COPPER COMPLEXES OF DINUCLEATING OCTA-AZAMACROCYCLIC LIGANDS

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Keith Philip Dancey
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by KEITH PHILIP DANCEY

Abstract

The synthesis of mono and dinucleating ligands and their copper complexes are described. Three types of dinucleating tetraimine macrocycles have been prepared from 4,7-diaza-2,3;8,9-dibenzodecane-1,10-dione by condensation with the appropriate polyamine; I, large-ring octa-aza macrocycles e.g. the 28-membered ring compound 5,6,7,8,15,16,23,24,25,26,33,34-dodecahydrotetrabenzo[*e*,*m*,*s*,*a*'][1,4,8,11,15,18,22,25]octaazacyclooctacosine and related 30- and 36-membered ring compounds; II, the "fused" bis(tetra-azamacrocycle) 5,6,7,8,22,23,24,25-octahydrotetrabenzo[*f*,*f*',*l*,*l*']benzo[1,2-*b*:4,5-*b*']-bis[1,4,8,11]tetraazacyclotetradecine; III, the "Linked" bis(tetra-azamacrocycle) 5,6,7,8,24,25,26,27-octahydrotetrabenzo[*f*,*f*',*l*,*l*']diphenyl[3,4-*b*:3',4'-*b*']bis[1,4,8,11]tetraazacyclotetradecine. For the type I and III ligands reduction of the imine linkages yielded the related octa-amines. The preparation of copper complexes is described. For many of the neutral copper complexes (formed by deprotonation of anilino nitrogen atoms) a novel synthetic route had to be used to overcome problems associated with the very low solubility of both ligand and complex.

An alternative route was investigated to other "linked" tetra-imines (type III) by reacting two moles of the amino-substituted macrocycle 17,18,19,20-tetrahydro-9-aminotribenzo-[*e*,*i*,*m*][1,4,8,11]tetra-azacyclotetradecine with one mole of diacyl halide. The most successful example of this type involved oxalyl dichloride. A mixture containing a number of high molecular weight species (including large-ring polyaza macrocycles of type I) was obtained from the reaction of 4,7-diaza-2,3;8,9-dibenzodecane-1,10-dione with hydrazine hydrate.

A dinuclear copper complex which was isolated as a diperchlorate salt from the 2:2 reaction of 1,6-diformaldoxime-4-methylphenol with copper(II) perchlorate has been shown to have a pseudo-macrocyclic structure (type IV) by virtue of intramolecular hydrogen bonding.

Single crystal X-ray structure determinations are reported for three biscopper complexes (types I and IV), one monocopper complex, and one metal-free dinucleating ligand (type I). Comparison are made with structures of a number of closely related compounds which have been determined recently at the Polytechnic of North London. In the cationic complexes, isolated as the perchlorate salts, three different types of enviroment have been found for the ClO_4^- groups and these are correlated with infrared spectra.

Magnetic data (obtained at University of North Carolina) are presented which indicate subnormal magnetic moments due to direct and/or superexchange interactions between copper ions in many of the dinuclear complexes.

Preface

While registered as a candidate for the degree for which submission is made the author has not been a registered candidate for another award of the CNAA or of a University during the research program. The results and conclusions presented in this thesis represent original work by the author unless specific reference is made.

In partial fulfilment of the requirements of the degree the author completed the following courses: a) Biological chemistry of dioxygen; b) Recent advances in inorganic chemistry; c) Advanced structural methods (NMR and X-Ray diffraction).

To my wife

Alison

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Abbreviations

Å	Angstrom 10^{-10} metre
BM	Bohr Magneton
bpim	4,5-bis[(2-(2-pyridyl)ethylimino)methyl]imidazolate
cm	centimetre
CuR	copper reagent
dma	dimethylacetamide
dmf	dimethylformamide
dmso	dimethylsulphoxide
dpt	diphenyltriazene
en	1,2-diaminoethane
Eims	Emission impact mass spectrometry
EPR	Electron paramagnetic resonance
Et_2O	Diethylether
Fc	Observed structure factor
Fdms	Field desorption mass spectrometry
Fo	Calculated structure factor
G	Gauss
g	grams
^1H nmr	Proton nuclear magnetic resonance
im	imidazolate
K_m	Michaelis constant
M	Moles
Me	Methyl
MeOH	Methanol
mmol	millimoles

nm	nanometres 10^{-9} metres
o-	ortho
OAc	Acetate
p-	para
Ph	Phenyl
py	pyridine
R	Residual index
R_w	Weighted residual index
thf	tetrahydrofuran
μ_{eff}	Effective magnetic moment

Infrared Abbreviations

b	broad
s	strong
m	medium
w	weak
sh	shoulder

^1H nmr Abbreviations

s	singlet
d	doublet
t	triplet
m	multiple

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Chapter 1

Introduction

1.1 General:

The work decribed in this thesis was carried out in collaboration with ICI Organics Division under a CASE Studentship, and involves the design and synthesis of dinucleating ligands and their copper complexes. Dinuclear complexes have been much studied recently because of their biological significance[1] and/or their potential as oxidation catalysts in the fine chemicals industry.
The background to these two areas is surveyed in section 1.2 and 1.3 below. Synthetic model systems for binuclear copper sites *in vivo* are considered in section 1.4. The general aims, a description of the systems studied and the layout of the thesis are described in chapter 2.

A feature of interest in such complexes is the possibility of copper to copper interaction (direct or via bridging ligands) as judged by various physical techniques including X-ray structural determination, EPR measurements and magnetic data. The complexes were tested for solution stability which indicates their suitability for testing as oxidation catalysts. The complexes prepared are also discussed where appropriate as possible models for copper-copper interaction in enzymes and proteins.

1.2 Biological Significance.

Three distinct forms of copper found in biological systems can be identified[1]:

Type 1 Cu^{2+} (or blue cupric). This is characterised by two unique and apparently inseparable properties: an intense multi-banded absorption envelope in the region of 600 nm and an EPR spectrum having an unusually small hyperfine coupling constant.

Type 2 Cu^{2+}. This form of copper is present in all blue multi-copper oxidases, but is lacking sufficient optical absorption to be observed above that of other copper-chromophores in these molecules.

Type 3 Cu. This form of copper is also found in all multi-copper oxidases and is charaterised by 1) its ability to act as a two electron acceptor/donor system, 2) an absorption band at 330nm, 3) the lack of an EPR spectrum, and 4) its non-paramagnetic nature over a wide range of temperatures. This centre appears to consist of two Cu^{2+} ions, in close proximity, which are strongly antiferromagnetically coupled.

1.2.1 Copper Proteins Containing Single or Independent Blue Centres.

Certain species of bacteria, non-photosynthetic plant material and chloroplasts have been found to contain relatively low molecular weight proteins having either a single or two identical and independent copper centres. Examples of these proteins are:

1) Azurins[2], originally named by Sutherland and

Wilkinson[3] in 1963. Proteins of this class which have received most attention were isolated from four bacterial species: psuedomonas aeruginosa, ps. flurescens, ps. denitrificans and bordetella pertussis.

2) Stellacyanin[4], umecyanin[5] and mung bean blue protein[6] all of which are isolated from non-photosynthetic plant tissue.

3) Plastocyanin[7], found exclusively in chloroplast when its involved in electron transfer from photosystem II to photosystem I.

1.2.2 Multicopper Oxidase

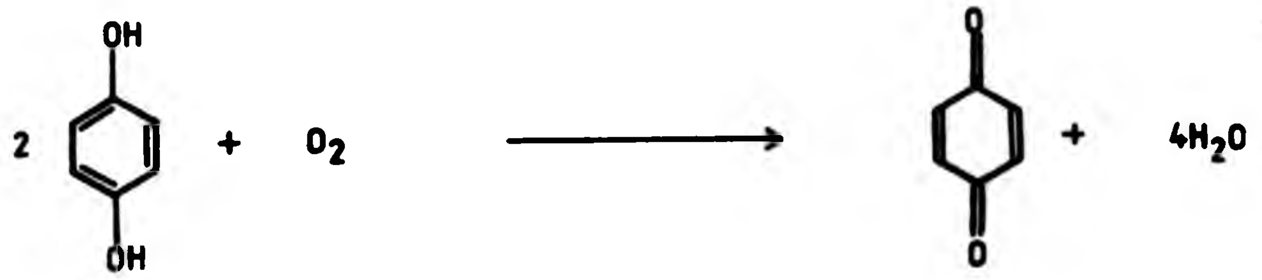
Multi-copper oxidases are enzymes which in addition to a blue centre contains several other coppers per molecule[8]. The different classes of this type of enzyme are laccase, ceruloplasmin and ascorbic acid oxidase, and these enzymes catalyse the general reactions:

$$2AH_2 + O_2 \longrightarrow 2A + 2H_2O \quad 2 \times 2e^- \text{ reduction}$$

$$4A^- + 4H^+ + O_2 \longrightarrow 4A + 2H_2O \quad 4 \times 1e^- \text{ reduction}$$

1.2.2.1 Laccase

Laccases catalyse the oxidation of a variety of materials[9] including p-diphenols according to the reaction shown in scheme 1.1.



Scheme 1.1

The name laccase was given to the latex of the lac tree 'rhus succeddanea' by G. Bertrand[10] in 1894. Since then many types of laccases have been studied, and will be referred to later on in the text.

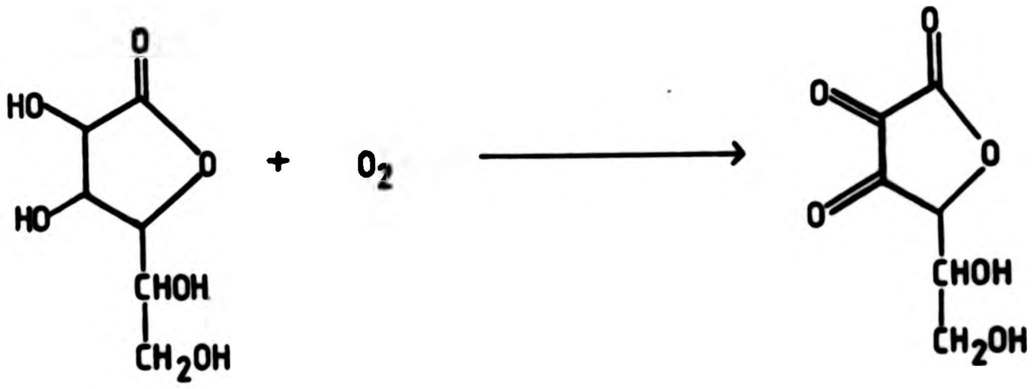
In studying proteins, to establish the nature of multi-copper sites, model systems are often compared to the proteins. The type of results which are used for comparison are those suggesting protein mediated Cu-Cu interaction where perturbation at one copper site influences the properties of another.

<u>1.2.2.2 Ceruloplasmin</u>

It was observed by Holmberg[11] that a particular serum protein fraction which was bluish in colour possessed oxidase activity toward p-phenylene diamine, p-cresol and catechol. The blue protein was purified by Holmberg and Laurell[12] and given the name ceruloplasmin. The exact role that ceruloplasmin plays in mammalian organism is unknown, although it is believed to be required for the efficient incorporation of iron into transferrin[13], and that it is an essential component of copper mobilisation[14]. The mechanism of the oxidase activity is very complex but some overall features of the reaction have become established: (a) Types 1 and 3 Cu are involved in the oxidation-reduction cycle and it is possible that other copper ions are likewise involved. (b) The catalytic role is independent of the nature of the substrate. (c) The form of enzyme that can react with O_2 does so with a very high affinity ($K_mO_2 = 4 \times 10^{-6}$m/l). (d) The reaction between O_2 and fully reduced enzyme results in formation of the complex composed of the elements of oxygen and enzyme which absorb at 420nm radiation.

1.2.2.3 Ascorbate Oxidase

Ascorbate oxidase is obtained from vegetation such as cucumber[15] (Cucumis salivus) and the courgette[16] (Cucurbita pepo medullosa). The reaction[17] catalysed by ascorbate oxidase is shown in scheme 1.2 for which it shows a strong but not absolute specificity[17b].



Scheme 1.2

The characterisation of ascorbate oxidase has not been as thorough as that of ceruloplasmin or the laccases due to the greater difficulty in purifying large enough quantities. However, recent developments[15a,18] have allowed measurements which show a similarity of the Cu-binding sites to those of the other blue multicopper oxidases.

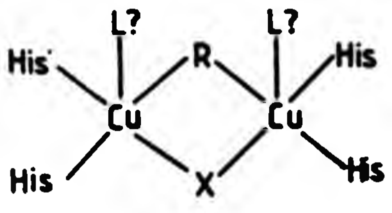
1.2.3 Tyrosinase

Tyrosinase is an enzyme isolable from the common commercial mushroom (Agaricus bisporus)[24]. The enzyme is an oxygen- and 4 electron-transferring phenol oxidase which catalyses phenol o-hydroxylation and dehydrogenation in plants and animals[25]. The active site of the enzyme is postulated[26] to contain a pair of antiferromagnetically coupled Cu(II) ions, for the following reasons; (a) There is a lack of any EPR absorption[24c]. (b) The apoenzyme can be wholly reconstituted with Cu(II) to an active product without an EPR signal[27], and that on reaction with H_2O_2, tyrosinase forms an O_2- and NO- binding compound which has chemical and spectroscopic characteristics similar to those of the bicuproprotein hemocyanin[28].

1.2.4 Hemocyanin

Hemocyanin is a copper-containing dioxygen-binding protein[29] found in the plasma of certain types of invertebrate[32], cephalopoda (molluscs) and xiphosura, arachnida and crustacea (anthropods). The deoxy form is colourless, but the absorption spectrum of the blue oxy form, which contains the copper-oxygen complex, consists of an intense ($\varepsilon \simeq 10^{+4}$ $M^{-1}cm^{-1}$) band near 340 nm and a weaker band near 570 nm[31]. In the oxy form the oxygen binds as peroxide[24a] and therefore the coppers are formally copper(II). The lack of an EPR signal is due to antiferromagnetic coupling between the coppers via an endogenous protein bridge[28a,27a].

Recent studies[22,29c] suggest a dinuclear copper(II) site (fig 1.1) having an endogenous and exogenous bridging ligands which mediate strong antiferromagnetism resulting in no paramagnetic behaviour.



$X = O_2^{2-}$ (oxyhemocyanin).

$X = N_3^-, OAc^-$ (methemocyanin).

R = ?

Fig 1.1 Structural representation of the oxyhemocyanin active site

1.2.5 Superoxide Dismutase

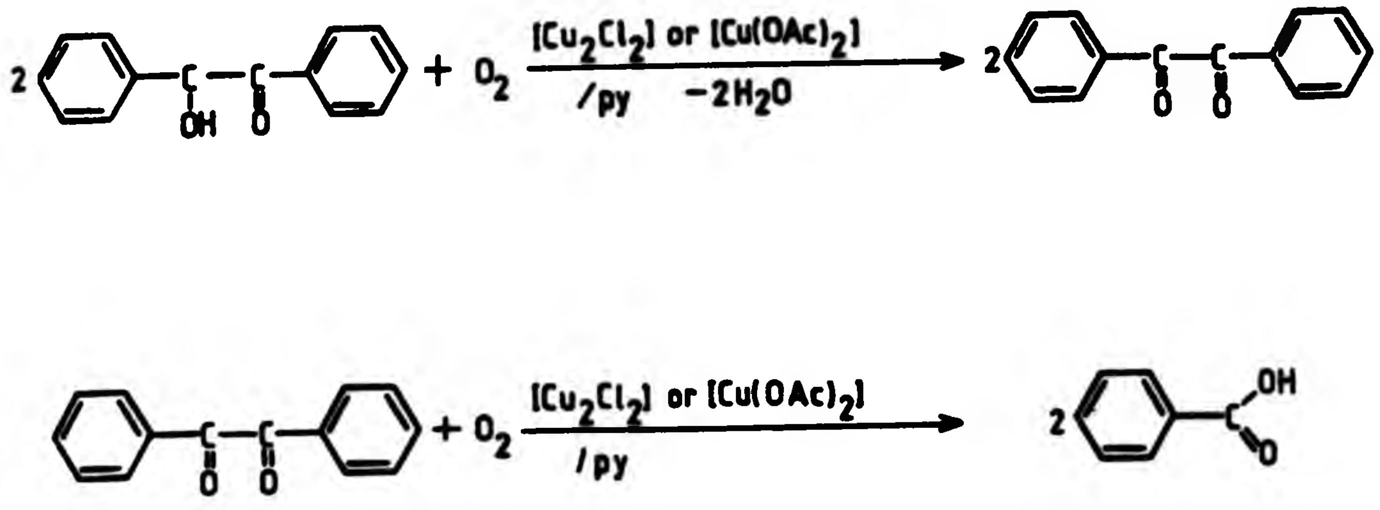
This protein has been purified from a variety of sources[33], including bovine and human erythrocytes, bovine heart, yeast, escherichia coli[34], streptococcus mutans, wheat germ, summer squash, garden peas, neurospora crussa and chicken liver. The enzymes obtained from eucaryotic sources were uniformly blue-green and contained copper and zinc. The bacterial superoxide dismutase had a molecular weight of 40000 and was composed of two subunits of identical size, held together by non-covalent forces[34].

1.3 Copper Complexes as Oxidation Catalysts

Copper(I) and Copper(II) salts have been widely used as catalysts for a variety of oxidation reactions. This aspect is important commercially in producing low cost materials in an increasingly competitive market. One such reaction is the aerial oxidation of aromatic amines to azo compounds which is catalysed by copper(I) chloride in pyridine (see below).

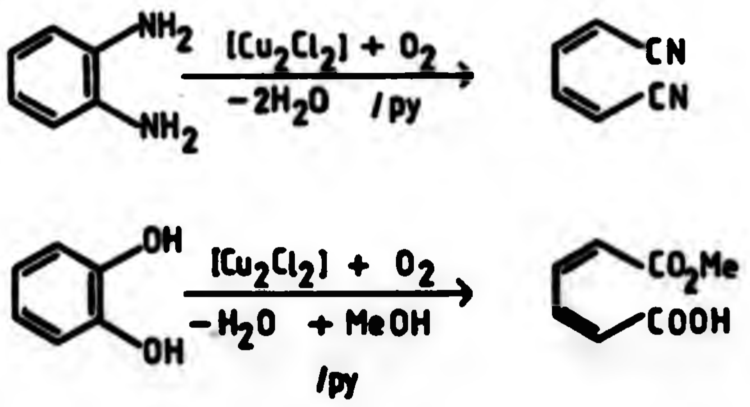
$$2ArNH_2 + O_2 \xrightarrow[/pyridine]{[Cu_2Cl_2]} Ar{-}N{=}N{-}Ar + 2H_2O$$

Terentiev et al[35] found that for effective catalysis, pyridine could not be replaced by other solvents such as dioxan, alcohol, dichloromethane or quinoline, and that other copper(I) or copper(II) compounds were inactive. Copper(I) chloride has also been used to catalyse the aerial oxidation of benzoin to benzil and subsequently to benzoic acid[36](scheme 1.3).



Scheme 1.3

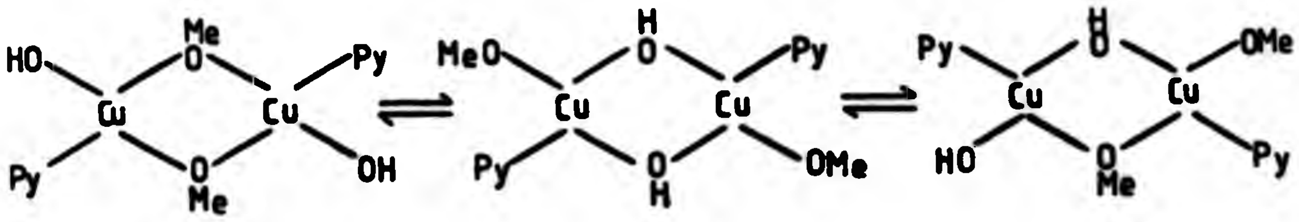
Aerial oxidation of 1,2-diaminobenzene[37] and catechol[38] to give *cis*,*cis*-muconitrile and *cis*,*cis*-monomethylmuconoate respectivly are catalysed by copper(I) chloride in pyridine (scheme 1.4). The reaction in each case involves ring fission.



Scheme 1.4

Brackmann et al[39] have investigated the oxidation of monohydric phenols using molecular oxygen as the oxidant and copper(II) amines as catalysts. These reactions are rapid at room temperature and may be applied to a variety of phenols using a number of different amines as catalysts.

Investigation by Rogic and Demmin[40] into the nature of the copper species responsible for such ring cleavage reactions have revealed activity from binuclear copper complexes. The "copper reagent" was prepared by action of oxygen with four molar equivalents of copper(I) chloride in a pyridine solution containing five equivalents of methanol, and the active component is thought to be the di-μ-methoxy and hydroxy bridged copper species (scheme 1.5).



Scheme 1.5

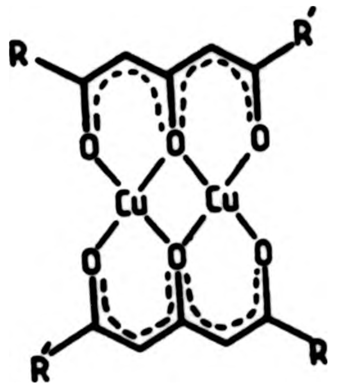
The dimeric copper(II) methoxy hydroxy system described by Rogic and Demmin is analogous to the copper containing centres in laccase[41] where two of the four copper(II)-centres in the fully oxidised laccase exist as an EPR-nondetectable copper(II) pair. The absence of an EPR signal in this system was also attributed to total antiferromagnetic coupling of the unpaired spins on the two adjacent copper(II) centers. This non-enzymatic reaction sequence for the cleavage of the carbon-carbon bonds in the absence of molecular oxygen is not evidence that enzymatic reactions proceed by such a reaction but must be considered an alternative to the widely accepted[42] mechanistic scheme based on enzymatic activation of molecular oxygen. The ability for binuclear copper complexes to act as specific oxidising catalysts, providing low energy routes to produce low cost materials will be of great commercial interest. The activity of catalysts such as 'CuR' may depend on direct or super exchange interactions between the two copper atoms. In order to control the separation and disposition of the two copper centres it is necessary to use relatively rigid multidentate ligands.

1.4 Copper Complexes as Models for Copper Containing Proteins

The information given in the previous section, outlines the physical properties of different types of copper protein. The types of copper site described in 1.2 above have been categorised in an attempt to help define the structure of the copper site.

Many polynuclear copper complexes have been synthesised, (some structually characterised) and then their physical properties compared to those of a variety of proteins, leading to postulations concerning the nature of the copper sites. For example, there is evidence[19] for high potential electron accepting sites in laccases. The reason suggested for this phenomenon is the presence of copper(II) atoms present as Cu-Cu pairs[19a].

1.4.1 Bis(1,3,5-triketo)dicopper(II) Complexes $Cu_2(TKO)_2$

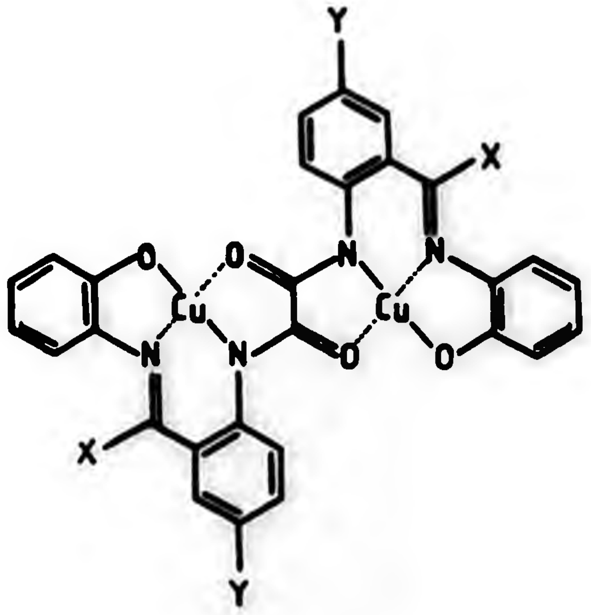


$Cu_2(TKO)_2$

Several of these complexes have magnetic and spectral properties[20] similar to type 3 coppers in metalloenzymes. Fenton and Lintvedt[21] have investigated the electrochemistry of several of these complexes, and found they exhibit a two-electron reversible reduction of the Cu(II),Cu(II) complex to the Cu(I),Cu(I) product. Since the redox reactions of type 3 coppers involve a 2-electron transfer, then these compounds are suggested as potential mimics for type 3 coppers in metalloenzymes.

Note: While many binuclear copper(II) complexes have been shown to exhibit antiferromagnetism, very few are diamagnetic at room temperature such as $Cu_2(TKO)_2$.

1.4.2 Amido-Bridged Binuclear Copper(II) Complexes

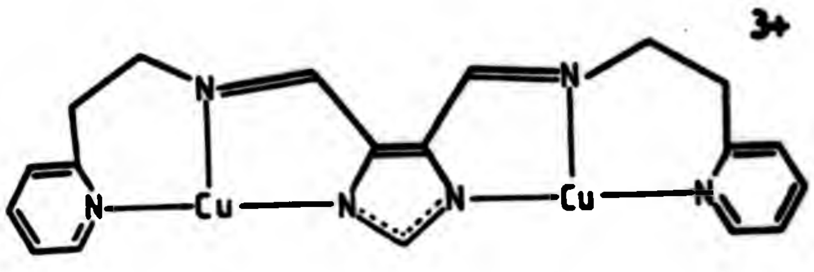


X	**Y**
H	H
	H
"	NO
"	Cl
"	F

This range of complexes has been studied[43] for comparability to the metal centres in biological systems, particularly the copper/heme a_3 site in cytochrome c oxidase[44]. The magnetic data has been recorded, and the magnitude of the coupling constant used for the identification of bridging groups. Because the a_3 site in cytochrome c oxidase shows similar coupling characteristics to those in model systems it was concluded[43] that this kind of bridge should be seriously considered as a possibility for the Cu-Cu sites in biological molecules.

1.4.3 Imidazolate-Bridged Copper Complex

It has been shown[47a] that by varying the pH, the bridge involving the imidazolate group can be broken. This was attempted[47b] for two compounds, Cu_2bpim^{3+} (1.2) and $[(Me_4dien)_2Cu_2(im)(ClO_4)_2]^+$ (1.3). In these complexes the bridge was stable but a new ligand system was devised leading to further complexes for study (fig 1.2).



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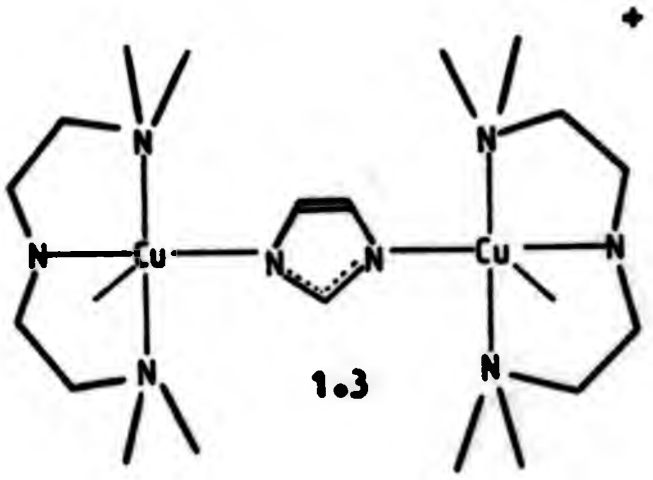

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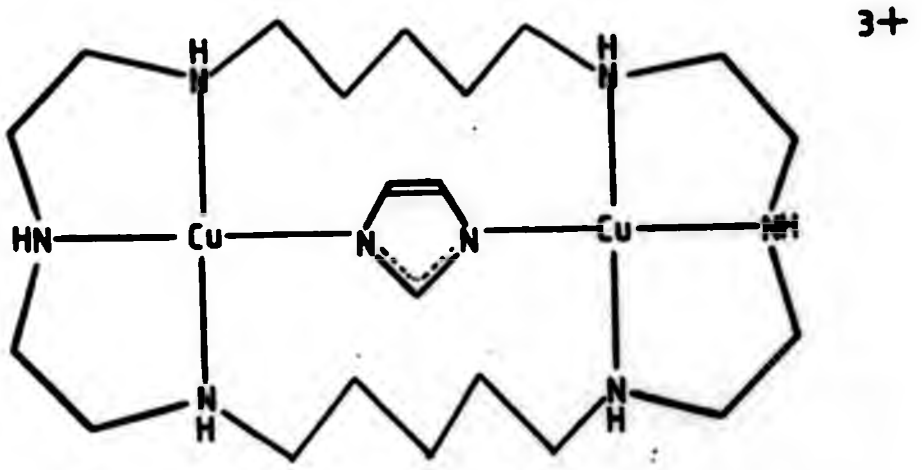


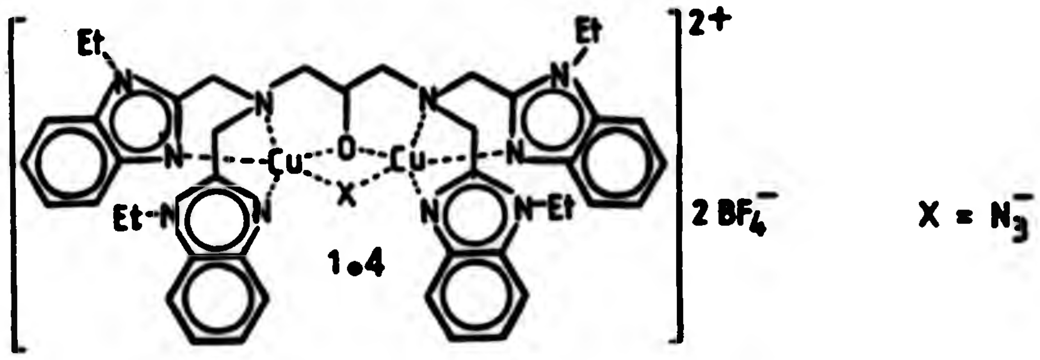
Fig 1.2 An imidazolate-bridged dicopper(II) unit

The imidazolate-bridged dicopper(II) ion is stabilised by the macrocycle (fig 1.2), and is suggested[45] to show similar properties to those observed in forms of the bovin erythrocyte superoxide dismutase protein[46].

Many other examples of complexes synthesised as models for the blue copper site are available[42].

Binuclear Cu(I) and Cu(II) complexes have been synthesised by Karlin [49] with a bridging pyridazine nucleus, as a model for metalloproteins.

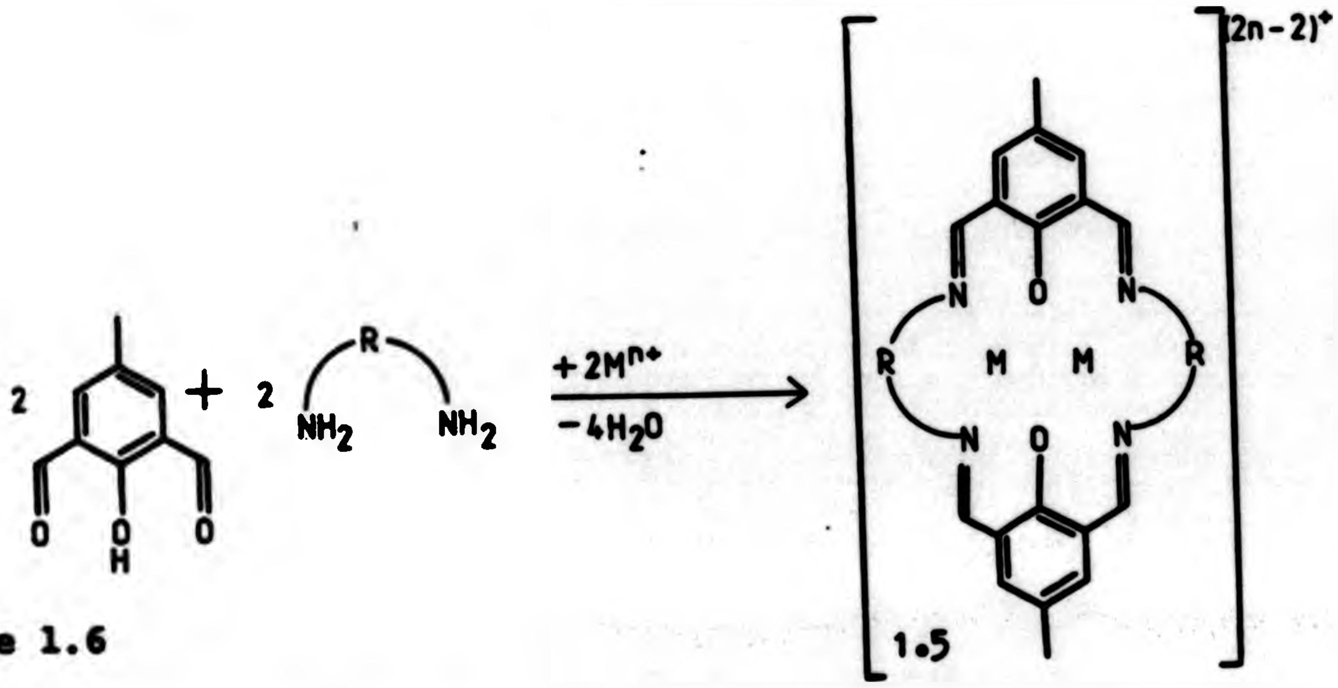
1.4.4 Copper hemocyanin models.



1.4

The azide complex 1.4, was found[29c] to be fully diamagnetic at room temperature, which is a rare occurance for copper(II) dimers. This complex was proposed as a model for Cu(II) hemocyanin due to recent chemical and spectroscopic studies[29c] (section 1.2.4).

1.5 Complexes from the condensation of 2-Hydroxy-3-methyl isonaphthaldehyde with various diamines.



1.5

Scheme 1.6

This basic structure (1.5, scheme 1.6) represents one of the most intensely studied binucleating systems[50]. The electrochemical properties of a range of binuclear metal complexes have been investigated by Gagne et al[49].

The magnetic properties of a wide range of biscopper complexes with monoatomic bridges (scheme 1.6) have been reported[51], whereby the degree of antiferromagnetic coupling is dependent on the Cu-O-Cu angle.

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Chapter 2 Dinucleating ligands

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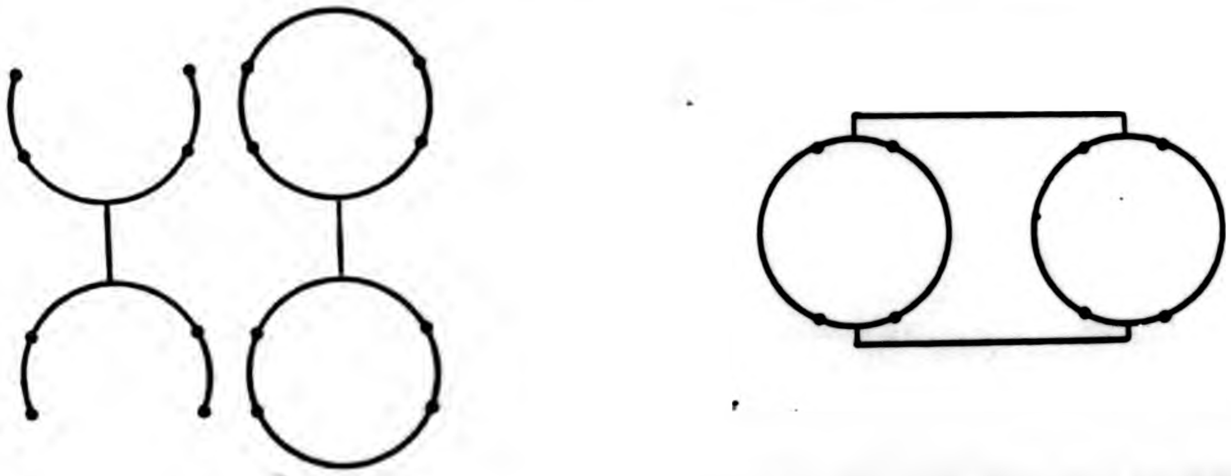
Chapter 2

Dinucleating ligands

A large number of dinucleating ligands and their metal complexes have been reported[1] over the past few years. Many such complexes have had their physical properties compared to those of metallo proteins. A comprehensive review[1] of dinucleating ligands appeared in 1977. In this section only those macrocyclic ligands with eight donor atoms are considered. The systems have been grouped into four classes as shown below, depending on how the macrocyclic units are incorporated into the ligand. For two of these classes it is relevent to consider their non-cyclic analogues.



Type I Mono-bridged bis-quadridentate systems

Type II Multiply-bridged bis-quadridentate systems

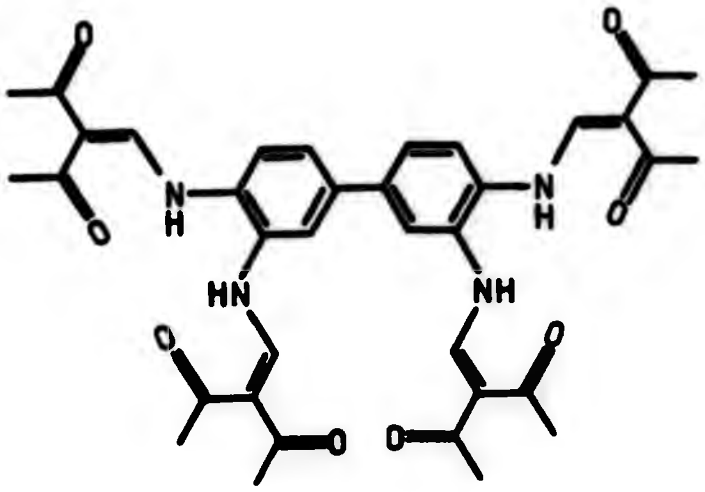
Type III Fused bis-quadridentate systems

Type IV Large ring octadentate systems

Scheme 2.1

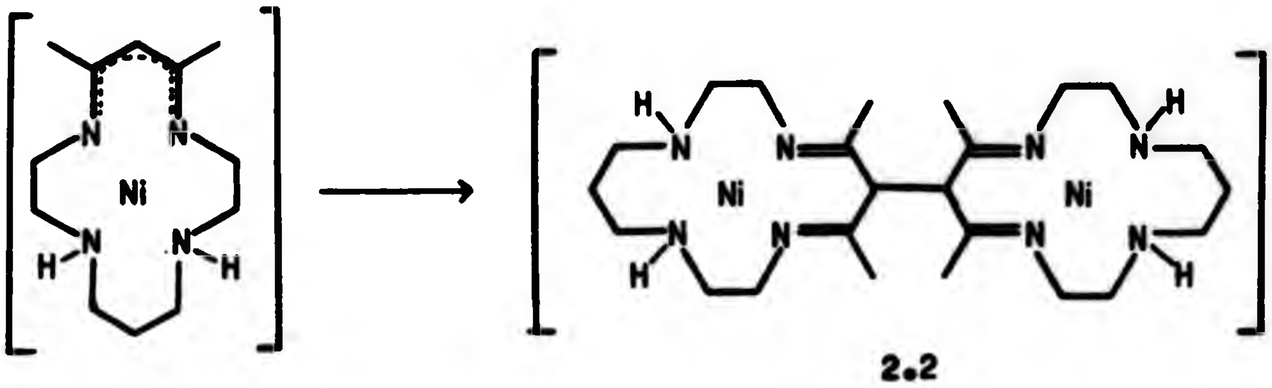
2.1.1 Mono-bridged bis-quadridentate systems (type I)

Ligands of this type have a single point of attachment between the two halves of the ligand, and depending on the bridging moiety, may exhibit a a degree of flexibility. The dinucleating non-cyclic ligand 2.1 was prepared[2] from the diamino benzidine precursor, and may show a degree of rotation about the single C-C bond. It has been reported[3] that such a molecule will exist in the skew configuration. Other compounds may have longer bridging units which would show much more flexibility.



2.1

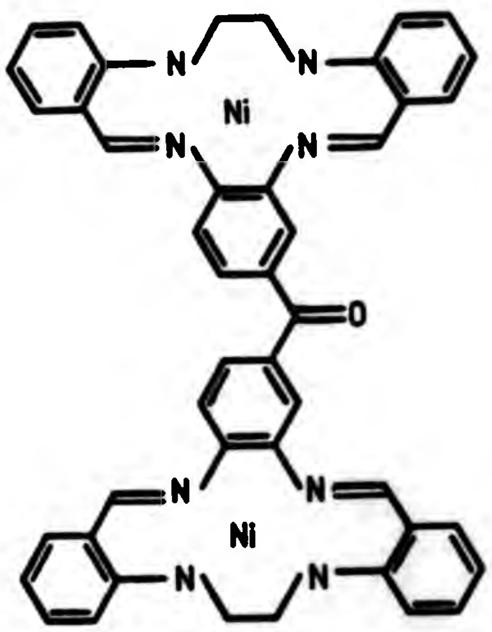
The coupling of two macrocyclic ligands gave[4] the bisNi(II) complex 2.2 (scheme 2.2). The free ligand was not isolated.



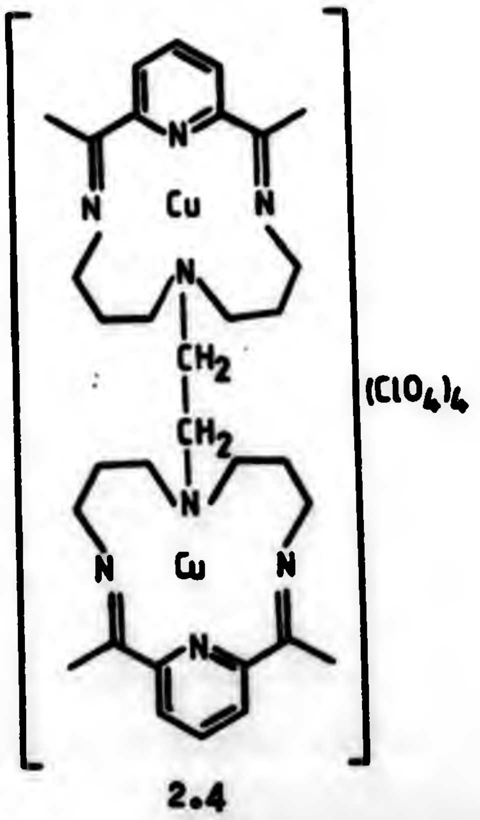
2.2

Scheme 2.2

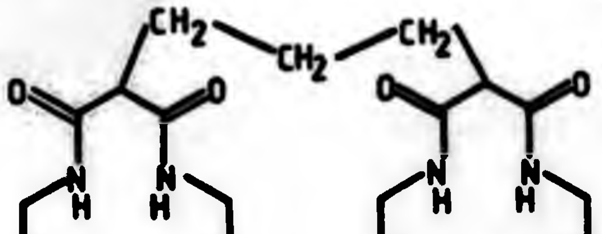
Other ligands and their copper complexes which fall into this class of bis-quadridentate systems are 2.3[5], 2.4[6] and 2.5[7].



2.3



2.4

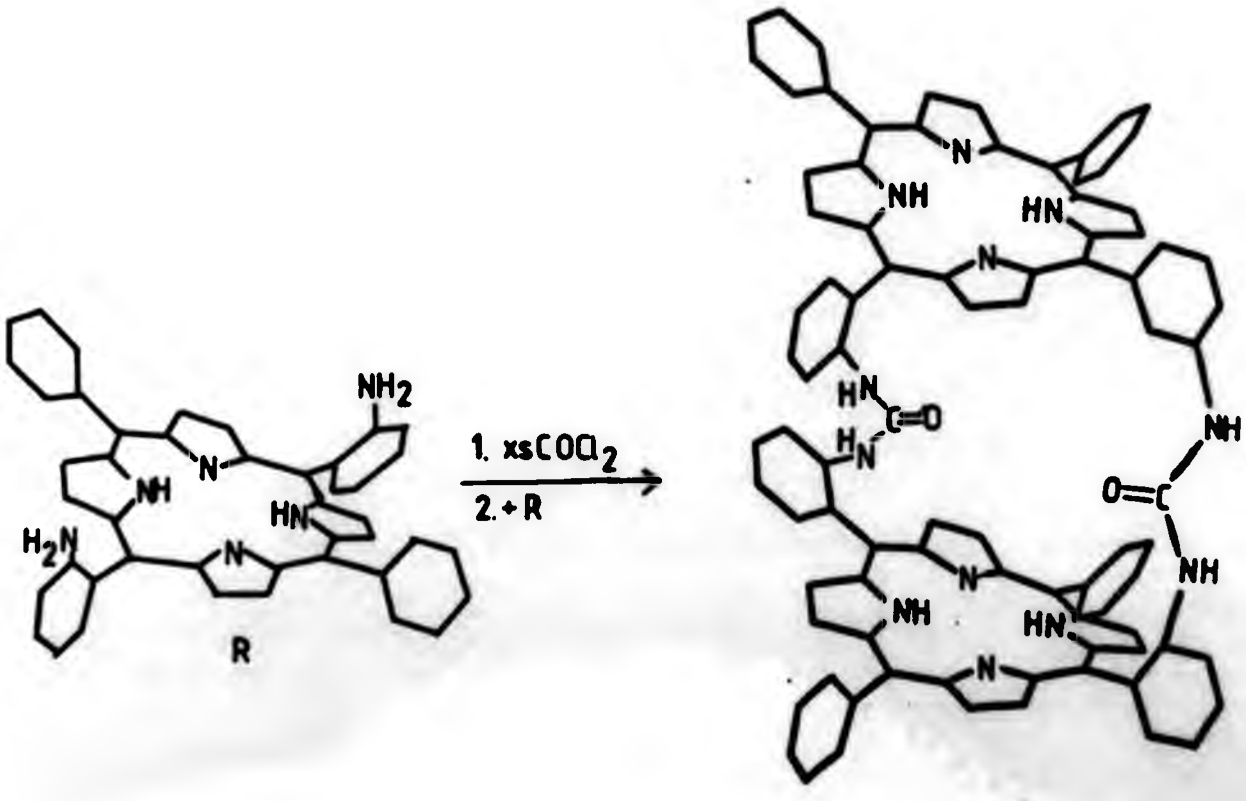


2.5

The main problem with flexible linking is that the coupling of two macrocyclic ligands involving a single point of attachment on each ligand, may result in an undesired amount of flexibility. This creates problems in estimating the distance between the two coordinated metal atoms, and in solution more than one conformation of the structure may be possible.

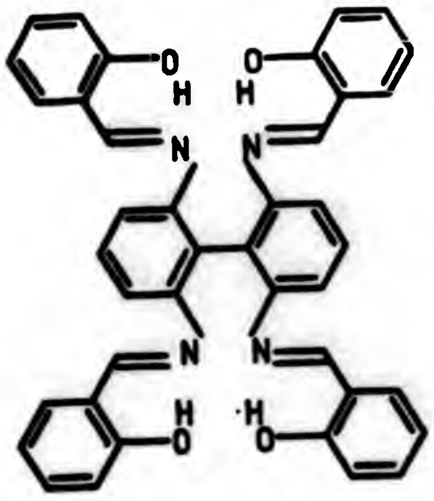
2.1.2 Type II Multiply-bridged bis-quadridentate systems

Multiple linking between two macrocycles results in rigid structures, which will hold two metal ions in fixed positions. Many cofacial porphryins fit into this category[8] (scheme 2.3). Variation of the bridging group can give a range of metal-metal contact distances.



Scheme 2.3

Condensation reactions with 2,2'6,6'-tetra-aminobiphenyl and 2-hydroxy benzaldehyde has given the structure of a open chain binucleating ligand 2.6.

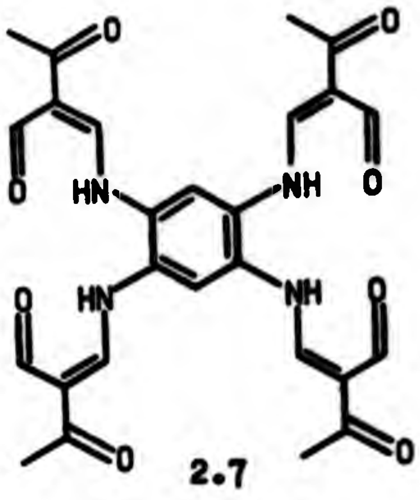


2.6

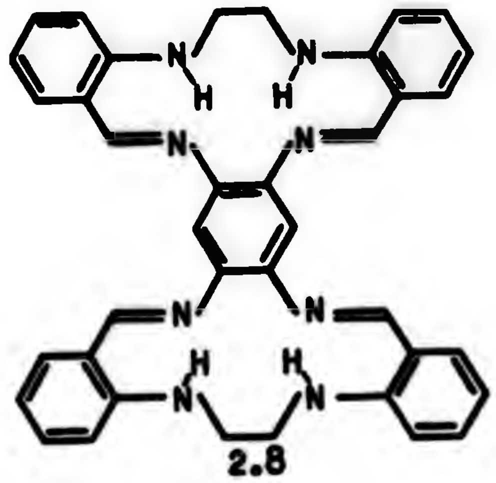
2.1.3 Type III Fused bis-quadridentate systems

These systems have at least two atoms common to the rings of both quadridentate units. They have the advantage over the mono-bridged previous systems that the ligands can be rigid and the bridging between the two metal atoms could consist of a aromatic moiety capable of propagating super exchange interaction.

Rigid systems such as 2.7[2] and 2.8[9] will be planar, and likely to show extensive conjugation between the two halves of the molecule. These systems are unlikely to show direct Cu-Cu interaction due to the large separation (~8 Å) of two copper atoms, unless close intermolecular contacts are made.

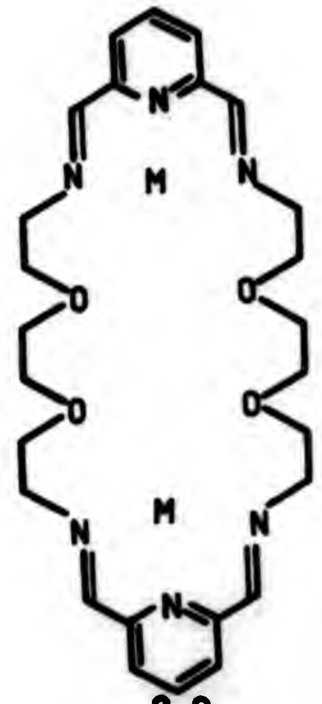


2.7



2.8

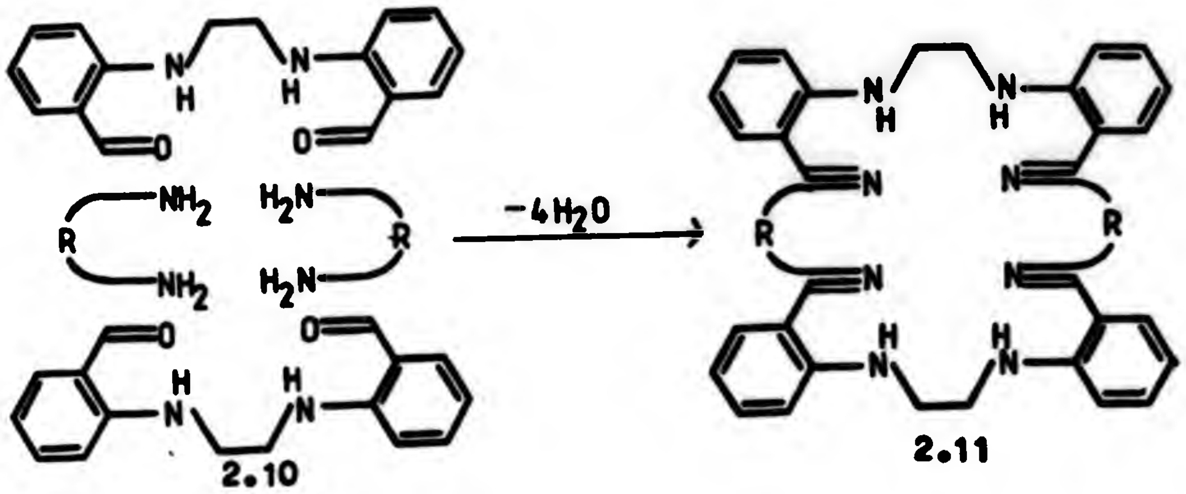
2.1.4 Large ring octadentate systems



2.9

Many [2+2] condensations based on the precursor 2,6-diacetyl pyridine to give macrocyclic metal complexes 2.9 have been reported[10]. These complexes undergo metal exchange reactions to form various binuclear complexes, sometimes capable of incorporating additional bridging ligands. The free ligands for these systems have not been isolated.

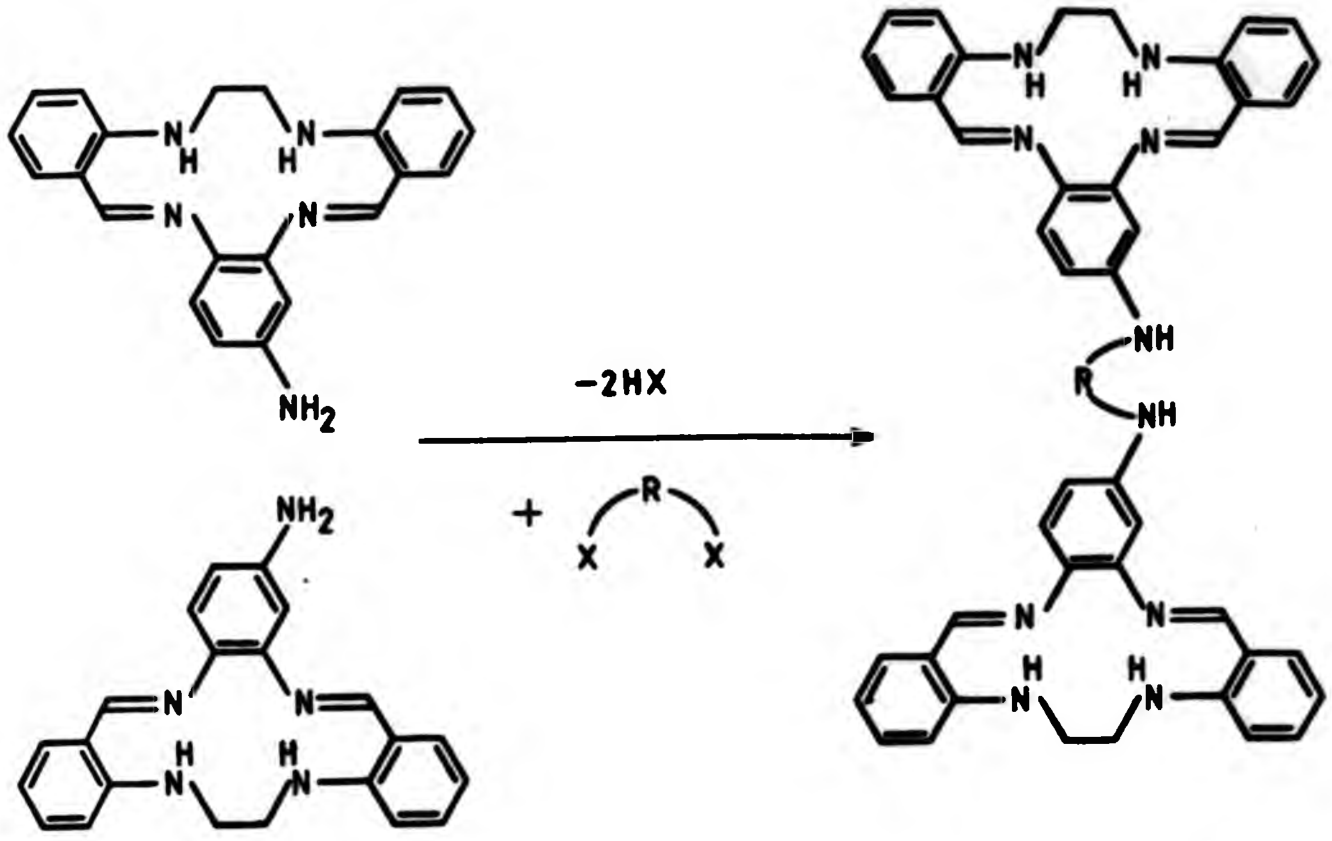
Preliminary reports[11] have suggested [2+2] condensation take place between C_2-dialdehyde (2.10) and various diamines to give large ring macrocycles (2.11 scheme 2.4). No metal complexes have been reported.



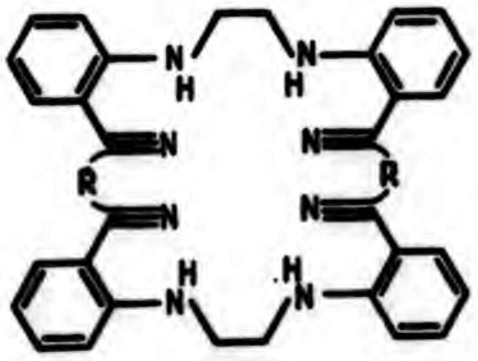
Scheme 2.4

2.2 Systems for study

The C_2-dialdehyde (2.10) precursor was chosen for study due to the preliminary evidence[11] for forming the dinucleating macrocycles 2.8 (type III) and 2.11 (type IV) with various diamino compounds. It was thought likely that these ligands could be used to form biscopper(II) complexes which would show interesting spectral properties. It was also possible to propose a method of linking two preformed macrocycles based on the precursor C_2-dialdehyde (scheme 2.5). The following section describes the layout of this thesis and a brief resume of each chapter.

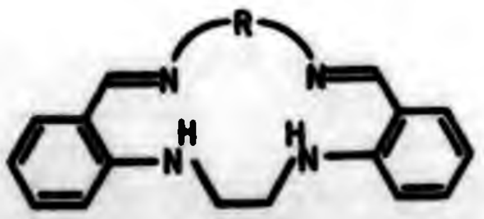


Scheme 2.5



2.11

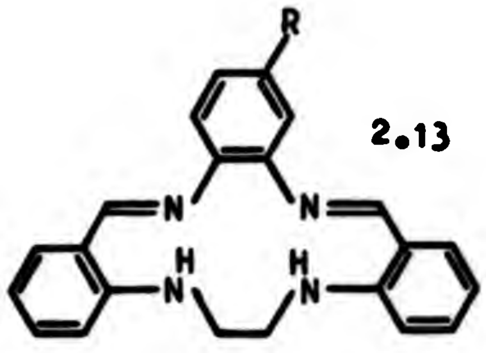
Chapter 3 considers ligands of the general type IV, i.e. large ring octadentate systems. These octa-aza ligands are derived from the [2+2] condensations of the type giving 2.11. Related tetra-aza systems (2.12) for the equivalent [1+1] condensation reactions are also considered. The copper complexes of these macrocycles are also discussed in terms of preparation, solution stability and structural points of interest for those compounds characterised by X-ray crystallography.



2.12

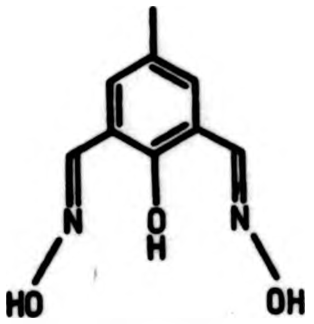
Fused bis- and mono-bridged quadridentate systems of type III and I respectively are considered in chapter 4. These systems are also formed from condensation reactions but require the presence of a catalyst. Emphasis is placed on the difficulty encountered with the preparation of ligands and their copper complexes (due to their low solubility).

The linking of two macrocycles (2.13) by bridging groups which may be varied in length to provide a series of biscopper(II) complexes are considered in chapter 5.



2.13

As part of the CASE/SRC award, a ligand H_3DFMP (2.14) was supplied by I.C.I. for investigation of the structural and magnetic properties of the biscopper(II) complex. The copper(II) complex of the hydrogen bridged macrocycle is discussed in chapter 6.



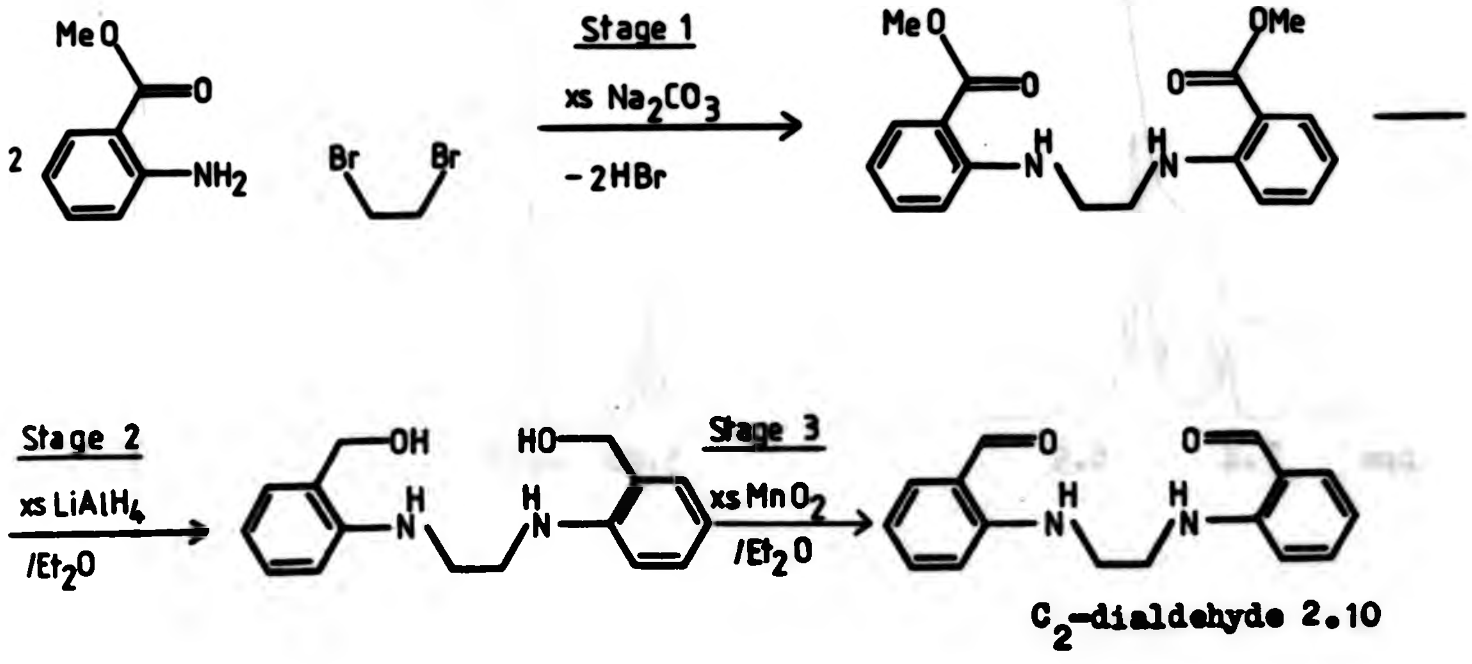
2.14

Chapter 7 describes how the five structures in this thesis were solved (either by heavy atom solutions from the Patterson synthesis or direct methods).

The experimental section (chapter 8) details the preparative method for each compound, together with full systematic naming.

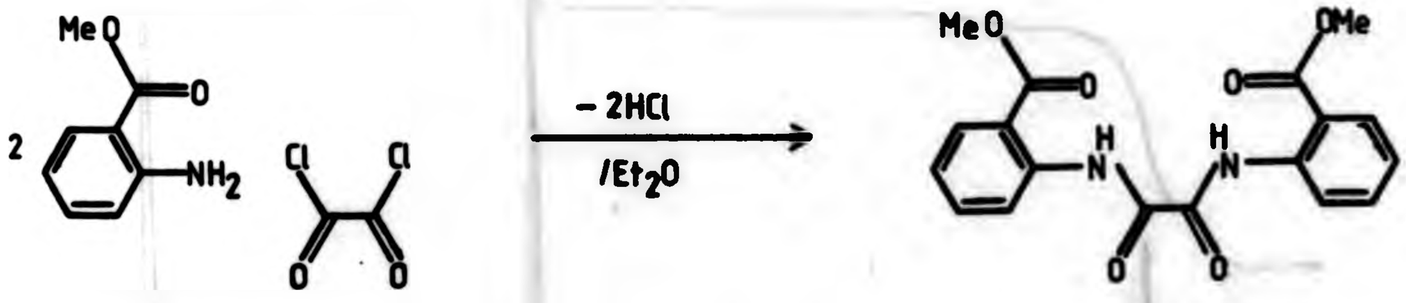
2.3 Synthesis of the precursor C_2-dialdehyde (2.10)

The preparation of C_2-dialdehyde was originally described[12] by a three step sequence reaction starting with methyl anthranilate (scheme 2.6).



Scheme 2.6

Black and co-workers[13] reported an improved synthesis for stage 1, but stage 2 would then require exceptionally large quantities of reducing agent (scheme 2.7).



2.15

Scheme 2.7

For economic reasons the original method was used, but changes in solvent (from diethyl ether to thf) were considered for stages 2 and 3 (scheme 2.6). The reduction of the C_2-diester in thf gave a good yield of C_2-dialcohol, but

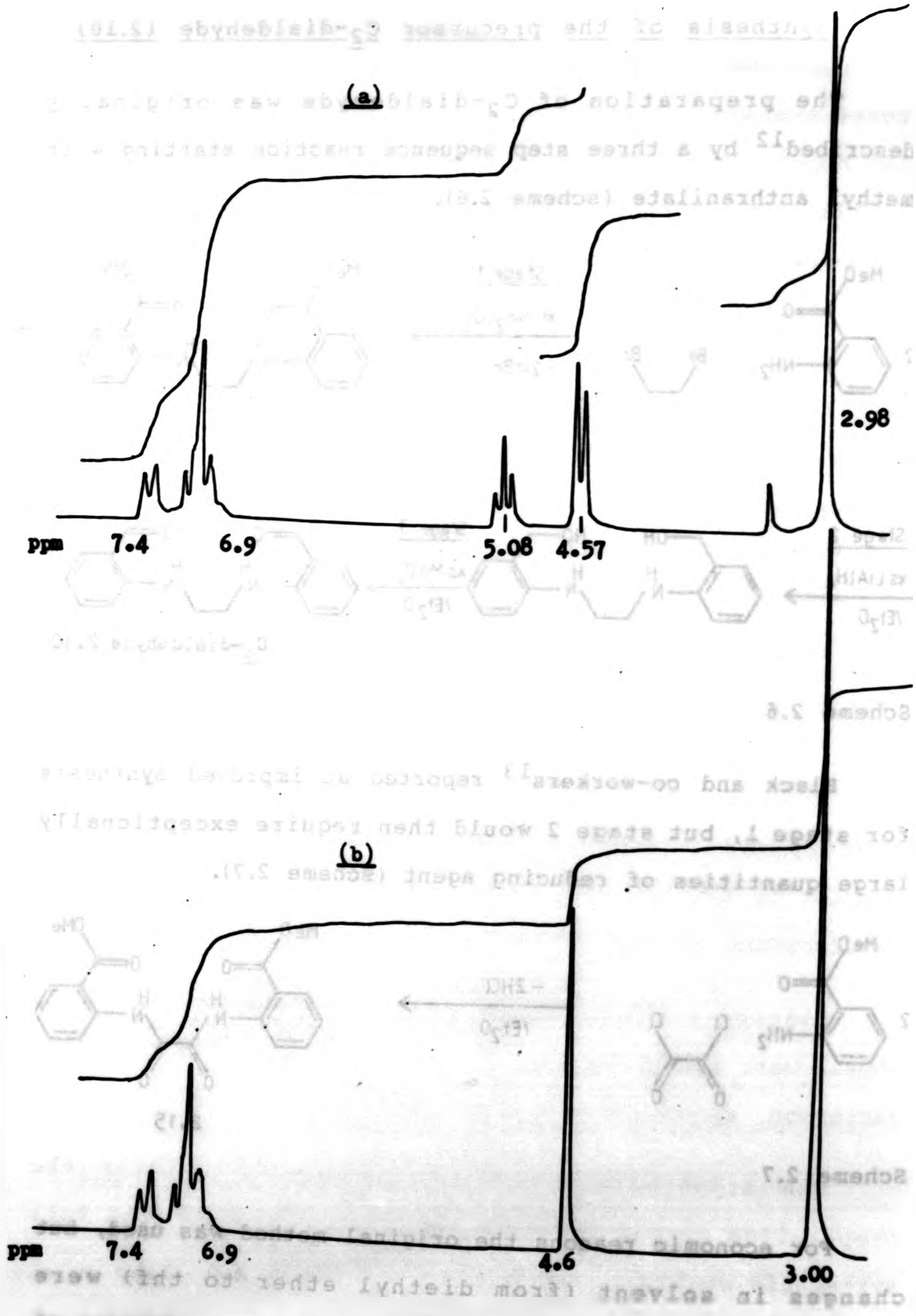
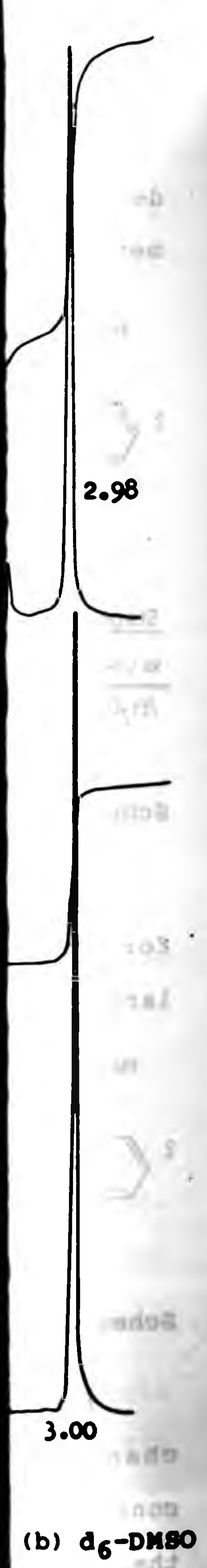


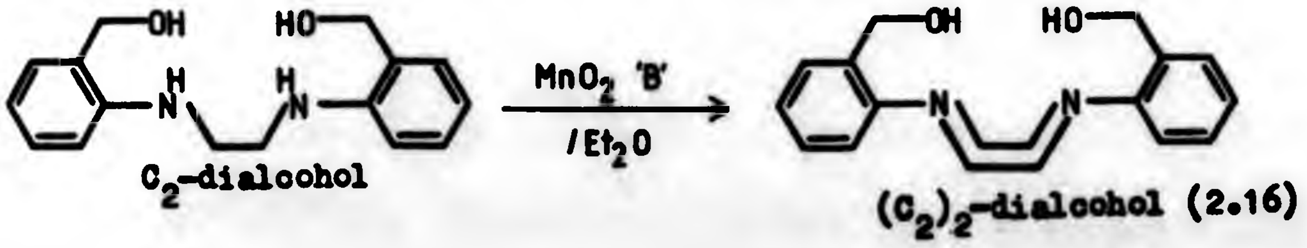
Fig 2.1 ^1H nmr of $(C_2)_2$-dialcohol. (a) d_6-DMSO. (b) d_6-DMSO + D_2O



the manganese dioxide oxidation resulted in an unexpected product which is described in the following section. Preparation of C_2-dialdehyde (2.10) was made by the original method[12] (scheme 2.6) showing reproducible results.

2.4 Preparation of $(C_2)_2$-dialcohol (2.16)

When thf was added dropwise to mangenese dioxide (type 'A')[14] under nitrogen, a strongly exothermic reaction was observed. It has been reported[14] that when diethyl ether was added slowly to manganese dioxide, local hot spots developed, and to overcome this the ether was added in one portion to wet all the manganese dioxide. This procedure was not followed for the addition of thf, since a fast addition may have been dangerous, and therefore thf was added slowly under a nitrogen atmosphere until the reaction subsided. Then a solution of C_2-dialcohol in thf was added and the mixture refluxed for a short time. The product extracted from this mixture in good yield (~90%, Scheme 2.8) showed only traces of C_2-dialdehyde (2.10), and spectral evidence indicated the principle product was N,'N-di(o-benzylalcohol) piperazine($(C_2)_2$-dialcohol)(2.16).



Scheme 2.8

This new dialcohol was identified by elemental analysis, eims (M* = 298) (Section 8) and ^1H nmr (table 2.1, fig 2.1 facing page).

Chemical Shift (ppm)	Integration Ratio	Assignment	Chemical Shift after D_2O exchange.
2.98 s	8	$-N-C\underline{H}_2-$	3.00 s
4.57 d	4	$-C\underline{H}_2-OH$	4.60 s
5.08 t	2	$-O\underline{H}$	
6.9 - 7.4 m	8	Aromatic C$\underline{H}$	6.9 - 7.4 m

Table 2.1 ^1H nmr (d_6-DMSO 60°C) of $(C_2)_2$-dialcohol.
(s=singlet, d=doublet, t=triplet, m=multiple)

The -OH proton is coupled to the protons of the methylene group, giving the observed n+1 splitting pattern. Because the -O$\underline{H}$ protons usually exchange rapidly, this effect indicates a degree of intramolecular hydrogen bonding (fig 2.2). On addition of D_2O the doublet at 4.57 ppm collapses to a singlet at 4.6 ppm, while the triplet at 5.08 ppm is lost from the spectrum. This would confirm the previous indication of intramolecular hydrogen bonding, since the -O$\underline{H}$ protons have been exchanged for deuterium and would not be detected in the ^1H nmr spectrum.

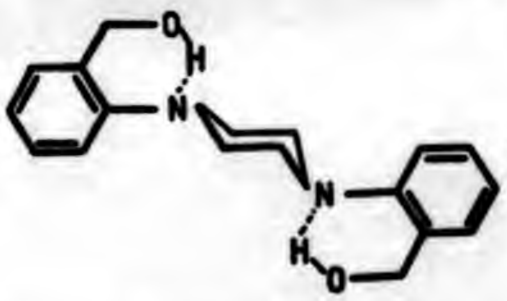


Fig 2.2 Hydrogen bonding for $(C_2)_2$-dialcohol in solution

The material $(C_2)_2$-dialcohol (2.16) was identified previously [15] as a byproduct from a reaction and may have been present as an impurity in the starting material C_2-dialdehyde. Of the few crystals obtained from this synthesis an X-ray structure determination confirmed the formulation, and showed extensive intermolecular* hydrogen bonding throughout the crystal (fig 2.3).

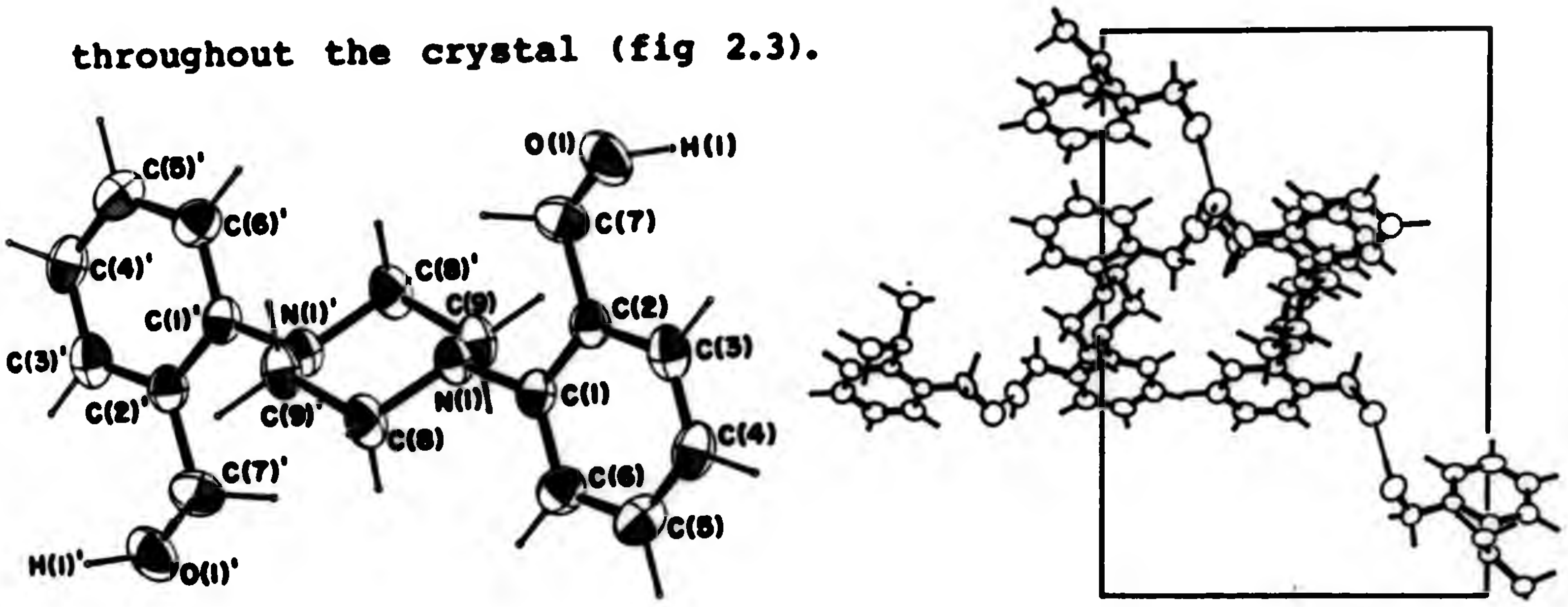
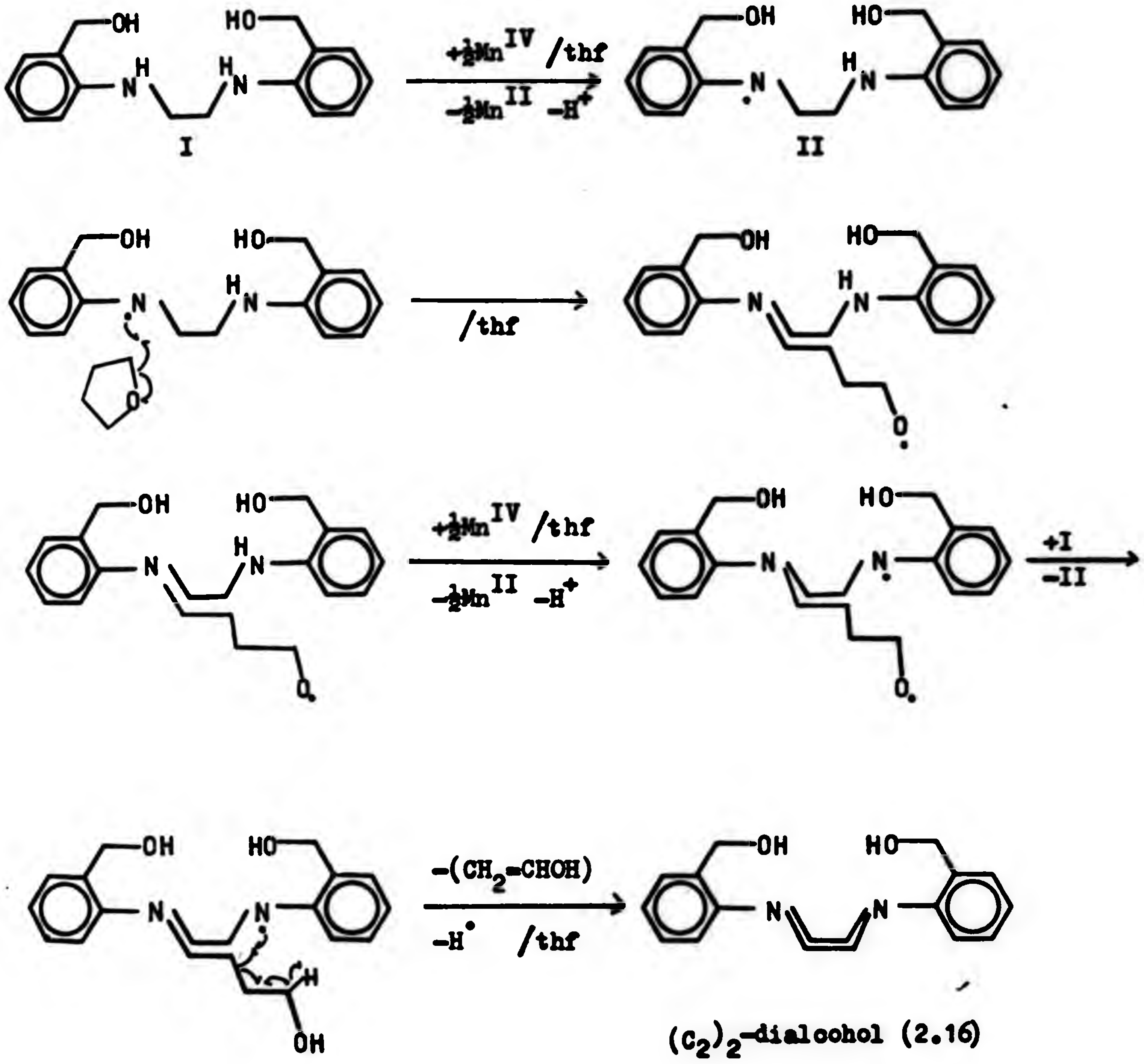


Fig 2.3 Ortep diagrams of $(C_2)_2$-dialcohol[15] (2.16).

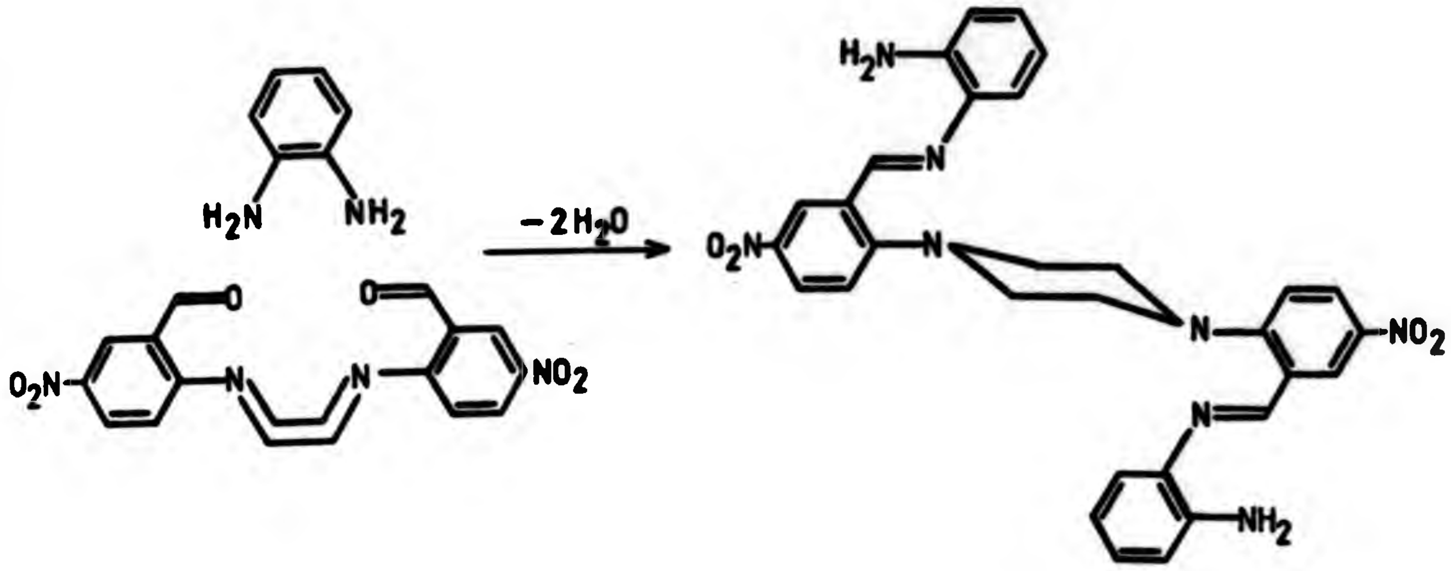
* It is unlikely that intermolecular hydrogen bonding will persist in solution.

The $(C_2)_2$-dialcohol may have arisen as an impurity during the preparation of C_2-dialdehyde (scheme 2.6) if excess dibromoethane had been used during the 1st stage[16]. This would lead to a small percentage of doubly bridged diester which would have been reduced at the second stage to $(C_2)_2$-dialcohol. However, the isolation of $(C_2)_2$-dialcohol in this work was made with very high yields (-90%), and probably results from a reaction involving thf and C_2-dialcohol (scheme 2.9).



Scheme 2.9 Tentative mechanism for the formation of $(C_2)_2$-dialcohol (2.16).

Other related doubly bridged dialdehydes[17] have been of no use in the preparation of macrocyclic di-imines (scheme 2.10) since only the [2+1] condensation products were formed.



Scheme 2.10

The lack of anilino hydrogens and the inability to form macrocyclic ligands, reflect the importance of intramolecular hydrogen bonding needed to stabilise metal free complexes of this type. When no anilino-hydrogens are present, a theoretical macrocycle would experience lone-pair:lone-pair repulsion from the four nitrogen atoms (fig 2.4).

Fig 2.4 Lone-pair:Lone-pair repulsion

It is believed to be for the previous reasons and the more stable chair conformation of the piperazine bridge, that there are no reports of successful ring closure reactions to give metal free 14, 15 and 16 membered 'N_4' macrocycles, unless there are at least two secondary amine groups present[18]. No further investigations were made with $(C_2)_2$-dialcohol, although a project[19] based on the findings in this section confirmed the results, and went further to prepare the $(C_2)_2$-dialdehyde. As expected no macrocycles could be prepared.

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Chapter 3 Tetra-aza and octa-aza large ring macrocycles

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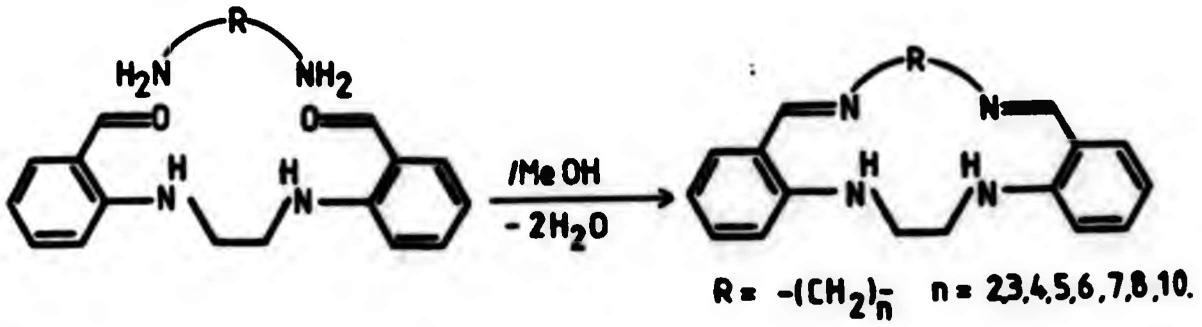
CHAPTER 3

Tetra-aza and octa-aza large ring macrocycles

This chapter concerns the large ring macrocycles of the schematic type IV which were described in the preliminary discussion (chapter 2). The related tetra-aza systems have also been studied to allow comparison to be made between the mononucleating and dinucleating ligands.

3.1.1 Introduction: Tetra-aza macrocycles

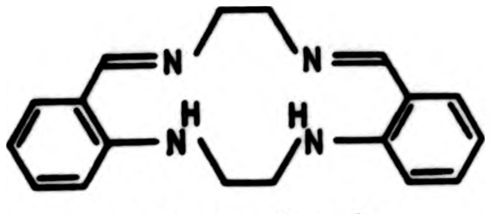
Aliphatic bridged macrocycles can be prepared by simple imine condensation reactions of C_2-dialdehyde (3.1) with a diamino compound (scheme 3.1) which do not require the presence of a catalyst. A range of macrocycles have been reported[1] where the bridging portion 'R' can vary in length from ethane to decane* (scheme).



Scheme 3.1

* No results were reported for Nonane

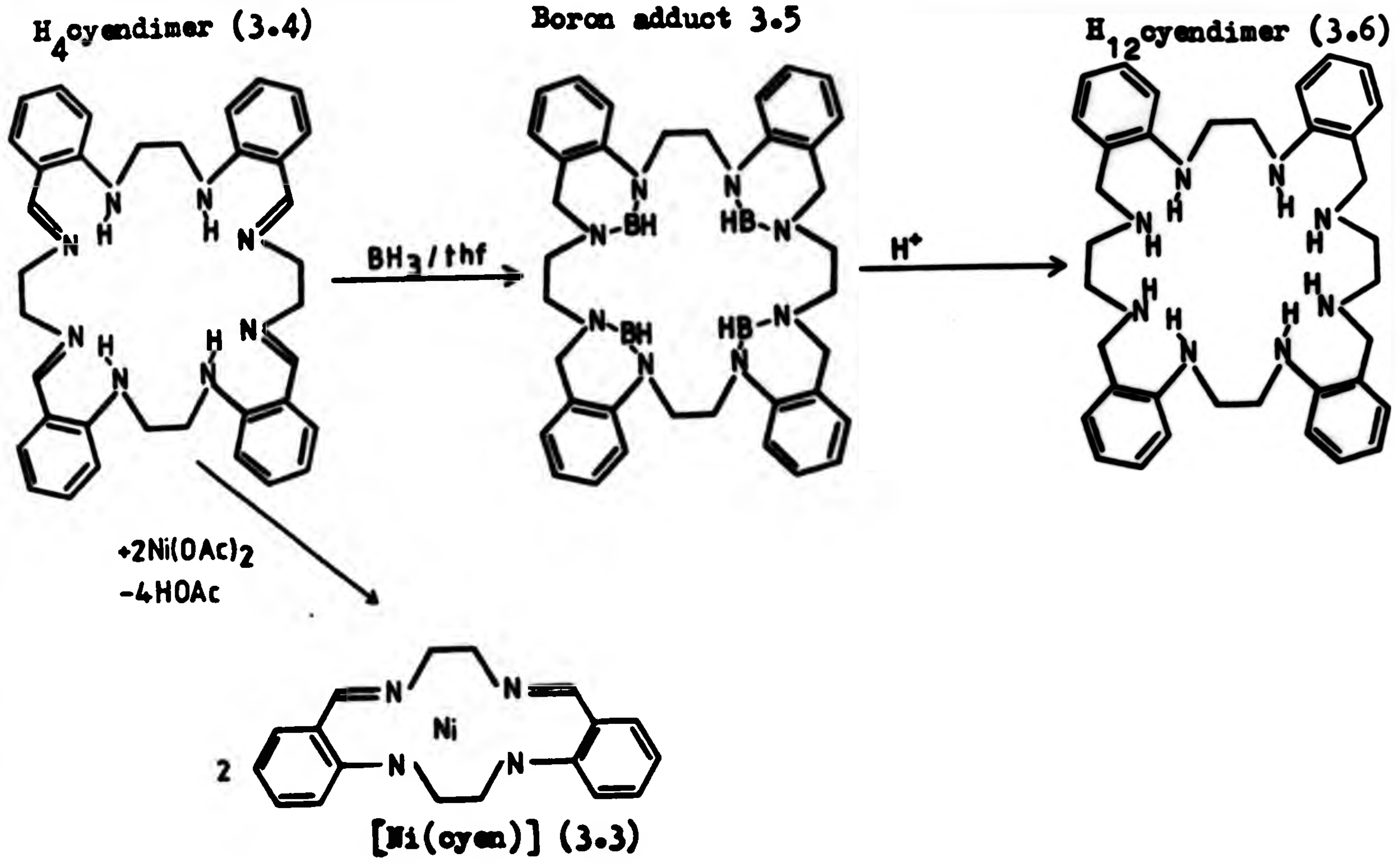
3.1.2 Introduction: Octa-aza large ring macrocycles


H_2cyen (3.2)

A very insoluble material which was isolated from the preparation of H_2cyen (3.2) was originally assigned a polymeric structure[2].

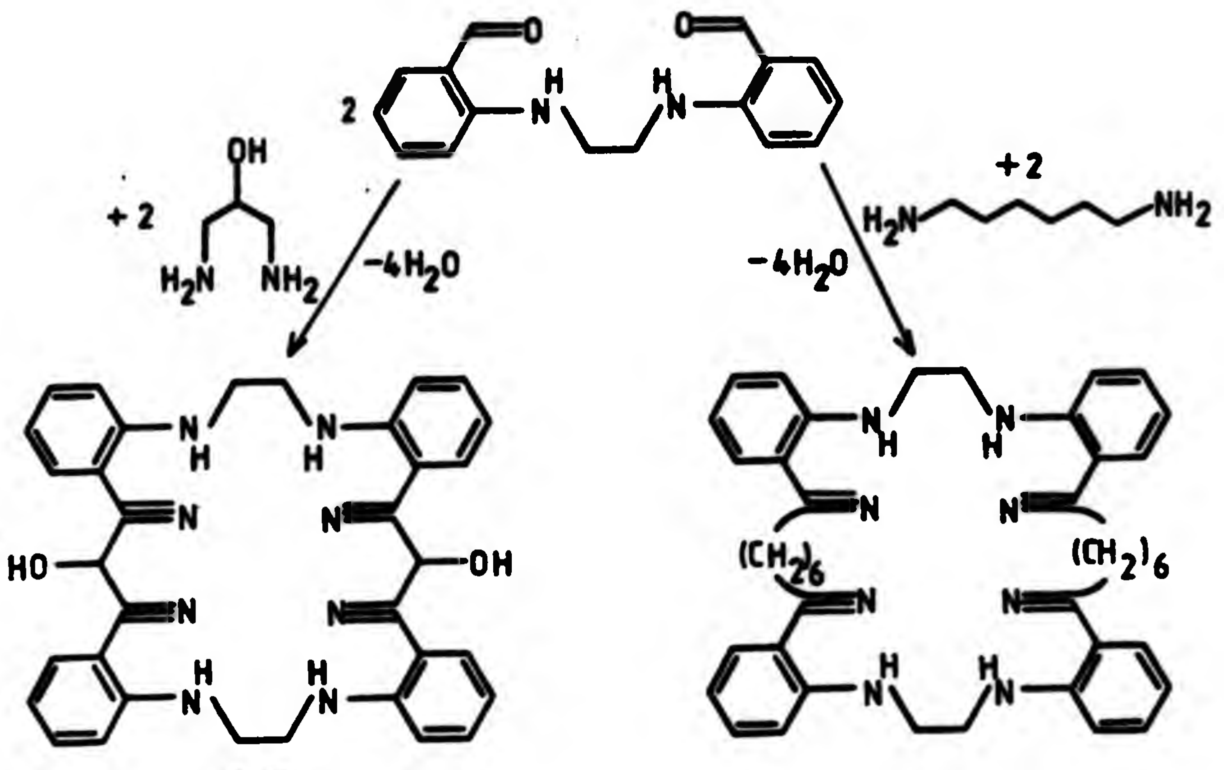
The 'polymeric material' was shown[3] by field desorption mass spectrometry (fdms) to have a relative molecular mass of m/e=584 which is double that of H_2cyen (3.2). On this basis the material was assigned the structure H_4cyendimer (3.4). It was found that after addition of nickel acetate followed by a long period of refluxing in methanol, only the tetra-aza macrocyclic complex [Ni(cyen)] (3.3) was formed[2] (scheme 3.2).

The structure for the 28-membered ring (3.4) was indirectly confirmed by the X-ray structural analysis[3] of an unusual boron adduct (3.5) which was isolated during the attempted reduction of 3.4 with BH_3/thf to give the corresponding octaamine H_{12}cyendimer (3.6) (scheme 3.2).



Scheme 3.2 Reactions of H_4cyendimer (3.4).

These results gave rise to speculation that the condensation reactions forming the other tetra-aza macrocycles may be accompanied by formation of larger ring analogues. During the course of an investigation[4] on the preparation of a wide range of tetra-azamacrocycles (scheme 3.1) it appeared that two other octa-aza macrocycles could be formed (scheme 3.3)



Scheme 3.3 H_4cyprodimer (3.7) and H_4cyhexdimer (3.8)

Characterisation of these large-ring tetra-imines (3.7 and 3.8) is particularly difficult due to their low volatility and solubility. Electron impact mass spectrometry (eims) is usually accompanied by extensive fragmentation of the parent ion, sometimes symmetrically giving peaks with maximum m/e values corresponding to the monomer species. Fdms is more successful, and X-ray crystallography has been employed when suitably crystalline samples were available.

3.2 Results and discussion for aliphatic bridged macrocycles

3.2.1 Preparation of tetra-aza macrocycles

The experimental details for the preparation of tetra-aza macrocycles (fig 3.1) are described in section 8. These methods were based on previous results[5], but not identical as the details of the procedures were not initially available.

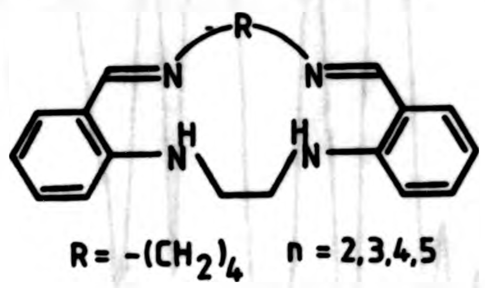


Fig 3.1 Tetra-aza macrocycles prepared in this project.

The times necessary for complete reaction were judged by removing aliquots every few hours, and examining the infrared spectrum of the isolated material. The disappearence of the carbonyl stretch at 1660 cm^{-1} indicated complete conversion of the C_2-dialdehyde (3.1) precursor. A slight excess of diamino compound was added to ensure high yields based on the C_2-dialdehyde (3.1).

3.2.2 Octa-azamacrocycles

3.2.2.1 Preparation of the 28-membered ring compound H_4cyendimer (3.4)

For the dimer 3.4, two preparative methods were possible (scheme 3.4).

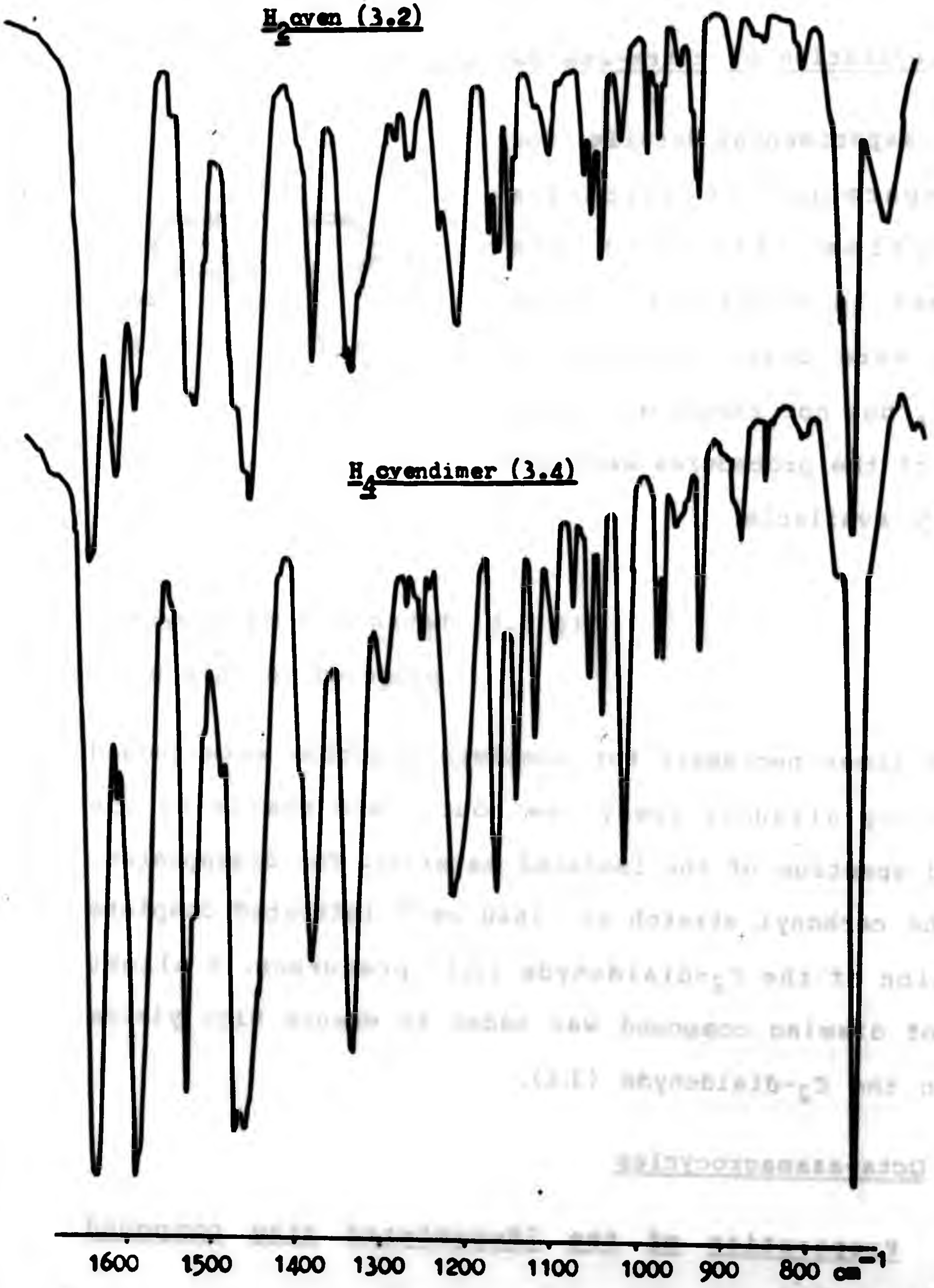
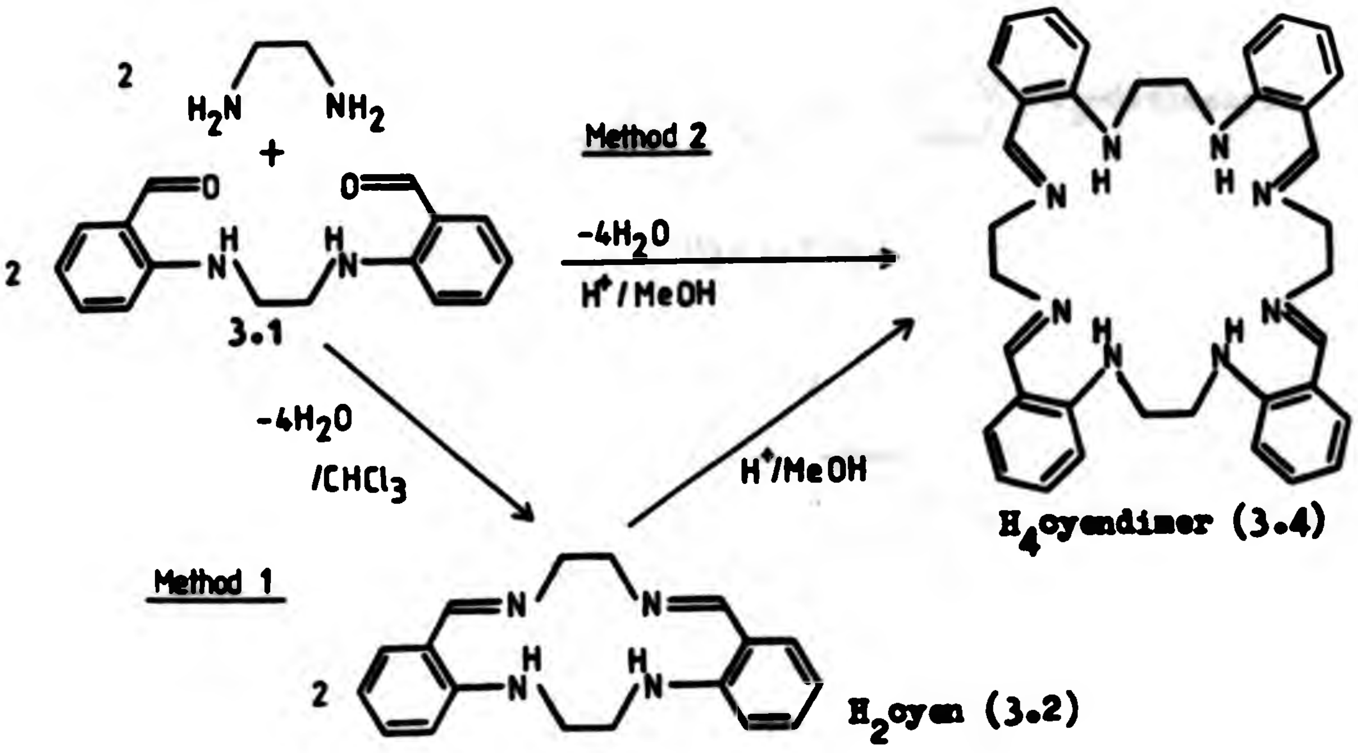
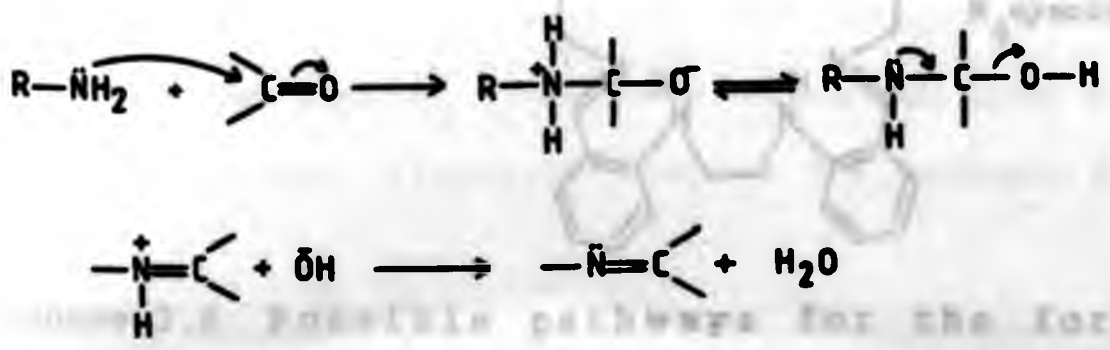


Fig 3.2 Infrared spectra of H_2cyen (3.2) and H_4cyendimer (3.4) (prepared as the nujol mull).

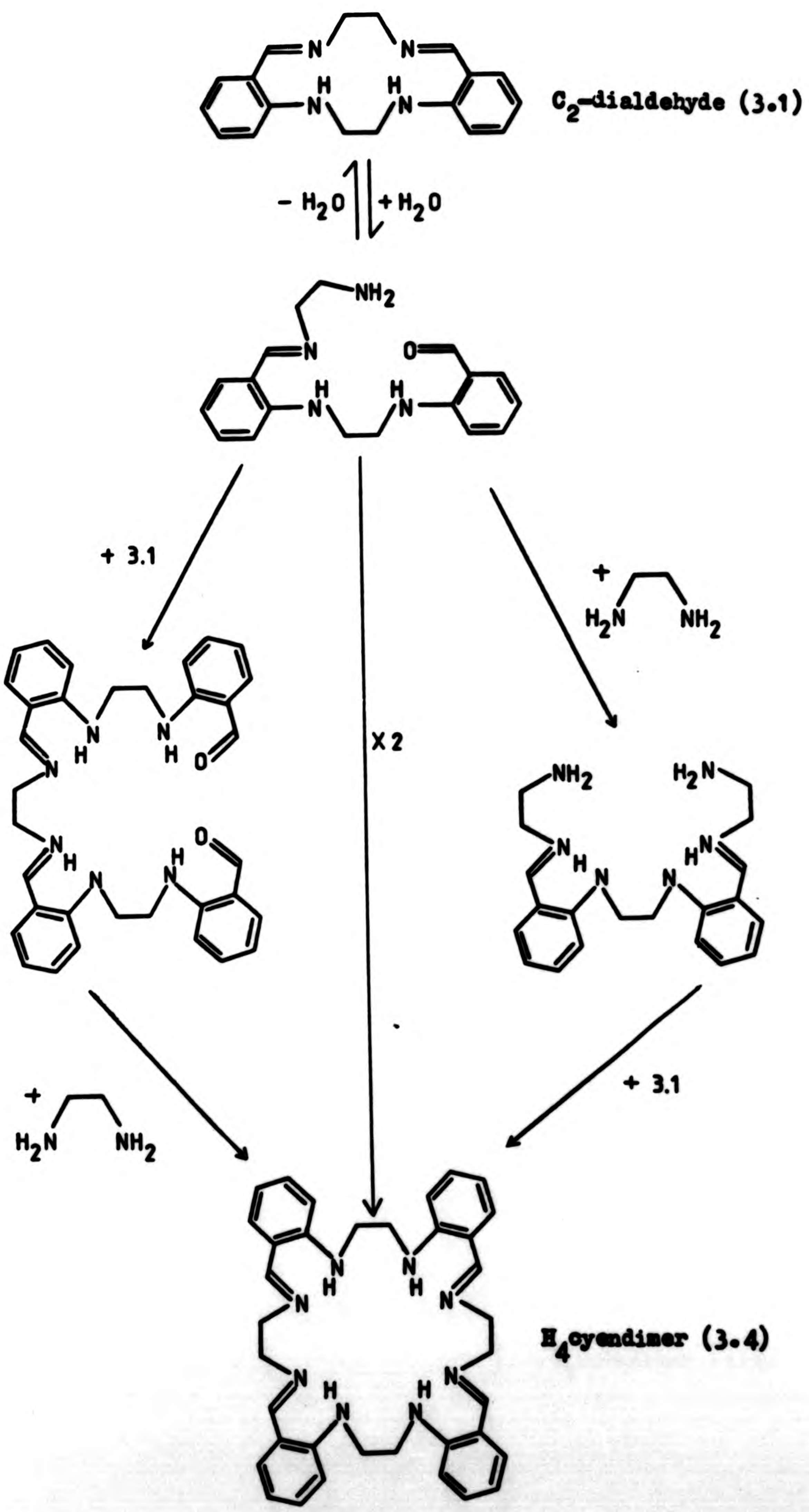


Scheme 3.4 Two methods for the formation of H_4cyendimer (3.4).

Method 1 involves isolation of the monomer H_2cyen (3.2), followed by conversion to the dimer 3.4. This reaction can be followed by the different infrared spectra of 3.4 and H_2cyen (fig 3.2 facing page). Method 2, an <u>in situ</u> reaction can be followed by removing aliquots every few hours, and comparing their infrared spectra to those from method 1. The reaction path for imine formation from carbonyl and amine groups[5] (scheme 3.5) is reversible, and conversion of the monomer to the dimer could take place by one or more pathways[6] (scheme 3.6). The imine intermediates shown in the pathways in scheme 3.6 could also exist with one or more of the imine bonds in the carbinolamine form.



Scheme 3.5 Imine formation.



C_2-dialdehyde (3.1)

H_4cyendimer (3.4)

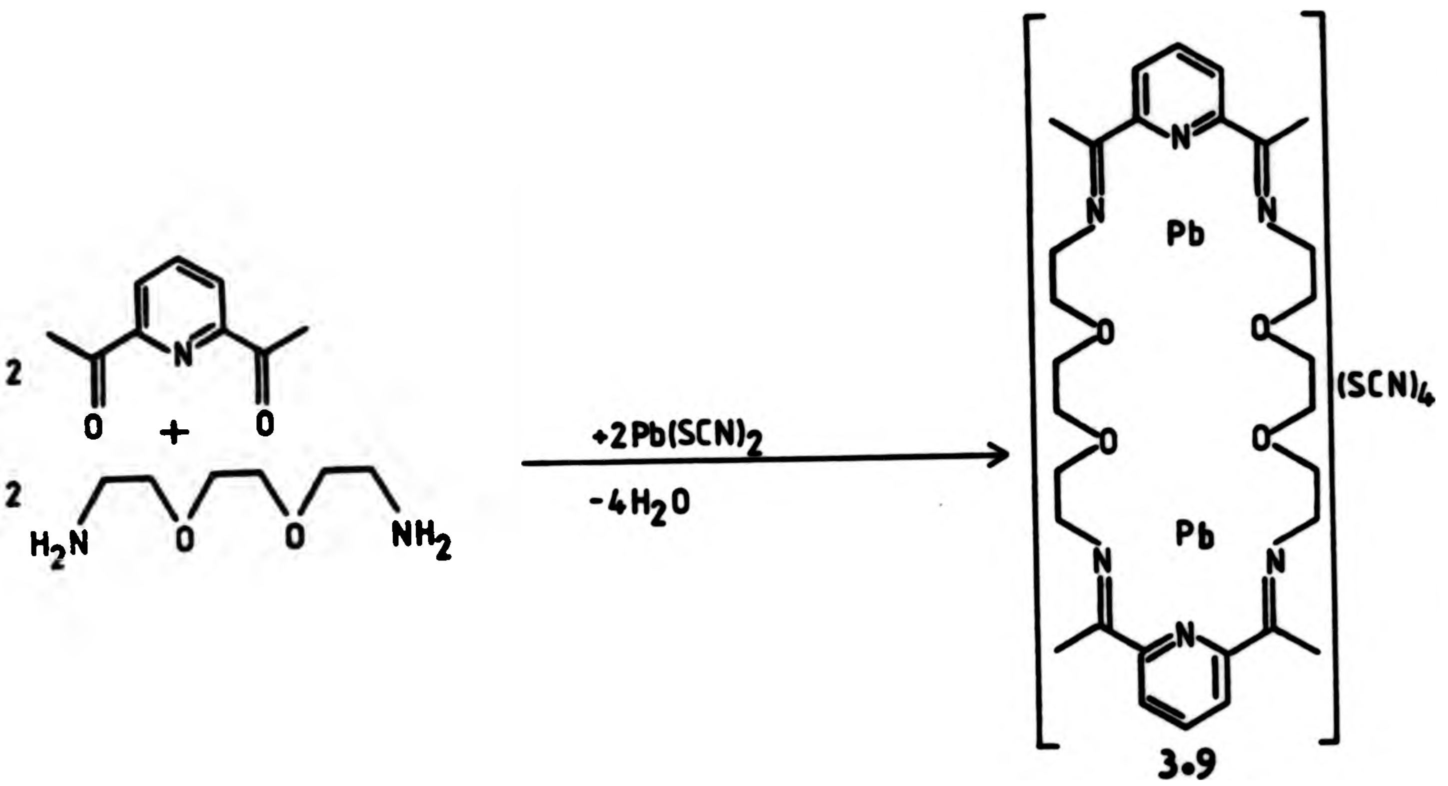
Scheme 3.6 Possible pathways for the formation of H_4cyendimer (3.4).

3.2.2.2 30 and 36 membered ring, H_4cyprodimer (3.7) and H_4cyhexdimer (3.8)

The reaction of the 1,6-diaminohexane or 1,3-diaminopropan-2-ol with C_2-dialdehyde (3.1) in methanol (section 8) formed their respective tetra-imine macrocycles directly without the related di-imines being detected. No catalyst was required for either of these reactions. Characterisation was made by elemental analysis and infrared spectra which compared with previously characterised samples[4]. Other diamino compounds were reacted with C_2-dialdehyde and found to form the mononucleating macrocycles (fig 3.1) previously reported by Peters[4]. The macrocyclic tetra-imine H_4cyendimer (3.4) has been shown to yield the di-imine nickel(II) complex[2] (3.3, scheme 3.2) on prolonged heating in methanolic nickel(II) acetate. Apart from this result, no reports on the interaction of 3.4 with metal ions have been reported.

3.2.3 Related ligands and the importance of intramolecular hydrogen bonding

Other [2+2] condensations to give large ring macrocycles have been reported, for example the 30-membered tetra-imine ligand[7] has been obtained from a 'template' reaction as its bilead(II) complex 3.9 (scheme 3.7).



Scheme 3.7

The free ligand of 3.9 has not been isolated, but other metal complexes can be prepared by transmetallation[6] procedures. This suggests that the lead(II) ion is essential in the ligand formation, and plays a major role in stabilising the macrocycle. A different stabilising influence is present in the macrocycles based on the precursor C_2-dialdehyde (3.1). It has been suggested[1] that the o-iminoanilino units present in the free ligands are stabilised by intramolecular hydrogen bonding (fig 3.3). This intramolecular hydrogen bonding will have the effect of reducing the repulsions between lone-pairs of electrons in the macrocycle cavities. A similar role can be assigned to metal ions in stabilising macrocyclic imines e.g. the Pb^{2+} ions in the complex 3.9.

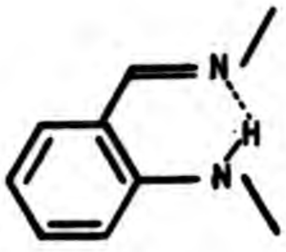
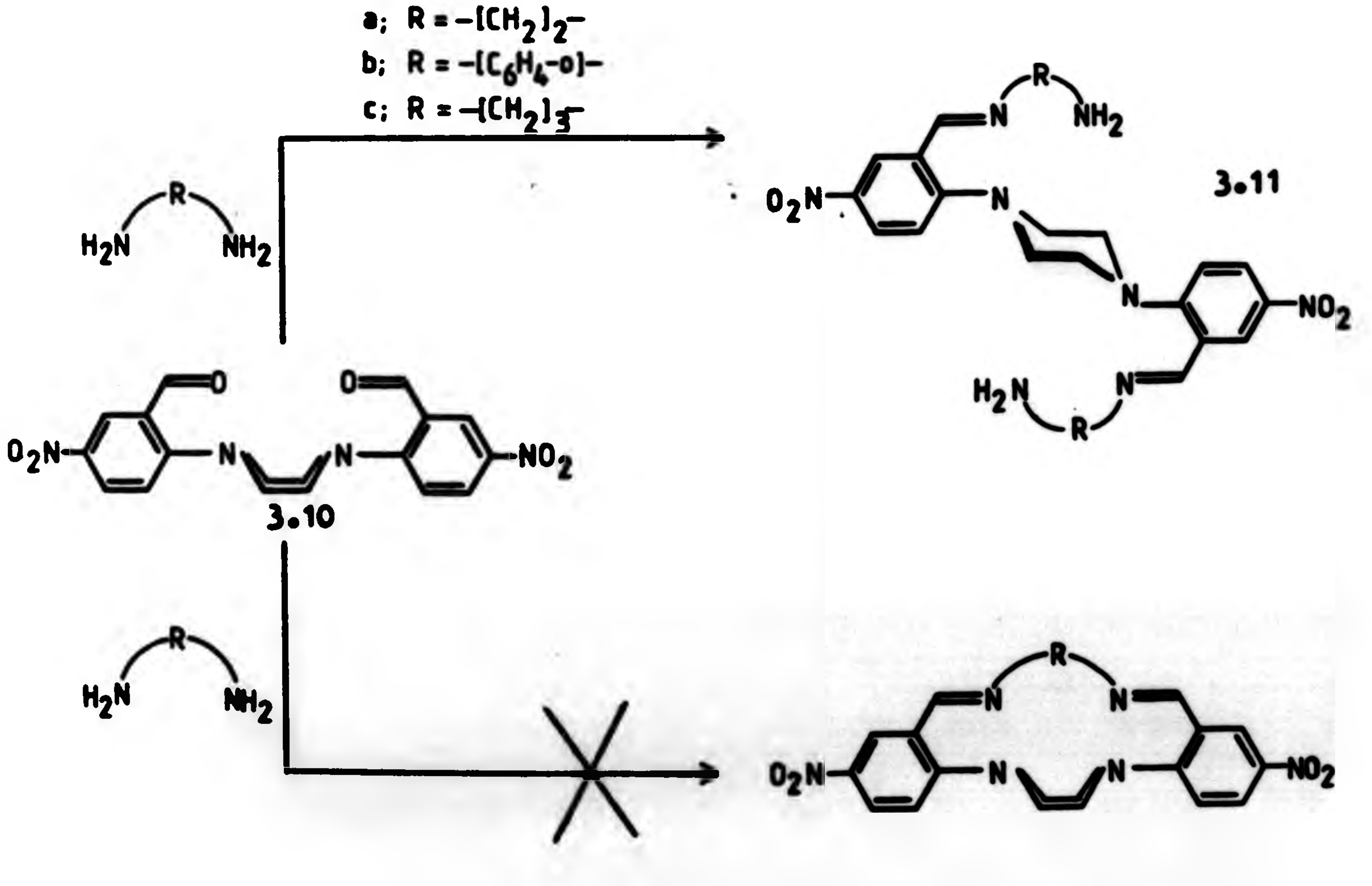


Fig 3.3 Intramolecular hydrogen bonding in the o-imino-anilino unit

A precursor (3.10) related to C_2-dialdehyde (3.1) but without the anilino hydrogens, has been shown[1] to form [2+1] condensation products (3.11, scheme 3.8) when treated with a molar equivalent of a diamino compound. No cyclic monomers equivalent to those shown in scheme 3.1 were obtained using conditions which had been successful in obtaining cyclic di-imines from the C_2-dialdehyde (3.1).



Scheme 3.8

There are two main reasons why the [2+1] condensation product is preferred in reactions of 3.10.

1). The conformation of the precursor (3.10) will probably be in the staggered conformation, due to the more stable 'chair' arrangement of the piperazine bridge[8]. This gives an extended conformation with the terminal aldehyde functional groups well separated from each other. A higher energy 'boat' form of the piperazine bridge would be required in the cyclic monomer.

2). There would be a very unfavourable interaction in the centre of the ring (fig 3.4) between the lone-pairs on the four nitrogen atoms. The structure determination for two of the [2+1] products (3.11 a and b) shows that they adopt an extended configuration which minimises lone-pair:lone-pair repulsion (fig 3.4).

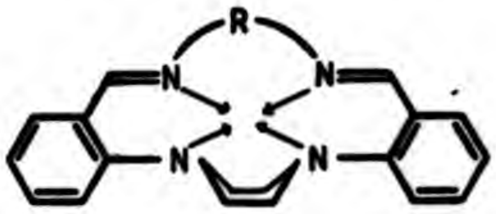
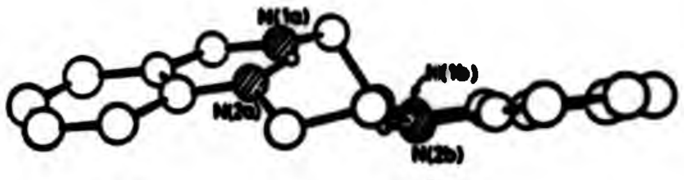
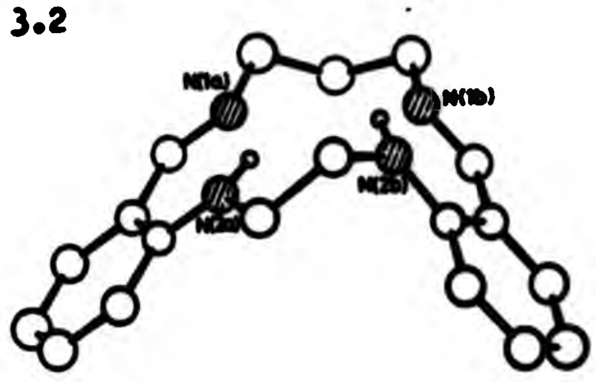


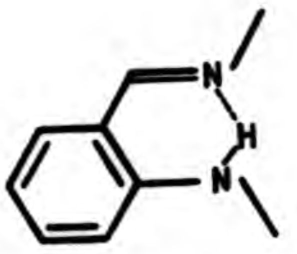
Fig 3.4 Lone-pair:lone-pair interaction for the piperazine bridged tetra-azamacrocycle

The structures of a number of related macrocyclic di-imines (see 3.2 and 3.12, fig 3.5) have been determined[1], and while the overall configuration of the macrocycles differ considerably, in each case the planarity of the o-iminoanilino units (3.13) are preserved (fig 3.5).



3.2





3.12 3.13

Fig 3.5 (a) The molecular configurations of the 14 and 15-membered macrocyles (3.2 and 3.12). (b) The o-iminoanilino unit.

3.2.4 Analysis of physical data

In solution the intramolecular hydrogen bonding can sometimes be supported by ^1H nmr spectra. Usually the rate of exchange for anilino hydrogens with the solvent is very fast and no coupling can be observed. However, intramolecular hydrogen bonding reduces the rate of exchange and weak coupling can sometimes be found.

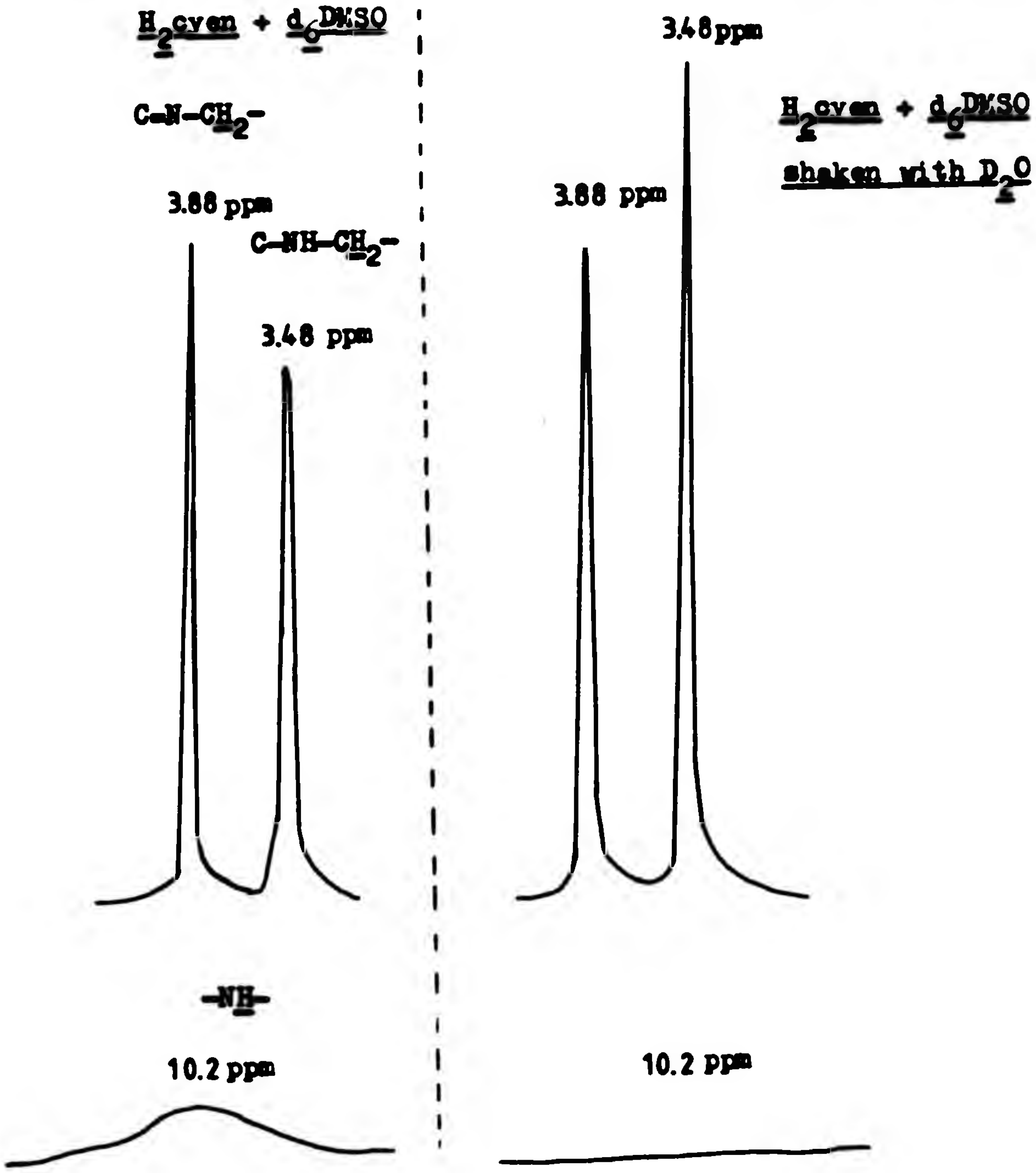


Fig 3.6 Observed ^1H nmr for H_2cyen (3.2) (d_6-DMSO).

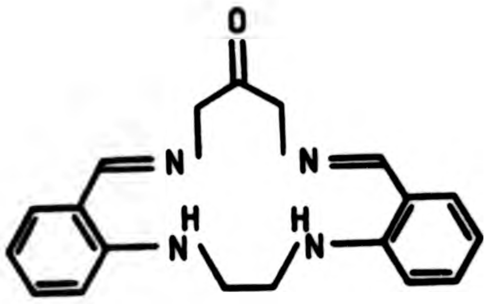
The coupling of the anilino protons with those protons on the adjacent carbon atom (fig 3.6) should give rise to a doublet at 3.48 ppm, and a triplet for the anilino protons at 10.24 ppm but the weak coupling only causes a broadening of the signal (3.48 ppm). After deuterium exchange, the coupling disappears, and the sharpness of the signal (3.48 ppm) increases relative to the rest of the spectrum. No other structural information can be deduced from the ^1H nmr, and as both monomer H_2cyen (3.2) and dimer 3.4 show similar spectra (table 3.1) therefore it is not possible to use ^1H nmr to differentiate between the two compounds.

H_2cyen (3.2) ppm	H_4cyendimer (3.4) ppm		Assignment
23°C	23°C	60°C	
3.48 s	3.40 s	3.50 s	$C-NH-C\underline{H}_2-$
3.88 s	3.8 s	3.75 s	$C=N-C\underline{H}_2-$
10.24 b	10.1 b	9.23 b	$-N\underline{H}-$
8.38 s	8.50 s	8.43 s	$N=C\underline{H}-$
6.45-7.3 m	6.40-7.30 m	6.57-7.30 m	Aromatics $-C\underline{H}$

Table 3.1 Comparison of ^1H nmr of H_2cyen (3.2) and H_4cyendimer (3.4) (d_6-DMSO). (s=singlet, m=multiple, b=broad).

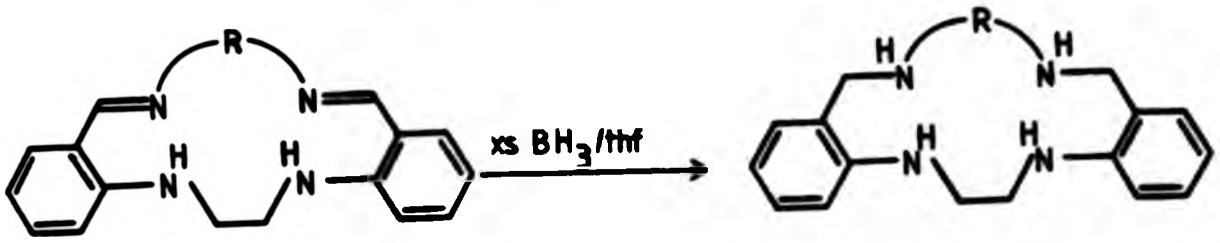
H_4cyendimer (3.4) was very involatile, and gave a low intensity mass spectrum (from eims) which could not be used for comparison with that of the monomer. The eims of H_4cyprodimer (3.7) contained a molecular ion at m/e = 340 corresponding to a dehydrogenated version of the monomer (3.14). The appearence of the monomer could be due to symmetrical fragmentation and dehydrogenation of the dimer or a small amount of monomer impurity which would be more volatile than 3.7 and give a misleading mass spectrum. However, the high probe temperature required to volatilise the material suggests that this latter possibility is not the case. An eims of H_4cyhexdimer (3.8) could not be obtained.

All three dimers showed infrared spectra which corresponded to samples which had previously[3] been characterised by fdms and X-ray crystallography.



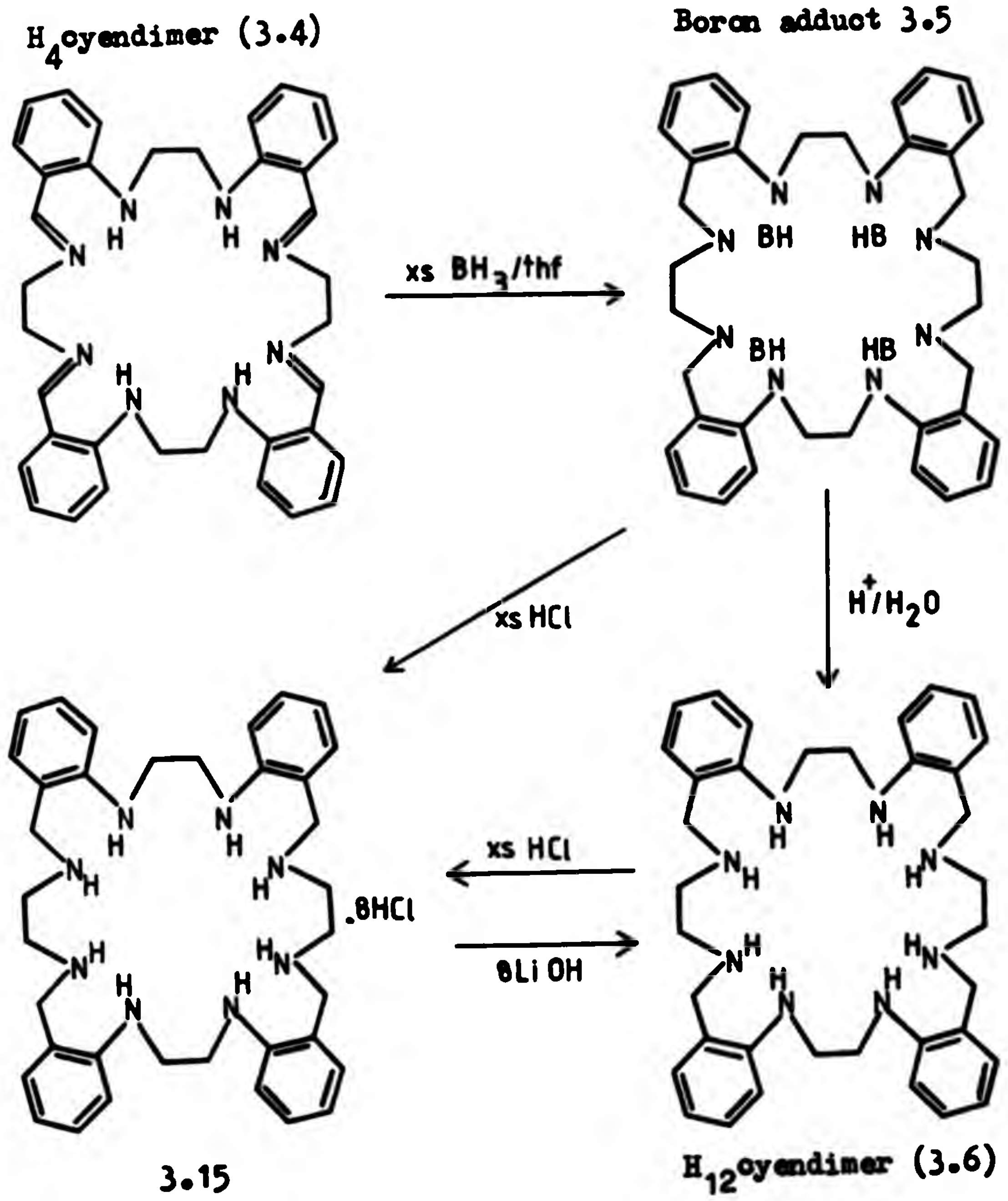
3.14

3.2.5 Reduction of di- and tetra-imines (scheme 3.9)



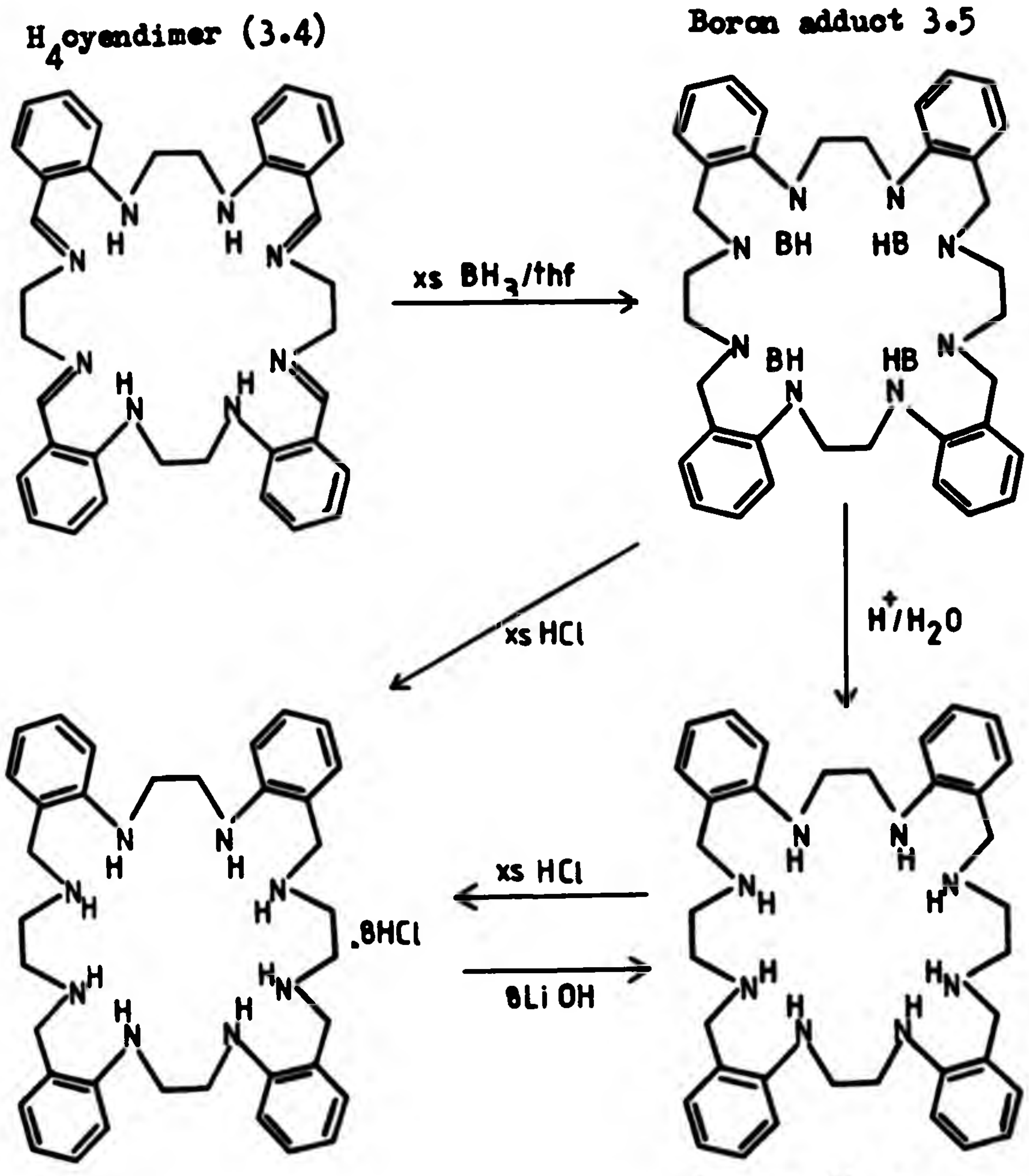
Scheme 3.9

A number of literature methods[9] are available for hydrogenation of imine functions, including H_2/Pt, $NaBH_4$ or $LiAlH_4$. The hydride reducing agents have one disadvantage, that the spent reducing agent sometimes contaminates the insoluble product. An improved method[3] involves the use of a solution of BH_3 in thf (BH_3/thf) which reduces an imine to a secondary amine (scheme 3.10).



Scheme 3.10

An intermediate boron adduct 3.5 has be isolated during the reaction of BH_3/thf with H_4cyendimer (3.4) and structurally characterised[4]. Addition of hydrochloric acid was reported[6] to hydrolyse the boron adduct 3.5 and liberate the free octa-amine ligand 3.6. Excess hydrochloric acid will produce the hydrochloride salt 3.15 of the octa-amine 3.6, which can be particularly useful if the free polyamine is air sensitive (eg tri and tetraamino benzene are isolated as their hydrochloride salts see chapter 4). The BH_3/thf reduction of a polyimine macrocycle can be monitored by the changing infrared spectra (scheme 3.11).



Scheme 3.10

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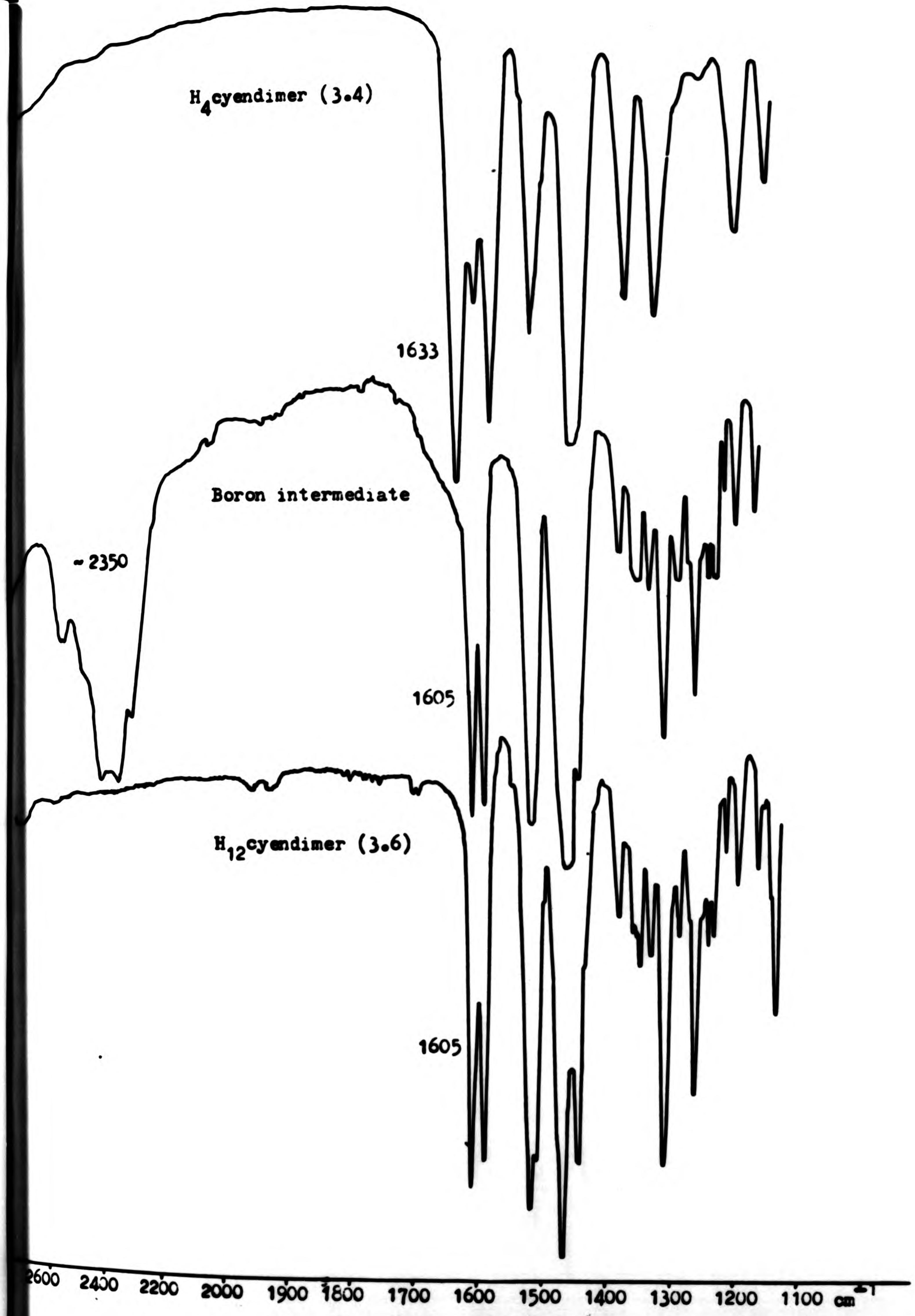


Scheme 3.11 Infrared changes during the BH$_3$/thf reduction of the tetraimine macrocycle 3.4.

The reduced monomers were characterised by eims, elemental analysis, and ^{1}H nmr. Methods for characterisation of the dimers depended on their solubility and volatility. H_{12}cyendimer (3.6) was characterised by X-ray structural analysis, eims, elemental analysis, infrared and ^{1}H nmr, whereas the less soluble H_{12}cypro and H_{12}cyhexdimers were identified on the basis of C,H,N analytical data, and comparison of their infrared spectra with those of H_{12}cyendimer (3.6) and "monomer" tetra-aza analogues. A description of the structure of 3.5 determined by X-ray crystallography is presented below.

3.2.6 The crystal structure of H_{12}cyendimer (3.6)

The macrocycle has a centre of symmetry as shown in fig 3.7. No evidence for intermolecular hydrogen bonding or solvates was found from the structure determination. The structure was solved using direct methods as described in section 7.4.

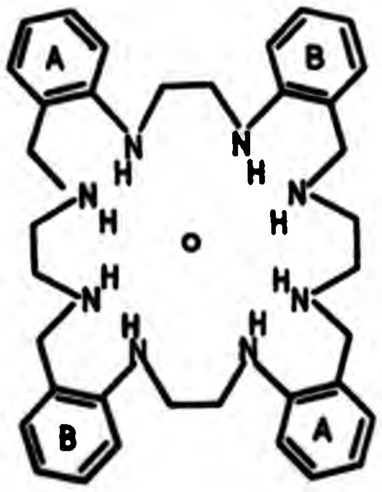
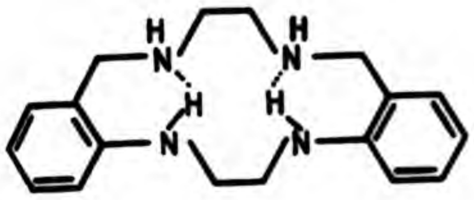


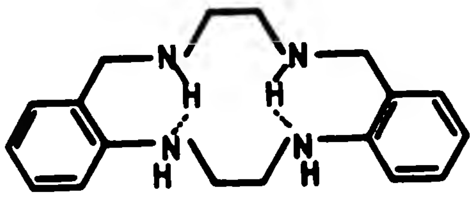
Fig 3.7 Schematic diagram of the H_{12}cyendimer (3.6) showing the crystallographic inversion centre.

3.2.6.1 Intramolecular hydrogen bonding

As described earlier (section 3.2.4) the stability of the o-iminoanilino units (fig 3.3) present in the polyimine macrocycles is at least partly due to intramolecular hydrogen bonding involving the anilino hydrogen atom (3.16). For the reduced macrocycles a variation may be possible involving the benzylamino hydrogen atom (3.17) (fig 3.8).



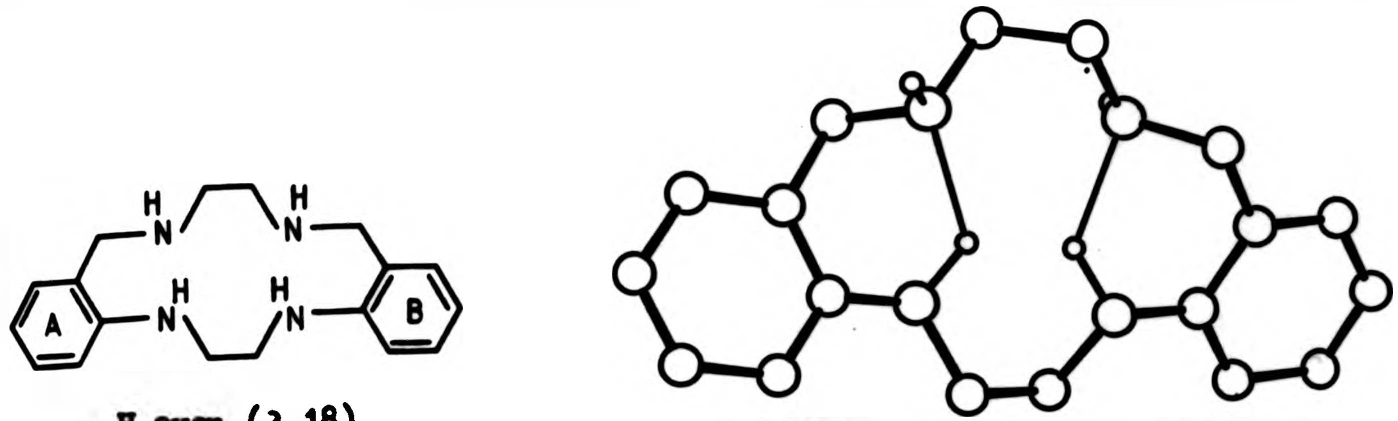
3.16



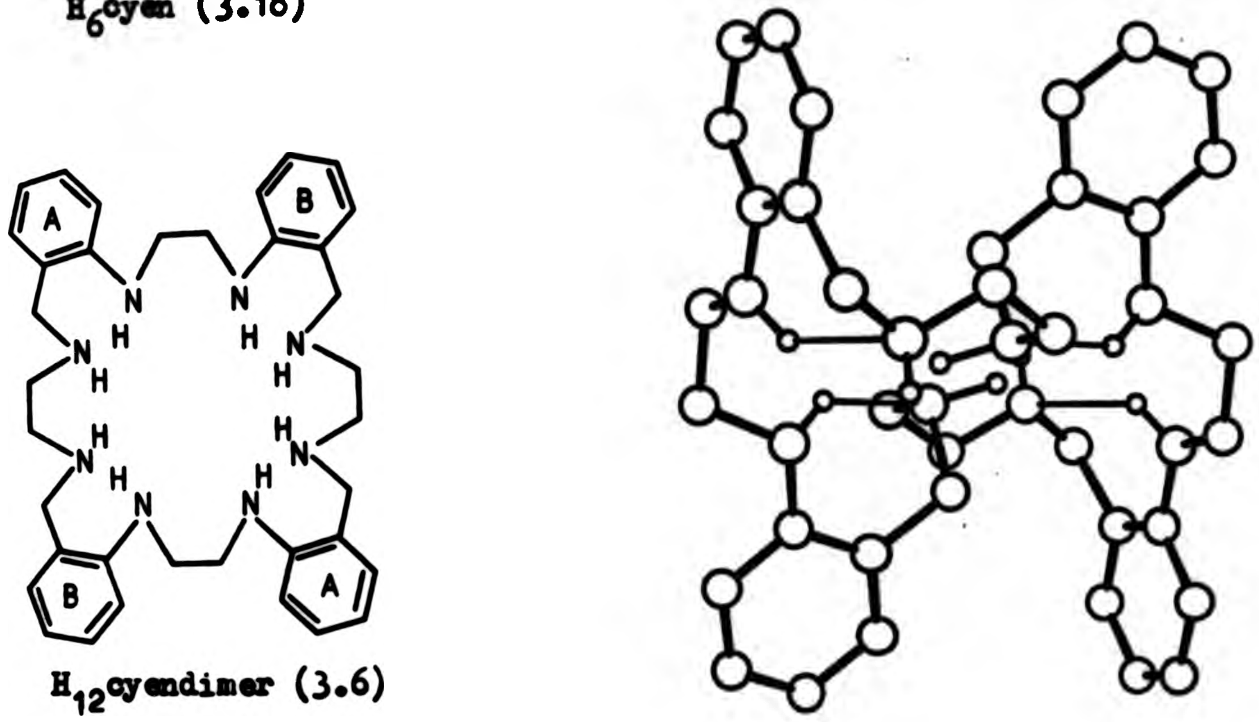
3.17

Fig 3.8 Two types of intramolecular hydrogen bonding.

It was found from the structural analysis of H_{12}cyendimer (3.6) that the intramolecular hydrogen bonding was of the type shown in 3.16. This type was also found[4] for the reduced monomer H_6cyen (3.18). The ortep diagrams of these two structures are shown in fig 3.9.



H_6cyen (3.18)



H_{12}cyendimer (3.6)

Fig 3.9 Schematic and ortep diagramsof H_6cyen (3.18) and H_{12}cyendimer (3.6).

The intramolecular hydrogen bonding (3.16) results in the anilino nitrogen atoms (N2) having a more planar enviroment than the benzylamino nitrogen atoms (N1) (table 3.2). The anilino nitrogen atoms will be encouraged to adopt a planar configuration (sum of bond angles approach 360°), therefore adopting an orientation of the lone-pair to provide orbital overlap with the pi orbitals from the phenyl ring (fig 3.10). The anilino nitrogen atoms thus have a higher degree of sp^2 hybridisation than the benzylamino nitrogen atoms. This is shown for both monomer 3.18 and dimer 3.6 in table 3.2. The sums of the bond angles of the benzylamino nitrogen atoms are close to the theoretical value of 321-324° estimated for the tetrahedral angles of trimethylamine[10] (fig 3.11). One exception to this are the angles at N(1b) in the tetra-aza system 3.18 which are anomalously large, possibly due to the atom N(1b) being involved in intermolecular hydrogen bonding.

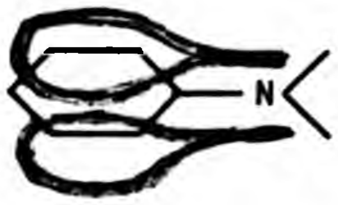


Fig 3.10 Pi - Pi overlap of a sp^2 hybridised anilino nitrogen atom with the phenyl ring.

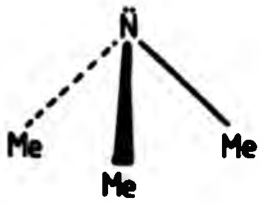


Fig 3.11 The tetrahedral structure of trimethylamine

Anilino Nitrogen Atoms (N2)

Bond angles/Å	H_6cyen (3.18)		H_{12}cyendimer (3.6)	
	Part A	Part B	Part A	Part B
C1-N2-C2	119.7(6)	119.5(5)	119.3(9)	123.5(9)
C1-N2-H	110.8(5)	107.5(5)	108.6(4.8)	120.4(7.1)
C2-N2-H	120.1(6)	115.6(6)	113.2(5.0)	108.8(5.8)
Sum of angles	350.6	342.6	341.1	352.7

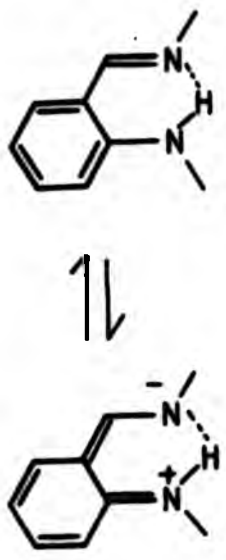
Benzylamino Nitrogen Atoms (N1)

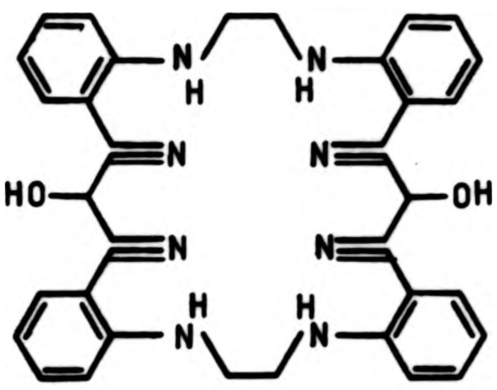
Bond angles/Å	H_6cyen (3.18)		H_{12}cyendimer (3.6)	
	Part A	Part B	Part A	Part B
C8-N1-C9	113.2(6)	112.7(6)	113.6(8)	111.8(8)
C8-N1-C2	100.9(5)	115.5(5)	107.1(5.3)	112.8(7.0)
C8-N1-H	99.8(5)	111.8(5)	100.4(5.2)	98.3(6.9)
Sum of angles	313.9	340.0*	321.1	322.9

Table 3.2 Angles about the nitrogen atoms in the macrocycles 3.6 and 3.18.

* Intermolecular hydrogen bonding causes this anomalous value (see text).

For the polyimine macrocycles e.g. H_4cyprodimer (3.7), the anilino nitrogen atoms are very nearly planar (table 3.3). In these systems the sp^2 hybridisation at the anilino nitrogen atoms allows delocalisation of electrons over the o-imino-anilino portion of the molecule, as represented by the resonance forms shown in fig 3.12. A comparison of bond angles about the anilino nitrogens is made in table 3.3 between H_4cyprodimer (3.7) and the boron adduct 3.5.





H_4cyprodimer (3.7)

Fig 3.12 Resonance forms of H_4cyprodimer (3.7) contributing to the sp^2 hybridisation of the anilino nitrogen atoms.

	<u>Anilino nitrogen atoms</u>		
	Boron adduct (3.5)		H_4cyprodimer (3.7)
<u>Bond angles/Å</u>	<u>Part A</u>	<u>Part B</u>	
C1-N2-C2	120.7(7)	120.3(7)	123.2(4)
C1-N2-H(or B)	120.2(8)	119.4(7)	115.3(4)
C2-N2-H(or B)	118.7(8)	120.1(8)	121.5(4)
Sum of angles	359.6	359.8	360.0

	<u>Benzylamino nitrogen atoms</u>		
	Boron adduct (3.5)		
<u>Bond angles/Å</u>	<u>Part A</u>	<u>Part B</u>	
C8-N1-C9	113.4(7)	113.5(7)	-
C8-N1-B	124.5(8)	123.3(8)	-
C8-N1-B	120.4(7)	121.3(8)	-
Sum of angles	358.3	358.1	

Table 3.3 Angles around the nitrogen atoms in 3.5 and 3.6

3.2.6.2 Conformational variations

The o-aminobenzyl six-membered rings of H_6cyen (3.18) and H_{12}cyendimer (3.6) are approximately planar (table 3.4). The atomic coordinates of the atoms N1,N2,C2,C7 and C8 used in the calculation of the plane do not deviate by more than 0.45 Å from the plane. From the data in table 3.4, it can be seen that the deviation of the atoms in part A of 3.18, resemble those deviations in part A of 3.6, and similarly for part B of both ligands. The root mean square deviation for both compounds are 0.28. Given that the o-aminobenzyl fragments are approximately planar the conformation of the molecule H_{12}cyendimer (3.6) will depend on the nature and geometry of the bridges between the o-aminobenzyl units. The two types of bridging units L1 and L2 are shown in fig 3.13.

	H_{12}cyendimer (3.6)		H_6cyen (3.18)	
Part	**A**	**B**	**A**	**B**
N1	0.29	-0.33	0.32	-0.31
N2	-0.22	0.24	-0.24	0.23
C2	0.20	-0.24	0.22	-0.20
C7	0.12	-0.11	0.12	-0.13
C8	-0.39	0.45	-0.41	0.42
RMSD	0.28		0.28	

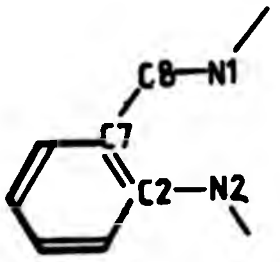


Table 3.4 Deviation of atoms from their best plane (Å), and the root mean square deviation (RMSD) of the o-aminobenzyl fragments.

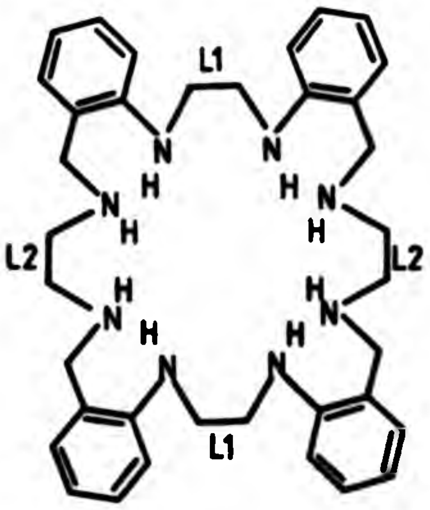


Fig 3.13 The two types of bridge between the o-aminobenzyl units in H_{12}cyendimer. The torsion angles for the two types of bridge are shown for four related structures in table 3.5.

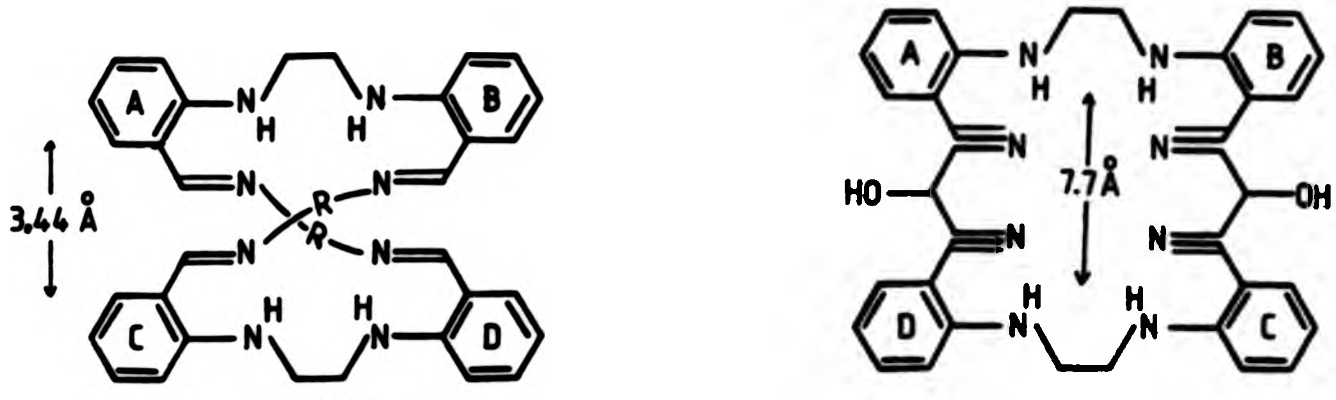
	H_6cyen (3.18)	H_{12}cyendimer (3.6)	H_4cyendimer (3.4+)	Boron adduct (3.5)
L1 (N2C1C1N2)	62.14	70.66	58.76*	-70.16
L2 (N1C9C9N1)	70.04	59.60	59.76*	171.92

*Average of two values.
+Ligand 3.6 of complex $[Cu_2(H_4cyendimer)](ClO_4)_3$ (section 3.4)

Table 3.5 Torsion angles for the L1 and L2 bridges in four related structures.

In each structure the ethane bridge L1 between the anilino nitrogen atoms has a gauche configuration with torsion angles fairly close to the value (60°) expected for the lowest energy form of this configuration. The overall molecular configurations of the dimers (table 3.5) are dictated by the ethane bridges (L2, fig 3.13) between the benzylamino or imino nitrogen atoms (N1). The conformation of the bridge L2 (N1C9C9N1) may allow the molecule to twist (fig 3.14). The configuration of the ligand H_4cyprodimer

(3.7) was the first dimer (based on the precursor C_2-dialdehyde) structurally determined. The L2 bridges contain three carbon atoms and not two as for the other dimers (table 3.5). It can be seen in fig 3.14 that the ligand H_4cyprodimer is twisted so that the two halves of the molecule (AB and CD) become very close. The distance between the centroids* of the two sets (AB and CD) of nitrogen atoms (3.20) is 3.44 Å compared with a calculated value (based on flat molecule 3.21) of 7.7 Å.



3.20 3.21

Fig 3.14 Distance between the two sets of nitrogen atoms in H_4cyprodimer (3.7).

The calculation of the distance between the centroids of two sets of nitrogen atoms were made in the following way.
The coordinates of the centroids were calculated by averaging the x,y and z coordinates for each of the two sets of four nitrogen atoms (when one set was related by symmetry only one needed to be calculated). These coordinates were assigned to 'dummy atoms' and used in a XANADU[12] calculation to retrieve the contact distances between the dummy atoms. If the the same type of molecular configuration is found in the dimers with shorter bridges(L2) than those in H_4cyprodimer, then the centroids of the two N_4 donor sets will be close together and a

dinuclear copper complex may be forced to adopt a very short copper-copper distance. This was found for a copper complex of H_4cyendimer (3.4) and is discussed in section 3.4. Reduction of the tetraimine compounds are expected to cause significant changes in the overall molecular configuration due to the tetrahedral disposition of the bonds about the benzylamino nitrogen atoms (table 3.2) as opposed to the planar arrangement found for the benzylimine nitrogen atoms. The benzylamino nitrogen atoms are part of the L2 bridge which may control the conformation of the molecule. In the following discussion the two terms "twisted" and "folded" are defined in fig 3.15.

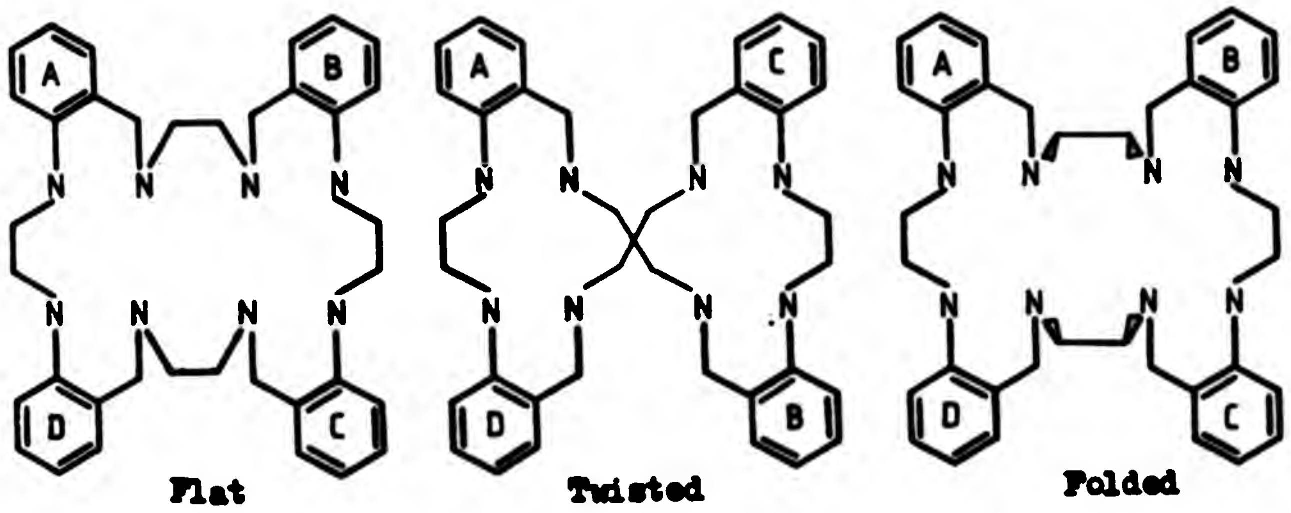


Fig 3.15 The twisted and folded conformations of the 28 membered ring

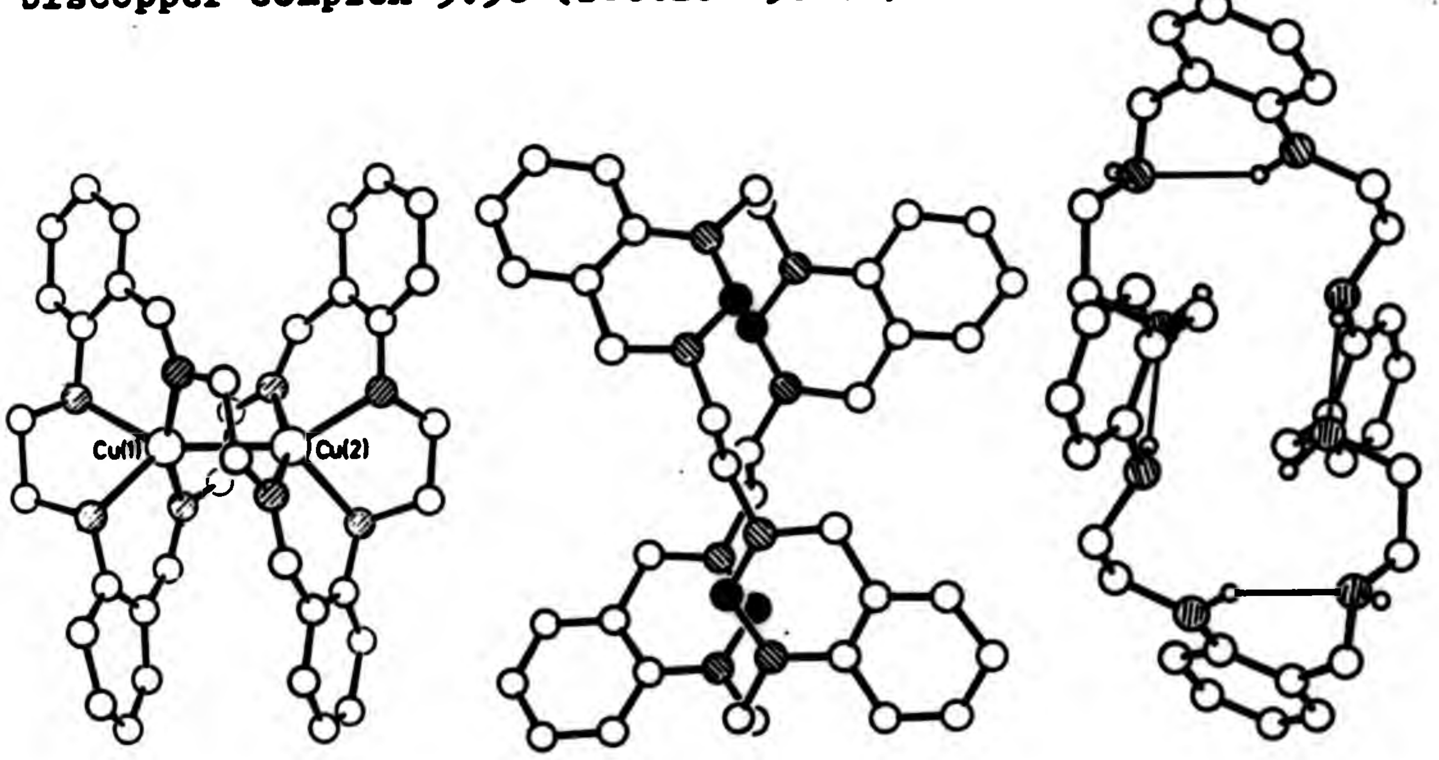
The reduction of H_4cyendimer caused the following changes in molecular configuration:

1). The tetraimine 3.4 is a twisted molecule (structually determined as the biscopper complex section 3.4) with a centroid-centroid (of the two sets of coordinating nitrogen atoms) distance of 3.71 Å.

2). Reduction of the free ligand 3.4 with BH_3/thf initially gave a boron adduct found to be partially twisted, with the L2 bridges in the transoid configuration.

3). The boron adduct hydrolysed to yield the octaamine and was shown to give a partially folded conformation as opposed to the twisted analogues. The three ortep diagrams of 3.4, 3.5 and 3.6 are depicted in fig 3.16.

Note: The structure of H_4cyendimer was determined as the biscopper complex 3.36 (section 3.4.1).



3.4 3.5 3.6

Fig 3.16 Ortep diagrams of H_4cyendimer (3.4), the boron adduct (3.5) and H_{12}cyendimer (3.6).

The close contact distance between the two sets of nitrogen atoms for 3.4 is dependent on the torsion angle of L2 (N1C9C9N1) being in a gauche configuration as opposed to a transoid arrangement which would extend the two halves of the molecule.

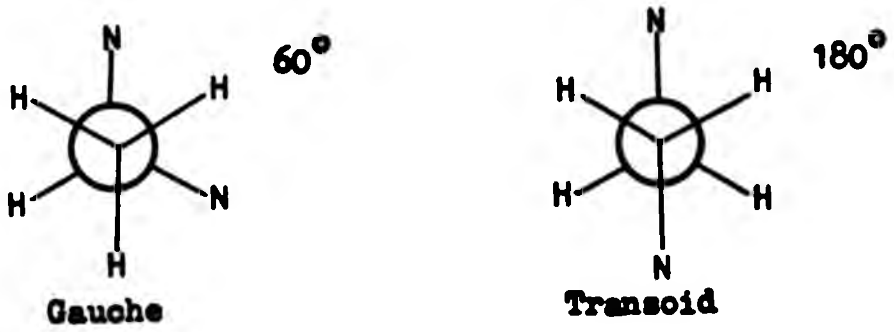
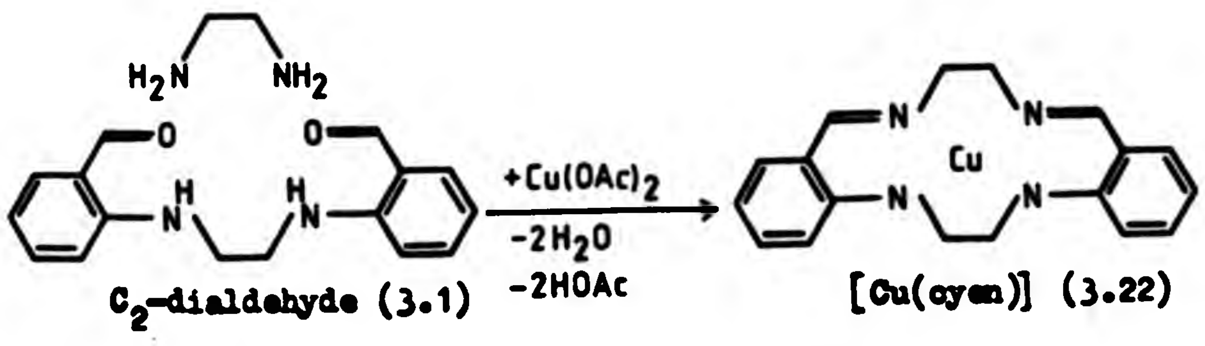


Fig 3.17 Schematic diagrams of the gauche and transoid[11] arrangements of a ethane bridge.

3.3.1 Copper complexes of aliphatic bridged tetra-aza macrocycles

3.3.1.1 Neutral copper(II) complexes

These are formed in reactions which involve the loss of hydrogen atoms from the anilino nitrogen atoms (scheme 3.12).



Scheme 3.12 Preparation of neutral copper(II) complexes (template method).

The template method[13] (scheme 3.12) involves an <u>in situ</u> reaction of the ligand precursors and copper(II) acetate. A reaction between the preformed ligand and copper(II) acetate did not give good yields or analytically pure samples for the macrocycles with aliphatic bridges between the imine nitrogen atoms. Yields for a series of complexes with different length bridging groups obtained from the template method are recorded in table 3.6.

Copper complex	Bridging group	Yield %	Reaction Time
[Cu(cyen)] (3.22)	$-(CH_2)_2-$	50	48
[Cu(cypr)] (3.26)	$-(CH_2)_3-$	53	18
[Cu(cybut)] (3.28)	$-(CH_2)_4-$	32	18
[Cu(cypen)]	$-(CH_2)_5-$	0	48
[Cu(cyhex)]	$-(CH_2)_6-$	0	96

Table 3.6 Template reactions

The reactions were monitored by withdrawing aliquots every few hours and examining the infrared spectra. Loss of the C_2-dialdehyde (3.1) characteristic absorption frequencies indicated the end of a reaction, and other analyses (C,H,N and Cu% and eims) were used to complete the characterisation. The X-ray structure of [Cu(cybut)] (fig 3.18) has been reported[14] as having an approximately planar N_4 coordination sphere[14], with the tetramethylene bridge in a half boat form.

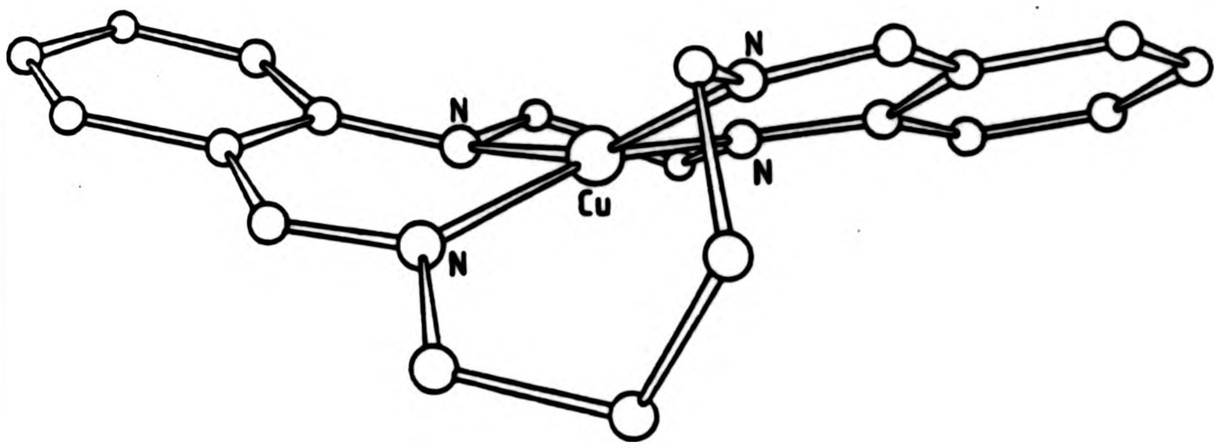


Fig 3.18 Ortep diagram of [Cu(cybut)] (3.28).

If the bridge is increased to five or more carbon atoms, then the four coordinating nitrogen atoms will be forced away from the approximately planar enviroment found for [Cu(cybut)] (3.28) and H_2cyen (3.2). The thermodynamic stability of the copper complexes [Cu(cypen)] and [Cu(cyhex)] are probably very low and cannot be easily isolated (table 3.6). No neutral copper(II) complexes have been prepared from the reduced ligand H_6cyen (3.18). The ease in preparing neutral copper(II) complexes from the di-imine macrocycles may be due to the stabilisation from resonance forms of the final complex (fig 3.19). The difficulty in preparing the neutral copper(II) complex of the ligand H_6cyen may be due to the lower thermodynamic stability of [Cu(H_4cyen)] (the lack of imine bonds prevents the resonance stabilisation found for [Cu(cyph)]).

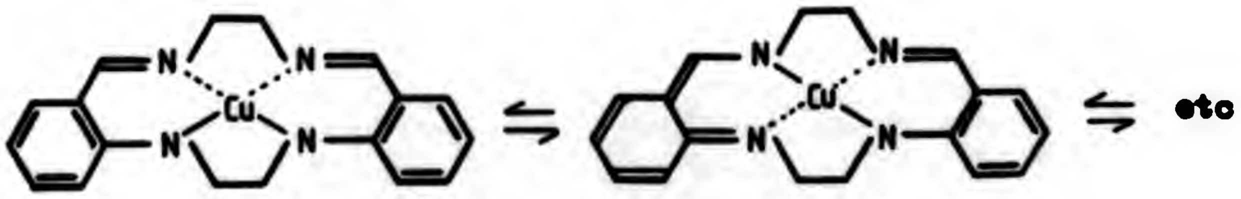
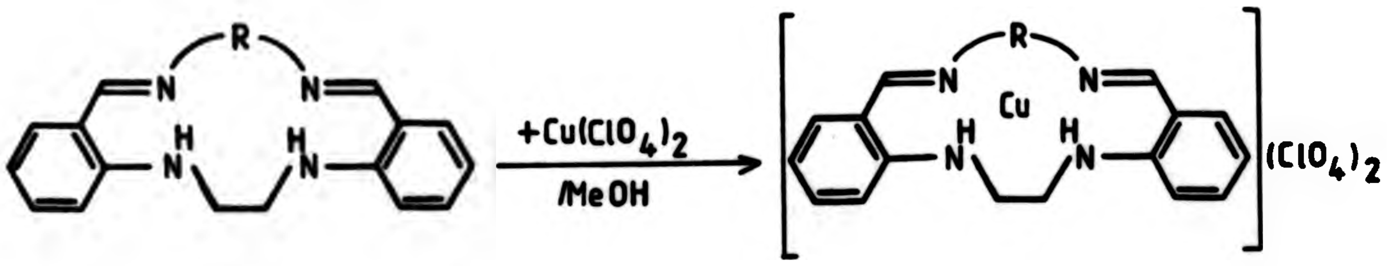


Fig 3.19 Resonance forms of [Cu(cyen)].

3.3.1.2 Cationic copper(II) complexes

The reaction between the preformed ligands and copper(II) perchlorate gave the copper(II) complexes without loss of the hydrogens from the anilino nitrogens (scheme 3.13), which were isolated as their relatively insoluble perchlorate salts. These reactions were fast (approximately 1 min) and only required gentle heating in methanol. Characterisation was made by elemental analysis and infrared (νClO_4 = 1100B). For ligands with bridges higher than four carbon atoms, no solid complexes were isolable. The reduced ligand H_6cyen (3.18) also formed a copper(II) perchlorate complex rapidly. Analytical and spectroscopic data for the monomer ligands and their complexes are given in table 3.7. The preparation of the reduced ligand H_6cyen could be monitored by the disappearence of the imine absorption band (infrared 1636 cm^{-1}) and the appearence of the NH stretch at 1606 cm^{-1} . The formation of the copper(II) complexes were monitored by withdrawing aliquots from the reaction mixture and observing their infrared spectra for absorption bands characteristic of the precursors.



Scheme 3.13

Table 3.7 Analytical and spectroscopic data for the mononucleating ligands and their copper(II) complexes.

	C %	H %	N %	Cu %
H_2cyen (3.2)	73.9	6.9	19.2	
(Calc. for $C_{18}H_{20}N_4$)	(73.4)	(7.0)	(18.6)	
Infrared absorptions cm^{-1}	3240,3146,3046,3016,2928,1636, 1616,1583,1577,1521,1516,1511, 1416,1401,1372,1332,1328,1202.			
[Cu(cyen)] (3.22)	60.1	4.6	15.7	17.0
(Calc. for $CuC_{18}H_{18}N_4$)	(61.1)	(5.1)	(15.7)	(18.0)
Infrared absorptions cm^{-1}	3018,2908,2876,2856,2826,2794, 1615,1597,1320,1467,1453,1442, 1060,1032,955,936.			
[Cu(H_2cyen)](ClO_4)$_2$ (3.23)	38.0	3.7	10.1	11.6
(Calc. for $CuC_{18}H_{20}N_4Cl_2O_8$)	(39.0)	(3.6)	(10.1)	(11.5)
Infrared absorptions cm^{-1}	3548,3258,2953,2898,1666,1620, 1602,1578,1494,1460,1412,1303, 1090.			
Uv/vis (methanol)	220(14028), 270(5550), 446(226).			
H_6cyen (3.18)	71.9	8.2	19.4	
(Calc. for $C_{18}H_{24}N_4$)	(72.9)	(8.2)	(18.9)	
Infrared absorptions cm^{-1}	3313,3251,3222,3182,3121,1606, 1582,1518,1502,1399,1334,1320, 1334,1320,1272,1142.			
Uv/vis (methanol)	220(14028),270(5550),446(226).			
[Cu(H_6cyen)](ClO_4)$_2$ (3.24)	38.8	4.4	9.9	11.0
(Calc. for $CuC_{18}H_{24}N_4Cl_2O_8$)	(38.8)	(4.4)	(9.9)	(11.0)
Infrared absorptions cm^{-1}	3528,3238,3193,1610,1587,1497, 1465,1369,1220,1188,1170,1090, 995,963.			
Uv/vis (methanol)	218(3073),278(1100),310(664), 510(285).			
H_2cypr (3.25)	74.3	7.5	18.2	
(Calc. for $C_{19}H_{22}N_4$)	(74.5)	(7.2)	(18.3)	
Infrared absorptions cm^{-1}	3208,3168,3140,1627,1594,1576, 1134,1064,1042,974,965,928,918.			

[Cu(cypr)] (3.26)	62.1	5.0	14.8
(Calc. for $CuC_{19}H_{20}N_4$)	(62.0)	(5.5)	(15.2)
Infrared absorptions cm^{-1}	3020,1610,1524,1510,1478,1432,1402,1392,1362,1340,1252,1200,1165,1132,1100,1072,1040,1032,953,935.		
H_2cybut (3.27)	75.2	7.1	17.3
(Calc. for $C_{20}H_{24}N_4$)	(75.0)	(7.5)	(17.5)
Infrared absorptions cm^{-1}	3230,3085,1638,1620,1597,1586,1532,1345,1288,1213,1280,1162,1088,1080,1052,1002,986.		
[Cu(cybut)] (3.28)	61.7	5.8	14.0
(Calc. for $CuC_{20}H_{22}N_4$)	(62.9)	(5.8)	(14.7)
Infrared absorptions cm^{-1}	3072,3027,2980,2890,1604,1524,1454,1440,1401,1364,1350,1439,1257,1214,1204,1194,1172,1164,1132,1094,1074,1042,1035,1008,1000,970.		

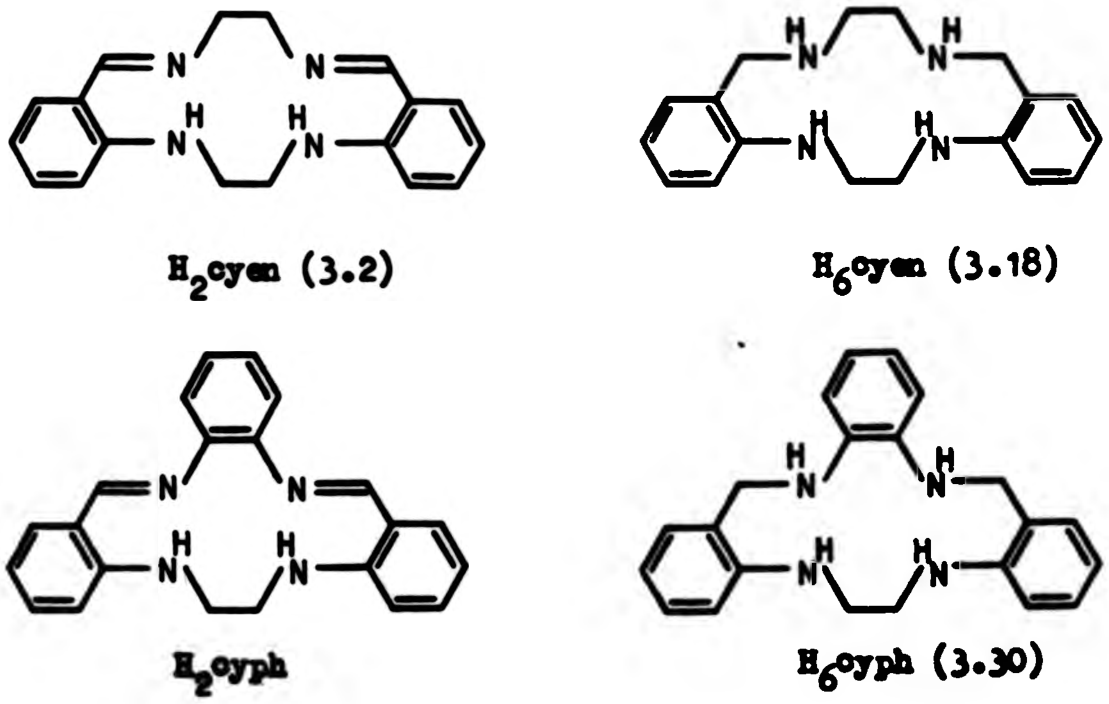
Table 3.7 Analytical and spectroscopic data for the mononucleating ligands and their copper(II) complexes.

[Cu(cypr)] (3.26)	62.1	5.0	14.8
(Calc. for $CuC_{19}H_{20}N_4$)	(62.0)	(5.5)	(15.2)
Infrared absorptions cm^{-1}	3020,1610,1524,1510,1478,1432,1402,1392,1362,1340,1252,1200,1165,1132,1100,1072,1040,1032,953,935.		
H_2cybut (3.27)	75.2	7.1	17.3
(Calc. for $C_{20}H_{24}N_4$)	(75.0)	(7.5)	(17.5)
Infrared absorptions cm^{-1}	3230,3085,1638,1620,1597,1586,1532,1345,1288,1213,1280,1162,1088,1080,1052,1002,986.		
[Cu(cybut)] (3.28)	61.7	5.8	14.0
(Calc. for $CuC_{20}H_{22}N_4$)	(62.9)	(5.8)	(14.7)
Infrared absorptions cm^{-1}	3072,3027,2980,2890,1604,1524,1454,1440,1401,1364,1350,1439,1257,1214,1204,1194,1172,1164,1132,1094,1074,1042,1035,1008,1000,970.		

Table 3.7 Analytical and spectroscopic data for the mononucleating ligands and their copper(II) complexes.

3.3.2 Stability of copper(II) complexes

The objective of preparing the mononuclear copper(II) complexes (table 3.7) was to help define the conditions which would be required for preparation of the more complicated dinuclear copper complexes. The stability of the ligands and their copper(II) complexes must be considered, since long reaction times may induce decomposition. Preliminary experiments involving uv/vis measurements were carried out to test their solution stability over extended periods of time in the presence of copper ions. The following ligands and their copper(II) complexes were studied (fig 3.20).


H_2cyen (3.2)

H_6cyen (3.18)

H_2cyph

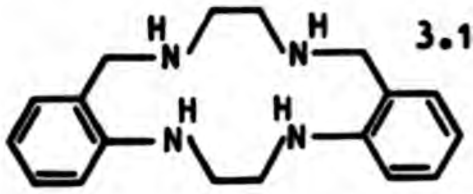
H_6cyph (3.30)

Fig 3.20 Tetra-aza macrocycles which were tested for solution stability.

It was expected that the reduced macrocycles H_6cyen (3.18) and H_6cyph (3.30) may be susceptible to oxidation. To examine whether these ligands were sensitive to oxygen in the absence of copper(II) ions solutions of H_6cyen and

H_6cyph were prepared in methanol and periodically examined by uv/vis (table 3.8). These results confirmed that the reduced macrocycles are stable to air in methanol.

H_6cyen (3.18)	nm	Abs	Abs (2 days)
	294	0.94	0.90
	250	1.06	1.02
H_6cyph (3.30)			
	208	0.75	0.73
	250	0.38	0.39
	295	0.10	0.10


3.18

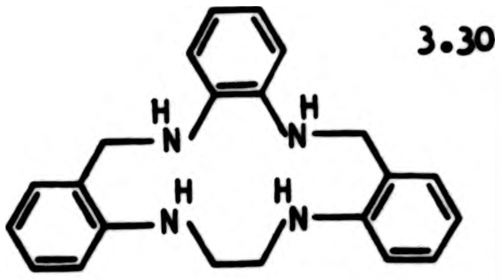
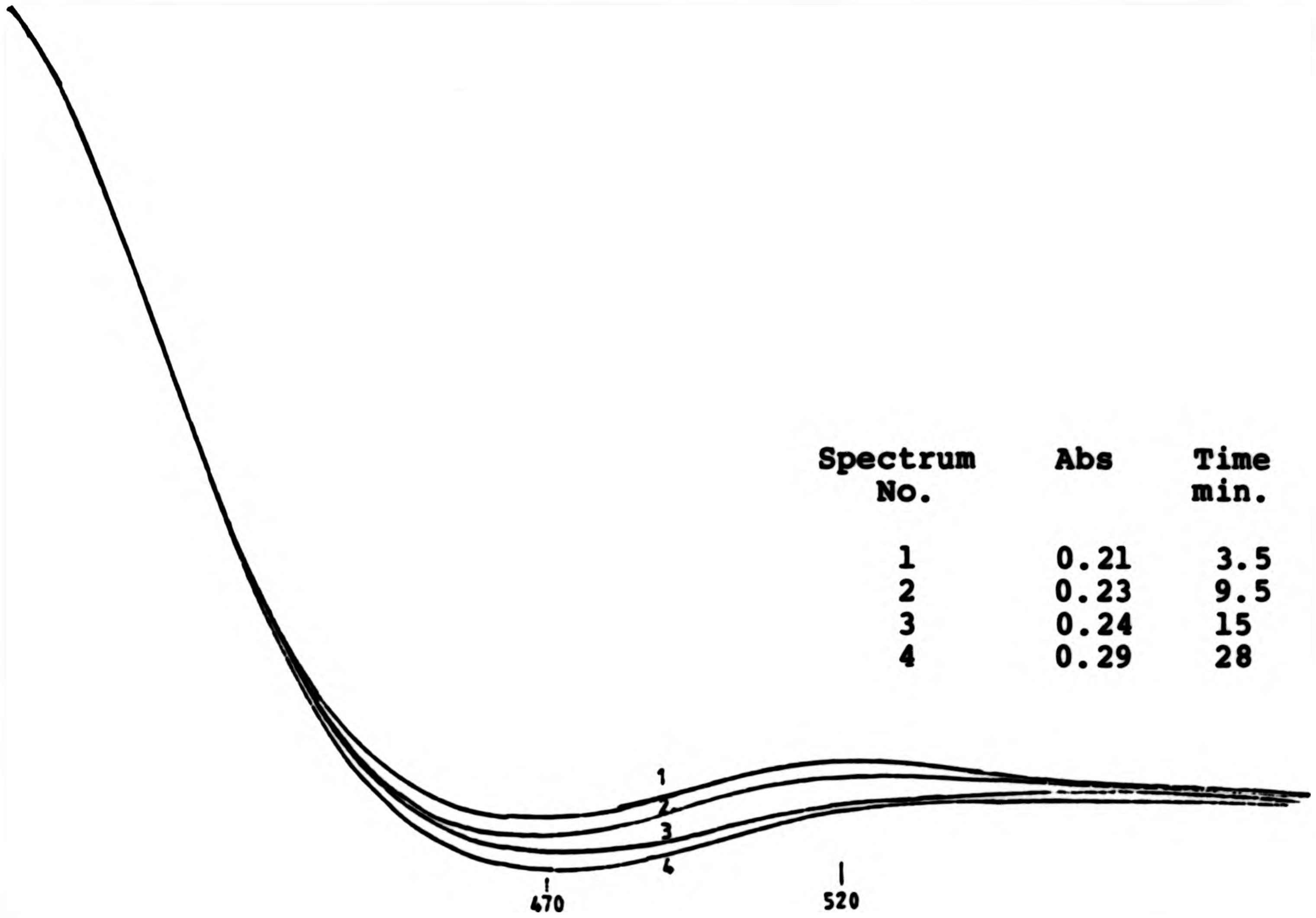

3.30

Table 3.8 Uv/vis results for H_6cyen (3.18) and H_6cyph (3.30)

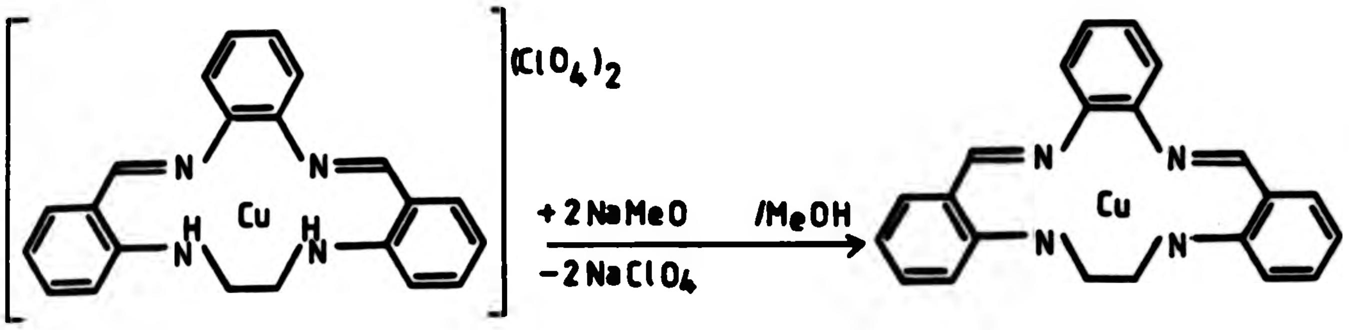
The solution stability of [Cu(H_6cyph)]$(ClO_4)_2$ (3.31) was tested in the presence of excess copper(II) perchlorate. The stability of the copper complex was monitored by following the changes in the uv/visible spectra. It was found that at low concentrations of ligand to copper, decomposition or oxidation takes place, as shown by the increasing absorption band at 520 nm (fig 3.21) which is also characteristic of the related imine copper complex [Cu(cyph)]. The oxidation/decomposition was inhibited as the molar ratio of ligand to copper(II) approached 1:1.



Spectrum No.	Abs	Time min.
1	0.21	3.5
2	0.23	9.5
3	0.24	15
4	0.29	28

Fig 3.21 The changes in the uv/vis spectum of [Cu(H_6cyph)](ClO_4)$_2$ (3.31) with time

The cationic copper complex 3.24 of the reduced ligand H_6cyen (3.18) was stable in a solution of copper(II) perchlorate, and showed no significant change in the uv/vis absorption spectra over 2 days. The neutral and cationic complexes of both of the imine ligands H_2cyen and H_2cyph were stable in solution in methanol, whether in the presence of excess copper(II) ions or not. It was found that the addition of a base (sodium methoxide solution) to [Cu(H_2cyph)](ClO_4)$_2$ (3.32) formed the neutral complex [Cu(cyph)] (3.33, scheme 3.14).



Scheme 3.14

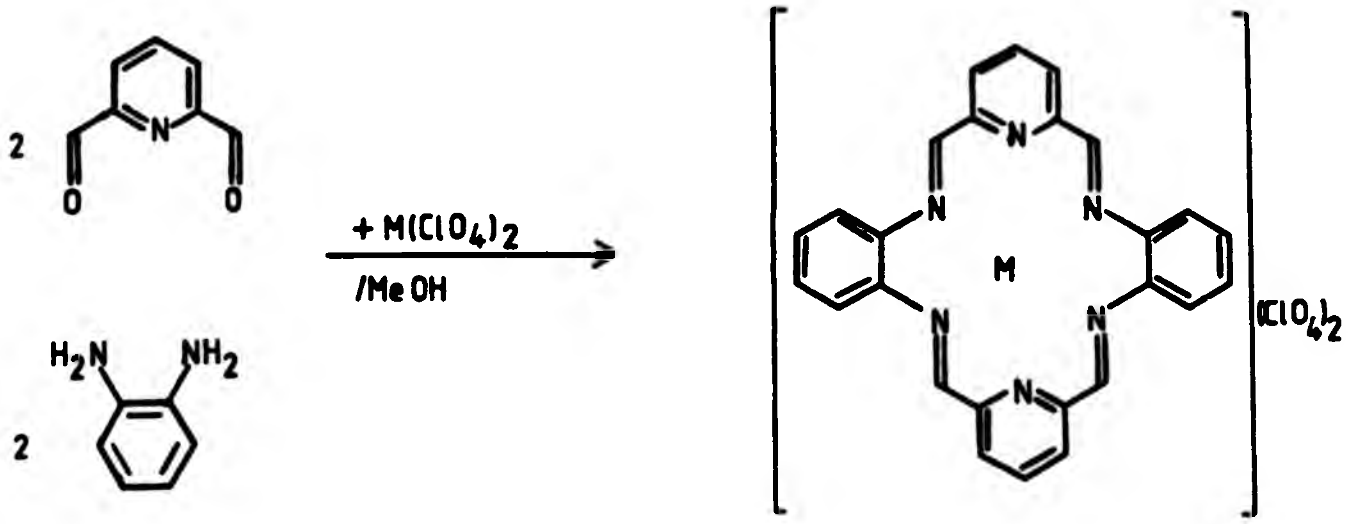
The deprotonation of the cationic complex 3.32 to give the neutral complex 3.33 was observed in solution by uv/vis measurements. The neutral complex could not be protonated by addition of perchloric acid, probably due to the greater thermodynamic stability of [Cu(cyph)] (3.33). For larger quantities of [Cu(H_2cyph)](ClO_4)$_2$ (3.32), conversion to [Cu(cyph)] (3.33) could be effected by addition of the base to a suspension of the perchlorate complex in methanol. This method could provide a novel synthetic route for the preparation of deprotonated species. The conversion of solid [Cu(H_2cyen)](ClO_4)$_2$ (3.23) to [Cu(cyen)] (3.22) did not proceed so readily but required a period at reflux.

Conclusion

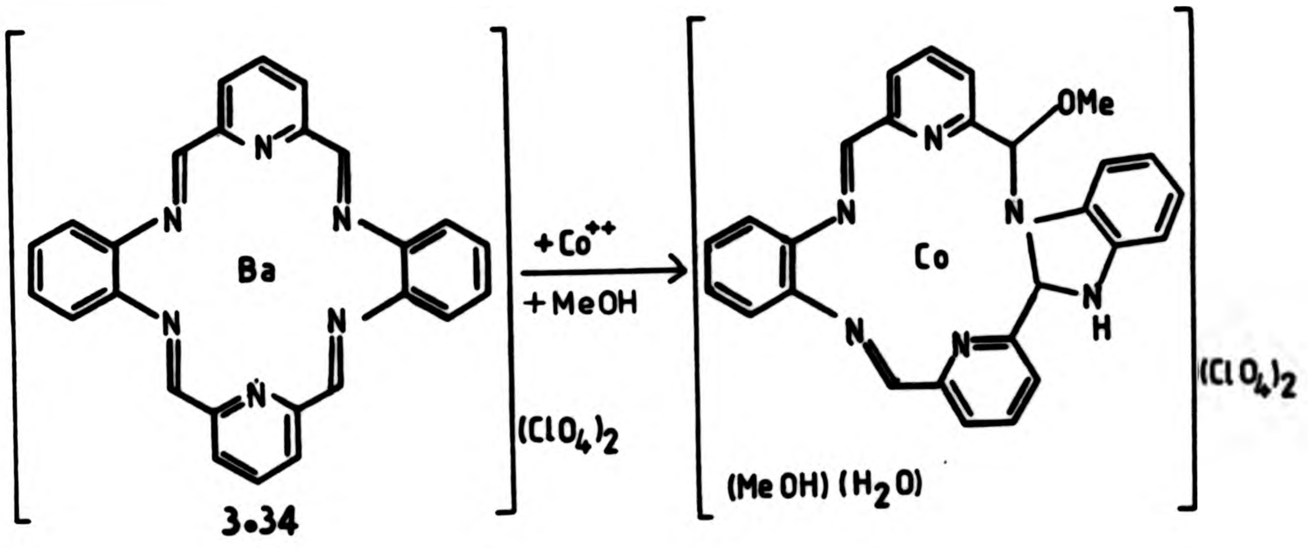
The stability of the copper complexes of the mononucleating ligands appear to be good providing they are not left in solution for extended periods of time, and that approximately equimolar amounts of ligand and copper(II) salt are used. The deprotonation of [Cu(H_2cyen)](ClO_4)$_2$ was not found to be effective for the preparation of [Cu(cyen)] due to contamination from the perchlorate complex. The deprotonation of [Cu(H_2cyph)](ClO_4)$_2$ to give the corresponding neutral complex [Cu(cyph)] is discussed in further detail in chapter 4.

3.4.1 Preparation of copper complexes of H_4cyendimer (3.4)

The low solubility of H_4cyendimer (3.4) results in ligand contamination of copper complexes prepared in most solvents. Highly polar solvents such as dmf or dmso which are suitable for dissolution of the ligand resulted in decomposition of the copper complexes as judged by the formation of black solids which could not be characterised. It has been reported[15] that metal ions in complexes can induce ring contraction to accomodate the stereochemical requirements of the metal ion. For example a [2+2] condensation reaction between 2,6-diacetylpyridine with 1,2-diaminobenzene in the presence of certain divalent metal ions (M^{2+}, M = Ca,Sr,Ba and Pb) occurs to accomodate the metal ion (scheme 3.15) No macrocyclic products were isolated when this template reaction was attempted with the perchlorate salt of the transition metals Mn to Zn. However reaction of the barium complex (3.34) with Co(II) was shown[16] by X-ray crystallography to have induced a ring contraction (scheme 3.16). Other metals of the same transition series show similar reactions.



Scheme 3.15



3.34

Scheme 3.16

Various solvent systems were used in an attempt to prepare copper(II) complexes of the neutral ligand H_4cyendimer (3.4) (i.e. without loss of the anilino protons). The first crystalline sample of a copper complex was obtained using a solvent system of thf/CH_3OH which gave translucent green prisms. Elemental analysis data did not correspond to the expected $[Cu_2(H_4cyendimer)](ClO_4)_4$ (3.35) complex or any other reasonable formulation. A single crystal X-ray structure determination showed the compound to be a triperchlorate complex $[Cu_2(H_4cyendimer)](ClO_4)_3$

(3.36). The formation of a tricationic complex was unexpected. It contains (section 7.1) two copper atoms in close proximity, with a particularly short Cu-Cu bond (2.444(4) Å). The formulation of the electronic structure of this complex presents some interesting problems and is discussed in detail later in this chapter. One assignment gives the copper atoms identical electronic enviroments in a $[Cu_2]^{3+}$ unit and therefore formal oxidation states of 3/2. Since the complex was relatively easily obtained and appears to be stable indefinitely in the solid state, it was of interest to compare the properties with related complexes which would contain the copper in more conventional oxidation states of 2 and 1. The biscopper(II) complex $[Cu_2(H_4cyendimer)](ClO_4)_4$ (3.35) was prepared using a solvent system of chloroform/methanol with the addition of diethyl ether, and characterised by elemental analysis. Attempts to prepare the biscopper(I) complex $[Cu_2(H_4cyendimer)](ClO_4)_2$ were made using tetra-acetonitrilecopper(I) perchlorate $[Cu(CH_3CN)_4](ClO_4)$ and H_4cyendimer (3.4) in the solvent thf. Preliminary results revealed that the thf must be dried (distilled from $LiAlH_4$) and degassed with argon. Preparation of the biscopper(I) complex was hampered by rapid oxidation which gave a green complex (assumed to be a biscopper(II) species) even under an argon atmosphere. The complex formed in this reaction was filtered, and the filtrate left to stand in an open necked vessel. After a few days, some brown-green crystals were filtered which were shown by infrared spectra to resemble a copper(II) perchlorate complex of the macrocyclic ligand. A crystal was examined by X-ray crystallography, and when the structure was solved it became clear the complex was a biscopper(II) with two perchlorates (3.37) and a deprotonated dianionic ligand. The preparation of the compound was improved by excluding the oxygen from the reaction mixture, although yields were still low and not reproducible. In an attempt to isolate a stable biscopper(I) complex, carbon monoxide was diffused through the reaction mixture to convert the reactive species to a carbon monoxide adduct. The $[Cu(CH_3CN)_4](ClO_4)$ was suspended in thf and found to be unreactive towards carbon monoxide. After twenty minutes diffusion of carbon monoxide through the suspension the free ligand was added to give a mole ratio of 1:2 ligand:Cu(I). The solution immediately turned pale-yellow green and remained so for 1 h, until filtration and drying gave a pale green compound with the infrared spectra showing a weak absorbance (νmax=2100 cm^{-1}) due to carbon monoxide. Other absorbances demonstrated that a substantial quantity of the unchanged ligand was still present. It was determined experimentally that a mole ratio of 1:4 ligand :Cu(I) gave high yields of a white compound for which the infrared spectra showed no unreacted starting materials, but did show a strong C=O stretch at 2100 cm^{-1}. The complex analysed as a biscopper(I) diperchlorate complex 3.38, with an unknown quantity of carbon monoxide ligand. All the reactions described above for the preparation of biscopper(I) complexes were carried out at room temperature, since heating apparently promoted oxidation of Cu(I) to Cu(II). These oxidised products analysed as a biscopper(II) diperchlorate complex (section 8) similar to the structually characterised diperchlorate 3.37, but with minor differences shown in the infrared.

A summary of copper complexes and their ligands are shown in table 3.9 with their analytical data.

Table 3.9 Analytical and spectral data for the dinuclear ligands and their copper(II) complexes

Compound	C%	N%	H%	Cu%
H_4cyendimer (3.4)	73.4	6.9	18.9	
(Calc. for $C_{36}H_{40}N_4$)	(73.9)	(6.9)	(19.2)	
$[Cu_2(H_4\text{cyendimer})](ClO_4)_4$ (3.35)	39.5	3.7	10.0	
(Calc. for $Cu_2C_{36}H_{40}N_8Cl_4O_{16}$)	(39.0)	(3.6)	(10.1)	
$[Cu_2(H_4\text{cyendimer})](ClO_4)_3$ (3.36)	42.2	4.0	10.9	12.3
(Calc. for $Cu_2C_{36}H_{40}N_8Cl_3O_{12}$)	(42.8)	(4.0)	(10.9)	(12.6)
$[Cu_2(H_2\text{cyendimer})(ClO_4)(H_2O)](ClO_4)$ (3.37)	48.8	4.6	11.5	
(Calc. for $Cu_2C_{40}H_{48}N_8Cl_2O_{10}$)	(49.5)	(4.9)	(11.3)	
$[Cu_2(H_4\text{cyendimer})(CO)_2](ClO_4)_2$ (3.38)	46.6	4.1	11.2	13.4
(Calc. for $Cu_2C_{38}H_{40}N_8Cl_2O_{12}$)	(47.2)	(4.2)	(11.6)	(13.1)
H_{12}cyendimer (3.6)	73.0	8.1	18.9	
(Calc. for $C_{36}H_{48}N_8$	(72.9)	(8.2)	(18.9)	
$[Cu_2(H_{12}\text{cyendimer})](ClO_4)_4$ (3.39)	37.9	4.3	10.0	11.2
(Calc. for $Cu_2C_{36}H_{44}N_8Cl_4O_{16}$)	(38.7)	(4.3)	(10.0)	(11.4)
H_4cyprodimer (3.7)	71.2	6.8	17.9	
(Calc. for $C_{38}H_{44}N_8O_2$)	(70.8)	(6.7)	(17.8)	
$[Cu_2(H_4\text{cyprodimer})](ClO_4)_4$ (3.40)	39.5	3.6	9.8	
(Calc. for $Cu_2C_{38}H_{44}N_8Cl_4O_{18}$)	(39.2)	(3.8)	(9.6)	
H_4cyhexdimer (3.8)	75.3	8.1	16.3	
(Calc. for $C_{44}H_{56}N_8$)	(75.8)	(8.1)	(16.8)	
$[Cu_2(H_4\text{cyhexdimer})](ClO_4)_4$ (3.41)	42.3	4.5	8.6	
(Calc. for $Cu_2C_{44}H_{56}N_8Cl_4O_{16}$)	(43.3)	(4.6)	(9.2)	
H_{12}cyprodimer.8HCl (3.42)	49.6	3.6	12.0	
(Calc. for $C_{38}H_{60}N_8O_2Cl_8$)	(49.7)	(3.7)	(12.2)	

Compound	C%	N%	H%
H_{12}cyhexdimer (3.43)	74.2	9.5	15.8
(Calc. for $C_{44}H_{64}N_8$)	(74.9)	(9.2)	(15.9)
H_{12}cyhexdimer.8HCl	54.7	7.3	10.4
(Calc. for $C_{44}H_{72}N_8Cl_8$)	(53.0)	(7.2)	(11.2)

Compound	Description	Infrared absorptions cm^{-1}
3.4	white needles	3240,3163,3088,1633,1626,1606, 1585,1582,1526,1484,1469,1458.
3.35	green powder	3280,3200,3100,1600,1605,1581, 1499,1324,1238,1220,1204,1100 b.
3.36	green crystals	3578 b, 3258,3058,1617,16001,1576, 1426,1407,1365,1248,1075 b.
3.37	brown-green crystals	3500 bw,1660,1632,1601,1532, 1409,1344,1305,1198,1187,1090 b.
3.38	white powder	3400 b,3270,3250,2088,1627,1602, 1588,1502,1309,1205,1100,970,787,752.
3.6	clear crystals	3317,3271,3210,3170,1605,1584, 1563,1505,1454,1441,1355,1347.
3.39	light brown powder	3560,3260,1635,1620,1595,1502, 1470,1420,1370,1219,1080 b.
3.7	white crystals	3210,3090,3025,1630,1600,1578, 1518,1463,1453,1327,1320.
3.40	dark red powder	3250 b, 2980,2940,1650,1612, 1590,1509,1100 b,935,768.
3.8	white needles	3250,3175,1640,1621,1595,1530, 1370,1333,1284,1212,1167.
3.41	red powder	3500 b, 3370,3180,1680,1648,1640, 1611,1586,1503,1315,1240,1100 b.
3.43	white powder	3405,3340,1613,1593,1525,1348, 1319,1295,1277,1232,1222,1199.

Table 3.9 Analytical and spectral data for the dinuclear ligands and their copper(II) complexes

3.4.2 DISCUSSION

The reaction between the ligand H_4cyendimer (3.4) with copper(II) perchlorate in thf/CH_3OH gave translucent green crystals. Preliminary analysis confirmed the presence of a perchlorate complex (νmax = 1100 cm^{-1}). X-ray structural analysis (section 7.1) showed the complex to be biscopper triperchlorate with a short copper-copper bond of 2.444(4) Å (fig 3.22).

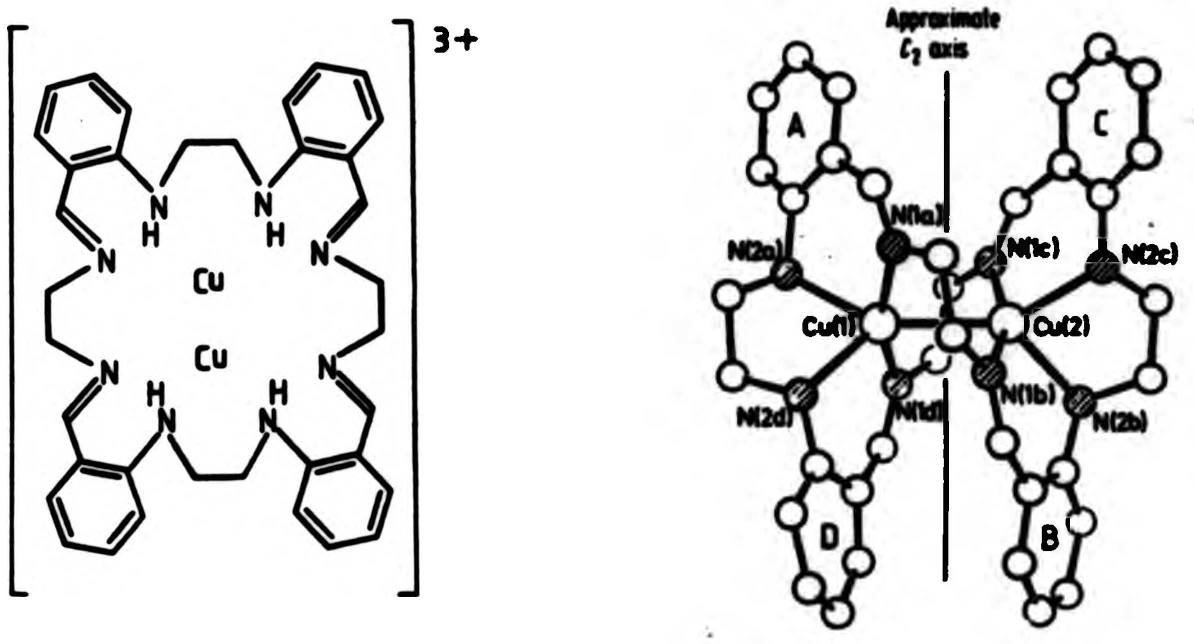


Fig 3.22 Schematic and ortep diagram of $[Cu_2(H_4cyendimer)]^{3+}$

The twisted conformation of the ligand H_4cyendimer (section 3.2.6.2) forces the two copper atoms to within bonding distance. The crystals of $[Cu_2H_4cyendimer](ClO_4)_3$ (3.36) are stable when in the solid state, but decomposition occurred when this material was allowed to stand for protracted periods in solution or when recrystallisation was attempted from a range of solvents (dmf, $CHCl_3$, CH_2Cl_2, thf and acetone). The ligand has low solubility, but during the course of the reaction with copper(II) perchlorate a soluble intermediate was formed, which then slowly deposited crystals of the $[Cu_2(H_4cyendimer)](ClO_4)_3$ (3.36) in ~50% yield. The mother liquor gradually darkens, leaving a black gummy material which could not be characterised. Reaction of the ligand with one molar eqivalent of copper(II) perchlorate resulted in a partial dissolution of the ligand followed by formation of the $[Cu_2(H_4cyendimer)](ClO_4)_3$ (3.36) complex. The nature of the intermediate is unknown, but could be a mono-copper complex in which the conformation of the ligand differs such to enhance the solubility. It is unlikely to be the biscopper(II) complex $[Cu_2(H_4cyendimer)](ClO_4)_4$ (3.35) because this was shown to be relatively insoluble (this chapter). A 30-membered Schiff base macrocyclic ligand (fig 3.23) has been reported[20] to incorporate one or two copper atoms per ligand. The mono-copper(II) complex is believed to have a pseudo-octahedral 'CuN_6' structure. This complex can be used to form biscopper(II) complexes on addition of a copper(II) salt. The free ligand has not been isolated, but was prepared as the dilead(II) complex, which can be used in transmetallation reactions to enable other metal ions to be incorporated.

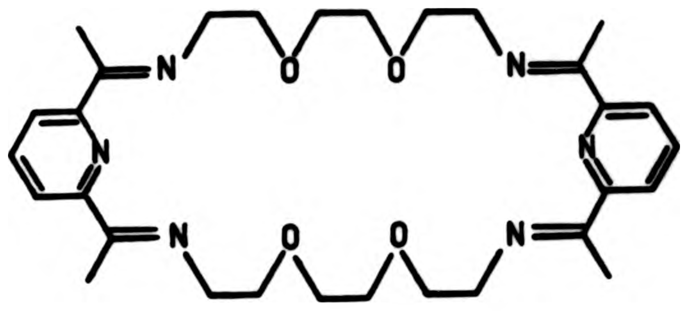


Fig 3.23 The free ligand of a dilead(II) complex[7].

The formation of a triperchlorate complex $[Cu_2(H_4cyendimer)](ClO_4)_3$ could arise in one of four ways: (i) by the transfer of a single electron to the dicopper(II) centre, (ii) by the loss of one of the anilino protons from the ligand, (iii) by the reduction of both copper atoms to copper(I) accompanied by simultaneous oxidation of the macrocyclic ligand, or (IV) by complexation of a pair of copper(II) ions with a reduced form of the ligand. The second possibility can be excluded on the basis of the structure determination, which shows all four anilino-nitrogen atoms have approximate tetrahedral geometry (table 3.13) rather than a trigonal planar arrangement which has been found[14] for the deprotonated anilino-nitrogen atoms in related mononuclear complexes. The structure of the free ligand H_4cyendimer (3.4) has not been determined but a related macrocycle H_4cyprodimer (3.7) (this chapter) shows a similarly twisted conformation, stabilised by intramolecular hydrogen bonding involving the anilino protons. This type of stabilisation has been considered to be important in determining the ease of isolation of metal free tetra-aza macrocycles, and is probably just as important for larger ring systems (see section 3.2). On complexation, these intramolecular hydrogen bonds are broken. The two copper atoms in the complex [Cu_2(H_4cyendimer)](ClO_4)$_3$ have very similar geometries (table 3.10) and the cation has approximate two fold symmetry about an axis which passes through the midpoint of the copper-copper bond and relates ligand portions A to C and B to D (fig 3.22). The stereoscopic view of the packing diagram depicts the cations and anions in a column arrangement (fig 3.24).

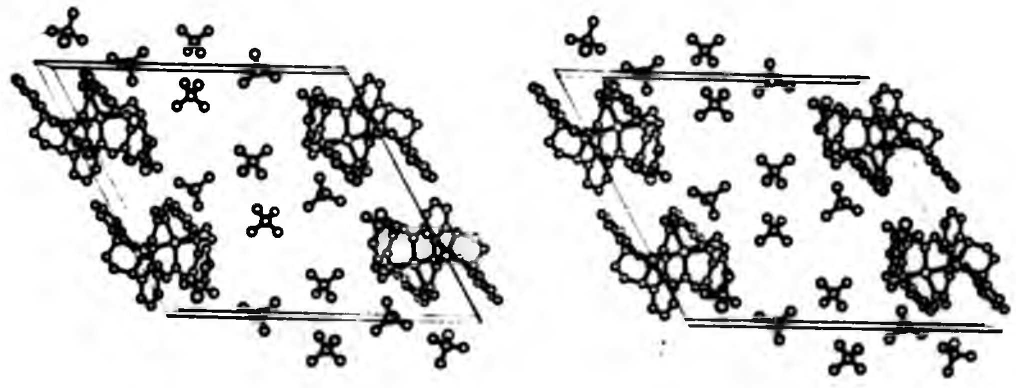


Fig 3.24 Stereoscopic view of [Cu_2(H_4cyendimer)](ClO_4)$_3$ (3.36)

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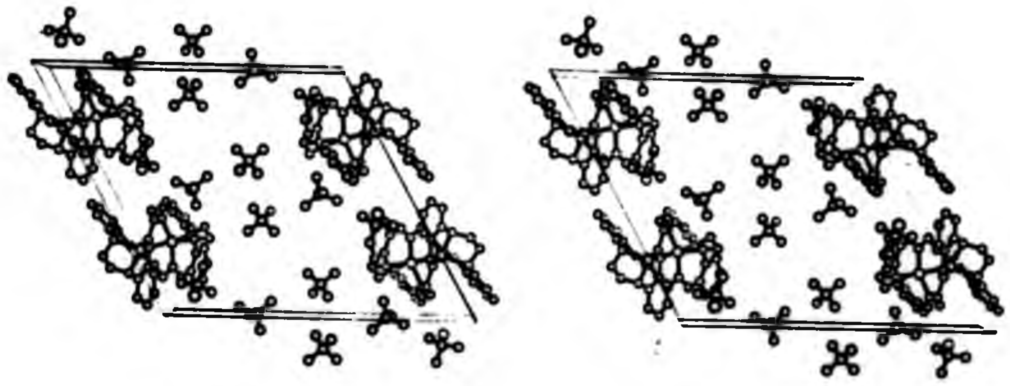


Fig 3.24 Stereoscopic view of [Cu_2(H_4cyendimer)](ClO_4)$_3$ (3.36)

	Part A	Part D	Part B	Part C
Bondlengths/Å				
Cu-N(1)	1.92(2)	1.90(2)	1.91(2)	1.95(2)
Cu-N(2)	2.18(2)	2.20(2)	2.20(2)	2.13(2)
Angles/Å				
N(1)-Cu-N(2)	91.5(8)	91.08(7)	93.5(8)	91.9(7)
N(1)-Cu-N(1)[a]	160.1(7)		158.2(7)	
N(1)-Cu-N(2)[a]	107.1(8)	99.2(7)	101.5(8)	104.9(7)
N(2)-Cu-N(2)[a]	83.5(7)		84.5(7)	
N(1)-Cu-Cu[b]	80.8(6)	80.7(5)	78.5(5)	80.8(5)
N(2)-Cu-Cu[b]	144.6(5)	131.9(5)	129.2(5)	146.2(5)

Table 3.10 Geometry about the copper atoms Cu(1) and Cu(2) for complex 3.36. a) denotes an atom in the alternative quarter of the ligand which is co-ordinated to the same Cu atom. b) denotes the Cu atom in the other half of the complex.

The similarity of the envirnments of both copper atoms and the short bond between them suggest they should not be assigned the discrete formal oxidation states +1 and +2, but that the single unpaired electron is delocalised over both metal centers, or that the metal centers are identical and that the unpaired electron resides on the ligand. This evidence would suggest this is a 'type 3A' mixed valence compound, where by the two copper atoms are equivalent and indistinquishable[17]. A number of copper ensymes contain more than one copper per molecule and in some cases[18], not all the copper can be accounted for by ESR as Cu(II) in the oxidised ensyme. To explain this and other unusual absorption spectra of these ensymes, one of the many suggestions has been a Cu(II)-Cu(I) interaction, categorised as a 'type 3A' mixed valence complex. A dinuclear mixed valence copper acetate complex (fig 3.25) has been proposed[19] as a model for such copper-copper interaction in enzymes, and similarly to [$Cu_2(H_4$cyendimer)]$(ClO_4)_3$ the two copper atoms were indistinquishable and their formal oxidation states indeterminate.

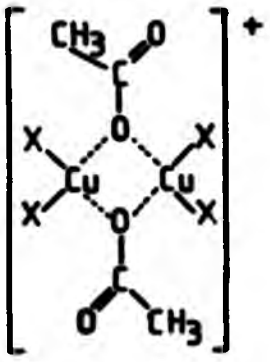


Fig 3.25 Proposed structure for a dinuclear mixed valence acetate complex.

A 30 membered Schiff base macrocyclic ligand (fig 3.23) previously described was reported[20] to coordinate two copper atoms, incorporating bridging ligands between them. The variation of the copper-copper distance is dependent on the flexibility of the ligand, which can alter to accomodate Cu-Cu bridging ligands of differing sizes (table 3.11,fig 3.26).

Bridging ligand	Cu-Cu /Å
OH	3.57
Imidazolate	5.99
1,3-azido group	6.02

Table 3.11

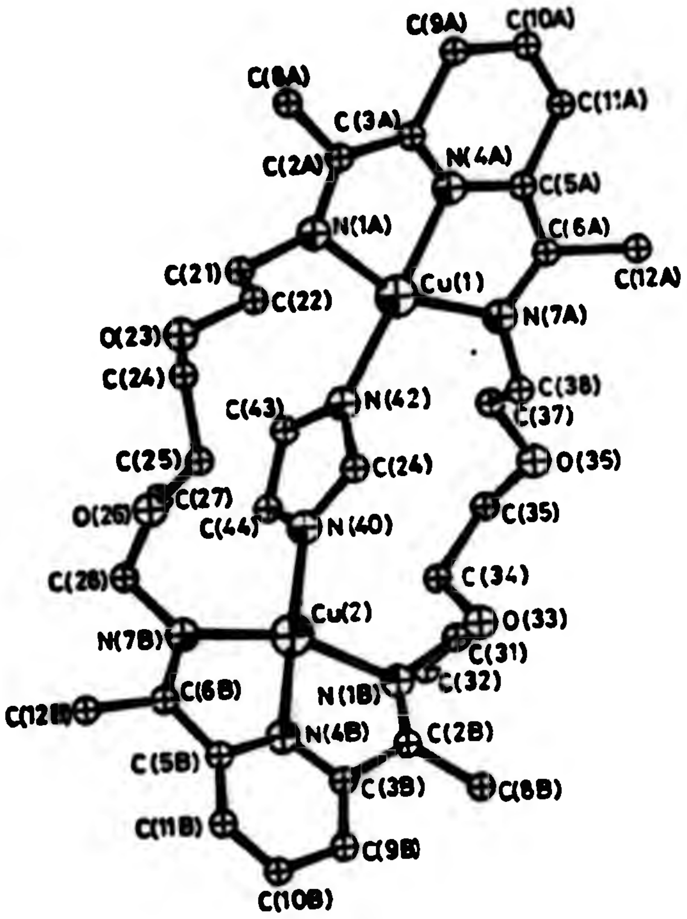


Fig 3.26 Ortep diagram of a 30 membered Schiff base macrocycle

The different conformations of the complexes above are achieved by folding of the ligand as opposed to the twisting of the ligand for the complex $[Cu_2(H_4cyendimer)](ClO_4)_3$ (3.36). An attempt by Nelson[20] to produce the mixed valence Cu(I)/Cu(II) complex of the ligand (fig 3.26), resulted in a mixture of the biscopper(I) and biscopper(II) complexes. Mixed valence copper complexes have become more common recently, although few known structures have been described[21]. A short Cu-Cu bond of 2.441(2) Å has been reported[23] for a biscopper(I) complex of 1,3-diphenyltriazene $[Cu_2(dpt)_4]$ (fig 3.27). The two N_4 planes are almost parallel, but the two sets of nitrogen atoms are twisted markedly (~15°) from the eclipsed configuration, no magnetic data have been reported.

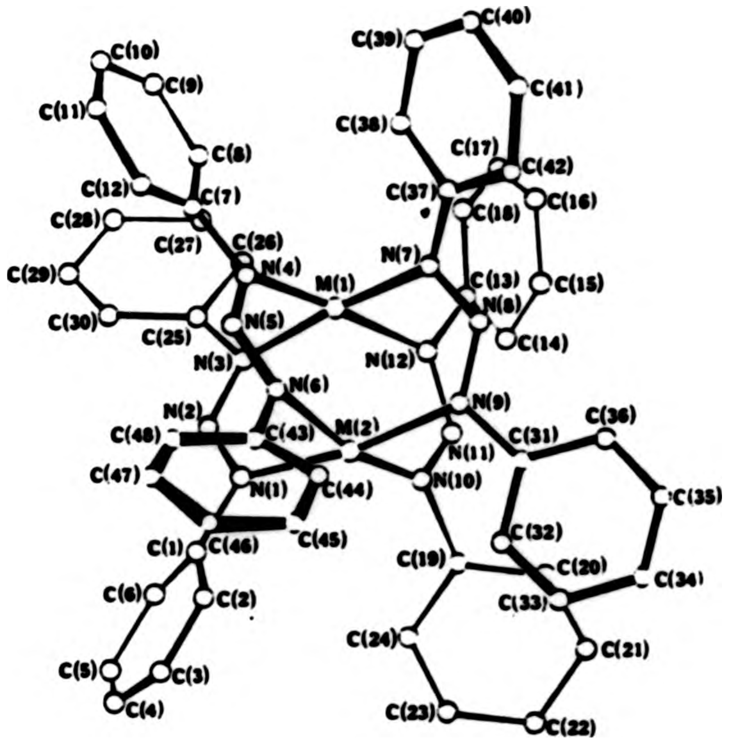


Fig 3.27 Ortep diagram of the structure of [$Cu_2(dpt)_4$]

Many metal-metal distances have been reported^{23} for structures related to that of copper(II) acetate monohydrate (table 3.12).

Compound	Distance /Å	Compound	Distance /Å
$[Cu_2(formate)_4(NCS)_2]^{2-}$	2.716	$[Cu_2(Decanoate)_4]$	2.63
$[Cu_2(formate)_4(urea)_2]$	2.657	$[Cu_2(aspirinate)_2]$	2.621
$[Cu_2(acetate)_4(py)_2]$ (orthorhombic)	2.645	$[Cu_2(acetate)_4(H_2O)_2]$ (neutron study)	2.614
$[Cu_2(acetate)_4(NCS)_2]^{2-}$	2.643	$[Cu_2(succinate)1]$	2.610
$[Cu_2(acetate)_4(H_2O)_2]$ (X-ray study)	2.64	$[Cu_2(octonoate)_4]$	2.59
$[Cu_2(acetate)_4(qn)_2]$	2.64	$[Cu_2(formate)_4(dx)]$	2.58
$[Cu_2(acetate)_4(py)_2]$ (monoclinic)		$[Cu_2(butyrate)_4]$	2.565
		$[Cu_2(dpt)_4]$	2.441

Table 3.12 Short Cu - Cu distances[23]

Many of these complexes have Cu-Cu distances close to the value of 2.56 Å for the pure metal[24]. Short Cu-Cu distances are indicative of metal-metal bonding. However, large exchange interactions do not always arise from short Cu-Cu distances[25], and very few inorganic dinuclear biscopper(II) complexes exhibit complete spin pairing at room temperature. One such compound (others have been reported[25]) was illustrated by Decourcey et al[26], in which the two coppers are separated by 3.05 Å and bridged by the two oxygens (fig 3.28).

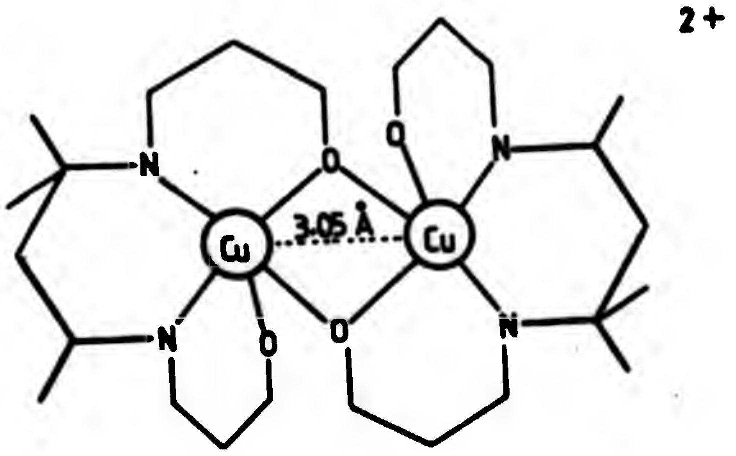


Fig 3.28 An outline of the structure of a di-μ-alkoxybridged Cu(II) complex which exhibits complete spin pairing at room temperature.

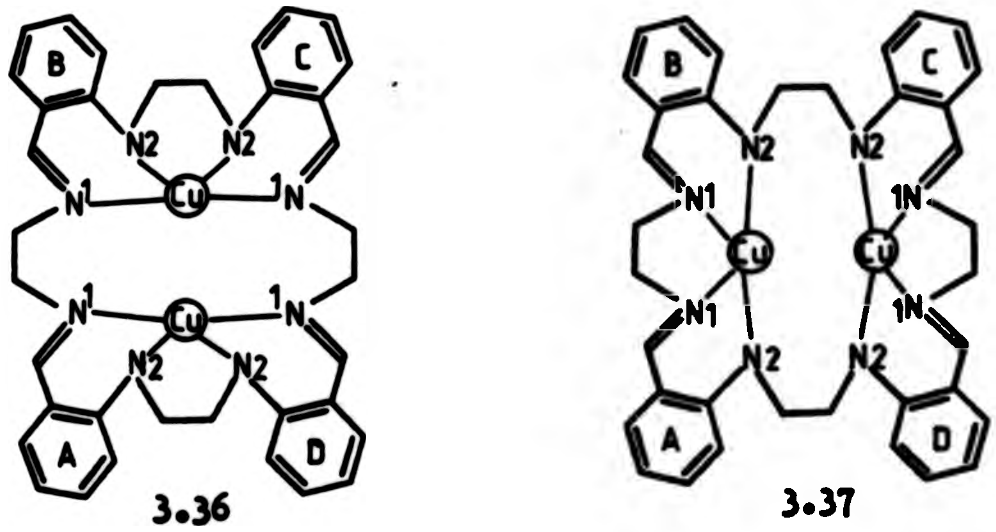
In these type of complexes it has been found that the degree of coupling increases as the distance between the two coppers increases and the bridge geometry varies, thus indicating the importance of exchange coupling in ligand-bridged copper(II) dimers. Even shorter Cu-Cu bonds have been reported[22,27] for tetranuclear cluster complexes of copper(I) (with bridging ligands) showing the copper(I) atoms separated by just 2.38 Å and 2.42 Å, however, these complexes are diamagnetic, and therefore cannot be used to study how exchange interaction depends on geometry. For $[Cu_2(H_4cyendimer)](ClO_4)_3$ (3.36) the ESR spectrum at the X-band of a powdered sample of a frozen acetonrile solution (77°K) exhibited one line at g=2.09 G. This does not unambiguously support the immediate conclusions from the X-ray structural study that the copper ions are equivalent and that this is a 'type 3A' mixed valence compound[17]. An ESCA spectrum[28] provided evidence for the assignment of equal oxidation states to the two copper atoms. All the data did not conclude whether $[Cu_2(H_4cyendimer)](ClO_4)_3$ contained a $[Cu_2]^{4+}$ unit or a $[Cu_2]^{3+}$ unit and a comparison of magnetic data with that of $[Cu_2(H_4cyendimer)](ClO_4)_4$ is made in section 3.7.1. The biscopper(II) complex$[Cu_2(H_4cyendimer)]$-$(ClO_4)_4$ (3.35) was prepared using a different solvent system and was characterised by elemental analysis. If the ligand 3.6 is capable of stabilising a $[Cu_2]^{3+}$ unit, then it may be possible to stabilise a biscopper(I) unit.

3.4.3 Biscopper(I) complex

Preparation of a biscopper(I) complex was attempted using $[Cu(CH_3CN)_4](ClO_4)$ as the source of copper(I). This copper(I) salt was made by the reduction of $Cu(II)(ClO_4)_2\cdot6H_2O$ with copper bronze in acetonitrile. Preliminary experiments to ascertain the stability of copper(I) compounds of 3.6 revealed that the solvents must be dried and used in an oxygen free atmosphere. The reaction was tested in a variety of solvents, but thf was found to be the most suitable in preventing oxidation of the copper(I) starting material. Without special oxygen free conditions, a green complex separated from solution rapidly. This was characterised as a biscopper(II) complex but was lightly contaminated with the free ligand. The filtrate was left to stand for approximately 5 days, when green-brown crystals of copper complex 3.37 formed. The infrared spectrum showed that the complex contained perchlorate. The dark colour suggested a copper(II) complex, although a biscopper(I) complex has been reported[20] where the colour was due to charge transfer. Other possibilities were that the complex was a mononuclear copper complex, or that the "dimeric" octa-aza ligand had reverted to a "monomeric" tetra-aza form (3.2) which gave a mononuclear copper(II) complex. This type of "dimer" to "monomer" conversion has been suggested[2] to account for the reaction when a polymeric material (now thought to be 3.4) was treated with a refluxing solution of nickel(II) acetate, when the tetra-azamacrocyclic complex [Ni(cyen)] was formed (see section 3.1). The infrared data for the green-brown copper(II) complex (3.37) were not compatible with formation of the analogous copper(II) complex [Cu(cyen)] or its related cationic form [Cu(H_2cyen)](ClO_4)$_2$. Consequently an X-ray structure determination was undertaken.

3.4.4 The Structure of [Cu_2(H_2cyendimer)(H_2O)(ClO_4)]-(ClO_4)thf (3.37)

The unit cell had a slightly smaller volume than the triperchlorate [Cu_2(H_4cyendimer)](ClO_4)$_3$, consistent with the presence of only two perchlorates. The formulation as a mononuclear copper(II) complex seemed reasonable, but when the structural analysis was completed a dinuclear copper(II) complex of a dianionic form of the ligand was revealed. The schematic diagrams of [Cu_2(H_4cyendimer)](ClO_4)$_3$ (3.36) and 3.37 are shown in fig 3.29.



3.36 3.37

Fig 3.29 Schematic diagram of 3.36 and 3.37

The two copper atoms in the diperchlorate 3.37 are bonded to different sets of nitrogen atoms from those in the triperchlorate 3.36. The molecule does not have crystallographic symmetry, and the coppers do not have the same coordination spheres. The angles around the anilino nitrogen atoms are given in table 3.13. These angles are compatible with deprotonation having occurred at nitrogen atoms N(2b) and N(2c), where the sums of angles are close to 360°. The planar disposition of bonds from these nitrogen atoms is consistent with an sp^2 hybridisation which has been observed[20] in other metal complexes containing deprotonated o-aminobenzaldehyde imines. The aniline nitrogen atoms N(2a) and N(2d) have a tetrahedral disposition of bonds, with sums of the C-N-C and C-N-Cu bond angles close to the theoretical value for a sp^3 hybridised atom. A comparison for these data is made with the complex $[Cu_2(H_4cyendimer)](ClO_4)_3$ (3.36) where the anilino nitrogen atoms have retained their protons and have values close to those expected for tetrahedral nitrogen atoms (table 3.13).

$[Cu_2(H_2cyendimer)(ClO_4)(H_2O)](ClO_4)thf$ (3.37)

	Part A	Part B	Part C	Part D
C1-N2-C2	111.0(9)	117.8(10)	117.1(11)	109.6(10)
C1-N2-Cu	109.7(7)	116.2(7)	116.9(8)	108.7(7)
C2-N2-Cu	109.5(7)	124.2(8)	125.6(8)	115.4(7)
Total	330.2	358.2	359.6	333.7

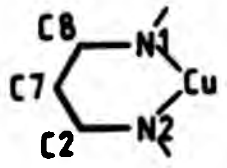
$[Cu_2(H_4cyendimer)](ClO_4)_3$ (3.36)

	Part A	Part D	Part B	Part C
C1-N2-C2	115.0(18)	114.2(19)	115.8(19)	111.3(17)
C1-N2-Cu	115.1(14)	106.0(14)	102.1(14)	105.1(14)
C2-N2-Cu	104.2(15)	114.8(14)	114.4(14)	118.8(14)
Total	334.3	335.0	332.3	335.2

Table 3.13 Bond angles about the anilino nitrogen atoms for complexes 3.36 and 3.37

For [Cu$_2$(H$_4$cyendimer)](ClO$_4$)$_3$, the anilino hydrogen atoms could not be located from the difference fourier electron density map. The presence of all four anilino hydrogens was suggested by the the tetrahedral disposition of the other bonded atoms around the nitrogen atoms (see above). In contrast, for 3.37 the two hydrogen atoms attached to the anilino nitrogen atoms N(2a) and N(2d) were located directly from a difference Fourier map due to the better quality of the reflection data (section 7.2). However, no electron density maxima could be detected in the region of the N(2b) and N(2c) atoms again suggesting that these have been deprotonated in the complex 3.37. The chelate rings of B and C (3.44) in 3.37 which have the deprotonated anilino nitrogen atoms, are more planar than a) the chelate rings of A and D, and b) the chelate rings A,B,C, and D in 3.37 which contain deprotonated anilino nitrogen atoms. This is shown in table 3.14 by the root mean square deviation of the plane of the six atoms N2, N1, Cu, C2, C7 and C8 in each unit.

Chelate ring	3.37	3.36
A	0.2874	0.2018
B	0.0428	0.1728
C	0.0457	0.1780
D	0.2398	0.1873



3.44

Table 3.14 Root mean square deviation of atoms in the six membered chelate rings A,B,C, and D (see 3.44) in the copper complexes 3.36 and 3.37.

Whereas $[Cu_2(H_4cyendimer)](ClO_4)_3$ (3.36) shows similar geometries (table 3.10) around each copper atom, the complex 3.37 has two different copper environments (table 3.15). The most significant difference between the environments of the two copper(II) atoms is the fifth coordination site, which for Cu1 is a strongly bound water, and Cu2 is a very weakly bonded oxygen of a perchlorate.

	Cu1		Cu2	
	Part A	Part B	Part C	Part D
Cu-N1	1.94(1)	1.94(1)	1.93(1)	1.95(2)
Cu-N2	2.10(1)	2.01(1)	1.97(1)	2.06(1)
Angles/Å				
N1-Cu-N2	85.2(4)	92.8(4)	93.4(5)	87.0(5)
N1-Cu-N(1)[a]	84.8(4)		84.0(6)	
N1-Cu-N(2)[a]	174.6(5)	160.2(5)	154.3(5)	175.2(5)
N2-Cu-N(2)[a]	95.6(4)		96.9(4)	
O-Cu	2.369(1)		2.632(1)	
O-Cu-N2	101.2(4)	93.8(4)	91.9(5)	97.97(5)
O-Cu-N1	91.3(4)	96.1(5)	105.2(6)	84.9(5)

Table 3.15 Geometry about the copper atoms Cu(1) and Cu(2) for complex 3.37. a) denotes an atom in the alternative quarter of the ligand which is coordinated to the same copper atom.

For the complex $[Cu_2(H_4cyendimer)](ClO_4)_3$ (3.36) a pseudo diad relates the ligand portions A to C, and D to B but with 3.37 no such comparison can be made (fig 3.30). The two halves of the complex are not related by any pseudo symmetry, and this is more pronounced because of the different coordination environments of the two copper(II) atoms. Both copper atoms in 3.37 have irregular coordination polyhedra. Cu1 has an approximately square pyramidal arrangement of the four nitrogen atoms and (axial) oxygen of the strongly bound water molecule. Cu2 has an irregular coordination geometry, described as inbetween square pyramidal and a trigonal planar arrangement. The four nitrogen atoms experience little repulsion from the very weakly coordinated perchlorate oxygen. The best geometric plane has been calculated through the four nitrogen atoms coordinated to each copper(II) atom, and the displacement of the coordinating atoms from their respective planes given in table 3.16.

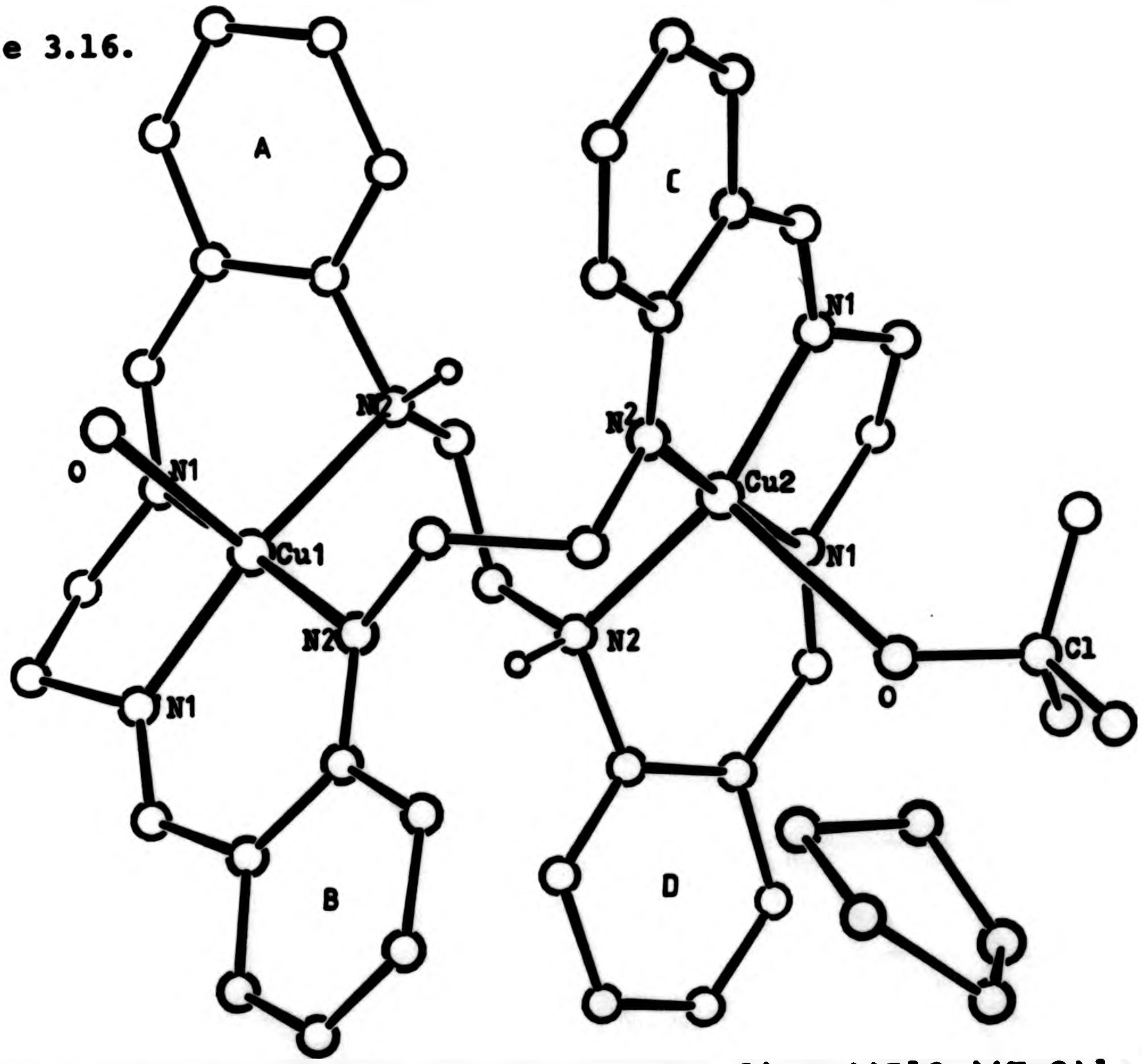
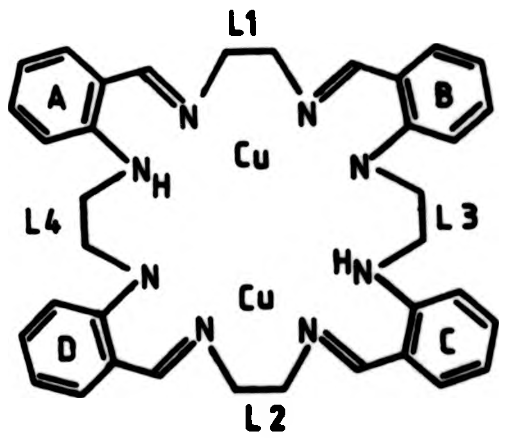


Fig 3.30 Ortep diagram of [$Cu_2(H_2cyendimer)(ClO_4)(H_2O)$]-($ClO_4$)thf (3.37)

	Cu1	Cu2
Cu-O bond length Å	2.369	2.632
Copper displacement from N_4 plane Å	-0.20	0.18
Oxygen displacement from N_4 plane Å	-2.564	2.801
Displacement of nitrogen atoms Å		
N1	0.10	-0.25
N2	-0.11	0.21
N1	0.11	0.25
N2	-0.10	-0.22

Table 3.16 Displacement of the coordinating atoms from their respective planes.

The overall conformation of the ligand in 3.37 depends on the arrangement adopted by the relatively flexible ethane linkages (ie upon the torsion angles of the C1-C1 and C9-C9 bridges (3.45) because the four chelate rings (3.46) are constrained to be approximately planar (see above).



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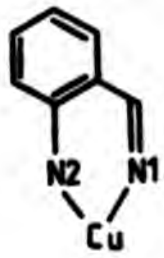


3.46

The linking of A-B and C-D is comparable in terms of torsion angles at the C9 bridge. The principle difference between the A-D and B-C halves of the molecule arise from the different torsion angles in the C1 bridge (table 3.17).

L1 (N(1a) C(9a) C(9b) N(1b)) Torsion angle = -44.3
L2 (N(1c) C(9c) C(9d) N(1d)) Torsion angle = -23.8
Difference = -20.5
L3 (N(2b) C(1b) C(1c) N(2c)) Torsion angle = 104.0
L4 (N(2d) C(1d) C(1a) N(2a)) Torsion angle = -52.8
Difference = 156.8

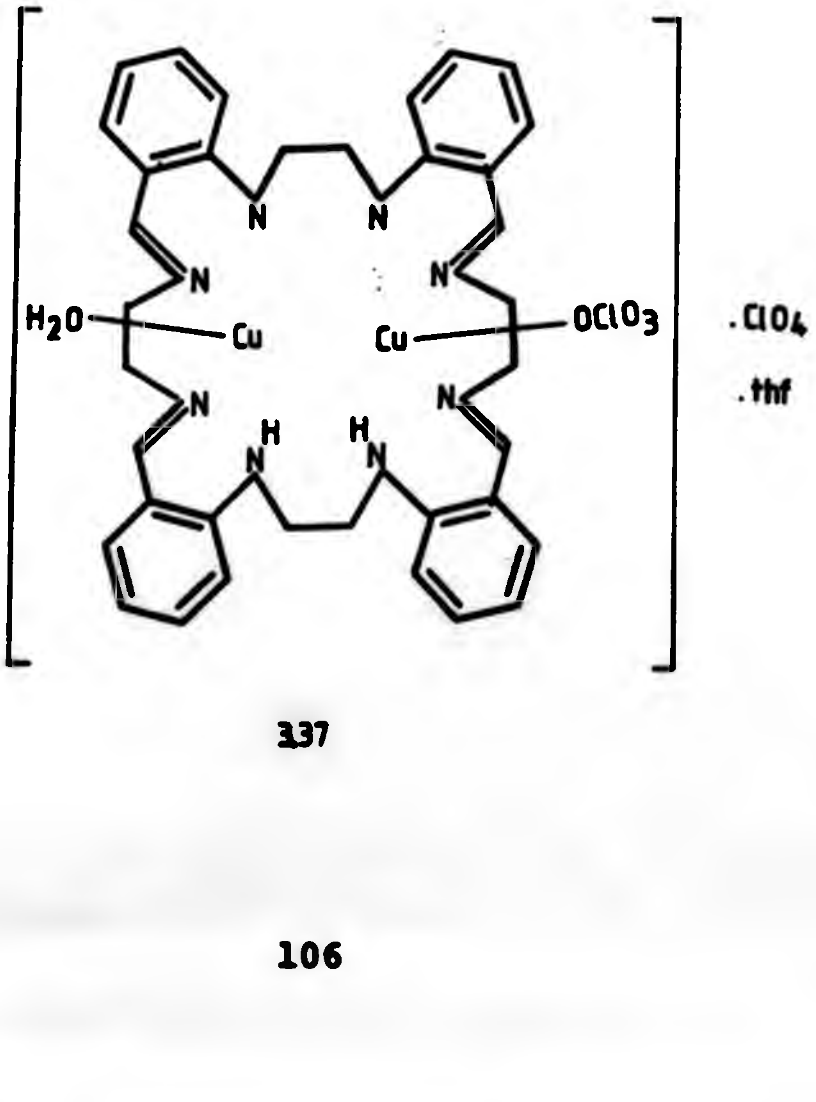
Table 3.17 Dihedral angles in $[Cu_2(H_2cyendimer)-(ClO_4)(H_2O)](ClO_4)$ (3.37).

The deprotonation of the anilino nitrogen atoms N(2b) and N(2c) for complex 3.37 is accompanied by a shortening of the aromatic carbon-nitrogen bonds (C(2b)-N(2b) and C(2c)-N(2c)), due to the increased conjugation as a consequence of sp^2 hybridisation. Thus these two C(2)-N(2) bonds in 3.37 have a mean length 1.35 Å compared with 1.44 Å for the other C(2)-N(2) bonds which do not have deprotonated nitrogen atoms (see table 3.18).

Complex	C(2a)-N(2a)	C(2b)-N(2b)	C(2c)-N(2c)	C(2d)-N(2d)
3.37	1.447(18)	1.358(14)	1.351(17)	1.483(31)
3.36	1.484(31)	1.442(28)	1.401(27)	1.399(30)

Table 3.18 Bond lengths for the aromatic carbon-nitrogen atoms in complexes 3.36 and 3.37. (Å).

The different conformation of the 28-membered ligand in 3.37 gives a much greater Cu1-Cu2 separation (5.7 Å) than in 3.36 (2.44 Å), and consequently is not expected to show any direct interaction. In the final refinement of this structure, the two atoms C(9c) and C(9d) were found to have a bond length of approximately 1.4 Å. A bond this short suggested that dehydrogenation had occurred. A complex with this formulation (3.37) would be a reasonable product from the reaction of the ligand H_4cyendimer (3.4) with the biscopper(I) salt and dioxygen (scheme 3.17). The reaction pathways shown in scheme 3.17 involves the formation of a dioxygen adduct of a biscopper(I) complex 3.48, followed by dehydrogenation of the ethane bridge (C(9c)-C(9d)) and semi-deprotonation of the anilino hydrogens to give the biscopper(II) complex plus two moles of water (one is coordinated to Cu1).



3.37

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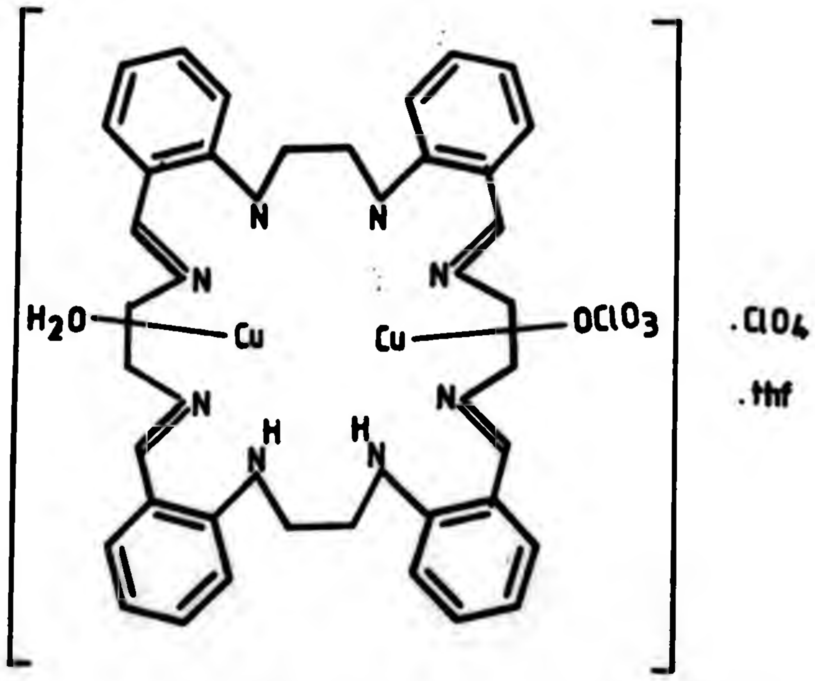

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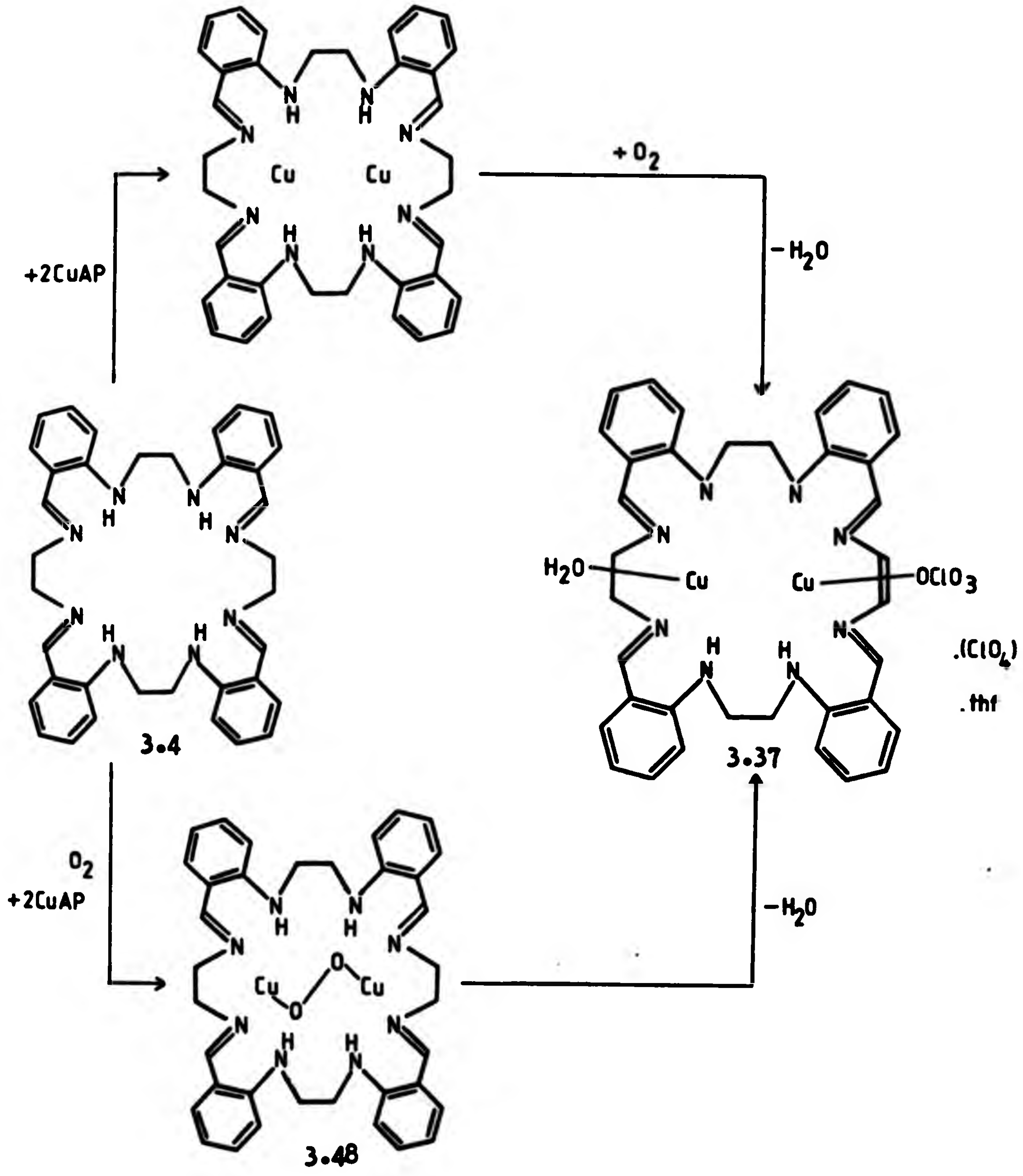


Scheme 3.17

Further examination of the crystallographic data for the complex 3.37 revealed high thermal parameters for both C(9c) and C(9d) atoms. It has been shown[29] that high thermal parameters can sometimes be accounted for by a disordered

ethane bridge (fig 3.31), which generates during refinement a short carbon-carbon bond length. In such a situation the four carbon atoms have half occupancy and sometimes it is possible to resolve electron density maps so that the positions of the four atoms can be defined (fig 3.31).

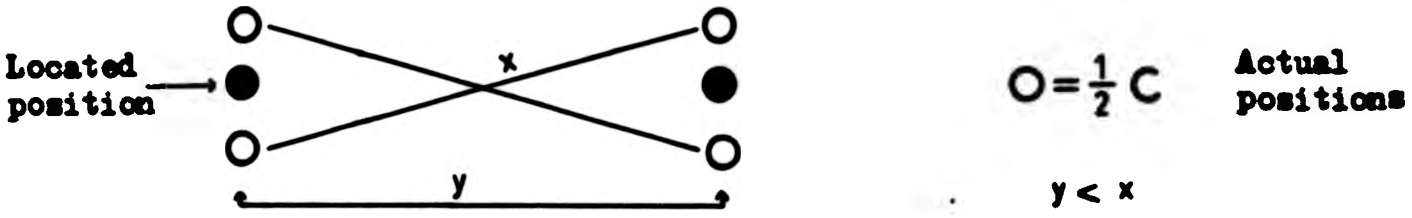


Fig 3.31 The four carbon atoms (half occupancy) of a disordered etane bridge.

Detailed examination of the Fourier electron difference maps revealed the electron density of the two carbon atoms C(9c) and C(9d) were smeared out in the x-z plane, rather than resolved into separate peaks. In conclusion, from the structural study the presence of a double bond is unlikely but cannot be ruled out. Other physical methods such as infrared could not be interpreted in terms of one double bond, and other methods (nmr spectra and mass spectra) could not be used due to the nature of the complex. For a transient biscopper(I) complex (3.48), the conformation to form a dioxygen adduct would require the two copper(I) atoms to be separated by a distance of 3.5-6 Å[30]. Several examples of biscopper(I) complexes have been reported recently[30] which have been found to react reversibly with dioxygen or carbon monoxide in the solid state (fig 3.32).

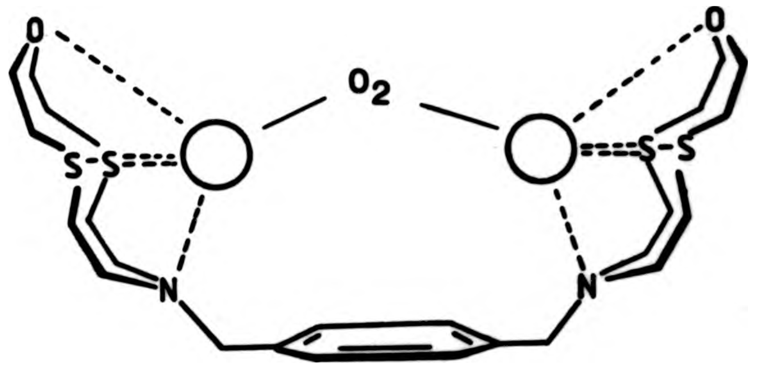
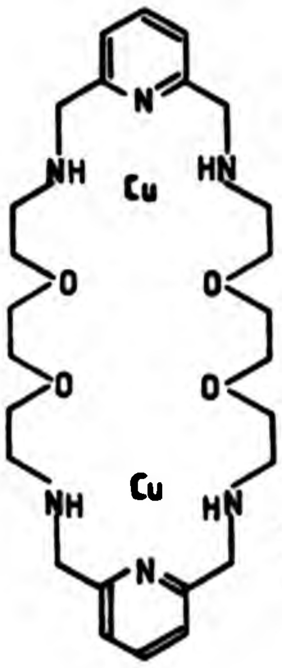
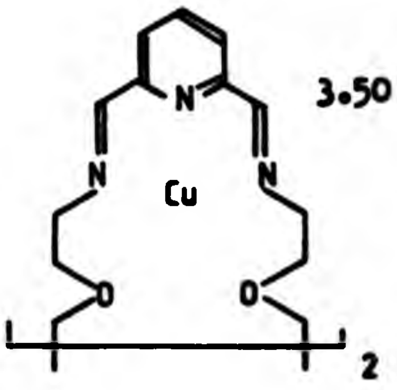


Fig 3.32 The dioxygen adduct of a biscopper(I) complex

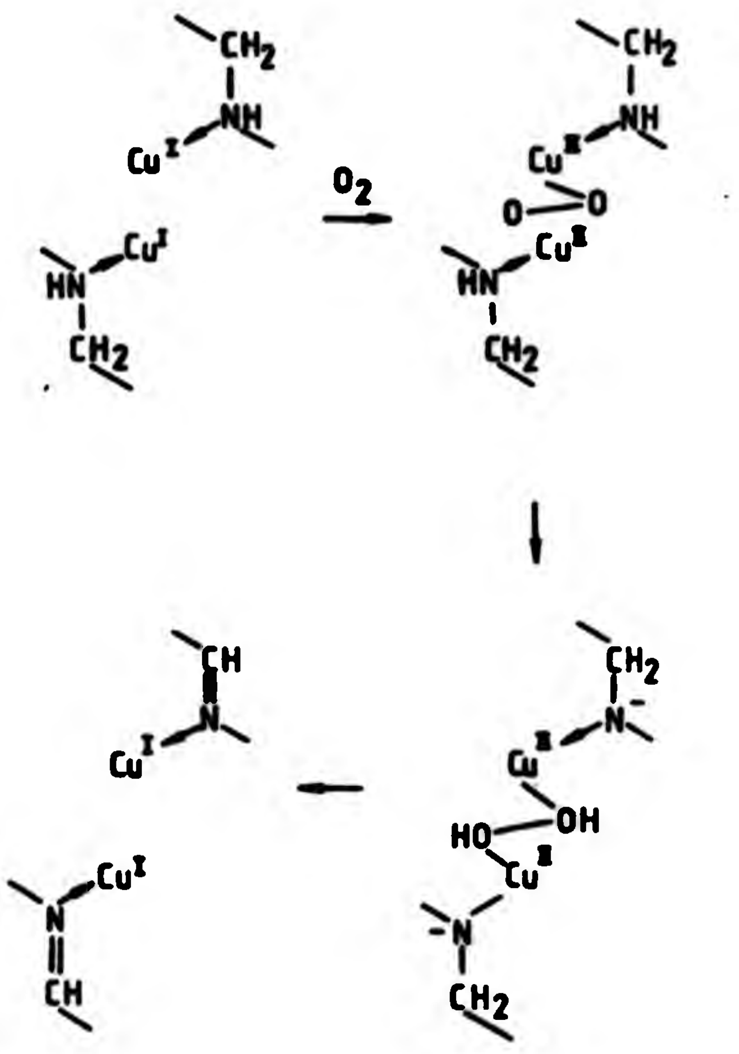
A biscopper(I) complex 3.49 of a 30 membered macrocycle has beendescribed[31] which reacts with dioxygen (scheme 3.18) resulting in the oxidative dehydrogenation of the ligand (secondary amine groups to imines) to regenerate a biscopper(I) complex. The regenerated biscopper(I) complex 3.50 will then repeat the cycle once more, and the resulting complex is thought to have been dehydrogenated in one of the ethane bridges as shown by the appearence of an infrared band at 1642 cm^{-1}. A comparable band (1660 cm^{-1}) is present in 3.37 which suggests that dehydrogenation may have occurred for the bond C(9c)-C(9d).



3.49



3.50



Scheme 3.18

Karlin et al have reported[32] the uptake of dioxygen by a biscopper(I) complex, resulting in hydroxylation of the ligand to produce a phenoxy-bridged biscopper(II) complex (fig 3.33).

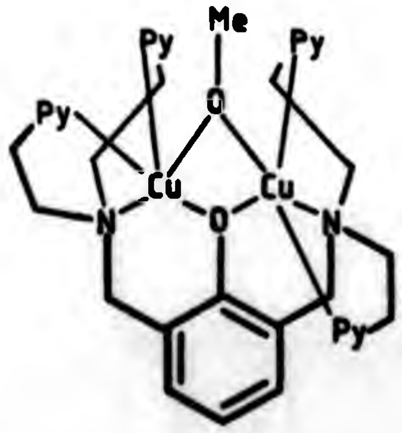
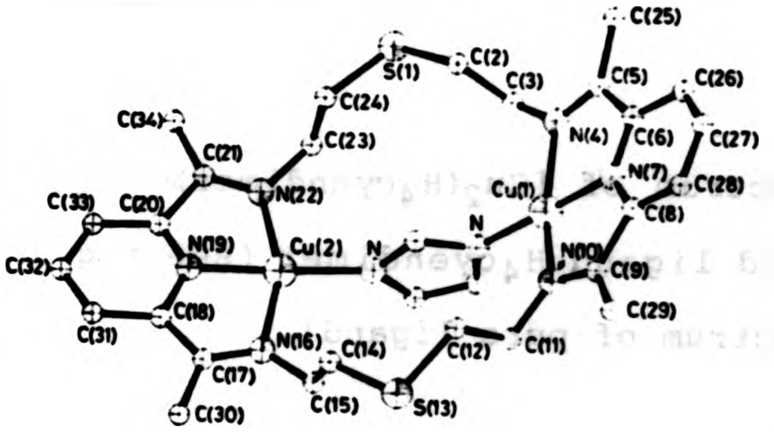
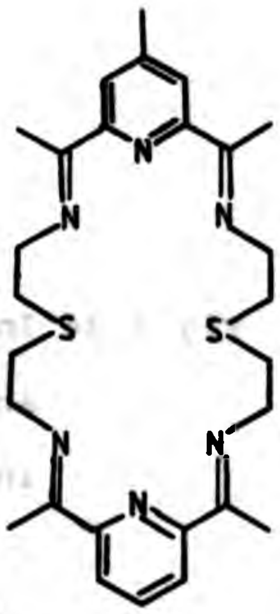


Fig 3.33 A phenoxy-bridged biscopper(II) complex

A dinuclear copper(II) complex of a 24 membered macrocyclic Schiff's base ligand 3.51 has been reported[33]. A structure determination has shown the metal centers to be linked intramolecularly by the imidazolate anion. Each copper is 6 coordinate and is bonded to 3 nitrogen atoms of the macrocycle, and to one nitrogen of the imidazolate. Both copper atoms are also bonded to oxygen atoms of perchlorate and water in axial positions.



Biscopper(II) complex of ligand 3.51



3.51

From the above results it is likely that the biscopper(I) complex of 3.4 would react readily with dioxygen, and strictly anaerobic conditions would be essential to isolate $[Cu_2(H_4cyendimer)]](ClO_4)_2$. The preparation was attempted under argon using carefully dried solvents, but only a green complex could be isolated, which corresponded to a dinuclear copper(II) complex (compound 3.35). The possibility of introducing a bridging ligand to stabilise the biscopper(I) complex by blocking the approach of O_2 to the Cu_2 site was considered. On the basis of a

Fig 3.34 Infrared spectrum of $[Cu_2(H_4cyendimer)(CO)_x](ClO_4)_2$ and unreacted ligand H_4cyendimer (see fig 3.2 for infrared spectrum of pure ligand).

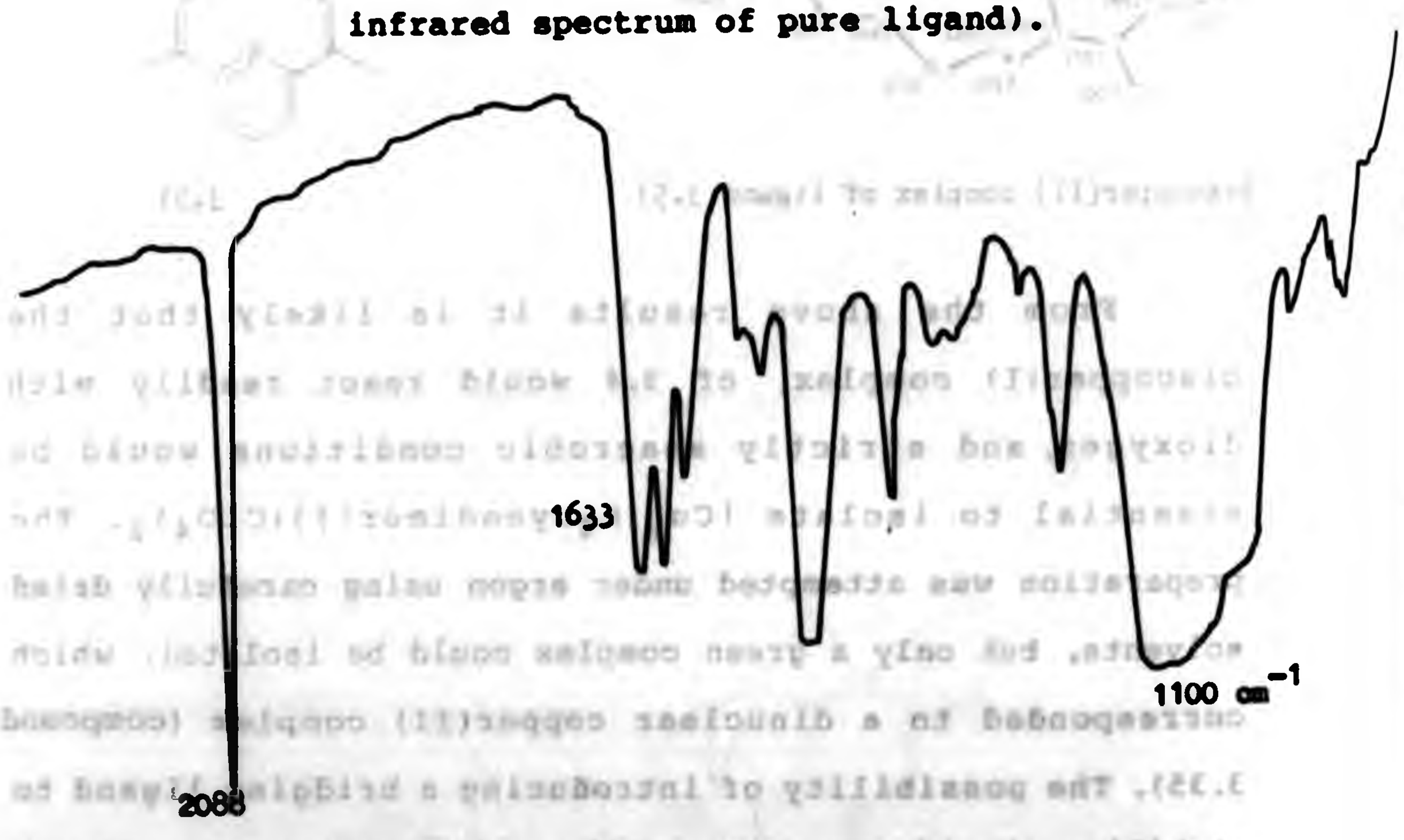


Fig 3.35 Infrared spectrum of $[Cu_2(H_4cyendimer)(CO)_x](ClO_4)_2$

cyendimer)(CO)$_x$](ClO$_4$)$_2$
dimer (see fig 3.2 for
and).

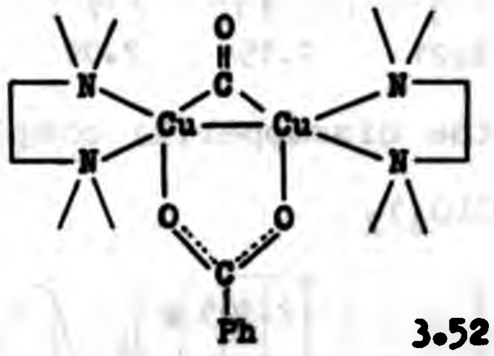
cyendimer)(CO)$_x$](ClO$_4$)$_2$

---

literature search, carbon monoxide was considered as an additional ligand to stabilise the Cu(I) center (see below).

3.5.1 Biscopper(I) - carbon monoxide adducts

Many Cu(I) complexes have been prepared which react reversibly and irreversibly with carbon monoxide[34]. The mode of bonding[35] for some complexes have been shown to be terminal, although other types have been suggested, and recently the bridging mode (3.52) has been confirmed.



3.52

3.5.2 Preparation of the biscopper(I) carbon monoxide adduct of the ligand H_2cyendimer

The preparation of this compound was attepted by the slow diffusion of carbon monoxide through a suspension of $[Cu(CH_3CN)_4](ClO_4)$ in thf, followed by the addition of H_4cyendimer to give a mole ratio of 1:2 L:Cu(I). The mixture changed from white to pale yellow, and the infrared spectrum of this material (fig 3.34, facing page) showed it to contain large quantities of unreacted ligand but with a small amount of carbon monoxide adduct (ν_{max} = 2100 cm^{-1}). Other solvents (dmf, dmso, acetonitrile, methanol or nitromethane) showed no improvement, but by using thf with an excess of the copper(I) salt, a white compound was

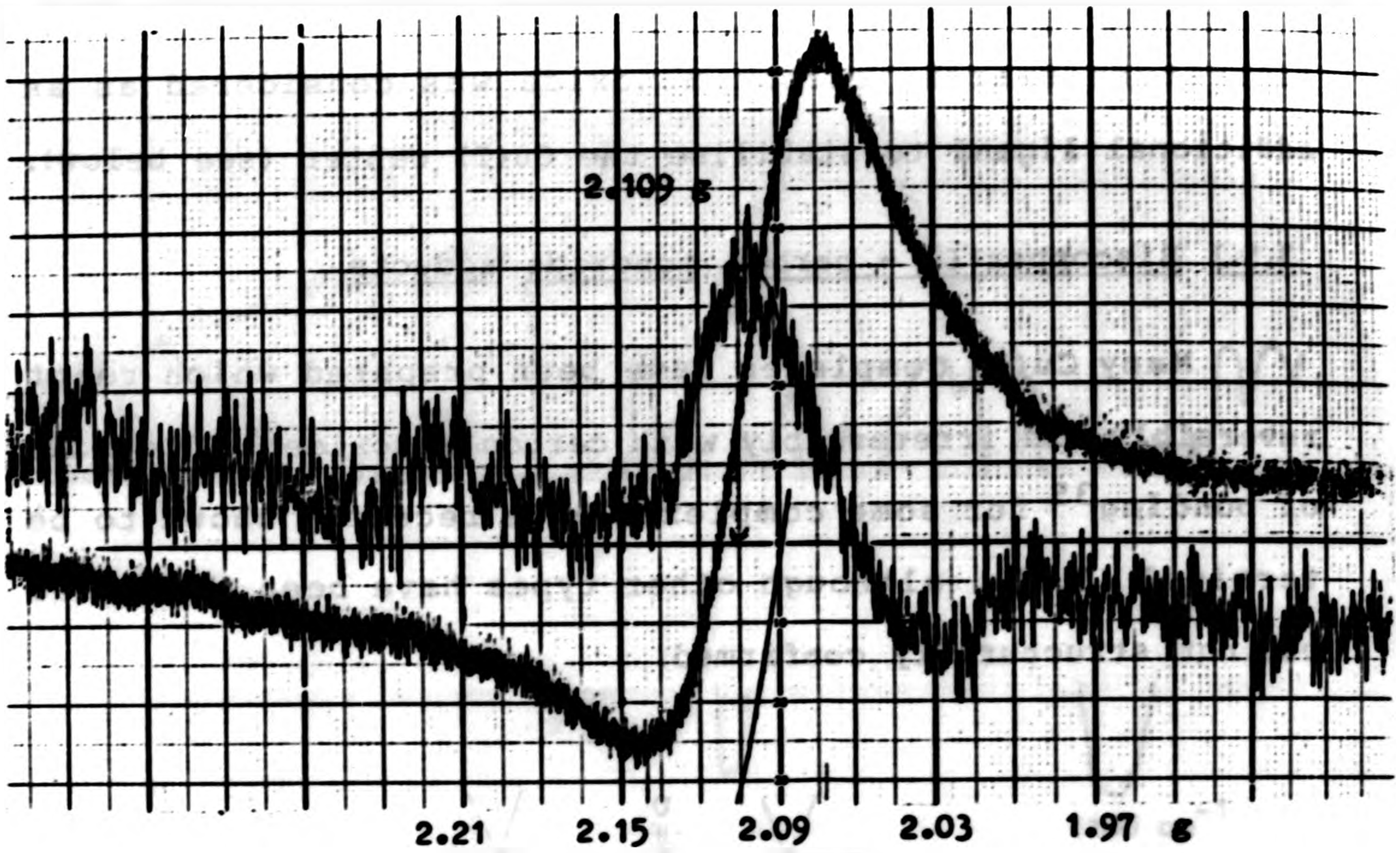
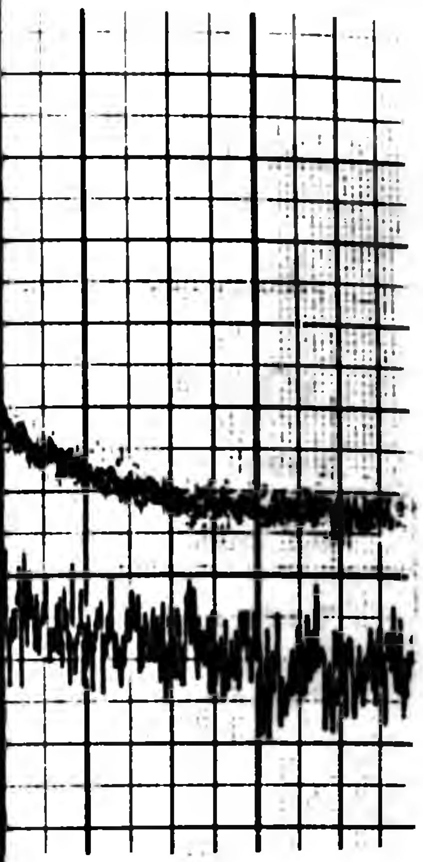
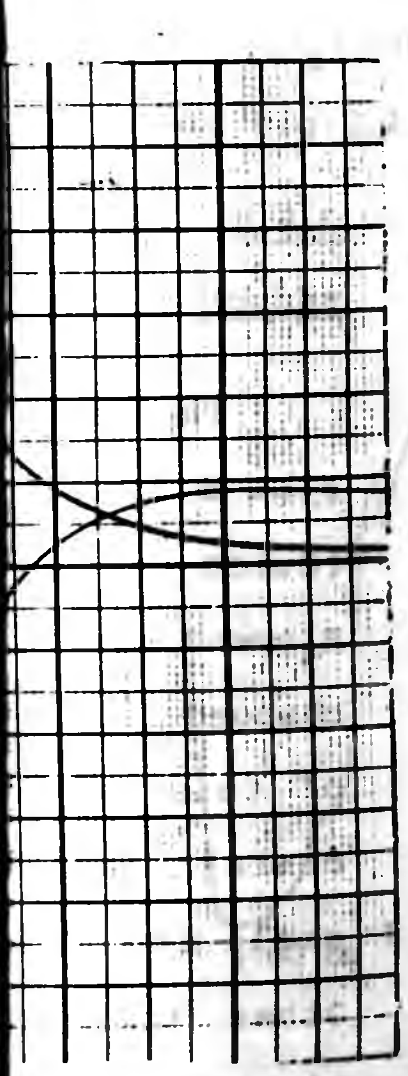


Fig 3.36 EPR of the biscopper(I) complex $[Cu_2(H_4cyendimer)-(CO)_x](ClO_4)_2$

Fig 3.37 EPR of the biscopper(I) complex $[Cu_2(H_4cyendimer)-(CO)_x](ClO_4)_2$ after exposure to air for two weeks.



$_2$(H$_4$cyendimer)-



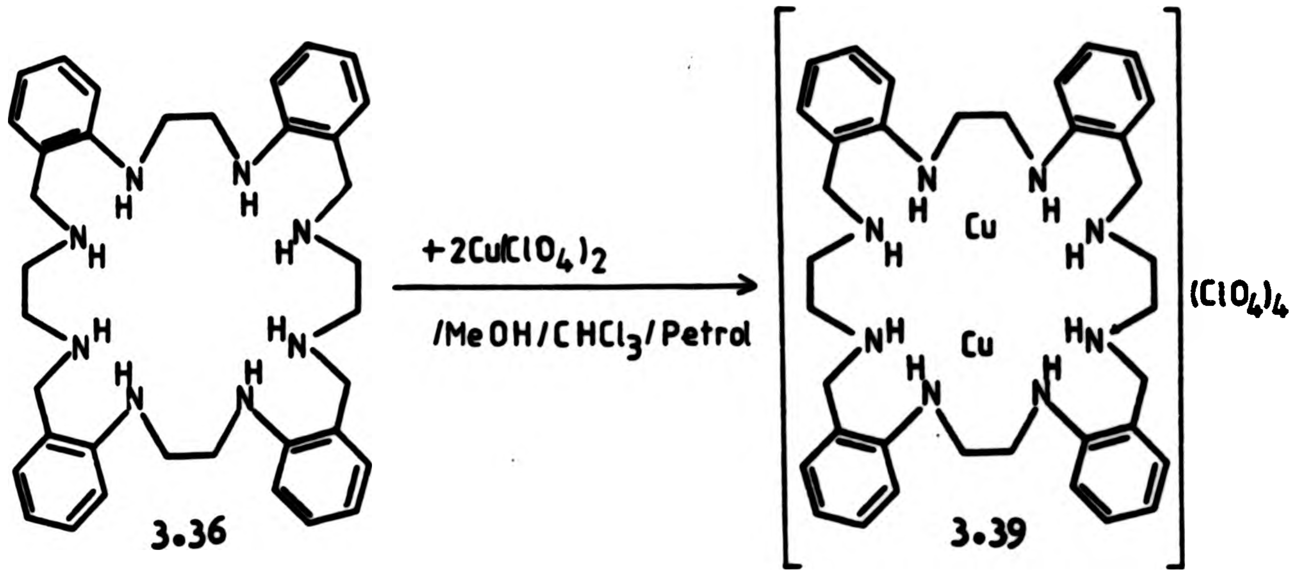
$_2$(H$_4$cyendimer)-

for two weeks.

isolated of which the infrared spectrum showed a significant uptake of carbon monoxide had taken place (fig 3.35, facing page). Quantitative experiments revealed optimum yields when the mole ratio of L:Cu was at least 1:4. All these experiments with carbon monoxide took place at room temperature, since heating resulted in a loss of carbon monoxide to yield a green (probably Cu(II) complex) compound. Elemental analysis confirmed the formulation of the carbon monoxide adduct as $[Cu_2(H_4cyendimer)(CO)_x](ClO_4)_2$, but was unable to determine the amount of carbon monoxide in the complex. Attempts to monitor the weight lost due to carbon monoxide when the complex was gently heated was hampered by the complex not being completely dry therefore giving false readings, and because it was difficult to remove all the carbon monoxide from the adduct. The EPR spectrum of the complex was very weak (fig 3.36, facing page) but observable due to Cu(II) impurities. After the complex had been exposed to air for two weeks a signal 100 times as intense was obtained (fig 3.37, facing page). The positions of the central bands are very similar at g= 2.109 and 2.105, and also correspond to that shown by the triperchlorate complex 3.36 at g = 2.09.

3.6.1 Copper complexes of H_{12}cyendimer (3.6)

The ligand H_{12}cyendimer (3.6) showed low solubility in most solvents, but formed a soluble copper(II) perchlorate complex in a mixture of chloroform/methanol. Addition of petrol induced crystallisation of $[Cu_2(H_{12}cyendimer)](ClO_4)_4$ scheme 3.19.

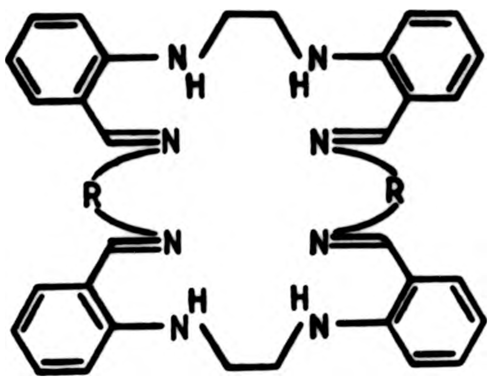


Scheme 3.19

The structure of the ligand Hl2cyendimer has been determined (section 7.4) and the distance between the centroids of the two sets of nitrogen atoms calculated at 4.605 Å (section 3.2.6). It is possible that this distance may represent the copper(II)–copper(II) distance in the complex [Cu$_2$(H$_{12}$cyendimer)](ClO$_4$)$_4$, but since the conformation of the ligand may vary, there is no definite way of knowing without an X-ray structure analysis which was not possible to undertake due to the lack of suitable crystals. The magnetic properties of this complex are discussed in section 3.7.

3.6.2 Copper complexes of large ring macrocycles (30 and 36 membered ring).

It was shown (this chapter) that the 28 membered ring H$_4$cyendimer (3.4) and H$_{12}$cyendimer (3.6) were capable of coordinating two copper atoms. The larger ring macrocycles H$_4$cyprodimer (3.7) and H$_4$cyhexdimer (3.8) may offer an interesting variation on the previously described systems, by increasing the bridging distance between the two N_4 donor sets (fig 3.38).



R = $-CH_2CHOHCH_2-$ (3.7)
R = $-(CH_2)_6-$ (3.8)

Fig 3.38 Schematic diagrams of 30 and 36 membered rings.

3.6.2.1 Copper(II) complexes of the reduced ligands H_{12}cyprodimer (3.42) and H_{12}cyhexdimer (3.43)

The very low solubility of the 30- and 36- membered octa-aza macrocycles (3.42 and 3.43) presented problems in forming copper complexes. Soxhlet extraction of the ligand into a solution of copper(II) perchlorate in a highly polar solvent (pyridine or dmf) for protracted periods did not produce a colour change which would have indicated a reaction between the ligand and copper(II) salt. The reduced ligands were not investigated any further for these reasons.

3.6.2.2 Copper(II) complexes of the tetraimine ligands H_4cyprodimer (3.7) and H_4cyhexdimer (3.8)

These tetraimine ligands showed a greater solubility in most solvents than their reduced analogues. Although a green colouration was produced when the ligands were added to a solution of copper(II) perchlorate in most solvents, any attempt to induce precipitation of the copper(II) complex resulted in recovery of the ligand. It has been reported that certain complexes cannot be prepared in the presence of water. It is possible that the water may influence the thermodymamic stability of the copper(II) complex and it therefore becomes necessary to remove all traces of water before the copper complex can be isolated. To overcome these problems two approaches can be made.

1) All solvents and starting materials can be vigourously dried.
2) A dehydrating solvent such as triethylorthoformate[36] or 2,2-dimethoxypropane[37] must be used.

The latter method was attempted due to the solubility of both the copper(II) perchlorate and the ligand in the triethylorthoformate (teof). Triethylorthoformate will react with water according to the following equation:

$$(C_2H_5O)_3CH + H_2O \longrightarrow 2C_2H_5OH + C_2H_5OOCH$$

Both the ligands (3.7 and 3.8) reacted with copper(II) perchlorate in heated triethylorthoformate (200°C) to give high yields of a dinuclear copper(II) complex. The yield was almost 100% based on a formlation as the tetraperchlorate complexes, which was confirmed by elemental analysis (table 3.9). The perchlorate complexes of both ligands were insoluble in most solvents and could not be recrystallised. On heating in dmf, dissociation occurred to give the free ligands. The neutral copper(II) complexes could not be prepared by reaction of the ligands with copper(II) acetate, or by neutralisation of the perchlorate complexes with a base, as had been found for other systems (section 3.3.2). The magnetic properties are discussed below.

3.7.1 Magnetic data.

The copper(II) ion has one unpaired electron and will thus be expected to give rise to a magnetic moment close to the spin-only value of 1.73 Bohr Magnetons (BM). For biscopper(II) complexes there are at least two types of copper-copper interaction which may occur to give an abnormal magnetic moment.

1) Direct interaction[38].

Compounds having this type of interaction have two or more copper(II) ions in close proximity, and a pairing of spins on the copper atoms by direct overlap of the metal orbitals containing the unpaired electrons gives rise to a subnormal magnetic moment.

2) Superexchange interaction[39].

The copper(II) compounds belonging to this category usually have a larger copper-copper distance than those with direct interaction, and the coupling of the spins takes place using orbitals on one or more atoms in a bridging ligand.

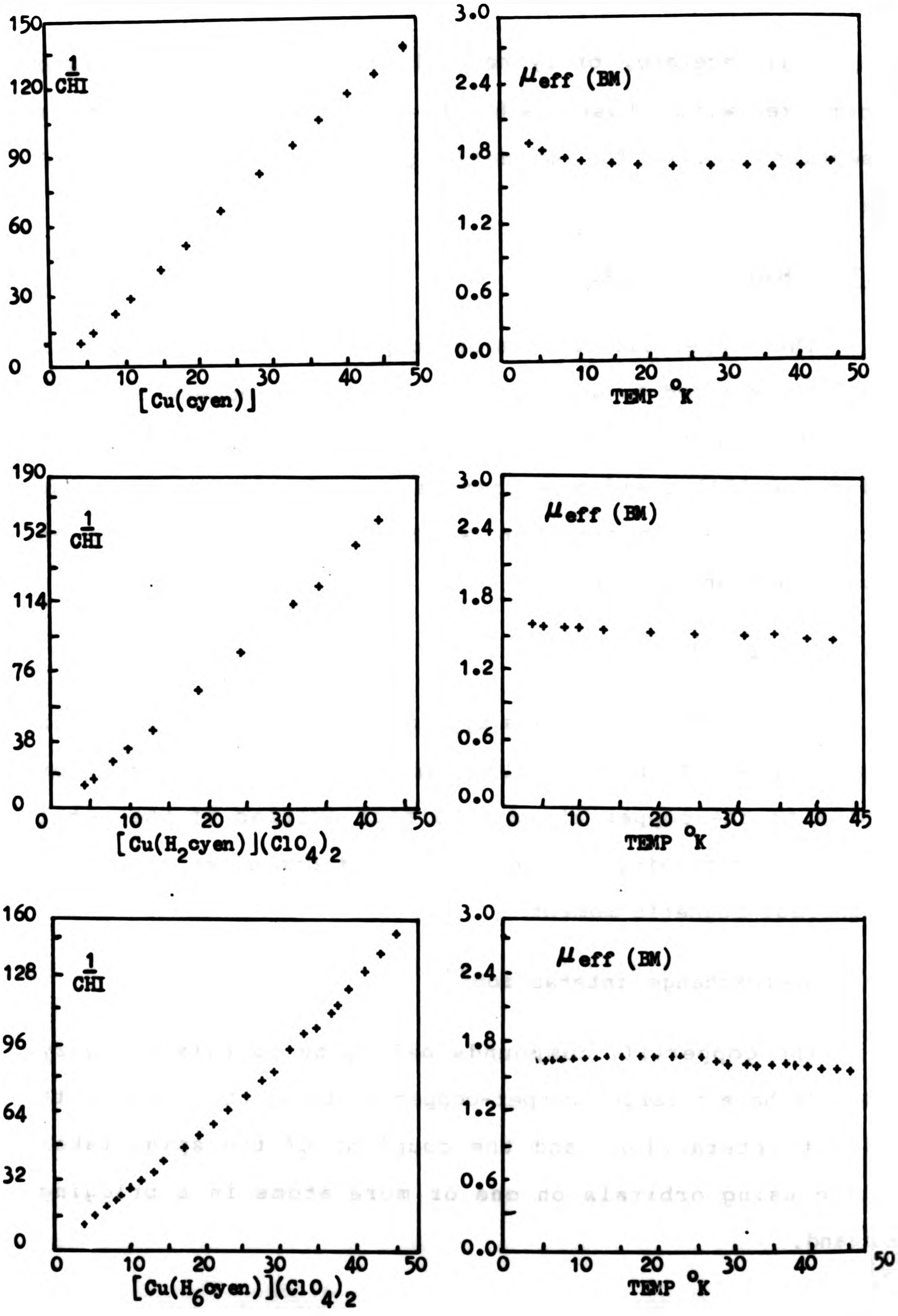


Fig 3.39 Magnetic data for the copper(II) complexes of H_2cyen and H_6cyen

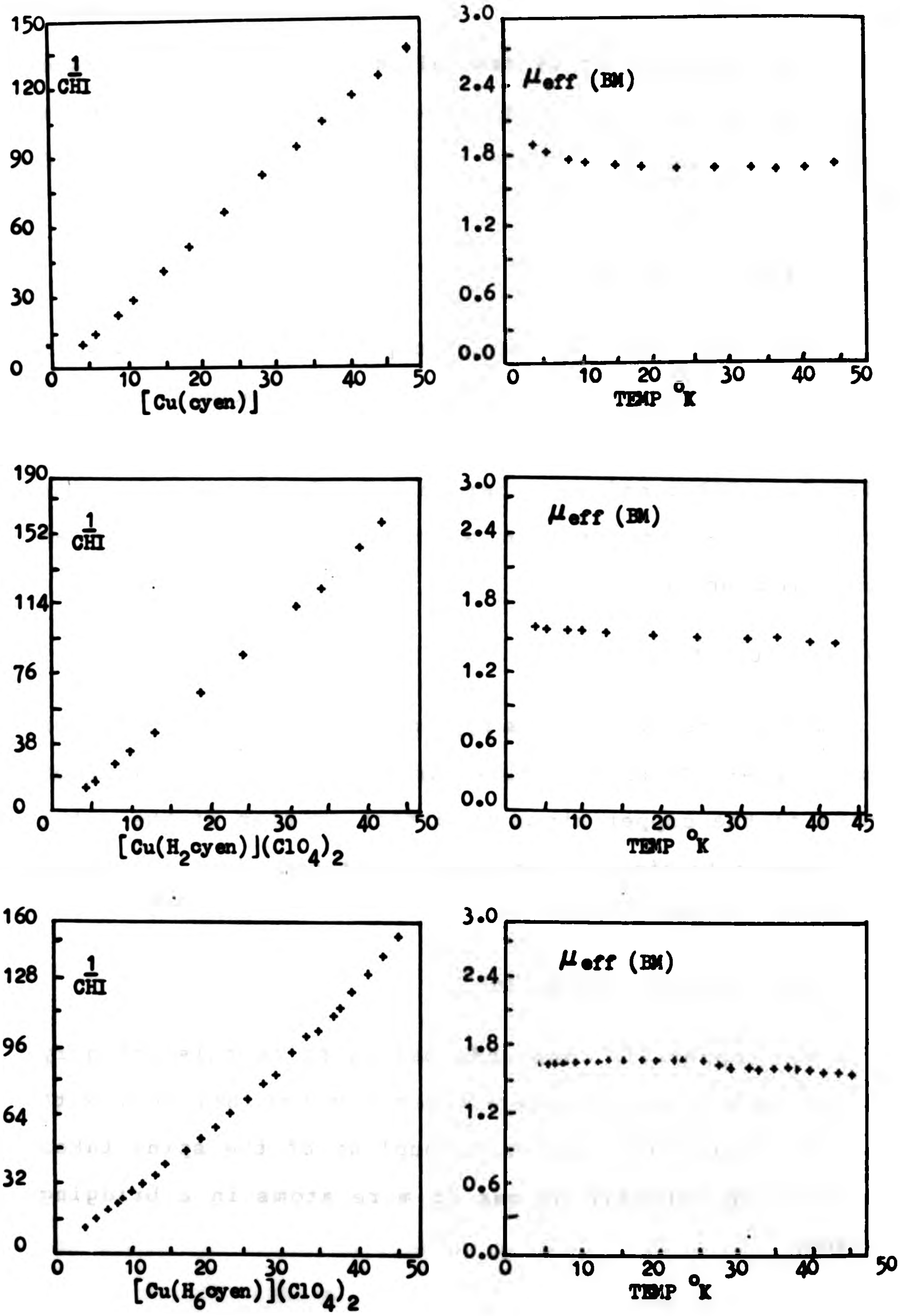
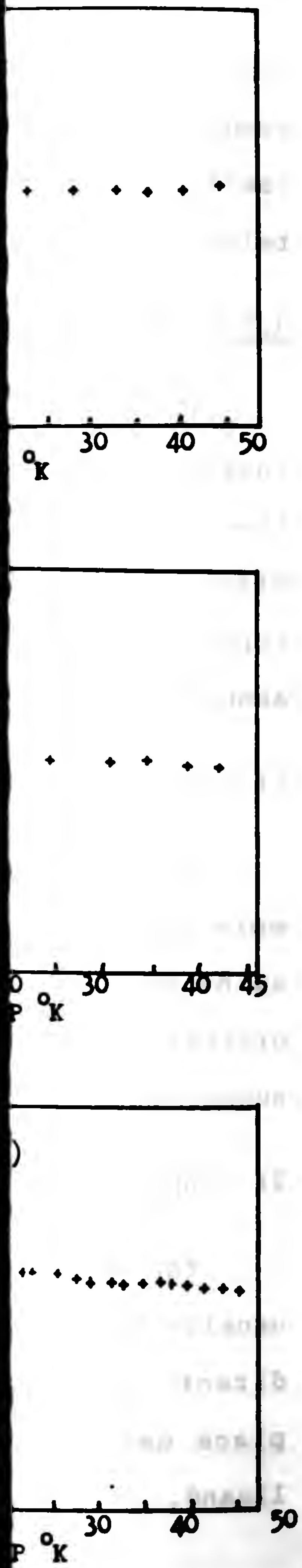


Fig 3.39 Magnetic data for the copper(II) complexes of H_2cyen and H_6cyen



) complexes of

3.7.2 Mononuclear copper(II) complexes.

In the series of copper(II) complexes discussed in this chapter, the mononuclear complexes will be expected to show normal Curie Weiss behaviour which is dependent on a linear relationship between temperature and the reciprocal of the magnetic susceptibility. Results for the copper(II) complexes of H_2cyen and H_6cyen are given in fig 3.39, facing page. The magnetic moments for these three complexes are close to the expected value of 1.73 BM and they show normal Curie Wiess behaviour (see figure 3.39). Anomalously low values would only be expected if there were short intermolecular contact distances between copper atoms, or superexchange interaction in which a copper atom makes a close contact with a neighbouring ligand atom.

3.7.3 Dinuclear copper complexes.

The dinuclear copper complexes discussed in this chapter are expected to be capable of showing direct copper-copper interactions, because the ligands can constrain the copper atoms to lie very close together. For example, the complex [Cu(H_4cyendimer)]$(ClO_4)_3$ (3.36), the particularly short Cu-Cu distance (2.444 Å) was due to the "twisted" conformation of the ligand (see section 3.2.6) which has also been found[3] in the related free ligand H_4cyprodimer (3.7).

The variable temperature magnetic measurements are shown in fig 3.40, facing p119. All three biscopper(II) complexes (fig 3.40) have subnormal magnetic moments

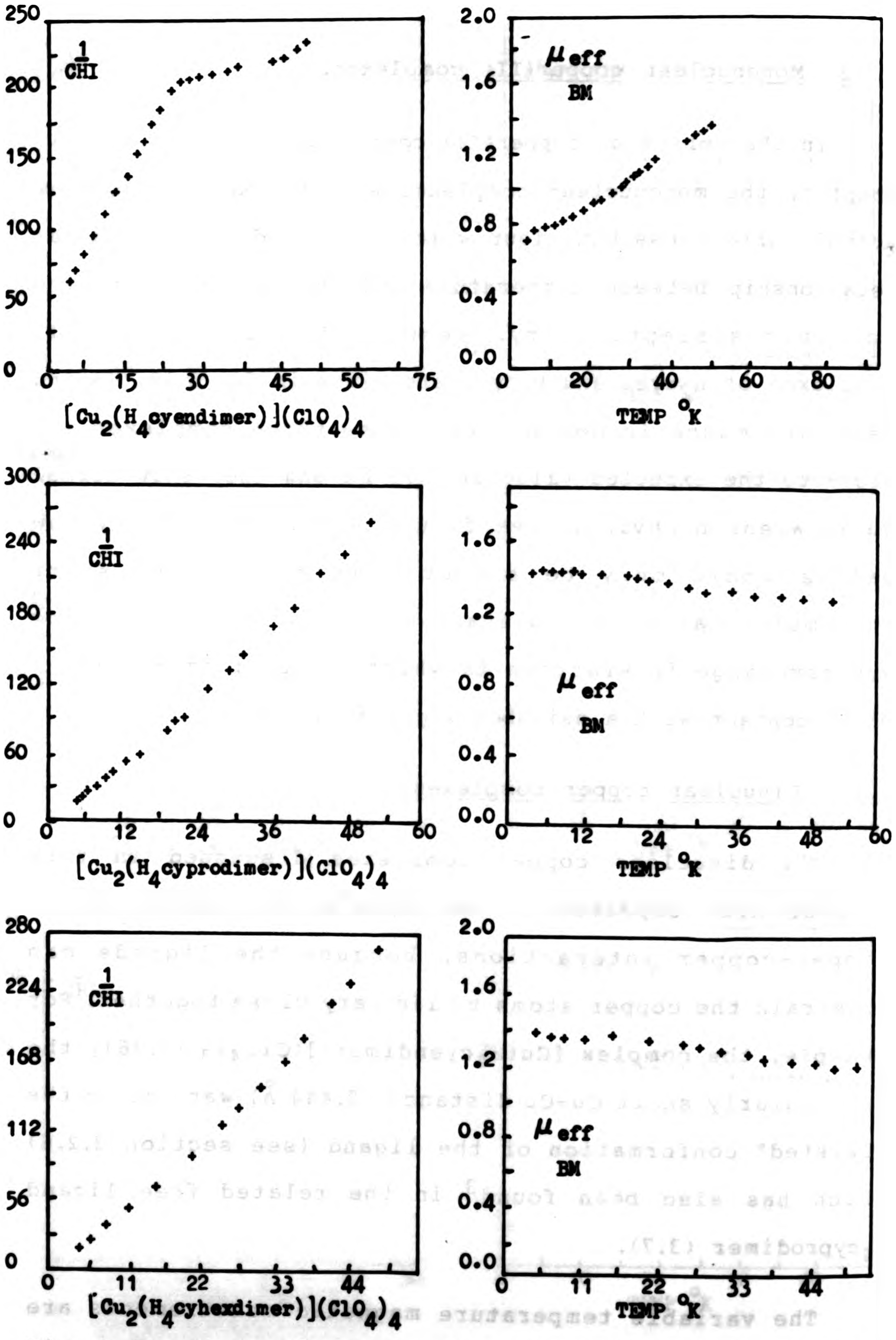


Fig 3.40 Magnetic data for the three tetraimine biscopper(II) complexes

compared to the expected value of 1.73 BM for one copper(II) atom per molecule. The slight increase in the magnetic moment as the temperature decreases is suggestive of a triplet ground state molecule resulting from a ferromagnetic interaction between the two copper(II) atoms in the dimer.

The last biscopper(II) complex to be considered in this chapter is $[Cu_2(H_{12}cyendimer)](ClO_4)_4$. The ligand H_{12}cyendimer is more flexible (section 3.2.6) and would be expected to allow greater copper-copper separations than that found in the related complex $[Cu(H_4cyendimer)](ClO_4)_4$ (3.35). As expected, the magnetic data for $[Cu_2(H_{12}cyendimer)](ClO_4)_4$ does show normal Curie Weiss behaviour and a μ eff of ca. 1.8 BM per copper(II) atom (fig 3.41), thus confirming the absence of direct or superexchange interaction between the copper(II) atoms.

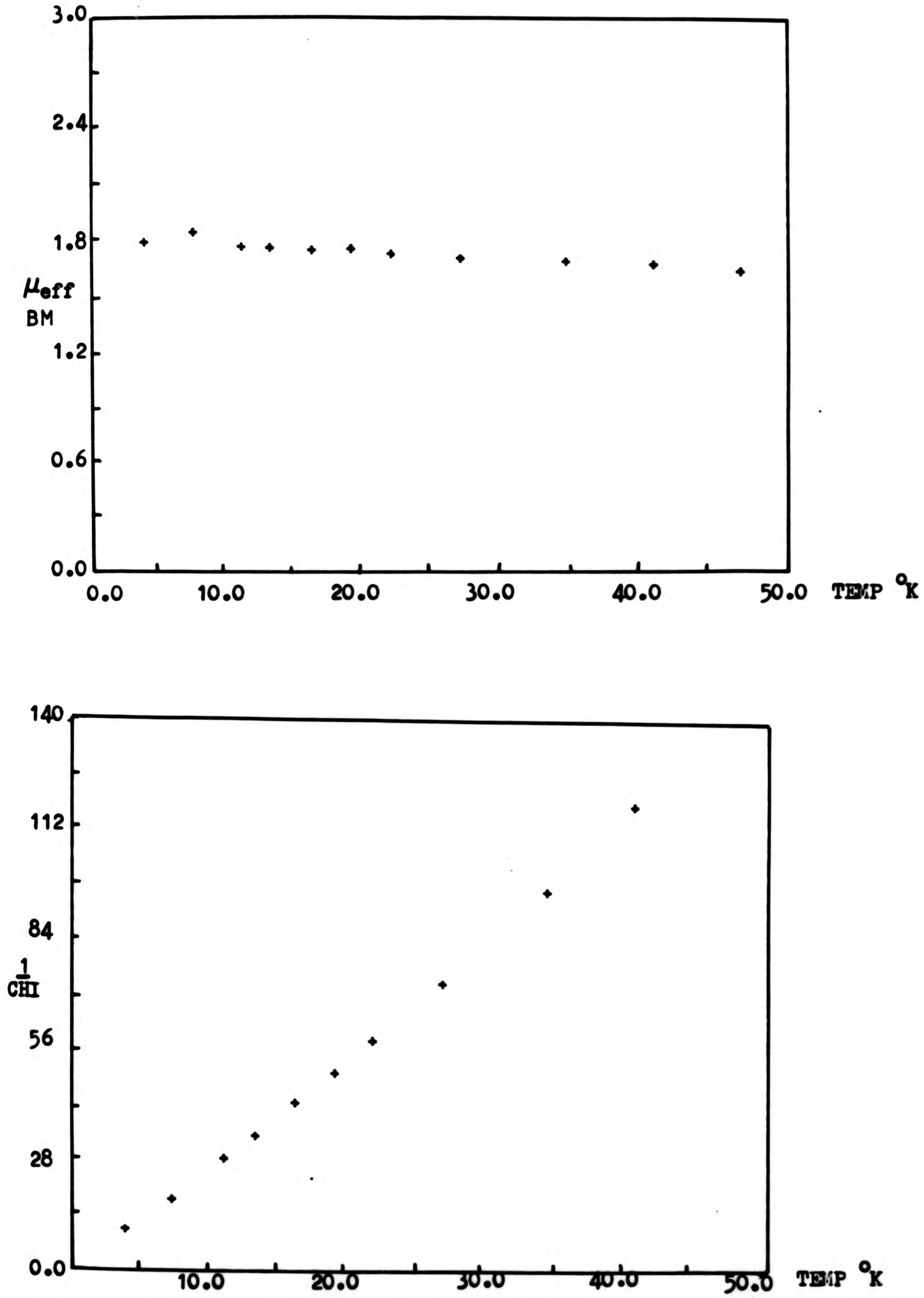


Fig 3.41 Magnetic data for $[Cu_2(H_{12}cyendimer)](ClO_4)_4$

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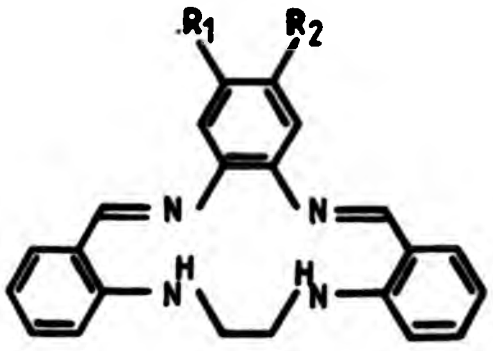
CHAPTER 4

4.1 Mono- and dinucleating aza-macrocycles containing 1,2-diaminobenzene units.

The dinucleating ligands discussed in this chapter correspond to the fused and mono bridged bisquadridentate types III and I respectively (chapter 2).

4.1.1 Introduction: Mononucleating aza macrocycles.

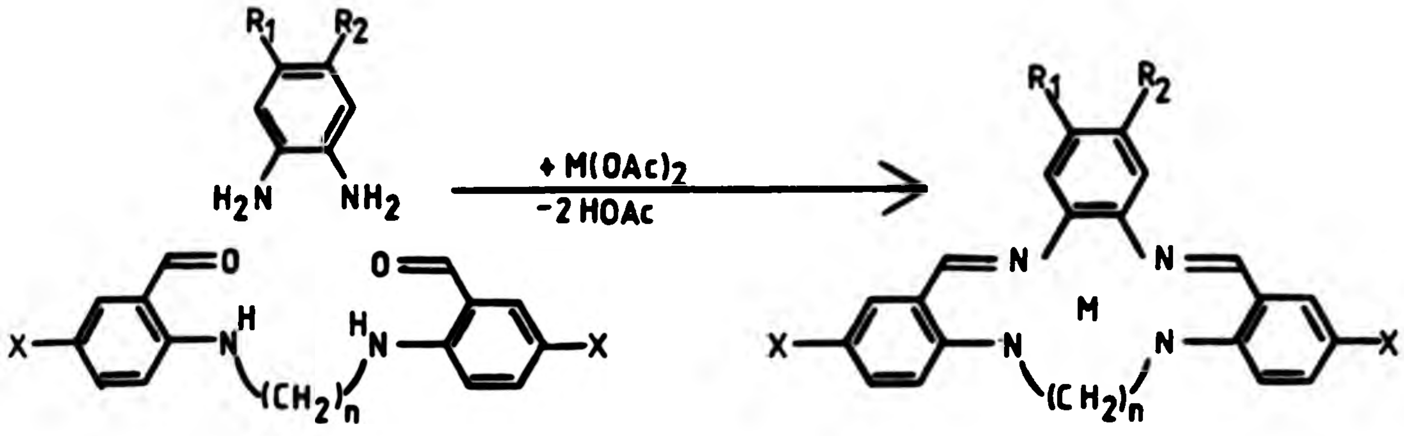
The tetra-aza macrocycles in this section are restricted to those with an aromatic bridging group between the imine nitrogen atoms (scheme 4.1). These ligands can be prepared by condensation of 4.4 and 4.5 in the presence of a catalyst such as zinc(II) acetate or PTSA[2]. Prior to the commencement of this project two free ligands had been reported[1]. Scheme 4.1 lists the free ligands independently prepared during this thesis[2].



		Ref
4.1	R1 = R2 = H	1a
4.2	R1 = R2 = CH_3	1b
4.3a	R1 = H, R2 = Cl	2
4.3b	R1 = H, R2 = NO_2	2
4.3c	R1 = H, R2 = CH_3	2
4.3d	R1 = H, R2 = COOH	2

Scheme 4.1 Tetra-aza macrocycles

Many metal complexes (mainly Cu(II), Co(II) and Ni(II)) have been prepared[1b] by in situ ("template") reactions of the ligand precursors and a metal salt (scheme 4.2).



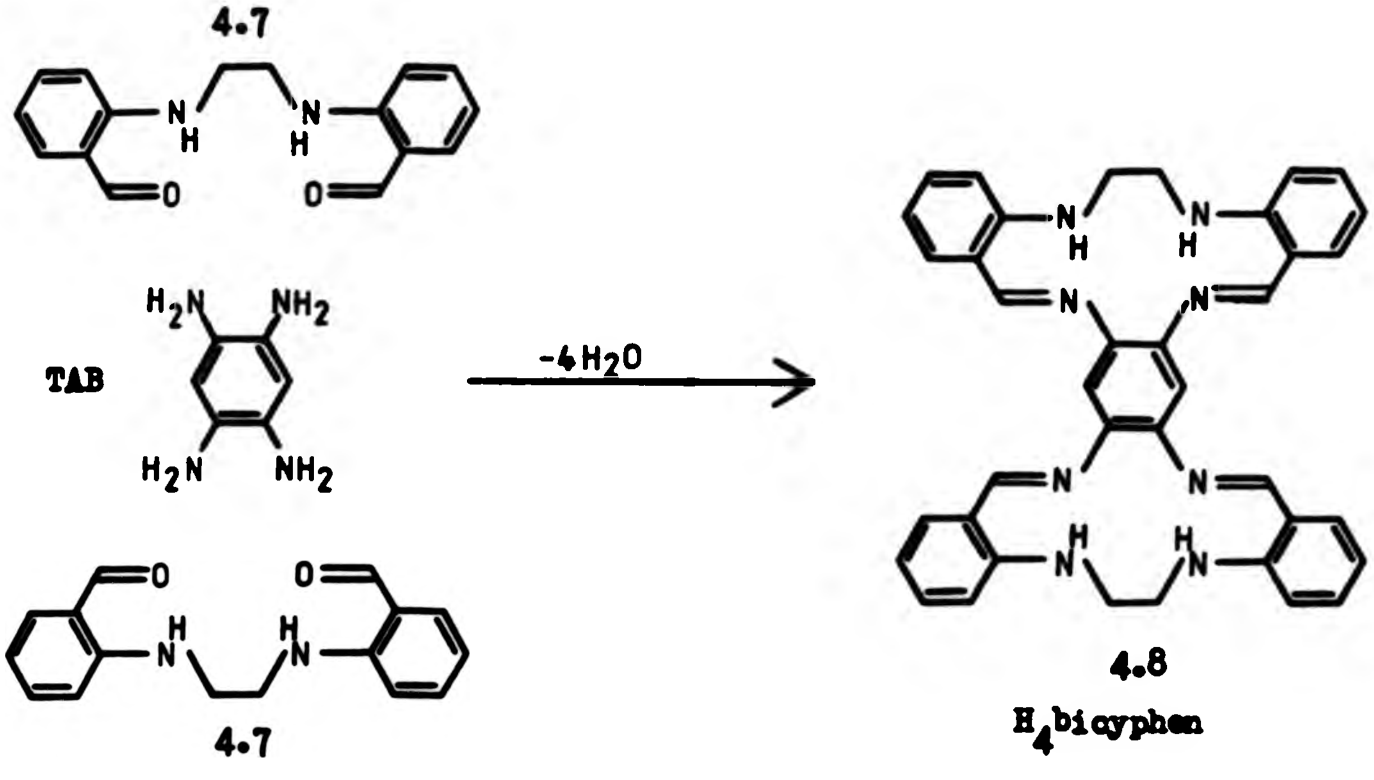
n	X	R1	R2
2	H	H	H
2	NO_2	Me	H
3	H	Me	Me
3	NO_2	-C4H4-	
3	NO_2	CL	H
		NO_2	H

Scheme 4.2 Template syntheses of macrocyclic metal complexes[1b].

A high proportion of all the possible permutations of Ni(II), Co(II) and Cu(II) complexes shown in scheme 4.2 have been prepared by Black and co-workers[1b]. These _in situ_ reactions have been termed[3] 'template reactions' and result in the neutral metal complex 4.6 formed after loss of the anilino protons. The free ligands for the complexes shown in the scheme had not been reported at the commencement of this work, with the exception of 4.1 and 4.2.

4.1.2 Introduction: Dinucleating-aza macrocycles.

This class of ligand could be prepared from the condensation of the dialdehyde (4.7) with a suitable tetra-amino precursor e.g. 1,2,4,5-tetraaminobenzene tetrahydrochloride (TAB.4HCl) (4.28) (scheme 4.3).



Scheme 4.3 Reported synthesis of H_4bicyphen (4.8)

A preliminary communication[4] reported the synthesis of H_4bicyphen (4.8). The reaction involved partial (~90 %) neutralisation of the TAB.4HCl with sodium methoxide solution followed by condensation with C_2-dialdehyde (4.7) in refluxing methanol. A yield of 28 % was recorded. Problems with solubility were encountered, and the dinuclear Cu(II) complex was prepared by extraction of the ligand from a Soxhlet thimble by refluxing pyridine from a solution of copper(II) acetate monohydrate (in pyridine). Characterisation of the ligand was made by infrared, elemental analysis and eims M^+ = 602. The copper(II) complex was to involatile to give an eims.

4.2.1 Results and discussion for mononucleating aza macrocycles.

The mononuclear analogue for all the dinucleating ligands considered in this chapter is H_2cyph (4.1). This ligand was prepared (section 8) along with the copper(II) (neutral 4.9 and dicationic 4.10) complexes (scheme 4.4, table 4.1). The reason for preparing these Cu(II) complexes was to investigate their stability to oxidation before testing them or their biscopper(II) analogues as oxidation catalysts, and to compare their physical and spectral properties with those of the related dinuclear systems. Reduction of the imine links in 4.1 gives the tetra-aza macrocycle 4.11 which contains only secondary type nitrogen atoms 4.11. Table 4.1 contains analytical data for the ligands and their copper complexes, and other closely related compounds which are discussed later in this chapter.

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4.2.1 Results and discussion for mononucleating aza macrocycles.

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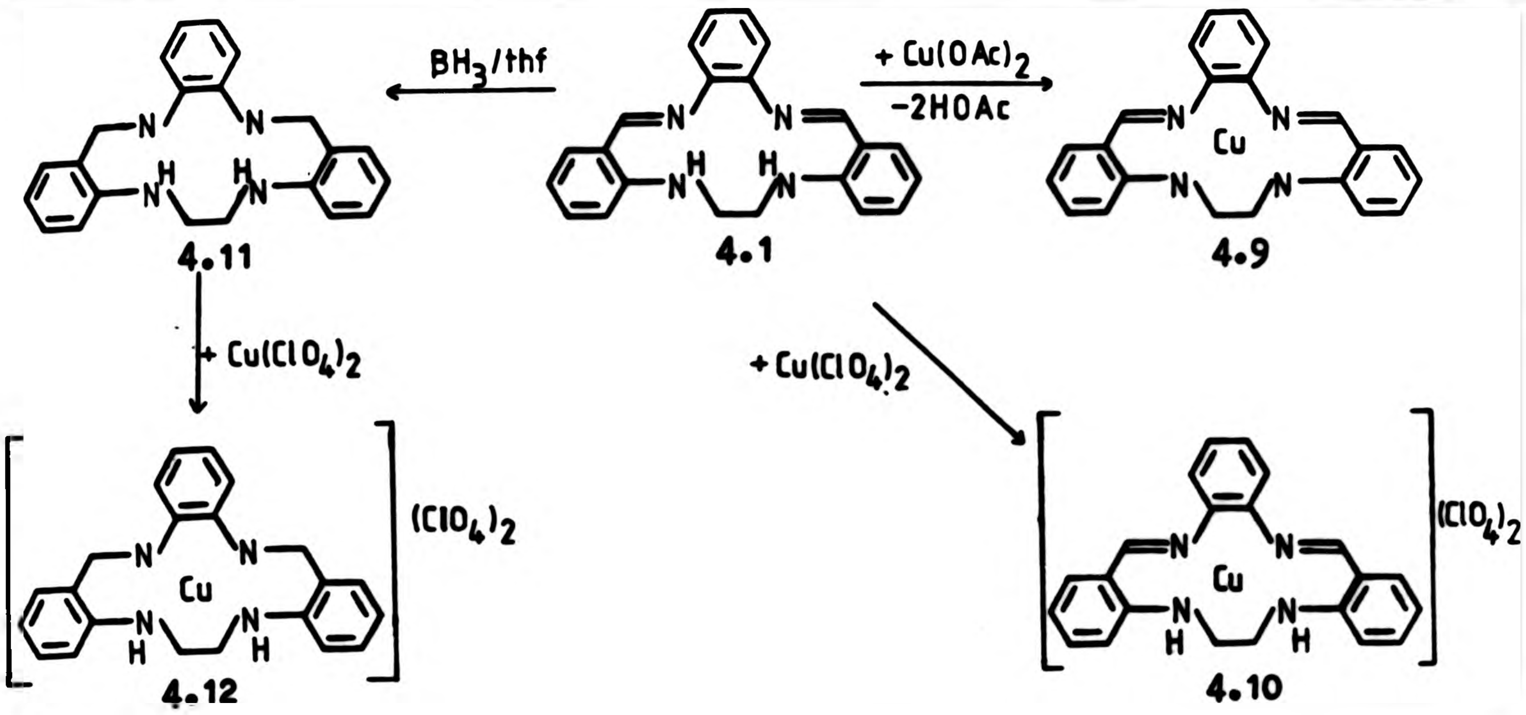
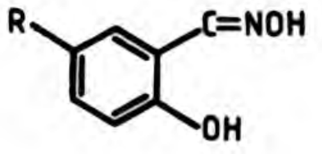


Scheme 4.4 Mononucleating ligands and their copper(II) complexes.

Compound	C%	H%	N%	Cu%
H_2cyph (4.1)	77.5	6.0	16.4	
(Calc. for $C_{22}H_{20}N_4$)	(77.6)	(5.9)	(16.5)	
[Cu(Cyph)] (4.9)	66.0	4.5	13.8	15.8
(Calc. for $CuC_{22}H_{18}N_4$)	(65.7)	(4.5)	(13.9)	(15.8)
[Cu(H_2cyph)]$(ClO_4)_2$ (4.10)	44.2	3.4	9.6	10.9
(Calc. for $CuC_{22}H_{20}N_4Cl_2O_8$)	(43.8)	(3.3)	(9.3)	(10.5)
H_6cyph (4.11)	76.6	7.0	16.3	
(Calc. for $C_{22}H_{24}N_4$)	(76.7)	(7.0)	(16.3)	
[Cu(H_6cyph)]$(ClO_4)_2$ (4.12)	43.4	4.0	9.2	10.4
(Calc. for $CuC_{22}H_{24}N_4Cl_2O_8$)	(43.5)	(4.0)	(9.2)	(10.5)
[Cu(H_2cyph)$(OMe)_2$] (4.18)	62.2	4.8	12.1	14.0
(Calc. for $CuC_{24}H_{22}N_4O_2$)	(62.4)	(4.8)	(12.1)	(13.8)
[Cu(cyphX)] (4.28)	60.9	3.4	13.4	
(Calc. for $CuC_{22}H_{24}N_4O_2$)	(61.5)	(3.3)	(13.0)	

Table 4.1 Analytical data for the mononucleating ligands and their copper(II) complexes, found (calculated).

The copper(II) perchlorate complex 4.10 of H_2cyph has retained the anilino protons while these have been lost in the neutral complex 4.9. It is an unusual situation for complexes to be stable at two different levels of protonation of the ligand. Many chelating ligands which coordinate copper(II) at medium or neutral pH, will on protonation release the copper(II), and recovery of the ligand can be achieved[5]. This is particularly useful for metal ore refining by solvent extraction.



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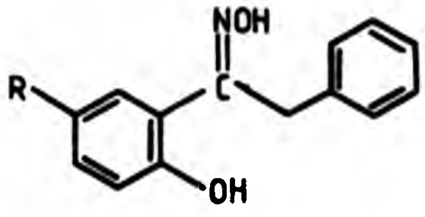
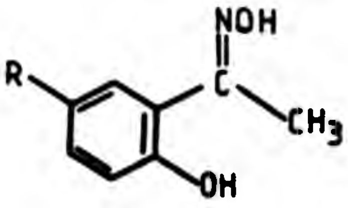


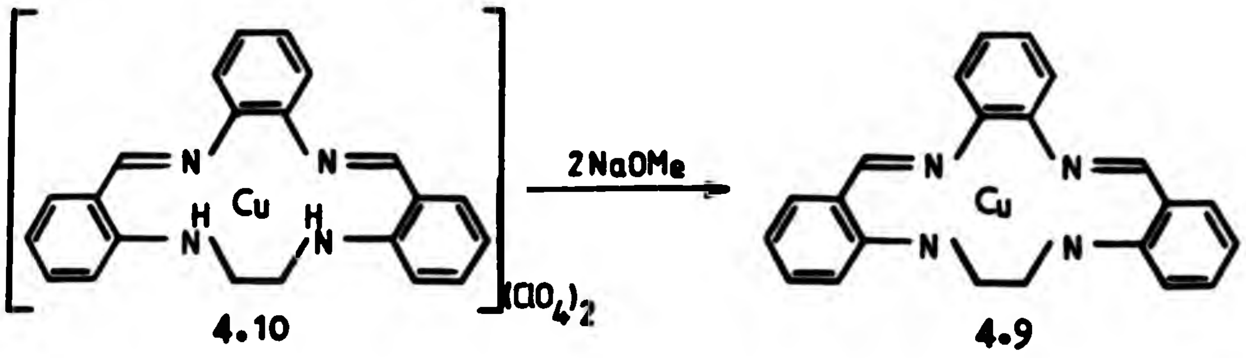
P17



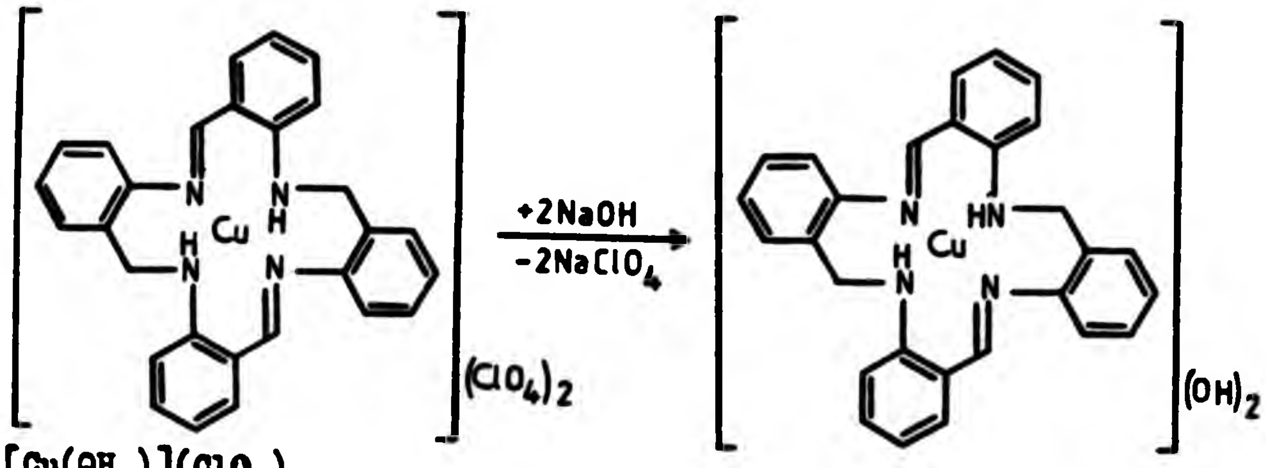
SME 529

Fig 4.1 Metal extractants[5] marketed by Acorgee ltd (P50,P17) and Shell Chemical Company (SME 529).

The conversion from the cationic complex $[Cu(H_2cyph)](ClO_4)_2$ (4.10) to the neutral complex [Cu(cyph)] (4.9) by the addition of sodium methoxide solution (scheme 4.5) has been confirmed by solid state infrared spectra and elemental analysis (also see section 3). In contrast, the copper(II) perchlorate complex 4.13 of a 16-membered ligand QH_4 which also contains the o-amino benzylimine unit was reported[6] to retain the anilino protons on addition of base, and only exchange of anions was effected (scheme 4.6).



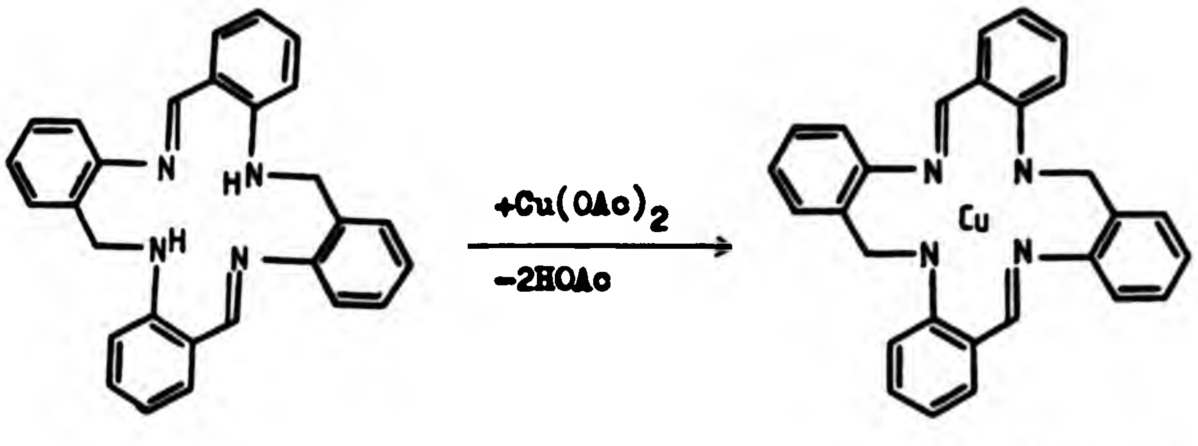
Scheme 4.5 Deprotonation of $[Cu(H_2cyph)](ClO_4)_2]$ (4.10).



$[Cu(QH_4)](ClO_4)_2$ (4.13)

Scheme 4.6 Typical anionic exchange reaction.

It is surprising that the neutral complex $[Cu(QH_2)]$ (4.14) was not formed by addition of base to the copper(II) perchlorate complex $[Cu(QH4)](ClO_4)_2$, since the ligand QH4 has been independently reported[7] to give the neutral complex $[Cu(QH_2)]$ (4.14) when treated with copper(II) acetate (scheme 4.7). The deprotonated nature of the latter has recently been confirmed by an X-ray structure determination[11] at the Polytechnic of North London.



QH_4

$[Cu(QH_2)]$ (4.14)

Scheme 4.7 Preparation of $[Cu(QH_2)]$ (4.14)

4.2.2 The Chemistry of H_2cyph (4.1)

Two methods have been reported[1b,8] for preparing the neutral complex [Cu(cyph)] (4.9).

1). Preparation of the ligand H_2cyph (4.1) followed by copper(II) complexation[8]. A mixture of preformed ligand and copper(II) acetate in refluxing methanol or dmf gave [Cu(cyph)] (4.9) (scheme 4.4).

2) Template reaction[1b]. A mixture of C_2-dialdehyde (4.7), 1,2-diaminobenzene and copper(II) acetate was heated in dmf or refluxing methanol to give the deprotonated copper(II) complex (scheme 4.2). Higher yields were recorded than method 1. Both methods gave a dark red compound which was

characterised as [Cu(cyph)]. Many closely related compounds have been prepared[1b] by method 2 (scheme 4.2). Thus in general it appears to be easier to prepare copper(II) complexes (scheme) than their free ligands. No mass spectral data were reported[1b] for the copper(II) complexes (scheme 4.2) due to their low volatility.

4.2.3 Discussion

A number of unexpected results were obtained when [Cu(cyph)] was prepared according to methods 1 and 2.

Method 1

Before recrystallisation, the crude product [Cu(cyph)] was shown by eims to contain trace amounts of oxygenated species (table 4.2). The percentage of these oxygenated species is low as the infrared spectra did not show any absorption ascribable to the carbonyl stretch (~1660 cm^{-1}). The relative abundancies of these species are not necessarily a useful guide to purity since the oxygenated species may be more volatile than [Cu(cyph)] or the ethene analogue [Cu(cyph-2H)] (4.15) (m/e = 399). The eims of a sample recrystallised from dmf showed a parent ion at m/e 399, corresponding to the complex [Cu(cyph-2H)] with a dehydrogenated ethane bridge. The colour of the compound when recrystallised from dmf varies from dark red to black, although no differences can be observed in the infrared or mass spectra to account for this. The uv/vis spectra in solution of the various samples are identical, and hence the variations in colours of the solids were attributed to the different crystalline forms.

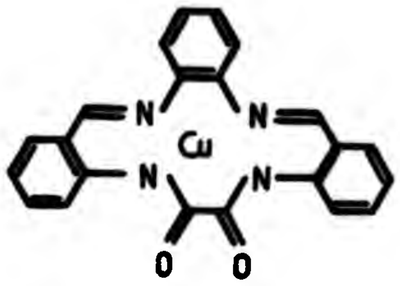
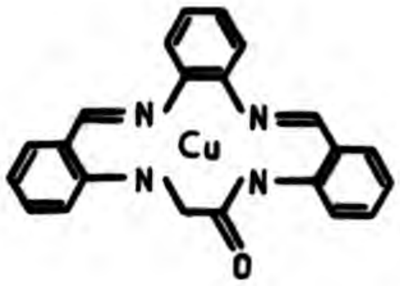
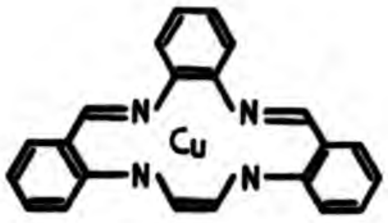
m/e	relative abundance	assignment
429	2%	
415	5%	
399	100%	 4.15

Table 4.2 Assignment of the three highest m/e peaks in the eims of [Cu(cyph)] (crude product) from method 1.

Method 2

The *in situ* reaction of the ligand precursors and copper(II) acetate gave a crude red powder, which showed an identical infra red and uv/vis (solution) spectra to the [Cu(cyph)] from method 1. The eims showed two molecular ions at 401 and 399 suggesting the presence of two types of parent ion (fig 4.2). A sample recrystallised from dmf gave dark red needles, of which an eims showed the presence of only one parent ion at m/e =399.

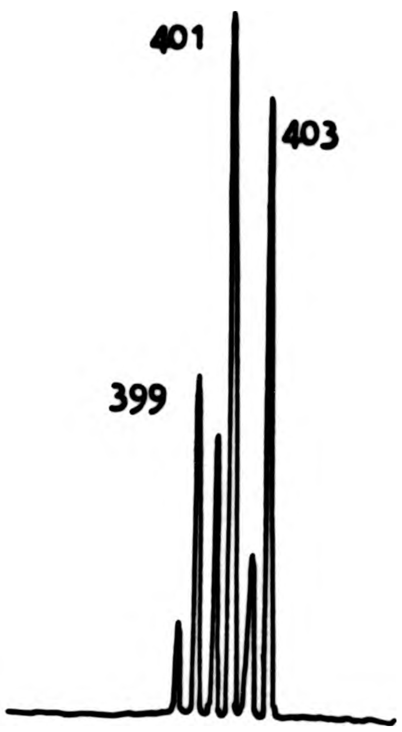
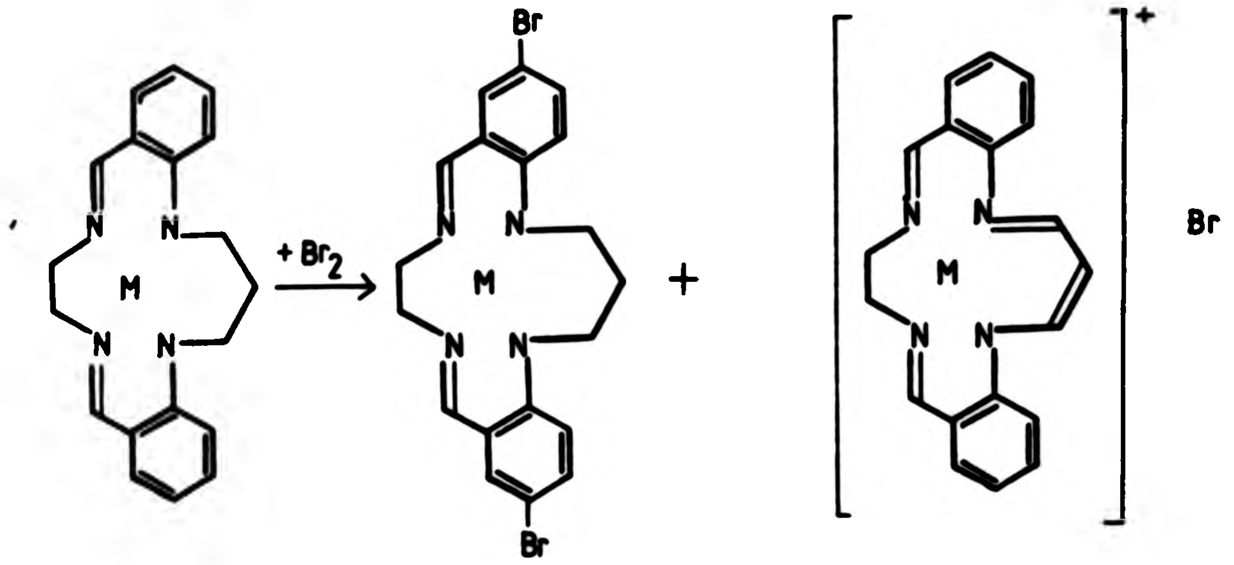


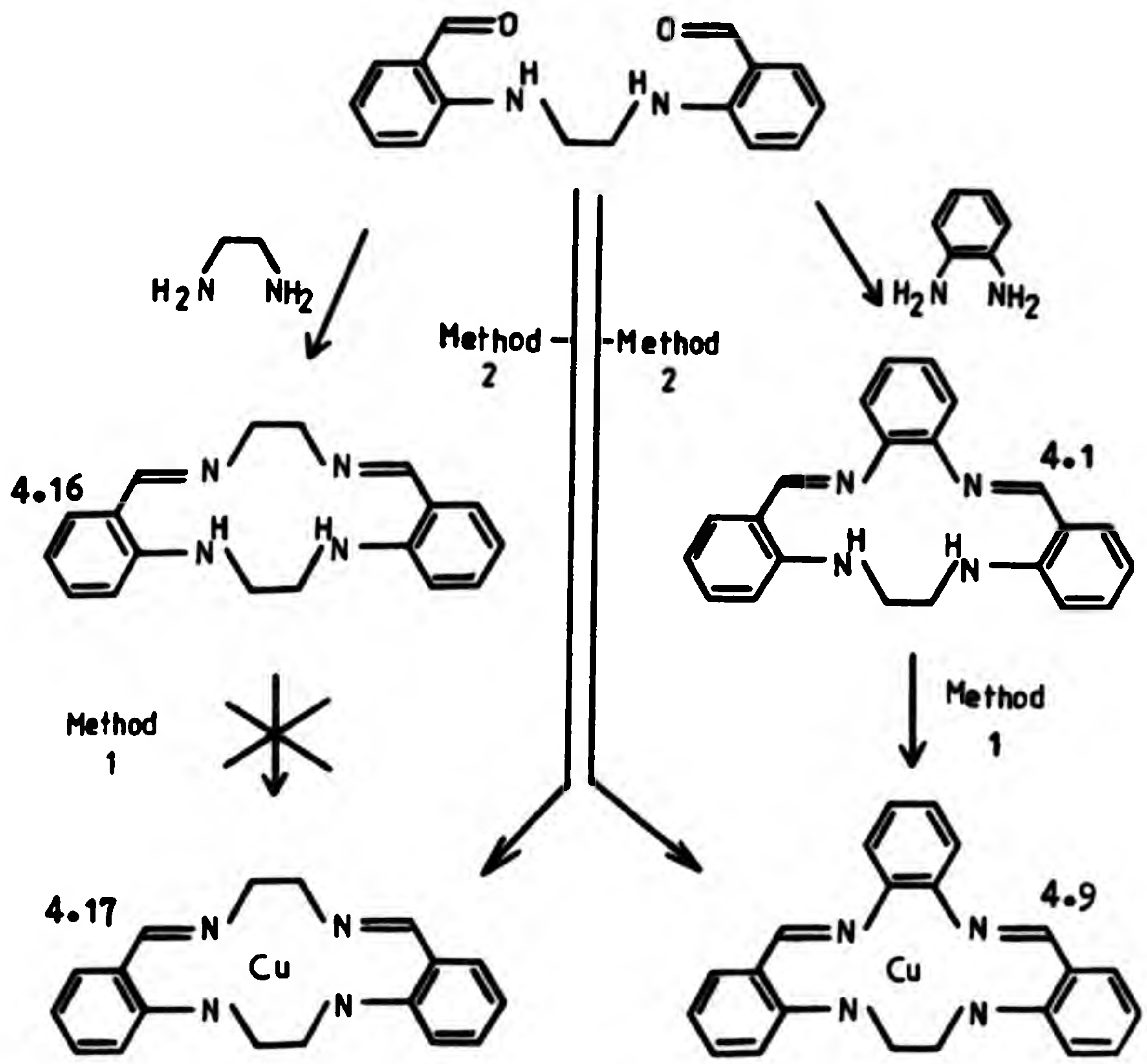
Fig 4.2 Eims of crude [Cu(cyph)] from method 2

It is possible that dehydrogenation could occur in the mass spectrometer to give 4.15. However, the observation that both 399 and 401 (m/e) peak in the 'crude' [Cu(cyph)] from the *in situ* preparation shows that it is possible to obtain a molecular ion for [Cu(cyph)] M^{+} = 401. Therefore it is probable that dehydrogenation occurs in the presence of dioxygen to give a more thermodynamically stable product. No material isolated from method 1 showed a molecular ion corresponding to [Cu(cyph)]. Only the m/e = 399 peak and traces of oxygenated impurities were observed. Therefore it is reasonable to suggest that the thermodynamic stability of [Cu(cyph)] and the dehydrogenated analogue 4.15 may be very close, but extended periods in solution in the presence of dioxygen (see section 4.2.4) may give the dehydrogenated species. The oxidative dehydrogenation of macrocyclic complexes (scheme 4.8) has been investigated by Black and co-workers[9], using a variety of oxidising agents (oxygen, hydrogen peroxide, bromine, iodine, hexa pyridine iron(II) chloride and 2,3-dichloro-5,6-dicyano-p-benzoquinone).



Scheme 4.8 The oxidative dehydrogenation of related tetra-aza macrocycles.

The successful incorporation of Cu(II) into the ligand H_2cyph (4.1) by method 1, contrasts with the situation for the ligand H_2cyen (4.16). It was shown (section 3.2) that copper incorporation using copper(II) acetate did not readily take place for the aliphatic bridged ligands (e.g. 4.16, method 1, scheme 4.9), whereas the template method (method 2) was effective for both types of ligand (e.g. 4.1 and 4.16, scheme 4 . 9).



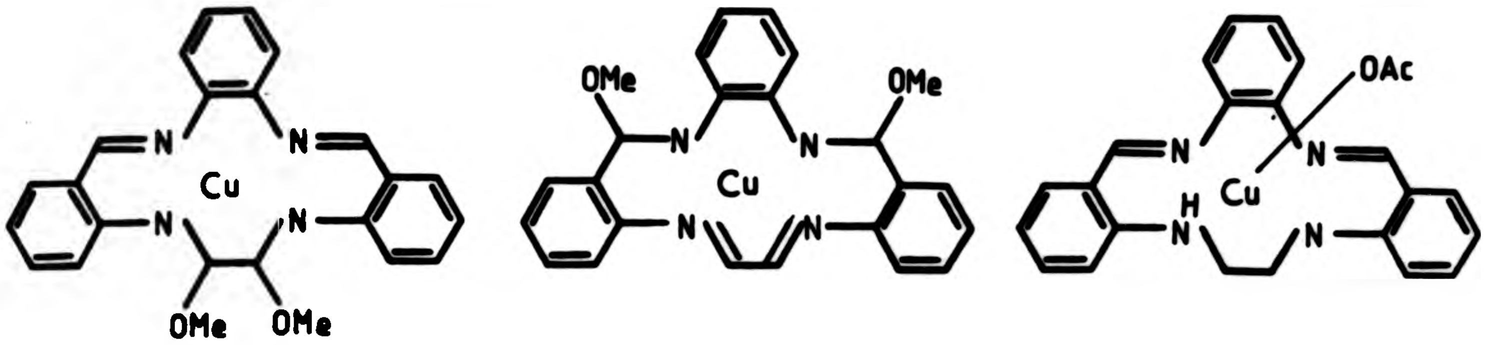
Scheme 4.9 Routes to deprotonated copper(II) complexes of H_2cyen (4.16) & H_2cyph (4.1).

* The addition of triethylamine to a mixture of H_2cyen (4.16) and copper(II) acetate in methanol resulted in partial incorporation of copper(II), but low yields and impure samples were obtained.

4.2.4 Other products from the preparation of [Cu(cyph)] (4.9) by method 1.

The reaction between H_2cyph (4.1) and copper(II) acetate in thf/methanol gave two products.
First the dark red neutral complex, either [Cu(cyph)] (4.9)

or [Cu(cyph-2H)] (4.15) (with M* = 399) was filtered from the reaction mixture. Secondly, after 20 h an unknown product (gold coloured needles) separated from the filtrate. From the molecular weight (M* = 461, from eims measurements) and elemental analysis results, an empirical formulae of $CuC_{24}H_{22}N_4O_2$ was calculated. From this information the product with M* = 461 could be formulated in one of several ways (fig 4.3).



4.18 4.19 4.20

Fig 4.3 Three possible formulations, each having the empirical formulae $CuC_{24}H_{22}N_4O_2$.

An accurate mass fragmentation pattern was obtained to help identify the correct assignment (table 4.3).

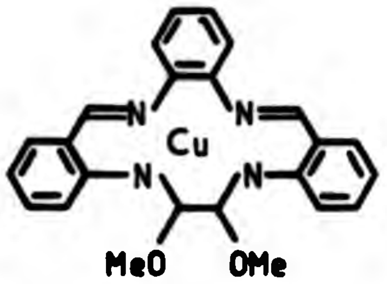
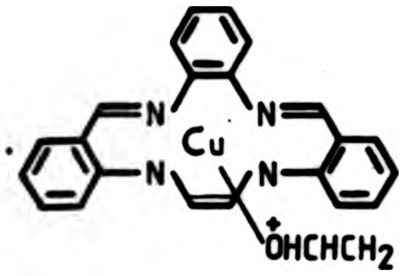
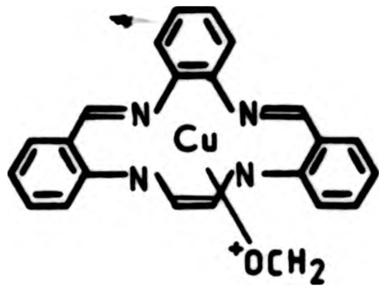
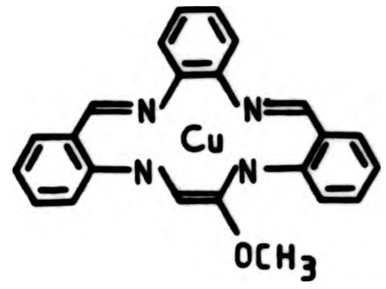
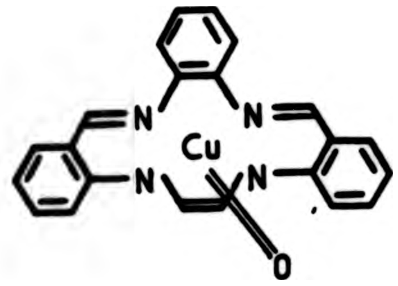
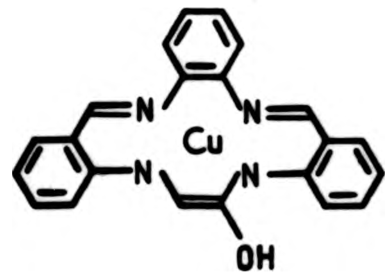
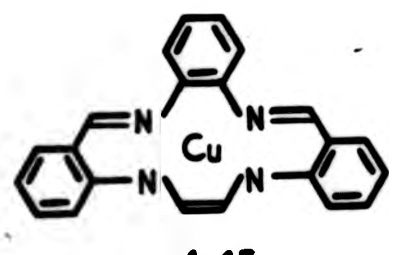
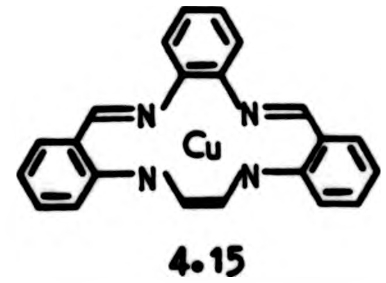
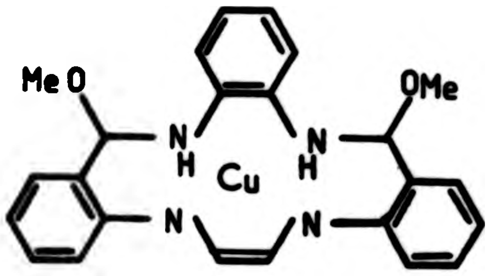
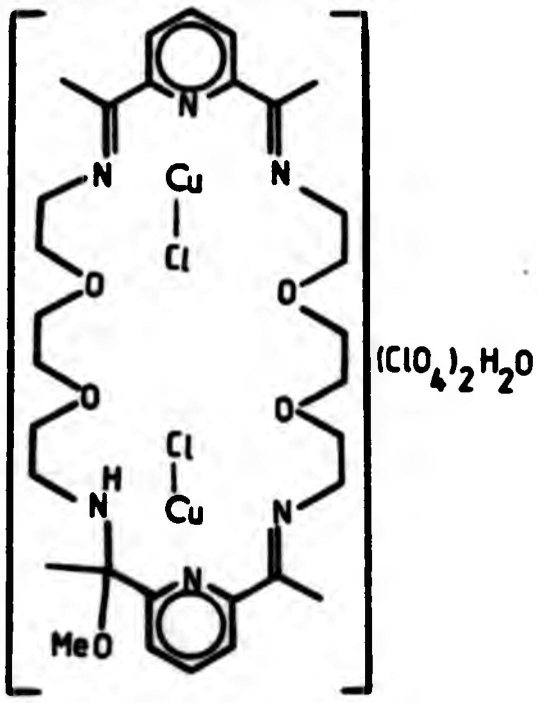
Accurate mass. Found (calculated)	Empirical Formulae	4.20	4.18
*461	$C_{24}H_{22}N_4O_2Cu$		
443.0945 (443.0935)	$C_{24}H_{20}N_4OCu$		
429.0797 (429.0778)	$C_{23}H_{18}N_4OCu$		
415.0662 (415.0662)	$C_{22}H_{16}N_4OCu$		
399.0686 (399.0673)	$C_{22}H_{16}N_4Cu$	 4.15	 4.15

Table 4.3. Accurate mass interpretation of unknown product.
* The molecular ion at 461 could not be detected at high resolution.

The accurate mass determination was interpreted on the basis of the two structures 4.18 and 4.20. Although a complete fragmentation pattern could be proposed for 4.20, the acetate structure was not confirmed by the infrared spectrum. The alternative structure 4.18 could not be fully interpreted for the accurate mass fragmentation pattern, but other evidence would suggest this possibility cannot be ruled out. The addition of methanol to an imine function has been reported[10] for a 30 membered Schiff's base macrocycle (4.22) mainly on the basis of infrared data. The unknown product cannot be formulated in a corresponding way (4.21) because the infrared spectrum did not show a N-H stretch (ca. 3300 cm^{-1}), and the molecular ion for 4.21 should be M* = 463.

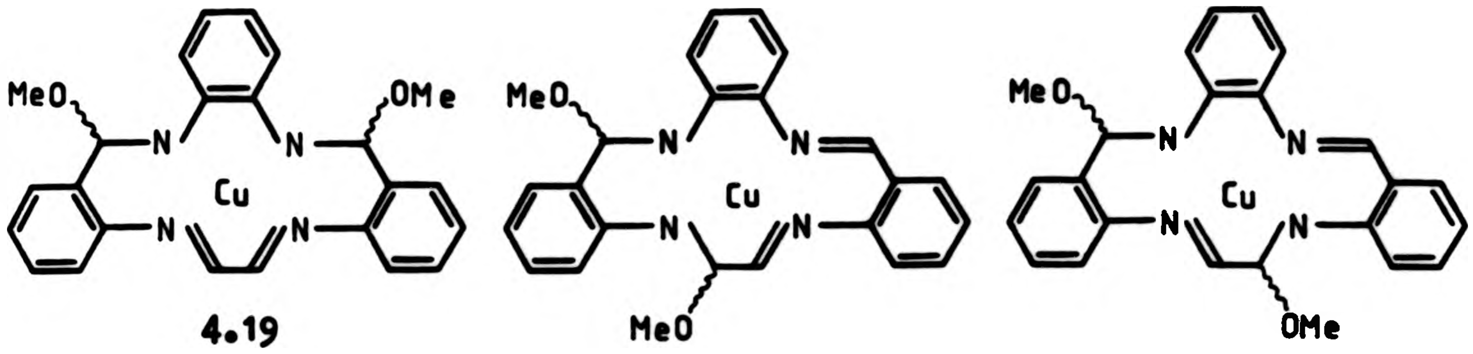


4.21



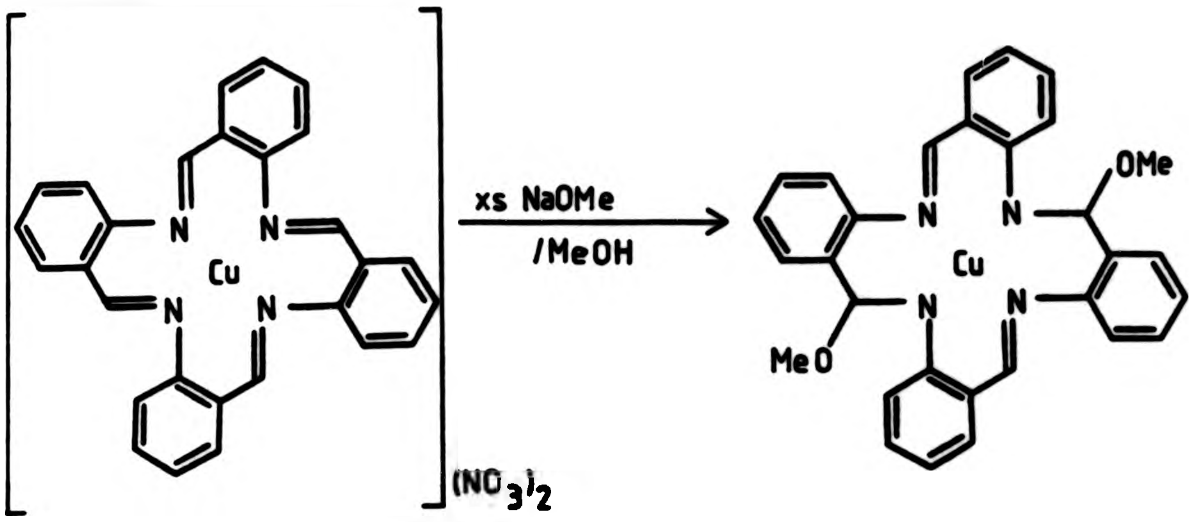
4.22

Neutral complexes having methoxy substituents[11] (e.g. 4.19) could result from the addition of methoxide to a dehydrogenated cationic complex (scheme 4.10). In this scheme there are four possible sites for the attack of the methoxide ion, and therefore several isomers are possible. The formulations 4.18 and 4.19 are the more symmetrical possibilities. The addition of methoxide to the imine carbon creates a chiral centre and therefore each dimethoxide adduct could exist as geometric isomers or in meso or racemic forms (scheme 4.10).



Scheme 4.10 Possible isomers of a dimethoxide adduct.

A cationic tetraimine copper(II) complex (see scheme 4.11) has been shown[11] to undergo nucleophilic addition of the methoxide ion to give a neutral complex.

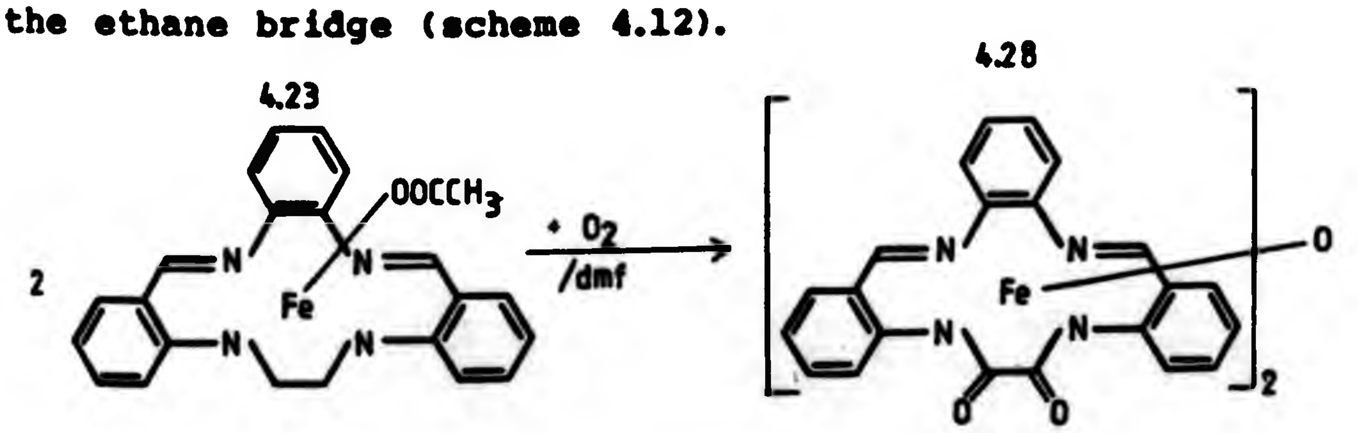


Scheme 4.11 Nucleophilic addition reaction of the methoxide ion to azomethine linkages.

The product (4.18) was not supported by a complete interpretation of the accurate mass fragmentation pattern (table 4.3), but can be related to other findings (section 4.2.5).

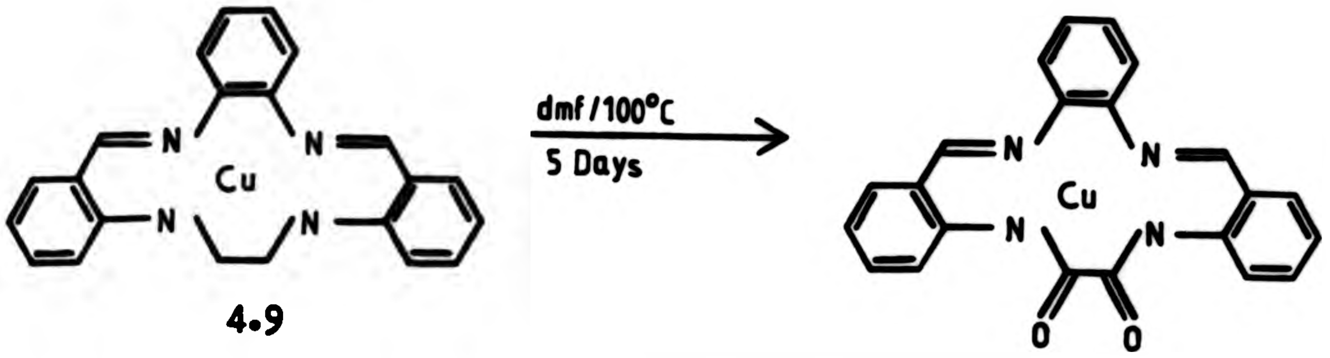
4.2.5 Reactivity of the ethane bridge in [Cu(cyph)].

The evidence presented already in the previous section suggests the ethane bridge may be dehydrogenated. Other reactions may occur, e.g. it has been reported[12] that [Fe(cyph)CH_3CO_2] (4.23) when dissolved in dmf deposits crystals of the oxygenated complex 4.28. This was shown by X-ray structural analysis to have undergone oxygenation at the ethane bridge (scheme 4.12).



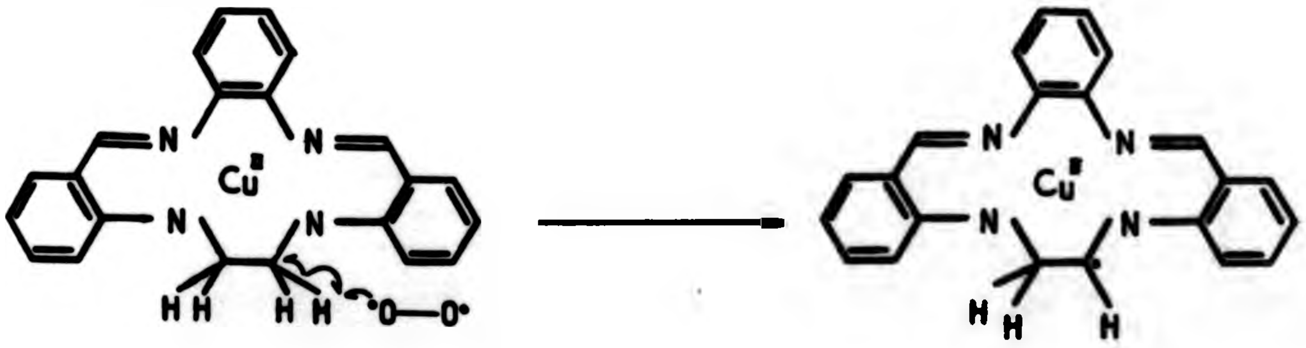
Scheme 4.12 Oxygenation of [Fe(cyph)CH_3CO_2] (4.23)

Preliminary reports[12] have suggested a similar result for [Cu(cyph)] (scheme 4.13).



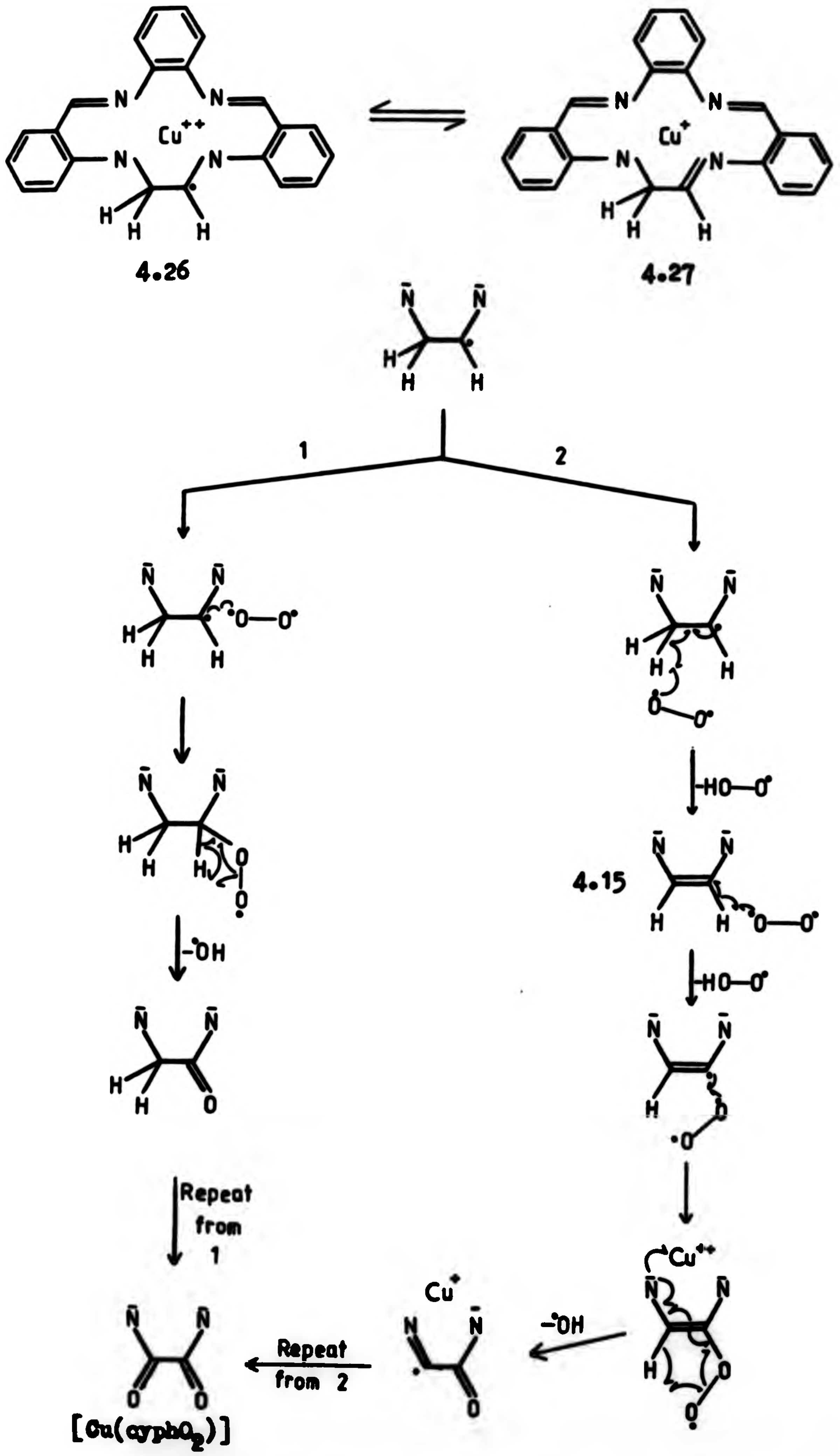
Scheme 4.13 Oxygenation of [Cu(cyph)].

The conditions for this oxygenation were reported[13] tobe 5 days at 100°C in dmf. The reaction mechanism is unknown, but may involve a radical reaction between [Cu(cyph)] and dioxygen (route 1, scheme 4.14). Routes 1 and 2 (scheme 4.14) would both involve the initial reation with dioxygen to give a radical species 4.26, which may be stabilised with a copper(I) analogue 4.27. Route 2 would then explain the formation of a dehydrogenated non-radical species 4.15, corresponding to the compound [Cu(cyph-2H)]. Route 1 depicts a radical reaction to give the dioxoproduct without forming 4.15. Both routes are speculative, although the autooxidation of unsaturated molecules is well established[14].



4.26

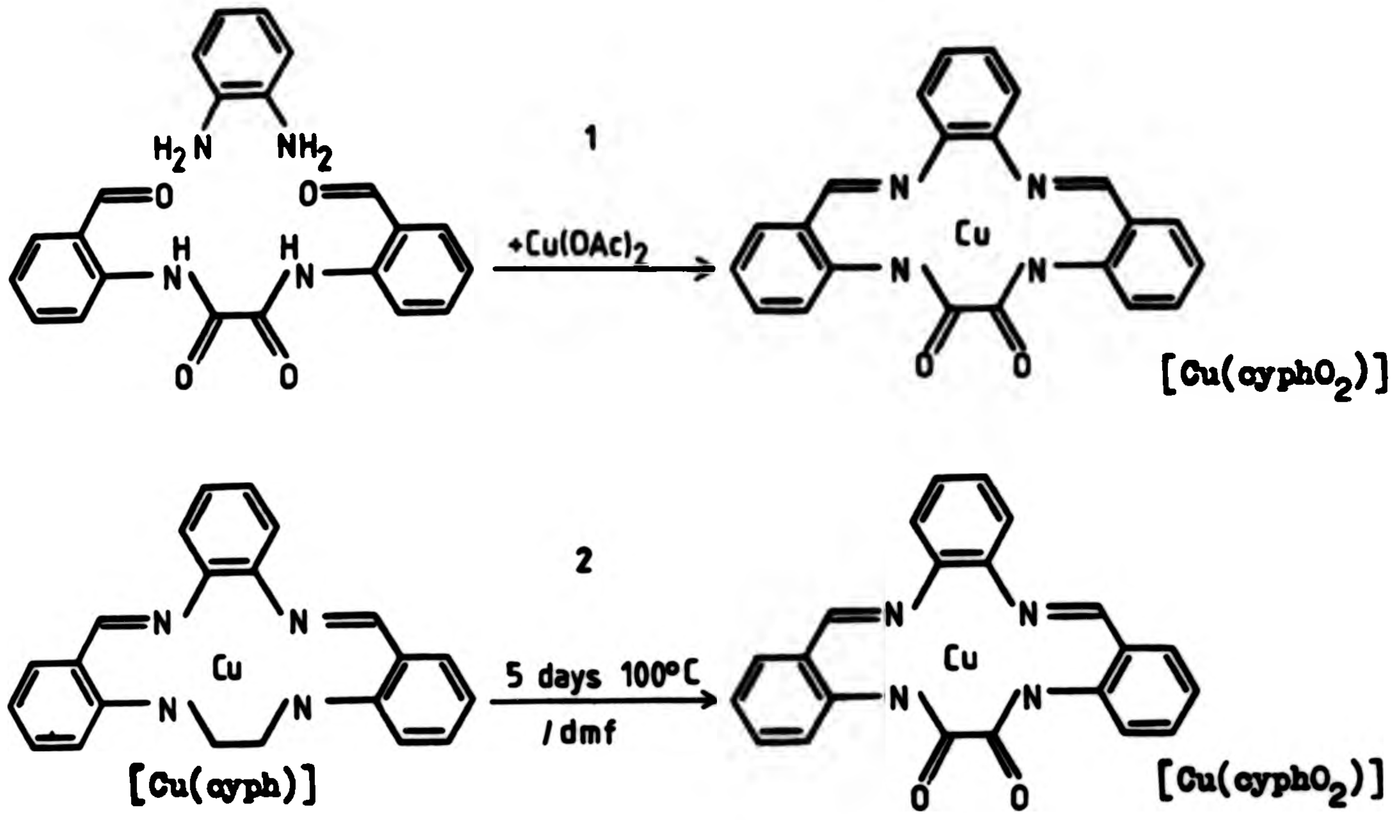
Scheme 4.14 (continued next page)



Scheme 4.14 Two possible mechanistic routes for the oxygenation of [Cu(cyph)].

4.2.6 Preparation of [Cu(cyphO_2)] (4.25)

The preparation of [Cu(cyphO_2)] has been reported using two different routes [12,15] (scheme 4.15).



Scheme 4.15 Two previously reported routes to [Cu(cyph)O_2].

The structure of [Cu(cyphO_2)] has been determined[7] on a crystalline sample from route 1 after recrystallisation from dimethylsulphoxide. It was reported[13] that the infrared spectra of a sample of [Cu(cyphO_2)] isolated from route 2 corresponded to the infrared spectra of a sample from route 1. When the preparation of [Cu(cyphO_2)] was attempted in this work using the conditions outlined previouly for route 2, a black solid was obtained on each occasion which could not be characterised. A material closely related to [Cu(cyphO_2)] which was initially labelled [Cu(cyphX)] (4.28) was obtained from an attempt to recrystallise [Cu(cyph)] from dimethylacetamide. The intention was to clarify whether

[Cu(cyph)] was dehydrogenated on recrystallisation (see section 4.2.3). The recrystallisation was attempted from dimethyl acetamide (dma) by dissolving a small sample of [Cu(cyph)] (4.9) at reflux and setting aside at room temperature. After 5 days the dark coloured solution had deposited deep burgandy coloured crystals of [Cu(cyphX)]. The few crystals obtained were compared to a sample of [Cu(cyphO_2)] (from route 1) which were a lighter colour. After a few days the surface of the crystals [Cu(cyphX)] (4.28) showed signs of decomposition. One was examined by X-ray crystallograhy (section 4.2.7). The recrystallisation of [Cu(cyph)] was also made using the same conditions as above but with the exclusion of oxygen (nitrogen atmosphere). On these occasions no product was isolable. This evidence did support the proposed radical reaction between dioxygen and [Cu(cyph)] (scheme 4.14).

4.2.7 The X-ray Structure of [Cu(cyphX)] (4.28)

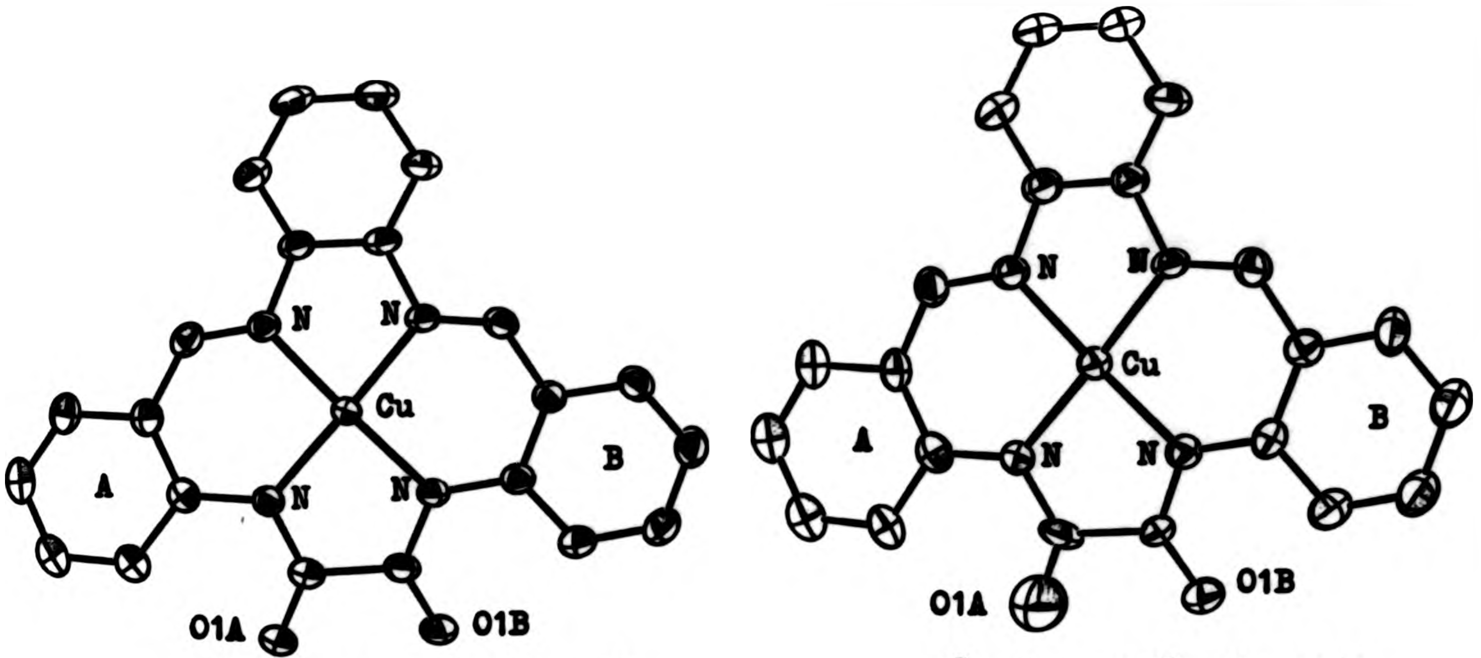
On the few crystals isolated from the method above, an eims and weak infrared spectra were obtained. The eims detected a molecular ion (m/e = 429) corresponding to [Cu(cyphO_2)]. The infrared spectrum on such a small sample was difficult to interpret, but did show a carbonyl stretch at 1660 cm^{-1}, and a spectrum similar to that of [Cu(cyphO_2)] (4.25). To confirm this analysis one of the crystals of [Cu(cyphX)] recovered from dma was examined by X-ray crystallography, and a unit cell was calculated and refined (section 7.5). The unit cell dimensions can often be used to 'fingerprint' a compound, although many compounds have more than one crystalline form. Table 4.4 compares the preliminary crystallographic data of [Cu(cyphO_2)] and [Cu(cyphX)].

UNIT CELL DATA

	[Cu(cyphO_2)]	[Cu(cyphX)]
a /Å	14.920	15.088
b /Å	15.918	16.034
c /Å	7.224	7.176
alpha = gamma	90.000°	90.000°
beta	95.031°	96.615°
Vol $Å^3$	1709.06	1724.47

Table 4.4 Refined unit cell data for [Cu(cyphO_2)] and [Cu(cyphX)].

The difference between the two sets of cell parameters was significant, and therefore the full structure determination was undertaken to establish the nature of the differences between the two materials. Due to the similarity of the cell parameters for both dioxocompounds (table 4.4), the structure of [Cu(cyphX)] was solved by using the same fractional coordinates of the non-hydrogen atoms (except oxygen) as those found for [Cu(cyphO_2)]. A difference Fourier map revealed the oxygen atoms in very similar positions to those found for [Cu(cyphO_2)]. The molecular configurations were very similar (fig 4.4), but the main difference was that in [Cu(cyphX)] atoms generally showed high thermal parameters, in particular the oxygen atom O(1A) (see figure 4.4 and table 4.5)



[Cu(cyphO$_2$)] (4.25) [Cu(cyphX)] (4.28)

Fig 4.4 Ortep diagram of [Cu(cyphO$_2$)] (4.25) and [Cu(cyphX)] (4.28) showing thermal ellipsoids at 50 % probability level.

<u>[Cu(cyphX)]</u>

	U11	U22	U33	U23	U13	U12
O(1A)	0.120(5)	0.116(5)	0.189(7)	-0.030(5)	-0.004(5)	0.007(4)
O(1B)	0.051(2)	0.061(3)	0.152(5)	-0.004(3)	-0.032(3)	0.011(2)

<u>[Cu(cyphO$_2$)]</u>

	U11	U22	U33	U23	U13	U12
O(1A)	0.039(1)	0.069(1)	0.093(2)	-0.020(1)	-0.017(1)	0.001(1)
O(1B)	0.044(1)	0.053(1)	0.143(2)	-0.009(1)	-0.037(1)	0.012(1)

Table 4.5 Anisotropic thermal parameters for oxygen atoms of the complexes [Cu(cyphO$_2$)] and [Cu(cyphX)].

The high thermal parameters could be due to:

1) a monooxygenated form of [Cu(cyph)], which showed a statistical disorder of the oxygen site in the ethane bridge (fig 4.5), or 2) an oxo-hydroxy species (fig 4.6), as a consequence of incomplete dehydrogenation. No

evidence for the existence of this incompletely oxygenated form (fig 4.5) or incompletely dehydrogenated form (fig 4.6) could be found from infrared or eims spectra.

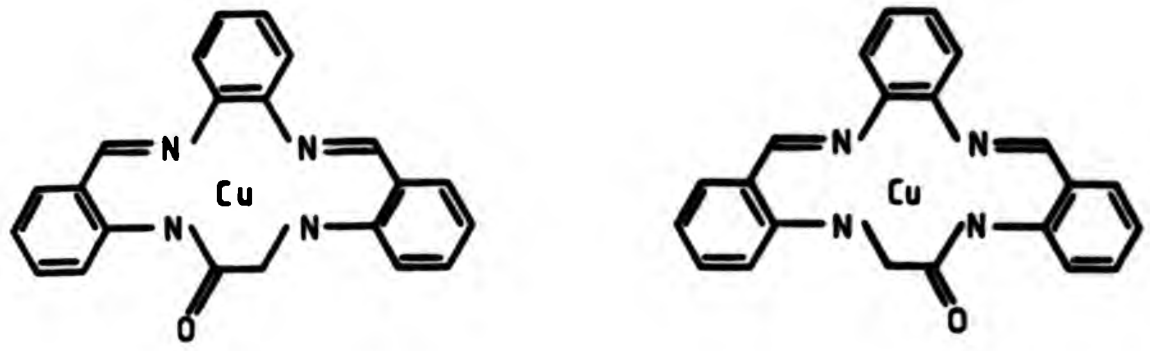


Fig 4.5 Statistical disorder of a mono-oxygenated ethane bridge in [Cu(cyphX)].

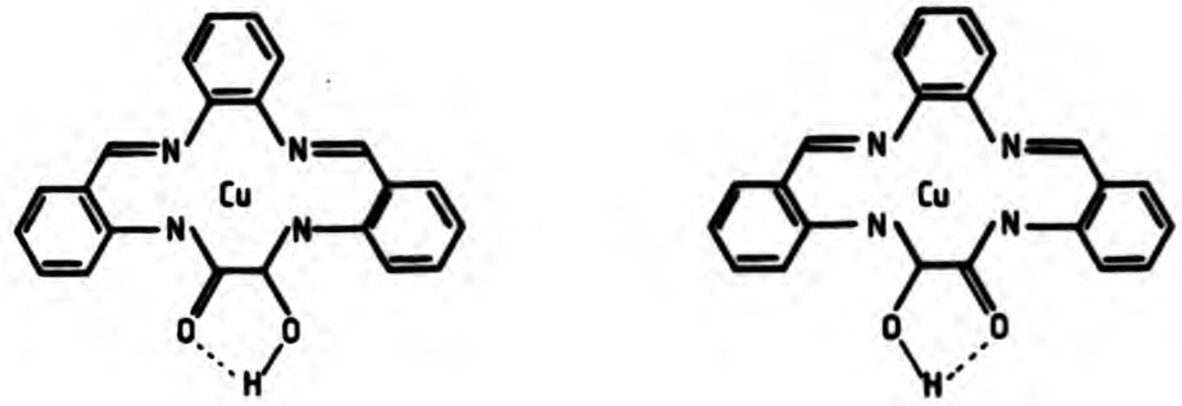


Fig 4.6 A oxo-hydroxy species of [Cu(cyphX)].

A thorough examination of the intermolecular contact distances in the solid state structures revealed some minor differences in the packing arrangement of [Cu(cyphX)] compared with [Cu(cyphO_2)].

4.2.8 A detailed examination of the two structures of [Cu(cyphX)] and [Cu(cyphO_2)].

The intense colour of the two compounds [Cu(cyphX)] and [Cu(cyphO_2)] will be due to the charge transfer between the copper(II) ion and the coordinated ligand. A close examination of the geometry about the copper atoms in both complexes, revealed a more tetrahedrally distorted arrangement of nitrogen atoms. Fig 4.7 depicts the distortion in milliangstroms from the least squares plane of the four nitrogen atoms.

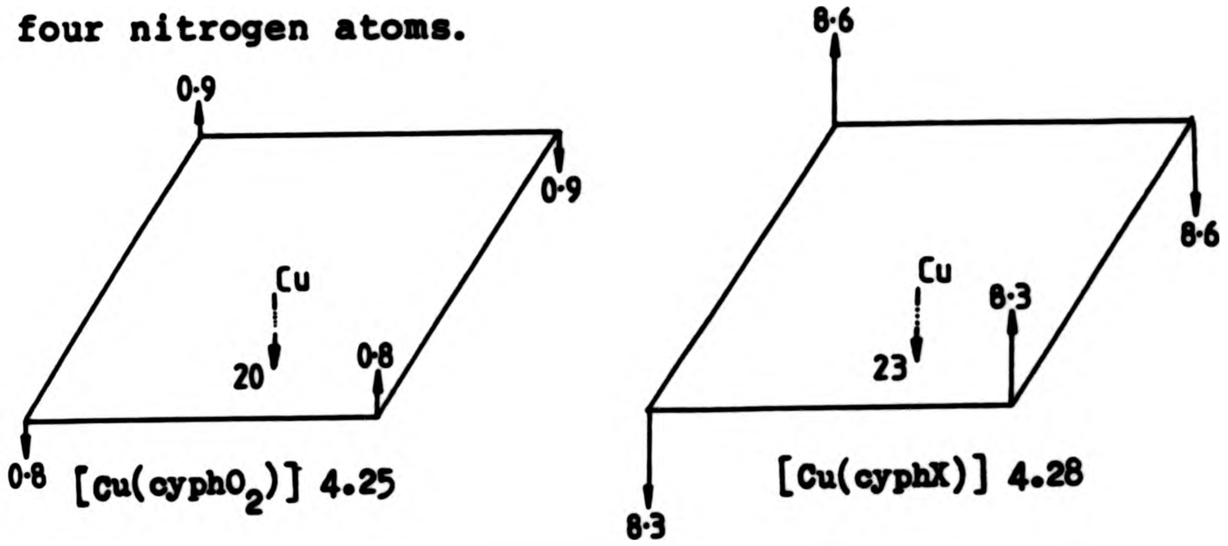


Fig 4.7 The geometry about the copper atom in the complexes [Cu(cyphX)] and [Cu(cyphO_2)]. Values (in milliangstroms) refer to the separation of the atoms from the best least squares plane of the four coordinating nitrogen atoms.

The intermolecular contact distances of the two structures [Cu(cyphO_2)] and [Cu(cyphX)] showed a number of significant differences. The extent of these differences varied between 0 to 0.43 Å. The differences are too small to be visually observed in the packing diagram, and therefore a comparison of intermolecular contact differences (greater than 0.2 Å) is made in table 4.6.

	[Cu(cyphX)] (4.28)	[Cu(cyphO$_2$)] (4.25)
C(11A)...N(2A)*	5.34	5.14
O(1B)....N(1A)*	4.72	4.51
C(2A)....N(2B)*	4.42	4.12
C(3A)....C(1A)*	5.22	5.02
C(4A)....C(1A)*	5.42	5.21
C(5A)....C(1A)*	4.87	4.66
C(2B)....C(3A)*	5.13	4.71
C(1B)....C(11A)*	4.80	4.60
O(1B)....C(11A)*	4.79	4.53
O(1B)....C(10A)*	4.25	4.04
O(1A)....C(11B)*	4.12	3.92
O(1B)....C(11B)*	5.42	5.19

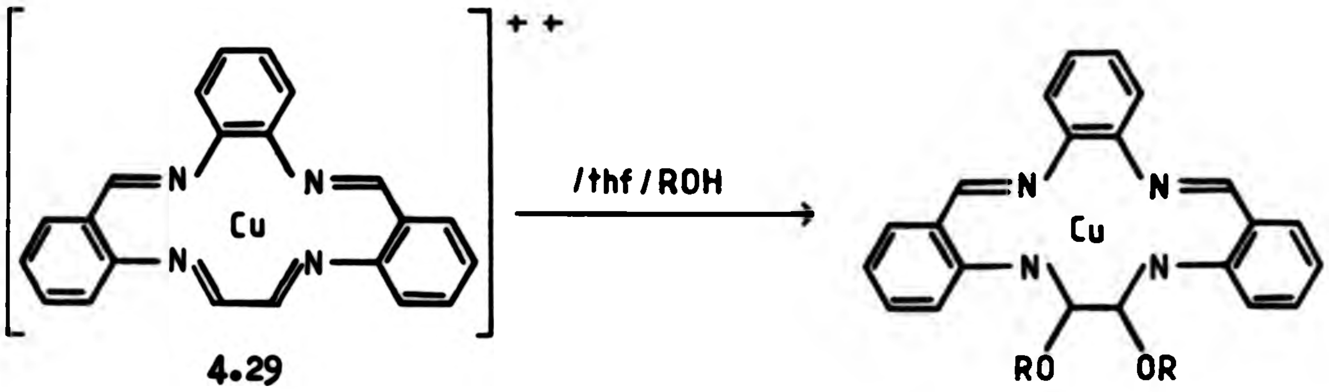
*(Symmetry transformation 1-x, 1-y, 1-z)

Table 4.6 Intermolecular Contact Distances(Å).

The experimental procedure for obtaining crystals of [Cu(cyphX)] was optimised (section 8) and further crystals showing the same intense colour were obtained. One of these was examined by X-ray crystallography and found to have the unit cell parameters previously found for the crystal [Cu(cyphX)] which was used in the structure determination above. The availability of larger quantities of crystals allowed a more intense infrared spectrum to be obtained (section 8). This was compared to the spectrum of [Cu(cyphO$_2$)] prepared by Peters[13] and found to be identical. The high thermal parameters of the oxygen atoms O(1A) could be due to a small percentage of hydroxy compound (Fig 4.6) distributed statistically throughout the lattice of [Cu(cyphO$_2$)]. However, the lack of any O-H stretch in the infrared spectra suggests that only a very small percentage of this species would be present.

4.2.9 Further reactions of [Cu(cyph)].

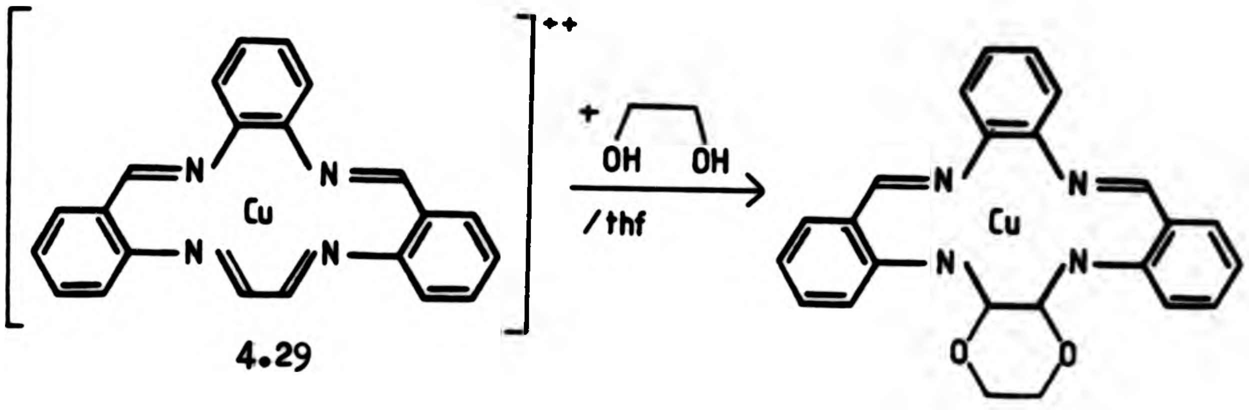
The formation of [Cu(cyph)(OMe)$_2$] (section 4.2.4) would suggest that the nucleophilic attack by methoxide has taken place on the imine bonds of a dehydrogenated complex 4.29 (scheme 4.16) This nucleophilic succeptibility of 4.29 has been further confirmed by the oxygenation to give [Cu(cyphX)] (4.28). The preparation of [Cu(cyph)(OMe)$_2$] (4.18) occurred in a solvent mixture containing methanol. This suggests that other alcohols may give rise to related compounds (scheme 4.16).



4.29

Scheme 4.16 Alcohol addition to the azomethine links in the complex 4.29

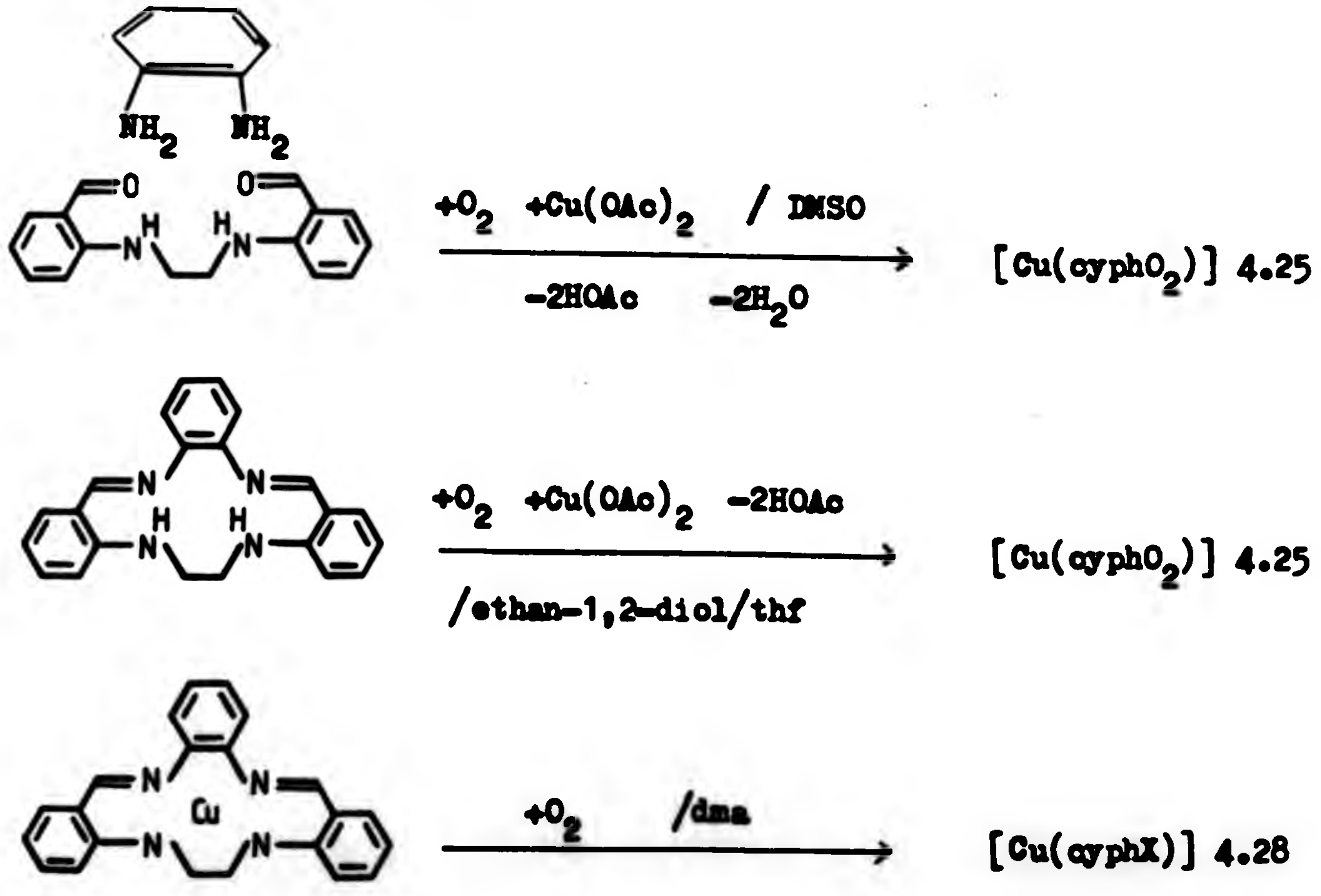
No addition reactions leading to products analogous to[Cucyph(OMe)$_2$)] **(4.18)** were detected when the reaction of H_2cyph with copper(II) acetate was carried out in the presence of ethanol, propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, or ethan-1,2-diol as prepared by the route described in section 4.2.4. The solvent ethan-1,2-diol was tried in an attempt to form the cyclised product 4.30 (scheme 4.17). This would have confirmed the addition of alcohol to the ethene bridge rather than the benzylimine linkages (section 4.2.4), however, from this solution crystals of a dioxocompound were formed. A single crystal was examined by X-ray crystallography for cell parameters, and was found to have a unit cell corresponding to that of the [Cu(cyphO$_2$)] (4.25) complex. Scheme 4.18 outlines the routes to both crystalline forms of the dioxo complex.



4.29

4.30

Scheme 4.17 Ethan-1,2-diol addition to the azomethine links in complex 4.29.



Scheme 4.18 Routes to the dioxocompounds characterised by X-ray crystallography.

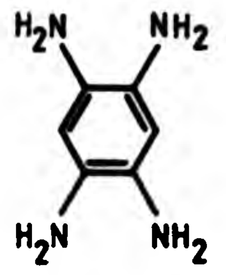
Conclusion

The solution chemistry of [Cu(cyph)] (4.9) is extensive and has shown many interesting features which were unexpected. The deprotonation of the perchlorate complex $[Cu(H_2cyph)](ClO_4)_2$ to give [Cu(cyph)], leads to a novel synthetic route for the more difficult to prepare neutral biscopper(II) complexes of the bicyclic ligands described later in this chapter. The side reactions found when preparing [Cu(cyph)], or recrystallisation of [Cu(cyph)] from dma has proved that the chemistry is by no means simple, and care must be taken to prevent leaving any copper(II) complexes for extended periods in solution. These unexpected results are not necessarily limited to the copper(II) complexes as other oxygenation reactions have been reported for related Ni(II)[16] and Fe(II)[12] complexes. Under conditions where the copper(II) complexes of this type are to be considered as catalysts for oxidative reactions it is probable that the complex would be first converted to oxygenated or dehydrogenated forms, and it would be necessary that these latter forms should show catalytic activity.

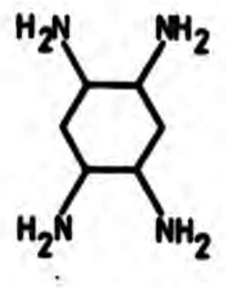
4.3.1 Results and discussion for dinucleating aza Macrocycles

Two tetra-amino compounds are commercially available which may react with C_2-dialdehyde to give a new series of bicyclic ligands. A third TAC (4.32) was supplied by I.C.I.

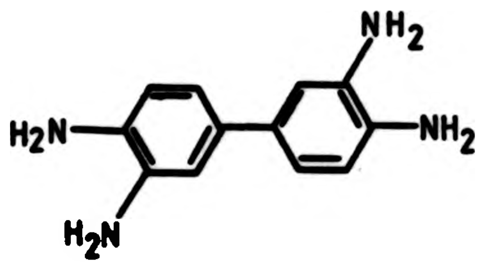
organics division, and is not commercially available (table 4.7). The two compounds TAC and TAB.4HCl on reaction (2:1 condensation) with C_2-dialdehyde could give bicyclic ligands with a "fused" bridge (see type III, section 2) whereas the DAB on condensation with C_2-dialdehyde would give rise to a linked bicyclic ligand (see type I, section 2).



TAB.4HCl
4.31



TAC
4.32

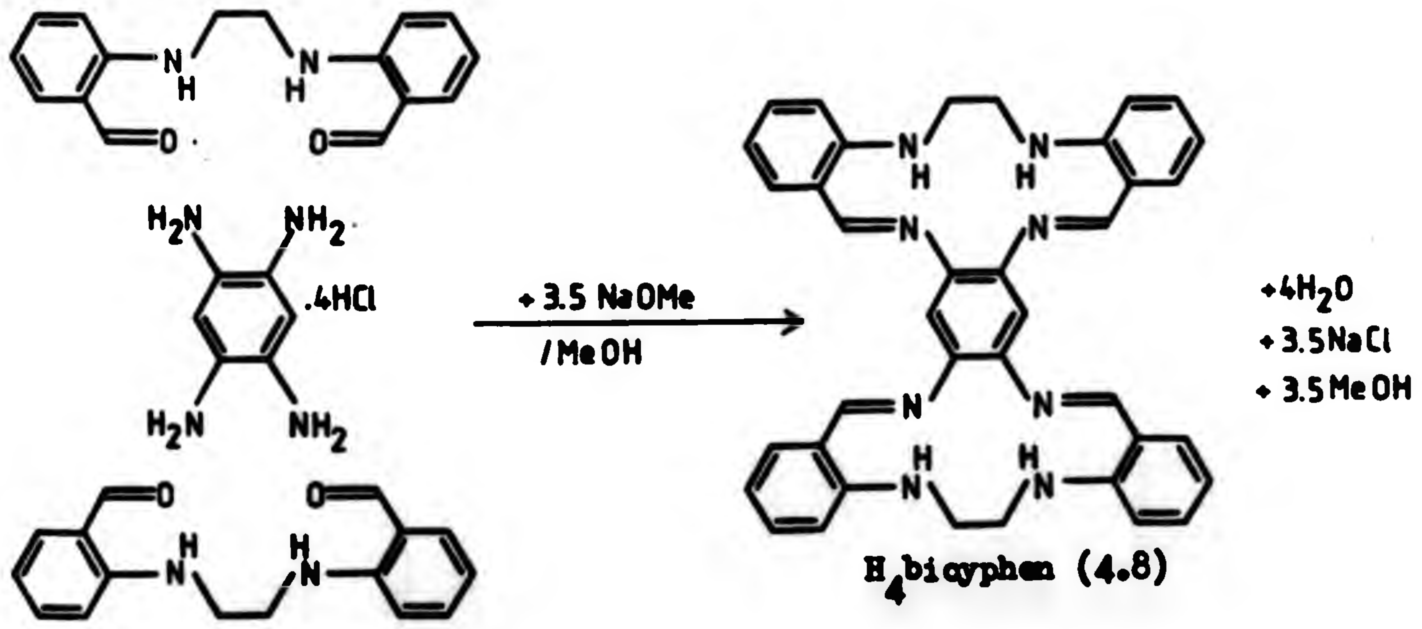


DAB
4.33

Table 4.7 Tetraamino compounds

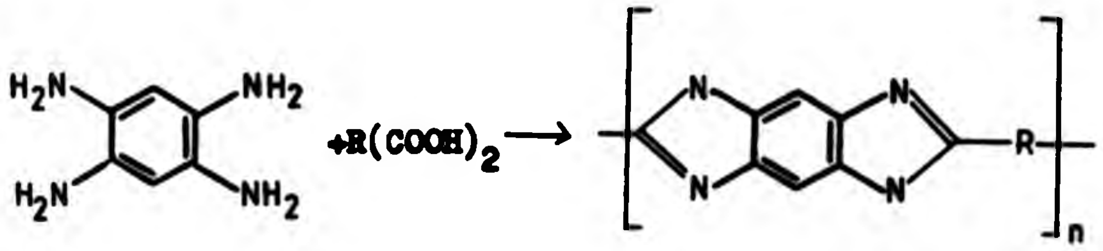
4.3.2 The reactions of 1,2,4,5-tetraaminobenzenetetrahydrochloride (TAB.4HCl, 4.31).

As discussed earlier (section 4.1.2) a preliminary communication[4] described the synthesis of H_4bicyphen (4.8, scheme 4.19) but recorded low yields of 28 %.



Scheme 4.19

The published method was repeated, but found to give little if any of the product H_4bicyphen (4.8). The reason was thought to be due to problems associated with the neutralisation of TAB.4HCl (4.31). This step involved the addition of sodium methoxide solution to the TAB.4HCl to partially neutralise (~90 %) the hydrochloride salt and to allow the remaining protons to catalyse the condensation reaction. Unfortunately, once neutralised the TAB is very sensitive to oxygen and forms a mixture of highly coloured products. The reactivity of TAB and other polyamines with various carboxylic acids has been well documented by Marvel[17] (scheme 4.20).

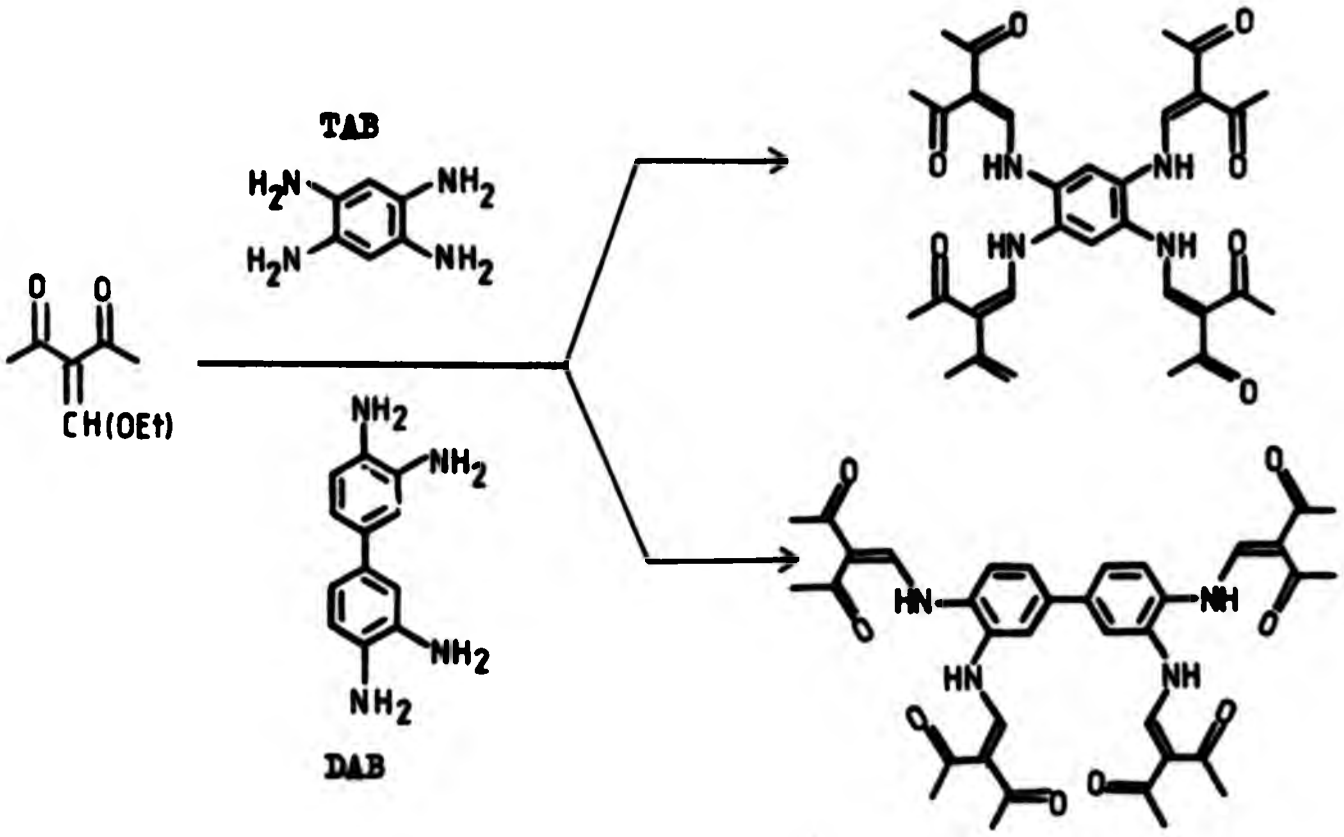


Scheme 4.20 Polymerisation of TAB.

The method for preparation of H_4bicyphen was improved by an in situ neutralisation of the hydrochloride salt, whereby small aliquots of TAB.4HCl were added to a stirred suspension of C_2-dialdehyde (4.7) in ethanol (under nitrogen). After each addition a red colour was produced, which was discharged by the dropwise addition of base (sodium methoxide). Refluxing for 20 h followed by recrystallisation from pyridine gave yields of ~75 %. H_4bicyphen has a low solubility and volatility (mp

330°C(d)), but was stable enough for the molecular ion to be detected by eims and fdms (m/e = 602, section 8). The copper complexes of this ligand are discussed in section 4.4.1.

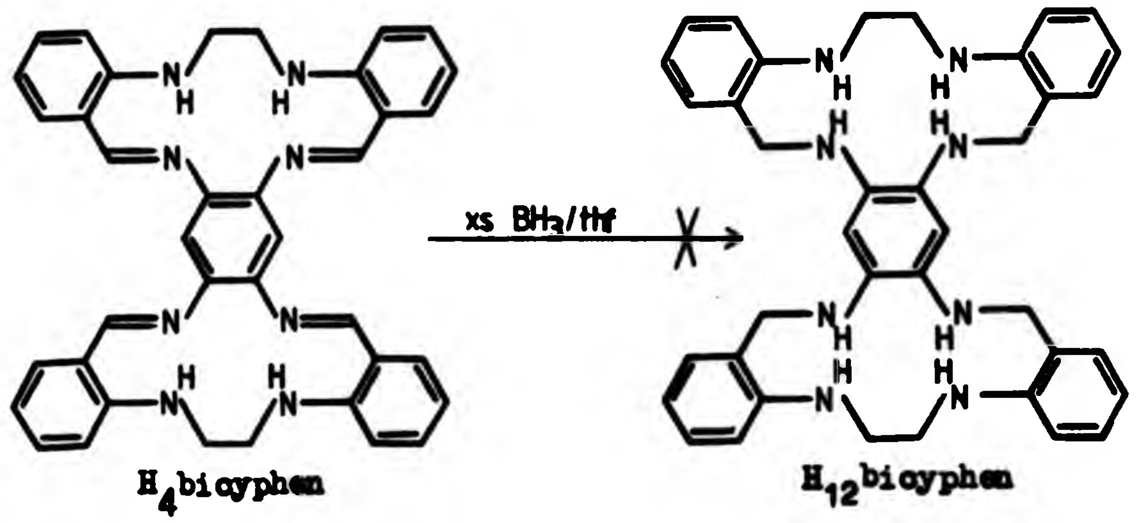
Relatively stable non-cyclic dinucleating ligands have been reported[18] by reaction of TAB or DAB with the ethoxymethylene derivative of acetylacetone (scheme 4.21).



Scheme 4.21 Other reactions with TAB and DAB.

4.3.3 Attempted Reduction of H_4bicyphen (scheme 4.22).

It was shown earlier in this section that reaction of BH_3/thf with the compound H_2cyph (4.1) gave the reduced tetraamine H_6cyph (4.11). One of the main problems when attempting to form copper(II) complexes from the ligand H_4bicyphen was the low solubility of the ligand and the copper complex. By reduction with BH_3/thf to give H_{12}bicyphen (4.34), it was hoped to form a more soluble ligand (scheme 4.22).

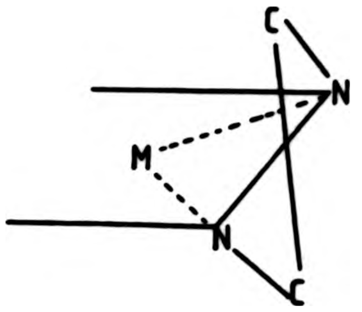


Scheme 4.22 Proposed synthesis of H_{12}bicyphen (4.34).

It was predicted that reduction of H_4bicyphen (4.8) would give a product as air sensitive as 1,2,4,5-tetraaminobenzene (TAB), and therefore all preparations were attempted in a glove box flushed with nitrogen. A solution of BH_3/thf was added to solid H_4bicyphen and gently heated. The reaction mixture darkened and thick brown fumes fiercely errupted, depositing a film of dust on the surrounding apparatus. The remaining solution was clear and no product was isolable. A similar observation has been reported[19] for a sodium borohydride reduction in dmf, where a runaway reaction occurred after a temperature dependent induction period of 45 min (90°C) to 45 h (62°C). No further attempts to prepare the reduced ligand H_{12}bicyphen were made on the assumption that the product would be too unstable to handle.

4.3.4 The reaction of 1,2,4,5-tetra-aminocyclohexane (TAC, 4.29).

A sample of unknown isomeric distribution of the compound TAC (4.32) was provided by the sponsoring establishment (I.C.I. Organics Division). No reactions were identified between TAC and C_2-dialdehyde either with or without the presence of copper(II) acetate. A variety of solvents (methanol, ethanol, thf and dmf) and catalysts (zinc(II) acetate and PTSA) were used but in each case the precursor C_2-dialdehyde was recovered. Attempts to obtain the biscopper(II) complex via a template method also failed, resulting in the recovery of the precursor C_2-dialdehyde from a highly coloured solution thought to be due to the oxidation of the tetraamine. The reason for TAC failing to react with C_2-dialdehyde may be due to the conformation of the amino substituents. It has been shown[20] that for the formation of a chelate ring from 1,2-diaminoethane a gauche conformation was the preferred arrangement (see 4.35). 1,2-diaminocyclohexane has two geometric isomers cis and trans, and only the trans can give the equivalent to the gauche form of 1,2-diamino ethane when it has the two amino substituents both in equatorial positions (although this would be in equilibrium with the bis axial form fig 4.8). For formation of large rings on condensation with C_2-dialdehyde, models show that similar considerations concerning the isomeric forms of cyclohexane apply. Since TAC has 4 substituent amino groups (two sets of adjacent amino groups), then the amino groups should be in equatorial positions for the [2+1] condensation with C_2-dialdehyde. The TAC used in the above experiment may contain one or more of the many different isomers, but since these isomers are not interconvertible, then unless the four substituents were all in equatorial positions then the TAC would be unlikely to condense with C_2-dialdehyde (scheme 4.23).



4.35

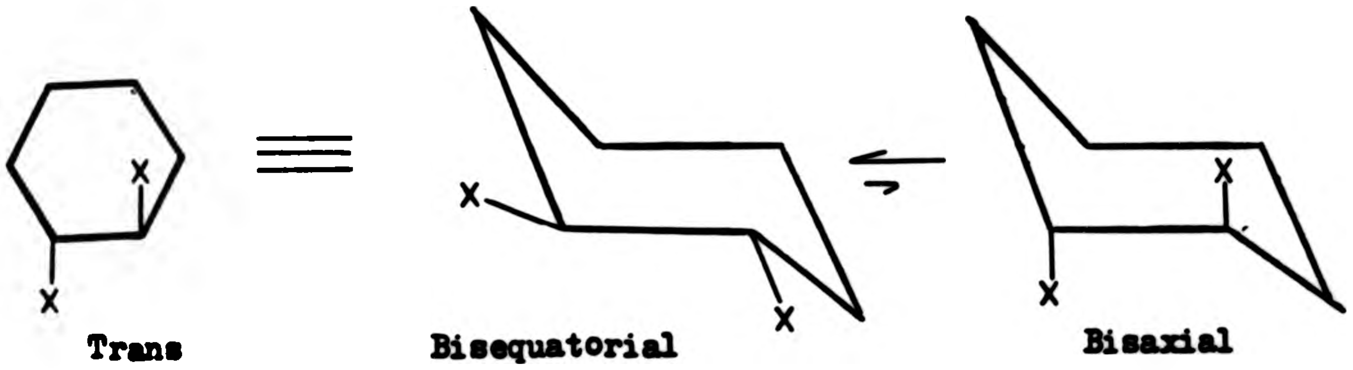
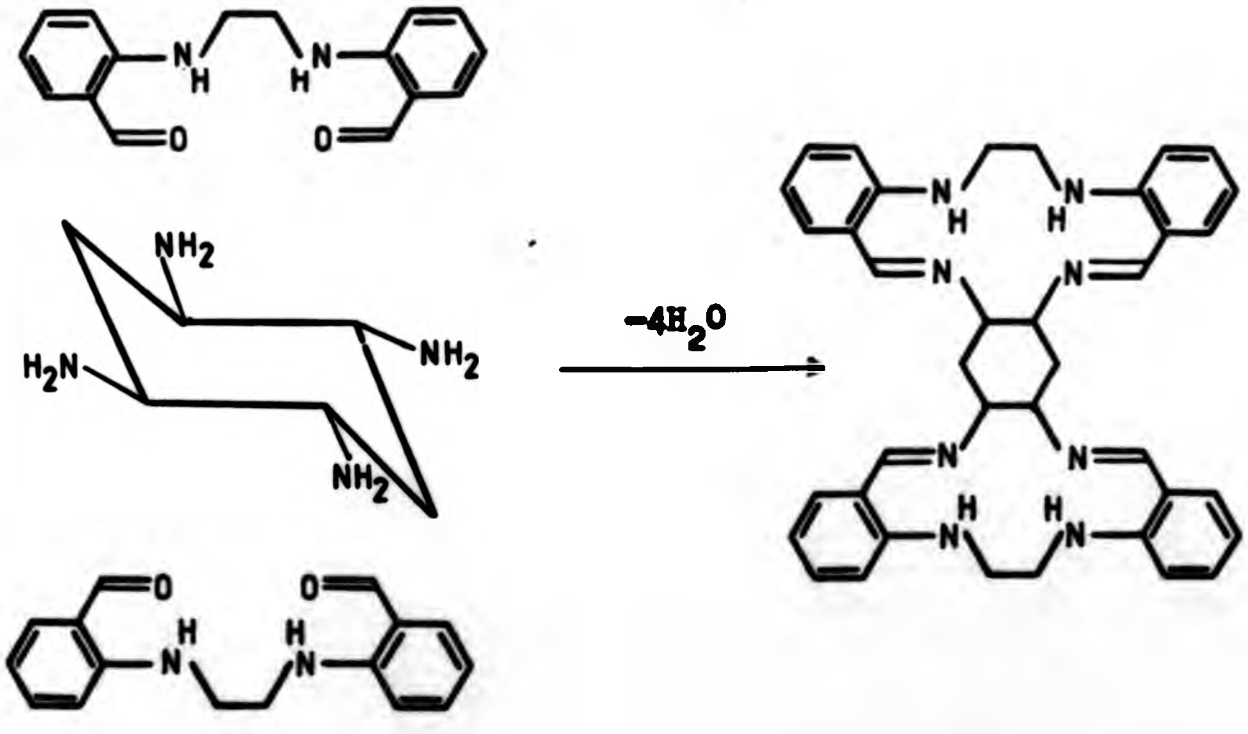


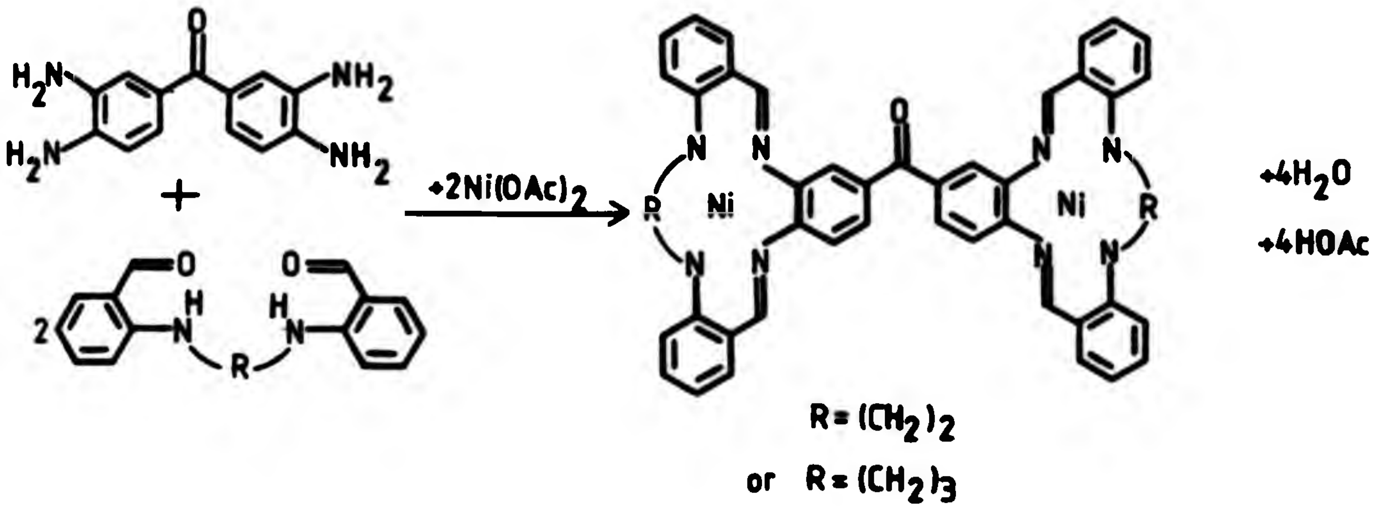
Fig 4.8 Equilibrium of the bisaxial with the bisequatorial form of 1,2-diaminocyclohexane. X = NH_2.



Scheme 4.23

4.3.5 The reactions of 4,4'-diaminobenzidine (DAB) 4.33.

A template reaction has been reported[1b] for the Ni(II) complex of 3,3',4,4'-tetra-aminobenzophenone with C_2- and C_3-dialdehyde (scheme 4.24), although no successful results were reported for any related Cu(II) complexes.



Scheme 4.24 A template reaction with 3,3',4,4'-tetra-aminobenzophenone.

To predict with confidence the distance between two copper atoms in a dinucleating ligand, it is necessary to have a rigid system. The benzidene nucleus provides a longer bridging system than that in the 1,2,4,5-tetraaminobenzene, but one which may show a degree of rotation while in the skew configuration[21]. This rotation will have a small effect on the distance between the two copper atoms, which molecular models show will vary between 11.7 Å (coplanar) and 11.4 Å (skew). The reaction between C_2-dialdehyde and DAB did not proceed until some zinc(II) acetate was added. This gave rise to a mixture of a zinc(II) complex (either the dinuclear 4.36 or the related mononuclear species) and free ligand H_4bicybenz (4.37) (scheme 4.25). Recrystallisation from pyridine/methanol gave the free ligand as microcrystals. The low solubility and volatility prevented analysis by eims and ^1H nmr, but characterisation was achieved by elemental analysis and infrared data (section 8). The three ligands H_2cyph, H_4bicyphen and H_4bicybenz all contain the same component ring system H_2cyph (4.1), and will be expected to show similar spectral properties. A comparison of the strongest absorptions in their infrared spectra is made in table 4.8 to show the similarity in the absorption pattern. Important features are the presence of the N-H (hydrogen bonded) stretch around 3165 cm^{-1} and the C=N stretch around 1610 - 1620 cm^{-1}. All these imine compounds are yellow whereas the reduced compounds H_6cyph (4.11) and H_{12}bicybenz (4.38) are white.

Main infrared^{a} absorptions/cm^{-1}

H_2cyph (4.1)	H_4bicyphen (4.8)	H_4bicybenz (4.36)
3170	3170	3165
3086	3095	
3060	3070	
3030	3030	3030
2956	2960	
2886	2890	2892
2838	2830	
1620	1618	1610
1601	1598	1595
1576	1572	1574
1337	1338	1361
1164	1162	1167

Uv/vis absorptions^{b}/nm (ε)

H_2cyph /MeOH	H_4bicyphen /dmf	H_4bicybenz /$CHCl_3$
270(1318)	270(1896)	256(7706)
285(1500)	320(1069)	-
	435(1974)	400(4155)

Table 4.8 Main infrared and uv/vis (solution) absorption bands of H_2cyph, H_4bicyphen and H_4bicybenz. ^{a}recorded in the range 4000 - 600 cm^{-1}, recorded as the nujol and HCB mull. ^{b}recorded in the range 260 - 850 nm in the solvents indicated, extinction coefficients in parentheses.

Main infrared^{a} absorptions/cm^{-1}

H_2cyph (4.1)	H_4bicyphen (4.8)	H_4bicybenz (4.36)
3170	3170	3165
3086	3095	
3060	3070	
3030	3030	3030
2956	2960	
2886	2890	2892
2838	2830	
1620	1618	1610
1601	1598	1595
1576	1572	1574
1337	1338	1361
1164	1162	1167

Uv/vis absorptions^{b}/nm (ε)

H_2cyph /MeOH	H_4bicyphen /dmf	H_4bicybenz /$CHCl_3$
270(1318)	270(1896)	256(7706)
285(1500)	320(1069)	-
	435(1974)	400(4155)

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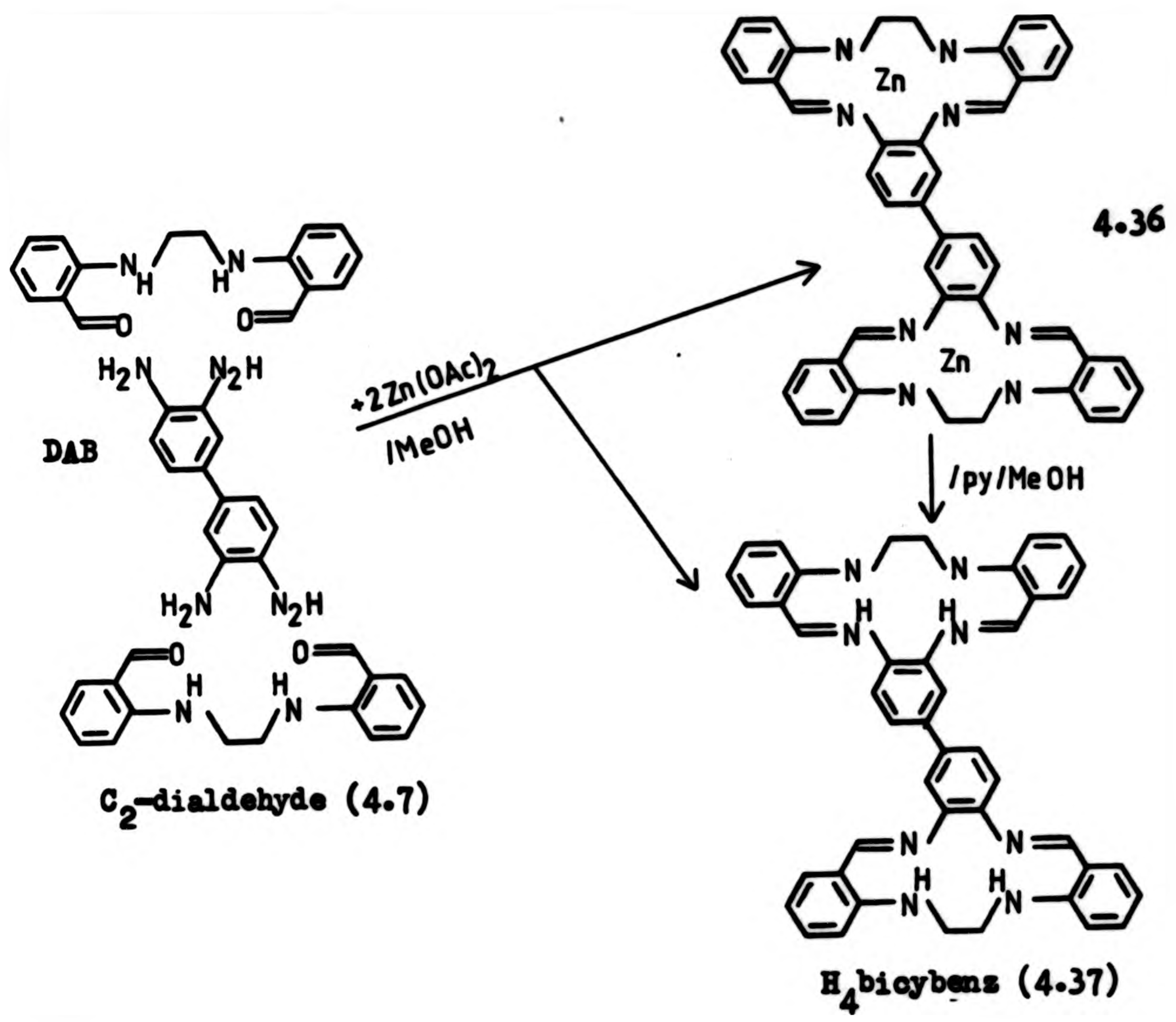
^{a}recorded in the range 4000 - 600 cm^{-1}, recorded as the nujol and HCB mull.
^{b}recorded in the range 260 - 850 nm in the solvents indicated, extinction coefficients in parentheses.

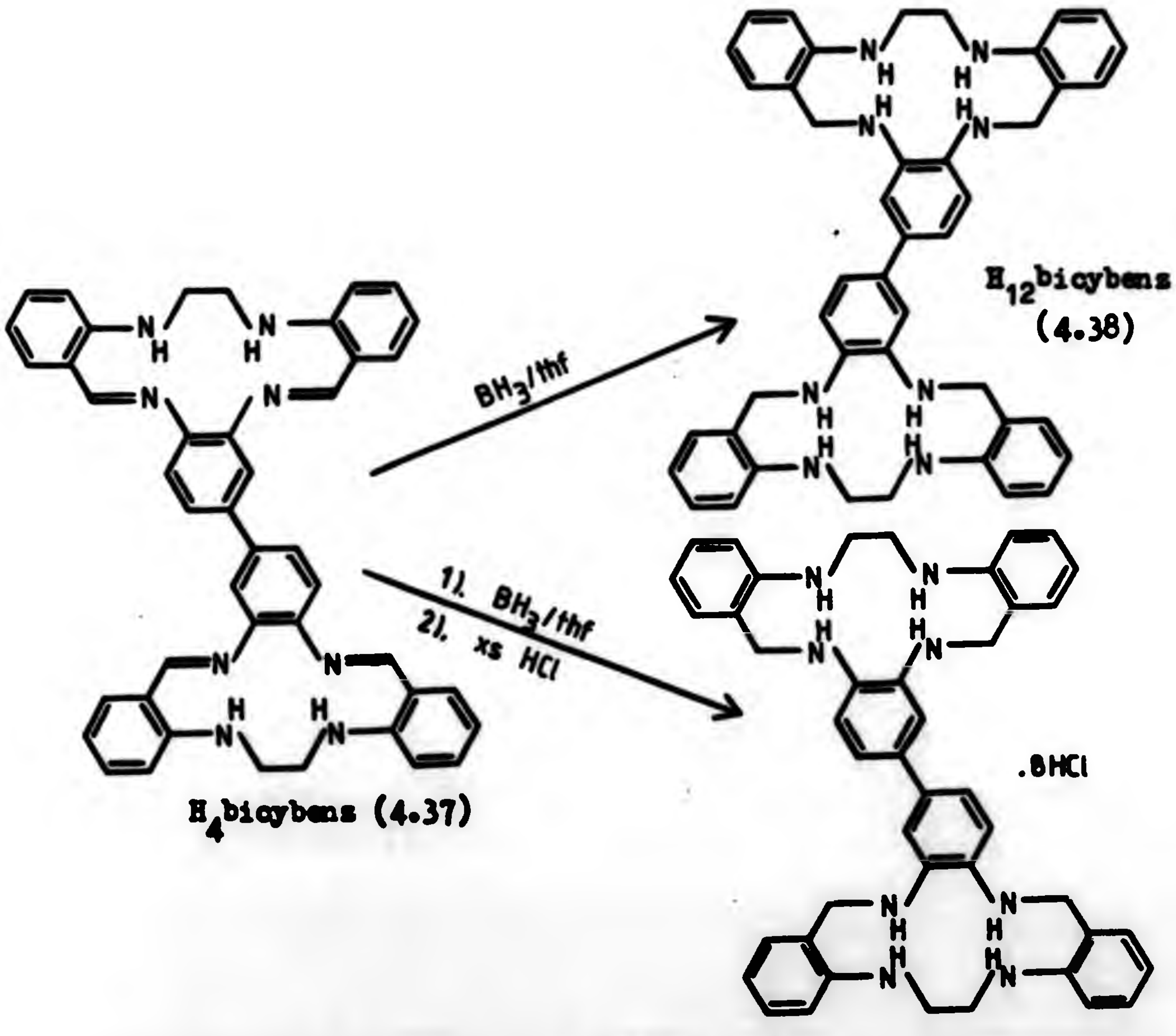


Scheme 4.25 Preparation of H_4bicybenz (4.37).

4.3.6 Reduction of H_4bicybenz.

Reduction of the imine linkages in H_4bicybenz was accomplished using BH_3/thf with no complications as experienced with H_4bicyphen. The hydrochloride salt of H_{12}bicybenz was prepared by addition of excess hydrochloric acid to the reduced ligand (scheme 4.26), but due to the stability of H_{12}bicybenz in air (4.38) it was found unnecessary to store further samples of the material in this way. Copper(II) complexes of the H_4bicybenz and H_{12}bicybenz ligands are described in section 4.4. This bicyclic ligand contains the same component ring system as H_6cyph, and a comparison of infrared data is made in table

4.9. It can be seen that the principle bands occur in very similar regions. Important features are the large number of bands in the region associated with N-H stretching modes (3320 - 3380 cm^{-1}) than in the parent imine molecules (see table 4.8). The bands associated with the imine units in H_2cyph (4.1) etc are not observed in the spectra of the reduced systems H_6cyph (4.11) or H_{12}bicybenz (4.38). The compounds H_6cyph (4.11) and H_{12}bicybenz both show only two bands in their electronic spectra, these in the uv region (see table 4.9). The main chromophore of the imine molecules H_2cyph etc thus apparently depends on delocalised pi orbitals involving the imine links (see table 4.8).



Scheme 4.26 Preparation of H_{12}bicybenz.

Main infrared absorptions^a.		Uv/vis absorptions^b/nm (ε)	
H_6cyph (4.11)	H_{12}bicybenz (4.38)	H_6cyph(/CH_3OH) (4.11)	H_{12}bicybenz/($CHCl_3$) (4.38)
3376	3370	250(2666)	260(2776)
3350	3320	295(2611)	300(2719)
3325			
1607	1607		
1598			
1584	1585		
1516	1516		
1502	1506		
1348			
	1321		
1302	1306		
1274			
1252	1259		
1244	1246		
1123	1136		
1042	1046		
	1021		
749	754		
732			

Table 4.9 Main infrared and uv/vis (solution) absorption bands for H_6cyph (4.11) and H_{12}bicybenz (4.38). ^{a}recorded in the range 4000 - 600 cm^{-1}, recorded as the nujol and HCB mull.
^{b}recorded in the range 260 - 850 nm in the solvents indicated, extinction coefficients in parentheses.

4.4.1 Preparation of copper complexes of the dinucleating aza ligands.

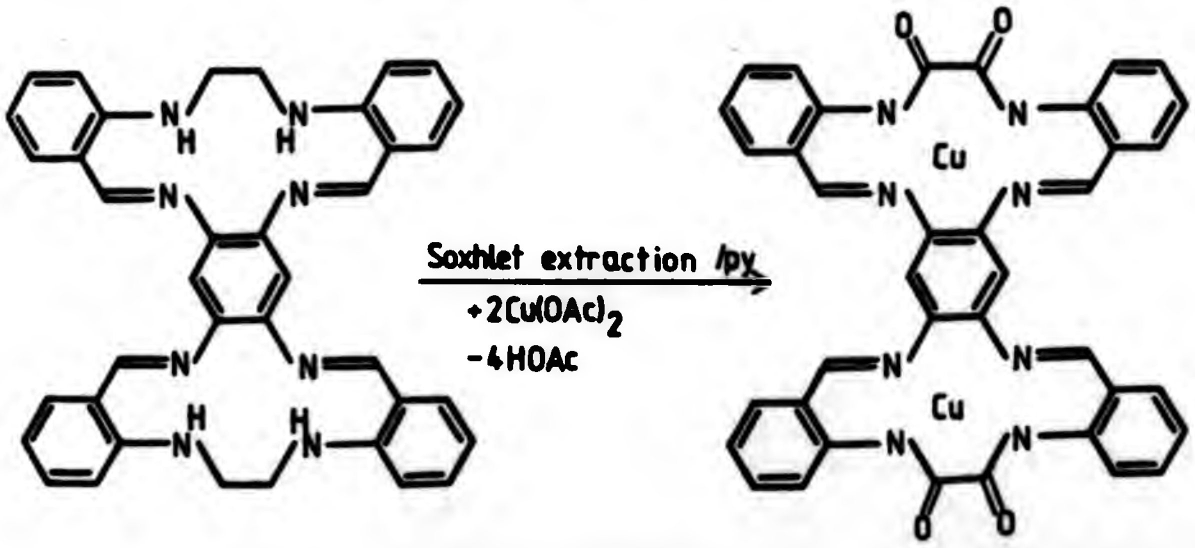
H_4bicyphen

It was reported that extraction of the free ligand H_4bicyphen (4.8) from Soxhlet thimbles by refluxing pyridine from a pyridine solution of copper(II) acetate for 30 h gave crystals of the neutral copper(II) complex 4.40. This method ensures total dissolution of the ligand when the complex formation takes place. This method was tried but was unsuccessful for two reasons:

1) The ligand was so insoluble, that even after 30 h very little had been extracted from the thimble.

2) The complex that had formed gave analytical data inconsistent with any expected formulation.

It is probable that long periods of continuous refluxing may result in oxygenation, similar to that found for the mononuclear analogue [Cu(cyph)] (section 4.2). A sample of [Cu_2(bicyphen)] originally prepared by Kendall-Torry was shown by fdms to contain oxygenated species (scheme 4.27). To avoid this possibility a quick reaction was necessary, but one which would ensure no contamination from unreacted ligand. Copper(II) complexes of the dinucleating ligands H_4bicyphen and H_4bicybenz which were prepared in this project are listed in table 4.10.



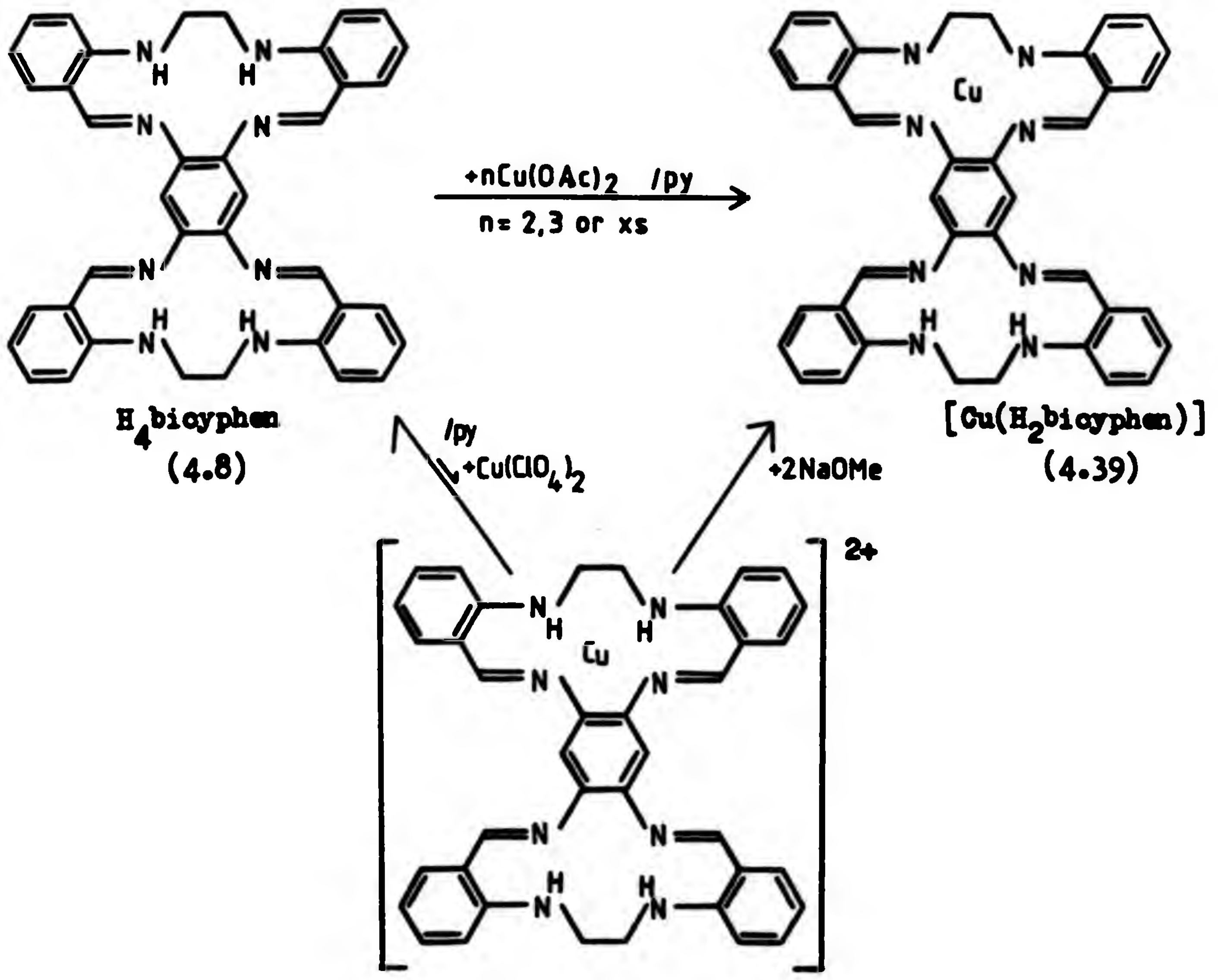
Scheme 4.27 Reported oxygenation of [Cu_2(bicyphen)] (4.40).

Compound	C%	N%	H%	Cu%
H_4bicyphen (4.8)	75.2	6.0	18.3	
(Calc. for $C_{38}H_{34}N_8$)	(75.7)	(5.7)	(18.6)	
[Cu(H_2bicyphen)] (4.39)	67.9	4.6	16.5	9.4
(Calc. for $CuC_{38}H32N_8$)	(68.7)	(4.10)	(16.9)	(9.6)
[Cu_2(bicyphen)] (4.40)	62.1	4.1	15.3	16.8
(Calc. for $Cu_2C_{38}H_{30}N_8$)	(62.9)	(4.2)	(15.4)	(17.5)
[Cu_2(H_4bicyphen)]$(ClO_4)_4$ (4.41)	41.2	3.4	9.9	11.0
(Calc. for $Cu_2C_{38}H_{34}N_8Cl_4O_{10}$)	(40.5)	(3.0)	(9.9)	(11.3)
H_4bicybenz (4.37)	77.4	5.4	16.1	
(Calc. for $C_{44}H_{38}N_8$)	(77.9)	(5.6)	(16.5)	
[Cu_2(bicybenz)] (4.42)	65.2	3.9	13.6	15.2
(Calc. for $Cu_2C_{44}H_{34}N_8$)	(65.9)	(4.3)	(14.0)	(15.8)
[Cu_2(H_4bicybenz)]$(ClO_4)_4$ (4.43)	44.1	3.0	9.6	10.1
(Calc. for $Cu_2C_{44}H_{38}N_8Cl_4O_{16}$)	(43.9)	(3.2)	(9.3)	(10.6)
H_{12}bicybenz (4.38)	76.2	6.6	16.0	
(Calc. for $C_{44}H_{42}N_8$)	(76.9)	(6.8)	(16.3)	
[Cu_2(H_{12}bicybenz)]$(ClO_4)_4$ (4.44)	44.3	3.5	9.2	
(Calc. for $Cu_2C_{44}H_{42}N_8Cl_4O_{16}$)	(44.0)	(3.9)	(9.3)	

Table 4.10 Analytical results for the dinucleating ligands and their copper(II) complexes.

4.4.2 Preparation of mononuclear copper(II) complexes of H_4bicyphen (4.8).

H_4bicyphen was dissolved in refluxing pyridine, and mixed with a solution of copper(II) acetate (2:1 Cu:Ligand) (in pyridine). The mixture instantly changed colour and precipitation occurred to give deep violet microcrystals with a green sheen. These crystals were characterised by elemental analysis (Cu,C,H and N, see table 4.10) as the mononuclear copper(II) complex (4.39). On the basis of this analysis, the only other formulation which could be proposed was a mixture of ligand and bisCu(II) complex in a ratio of 1:1. However, this was not the case since the infrared spectra did not indicate the presence of any uncomplexed ligand. The complex [Cu(H_2bicyphen)] was too insoluble for fdms and only at approximatly 60°C in pyridine did the complex dissolve to give a weak uv/vis spectrum (section 8). The preparation of the mono copper(II) perchlorate complex was attempted in the same manner using copper(II) perchlorate. To a solution of copper(II) perchlorate in pyridine a one molar equivalent of H_4bicyphen was added. No colour change was noted on this addition and it was possible that the copper(II) perchlorate at a 1:1 molar ratio with the ligand in pyridine has an equilibrium in favour of the pyridine complex. Evaporation of this solution and addition of various less polar solvents (methanol, diethylether, petrol or benzene) lead to the recovery of the free ligand H_4bicyphen. The addition of base (2 molar equivalents of sodium methoxide solution in methanol) to the mixture of ligand and copper(II) perchlorate in pyridine instantly gave a colour change (to almost black) and precipitation occurred to give the neutral mononuclear copper(II) complex (scheme 4.28).

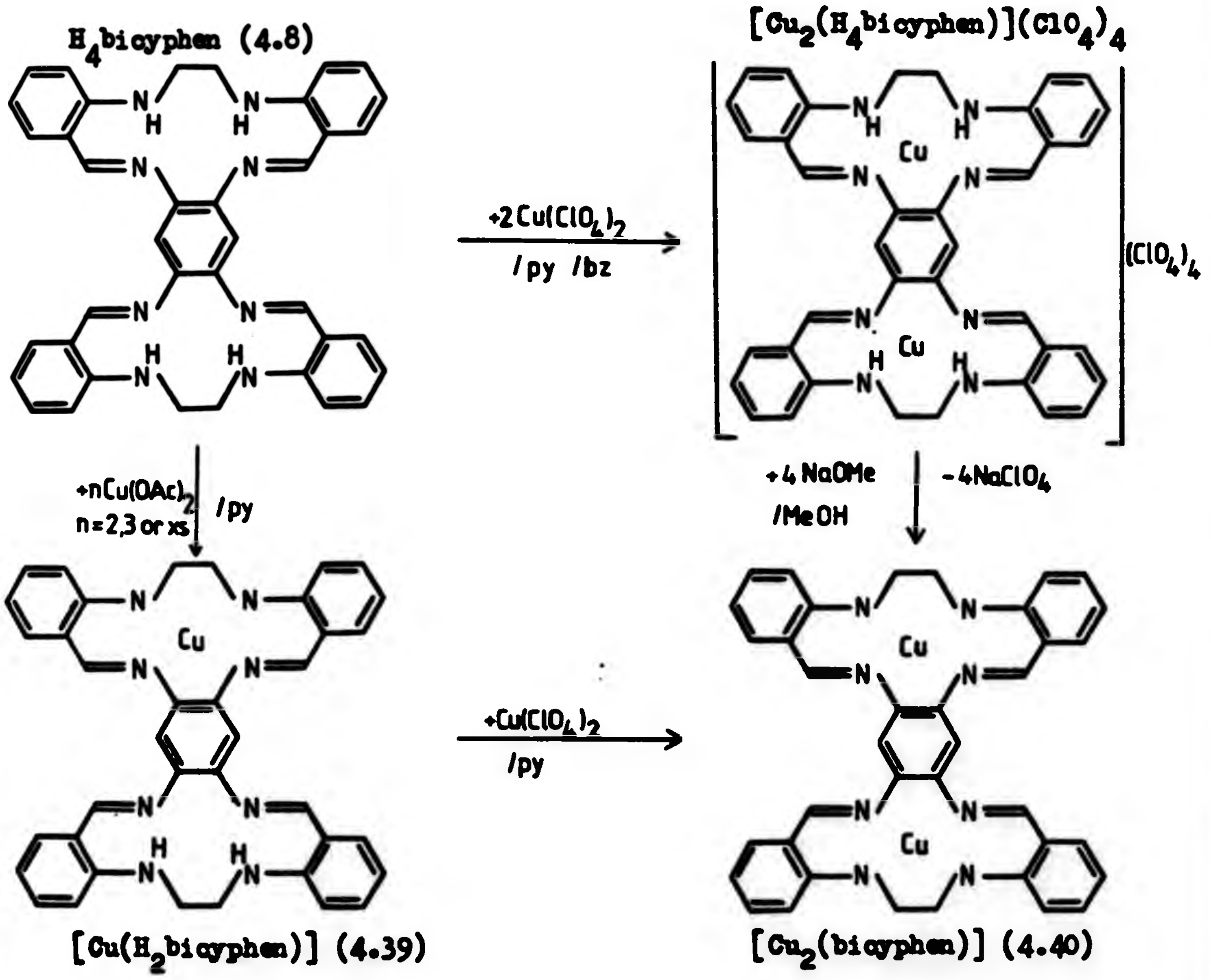


Scheme 4.28 Preparation of [Cu(H_2bicyphen)] (4.39).

4.4.3 Preparation of dinuclear copper(II) complexes of H_4bicyphen.

As stated above, direct reaction of the free ligand with copper(II) acetate is not an effective method for preparation of the neutral complex [Cu_2(bicyphen)] (4.40). Even in the presence of excess copper(II) acetate, the major product separating from a pyridine solution of the ligand is the mononuclear complex [Cu(H_2bicyphen)] (4.39). Continuous refluxing of this mononuclear complex 4.39 with excess copper(II) acetate in pyridine did not result in further copper(II) incorporation. Curiously however, when

[Cu(H_2bicyphen)] (4.39) was refluxed with one molar equivalent of copper(II) perchlorate, dissolution of the mononuclear complex occurred, and the neutral dinuclear copper(II) complex [Cu_2(bicyphen)] (4.40) separated (scheme 4.29). In this reaction the pyridine acts as base to deprotonate the biscopper(II) complex.



Scheme 4.29 Summary of preparative routes to dinuclear copper complexes of H_4bicyphen (4.8)

The reaction between two moles of copper(II) perchlorate and one mole of ligand in pyridine, gave a brown solution. This colour change indicated that the ligand had reacted with the copper(II) perchlorate to give a soluble complex. Addition of less polar solvents (methanol, diethylether, petroleum ethers or benzene) resulted in precipitation of the copper complex of the ligand. Benzene was found to be the most effective, giving the highest yield of $[Cu_2(H_4bicyphen)]-(ClO_4)_4$ (4.41). In the preparation just described, the brown solution contained a mixture of Cu:ligand in the molar ratio of 2:1. Apparently the addition of benzene produces the conditions needed to shift the equilibrium away from the pyridine soluble complex to give the less soluble biscopper(II) perchlorate complex. The nature of the soluble complex(es) is not clear, the brown solution may contain a number of different species in equilibrium but addition of the benzene precipitates the least soluble component; $[Cu_2(H_4bicyphen)](ClO_4)_4$ (4.41). Characterisation was made by elemental analysis, infrared spectra and additionally for $[Cu_2(bicyphen)]$ fdms was possible (fig 4.9).

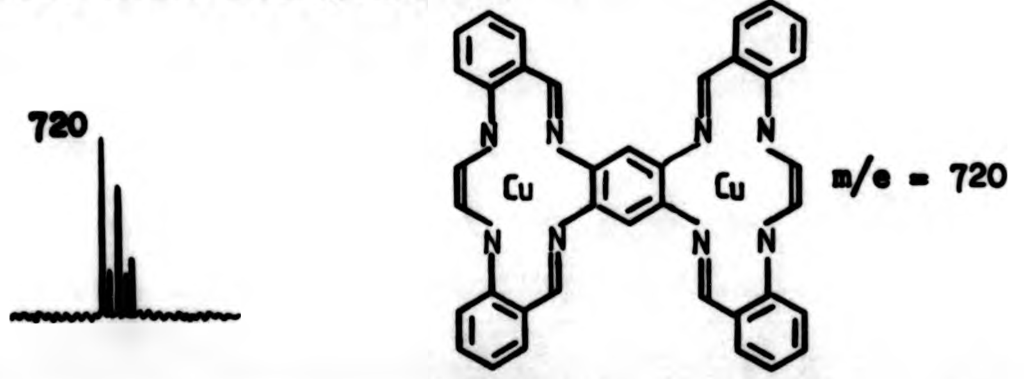


Fig 4.9 Fdms of $[Cu_2(bicyphen)]$ (4.40).

The appearence of three molecular ion peaks and separated by two mass units, characterises a dinuclear Cu(II) complex, since naturally occurring copper is composed of ^{63}Cu (69.09%) and ^{65}Cu (30.91%). The relative abundancies for the three peaks are dependent on the different isotopic combinations of ^{63}Cu and ^{65}Cu (table 4.11).

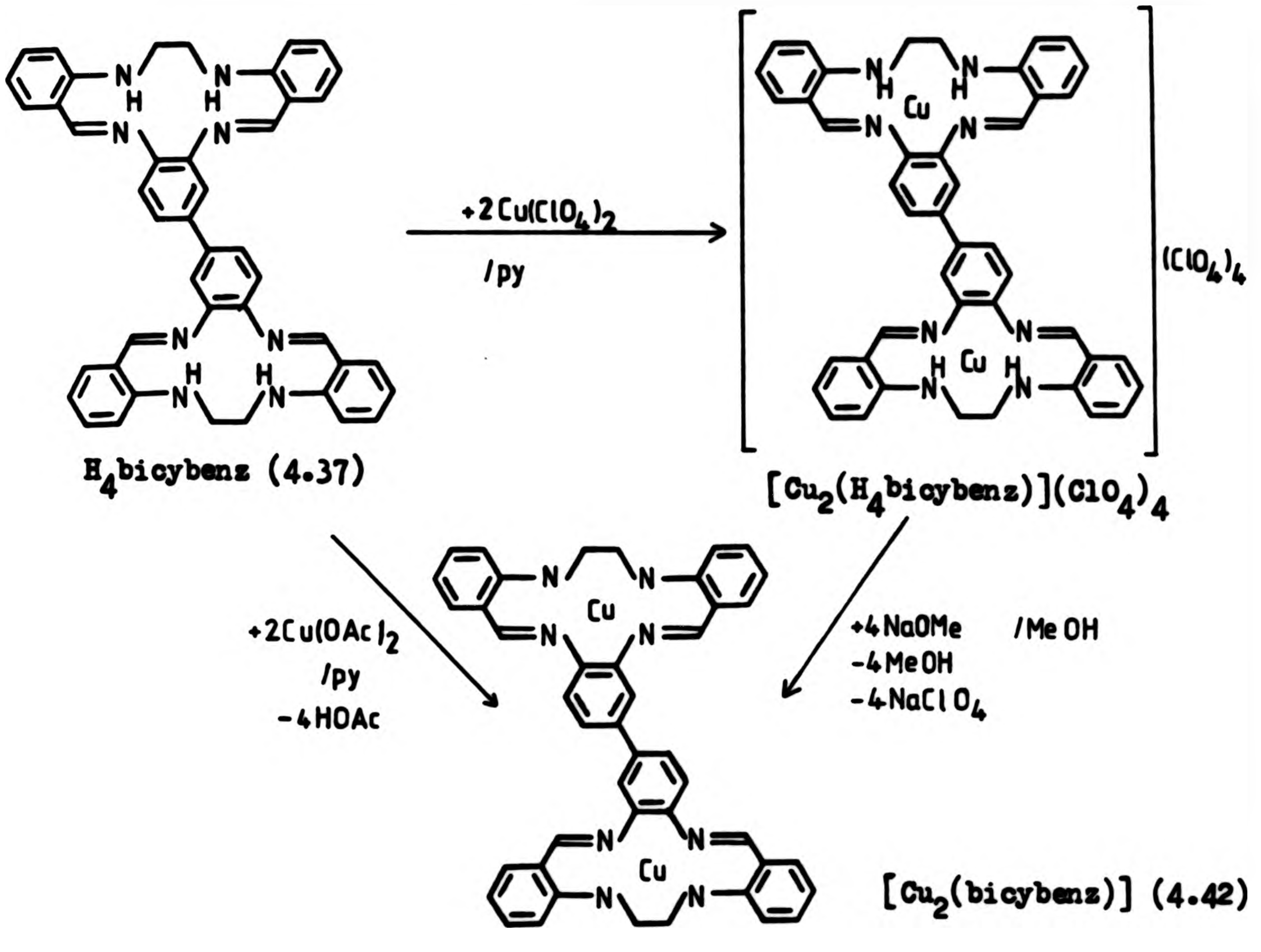
Nature of copper in macrocycle	% of isotopic biscopper(II) complex	Relative Abundancies Calc	Found
$^{63}Cu^{63}Cu$	0.6909 x 69.09 = 47.7 %	100.0	100
$^{63}Cu^{65}Cu$	2(0.6909 x 30.91) = 42.7 %	89.5	75
$^{65}Cu^{65}Cu$	0.3091 x 30.91 = 9.5 %	19.9	30

Table 4.11 Isotopic contributions of copper.

The molecular ion detected at M* = 720 corresponds to a form of the molecule in which both ethane bridges are dehydrogenated (fig 4.9). This is consistent with the data found for the mononuclear analogue [Cu(cyph-2H)] (section 4.2). Unlike [Cu(cyph)], no evidence has been found for oxygenation of the ethane bridge in the samples prepared by the methods outlined above.

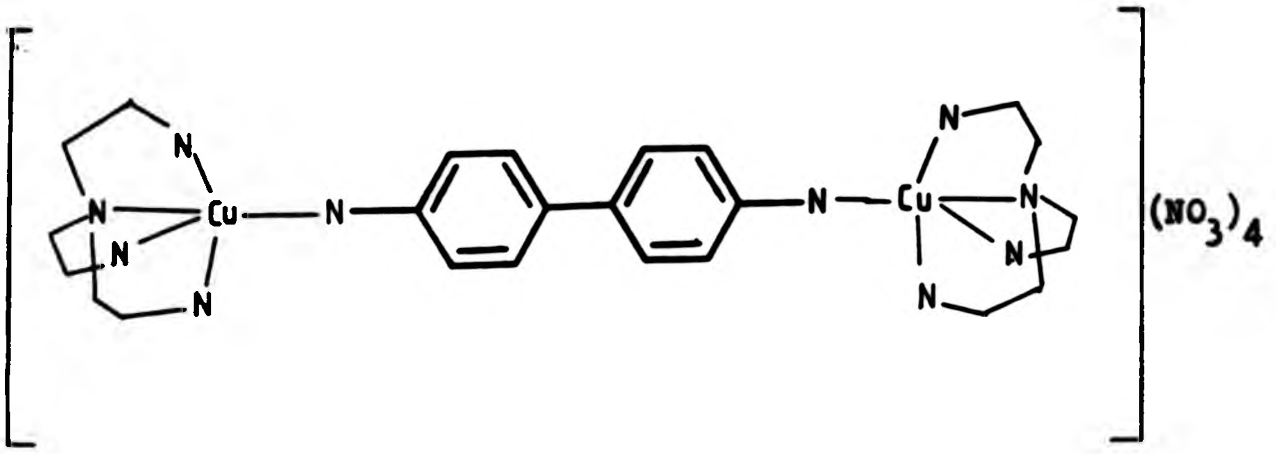
4.4.4 Copper(II) Complexes of H_4bicybenz.

The solubility of H_4bicybenz (4.37) is low, but the ligand will dissolve in hot pyridine containing copper(II) perchlorate to form the dinuclear copper(II) complex $[Cu_2(H_4bicybenz)](ClO_4)_4$ (4.43) (scheme 4.30). Deprotonation of the perchlorate complex to give $[Cu_2(bicybenz)]$ (4.42) was found under similar conditions to those for the copper(II) complexes of H_4bicyphen (section 4.4.1).



Scheme 4.30 Preparation of [$Cu_2(H_4bicybenz)](ClO_4)_4$ (4.43).

The intramolecular Cu-Cu distance was calculated from molecular models as approximately 11.4 Å, although some close intermolecular contacts in the solid state have been shown present in other bisCu(II) systems[23] (scheme 4.31).



Scheme 4.31

Due to the low solubility of the ligand H_{12}bicybenz, the biscopper(II) complex $[Cu_2(H_{12}bicybenz)](ClO_4)_4$ (4.44) was prepared in dmf. The complex 4.44 separated from the solution above after setting aside for 24h, and appeared to be stable in the solid state. The magnetic properties of these copper(II) complexes are discussed in section 4.5.

4.4.5 Conclusions concerning the methods of preparation of the copper complexes.

The method of deprotonation of the anilino nitrogen atoms in the perchlorate complexes, leads to a novel synthetic route to the less soluble neutral copper(II) compounds. Attempts to reverse this reaction by the addition of perchloric acid to the neutral copper(II) compound failed for all those complexes described in this chapter. It has not been possible to prepare any biscopper(II) complexes via a template reaction, and this is believed to be due to the rapid oxidation of the tetraamino compounds to give highly coloured polymer type species. This difficulty has not hindered the preparation of the copper(II) complexes since in all cases it was possible to prepare the metal free polyimine ligand which would then incorporate copper(II) atom(s).

4.4.6 Properties of the copper(II) complexes of the dinucleating aza ligands.

Some of the physical data is presented in table 4.12 for the copper(II) complexes described in this chapter, and it is interesting to note some similarities between the mononuclear and dinuclear copper(II) complexes. The table is divided into four groups of related compounds, which can be considered in the following ways.

Group 1 contains the neutral complexes.

[Cu(cyph)] (4.9) and [Cu_2(bicybenz)] (4.42) show similar electronic spectral properties because both compounds contain the same chromophore (assuming that there is little or no pi-interaction across the skew linkage of the two macrocyclic units in [Cu_2(bicybenz)] (4.42)). The complex [Cu_2(bicyphen)] (4.40) also shows a similar spectrum, but with the additional band in the visible spectrum at 630 nm possibly due to the extended conjugation through the 'fused' benzene ring. The mononuclear complex [Cu(H_2bicyphen)] (4.39) has a similar uv/vis spectrum to the dimer [Cu_2(H_2bicyphen)] (4.40) for the same reasons as above.

Group 2 contains the cationic complexes of the imine ligands.

There are no distinct similarities in this group of cationic complexes, possibly due to the more basic solvents required for the less soluble dinuclear complexes.

Group 3 contains the cationic complexes of the reduced ligands.

The copper(II) complexes of the reduced ligands do not show similar uv/vis spectra, but this could again be due to the different solvents used for the dissolution of the complexes. For example, The complex $[Cu_2(H_{12}bicybenz)](ClO_4)_4$ (4.44) requires dmf, whereas methanol is suitable for $[Cu(H_6cyph)](ClO_4)_2$ (4.12).

Group 4

These complexes do not have suitable dinucleating copper complexes for comparison, but [Cu(cyph(X))] shows a distinctive carbonyl stretch at 1658 cm^{-1}, and a different infrared spectra to that of the parent compound [Cu(cyph)].

Group 1.	**Colour**	**Infrared** cm^{-1}	**Uv/vis (ε)** nm
[Cucyph] (4.9)	black	3074 3024 2936 1616 1588 1573 1501 1481 1237	272(2860) 337(1131) 354(1031) 432(1247) 520(964)
[Cu_2(bicybenz)] (4.42)	black	3050 2850 1614 1577 1520 1362 1190 1143 748	270(1958) 328(1246) 440(1079) 520(1001) 600(734)
[Cu(H_2bicyphen)] (4.39)	purple	2940 2480 1611 1580 1516 1478 1448 1391	350(492)* 510(526)* 650(240)*
[Cu_2(bicyphen)] (4.40)	purple	2940 2480 1611 1580 1516 1478 1448 1391	355(823)* 510(769)* 630(491)*
Group 2			
[Cu(H_2cyph)](ClO_4)$_2$ (4.10)	brown	3500 3176 1627 1598 1571 1482 1100b 765	220(1340) 268(524) 320(411) 390(188)
[Cu_2(H_4bicybenz)](ClO_4)$_4$ (4.43)	brown	1620 1551 1420 1385 1300 1230 1192 1168 1100b 760 628	270(6019) 308(3760) 330(3700) 440(3310) 470(3310) 520(2295) 650(169)
[Cu_2(H_4bicyphen)](ClO_4)$_4$ (4.41)	brown	1612 1598 1542 1536 1517 1485 1362 1336 1100b	270(462)* 320(401)* 450(310)* 600(60)*

Table 4.12 Infrared and uv/vis data for copper(II) complexes of the mononuclear and dinuclear ligands (continued next page).

* The compound could not be fully dissolved.

Group 3.	**Colour**	**Infrared** cm^{-1}	**Uv/vis (ε)** nm
$[Cu(H_6cyph)](ClO_4)_2$ (4.12)	pink	3518 3238 1614 1590 1495 1462 1364 1308 1100b	222(3073) 260(1100) 318(664) 370(285) 520(720) 570(608)
$[Cu_2(H_{12}bicybenz)](ClO_4)_4$ (4.44)	brown	3550 3200 1610 1555 1495 1420 1305 1100b 770	268(5005) 320(3337) 400(1902) 440(2369) 464(2402) 526(2169) 646(267)
Group 4			
[Cu(cyphX)] (4.28)	burgandy	1658 1620 1600 1583 1547 1524 1494 1458	270* 340* 450* 520* 605*
$[Cu(cyph(OMe)_2)]$ (4.18)	gold	3103 3076 3026 1606 1580 1521 1460 1392 1373	275(3619) 315(1841) 336(1567) 354(1521) 420(1498) 480(1106) 510(1286)

Table 4.12 Infrared and uv/vis data for copper(II) complexes of the mononuclear and dinuclear ligands.

* The compound could not be fully dissolved.

4.5 Magnetic data for the copper(II) complexes.

In the previous chapter (section 3.7) abnormally low magnetic moments and non Curie-Weiss behaviour were explained in terms of direct[25] and superexchange[26] pathways in the copper(II) complexes of the large ring systems (section 3.6). The direct[25] interaction was possible due to

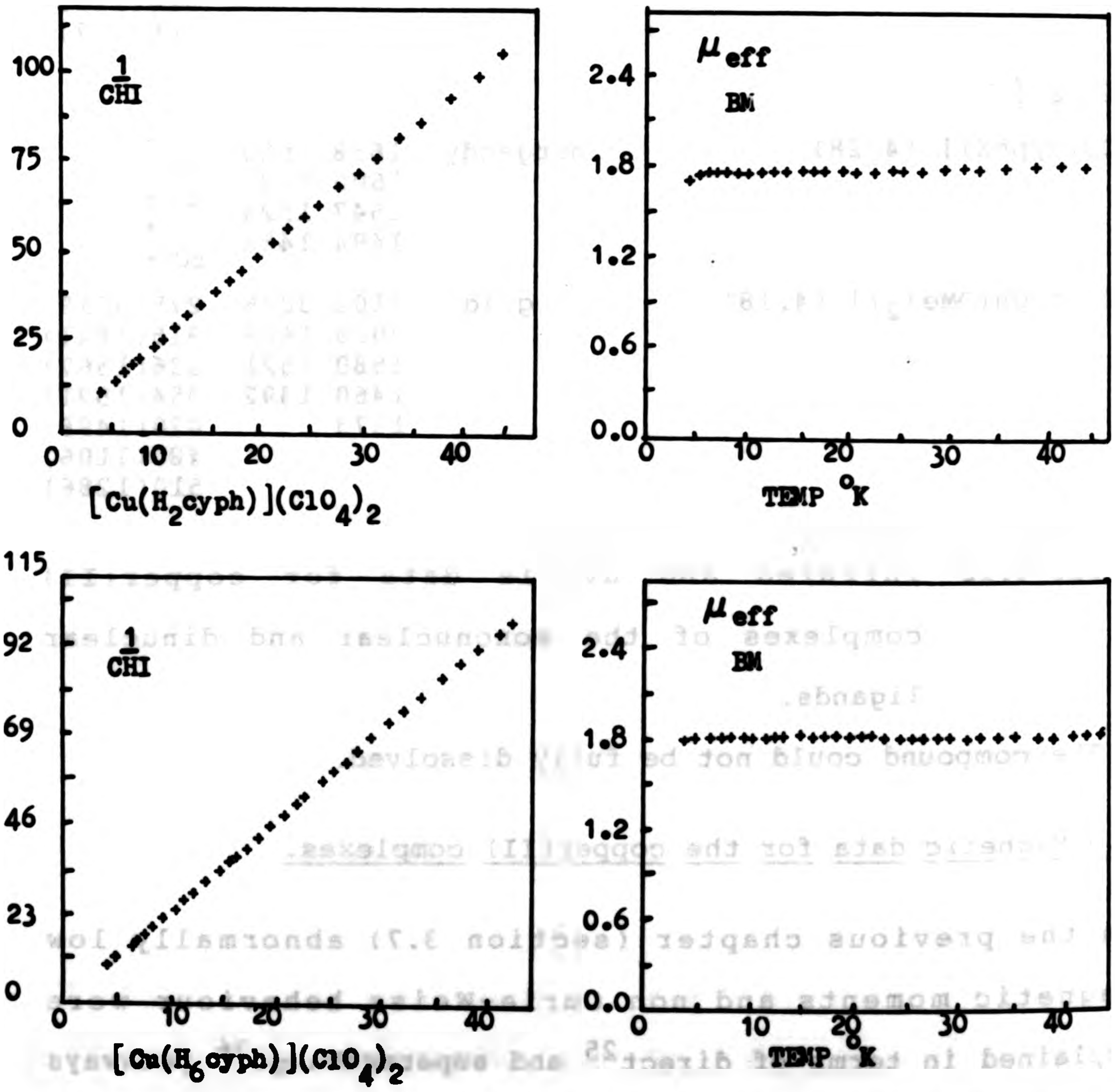


Fig 4.10 Magnetic data for [Cu(H$_2$cyph)](ClO$_4$)$_2$ and [Cu(H$_6$cyph)](ClO$_4$)$_2$

the twisted conformation of the ligand forcing the two copper atoms into close proximity. The ligand system H_4bicyphen discussed in this chapter is rigidly planar, and unlikely to show a subnormal magnetic moment due to direct interaction, unless intermolecular contacts are made between two copper(II) atoms. The monocopper complexes [Cu(H_2cyph)]-(ClO_4)$_2$ and [Cu(H_6cyph)](ClO_4)] show normal Curie Weiss behaviour (fig 4.10, facing page).

The biscopper(II) complexes of H_4bicyphen fall into two groups, cationic and neutral. The neutral biscopper(II) complex was expected to be more likely to show superexchange interaction because there is a fully unsaturated bridging unit between the two copper atoms. A highly delocalised ground state is possible for this molecule, shown schematically by the resonance forms in fig 4.11. Internal redox changes of this type leading to difficulties in formulating the formal oxidation levels of metal ions and ligand donor atoms have been noted previously in the so called "electron-transfer-series-complexes"[27]. The magnetic data (fig 4.12, facing page 183) confirms the presence of antiferromagnetic coupling, however the monocopper(II) complex [Cu(H_2bicyphen)] also shows a subnormal magnetic moment, and this can only be due to intermolecular exchange between copper(II) atoms. This would suggest for the biscopper(II) systems both types of interaction (intramolecular (via superexchange) or intermolecular (via either direct or superexchange)) may contribute to the lower magnetic moment.

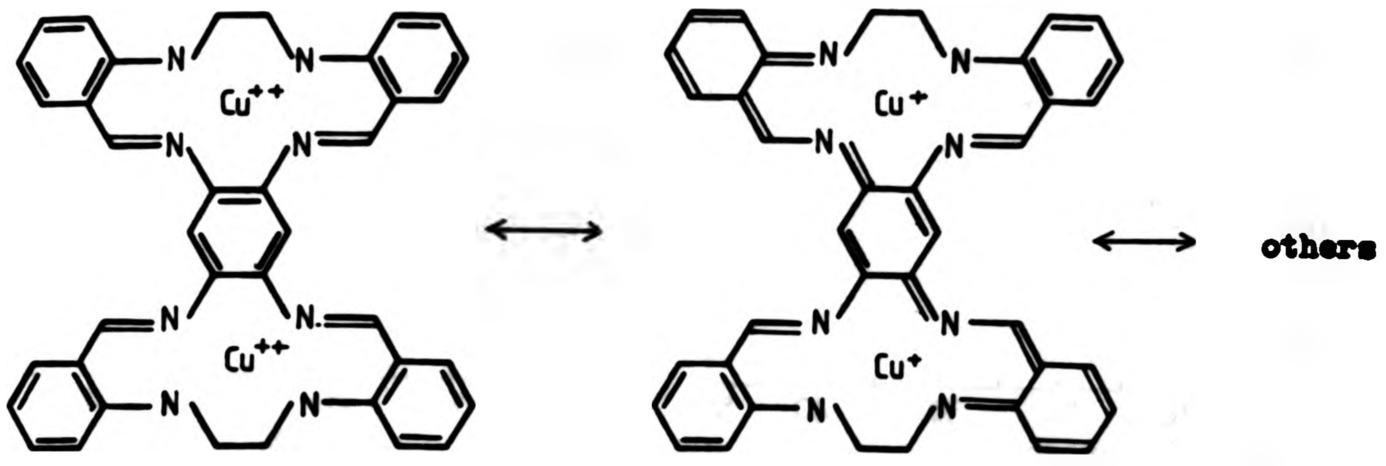


Fig 4.11 Resonance forms illustrating the possible delocalised electronic ground state in [Cu_2(bicyphen)].

An antiferromagnetic interaction was reported[24] for a biscopper(II) complex $Cu_2A^4(B^3)_2$ (4.45). The intramolecular nature of this superexchange was demonstrated by comparison of physical data to four monomeric copper(II) complexes. The antiferromagnetic exchange interaction in $Cu_2A^4(B^3)_2$ (4.45) was viewed as resulting from "a spin polarisation between the unpaired copper electron and the various nitrogen electrons, a polarisation that is propagated through the benzene moiety to the other copper atom"[24] (i.e. analogous to the systems described for [Cu_2(bicyphen)] above.

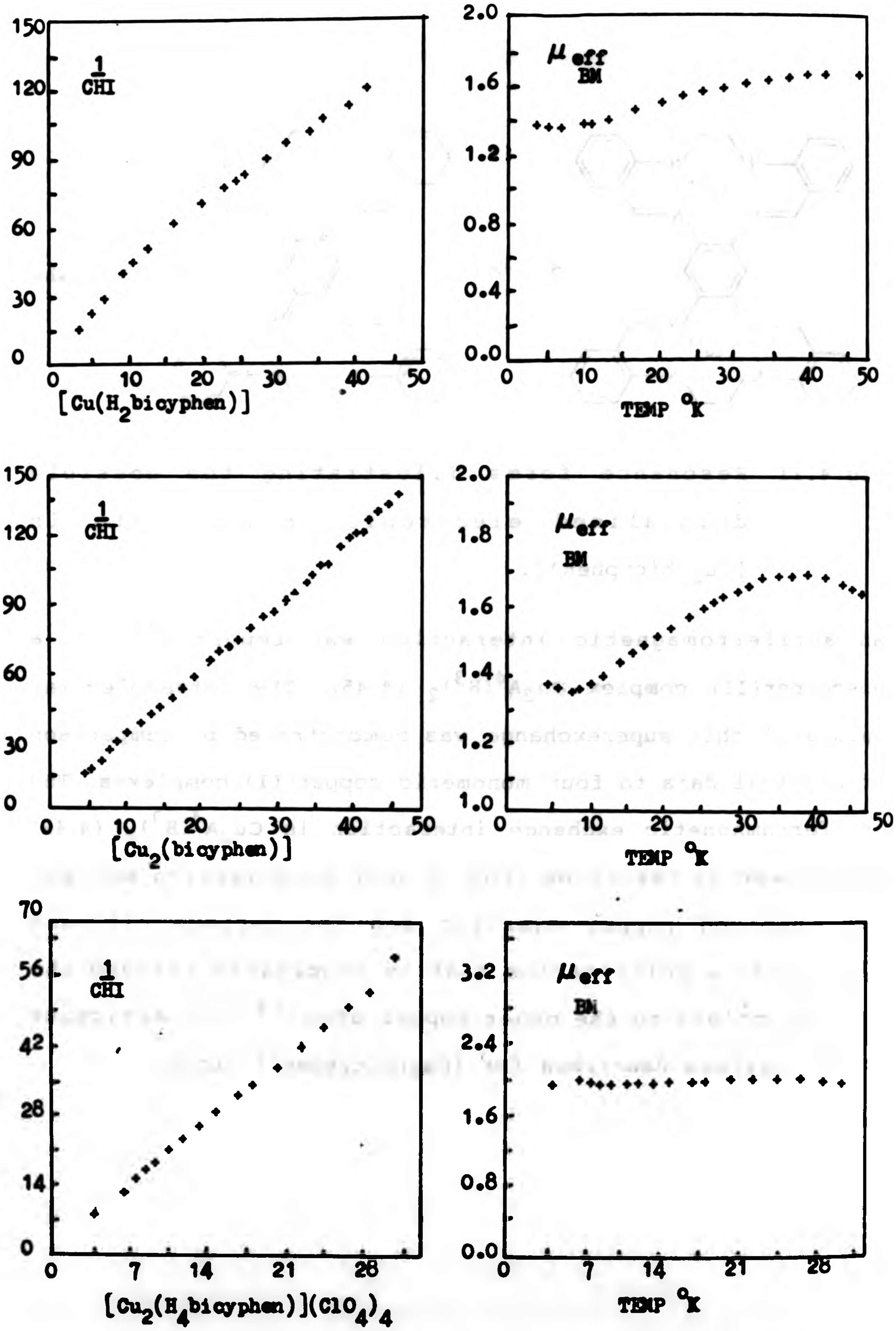
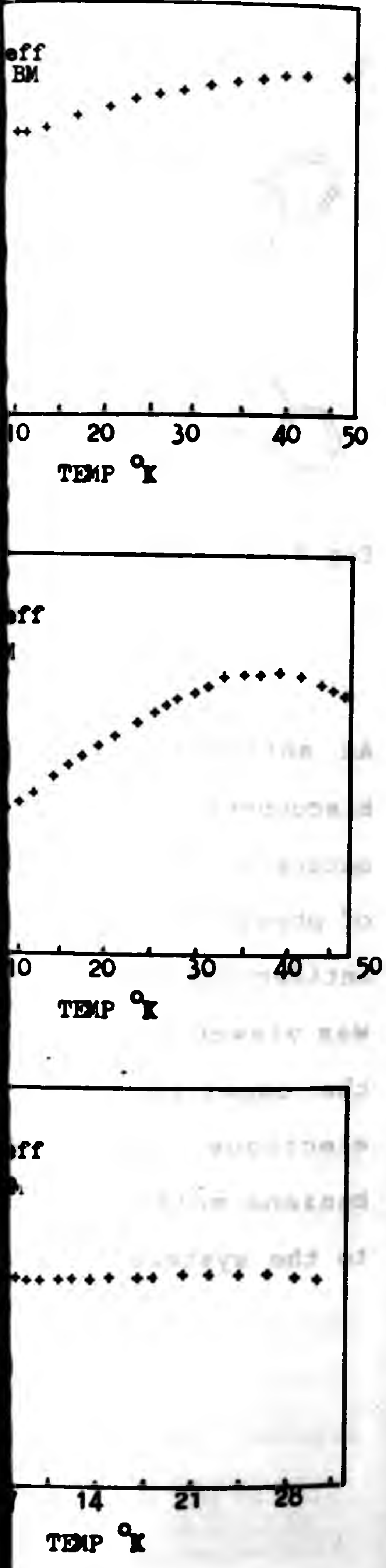
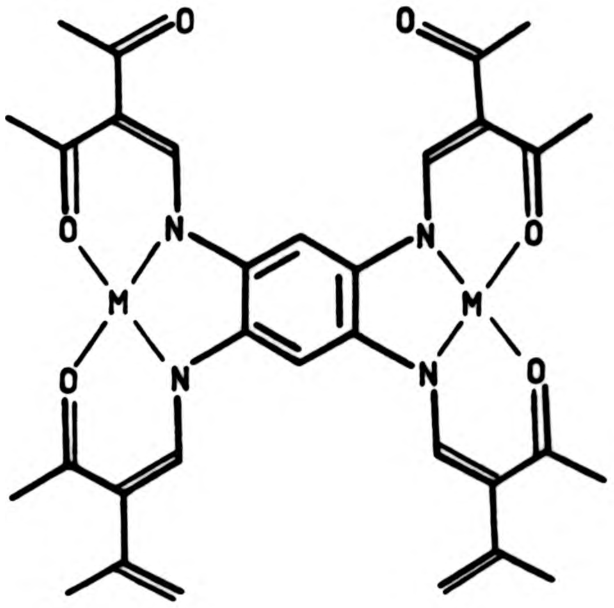


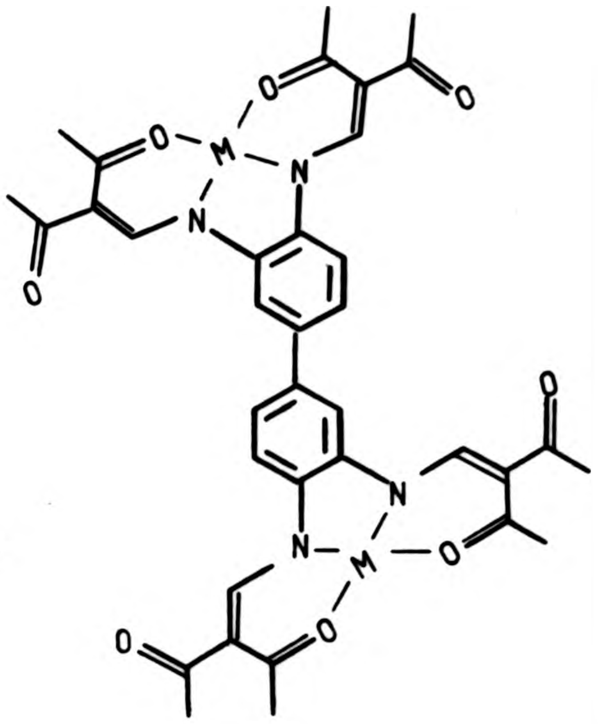
Fig 4.12 Magnetic data for the copper(II) complexes of H_4bicyphen



er(II) complexes of



Cu$_2$A^4(B^3)$_2$ (4.45)



4.46

The cationic complexes cannot utilise the same pathway as [Cu$_2$(bicyphen)] since the anilino nitrogen atoms retain their protons and delocalised ground states of the type shown in fig 4.11 are not possible. The variable temperature magnetic data confirm the normal Curie Weiss behaviour for [Cu$_2$(H$_4$bicyphen)](ClO$_4$)$_4$ (fig 4.12, facing page).

The biscopper(II) complexes of the ligand H$_4$bicybenz were not prepared in time for the magnetic measurements to be completed by the submission date of this thesis. However, biscopper(II) complexes based on non-cyclic ligands containing the benzidine nucleus have been reported^{24}. The complex 4.46 did not show exchange interaction, for reasons that "spin polarisation would be attenuated with distance, or perhaps there is little spin polarisation between the two phenyl groups in the biphenyl bridge". But it has subsequently been demonstrated^{23} that electrons can exchange between two copper(II) atoms separated by 12 Å via a benzidine moiety. The phenyl rings of the benzidine nucleus are planar with dihedral angles of 13.8 and 22.5° about the Carbon-Carbon bond connecting them for each of the two crystallographically independent dimers (fig 4.13). This approximately planar configuration would allow the presence of resonance forms (fig 4.14). These would then be capable of contributing to magnetic exchange in a manner analogous to that considered above for the neutral [Cu_2(bicyphen)] complexes (fig 4.11).

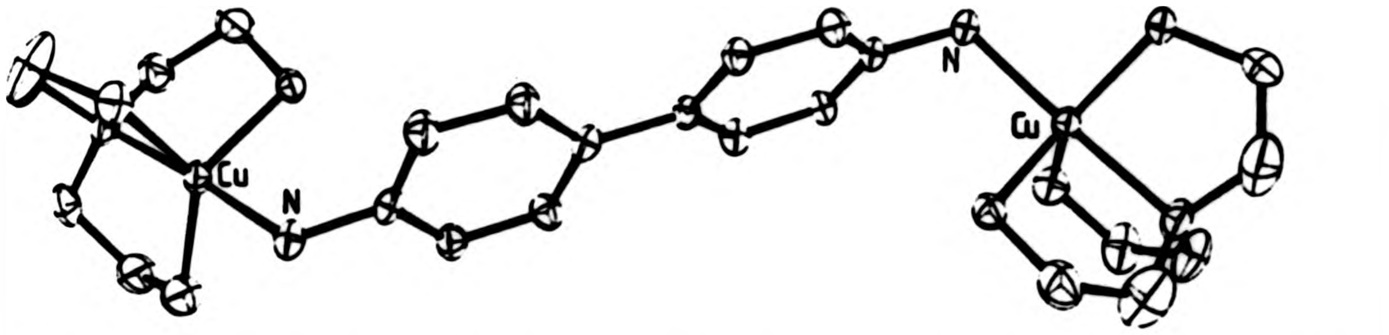


Fig 4.13 One of the two crystallographically independent dimers.

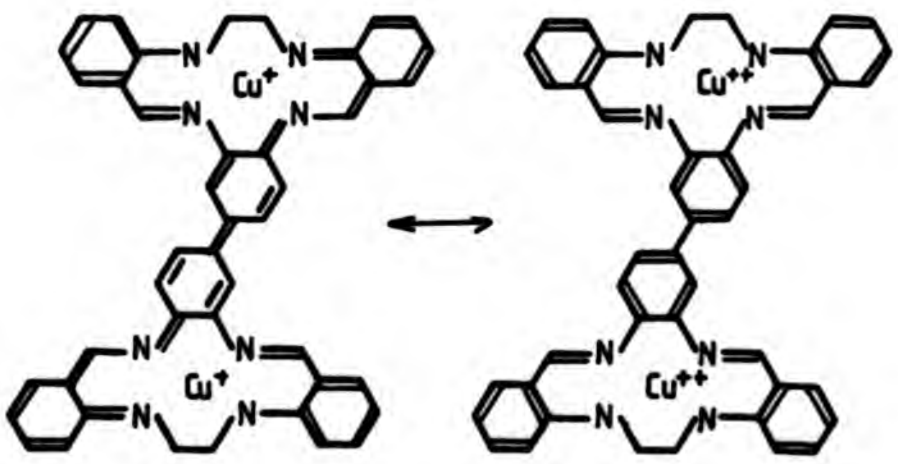


Fig 4.14 Resonance forms illustrating the possible electronic ground state for complexes based on the benzidine nucleus.

benzidine moiety. The phenyl rings of the benzidine nucleus are planar with dihedral angles of 13.8 and 22.5° about the Carbon-Carbon bond connecting them for each of the two crystallographically independent dimers (fig 4.13). This approximately planar configuration would allow the presence of resonance forms (fig 4.14). These would then be capable of contributing to magnetic exchange in a manner analogous to that considered above for the neutral [Cu_2(bicyphen)] complexes (fiq 4.11).

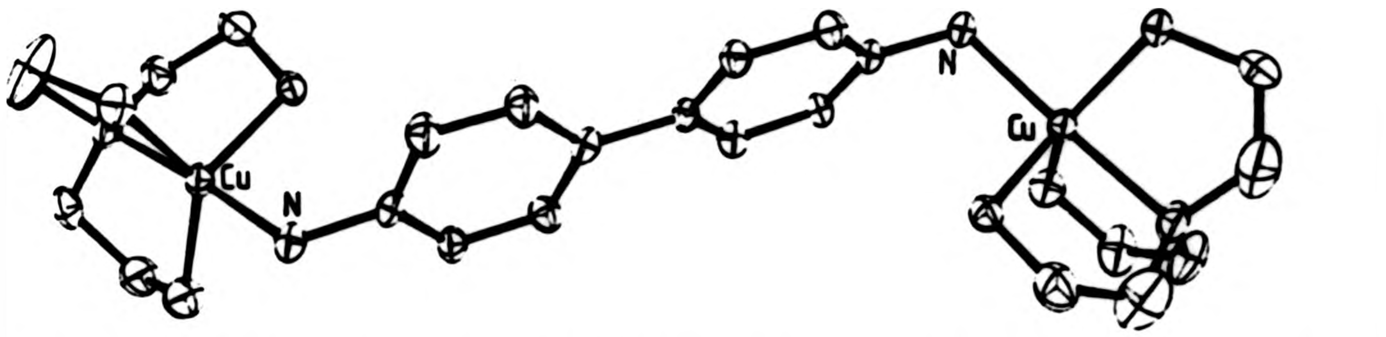


Fig 4.13 One of the two crystallographically independent dimers.

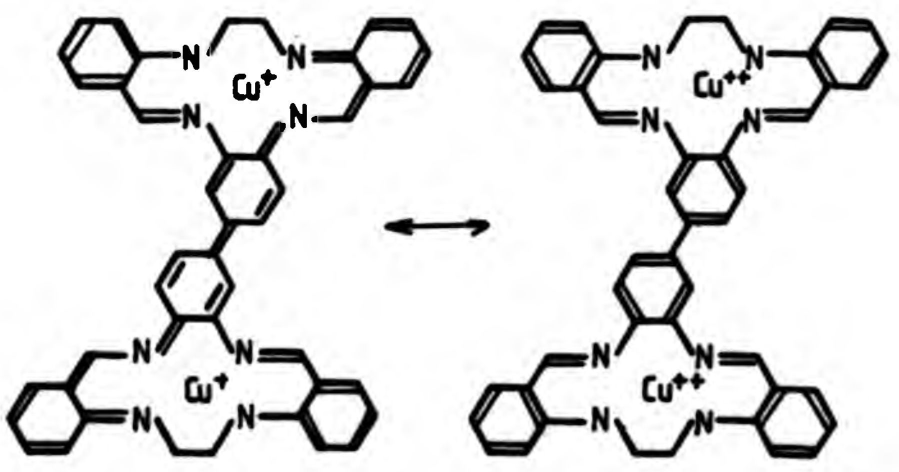


Fig 4.14 Resonance forms illustrating the possible electronic ground state for complexes based on the benzidine nucleus.

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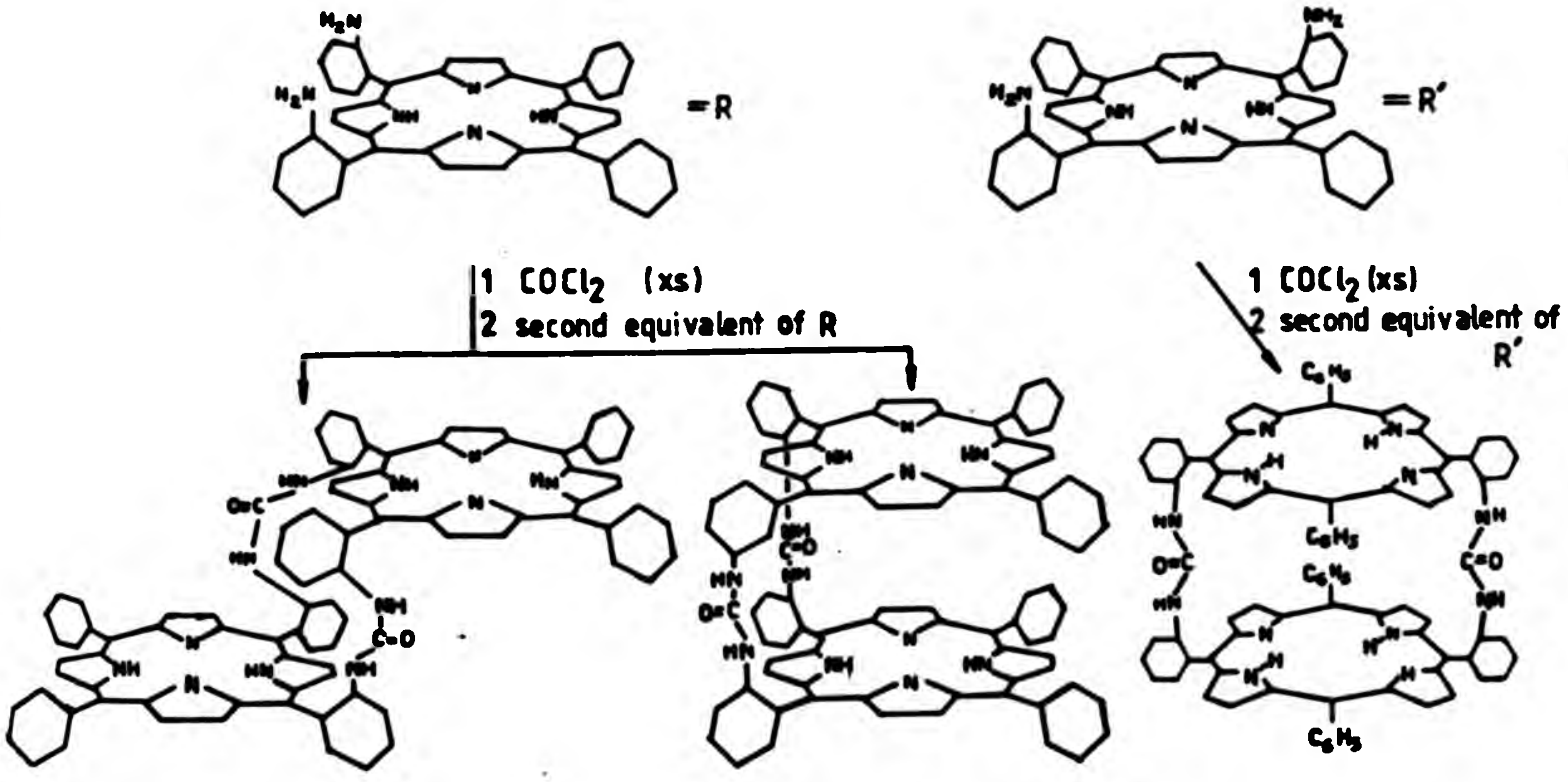
CHAPTER 5

Linked Macrocycles

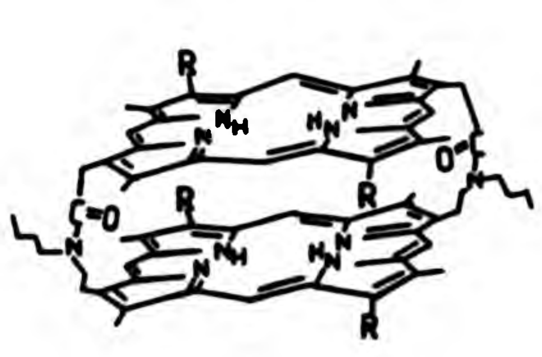
5.1.1 Introduction.

The linking of two macrocycles together with a bridge which could be varied in length and nature would provide an interesting range of binuclear metal complexes. Many examples are available[1] whereby two macrocycles (usually porphyrins) have been linked together by one or more bridging portions (scheme 5.1).



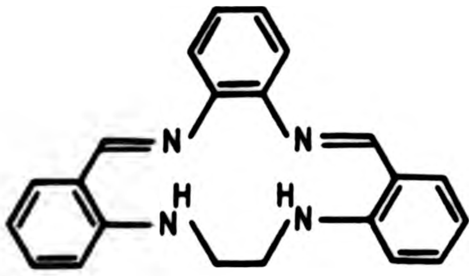
Scheme 5.1 Synthesis of cofacial porphyrins.

Cofacial porphyrins are capable of constraining two metal ions to lie in close proximity, and may posess unusual properties. For example, the dicobalt(II) complex[1d] of the cofacial diporphryin 5.1 reacts with oxygen to give a sandwiched complex.



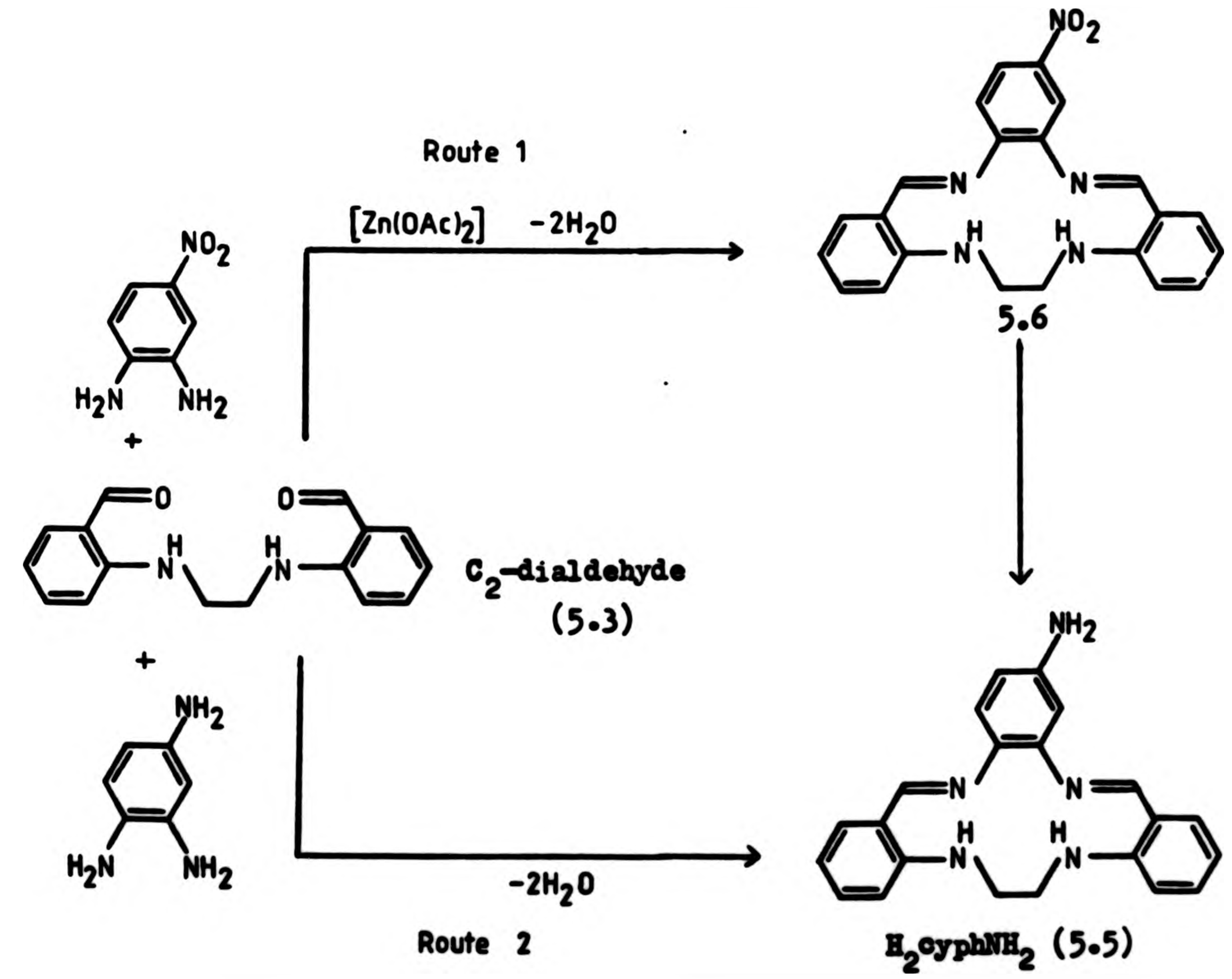
5.1 R = n-hexyl

5.1.2 Precursors based on C_2-dialdehyde (5.3).

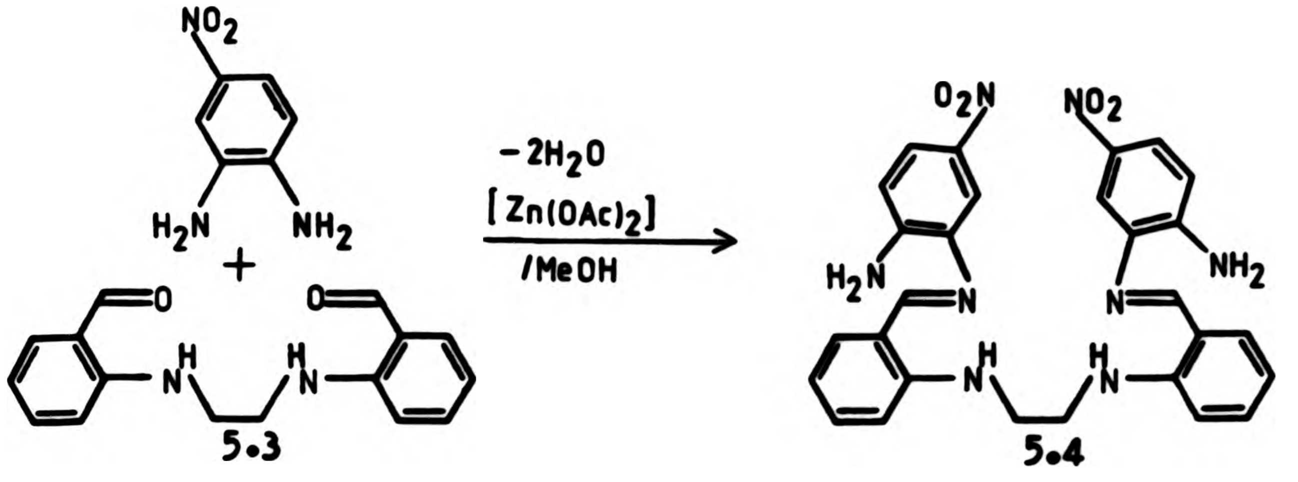


H_2cyph (5.2)

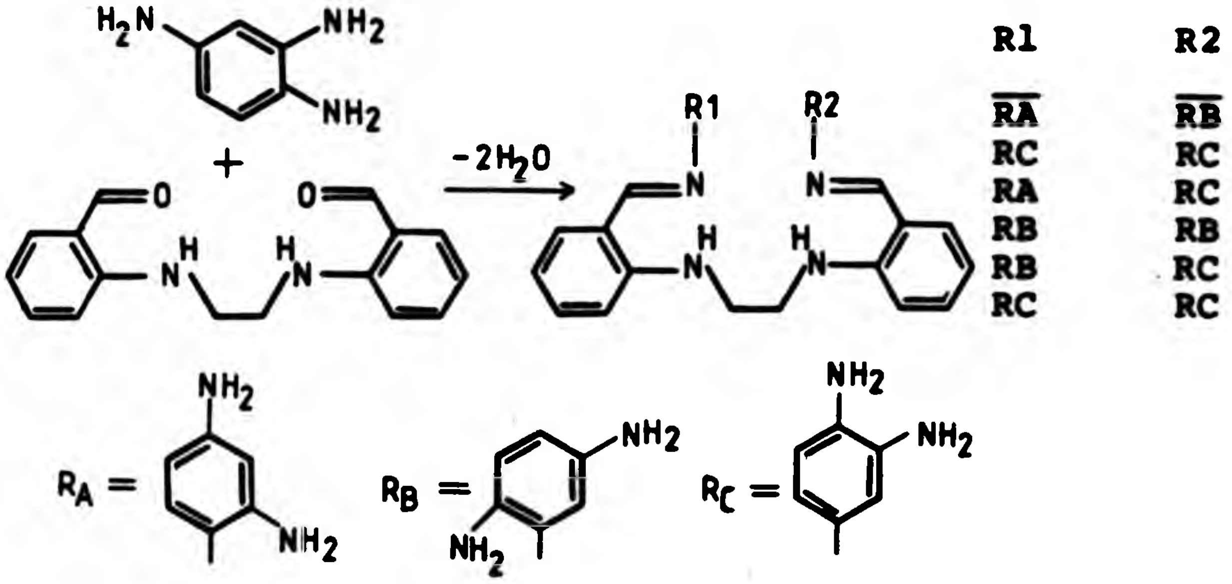
The precursors outlined above (section 5.1) have been linked together using substituent groups (on the porphryins) such as amines or acid chlorides. Related derivatives of H_2cyph (5.2) which are capable of being linked together have not been reported (see chapter 3). A derivative of this type which could be used in a "linking" reaction would be H_2cyphNH$_2$ (5.5, scheme 5.2), which could possibly be prepared by condensation of the C_2-dialdehyde with either 1,2,4-triaminobenzene (route 2) or with 1,2-diamino-4-nitrobenzene, followed by selective reduction of the nitrosubstituent (route 1). There was some doubt as to whether the [1+1] condensation of the C_2-dialdehyde with 1,2,4-triaminobenzene would occur successfully because it has been observed[2] that a [2+1] condensation product (5.4) was obtained in attempts to prepare the related nitro derivative $H_2cyphNO_2$ (5.6,scheme 5.3) from condensation with 1,2-diamino-4-nitrobenzene. If a similar [2+1] condensation reaction occurred between 1,2,4-triaminobenzene and the C_2-dialdehyde at least six di-imines could result which may be unstable and/or difficult to separate (scheme 5.4). Polymeric materials may separate in addition to the compounds described above (see section 5.4.3).



Scheme 5.2 Two possible routes for preparing $H_2cyphNH_2$ (5.5).



Scheme 5.3 Preparation of a [2+1] condensation product.



R1	R2
RA	RB
RC	RC
RA	RC
RB	RB
RB	RC
RC	RC

Scheme 5.4 Possible [2+1] condensation products.

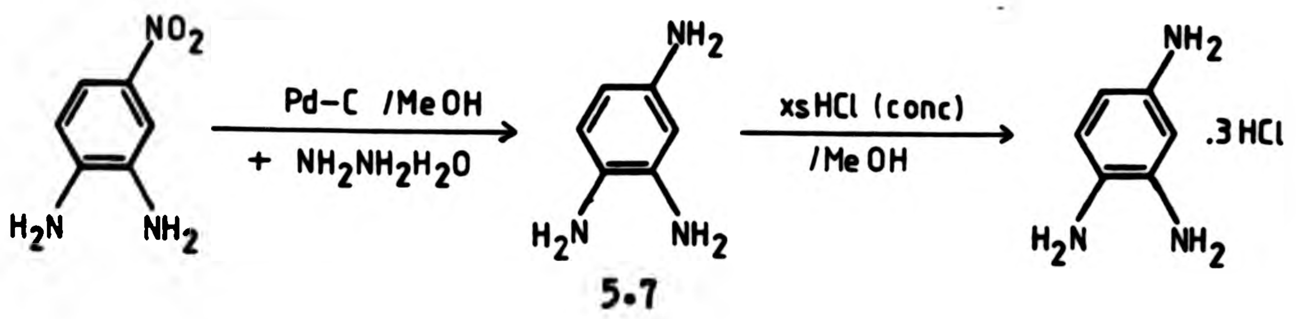
5.2 Results and Discussion.

The reaction between 3-nitro-1,2-diaminobenzene and C_2-dialdehyde (5.3, scheme 5.3) in the presence of zinc(II) acetate was examined, and after 5 days at reflux the [1+1] condensation product $H_2cyphNO_2$ (5.6) was isolated. The [2+1] product appeared initially, therefore confirming the previous results[3] (as shown by infrared data NH_2 = 3300 and 3500 cm^{-1}) but reverts to the more stable macrocycle on extended refluxing. At this stage there are two possible routes for attempting to prepare the amino derivative H_2cyphNH$_2$ (5.5) (scheme 5.2). Route 2 was chosen, since route 1 would involve difficulties in the selective reduction of a nitro substituent.

5.3.1 Preparation of 1,2,4-triaminobenzene (5.7)

The precursor 1,2-diamino-4-nitrobenzene (a red coloured solid) was commercially available, and had been used in the previously described reaction to give H_2cyphNO$_2$ (scheme 5.2). The reduction of the nitro group in 1,2-diamino-4-nitrobenzene was achieved by using hydrazine hydrate and the catalyst palladium on carbon. Care was taken as spontaneous ignition occurs when palladium on carbon is added to methanol in the presence of oxygen. The progress of the reduction was monitored by withdrawing a drop of reaction mixture with a capillary pipette, and placing it on a filter paper. When the intense red colour had disappeared all the 1,2-diamino-4-nitrobenzene had been reduced to give a clear supernatent liquid. CAUTION- The filter paper should be soaked in water for 24 h, or else spontaneous combustion will take place when the filter paper dries. Care was taken (see section 8) to avoid adding excess amounts of 1,2-diamino-4-nitrobenzene or hydrazine hydrate since both these reagents could react with C_2-dialdehyde. Methanolic solutions of 1,2,4-triaminobenzene were only stable under nitrogen and attempts to isolate the solid were accompanied by rapid oxidation to give a mixture of highly coloured products. A preliminary attempt to form the macrocycle

H_2cyphNH$_2$ (5.5) was made by filtering the reduction solution directly into a suspension of C_2-dialdehyde in degassed methanol. Rapid oxidation of the 1,2,4-triaminobenzene appeared to take place and only the precursor C_2-dialdehyde was recovered. On one occasion excess hydrazine hydrate was present in the solution of 1,2,4-triaminobenzene, and other condensation products were isolated (section 5.6). To avoid the problem of the 1,2,4-triaminobenzene oxidising it was converted into a hydrochloride salt by treatment with methanolic hydrochloric acid. The creamy coloured solid which was isolated was characterised as 1,2,4-triaminobenzene trihydrochloride (scheme 5.5) and was air stable.

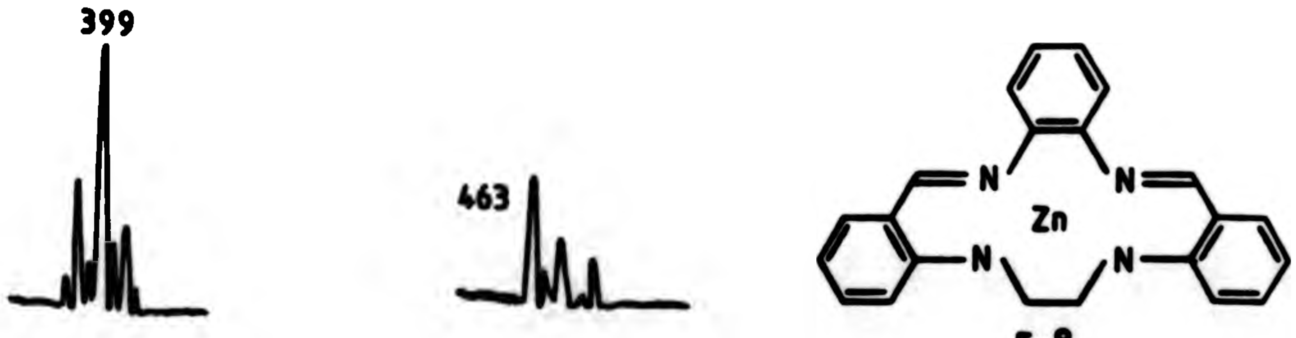


Scheme 5.5 Preparation of 1,2,4-triaminobenzene trihydrochloride.

5.3.2 Reactions of 1,2,4-Triaminobenzene trihydrochloride with C_2-dialdehyde

To prepare the ligand H_2cyphNH$_2$ (5.5) a similar procedure to that for the reaction of TAB.4HCl (chapter 4) with C_2-dialdehyde was used. However, the mixture of C_2-dialdehyde and 1,2,4-triaminobenzene (5.7) in refluxing ethanol showed no reaction until zinc(II) acetate was added.

The reaction of tetra-aminobenzene with C_2-dialdehyde (chapter 4) only required the presence of acid to catalyse the [2+1] condensation reaction, but this reaction gave rise to a very low soluble product. The addition of a lewis acid catalyst has been found necessary for all the aromatic bridged tetra-aza macrocycles (section 4). After the addition of zinc acetate to the mixture of C_2-dialdehyde and 1,2,4-triaminobenzene in refluxing methanol a yellow-orange precipitate separated, which was then shown to be the zinc complex [Zn(cyphNH$_2$)] (5.8) by elemental analysis (Zn,C,H,N), eims (M* = 463, fig 5.1) and infrared spectra. Optimisation of the reaction conditions led to a yield of 92% which was dependent on a reaction time of only one hour in refluxing ethanol. When the reaction time was prolonged the yield decreased (table 5.1). Only when these conditions were established could a high yield of [Zn(H$_2$cyphNH$_2$)] (5.8) be obtained, despite the many other possibilities shown previously in scheme 5.4. It is likely that the formation of the macrocyclic zinc(II) complex was more stable than any of the [2+1] condensation products



5.8

Fig 5.1 Eims of [Zn(cyphNH$_2$)] (5.8)

Reaction Time h	% Yield
24	8
6	35
3	45
1	92

Table 5.1 Effect of reaction time on yields of [Zn(cyphNH$_2$)] (5.8)

The zinc complex 5.8 was unstable, and slowly changed to a dark red coloured product on standing in air. Attempts to recrystallise [Zn(cyphNH$_2$)] (5.8) from pyridine/methanol resulted in the isolation of the free ligand (~60 % yield) as a bright yellow powder. This compound was air stable and was characterised by infrared spectroscopy, elemental analysis and eims (M^+ = 355).

5.4.1 Linking reactions.

To examine whether H$_2$cyphNH$_2$ (5.5) would react with acid chlorides, preliminary experiments were made with acetyl and benzoyl chloride, and with oxalyl dichloride. Two methods were originally considered:

1). The acid chloride (RCOCl) was added to a suspension of H$_2$cyphNH$_2$ in diethyl ether[4], and an alkaline water phase was added to absorb the liberated hydrogen chloride which occurred on addition of the H$_2$cyphNH$_2$ (eq 5.1). This was not successful due to the low solubility of H$_2$cyphNH$_2$ in diethyl ether.

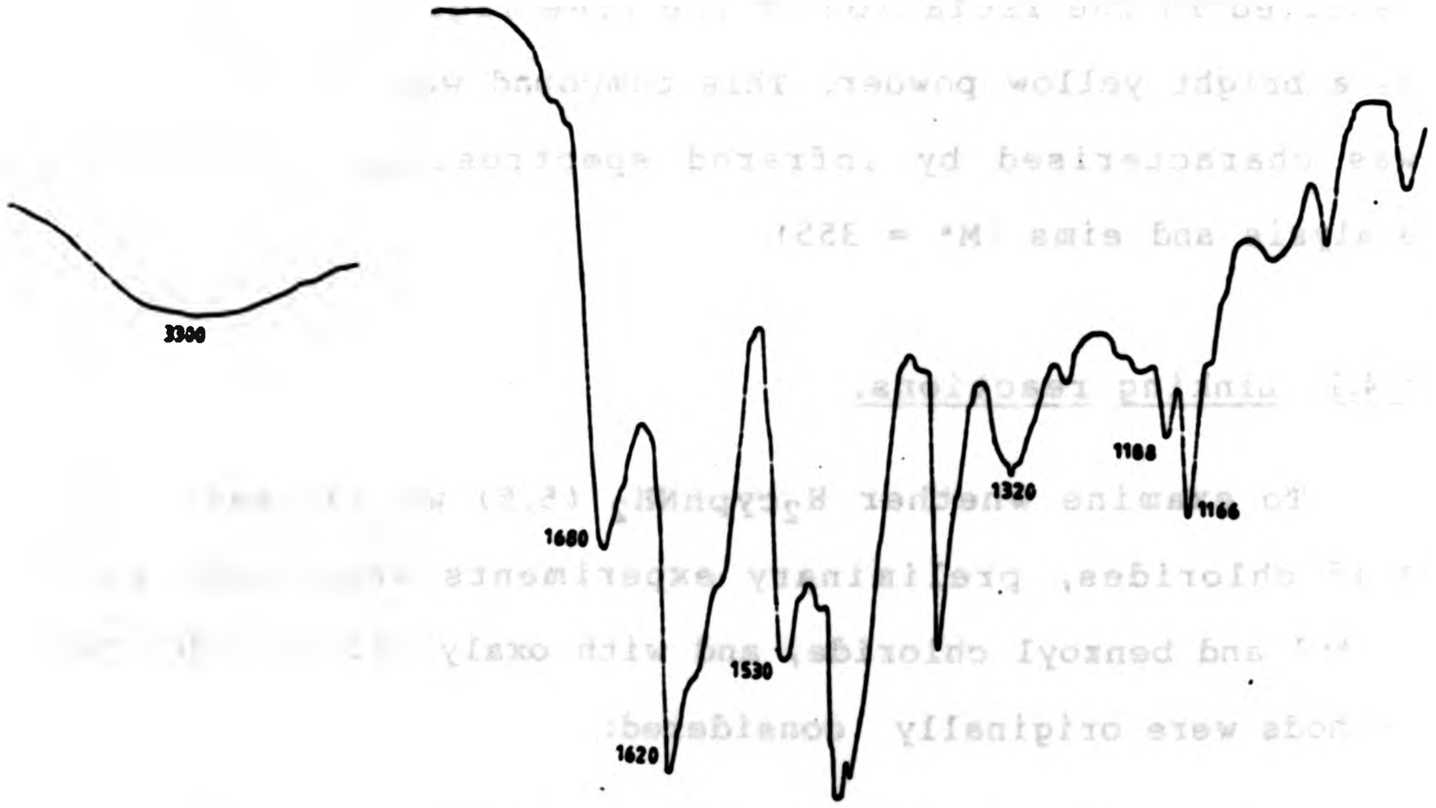
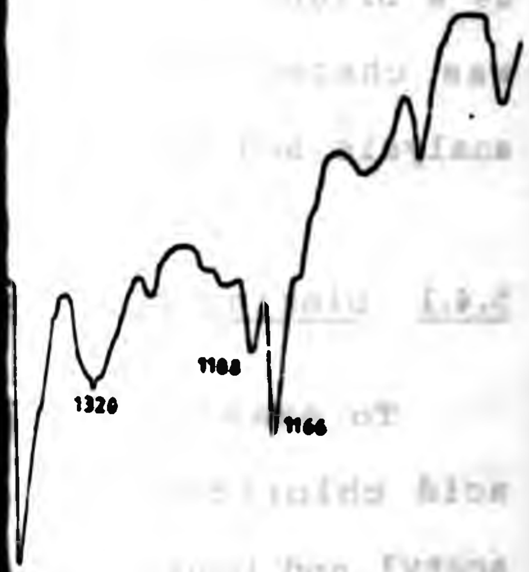


Fig 5.2 The infrared spectrum of RNHCOCONHR (5.11) (RNH_2 = $H_2cyphNH_2$).



m of RNHCOCONHR (5.11) (RNH$_2$ =

$$\text{H}_2\text{cyphNH}_2 + \text{RCOCl} \xrightarrow[\text{/diethylether}]{\substack{\text{+NaOH/H}_2\text{O} \\ \text{-NaCl}}} \text{H}_2\text{cyphNHCOR} \quad \text{...eq 5.1}$$

2). The second method[5] used the solvent pyridine to act as base and absorb liberated hydrogen chloride (eq 5.2).

$$\text{H}_2\text{cyphNH}_2 + \text{RCOCl} \xrightarrow[\text{-[pyH]Cl}]{\text{/py}} \text{H}_2\text{cyphNHCOR} \quad \text{... eq 5.2}$$

5.4.2 Results for acetyl and benzoyl chloride, and for oxalyl dichloride

A solution of acid chloride in benzene was added to a solution of H_2cyphNH$_2$ (5.5) in pyridine. The addition of methanol precipitated a yellow powder which had a strong absorbance at ~1670 cm^{-1} in the infrared spectrum ascribable to the carbonyl group (fig 5.2 facing page, table 5.2). This and elemental analyses confirmed that all three acid chlorides (acetyl, benzoyl and oxalyl) had reacted with H_2cyphNH$_2$ (5.5) (scheme 5.6). The three products were too involatile for a molecular ion to be detected in their electron impact mass spectra. However, for the oxalyl derivative a m/e peak at 528 was detected which may correspond to a fragment (fig 5.3) of the expected linked molecule.

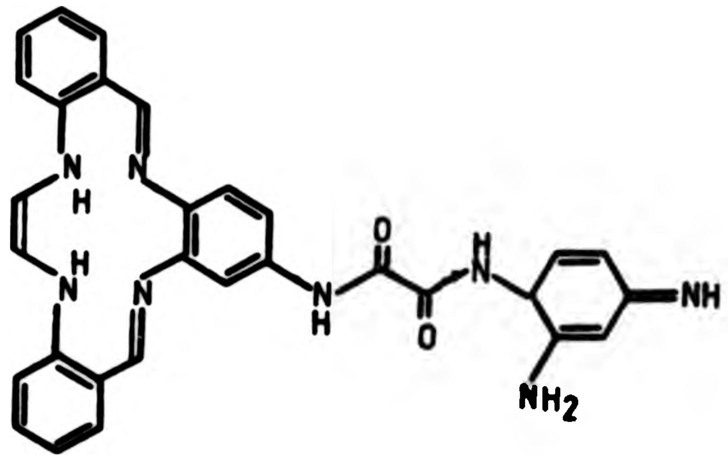
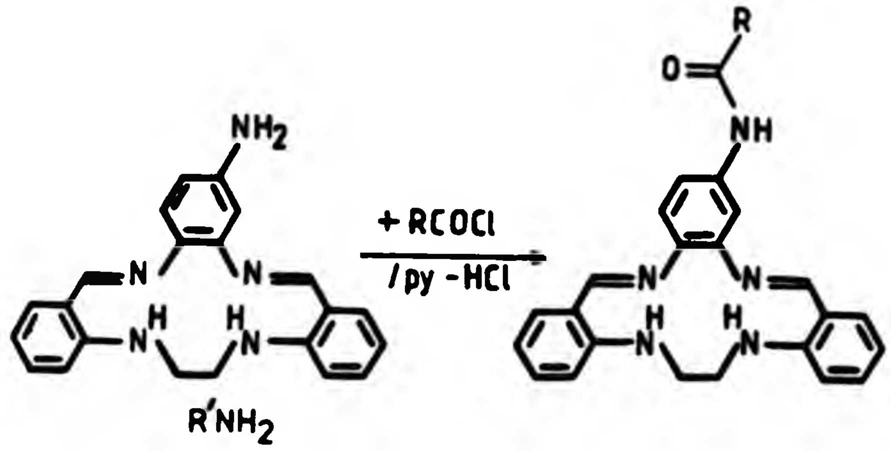


Fig 5.3 Eims assignment for m/e = 528



R = NHCOCH$_3$ (5.9)

R = NHCOPh (5.10)

R = CONHR' (5.11)

Scheme 5.6 Reactions of H$_2$cyphNH$_2$ (5.5) with acid chlorides.

RNH_2	$RNHCOCH_3$	RNHCOPh	RNHCOCONHR
(5.5)	(5.9)	(5.10)	(5.11)
3470			
3370	3300 BW	3300 BW	3300 BW
3240			
3090			
2950			
2880			
	1665	1665	1680
1622	1618	1618	1620
1600	1600	1600	1605
1580	1585	1582	1590
1562	1575		1530
1524 B	1522	1521	1520
	1505	1497	
	1485	1487	
		1415	
1330 B	1322 B	1325 B	1320
	1275	1281	
	1253	1256	1250
	1235	1237	1220
1210	1205	1213 W	
1183	1185	1185	1188
1165	1163	1163	1166
1150	1100 B	1100 B	1120
1100			
1082			
1049		1046 M	1048
		1031 M	
968		972 B	975
		933	
895		893	890

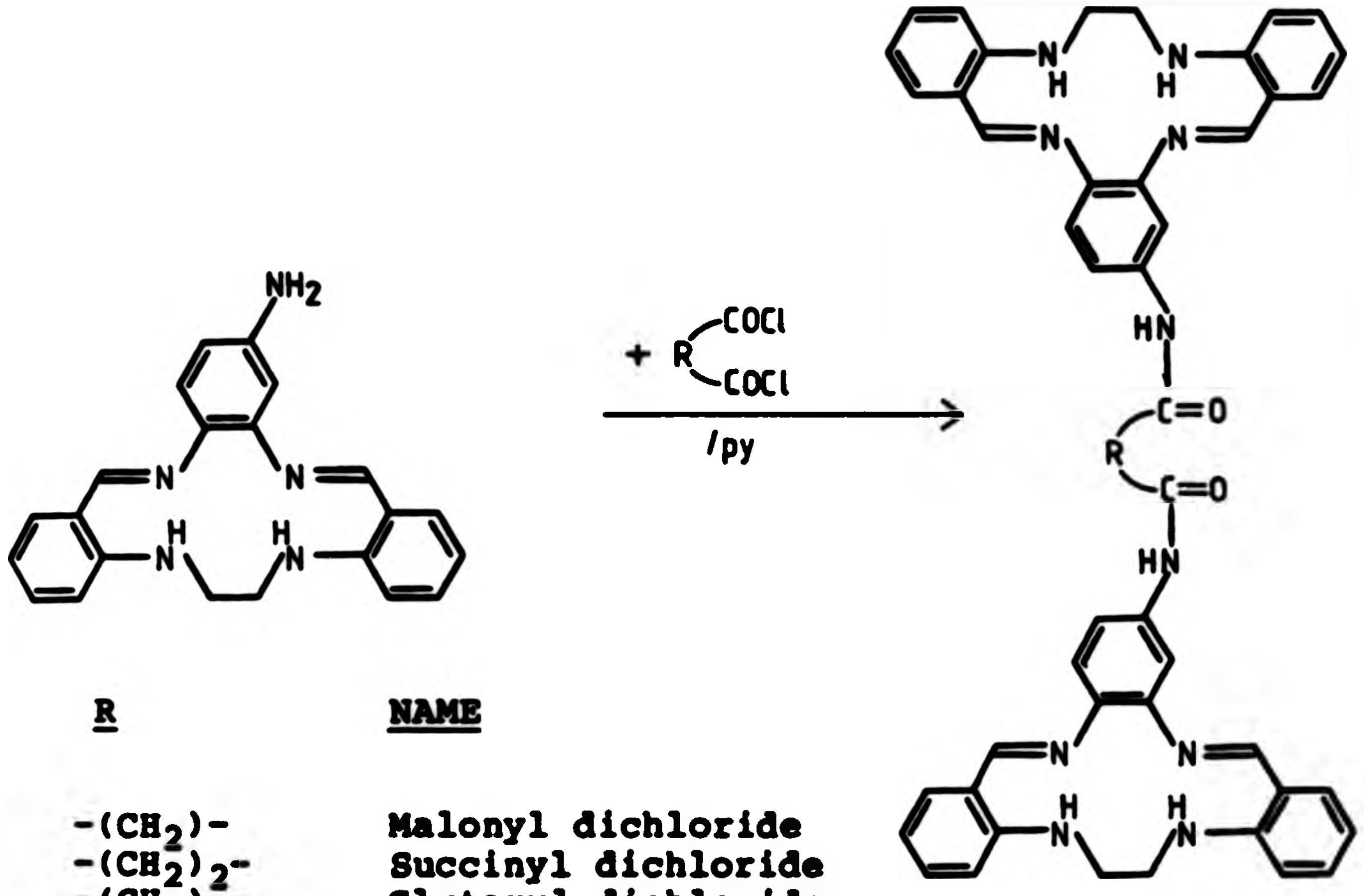
Table 5.2 Infrared absorption bands in the spectra of the derivatives of $H_2cyphNH_2$ (RNH_2). B = broad, W = weak, M = medium intensity bands.

	C%	H%	N%	CL%	Zn%
Triamine.3HCl (5.7)	30.5	5.3	17.7	44.1	
(Calc. for $C_6H_{12}N_3Cl_3$)	(31.0)	(5.2)	(18.1)	(45.7)	
H_2cyphNH$_2$ (5.5)	74.0	5.8	19.2		
(Calc. for $C_{22}H_{21}N_5$)	(74.3)	(6.0)	(19.7)		
[Zn(cyphNH$_2$)] (5.8)	63.9	4.6	17.0		14.1
(Calc. for $ZnC_{22}H_{19}N_5$)	(63.4)	(4.6)	(16.8)		(15.3)
RNHCOCH$_3$.2H$_2$O (5.9)*	66.1	5.9	16.0		
(Calc. for $C_{24}H_{27}N_5O_3$)	(66.5)	(6.2)	(16.2)		
RNHCOPh.2H$_2$O (5.10)*	70.9	5.9	13.8		
(Calc. for $C_{29}H_{29}N_5O_3$)	(70.3)	(5.9)	(14.1)		
RNHCOCONHR.H$_2$O (5.11)*	71.8	5.3	18.0		
(Calc. for $C_{46}H_{42}N_{10}O_2$)	(72.1)	(5.5)	(18.3)		
(RNH$_2$)$_2$CO.2H$_2$O (5.12)*	70.4	5.8	17.9		
(Calc. for $C_{45}H_{44}N_{10}O_3$)	(69.9)	(5.7)	(18.1)		

Table 5.3 Microanalytical data for the macrocycles derived from 1,2,4-triaminobenzene.
*In these amide derivatives the abbreviation RNH$_2$ refers to the aminosubstituted macrocycle H$_2$cyphNH$_2$ (5.5)

5.4.3 Reactions of the diacid chlorides with the amino substituted macrocycle H$_2$cyphNH$_2$ (5.5)

The reactions of a range of diacid chlorides with H$_2$cyphNH$_2$ (5.5) were considered (scheme 5.7).



R	**NAME**
$-(CH_2)-$	Malonyl dichloride
$-(CH_2)_2-$	Succinyl dichloride
$-(CH_2)_3-$	Glutaryl dichloride
$-(CH_2)_4-$	Adipoyl dichloride
$-(CH_2)_8-$	Sebacoyl dichloride
$-C_6H_4-$	Terephthayl dichloride

Scheme 5.7

For each of the reactions between H_2cyphNH$_2$ (5.5) and diacid dichloride (except terephthayl dichloride) two products were isolated. One product was insoluble in all the highly polar solvents tried (refluxing pyridine, dmso, dmf, thf) but was only isolated in 3 % yield. In each case both products had relatively similar infrared spectra (fig 5.4). The insoluble products from the different reactions were too involatile to be analysed by fdms and did not correspond to any expected formulation on the basis of elemental analysis (each product gave different elemental analyses). The second product from each reaction was soluble in pyridine and was isolated in approximately 60 % yield by the addition of methanol. The infrared spectra of these products showed only minor differences from that of H_2cyphNH$_2$ (5.5) and in all cases eims detected only a molecular ion at m/e = 355 which corresponded to the precursor H_2cyphNH$_2$.

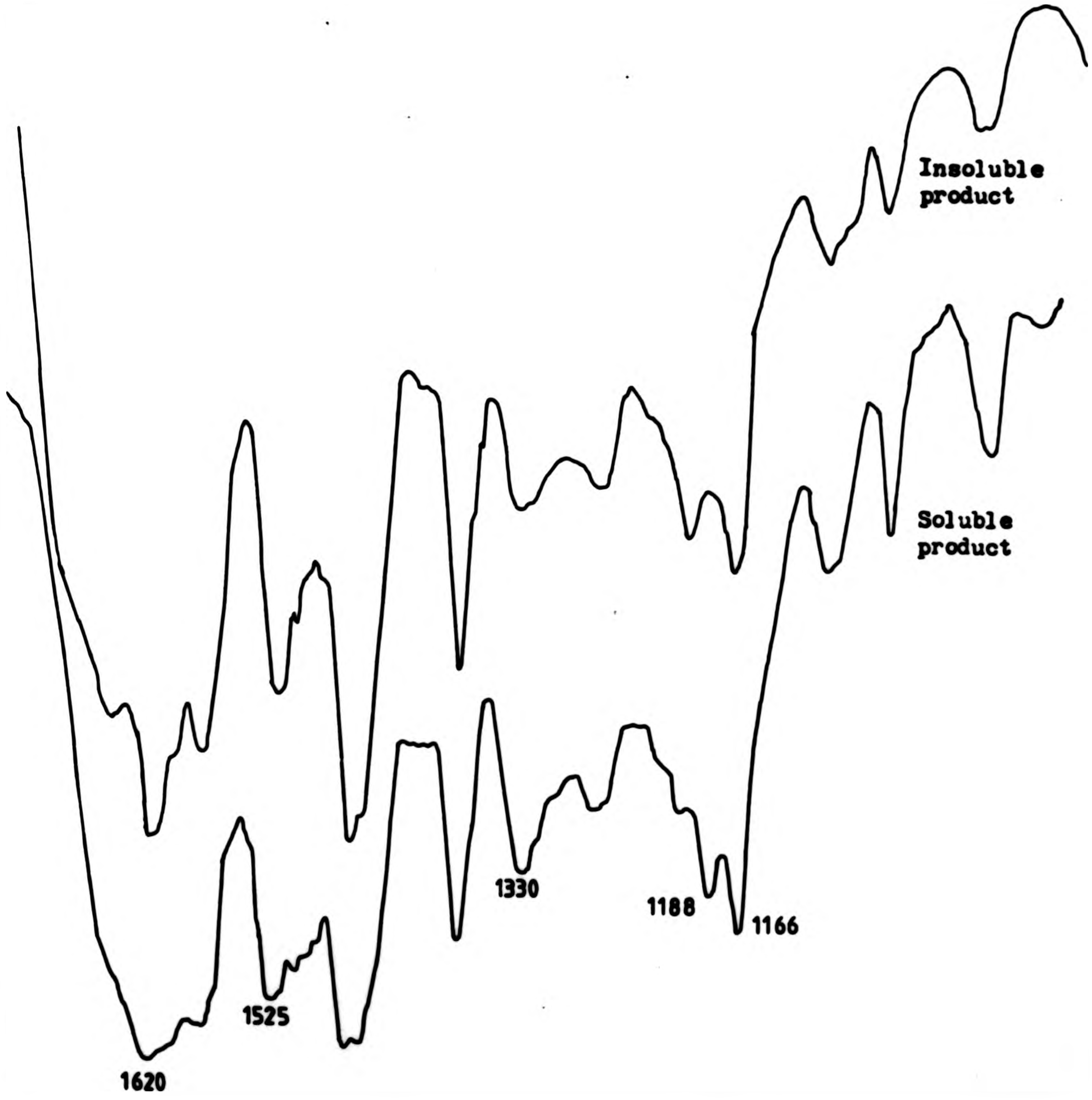
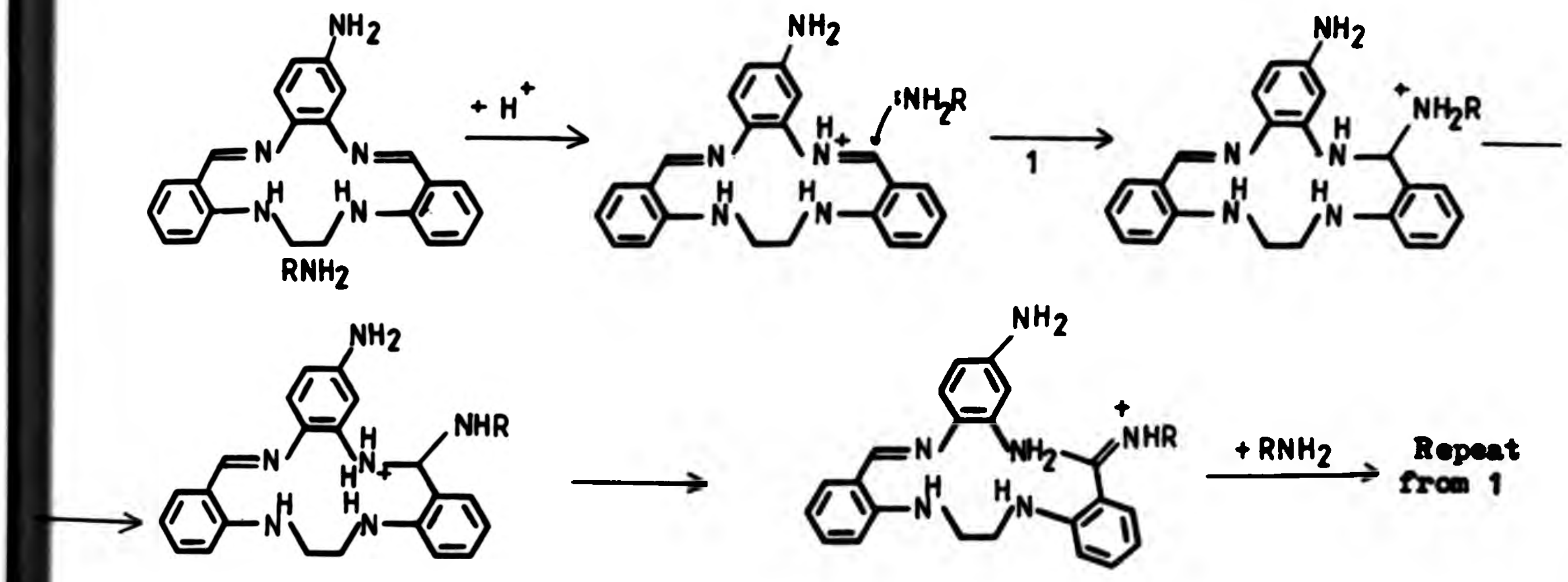


Fig 5.4 Infrared spectra of the products from the reaction of sebacoyl dichloride with H_2cyphNH$_2$

The first insoluble product could be formed for each of the above reactions, and the low solubility would suggest the material was a polymer (scheme 5.8). This polymer formation was one of the many problems anticipated for the preparation of H_2cyphNH$_2$ (section 5.1.2), but was overcome by the formation of the macrocyclic zinc complex [Zn(H_2cyphNH$_2$)]. The acidic conditions created with the addition of the acid chloride may be the cause of a transamination reaction^9.



Scheme 5.8 Possible polymeric formulation.

The second soluble product was considered to be a mixture of mainly H_2cyphNH$_2$ (shown by infrared spectra) and other minor amide compounds, (addition products as shown by a weak carbonyl stretch C=O stretch at ca. 1700 cm^{-1}). Two exceptions to the above results were the reactions involving terephthayl dichloride which did not give an insoluble product, and oxalyl dichloride as discussed earlier. The choice of pyridine as solvent for the reaction between H_2cyphNH$_2$ (5.5) and the diacidchloride was to absorb the liberated hydrochloride and prevent formation of the

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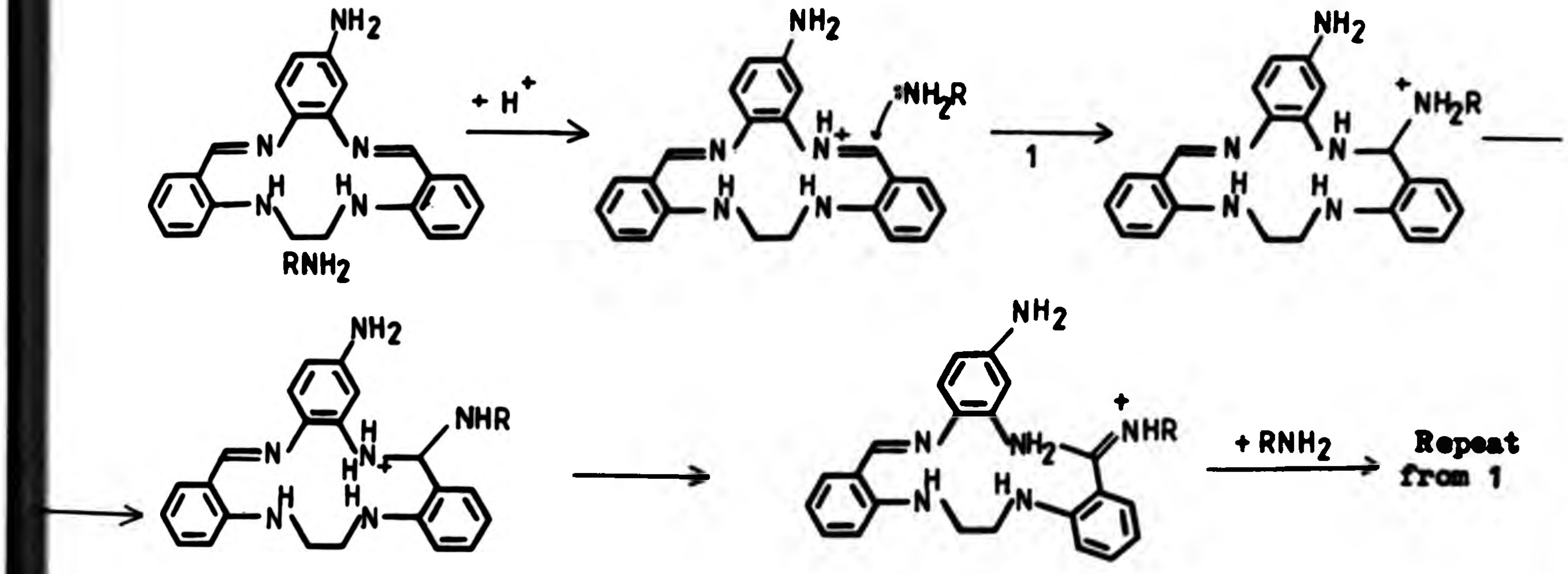

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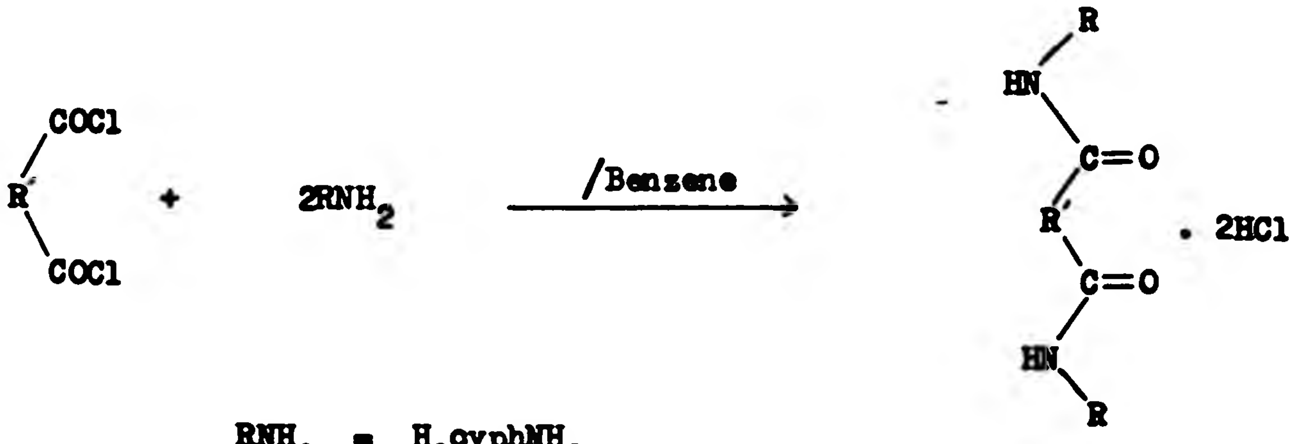


RNH_2 = H_2cyphNH$_2$

R′ = diacid chloride (see scheme 5.7)

Scheme 5.9 Preparation of the chloride salt of a dinucleating ligand.

The compounds shown in scheme 5.9 were isolated and found by elemental analysis to contain substantial amounts of chloride, but more importantly they all showed similar infrared spectra. The compounds could not be characterised by elemental analysis due to impurities (shown by infrared to possibly consist of small amounts of a carbonyl compound) and could not be recrystallised due to their low solubility in non-basic solvents (thf, $CHCl_3$, CH_3OH). Reaction of these chloride salts with sodium methoxide solution or pyridine gave yellow compounds which showed a similar infrared spectra to the soluble compounds isolated using the method in section 5.4.3.

5.5 Further reactions with H_2cyphNH$_2$.

A series of other linking reactions were attempted (table 5.4) using pyridine and thf as the solvent media.

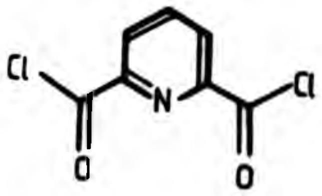
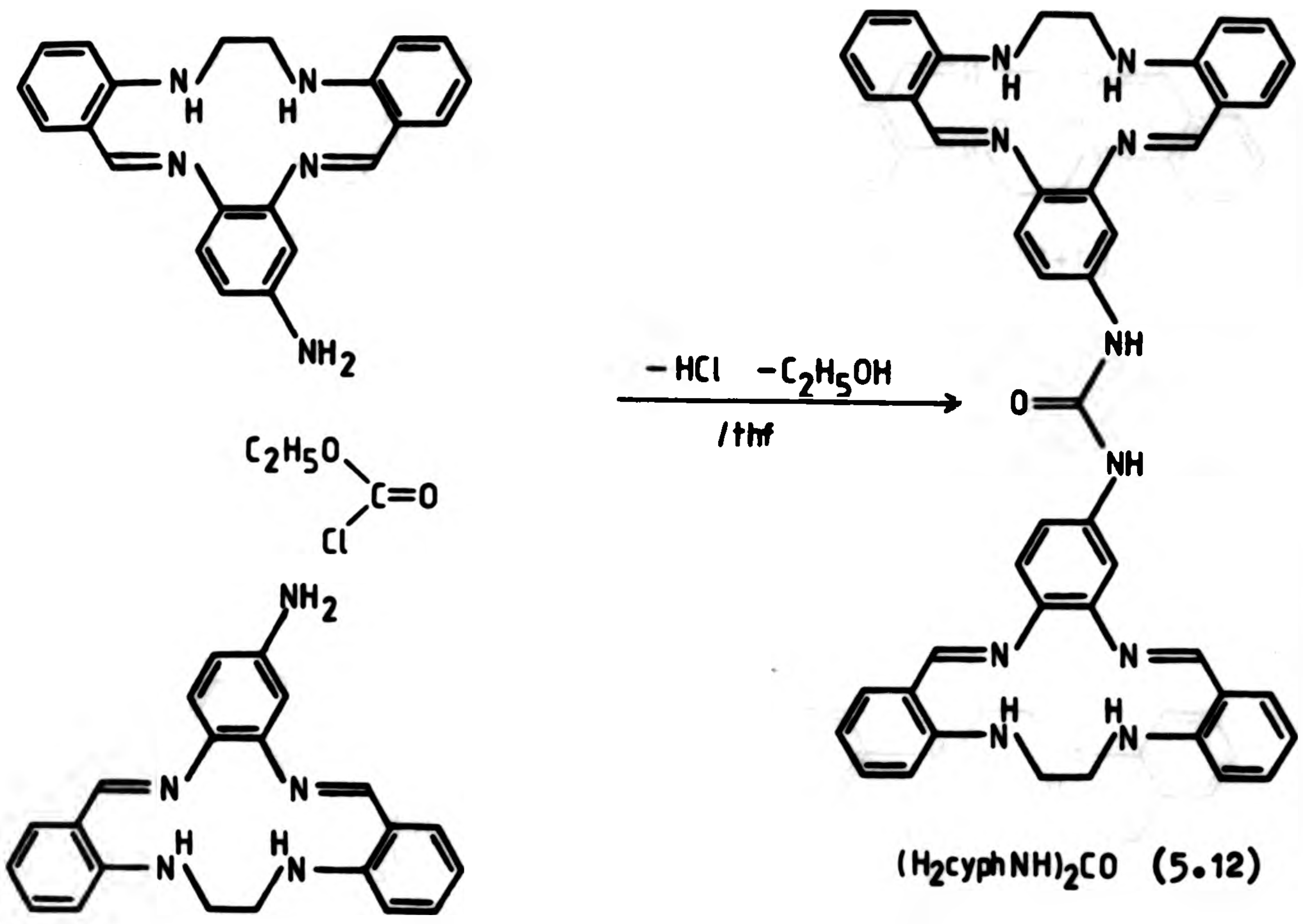
	Product
	Infrared spectrum indicates unchanged H_2cyphNH$_2$
$CH_3COCH_2COCH_3$	Infrared spectrum indicates unchanged H_2cyphNH$_2$
HCOHCO	Infrared spectrum indicates unchanged H_2cyphNH$_2$
$ClCOOC_2H_5$	Possible linking reaction see below

Table 5.4 Results for the attempted linking reaction of H_2cyphNH$_2$ (5.5)

Apart from ethylchloroformate, the results were negative and only the H_2cyphNH$_2$ precursor was recovered from the reaction mixture. For the reaction between H_2cyphNH$_2$ and ethylchloroformate a product separated, and the infrared spectrum showed distinct changes from that of H_2cyphNH$_2$ (including C=O stretch of 1720 cm^{-1}). The eims showed a weak spectrum trailing to above m/e = 500 which would be consistent for the high molecular weight of a linked macrocycle. The product was tooinsoluble to be characterised by ^{1}H nmr but was confirmed by elemental analysis (scheme 5.10).

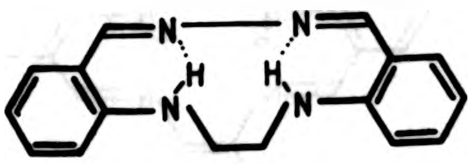


$(H_2cyphNH)_2CO$ (5.12)

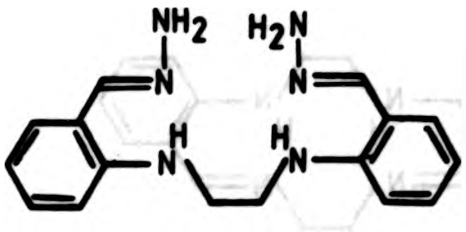
Scheme 5.10 Preparation of $(H_2cyphNH)_2CO$. (5.12).

Conclusion.

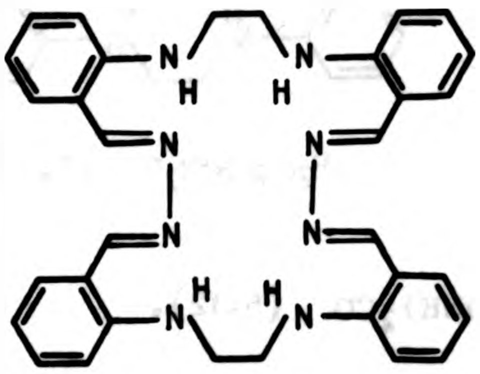
This section has described the successful reaction of $H_2cyphNH_2$ (5.5) with acetyl and benzoyl chloride, and with oxalyl dichloride and ethylorthoformate. Preliminary attempts to prepare the copper(II) complexes of these ligands resulted in the products heavily contaminated with unchanged ligand. These problems were experienced in chapter 4 with H_4bicyphen but were overcome by forming the cationic complex in pyridine. However, preliminary attempts have not shown comparable results and a lack of time has prevented further work in this area.



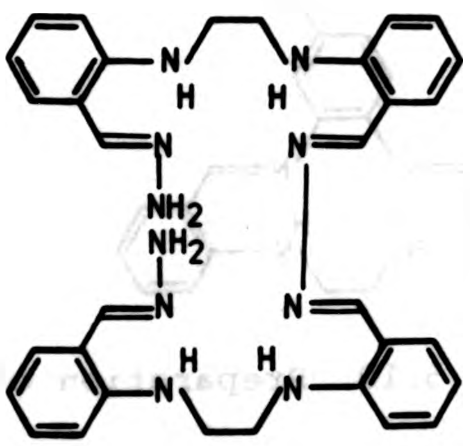
[1+1] monomer



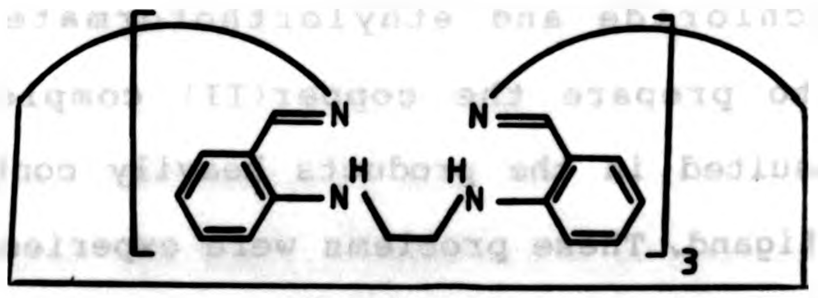
[2+1] 5.13



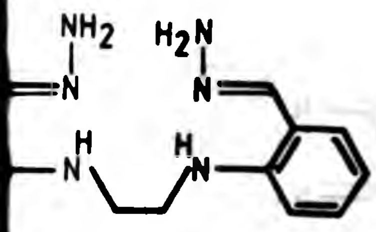
[2+2] 5.14



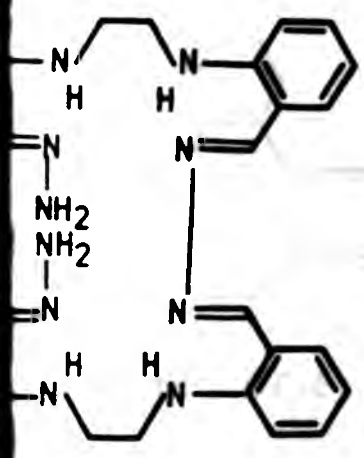
[3+2] 5.15



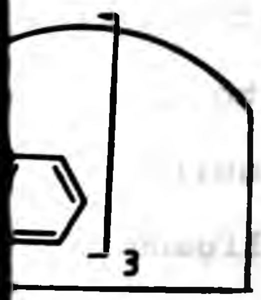
[3+3] 5.16



[2+1] 5.13



[3+2] 5.15



5.6.1 Reaction of hydrazine hydrate with C_2-dialdehyde.

Crystals of a hydrazine derivative were isolated from a reaction between C_2-dialdehyde and 1,2,4-triaminobenzene (section 5.3.2) where the 1,2,4-triaminobenzene had been heavily contaminated with hydrazine hydrate. These crystals were analysed by eims which showed a maximum m/e of 264, elemental analysis and infrared (section 8). On the basis of eims, a formulation corresponding to a monomer [1+1] was made. This structure probably results from the fragmentation of a larger molecule since the infrared spectrum showed two strong absorptions (3300 and 3416 cm^{-1}) (fig 5.5) indicative of a compound with one or more terminal NH_2 groups. On this evidence a [2+1] (5.13) or [3+2] (5.15) condensation product (hydrazine : C_2-dialdehyde) could be predicted (facing page).

The sample from above was analysed by field desorption mass spectrometry which detected two molecular ions (m/e = 528 and 560). One of these molecular ions corresponded to the predicted formulation $C_{32}H_{36}N_{10}$ of a [3+2] condensation product (5.15). This was also confirmed by elemental analysis, which was able to differentiate between [3+2] (5.15) and the other molecular ion (m/e = 528) which corresponded to a [2+2] condensation product (5.14). The dimer 5.14 would therefore be assigned a fragmentation product of 5.15.

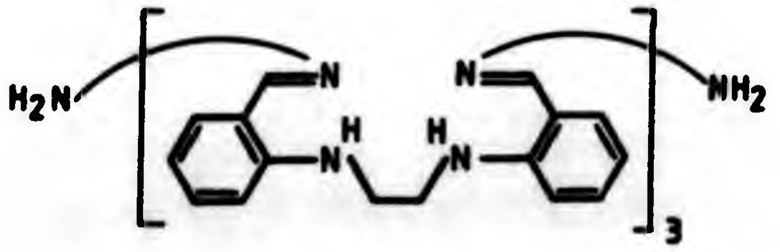
5.6.2 Attempts to prepare the [3+3] condensation product 5.16.

An attempt was made to form the [3+3] condensation product (5.16) by treating the [3+2] product (5.15) with a further molar quantity of C_2-dialdehyde (5.3) in refluxing methanol. After 24 h, a yellow crystalline compound was isolated which showed no absorptions in its infrared spectrum characteristic of terminal NH_2 groups which had been found for the [3+2] product (5.15). Field desorption mass spectrometry indicated that the material contained four species (table 5.5). The [3+3] condensation product 5.16 showed the largest molecular ion, but this does not identify the major constituent, since this would depend on the relative volatilities of all the possible species. However, elemental analysis was consistent with the [3+3] product.

m/e	Assignment
824	[4+3] 5.17
792	[3+3] 5.16
560	[3+2] 5.15
528	[2+2] 5.14

Table 5.5 Interpretation of the fdms results.

[4+3] 5.17



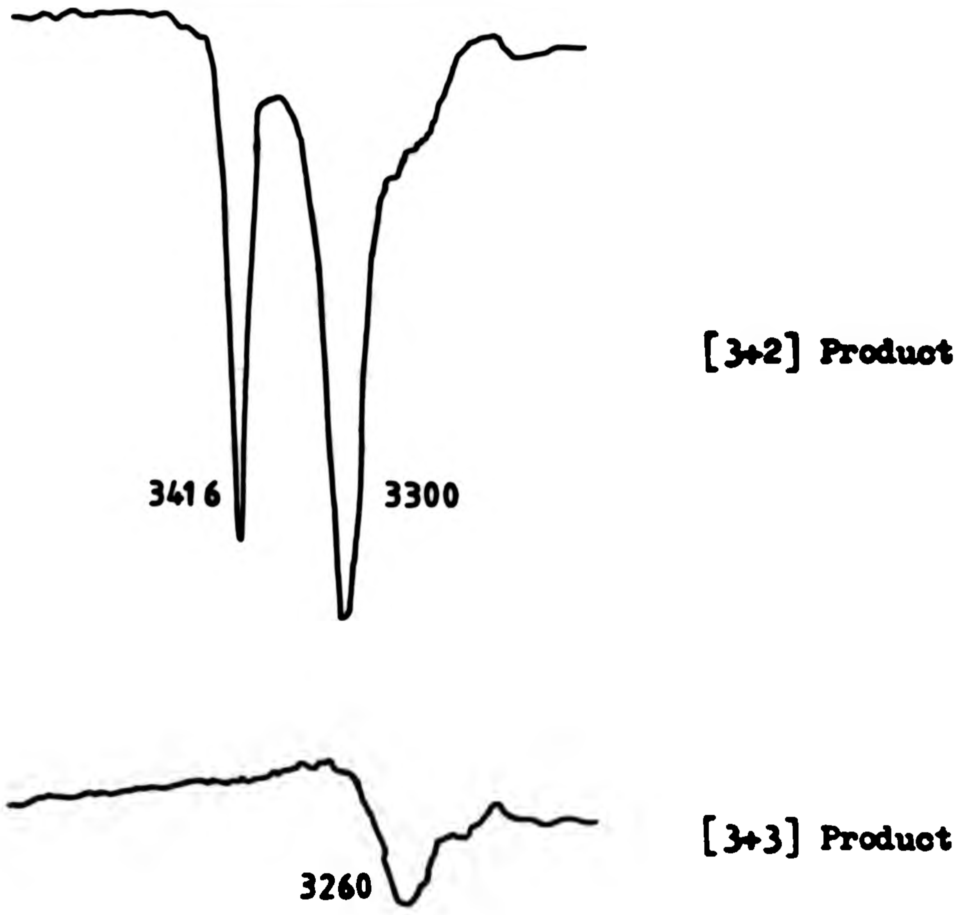
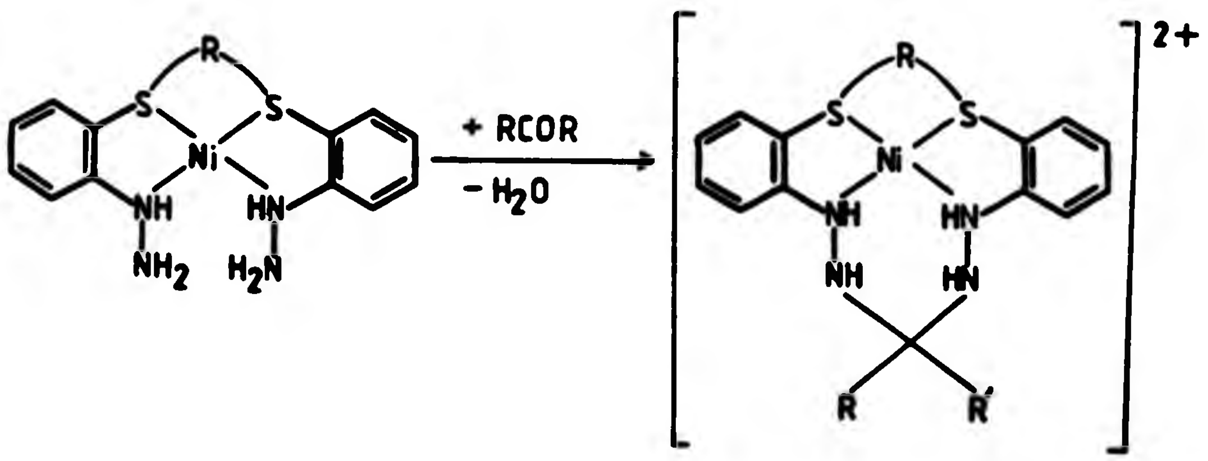


Fig 5.5 Infrared spectra (3000-3500 cm^{-1}) for the two compounds 5.15 and 5.16

The preparation and reactions of hydrazine ligands have been reported[7,8] as part of a program of the reactions of coordinated hydrazines (scheme 5.11).



Scheme 5.11

Conclusion

From the results described above, it is likely that the products consist of a mixture of species. These mixtures are unlikely to provide any useful dinucleating ligands because the different species may be difficult to separate, and could also be in equilibrium with eachother.

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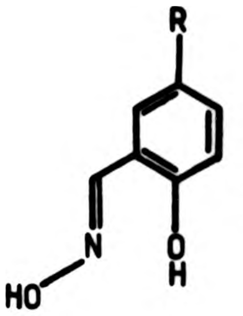
CHAPTER 6

Biscopper(II) complexes of a hydrogen bridged molecule.

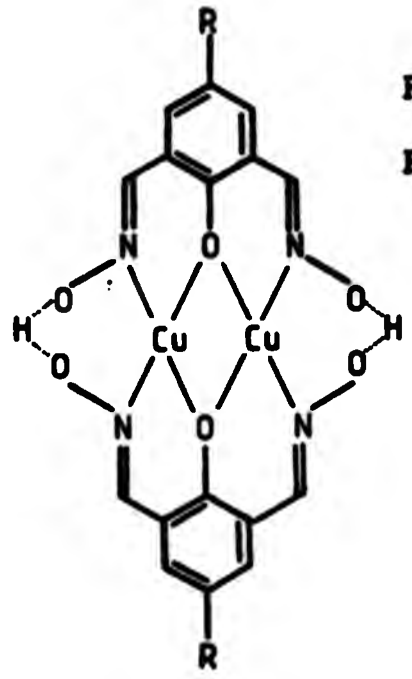
6.1 Introduction.

During a routine solvent extraction process of copper(II) using the ligand 2-formaldoxime-4-nonylphenol (6.1), a very low soluble material was isolated[1]. This was shown by elemental analysis to correspond to a neutral bis copper(II) complex $[Cu_2(H_2DFNP)_2]$ (6.2). Subsequent analysis of the ligand 6.1 showed it contained small amounts of 2,6-diformyl-4-nonylphenol (H_3DFNP) (6.1a) which when treated with copper(II) ions gave the very insoluble complex $[Cu_2(H_2DFNP)_2]$ (6.2)



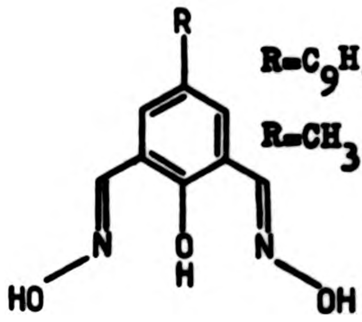
$R=C_9H_{19}$ (6.1)

$R=CH_3$ (6.3)



$R=C_9H_{19}$ (6.2)

$R=CH_3$ (6.4)



$R=C_9H_{19}$ (6.1a)

$R=CH_3$ (6.5)

A closely related biscopper(II) complex $[Cu_2(HDFMP)_2]$ (6.4) has been reported[2] as being practically insoluble in highly basic solvents such as pyridine and dmf, and also stable to cold concentrated hydrochloric and sulphuric acid or sodium hydroxide solution. The magnetic moment at room temperature was found to be subnormal (0.59 BM) and the magnetic susceptibility was measured over a large range 77-300°K. The temperature variation of magnetic susceptibility could be explained on the basis of the Bleaney Bowers equation[3]. It was also reported[2] that the mass spectra of $[Cu_2(HDFMP)_2]$ detected molecular ion peaks at 510 and 512, with relative intensities corresponding to to the isotopic ratios for binuclear copper complexes (see section 4.4). On the basis of the molecular formulae obtained from the mass spectra, the molecule was assumed to be deprotonated at two of the oxime hydroxy groups and an intramolecular hydrogen bonded structure (6.4) was proposed. It is improbable that 6.4 contains a symmetrical hydrogen bond as in fig 6.1 (c), but more likely a statistical distribution in the solid state of asymmetrical hydrogen bonds as in (a) and (b).

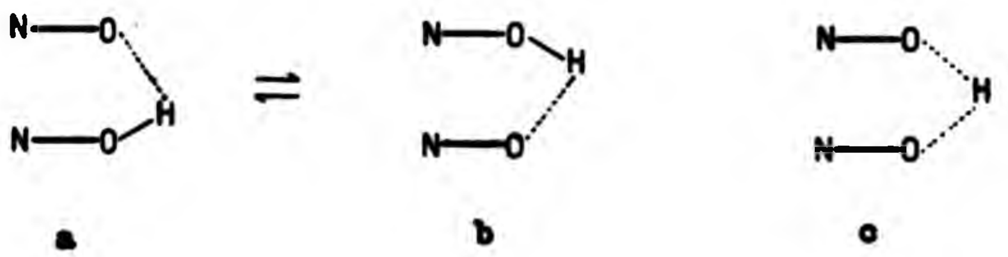
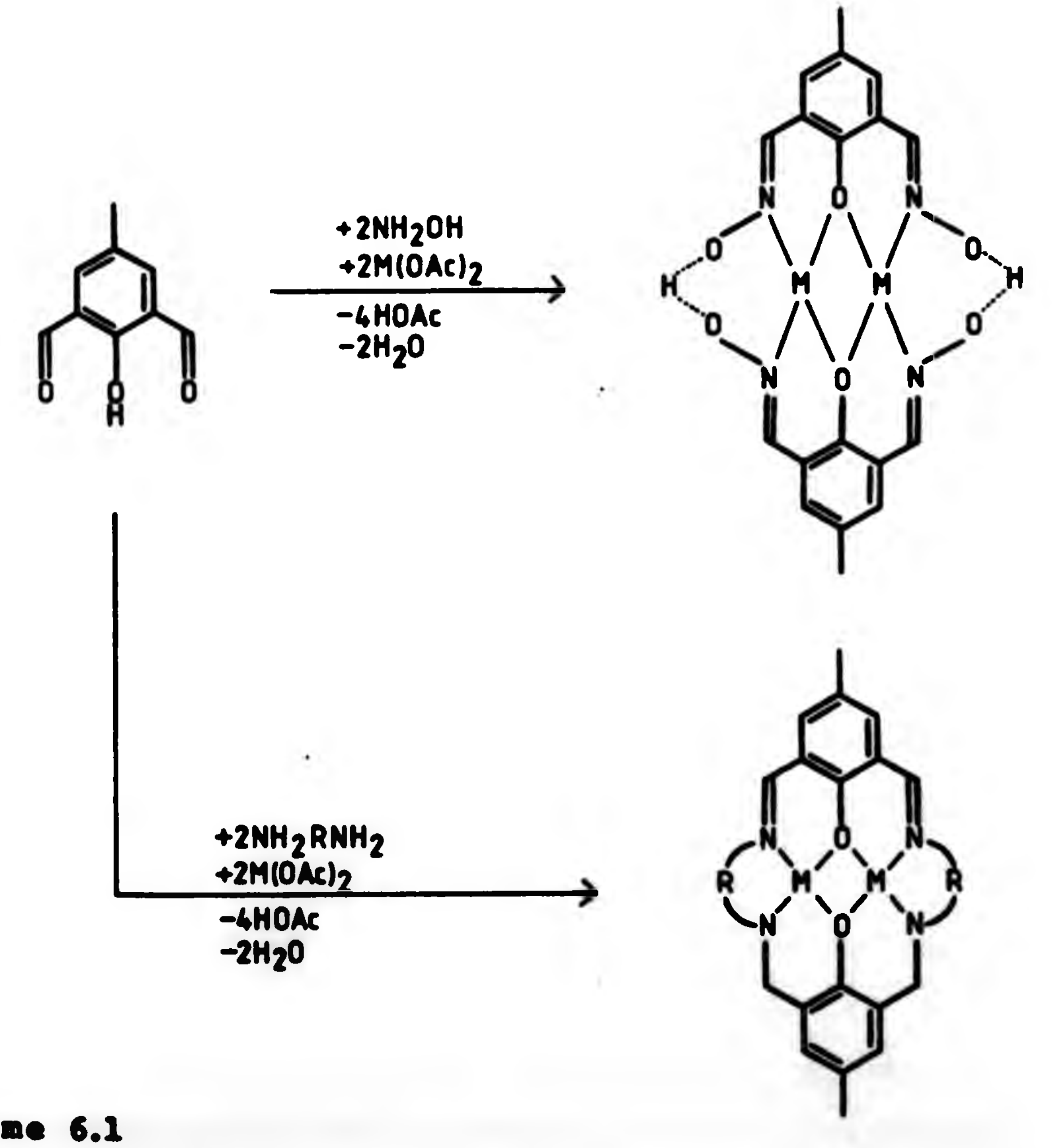


Fig 6.1 Hydrogen bonding schemes for the oxime groups in 6.4.

The interest in the nature of the hydrogen bonding in $[Cu_2(H_2DFNP)_2]$ (6.2) led us to consider attempting an X-ray structure determination. Also it was of interest to examine the separation and disposition of the two copper atoms in such a complex. The nonyl derivative H_3DFNP (6.1a) was unsuitable for the preparation of a crystalline copper(II) complex, since the nonyl chain would have given rise to many conformers. A methyl derivative H_3DFMP was used to prepare a biscopper(II) complex and model the hydrogen bonding suggested for the nonyl derivative $[Cu_2(H_2DFNP)_2]$ (6.2). The ligand 1,6-diformaldoxime-4-methylphenol (H_3DFMP) (6.5) was supplied by ICI Ltd Organics Division, and attempts were made to crystallise the bis copper(II) complex. A large number of macrocyclic complexes have been prepared[4] from the precursor 2,6-diformyl-4-methylphenol (scheme 6.1). The biscopper complexes and a series of heterobinuclear Cu(II)-M(II) complexes have been investigated[5]



Scheme 6.1

The complex $[Cu_2(H_2DFMP)_2]$ (6.4) was prepared by addition of copper(II) acetate to a solution of ligand in a range of solvents (thf, dmf, dma and pyridine). In each case only microcrystalline samples of the biscopper(II) complex could be obtained. These crystals were not large enough for X-ray structure determination.

6.2.1 Preparation and X-ray structural analysis of $[Cu_2(H_2DFMP)_2(ClO_4)_2]$.2thf (6.6)

An attempt was made to prepare the cationic copper(II) complex by the addition of a solution of copper(II) perchlorate to a solution of ligand H_3DFMP (6.5). It has been found (previous chapters 3 and 4) that the perchlorate salt of copper(II) complexes are generally more soluble than their neutral analogues. This would enable slow neutralisation (with a base) of the perchlorate salt to give a crystalline complex of the neutral biscopper(II) complex $[Cu_2(H_2DFMP)_2]$ (6.4). The biscopper(II) complex $[Cu_2(H_2DFMP)_2](ClO_4)_2$ has not been reported, although many related complexes have been studied as part of an investigation into the magneto chemistry of hydroxy bridged binuclear copper(II) compounds^6. The conditions used previously (see chapters 3 and 4) for the preparation of the copper(II) complexes were not suitable, as the reaction was instantaneous and gave rise to a precipitate which was difficult to purify due to its low solubility. In an attempt to grow larger crystals of the biscopper(II) complex the reaction rate was slowed down by carrying it out at a lower

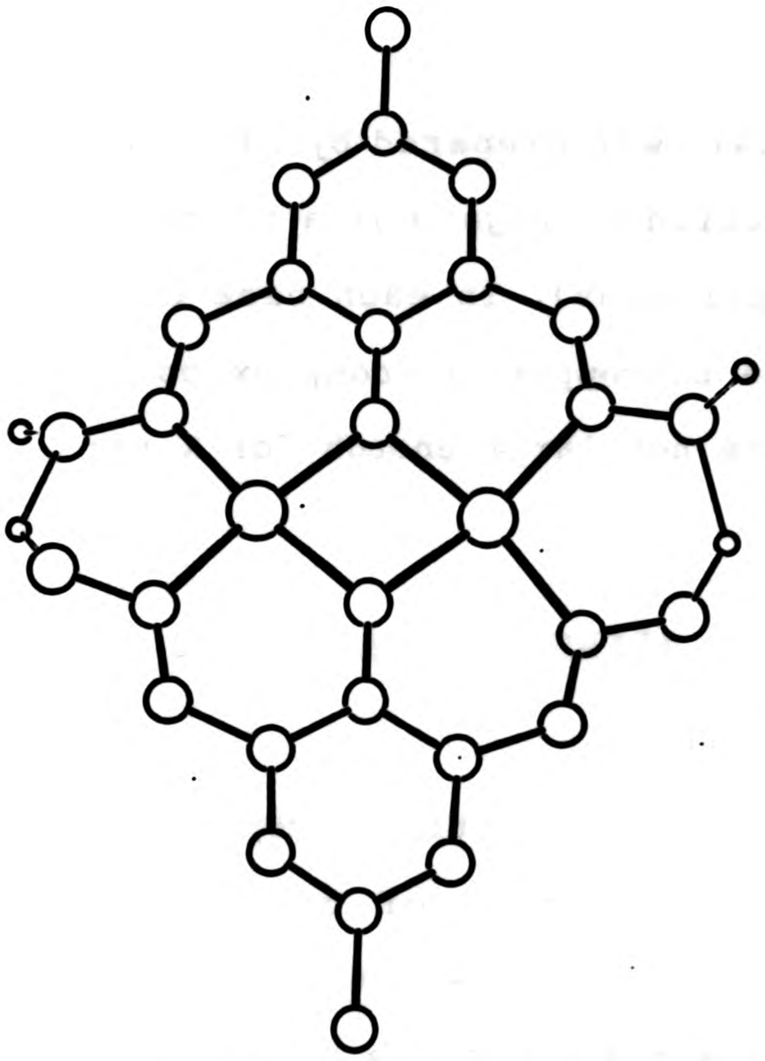


Fig 6.2 Ortep diagram of $[Cu_2(H_2(DFMP)_2]^{2+}$

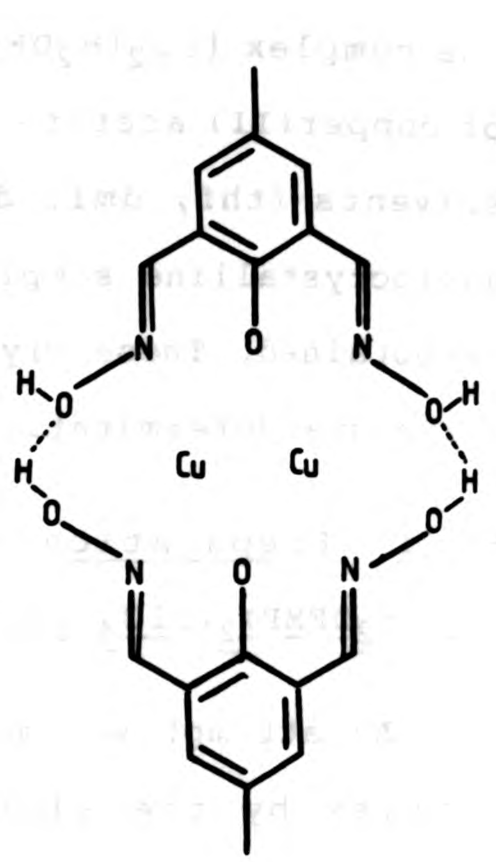


Fig 6.3 Schematic diagram of $[Cu_2(H_2(DFMP)_2]^{2+}$

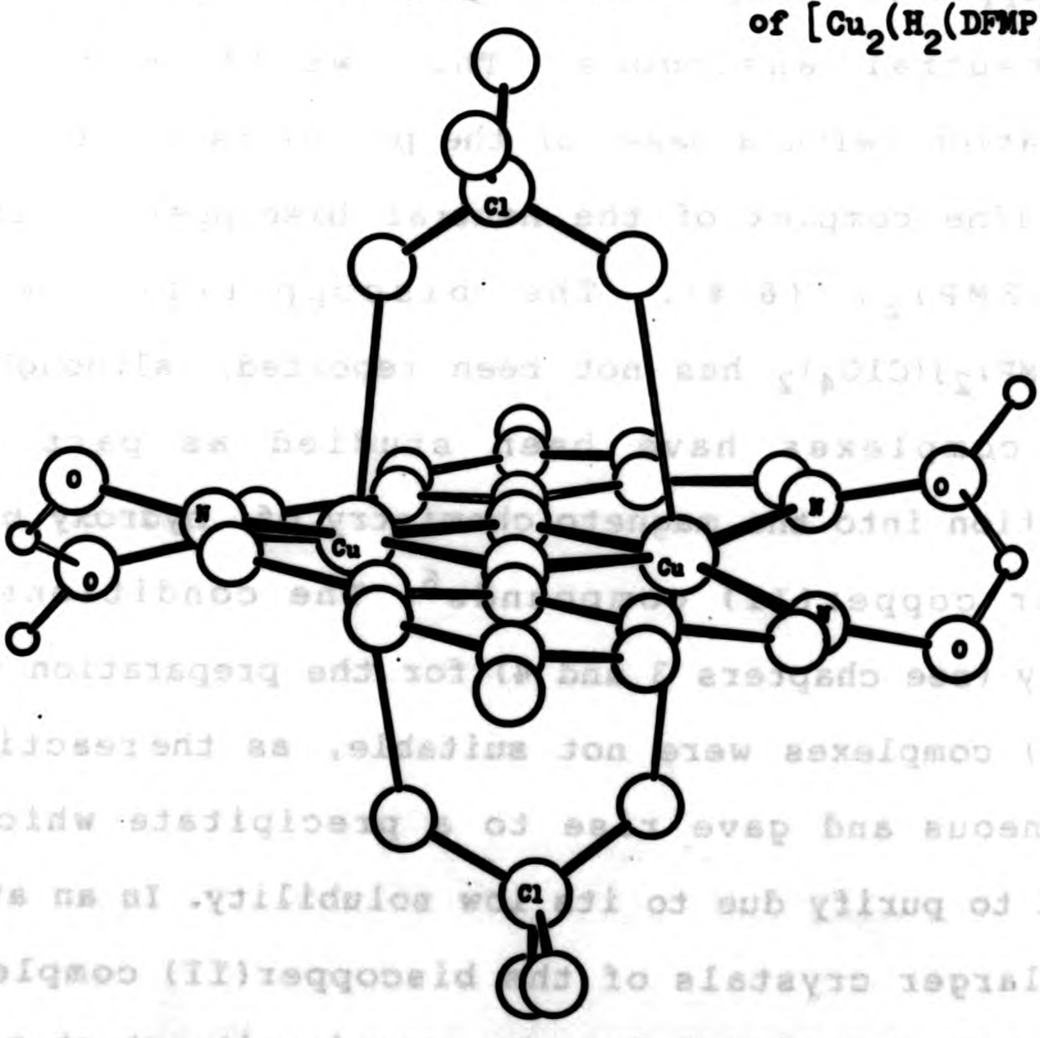


Fig 6.4 Ortep diagram of $[Cu_2(H_2DFMP)_2(ClO_4)_2]$.

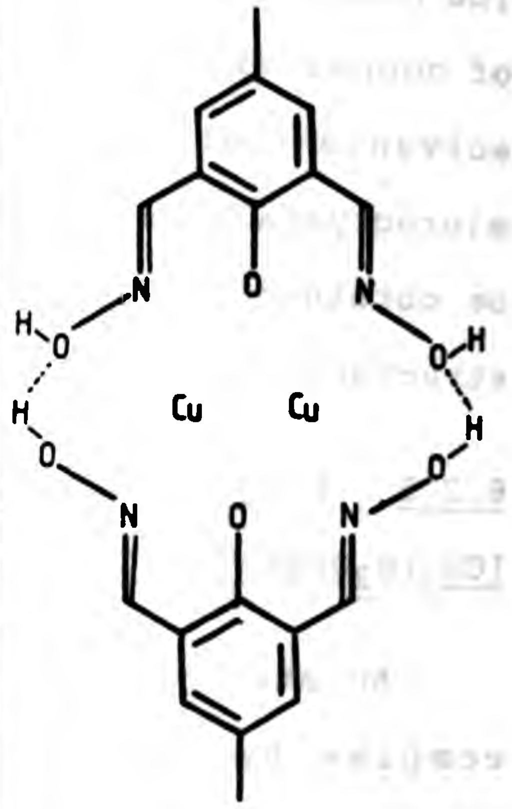
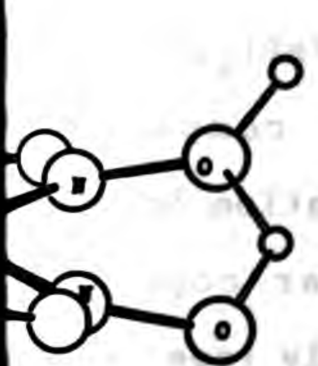


Fig 6.3 Schematic diagram of $[Cu_2(H_2(DFMP)_2]^{2+}$



].

temperature. A solution of H_3DFMP (6.5) in thf was cooled with liquid nitrogen until the solution just started to freeze. The addition of a methanolic solution of copper(II) perchlorate gave a translucent green solution, which on warming to room temperature deposited green prisms of a cationic complex $[Cu(H_2DFMP)_2(ClO_4)_2]$, as shown by the strong infrared absorptions ascribable to the perchlorate group at 1100 cm^{-1}. The addition of base to the solution above did not produce the neutral biscopper(II) complex, but induced precipitation of the perchlorate salt. The X-ray structure determination was undertaken to examine the nature of the hydrogen bonding.

6.2.2 The X-ray structure of $[Cu_2(H_2DFMP)_2(ClO_4)_2]$.2thf (6.6).

6.2.3 General.

The complex 6.6 consists of an approximately planar $[Cu_2(H_3DFMP)_2]$2+ unit to which there are bonded across the copper atoms two perchlorate groups (see fig 6.4). The structure of the dication unit $[Cu_2(H_2DFMP)_2]$2+ is shown in fig 6.2 and 6.3 (facing page). The Cu_2O_2 bridging unit is planar due to the crystallographic 2 fold axis which passes through the two μ- oxygen atoms O(1a) and O(1b).

In addition to the two phenolate bridges, there are symmetry related perchlorato bridges above and below the N2Cu-O2-CuN2 plane (fig 6.4, facing page) which have been found for many other related perchlorato complexes[6]. The perchlorate anion is coordinated in a bidendate fashion,

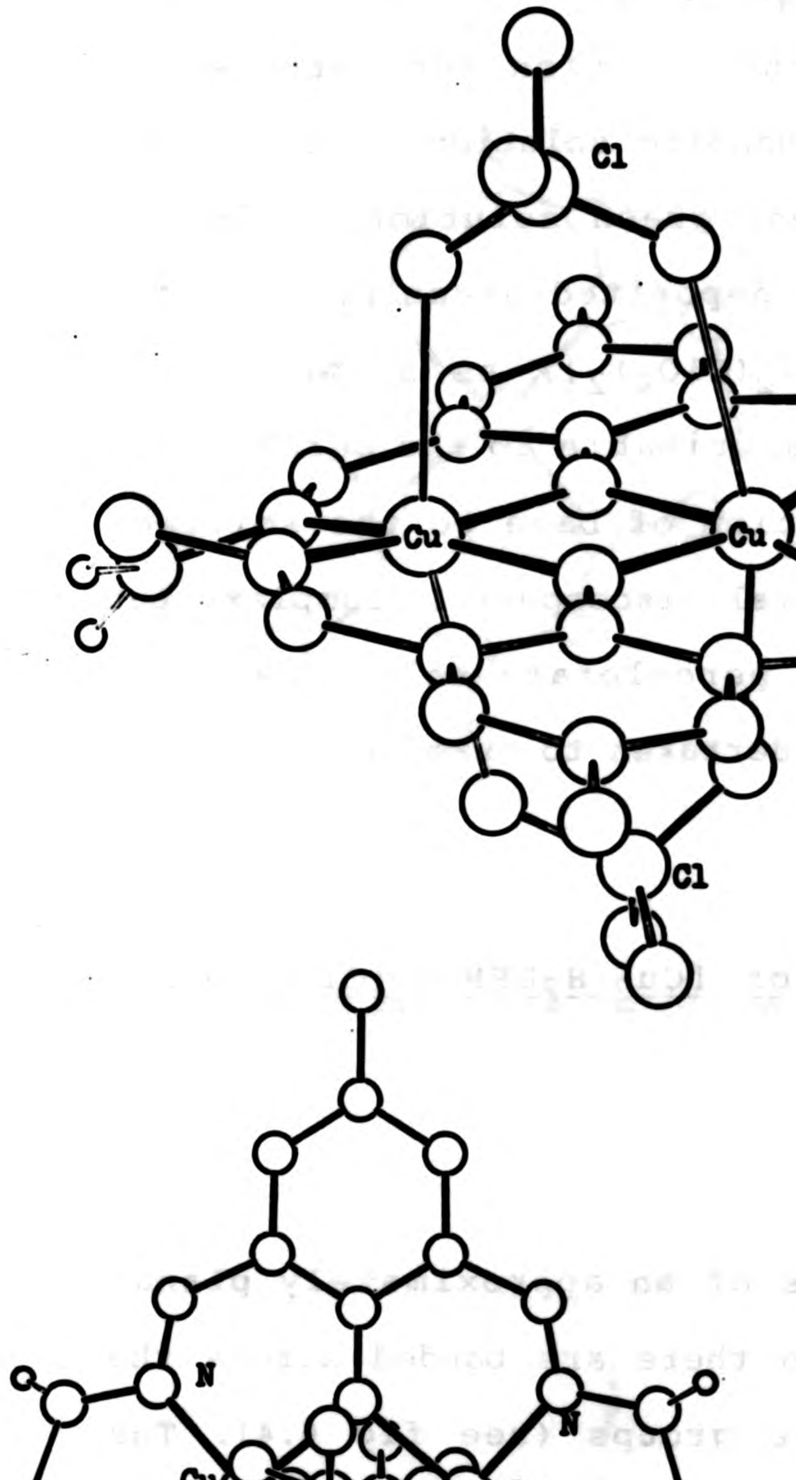


Fig 6.5 Ortep diagram of $[Cu_2(H_2DFMP)_2(ClO_4)_2]$

with one oxygen showing a relatively strong bond of 2.51 Å, and the other a much weaker bond of 2.76 Å. A range of bond lengths have been reported for semi-coordinated perchlorate groups in copper(II) complexes showing comparable bond lengths[7].

Two thf solvate molecules accompany each molecule, but show serious disorder (see section 7.3). Fig 6.5 (facing page) depicts the ortep diagrams, and the stereoscopic views are shown in fig 6.6.

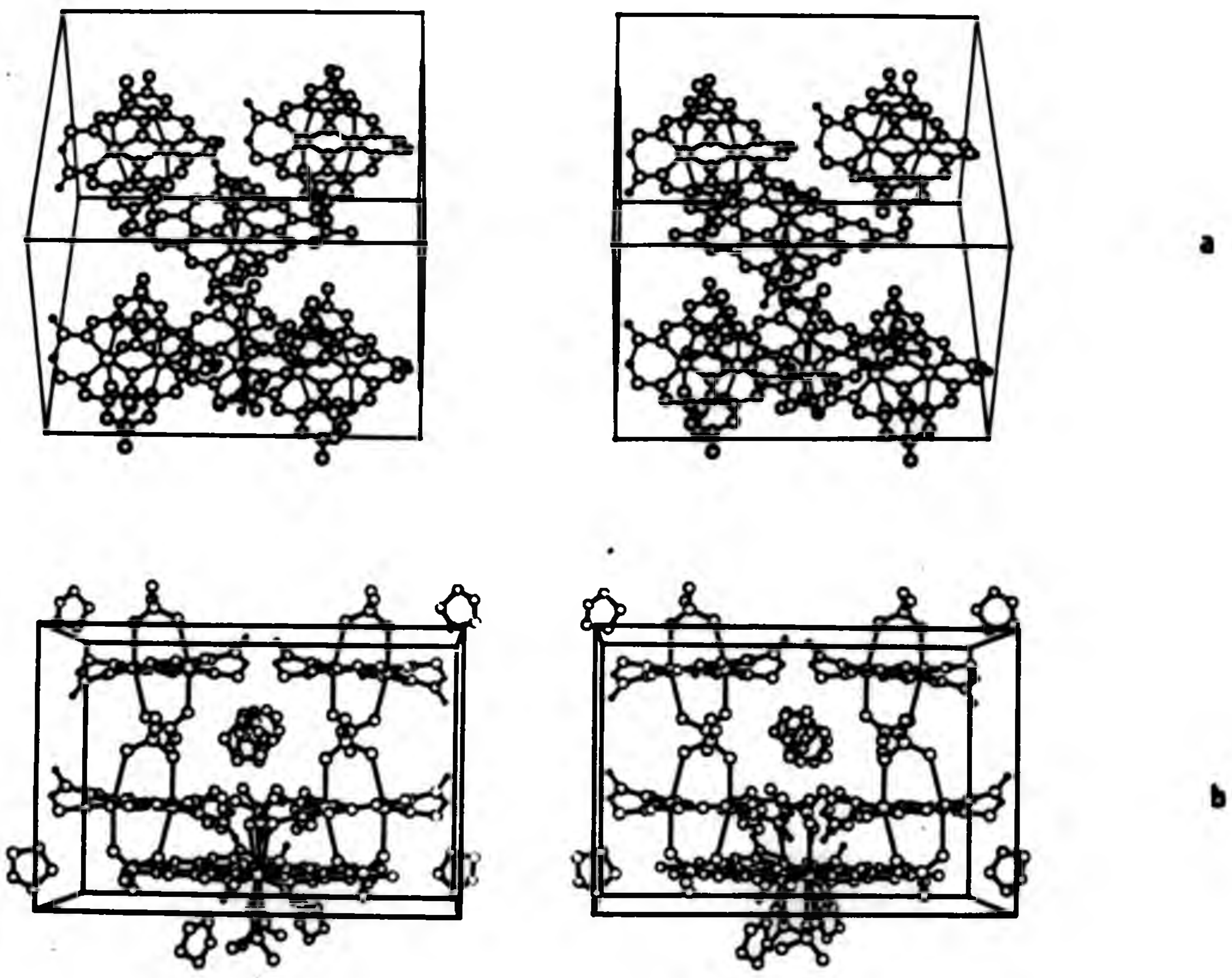


Fig 6.6 Stereoscopic views of the packing arrangement in $[Cu_2(HDFMP)_2(ClO_4)_2].2thf$. Fig 6.6a omits the thf solvate for clarity.

In addition to the crystallographic two fold axis which passes through the methyl and phenolate oxygens, the complex is theoretically capable of showing a pseudo mirror plane symmetry which would relate ligand framents A and B (fig 6.7). In practice this mirror plane relationship dose not exist (see fig 6.4). However, chemically equivalent bond lengths and angles in the A and B fragments agree reasonably well (table 6.1).

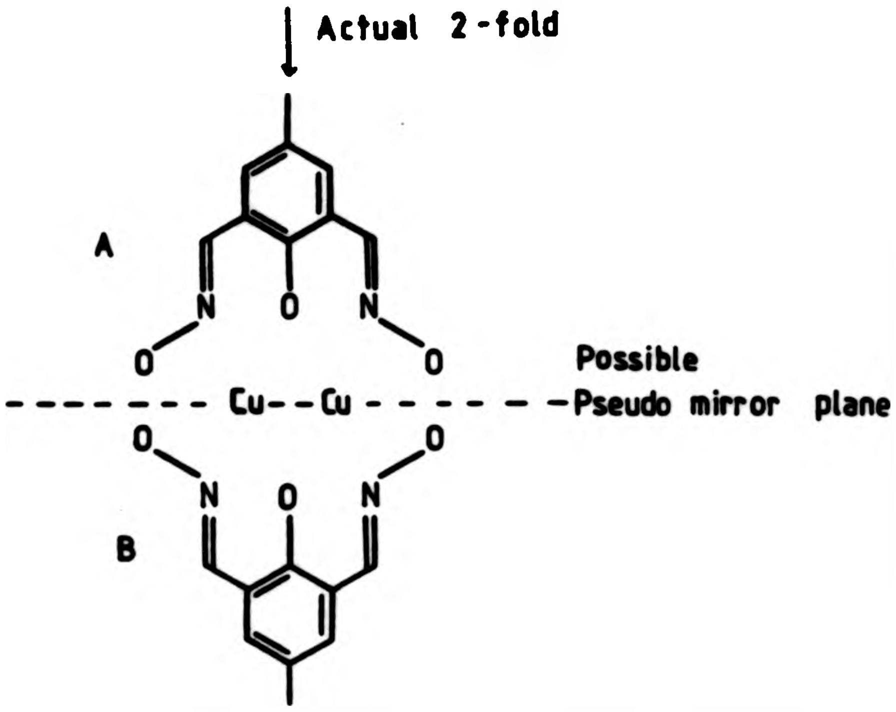


Fig 6.7 The possible and actual symmetry elements in $[Cu_2(H_2DFMP)_2(ClO_4)_2].2thf$

Bond length/Å	**Part a**	**Part b**
Cu-N(1)	1.945(16)	1.985(18)
Cu-O(1)	1.941(10)	1.965(12)
Bond Angles/Å		
Cu-N(1)-C(1)	129.3(1.4)	127.9(1.6)
Cu-N(1)-O(2)	115.5(1.1)	120.1(1.3)
O(2)-N(1)-C(1)	115.2(1.6)	111.9(1.8)
Sum of angles about N(1)	360.0°	359.9°
C(3)-O(1)-Cu	129.5(0.3)	130.4(0.4)
C(3)-O(1)-Cu	129.5(0.3)	130.4(0.4)
Cu-O(1)-Cu	100.9(0.7)	99.2(0.8)
Sum of angles about O(1)	359.9°	360.0°

Table 6.1 Comparison of bond lengths and angles in the chemically equivalent parts (a and b) of $[Cu_2(H_3DFMP)_2(ClO_4)_2]$

The non-hydrogen atoms of the dication unit $[Cu_2(H_2DFMP)_2]2+$ do not form a perfect planar system, this could be due to the steric repulsion of the two oxime oxygen atoms. The deviation from planarity (fig 6.8) allow the oxygen atoms O(2a) and O(2b) to become further apart.

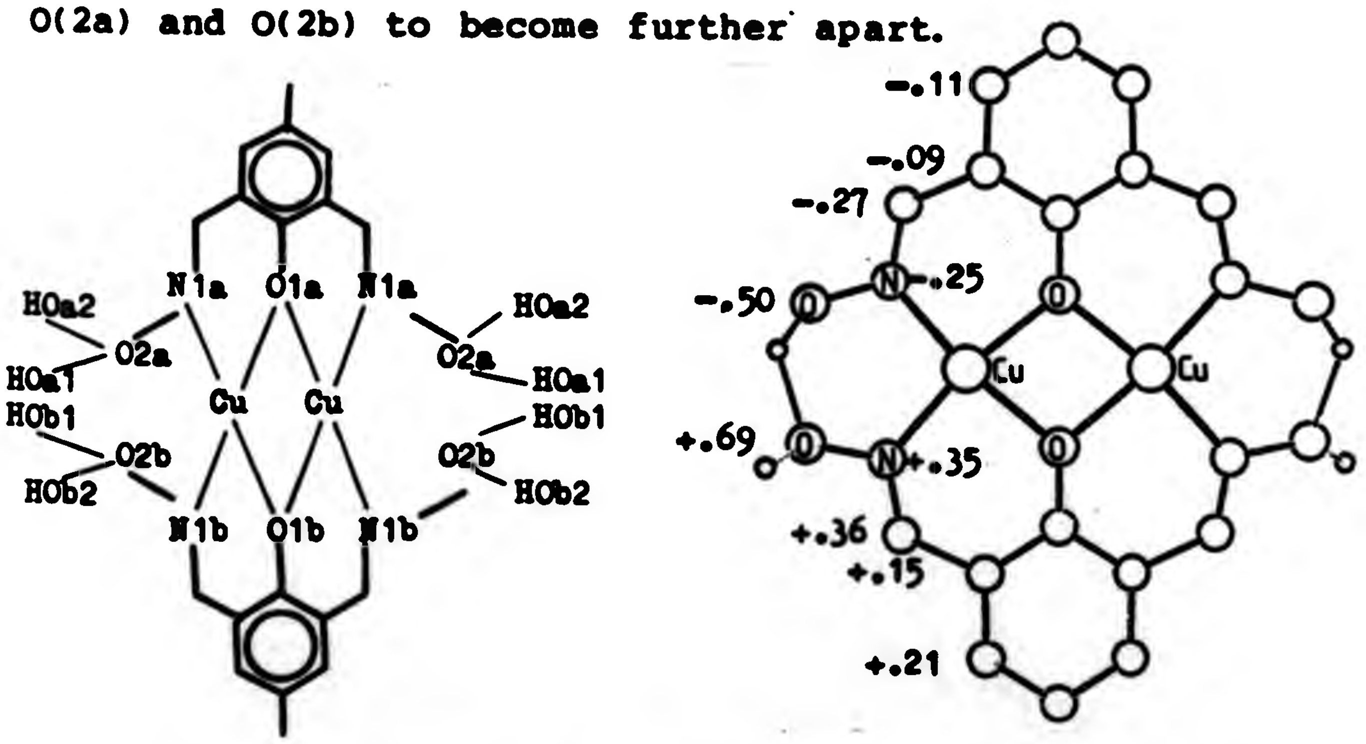


Fig 6.8 Deviation of the non-hydrogen atoms from the planarity of the Cu-O2-Cu bridging unit (mÅ)

In support of the electron density maxima near O(2a) and O(2b) as partial occupancy hydrogen atoms, the bond angles about the oxygen atoms in fig 6.9 (c) correspond to sp^2 hybridisation at the oxygen atoms (table 6.2).

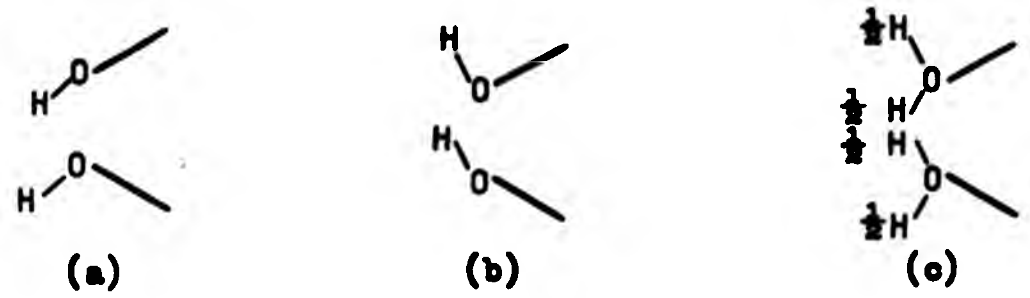


Fig 6.9 Statistically disordered hydrogen bonds (a) and (b), plus a schematic diagram (c) of the assignment of half occupancy hydrogen atoms to the electron density maxima found for the complex $[Cu_2(H_2DFMP)_2)(ClO_4)_2]$ (6.6)

N(1a)-O(2a)-HO(a2)	120.5(1.4)
N(1a)-O(2a)-HO(a1)	119.4(1.3)
HO(a2)-O(2a)-HO(a1)	120.1(1.3)
Sum of angles	360.0
N(1b)-O(2b)-HO(b2)	129.8(1.6)
N(1b)-O(2b)-HO(b1)	97.4(1.3)
HO(b2)-O(2b)-HO(b1)	132.8(1.6)
Sum of angles	360.0

Table 6.2 Bond angles about the oxygen atoms O(2a) and O(2b)

To explain the nature of the hydrogen bonds, there are three possible types that must be considered:

1) The oxygen is sp^2 hybridised (fig 6.10).

The most overlap of the sp^2 hybridised orbitals will occur if Hx forms bond angles of approximately 120° at the oxygen.

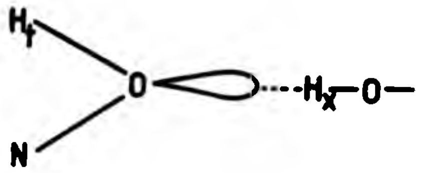


Fig 6.10 sp^2 hybridisation

2) The oxygen is SP^3 hybridised.

One lone pair is involved in hydrogen bonding (fig 6.11). The best overlap will occur when Hx forms bond angles of approximately 111°.

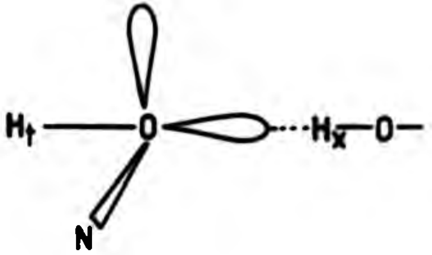


Fig 6.11 SP^3 hybridisation

3) Electrostatic hydrogen bond (fig 6.12).

The best overlap will occur when Hx forms bond angles of approximately 124.5°

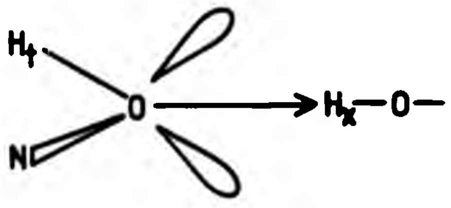


Fig 6.12 Electrostatic hydrogen bond

From the structure determination the sum of the bond angles about the oxygen atoms O(2b) and O(2a) (table 6.3) are shown to difficult to assign a definite type, but are probably closer to SP^3 hybridisation than the other two types.

N(1a)-O(2a)-HO(a2)	120.5(1.4)
N(1a)-O(2a)-HO(b1)	109.9(1.1)
HO(a2)-O(2a)-HO(b1)	119.1(1.1)
<u>Sum of angles</u>	<u>349.5</u>

N(1b)-O(2b)-HO(b2)	129.8(1.6)
N(1b)-O(2b)-HO(a1)	112.1(1.2)
HO(a1)-O(2b)-HO(b2)	113.5(1.2)
<u>Sum of angles</u>	<u>355.4</u>

Table 6.3 Bond angles about the oxygen atoms O(2a) and O(2b)

The separation of 2.99 Å between the two copper atoms is to great to allow a strong Cu-Cu interaction by direct overlap of metal orbitals. Also it has been reported[8] that for compounds of this type the degree of super exchange interaction is dependent on the angle between the bridging oxygens and the copper atom (fig 6.13).

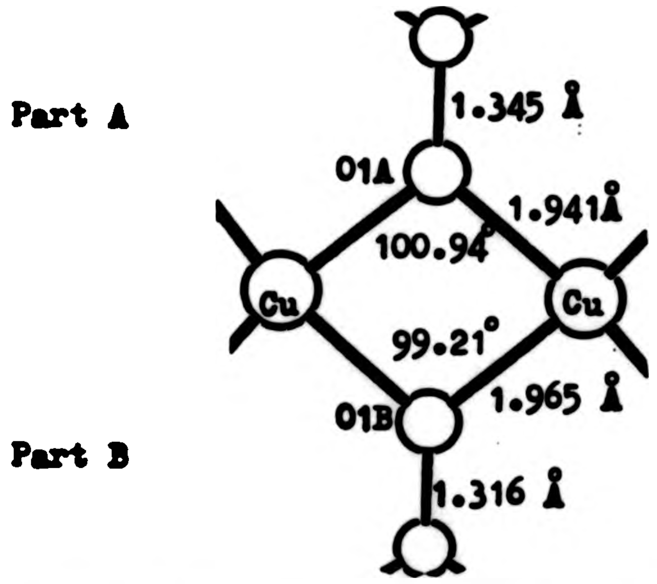
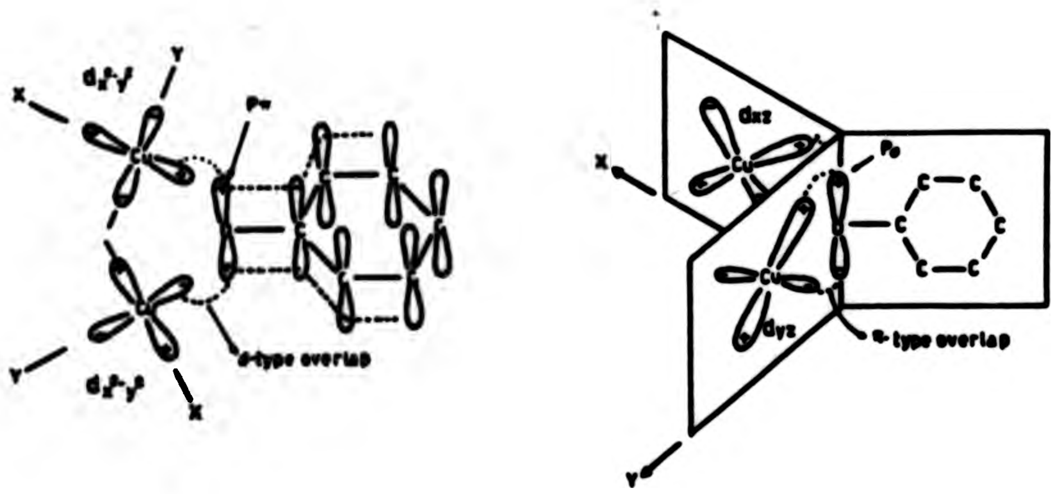


Fig 6.13 Bond angles about the bridging oxygen atoms O(1a) and O(1b).

	C-O/Å	Cu-O/Å	Cu-O-Cu/°
Part A	1.345(27)	1.941(10)	100.9(0.7)
Part B	1.316(31)	1.965(12)	99.2(0.8)

Table 6.4 Bond lengths about the bridging oxygen atoms O(1a) and O(1b).

The shorter Cu-O bond in portion A fig 6.13) and other data (table 6.4) would suggest a higher degree of coupling between the oxygen and copper(II) atoms than those in portion B. Therefore, any superexchange interaction that probably occurs for this compound, may be due more to one phenolic bridge than the other. It must be stressed however, that the difference between the bond lengths in part A and B (table 6.4) is not very large in comparison with the errors in their determination. Spin coupling between the two copper(II) atoms may take place using two superexchange pathways[9] (scheme 6.2).

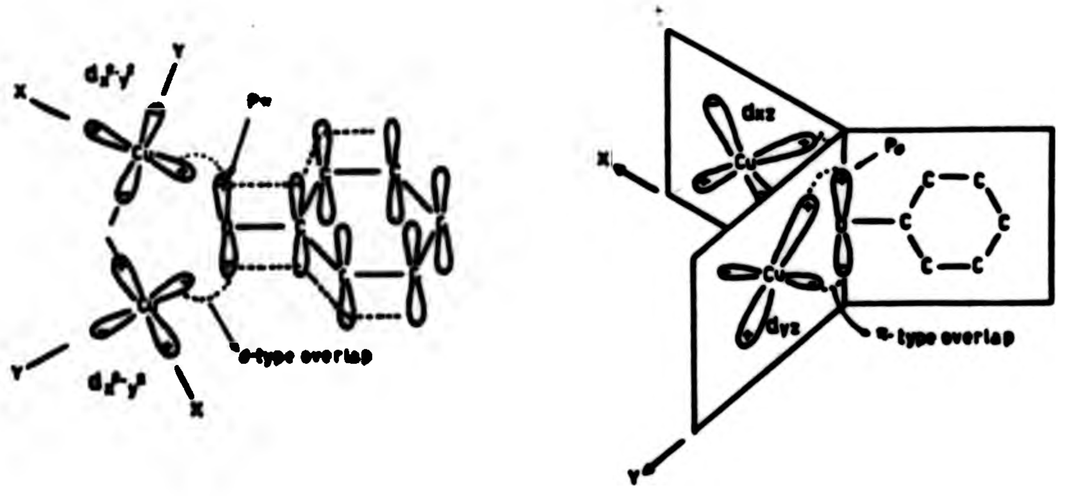


Scheme 6.2 Spin coupling pathways using d type orbitals.

	C-O/Å	Cu-O/Å	Cu-O-Cu/°
Part A	1.345(27)	1.941(10)	100.9(0.7)
Part B	1.316(31)	1.965(12)	99.2(0.8)

Table 6.4 Bond lengths about the bridging oxygen atoms O(1a) and O(1b).

The shorter Cu-O bond in portion A fig 6.13) and other data (table 6.4) would suggest a higher degree of coupling between the oxygen and copper(II) atoms than those in portion B. Therefore, any superexchange interaction that probably occurs for this compound, may be due more to one phenolic bridge than the other. It must be stressed however, that the difference between the bond lengths in part A and B (table 6.4) is not very large in comparison with the errors in their determination. Spin coupling between the two copper(II) atoms may take place using two superexchange pathways[9] (scheme 6.2).



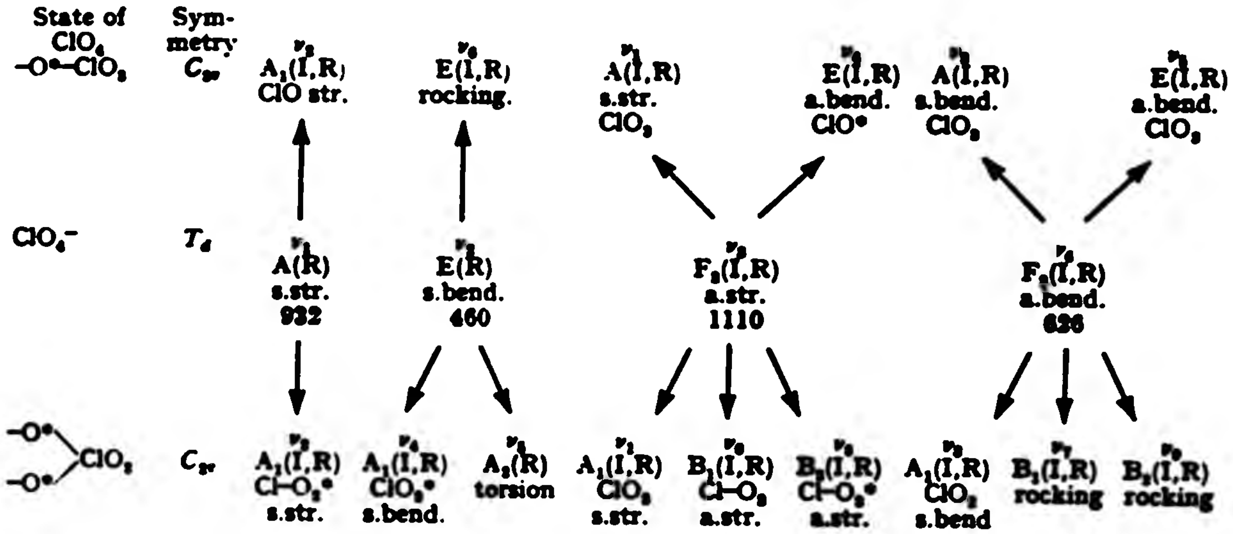
Scheme 6.2 Spin coupling pathways using d type orbitals.

Conclusion

The X-ray structure of $[Cu(H_2DFMP)_2(ClO_4)_2].2thf$ has shown the hydrogen bonding of the oxime groups to be asymmtrical as predicted in section 6.1. The preparation of the cationic complex was achieved using a novel synthesis of cooling the solutions before reaction to produce a crystalline complex suitable for X-ray structural determination. This procedure did not prove successful for producing the neutral complex. The lack of time has prevented the magnetic data being available at the conclusion of this project.

6.3 The infrared of coordinated perchlorates.

The difference between ionic and coordinated perchlorate can often be detected in the infrared spectrum[10]. The perchlorate ion has a regular tetrahedral structure and belongs to the point group Td, having nine vibrational degrees of freedom distributed between four normal modes of vibration (table 6.5).



† A and B, non-degenerate. E, doubly degenerate. F, triply degenerate. I, infrared active. R, Raman active. s., symmetric. a., antisymmetric. O* refers to oxygen co-ordinated to copper.

Table 6.5 Vibrations of the ClO_4 group as a function of symmetry[10]

For ionic perchlorates the characteristic infrared frequencies are:

1) A very broad strong band with a poorly defined maximum (νClO_4 1100cm^{-1})
2) A medium strong band at 625 cm^{-1}
3) A weak absorption at 930 cm^{-1} (this absorption is weakly allowed due to a slight distortion of the ion in a crystal field of lower symmetry than itself).

The degree of splitting of these absorptions will be dependent on the extent and type of coordination of the perchlorate ion. A bidentate bridged ligand shows a greater splitting pattern than a monodentate ligand[10](fig 6.14).

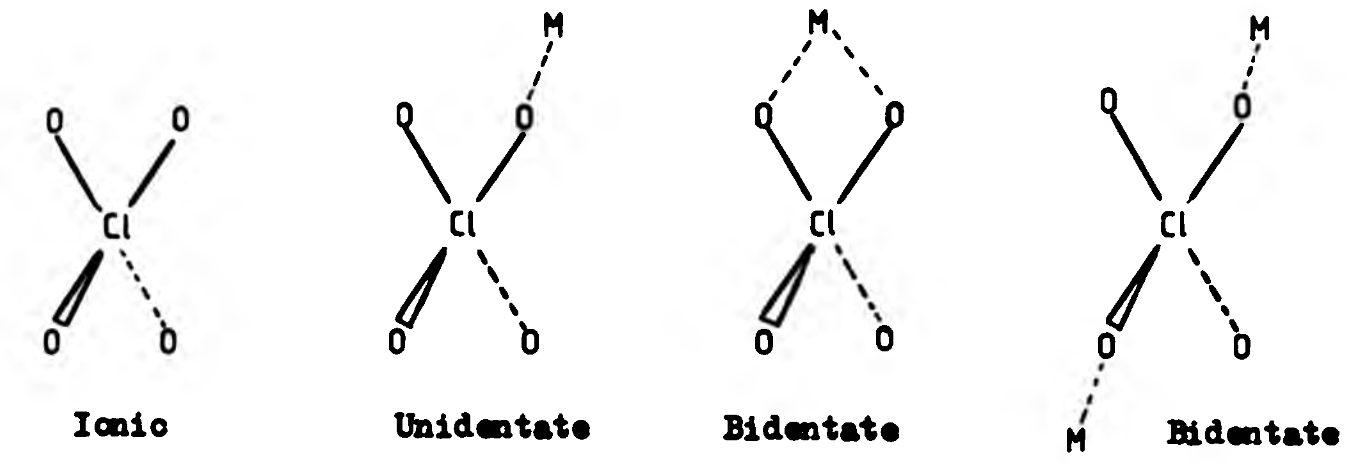


Fig 6.14 Different types of perchlorate enviroment.

The effect of coordination of the perchlorate group will bring major differences in the infrared spectra, and additionally minor shifts or splittings may result from a lowering of the site symmetry of the group from coupling of vibrations between perchlorate groups in the same unit cell, or purely from an isotopic effect within the group. In this thesis, three of the five structures discussed contain perchlorate anions, which have different types of enviroment (table 6.6).

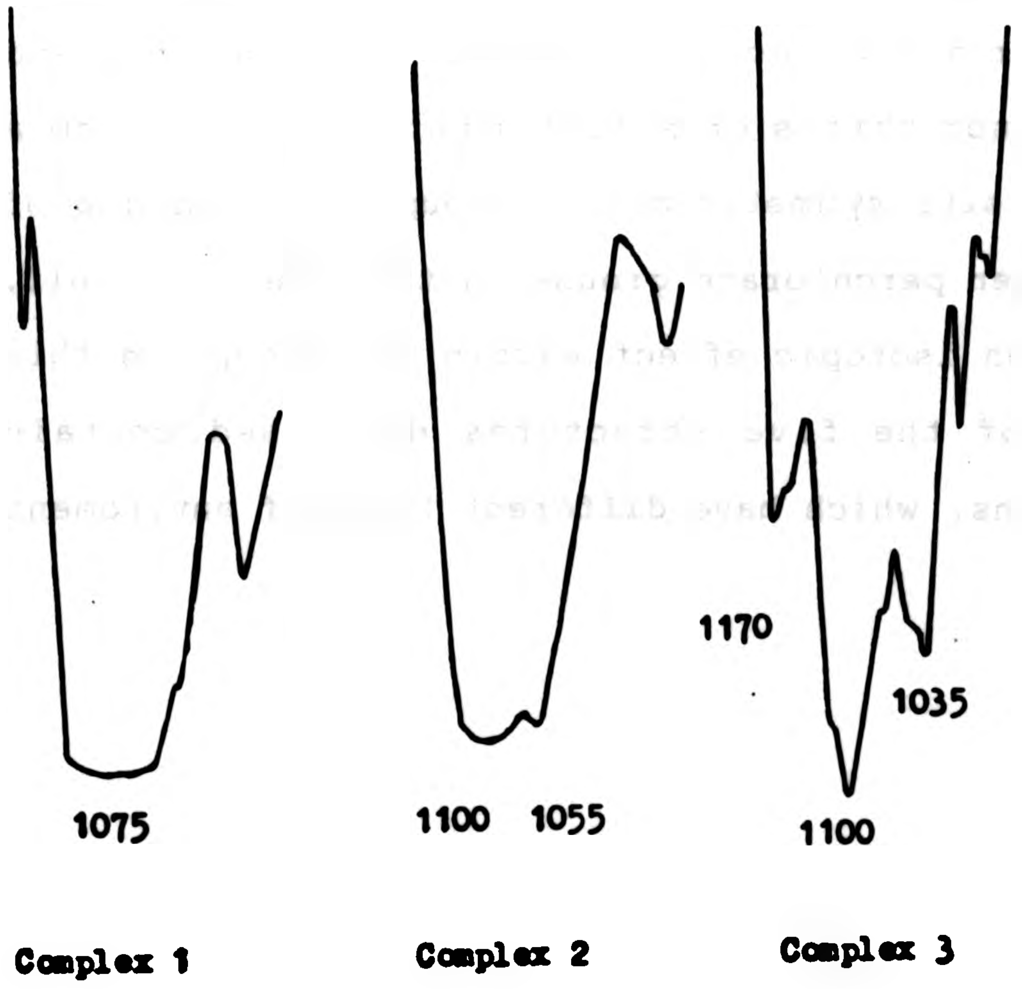


Fig 6.15 The infrared spectra of complexes 1, 2 and 3 in the region of 1100 cm^{-1}.

ex 3

2 and 3 in the region

Complex	Section	Perchlorate Type
[$Cu_2(H_4$cyendimer)]$(ClO_4)3$	(7.1)	Ionic
[$Cu_2(H_2$cyendimer)$(ClO_4)(H_2O)](ClO_4)$	(7.2)	One Ionic One Unidentate
[$Cu_2(H_2$DFMP)$(ClO_4)_2$].thf	(7.3)	Both Bidentate (Bridging)

Mode[8]	Complex 1 (Ionic)	Complex 2 (Unidentate)	Complex 3 (Bidentate)
1	930 w 936 w	932 w	922 w 930 w 936 w
4	624 s	625 s	625 s
3	1075 bs	1055 s 1100 bs	1035 s 1100 s 1170 s

Table 6.6 Observed infrared absorptions assigned to the perchlorate group

The main differences occur at 1100 cm^{-1}, which as shown in fig 6.15 (facing page) are strongly split for the bidentate perchlorate. The degree of splitting will increase with the distortion of the tetrahedral arrangement of the perchlorate oxygens, and this will depend on the strength of the $Cu-O(ClO_3)$ bond (fig 6.16).

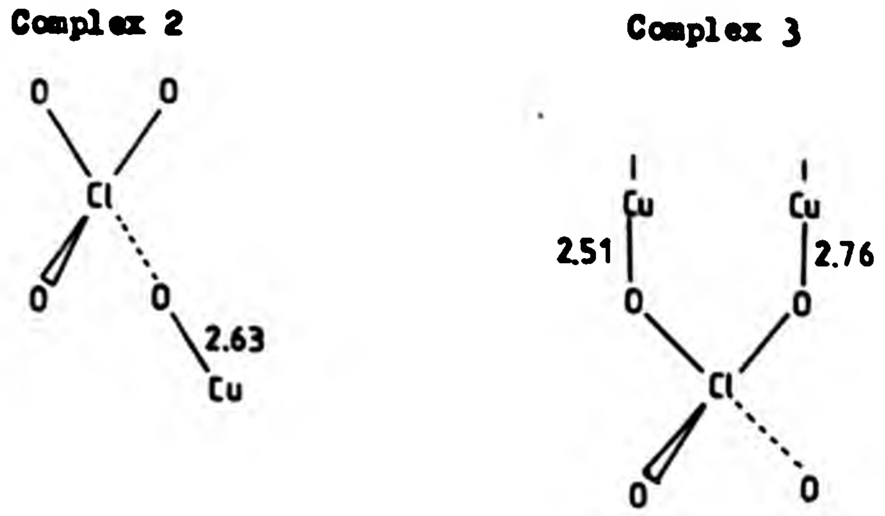


Fig 6.16 Bonding distance of the Cu-O(ClO_3) in complexes 2 and 3.

The most significant differences in the infrared spectra of the three complexes are at 1100 cm^{-1}, but complex 3 does not show as much splitting of the 1100 cm^{-1} band as expected due to only half the total amount of perchlorate being coordinated. No splitting was observed for the 4th mode at 625 cm^{-1} for any of the above complexes, whereas Nelson et al[11] have reported a splitting of the 4th mode for the complex $[Cu_2L(NCS)_2](ClO_4)_2$ (fig 6.17). No other infrared data for this complex were reported.

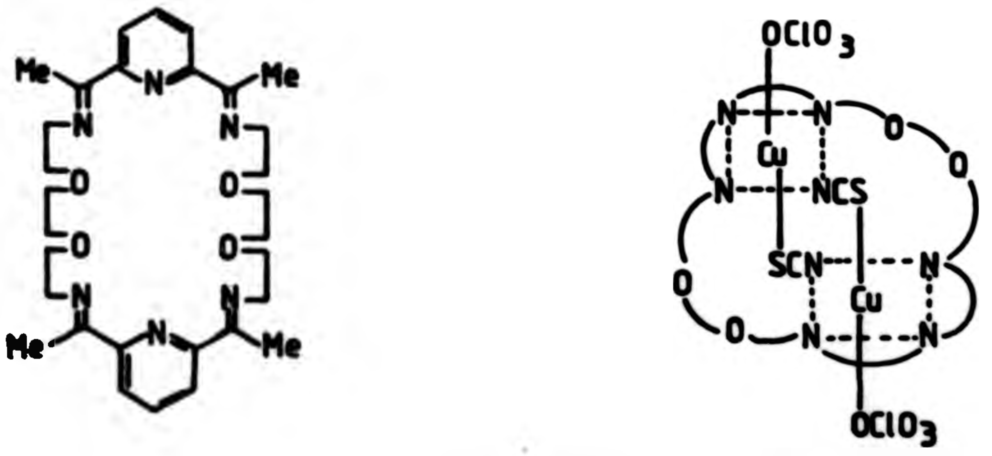


Fig 6.17 Schematic diagram of the ligand (L) and complex $[Cu_2L(NCS)_2](ClO_4)_2$

Conclusion

From the infrared data of other cationic complexes presented in this thesis it is proposed that $[Cu_2(H_4bicybenz)](ClO_4)_4$ has coordinated perchlorates shown by the split infrared band at 1100 cm^{-1} (fig 6.18). All other perchlorate complexes have shown no appreciable splitting at 1100 cm^{-1} although the possibility of a mixture of ionic and coordinated perchlorates cannot be excluded.

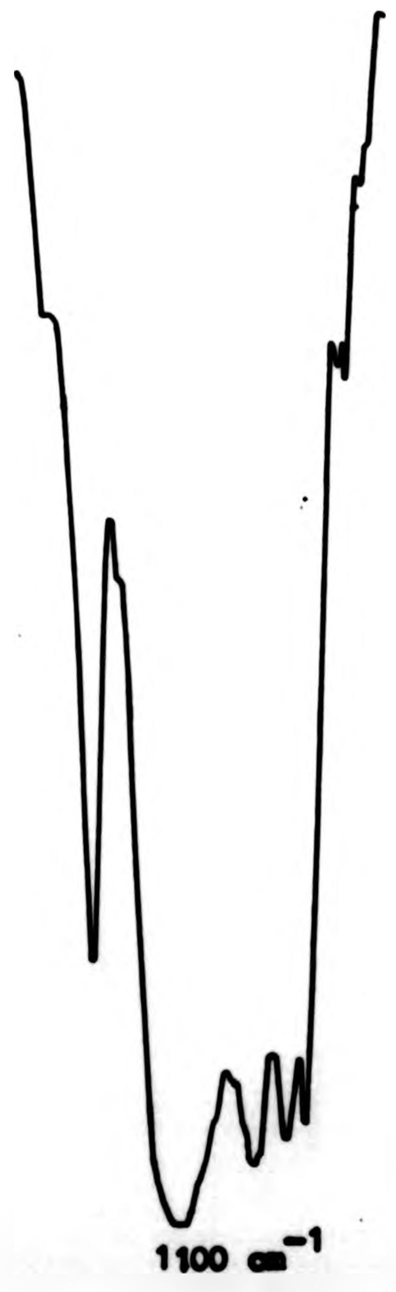


Fig 6.18 Infrared spectrum of $[Cu_2(H_4bicybenz)](ClO_4)_4$ in the region of 1100 cm^{-1} (prepared as nujol mull).

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Chapter 7 X-ray structure determination

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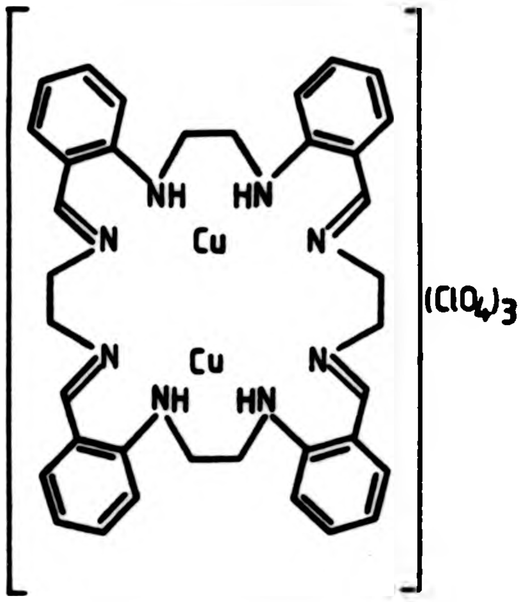
CHAPTER 7

X-ray Structure determination

7.1 X-ray structure of $[Cu_2(H_4cyendimer)](ClO_4)_3$ (7.1)

Crystal Data: $Cu_2C_{36}H_{40}N_8Cl_3O_{12}$ M wt = 1010.2, monoclinic space group Cc, a = 22.577(7), b = 11.016(4), c = 20.909(8) Å. Beta = 118.96°, V = 4550 $Å^3$, Z = 4, T = 22°C, d(calc) = 1.47 g cm^{-3}, Crystal Size = 0.13 x 0.26 x 0.32 mm, data = 1815 $[I > 3\sigma(I)]$. Absorption corrections were applied based on a pseudo-ellipsoid model[1].



$[Cu_2(H_4cyendimer)](ClO_4)_3$

General systematic absences in the data of the type h + k = 2n + 1 indicated that the lattice was C-face centered. The special absences h0l, l = 2n + 1 indicated the presence of a C-glide perpendicular to b. This suggested two possible monoclinic space groups Cc or C2/c. The two fold axis for C2/c would not show systematic absences.

A Patterson synthesis was calculated to resolve the ambiguity in the space group, and to determine the position of the copper atom(s). Early attempts at solving the Patterson were made with the assumption that the compound was a tetraperchlorate complex $[Cu_2(H_4cyendimer)](ClO_4)_4$, which requires the unit cell to contain eight copper atoms on the basis of the crystal density being in a reasonable range. For the space group C2/c the eight copper atoms are generated by the symmetry operations shown in table 7.1. For four dinuclear complexes per unit cell this would require the [$Cu_2(H_4$cyendimer)] unit to lie on a crystallographic symmetry element e.g. the diad as in fig 7.1. Alternatively, the space group Cc contains only four asymmetric units per unit cell (table 7.4) and therefore each asymmetric unit could contain two independent copper atoms in the complex 7.1 (fig 7.2).

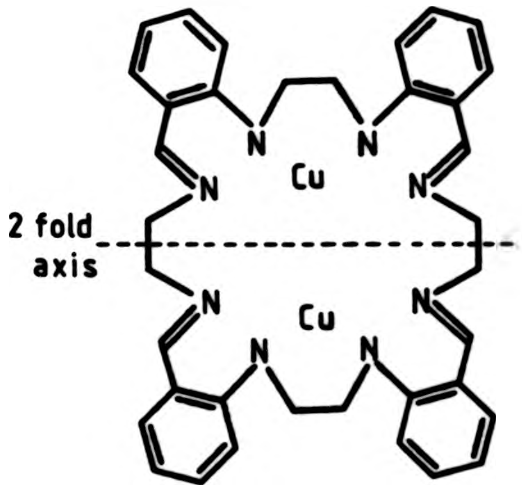


Fig 7.1 Schematic diagram of the dimer for C2/c space group

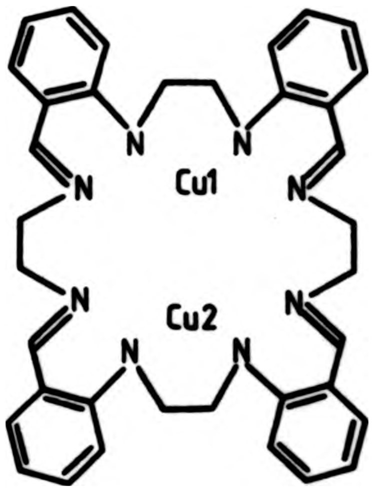


Fig 7.2 Schematic diagram of the dimer for Cc space group

x y z   -x -y -z   -x y 0.5-z   x -y 0.5 + z

Symmetry related positions (0 0 0   0.5 0.5 0)

Table 7.1 Equivalent positions for the space group C2/c.

A copper atom at the position x y z in the C2/c space group would give rise to three unique Cu-Cu vectors in the Patterson synthesis as listed in table 7.2.

2x	2y	2z
-2x	0	0.5 + 2z
0	2y	0.5

Table 7.2 The three Cu-Cu vectors for $[Cu_2(H_4cyen\text{-}dimer)](ClO_4)_3$ (7.1) in the space group C2/c.

Examination of the first twenty highest peaks in the Patterson map (table 7.3) did not produce a solution based on the above (table 7.2) vectors.

	HEIGHT	X/A	Y/B	Z/C
Q1	999.	0.0	0.000	-0.000
Q2	999.	0.0	0.000	1.000
Q3	999.	0.500	0.500	-0.000
Q4	999.	0.500	0.500	1.000
Q5	310.	0.000	0.500	0.500
Q6	310.	0.500	0.0	0.500
Q7	225.	0.000	0.337	0.500
Q8	225.	0.500	0.163	0.500
Q9	128.	0.380	0.086	0.464
Q10	128.	0.120	0.414	0.536
Q11	125.	0.120	0.072	0.037
Q12	125.	0.380	0.428	0.963
Q13	103.	0.158	0.315	0.876
Q14	103.	0.342	0.185	0.124
Q15	102.	-0.000	0.198	0.500
Q16	102.	0.500	0.302	0.500
Q17	94.	0.296	0.141	0.259
Q18	94.	0.204	0.359	0.741
Q19	79.	0.178	0.442	0.724
Q20	79.	0.322	0.058	0.276

Table 7.3 Patterson map from the diffraction data of the complex 7.1.

The above results suggested the dimer 7.1 did not belong to the C2/c space group, and the non-centrosymmetric space group Cc was investigated. The equivalent positions are shown in table 7.4.

x y z x -y 0.5 + z

Symmetry related positions (0 0 0 0.5 0.5 0)

Table 7.4 Equivalent positions for the space group Cc.

A copper atom Cu1 at the position x y z would give rise to one strong vector between the symmetry related copper atoms at 0 2y 0. Examination of the Patterson map revealed the peak (Q7) 0.0 0.337 0.5 which could correspond to the vector 0 2y 0.5. This would give a value for the y coordinate of 0.169 for Cu1. This solution only supplies the y coordinate of a copper atom, and further vectors need to be sought to find the the coordinates for Cu2. The vectors between the two copper atoms Cu1 and Cu2 in the asymmetric unit are calculated by subtracting the positions x, y, and z for Cu1, away from the two positions of the other Cu2 atom which gave the two vectors x_1-x_2 y_1-y_2 z_1-z_2 and x_1-x_2 y_1+y_2 $0.5+(z_1-z_2)$. These vectors between the two copper atoms Cu1 and Cu2 should appear at high intensity in the Patterson map. The length of the first vector will correspond to the Cu1-Cu2 contact distance in the dimer $[Cu_2(H_4cyendimer)](ClO_4)_3$ (7.1). From molecular models of the ligand it was found that this distance would be less than 7 Å, but will depend greatly on the conformation of the ligand. The vector which most obviously met the requirements of being less than 7 Å is Q11 which was particularly short at approximately 2.9 Å. If vector Q11 corresponds to x_1-x_2, y_1-y_2, z_1-z_2, then Q10 can be readily assigned as x_1-x_2, y_1+y_2, $0.5+(z_1-z_2)$ having an identical x value (0.120) and a similar height value (128 cf 125). The y coordinates of both copper atoms were evaluated by simultaneous equations giving $y_1 = 0.171$ and $y_2 = 0.243$. In the space group Cc the origin is not fixed in the "a" and "c" directions and therefore x_2 and z_2 were assigned arbitary values, and x_1 and z_1 were calculated using these arbitary values and the vectors Q10 and Q11. The coordinates for Cu1 and Cu2 are:

Cu2	0	0.243	0.250
Cu1	0.12	0.171	0.283

A Fourier electron difference map based on this solution for the two nonequivalent copper atoms showed a recognisable fragment of the expected molecule. The atoms which were located from this map were used for further Fourier maps which located all the non-hydrogen atoms. More than four positions were found for the oxygen atoms about two of the perchlorate anions, and a fine grid difference map was used to resolve the disordered positions. The oxygen atoms were fixed at these sites and assigned a common thermal parameter. The site occupation factors for the disordered oxygens were allowed to refine. In the final cycles of refinement anisotropic thermal parameters were assigned to the two copper atoms and Cl(1) and Cl(3) atoms where previously higher isotropic thermal parameters were found. Hydrogen atoms were included in fixed positions, "riding" at a fixed distance of 0.95 Å from the carbon atoms to which they were attached, having a common isotropic thermal parameter. The hydrogen atoms of the anilino nitrogen atoms were also included in calculated positions at a fixed distance of 0.9 Å, and assigned a common thermal parameter. This resulted in R = 0.0727 and R_w = 0.0712. Fig 7.3 depicts the schematic and ortep diagrams of the complex 7.1.

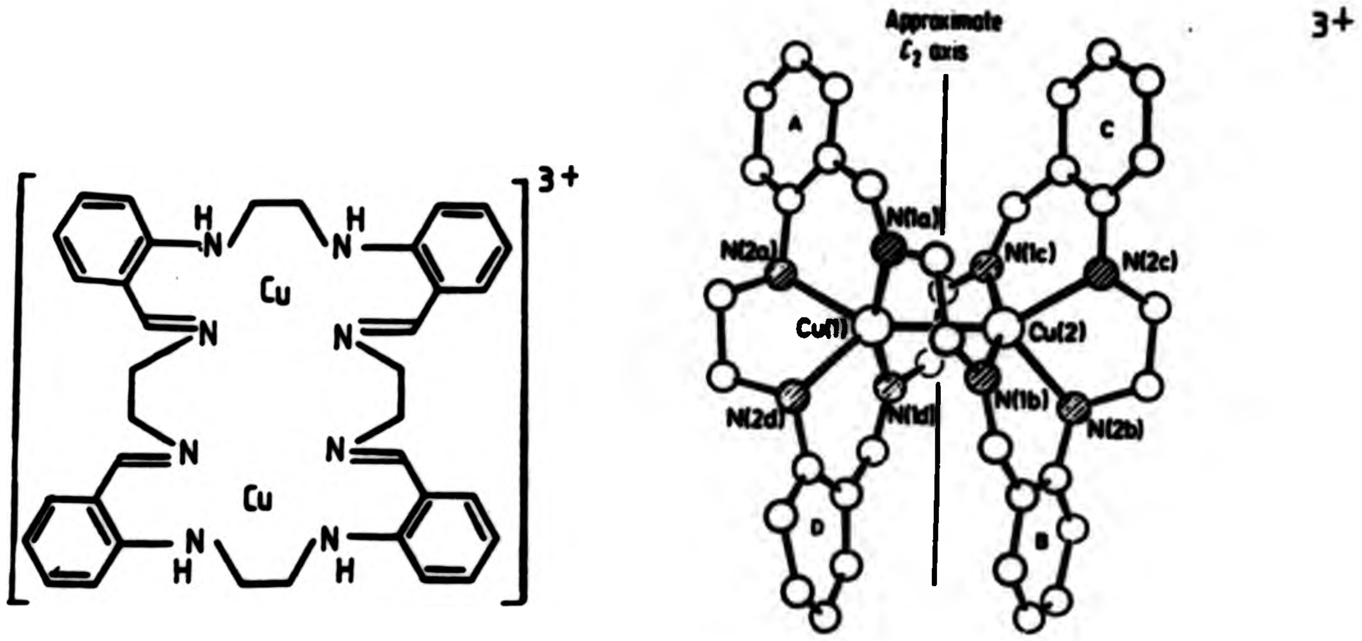
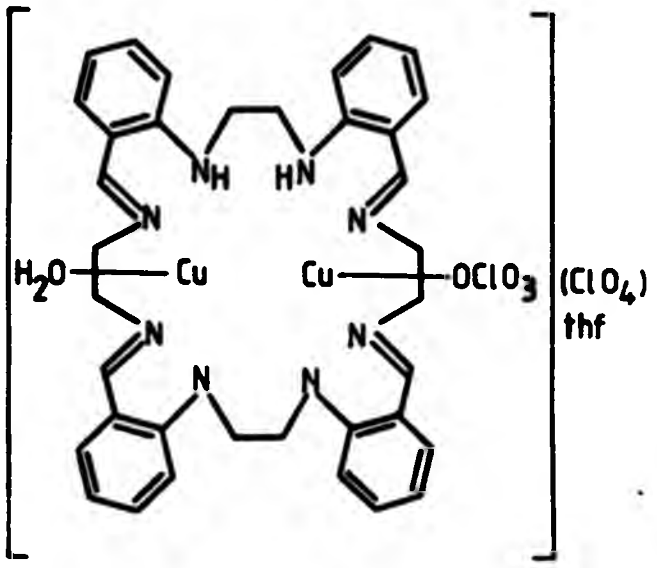


Fig 7.3 Ortep diagram of $[Cu_2(H_4cyendimer)]^{3+}$

7.2 X-Ray structure of [Cu_2(H2cyendimer)(H_2O)(ClO_4)]-(ClO_4).0.5thf

Crystal Data: $Cu_2C_{38}H_{44}N_8Cl_2O_9$ Mwt = 998.9, monoclinic space group Cc, a = 21.963(7), b = 16.326, c = 12.699(4) Å. Beta = 103.73°, V = 4423.3 $Å^3$, Z = 4, T = 22°C, d(calc) = 1.451 g cm^{-3}, Crystal Size = 0.36 x 0.43 x 0.35 mm, data = 2835. [$\underline{I} \geqslant 3\sigma(\underline{I})$]. Absorption corrections were not applied.



General systematic absences in the data of the type h + k = 2n + 1 indicated the lattice was C-face centered. The special absences h0l, l = 2n + 1 indicated the presence of a C-glide perpendicular to b. This indicated two possible monoclinic space groups Cc or C2/c. The two fold axis for C2/c would not show systematic absences. A Patterson Synthesis was calculated to resolve the ambiguity in the space group, and to determine the position of the copper atom(s). The volume of the unit cell was slightly smaller than that of [Cu_2(H_4cyendimer)](ClO_4)$_3$ (7.1) (4423.3 cf 4450 $Å^3$) and therefore approximate calculations were made with with the assumption that the compound was a biscopper diperchlorate complex [Cu_2(H_4cyendimer)](ClO_4)$_2$, which would require eight copper atoms per unit cell. The non-centrosymmetric space group Cc was considered first and the vectors between two copper atoms Cu1 and Cu2 in the same asymmetric unit are x_1-x_2 y_1-y_2 z_1-z_2 and x_1-x_2 y_1+y_2 $0.5+(z_1-z_2)$ as calculated in section 7.1.

Examination of the first twenty highest peaks in the Patterson map (table 7.5) produced a solution based on the above vectors.

	HEIGHT	**X/A**	**Y/B**	**Z/C**
Q1	1000.	0.0	-0.000	-0.000
Q2	1000.	0.0	-0.000	1.000
Q3	1000.	0.500	0.500	-0.000
Q4	1000.	0.500	0.500	1.000
Q5	185.	0.000	0.279	0.500
Q6	185.	0.500	0.221	0.500
Q7	162.	0.375	0.012	0.421
Q8	162.	0.125	0.488	0.579
Q9	160.	0.123	0.238	0.081
Q10	160.	0.377	0.262	0.918
Q11	100.	0.502	0.418	0.463
Q12	100.	0.002	0.082	0.463
Q13	100.	-0.002	0.082	0.537
Q14	100.	0.498	0.418	0.537
Q15	94.	0.217	0.000	0.081
Q16	94.	0.283	0.500	0.919
Q17	77.	0.451	0.500	0.870
Q18	77.	0.049	-0.000	0.130
Q19	76.	-0.000	0.111	-0.000
Q20	76.	-0.000	0.111	1.000

Table 7.5 Patterson synthesis from the diffraction data of the complex 7.2

The peak which corresponds to x_1-x_2 y_1-y_2 z_1-z_2 should be less than about 7 Å in length for the same reasons discussed in section 7.1. The highest peak to meet this requirement was Q9 which showed an approximate contact distance between Cu1 and Cu2 of 4.8 Å. If this vector Q9 corresponded to x_1-x_2, y_1-y_2, z_1-z_2, then Q8 can be readily assigned as x_1-x_2, y_1+y_2, $0.5+(z_1-z_2)$ having a similar x value (0.123 cf 0.125) and height (162 cf 160). The coordinates of the two copper atoms Cu1 and Cu2 can be evaluated in the same way as for the previous complex 7.1, and the coordinates for Cu1 and Cu2 are:

Cu1	0.000	0.125	0.250
Cu2	0.124	0.363	0.330

A Fourier difference map phased on this solution for the two nonequivalent copper atoms showed recognisable fragments of the expected molecule and gave an R factor of 0.33. The atoms which were located from this map were used for further Fourier maps which located all the non-hydrogen atoms plus the anilino hydrogen atoms. The hydrogen atoms attached to the carbon atoms were included in calculated positions, "riding" at a fixed distance of 1.08 Å and assigned a common thermal parameter. One of the two perchlorates was coordinated to Cu2, while the other perchlorate was disordered, and refined as described in section 7.1. In the final cycles of refinement, anisotropic thermal parameters were assigned to the two copper atoms and the following atoms C(9c), C(9d), O(1), Cl(1) and Cl(2) where previously higher isotropic thermal parameters were found. The atoms C(9c) and C(9d) showed disorder, and a fine grid difference map was examined to try to resolve the disordered positions, however, the electron density for these two atoms was smeared in the x-z plane rather than resolved into separate peaks (see chapter 3.4.4 for further details). A tetrahydrofuran (thf) solvate molecule accompanied each dimer molecule, but showed high thermal parameters for all the five atoms located from the Fourier electron difference map. These five atoms were assigned common isotropic thermal parameters which allowed their site occupation factors to refine to 0.5, thereby accounting for half a mole of thf per mole of complex 7.2. The final cycles of refinement gave an R = 0.0753 and R_w = 0.0727. Fig 7.4 depicts the ortep diagram of the biscopper(II) complex 7.2.

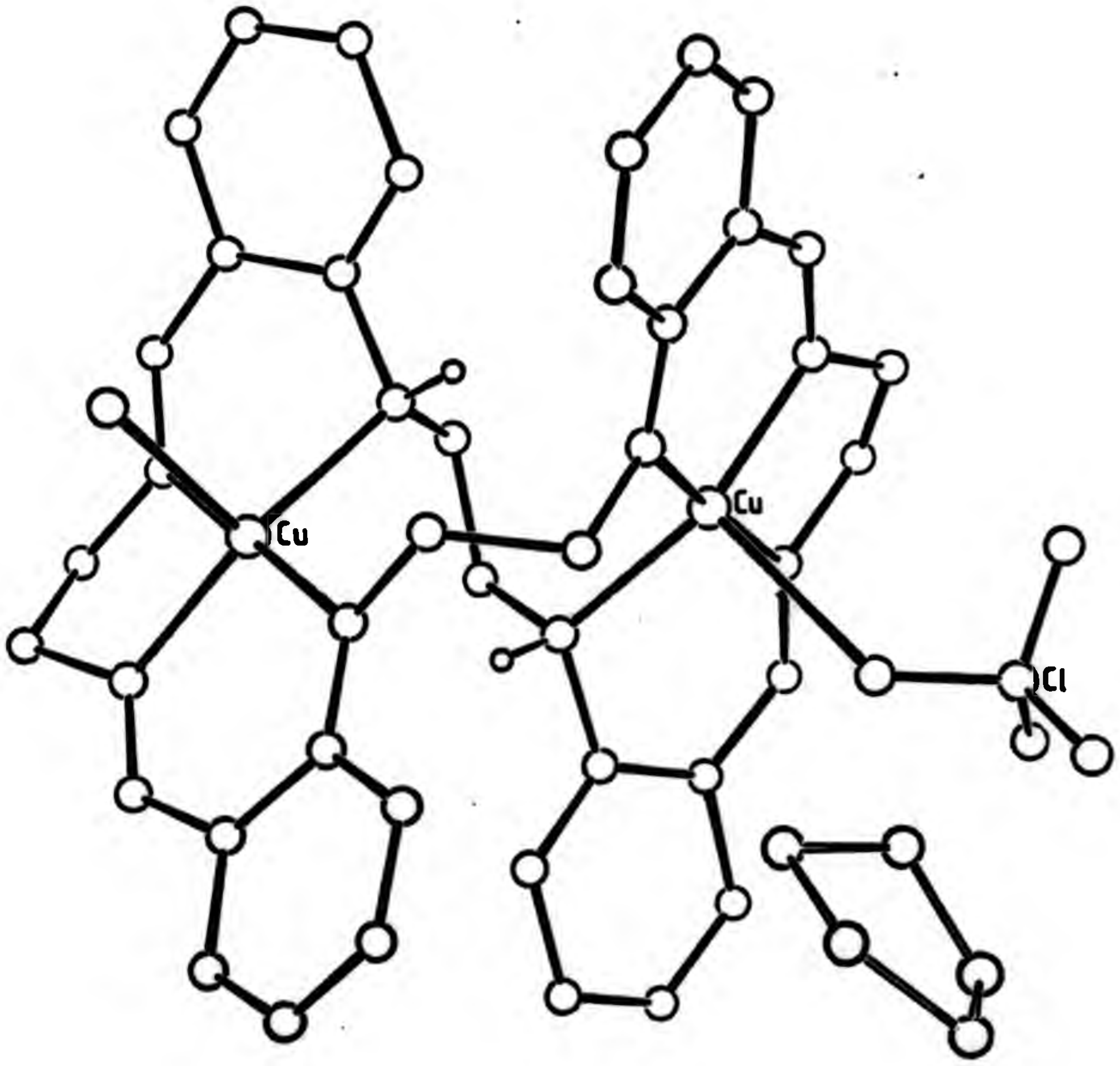
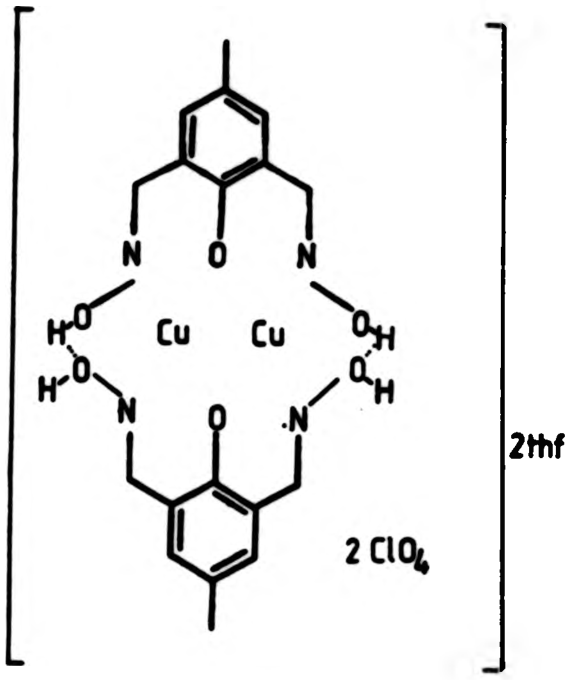


Fig 7.4 Ortep diagram of [Cu_2(H2cyendimer)(H_2O)(ClO_4)]-(ClO_4).0.5thf (7.2)

7.3 X-Ray structure of $[Cu_2(H_2DFMP)_2(ClO_4)_2].thf$ (7.3).

Crystal data: $Cu_2C_{26}H_{52}N_8Cl_2O_6$ Mwt = 855.7, monoclinic space group I42d, a = 21.527(3), c = 14.759(8) Å. V = 6839 $Å^3$, Z = 8, T = 22°C, d(calc) = 1.66 g cm^{-3}, 1st Crystal Size = 0.3 x 0.3 x 0.24 mm 2nd Crystal Size = 0.3 x 0.3 x 0.16 mm data = 929 and 481 respectively [$\underline{I} > 3\sigma(\underline{I})$]. Absorption corrections were not applied.



Two square pyridimal shaped crystals were used for data collection and both were coated in "Araldite Resin"[2] to prevent loss of the solvate thf. The first crystal was used to collect data within the theta range of 2.5 - 10° before disintergrating. The second crystal was used to collect data within the theta range 7 - 30° (an overlap of 3° to allow both sets of data to be scaled and merged). The two data sets were merged through common reflections by linear least squares[3] to give 1031 unique reflections (interlayer scale factors of 0.4687 and 2.133) with a merge R factor of 0.0436. From the original 25 refections the diffractometer calculated a orientation matrix and a Dirichlet reduced unit cell. The relationships of the parameters of the cell indicated that a body-centered unit cell with all angles 90° and two of the axis of equal length could be selected. The intensity relationships of a large range or reflections was tested and indicated that the Laue symmetry (table 7.6) corresponded to the tetragonal crystal system.

$$h\ k\ l = \bar{h}\ \bar{k}\ l = h\ k\ \bar{l} = \bar{h}\ \bar{k}\ \bar{l} = \bar{h}\ k\ l = h\ \bar{k}\ l = \bar{h}\ k\ \bar{l} = h\ \bar{k}\ \bar{l}$$

$$k\ h\ l = k\ \bar{h}\ l = \bar{k}\ h\ \bar{l} = k\ \bar{h}\ \bar{l} = \bar{k}\ h\ l = \bar{k}\ \bar{h}\ l = k\ h\ \bar{l} = \bar{k}\ \bar{h}\ \bar{l}$$

Table 7.6 Laue symmetry for the tetragonal crystal system.

Systematic absences in the full data set gave rise to two possible space groups, I42d and $I4_1md$, both having the same special conditions: 0 k l (k + l = 2n) and h k l (l = 2n and 2h + l = 4n).

<u>Number of positions</u>	<u>I42d</u>					
16	x,	y,	z;	$\bar{x}$,	0.5+y,	0.25-z
	$\bar{x}$,	$\bar{y}$,	z;	x,	0.5-y,	0.25-z
	$\bar{y}$,	x,	$\bar{z}$;	y,	0.5+x,	0.25+z
	y,	$\bar{x}$,	$\bar{z}$;	$\bar{y}$,	0.5-x,	0.25+z
8	x,	0.25,	0.125;	$\bar{x}$,	0.750,	0.125
	0.75,	x,	0.875;	0.25,	$\bar{x}$,	0.875
8	0,	0,	z;	0,	0,	$\bar{z}$
	0,	0.5,	0.25+z;	0,	0.5,	0.25-z

Table 7.7 Eqivalent positions for space groups I42d and $I4_1md$ (continued next page).

$I4_1md$

16	x,	y,	z;	y,	0.5+x,	0.25+z
	$\bar{x}$,	$\bar{y}$,	z;	$\bar{y}$,	0.5-x,	0.25+z
	$\bar{x}$,	y,	z;	$\bar{y}$,	0.5+x,	0.25+z
	x,	$\bar{y}$,	z;	y,	0.5-x,	0.25+z
	0,	y,	z;	y,	0.5,	0.5+z
	0,	-y,	z;	-y,	0.5,	0.5+z

Symmetry related positions (0 0 0, 0.5 0.5 0.5)

Table 7.7 Eqivalent positions for space groups I42d and $I4_1md$

From the expected structure both space groups are possible, one with a two fold axis and the other with a mirror plane (Fig 7.5).

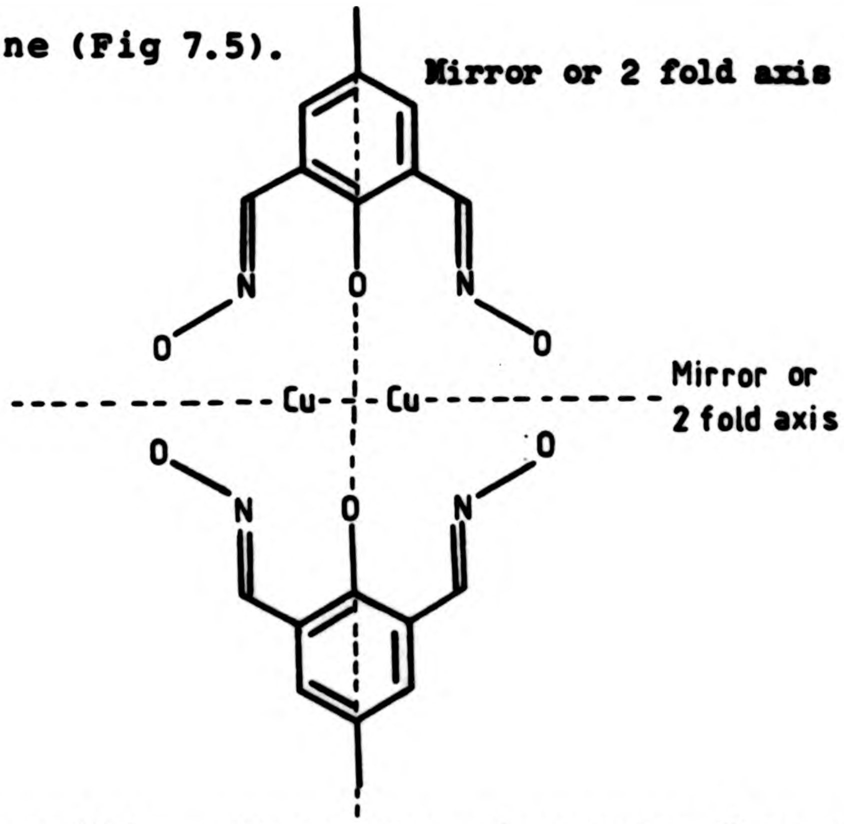


Fig 7.5 Possible symmetry elements for the cation $[Cu_2(H_2DFMP)2]^{2+}$ (7.3).

The space group $I4_1md$ was considered first, and table 7.8 shows the Cu-Cu vectors for the copper atoms in general (fig 7.6) and special (fig 7.7) positions.

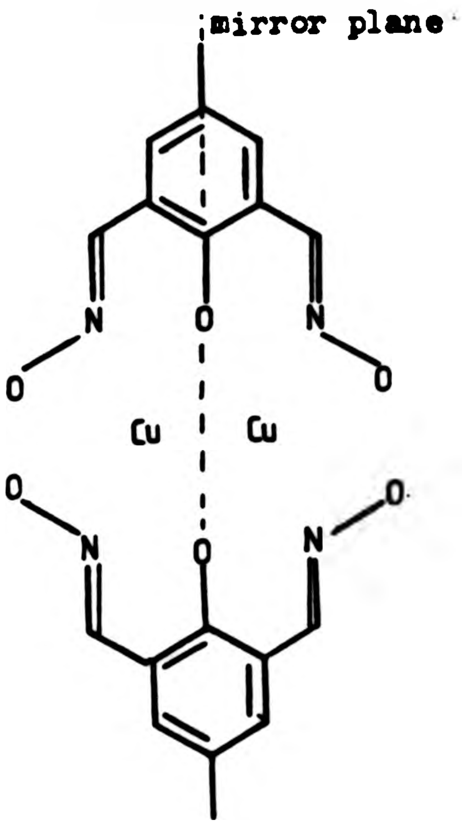


Fig 7.6 Schematic diagram for copper atoms in general positions

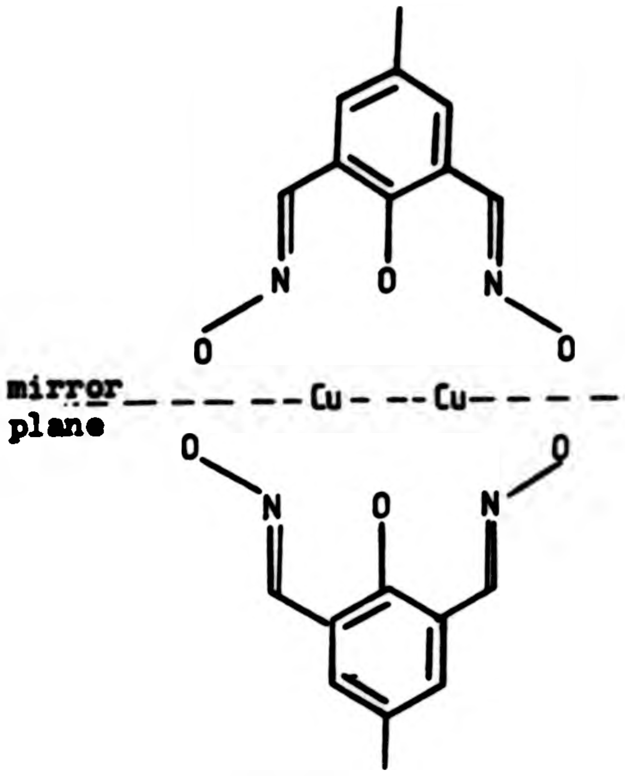


Fig 7.7 Schematic diagram for for copper atoms in in special positions

$I4_1md$

2x,	2y,	0;	x,	0,	0
(x-y),	0.5+(x-y),	0.25;	x,	2y,	0
(x+y),	0.5+(x+y),	0.25;	x-y,	y-0.5,	0.25
2x,	0,	0;	x+y,	y-0.5,	0.25
0,	2y,	0;			
(x+y),	0.5+(x-y),	0.25;			
(x-y),	0.5-(x+y),	0.25;	(x+y),	0.5+(x+y),	0.25

Table 7.8 Vectors between the copper atoms in general and special positions

	HEIGHT	X/A	Y/B	Z/C
Q1	999.	-0.000	0.000	-0.000
Q2	219.	0.034	0.500	-0.000
Q3	213.	0.000	0.465	0.500
Q4	194.	0.000	0.140	-0.000
Q5	170.	0.065	0.064	-0.000
Q6	85.	0.033	0.364	-0.000
Q7	76.	0.061	0.118	-0.000
Q8	76.	0.120	0.060	-0000
Q9	74.	0.048	0.000	-0.225
Q10	74.	0.095	-0.000	0.217
Q11	74.	0.000	0.095	0.217
Q12	70.	0.029	0.440	-0.000
Q13	69.	0.000	0.047	0.222
Q14	67.	0.090	0.437	-0.000
Q15	63.	0.061	0.472	0.500
Q16	63.	0.065	0.410	0.500
Q17	56.	0.060	0.260	-0.000
Q18	54.	0.000	0.318	0.500
Q19	52.	-0.000	-0.000	0.169
Q20	49.	0.034	0.404	0.233

Table 7.9 Patterson synthesis from the diffraction data of the complex 7.3

The Patterson was not readily interpreted, and a further Patterson (table 7.10) was obtained by examining a different part of the unit cell.

The highest 20 peaks from the second Patterson synthesis are tabulated in table 7.10.

	HEIGHT	X/A	Y/B	Z/C
Q1	999.	-0.000	-0.000	0.000
Q2	267.	0.500	0.031	0.000
Q3	257.	0.032	0.500	0.000
Q4	202.	0.064	0.064	0.000
Q5	192.	0.140	0.000	0.000
Q6	192.	-0.000	0.140	0.000
Q7	153.	0.298	0.202	0.250
Q8	153.	0.202	0.298	0.250
Q9	150.	0.257	0.242	0.250
Q10	150.	0.243	0.258	0.250
Q11	124.	0.198	0.165	0.245
Q12	123.	0.165	0.198	0.245
Q13	120.	0.450	0.025	0.000
Q14	120.	0.019	0.450	0.000
Q15	119.	0.337	0.163	0.250
Q16	119.	0.163	0.337	0.250
Q17	109.	0.000	0.049	0.228
Q18	105.	0.047	-0.000	0.224
Q19	103.	0.180	0.125	0.000
Q20	103.	0.121	0.186	0.000

Table 7.10 Patterson synthesis from the diffraction data of the complex 7.3

These results eliminated the space group $I4_1md$ since the vectors shown in table 7.8 could not all be assigned to the above Patterson. The alternative space group I42d was considered, and the vectors between two copper atoms in general positions are shown in table 7.11.

2x,	2y,	0.
x+y,	x-y,	2z.
x-y,	x+y,	2z.
2x,	0.5,	2z-0.25.
2x,	2y-0.5,	2z-0.25.
(x-y),	0.5+(x-y),	0.25.
(x+y),	0.5-(x+y),	0.25

Table 7.11 The vectors between two copper atoms in general position for the space group I42d.

The Patterson synthesis was solved for two copper atoms in general positions by assignment of all the vectors (table 7.12) as follows.

Vectors (table 7.11)			Patterson peak				(Patterson synthesis)
2x,	2y,	0	Q6	0.033	0.364	-0.000	(1)
x+y,	x-y,	2z	Q11	0.198	0.165	0.245	(2)
x-y,	x+y,	2z	Q12	0.165	0.198	0.245	(2)
2x,	0.5,	2z-0.25	Q3	0.032	0.500	0.000	(2)
0,	2y-0.5,	2z-0.25	Q6	-0.000	0.140	0.000	(2)
(x-y),	0.5+(x-y),	0.25	Q15	0.337	0.163	0.250	(2)
(x+y),	0.5-(x+y),	0.25	Q8	0.202	0.298	0.250	(2)

Table 7.12 Assignment of the Patterson peaks for the space group I42d.

The coordinates of the copper atom are:

Cu	0.517	0.182	0.123

After a series of fourier maps for the above solution a fragment of the expected molecule be recognised. The hydrogen atoms were included in calculated positions, "riding" on at a fixed distance of 1.08 Å from the carbon atoms to which they were attached having a common isotropic thermal parameter. Four sites of low electron density corresponded to the two hydroxyl hydrogens. These were assigned site occupation factors of 0.5 and refined (see chapter 6 for further details). Anisotropic thermal parameters were assigned to the Cu and Cl atoms in the final cycles of refinement. The dimer molecule was found to have one perchlorate (coordinated in a bidentate fashion to the two copper atoms) and one thf solvate per asymmetric unit. A fine grid difference map detected ten areas of high electron density, and these ten positions were assigned common thermal parameters to allow the site occupation factors to refine. These site occupation factors were fixed in the final cycles of refinement and accounted for two moles of thf per mole of complex 7.3. This resulted in R = 0.0753 and R_w = 0.0727.

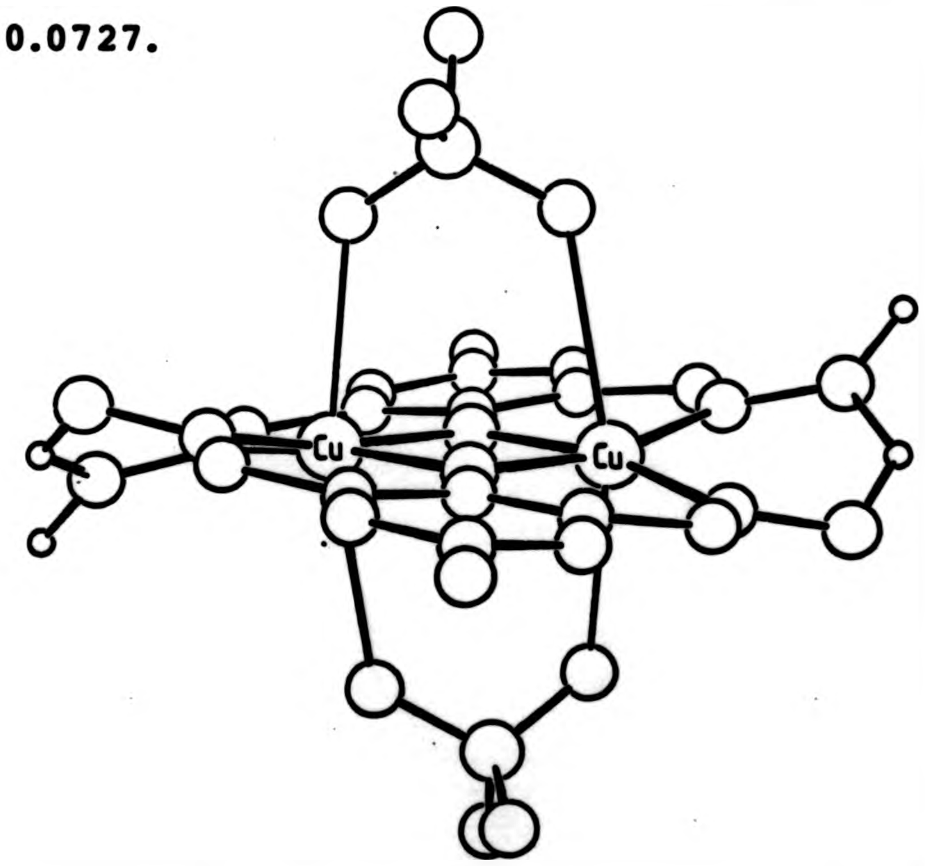
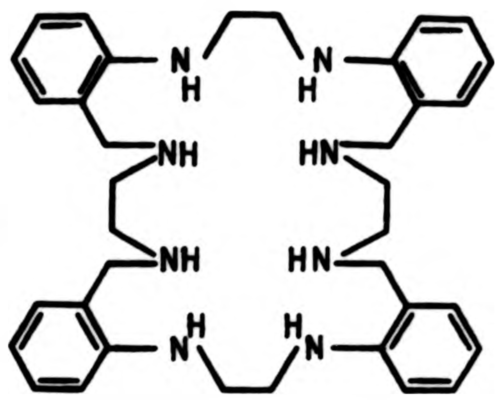


Fig 7.8 Ortep diagram of $[Cu_2(H_2DFMP)_2(ClO_4)_2]$.thf (7.3).

7.4 X-ray structure of H_{12}cyendimer



Crystal Data: $C_{36}H_{48}N_8$ Mwt = 592.8, monoclinic space group P21/n, a = 14.603(2), b = 9.846(2), c = 11.462(2) A. Beta = 97.25(2)°, V = 1648 A^3, Z = 4, T = 22°C, d(calc) = 1.194 g cm^{-3}, Crystal Size = 0.19 x 0.22 x 0.24 mm, data = 3236 [$\underline{I} \geqslant 3\sigma(\underline{I})$]. Absorption corrections were not applied.

From the original 25 reflections the diffractometer calculated a orientation matrix and a Dirichlet reduced unit cell. The relationships of the parameters of the cell confirmed a monoclinic space group. Sytematic absences in a range of the reflection data indicated the space group $P2_1/n$. The structure was solved using the SHELX program by TANGENT multisolution refinement with values of E > 1.3. The starting origin and multisolution phases were selected as in table 7.13.

Origin	E	Multisolutions of R	E
8 5 2	3.303	-1 0 5	3.214
1 8 3	3.443	1 0 3	2.992
1 1 9	4.336	0 1 9	2.970

Table 7.13 Origin and multisolution phases.

From the E map with the lowest RA(= 0.103) all the 22 non-hydrogen atoms were found from the highest 22 peaks.

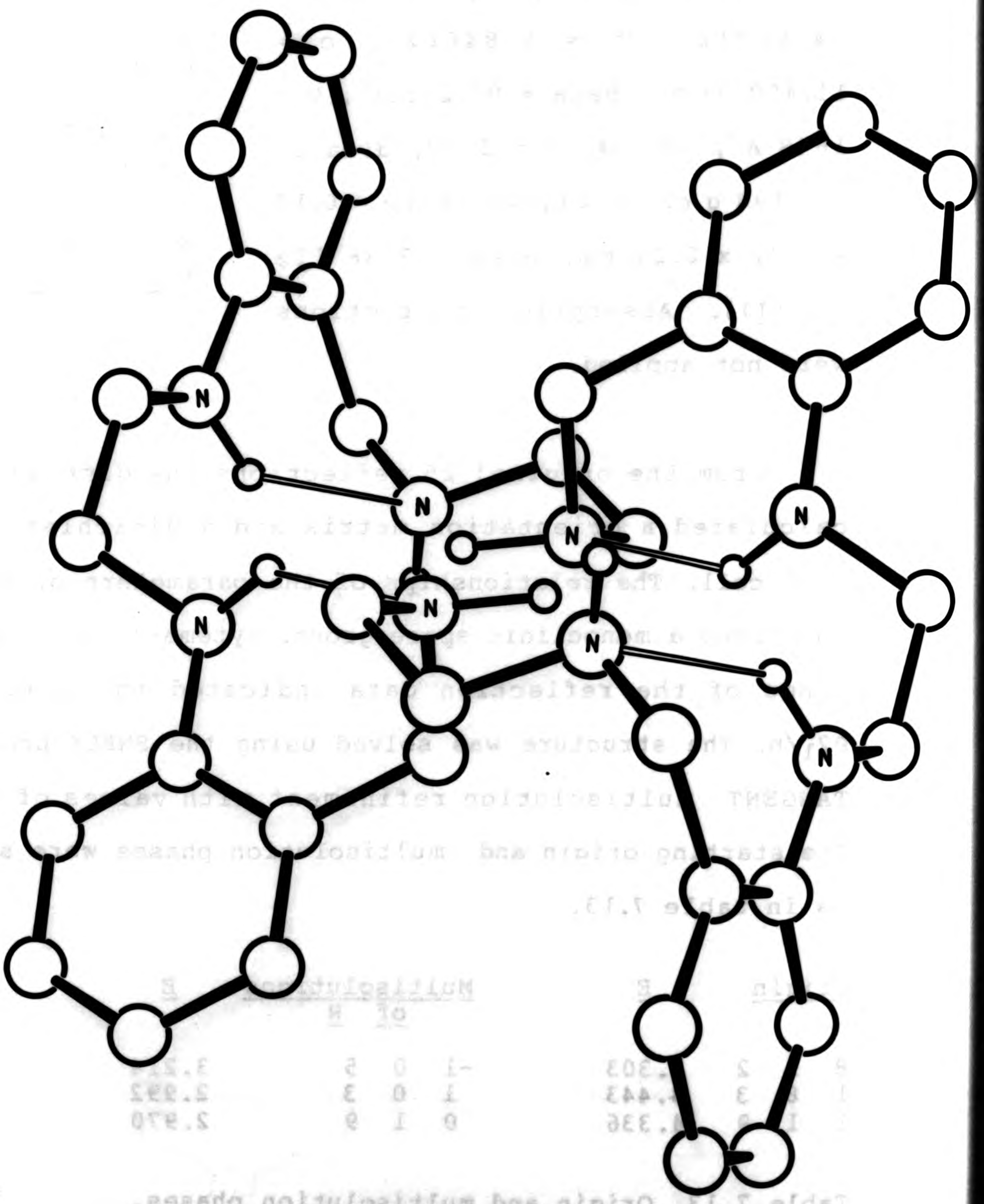


Fig 7.9 Ortep diagram of H_{12}cyendimer

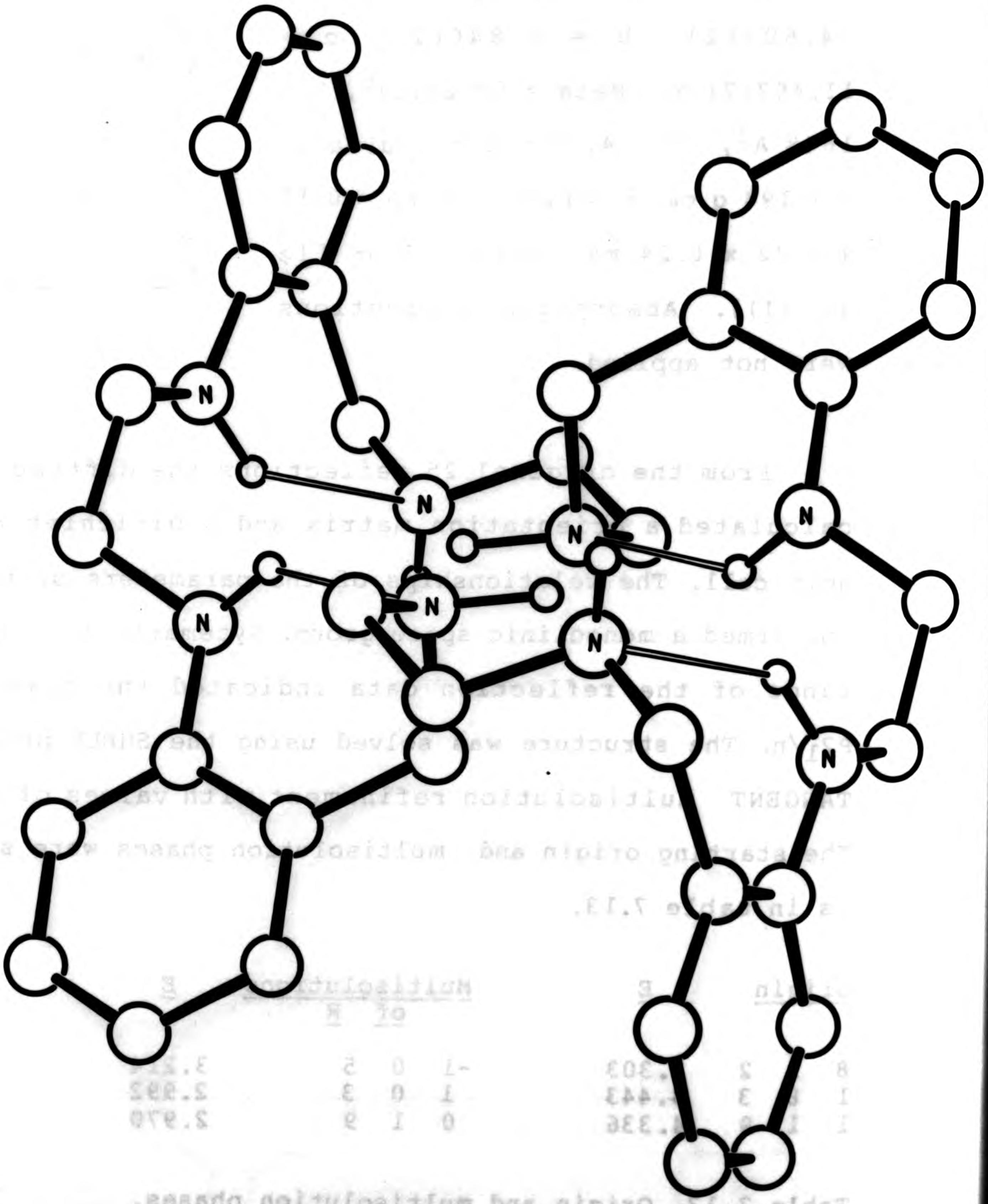


Fig 7.9 Ortep diagram of H_{12}cyendimer

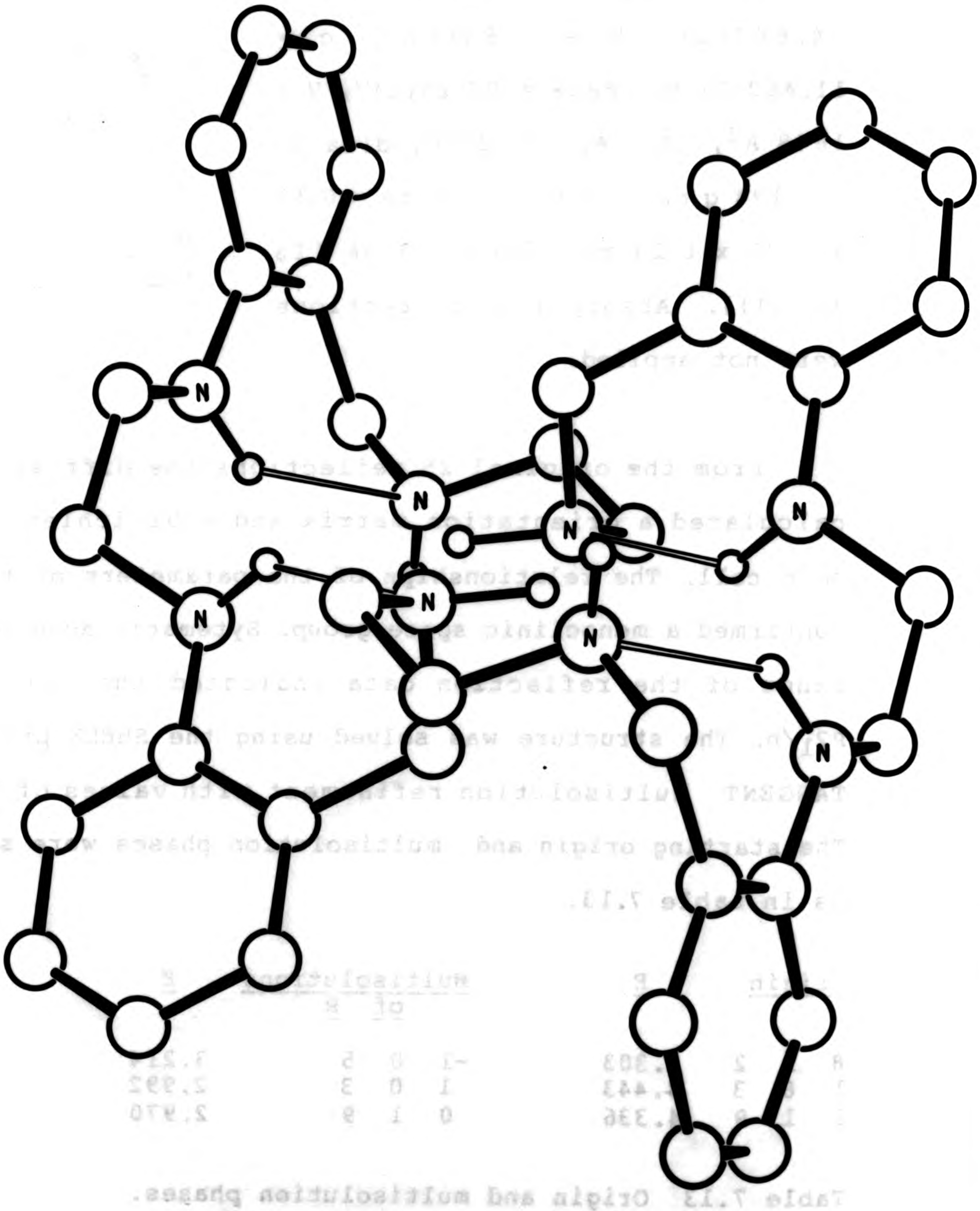


Fig 7.9 Ortep diagram of H_{12}cyendimer

Isotropic refinement on these 22 atoms gave R = 0.118. The C-H hydrogen atoms were included in calculated positions "riding" on the atoms to which they were bonded at a fixed distance of 0.95 Å. The N-H hydrogen atoms were located from a difference map and included in subsequent refinement. Anisotropic thermal parameters were assigned to the nitrogen atoms, while two different common thermal parameters were assigned to the phenylene and methylene hydrogen atoms. These two parameters were included as free variables in the refinement. This resulted in of R = 0.077 and Rw = 0.0734. Fig 7.9 (facing page) depicts the ortep diagram of H_{12}cyendimer. The stereoscopic view is shown below (fig 7.10).

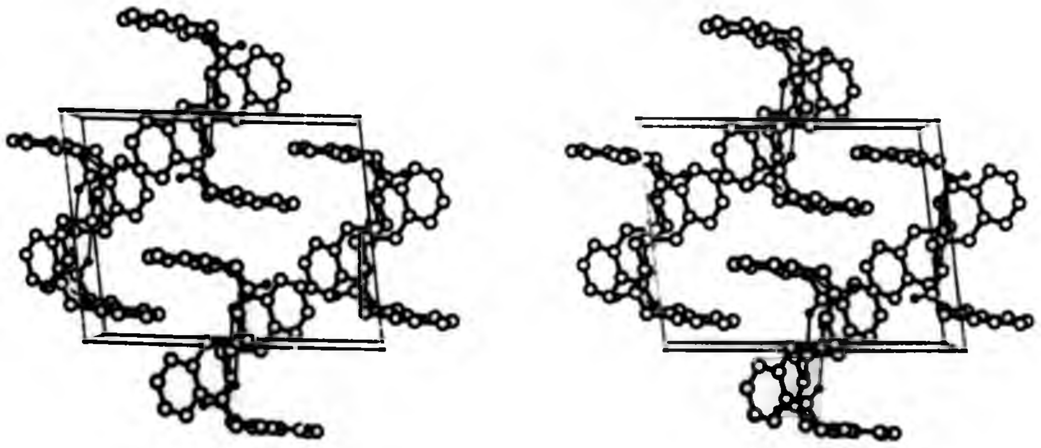
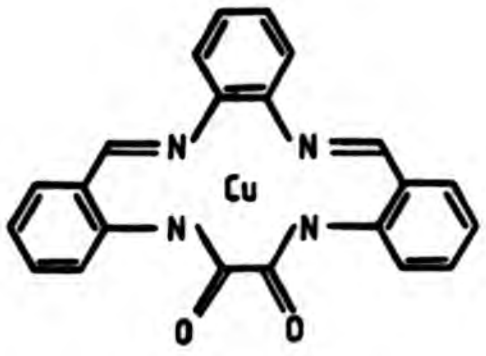


Fig 7.10 Stereoscopic view of H_{12}cyendimer

7.5 X-ray structure of [Cu(cyphX)]

Crystal Data: $CuC_{22}H_{18}N_4O_2$ M wt = 401, monoclinic space group P21/c, a = 15.088(5), b = 16.034(5), c = 7.176(3) Å. Beta = 96.15°, V = 1724 $Å^3$, Z = 4, T = 22°C, d(calc) = 1.55 g cm^{-3}, Crystal Size = 0.2 x 0.15 x 0.1 mm data = 2043 Absorption corrections were applied based on a pseudo ellipsoid model[1].



From the original 25 reflections the diffractometer calculated a orientation matrix and a Dirichlet reduced unit cell. The unit cell parameters were similar to those found for a previously characterised compound [Cu(cyphO_2)] (chapter 4). There was however a significant difference, and the full set of diffraction data were collected. The structure was solved using the same x, y and z coordinates of the non-hydrogen atoms found for the compound [Cu(cyphO_2)]. Anisotropic thermal parameters were assigned to all the non hydrogen atoms, while the 14 hydrogen atoms were assigned common thermal parameters and refined isotropically. This resulted in R = 0.0428 and Rw = 0.0430. Fig 7.11 depicts the ortep diagram of [Cu(cyphX)] where X = O_2.

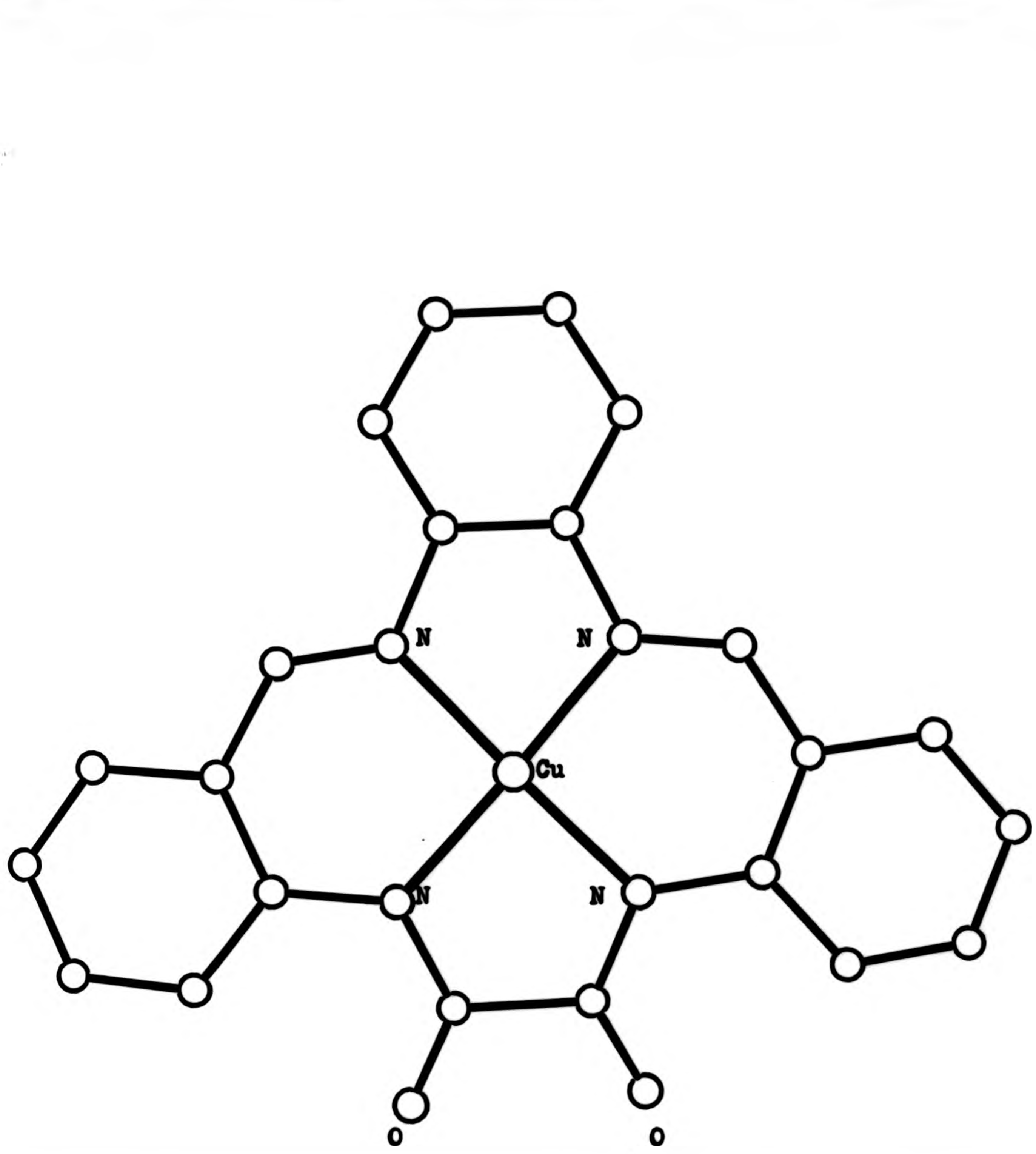


Fig 7.11 Ortep diagram of [Cu(cyphX)] (7.5) (X = O_2).

References

1 Sheldrick,G.M. *EMPABS* Program for absorbtion corrections. The University of Cambridge. 1976.

2 Any resin which does not contract on hardening can be used

3 Rae,A.D., Blake,A.B. *Acta. Cryst.* 1966, 209, 586.

General reference: Sheldrick,G.M. *SHELX Program.* The University of Cambridge. 1976.

Chapter 8 Experimental section

Compound	Page	Reference
H_2cyen 8.II	258	1
[Cu(cyen)] 8.IIA	259	
[Cu(H_2cyen)]$(ClO_4)_2$ 8.IIB	259	
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[Cu(H_6cyen)]$(ClO_4)_2$ 8.IIIB	261	
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H_2cypr 8.IX	273	2
[Cu(cypr)] 8.IXA	274	
H_2cybn 8.X	275	2
[Cu(cybn)] 8.XA	276	
[Cu(cyphX)] 8.XI	277	
[(Cucyph$(OMe)_2$)] 8.XII	278	

Compound	Page	Reference
H_4cyendimer 8.XIII	279	2
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$[Cu_2(H_4cyendimer)](ClO_4)_4$ 8.XIIIB2	281	
$[Cu_2(H_2cyendimer)(ClO_4)(H_2O)](ClO_4)$ 8.XIIIB3	282	
$[Cu_2(H_4cyendimer)(CO)_x](ClO_4)_2$ 8.XIIIB4	283	
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H_{12}cyhexdimer 8.XVI	288	
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$[Cu_2(H_4cyprodimer)](ClO_4)_4$ 8.XVIIB	291	
H_{12}cyprodimer8HCl 8.XVIIC	292	
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$[Cu(H_2bicyphen)]$ 8.XIXA1	294	
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$[Cu_2(bicybenz)]$ 8.XXA	298	
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H_{12}bicybenz 8.XXI	300	
$[Cu_2(H_{12}bicybenz)](ClO_4)_4$ 8.XXIB	301	
$[Cu_2(HDFMP)_2]$ 8.XXIIA	302	
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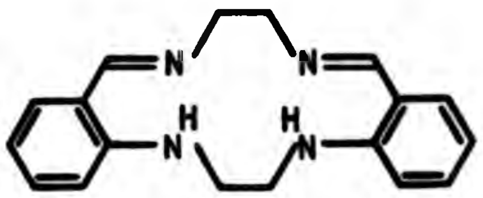
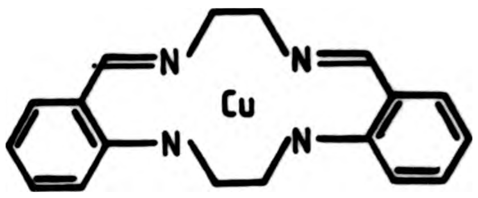
7,8,15,16,17,18-Hexahydrodibenzo[e,m][1,4,8,11]tetraazacyclotetradecine.



H_2cyen 8.II

1,2-Diaminoethane (0.63 g, 10.5 mmol) in chloroform (2 cm^3) was added to a refluxing solution of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (8.I) (2.68 g, 10 mmol) in chloroform (250 cm^3). After refluxing for 24 h the solution was evaporated to 80 cm^3 under reduced pressure at 50°C and addition of ethanol (80 cm^3), followed by cooling, gave 7,8,15,16,17,18-hexahydrodibenzo[e,m][1,4,8,11]tetraazacyclotetradecine (8.II) (2.75 g, 9.4 mmol, 94 % yield) as white crystals from methanol/chloroform (1:1 , 80 cm^3), mp 130°C, (found: C, 73.9; H, 6.9; N, 19.2. $C_{18}H_{20}N_4$ requires C, 73.4; H, 7.0; N, 18.6 %). Electronic Spectrum (methanol) λ_{max}/nm (ϵ): 250 (1935), 294 (428). ν_{max} /cm: 3240, 3146, 3046, 3016, 2928, 2918, 2888, 2841, 2834, 1636, 1616, 1583, 1577, 1521, 1516, 1511, 1416, 1401, 1372, 1332, 1328, 1202, 1165, 1158, 1141, 1044, 1032, 920, 915, 754, 742, 703. ^1H nmr Spectrum: δ/ppm 1.80 bs 2H NH; 3.55 s 4H; 3.88 s 4H; 6.65-7.29 m 8H aryl protons; 8.47 s CH. Mass Spectrum m/e: 292(M^* = 42 %), 231(9), 175(25), 174(14), 173(17), 149(29), 147(16), 146(30), 145(36), 133(26), 132(26), 131(66), 118(100), 117(38), 104(27), 99(16), 91(36).

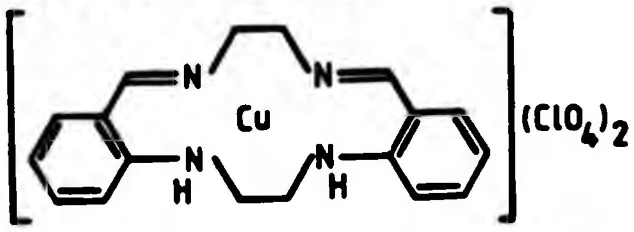
((7,8,16,17-Tetrahydrodibenzo[e,m][1,4,8,11]tetraazacyclotetradecinato(2-)N^6,N^9,N^{15},N^{18})copper(II)).



[Cu(cyen)] 8.IIA

1,2-diaminoethane (0.3 g, 5 mmol) was added to a suspension of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (8.I) (0.67 g, 2.5 mmol) and copper(II) acetate(0.5 g, 2.5 mmol) in refluxing methanol (100 cm^3). After refluxing for 48 h, cooling and filtering gave a deep brown powder of ((7,8,16,17-tetrahydrodibenzo[*e*,*m*][1,4,8,11]tetraazacyclotetradecinato(2-)N^6,N^9,N^{15},N^{18})copper(II)) (8.IIA) (0.44 g, 1.25 mmol, 50 % yield), mp 270°C, (found: Cu, 17.0; C, 60.1; H, 4.6; N, 15.7. $CuC_{18}H_{18}N_4$ requires: Cu, 18.0; C, 61.1; H, 5.1; N, 15.7 %). ν_{max}/cm: 3018, 2908, 2876, 2856, 2826, 2794, 1615, 1597, 1320, 1467, 1453, 1442, 1433, 1060, 1032, 955, 936, 927, 862, 820, 788, 746, 740, 730, 723, 646, 631, 618, 497, 433.

((7,8,15,16,17,18-Hexahydrodibenzo[e,m][1,4,8,11]tetraazacyclotetradecine-N^6,N^9,N^{15},N^{18})copper(II)perchlorate)

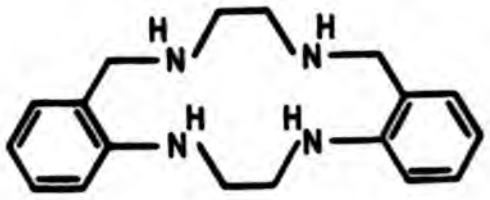


[Cu(H_2cyen)](ClO_4)$_2$ 8.IIB

H_2cyen (8.II) (0.12 g, 0.4 mmol) was added to a refluxing solution of copper(II) perchlorate (0.185 g, 0.5 mmol) in methanol (20 cm^3) under nitrogen. After 10 min the solution was cooled to give deep brown crystals of ((7,8,15,16,17,18-hexahydrodibenzo[*e*,*m*]-

[1,4,8,-11]tetraazacyclotetradecine-N^6,N^9,N^{15},N^{18})copper(II)perchlorate) (8.IIB) (0.12 g, 0.22 mmol, 54 % yield), mp 220°C, (found: C, 38.0; H, 3.7; N, 10.1; Cu, 11.6. $CuC_{18}H_{20}N_4Cl_2O_8$ requires: C, 39.0; H, 3.6; N, 10.1; Cu, 11.5 %). Electronic Spectrum (methanol) λ_{max}/nm (ϵ): 220 (14028), 270 (5550), 440 (226). ν_{max}/cm: 3548 B, 3258, 3138, 2953, 2898, 2838, 1666, 1652, 1620, 1602, 1578, 1494, 1460, 1412, 1307, 1225, 1090 B, 987, 952, 772, 624.

5,6,7,8,9,10,15,16,17,18-Decahydrodibenzo[e,m,][1,4,8,11]tetraazacyclotetradecine.

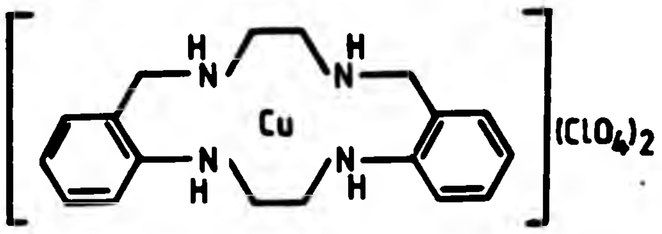


H_6cyen 8.III

BH_3/thf (250 cm^3, 1 mol dm^{-3} solution, 250 mmol) was added under nitrogen to H_2cyen (8.II) (6.4 g, 21.9 mmol). After refluxing for 24 h, distilled water (100 cm^3), KCl (5 g), and NaOH solution (2 mol dm^{-3}, 40 cm^3, 80 mmol) was added. Evaporation of the organic layer to 40 cm^3 under reduced pressure at 50°C and addition of methanol (100 cm^3) with evaporation to 60 cm^3 and addition of petrol (40:60 , 100 cm^3) gave white crystals of 5,6,7,8,9,10,15,16,17,18-decahydrodibenzo[e,m,][1,4,8,11]tetraazacyclotetradecine. (4.1 g, 15.2 mmol, 69% yield), mp 110-112°C, (found: C, 71.9; H, 8.2; N, 19.4. $C_{18}H_{24}N_4$ requires: C, 72.9; H, 8.2; N, 18.9 %). Electronic Spectrum λ_{max}/nm (ϵ): 250 (1963), 294 (435). ν_{max}/cm: 3313, 3251, 3222, 3182, 3121, 3074, 3034, 2944, 2924, 2884, 2864, 2824, 1606, 1582, 1518, 1512, 1502, 1399, 1334, 1330, 1320, 1303, 1272, 1259, 1230, 1142, 1123, 1110, 1038, 1000, 962, 943, 844, 757, 747, 728, 722, 654,

602. ^{1}H nmr Spectrum ($CDCl_3$) δ /ppm: 2.71 s 4H; 3.45 s 4H; 3.81 s 4H; 6.52-7.30 m aryl protons. Mass Spectrum m/e: 296(M^*=24%), 236(5), 176(22), 161(10), 149(28), 148(26), 147(31), 132(25), 120(42), 118(46), 106(41), 91(37), 77(11).

{(5,6,7,8,9,10,15,16,17,18-Decahydrodibenzo[e,m][1,4,8,11]tetraazacyclotetradecine-N^6,N^9,N^{15},N^{18})copper(II)}perchlorate.

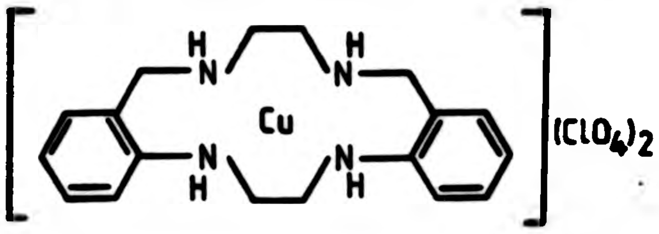


[Cu(H_6cyen)](ClO_4)$_2$ 8.IIIB

H_6cyen (8.III) (0.12 g, 0.4 mmol) was added to a refluxing solution of copper(II) perchlorate (0.19 g, 0.5 mmol) in methanol (10 cm^3) under nitrogen. After 3 min the solution was cooled and filtered to give red-brown crystals of {(5,6,7,8,9,10,15,16,17,18-decahydrodibenzo[*e*,*m*][1,4,8,11]tetraazacyclotetradecine-*N*^{6},*N*^{9},*N*^{15},*N*^{18}-)copper(II)}perchlorate (8.IIIB) (0.11 g, 0.2 mmol, 49 % yield), mp 265°C(e), (found: C, 38.8; N, 4.4; N, 9.9; Cu, 11.0. $CuC_{18}H_{24}N_4Cl_2O_8$ requires C, 38.7; H, 4.3; N, 10.0; Cu, 11.4 %). Electronic Spectrum (methanol) λ_{max}/nm (ϵ): 218 (3073), 278 (1100), 310 (664), 510(285). ν_{max}/cm: 3528 b, 3238, 3193, 3123, 3078, 3033, 2968, 2938, 2878, 2788, 1610, 1587, 1497, 1465, 1369, 1220, 1188, 1170, 1090 b, 995, 963, 960, 950, 930, 913, 833, 772, 737, 620, 590.

602. ^{1}H nmr Spectrum ($CDCl_3$) δ /ppm: 2.71 s 4H; 3.45 s 4H; 3.81 s 4H; 6.52-7.30 m aryl protons. Mass Spectrum m/e: 296(M^*=24%), 236(5), 176(22), 161(10), 149(28), 148(26), 147(31), 132(25), 120(42), 118(46), 106(41), 91(37), 77(11).

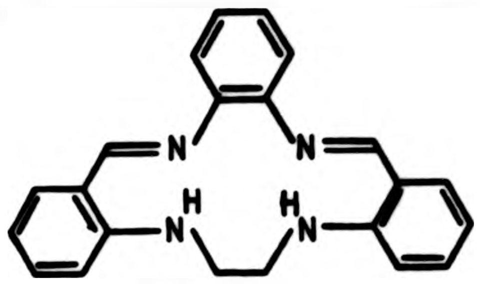
{(5,6,7,8,9,10,15,16,17,18-Decahydrodibenzo[e,m][1,4,8,11]tetraazacyclotetradecine-N^6,N^9,N^{15},N^{18})copper(II)}perchlorate.



[Cu(H_6cyen)](ClO_4)$_2$ 8.IIIB

H_6cyen (8.III) (0.12 g, 0.4 mmol) was added to a refluxing solution of copper(II) perchlorate (0.19 g, 0.5 mmol) in methanol (10 cm^3) under nitrogen. After 3 min the solution was cooled and filtered to give red-brown crystals of {(5,6,7,8,9,10,15,16,17,18-decahydrodibenzo[e,m][1,4,8,11]tetraazacyclotetradecine-N^6,N^9,N^{15},N^{18}-)copper(II)}perchlorate (8.IIIB) (0.11 g, 0.2 mmol, 49 % yield), mp 265°C(d), (found: C, 38.8; H, 4.4; N, 9.9; Cu, 11.0. $CuC_{18}H_{24}N_4Cl_2O_8$ requires C, 38.7; H, 4.3; N, 10.0; Cu, 11.4 %). Electronic Spectrum (methanol) λ_{max}/nm (ϵ): 218 (3073), 278 (1100), 310 (664), 510(285). ν_{max}/cm: 3528 b, 3238, 3193, 3123, 3078, 3033, 2968, 2938, 2878, 2788, 1610, 1587, 1497, 1465, 1369, 1220, 1188, 1170, 1090 b, 995, 963, 960, 950, 930, 913, 833, 772, 737, 620, 590.

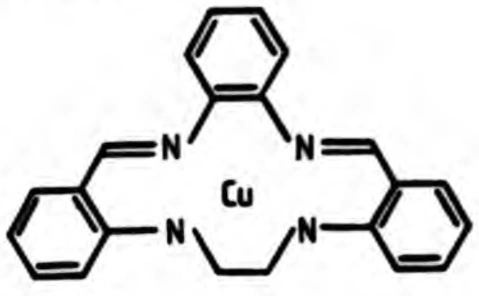
17,18,19,20-Tetrahydrotribenzo[e,i,m][1,4,8,11]tetraazacyclotetradecine.



H_2Cyph 8.IV

4,7-Diaza-2,3:8,9-dibenzodecane-1,10-dione (8.I) (1.0 g, 3.7 mmol), 1,2-diaminobenzene (0.488 g, 4.5 mmol) and zinc(II)acetate was heated in refluxing methanol (200 cm^3) under nitrogen for 18 h. Evaporation to 80 cm^3 under reduced pressure at 60°C and cooling gave 17,18,19,20-tetrahydrotribenzo[e,i,m][1,4,8,11]tetraazacyclotetradecine. (8.IV) (0.78 g, 2.3 mmol, 62 % yield) as fine yellow needles after recrystallisation from chloroform/methanol (60:40 , 50 cm^3), mp 174-176°C, (found: C, 77.5; H, 6.0; N, 16.4. $C_{22}H_{22}N_4$ requires: C, 77.6; H, 5.9; N, 16.45 %). Electronic Spectrum (methanol) λ_{max}/nm (ε): 206 (8182), 214 (7182), 230 (4045), 270 (1318), 285 (1500). ν_{max}/cm: 3170, 3086, 3060, 3030, 2956, 2886, 2835, 2830, 1620, 1601, 1576, 1588, 1533, 1483, 1455, 1337, 1320, 1183, 1164, 1154, 742, 713, 600. ^{1}H nmr Spectrum/ppm : 3.57 t 4H C$\underline{H}_2$; 6.57-7.60 m 12H aryl protons; 8.81 s 2H C$\underline{H}$; 10.28 bs 2H N$\underline{H}$. Mass Spectrum m/e: 340(M^*=18 %), 273(12), 231(12), 230(14), 222(6), 221(29), 220(31), 208(8), 207(8), 206(6), 205(12), 192(12), 147(100), 119(38), 118(46), 111(24), 105(28), 104(26), 97(40), 91(44).

{(18,19-Dihydrotribenzo[e,i,m][1,4,8,11]tetraazacyclotetradecinato(2--)N^6,N^{11},N^{17},N^{20})copper(II)}.



[Cu(Cyph)] (8.IVA)

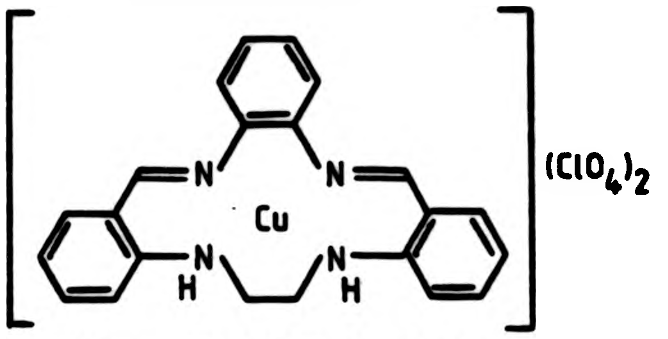
Method A

H_2Cyph (8.IV) (0.3 g, 0.88 mmol) was added to a refluxing solution of copper(II)acetate (0.2 g, 1 mmol) in methanol (40 cm^3). After 5 min the product was filtered and recrystallised from DMF (20 cm^3) to give black needles of {(18,19-dihydrotribenzo[e,i,m][1,4,8,11]tetraazacyclotetradecinato(2-)N^6,N^{11},N^{17},N^{20})copper(II)} (8.IVA) (0.18 g, 0.44 mmol, 51 % yield), mp 250°C(d), (found: Cu, 15.8; C, 66.0; H, 4.5; N, 13.8. $CuC_{22}H_{18}N_4$ requires: Cu, 15.8; C, 65.7; H, 4.5; N, 13.9 %). Electronic Spectrum (Chloroform) λ_{max}/nm (ϵ): 272 (2860), 337 (1131), 354 (1031), 432 (1247), 520 (964). ν_{max}/cm: 3074, 3024, 2936, 2900, 2862, 1610, 1588, 1573, 1501, 1481, 1448, 1364, 1246, 1237, 1184, 1171, 1158, 1140, 1032, 949. 920, 749, 617, 537, 503.

Method B

1,2-Diaminobenzene (0.54 g 5 mmol) in methanol was added to a refluxing suspension of 4,7-Diaza-2,3:8,9-dibenzodecane-1,10-dione (8.I) (0.67 g, 2.5 mmol) and copper(II) acetate (0.5 g, 2.5 mmol) in methanol (100 cm^3). After refluxing for 20 h the mixture was cooled and filtered to give a dark red powder, which on recrystallisation from DMF (50 cm^3) gave black needles of {(18,19-Dihydrotribenzo-[e,i,m][1,4,8,11]tetraazacyclotetradecinato(2-)N^6,N^{11},N^{17},N^{20})copper-(II)} (8.IVA) (0.9 g, 2.5 mmol, 90 % yield).

{(17,18,19,20-Tetrahydrotribenzo[*e*,*i*,*m*][1,4,8,11]tetraazacyclotetradecine-N^6,N^{11},N^{17},N^{20})copper(II)}perchlorate.



[Cu(H_2Cyph)](ClO_4)$_2$ **8.IVB**

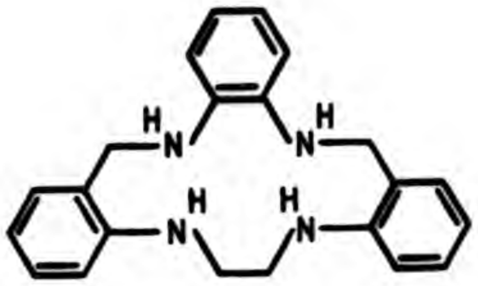
Method *A*

H_2Cyph (8.IV) (0.3 g, 0.88 mmol) was added to a refluxing solution of copper(II) perchlorate (0.37 g, 1 mmol) in methanol (20 cm^3) under nitrogen. After 10 min the solution was cooled and filtered to give a brown powder of {(17,18,19,20-tetrahydrotribenzo[*e*,*i*,*m*]-[1,4,8,11]tetraazacyclotetradecine-N^6,N^{11},N^{17},N^{20})copper(II)}perchlorate (8.IVB) (0.43 g, 0.71 mmol, 80 % yield), mp 270°C(e), (found: Cu, 10.9; C, 44.2; H, 3.4; N, 3.9. $CuC_{22}H_{20}N_4Cl_2O_8$ requires: Cu, 10.5; C, 48.8; H, 3.3; N, 9.3 %). Electronic Spectrum (methanol) λ_{max}/nm (ε): 220 (1340), 268 (524), 320 (411), 390 (188). ν_{max}/cm: 3500 b, 3176, 1627, 1598, 1571, 1482, 1100 b, 1012, 978, 962, 929, 906, 805, 765, 752, 623, 555.

Method *B*

A solution of H_2Cyph (8.IV) (0.1 g, 0.29 mmol) in thf (10 cm^3) was added to copper(II) perchlorate (0.13 g, 0.35 mmol) dissolved in methanol (20 cm^3). The mixture was allowed to stand for two days, and then filtered to give orange/brown crystals of {(17,18,19,20-tetrahydrotribenzo[*e*,*i*,*m*][1,4,8,11]tetraazacyclotetradecine-N^6,N^{11},N^{17},N^{20})copper(II)}perchlorate (8.IVB) (0.12 g, 0.2 mmol, 69 % yield), mp 275°C (e), (found: Cu, 10.9; C,43.8; H, 3.4; N, 9.29). ν_{max}/cm as for "method A" except 1547, 1416, 1215 which are missing.

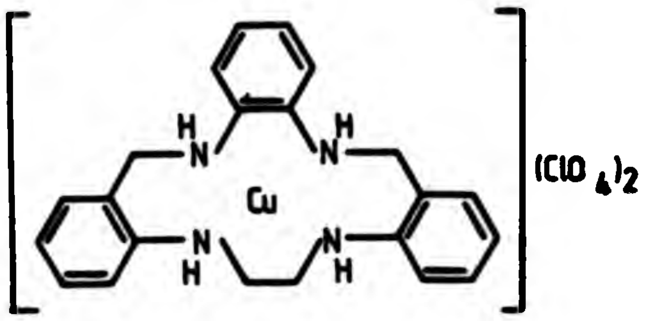
5,6,11,12,17,18,19,20-Octahydrotribenzo[e,i,m][1,4,8,11]tetraazacyclotetradecine.



H_6Cyph 8.V

BH_3/thf (350 cm^3 of 1 mol dm^{-3} solution, 350 mmol) was added in 20 cm^3 portions over a period of 20 min to H_2cyph (8.IV) (6.65 g, 19.6 mmol) under nitrogen. After refluxing for 3 h, distilled water (50 cm^3), potassium chloride (3 g), and sodium hydroxide solution (2 mol dm^{-3}, 20 cm^3, 40 mmol) was added. Evaporation of the organic layer under reduced pressure at 50°C and addition of methanol (40 cm^3) followed by further evaporation and addition of methanol gave a white powder after filtration. Recrystallisation from petrol (40:60)/dichloromethane (100:40 , 100 cm^3) gave white fluffy needles of 5,6,11,12,17,18,19,20-octahydrotribenzo[e,i,m][1,4,8,11]tetraazacyclotetradecine (8.V) (4.3 g, 12.5 mmol, 64 % yield), mp 188-190°C, (found: C, 76.6; H, 7.0; N, 16.25. $C_{22}H_{24}N_4$ requires: C, 76.7; H, 7.0; N, 16.3 %). Electronic Spectrum (methanol) λ_{max}/nm(ϵ): 208 (4111), 250 (2666), 295 (7611). H^1 nmr Spectrum (chloroform) δ /ppm: 3.28 s 4H $C\underline{H}_2$; 4.23 d 4H $C\underline{H}_2$; 4.89 t 2H $N\underline{H}$; 5.74 s 2H $N\underline{H}$; 6.50-7.22 m 12H aryl protons. ν_{max}/cm: 3376, 3350, 3325, 3312, 3046, 2870, 1607, 1598, 1584, 1516, 1502, 1455, 1348, 1302, 1274, 1252, 1244, 1123, 1047, 934, 922, 912, 749, 732. Mass Spectrum m/e: 344(M^*=77%), 237(17), 235(18), 225(23), 234(100), 222(61), 209(27), 120(71), 119(68), 118(85), 106(100), 91(73).

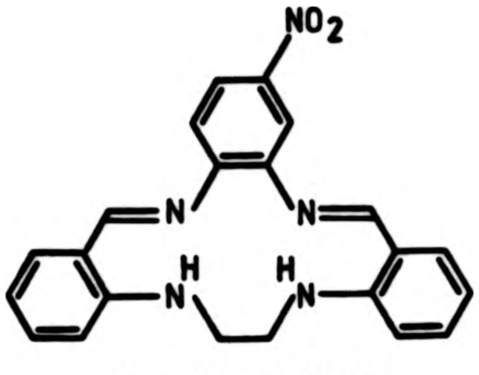
{(5,6,11,12,17,18,19,20-Octahydrotribenzo[e,i,m][1,4,8,11]tetraazacyclotetradecine-N^6,N^{11},N^{17},N^{20})copper(II)}perchlorate.



$[Cu(H_6Cyph)](ClO_4)_2$ **8.VB**

H_6Cyph (8 . V) (0.3 g, 0.87 mmol) was added to a refluxing solution of copper(II) perchlorate (0.37 g, 1 mmol) in methanol (25 cm^3) under nitrogen. The resulting suspension was dissolved by placing the flask in an ultrasonics bath for 1 min, and crystallisation occurred overnight. Filtering under nitrogen gave a deep pink powder of {(5,6,11,12,17,18,19,20-octahydrotribenzo[e,i,m][1,4,8,11]tetraazacyclotetradecine-N^6,N^{11},N^{17},N^{20})copper(II)}perchlorate (8.VB) (0.35 g, 0.58 mmol, 66.3 % yield), mp 240°C(e), (found: Cu, 10.4; C, 43.4; H, 4.1; N, 9.15. $CuC_{22}H_{24}N_4Cl_2O_8$ requires: Cu, 10.5; C, 43.5; H, 4.0; N, 9.2 %) Electronic Spectrum (methanol) λ_{max}/nm (ε): 222 (3073), 260 (1100), 318 (664), 370 (285), 520 (720), 570 (608). ν_{max}/cm: 3518, 3238 b, 3218, 3178, 3075, 3043, 2978, 2958, 2936, 2903, 2864, 1614, 1590, 1495, 1462, 1364, 1308, 1294, 1267, 1225, 1100 b, 1000, 961, 931, 919, 905, 874, 854, 822, 761, 748, 732, 722, 626, 590, 532, 493.

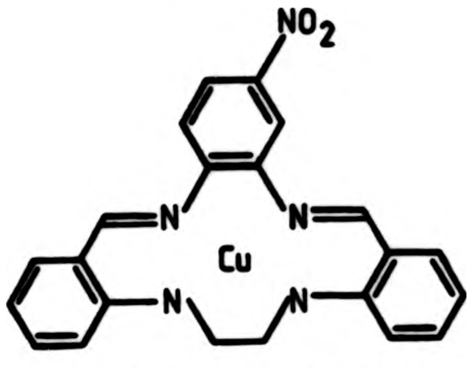
17,18,19,20-Tetrahydro-9-nitrotribenzo[e,i,m][1,4,8,11]tetraazacyclotetradecine.



H_2cyphNO$_2$ 8.VI

4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (8.I) (0.68 g, 2.5 mmol), 4-nitro-1,2-diaminobenzene (0.42 g 2.75 mmol) and zinc(II) acetate (1.1 g. 6 mmol) was heated in refluxing methanol (70 cm^3) for 5 days. Recrystallisation from chloroform (150 cm^3) gave a yellow powder of 17,18,19,20-tetrahydro-9-nitrotribenzo[*e*,*i*,*m*][1,4,8,11]-tetraazacyclotetradecine. (8.VI) (0.8 g, 2 mmol, 80 % yield), mp 200°C, (found: C, 69.1; H, 4.6; N 17.4. $C_{22}H_{19}N_5O_2$ requires C, 68.7; H 4.7; N, 18.2 %). ν_{max}/cm: 3490, 3480, 3080, 2970, 2890, 2860, 2820, 1620, 1600, 1574, 1560, 1520, 1510, 1488, 1335, 1300, 1265, 1190, 1162, 1095, 1082, 1048, 980, 955, 930, 900, 825, 750, 470.

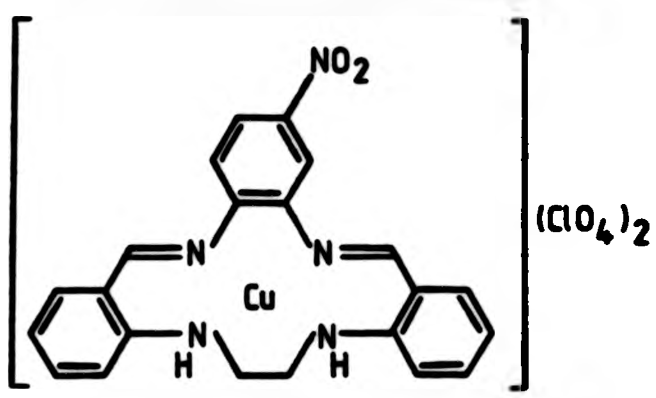
{(17,18,19,20-Tetrahydro-9-nitrotribenzo[e,i,m][1,4,8,11]tetraazacyclotetradecinato(2-)-N^6,N^9,N^{15},N^{18})copper(II)}.



[Cu(cyphNO$_2$)] 8.VIA

1,2-Diamino-4-nitrobenzene (0.16 g, 1.05 mmol) in methanol (10 cm^3) was added to a suspension of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (8.I) (0.27 g, 1 mmol) and in methanol (50 cm^3). After refluxing for 18 h under nitrogen the mixture was cooled and filtered to give brown crystals of [(17,18,19,20-tetrahydro-9-nitrotribenzo-[*e*,*i*,*m*][1,4-,8,11]tetraazacyclotetradecinato(2-)-*N*^{6},*N*^{9},*N*^{15},*N*^{18})copper-(II)] (8.VIA) (0.35 g, 0.79 mmol, 79 % yield), mp 214°C(d), (found: C, 57.2; H, 3.5; N, 14.8. $CuC_{22}H_{17}N_5O_2$ requires: C, 59.1; H, 3.5; N, 15.6 %). ν_{max}/cm: 3082, 3028, 2910, 2850, 1620, 1584, 1571, 1522, 1480, 1435, 1390, 1350, 1335, 1286, 1223, 1260, 1200, 1180, 1156, 1091, 1080, 968, 948, 928, 870, 833, 750, 740, 728, 626, 532, 512, 480, 389.

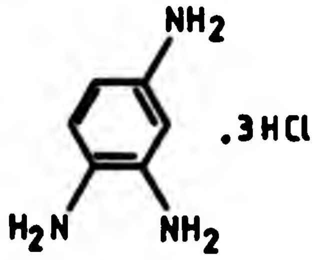
{(17,18,19,20-tetrahydro-9-nitrotribenzo[e,i,m][1,4,8,11]tetraazacyclotetradecine-N^6,N^9,N^{15},N^{18})copper(II)}perchlorate.



[Cu(H_2cyphNO$_2$)](ClO_4)$_2$ 8.VIB

H_2cyphNO$_2$ (8.VI) (0.2 g, 0.52 mmol) was added to a refluxing solution of copper(II) perchlorate (0.23 g, 0.61 mmol) in methanol (25 cm^3) under nitrogen. After 10 min the solution was cooled and filtered to give brown crystals of [(17,18,19,20-tetrahydro-9-nitrotribenzo[e,i,m][1,4,8,11]tetraazacyclotetradecine-N^6,N^9,N^{15},N^{18})copper(II)]-perchlorate (8.VIB) (0.24 g, 0.39 mmol, 70 % yield), mp >360°C, (found C, 40.7; H, 3.3; N, 10.5. $CuC_{22}H_{19}N_5Cl_2O_{10}$ requires: C, 40.8; H, 3.0; N, 10.8 %). ν_{max}/cm: 3350 b, 1610, 1590, 1575, 1480, 1462, 1120 b, 930, 750.

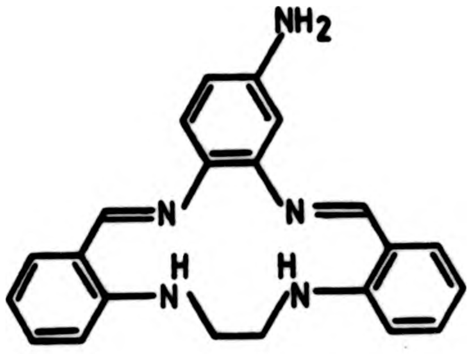
1,2,4-Triaminobenzenetrihydrochloride



TAB.3HCl 8.VII

Methanol (30 cm^3) was added to Pd-C (5 %, 1 g) under nitrogen, followed by 1,2-diamino-4-nitrobenzene (2 g, 13 mmol). The solution was refluxed and the addition of hydrazine hydrate (3 g, 60 mmol) was made in a dropwise fashion until the yellow coloured solution became clear. The mixture was then refluxed for a further 24 h, and then filtered through a celite filter under nitrogen into methanol (50 cm^3) containing concentrated hydrochloric acid (20 cm^3). Filtering and vacuum drying at 30°C for 10 days gave 1,2,4-triaminobenzenetrihydrochloride (8.VII) (2.8 g, 12 mmol, 93 % yield), (found: C, 30.5; H, 5.3; N, 17.7; Cl, 44.1. $C_6H_{12}N_3CL_3$ requires: C, 31.0; H, 5.2; N, 18.1; Cl, 45.7 %).

((17,18,19,20-Tetrahydro-9-aminotribenzo[e,i,m][1,4,8,11]tetraazacyclotetradecine

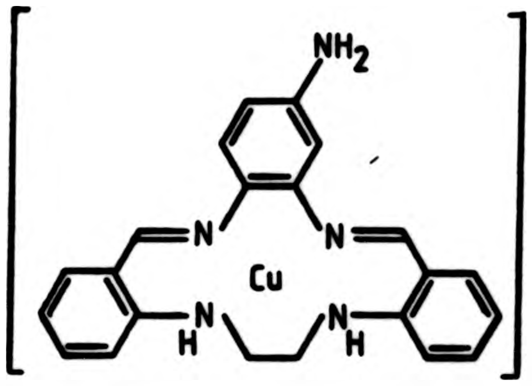


H_2cyphNH$_2$ 8.VIII

4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (8.I) (4.0 g, 15 mmol) was heated in refluxing ethanol (175 cm^3) under nitrogen and TAB3HCL (8.XXI) (4.0 g, 17.2 mmol) was added in twenty approximately equal aliquots over a period of 15 min. After each addition a deep red colour was produced which was discharged in each case by addition of sodium methoxide solution (2.0 mol dm^{-3}) until a yellow colouration was produced (total 24 cm^3, 48 mmol). Addition of zinc(II) acetate (6.4 g, 35 mmol) followed by refluxing for 1 h and filtering under dry nitrogen gave a orange powder. Recrystallisation from pyridine/methanol (1:8 , 360 cm^3) gave yellow flakes of ((17,18,19,20-tetrahydro-9-aminotribenzo[<u>e,i,m</u>][1,4,8,11]tetraazacyclotetradecine (8.VIII) (3.9 g, 11.0 mmol, 73 % yield), mp 190°C(d), (found: C, 74.0;

H, 5.8; N, 19.2. $C_{22}H_{21}N_5$ requires: C, 74.3; H, 6.0; N, 19.7 %). $_{max}$/cm 3470, 3370, 3240, 3090, 2950, 2880, 1622, 1600, 1580, 1524, 1510, 1330, 1100, 1183, 1165, 1150, 1100, 1049, 968, 895, 751. Mass Spectrum m/e: 355(M^{*}=20 %), 340(2), 249(8), 238(18), 237(20), 224(10), 223(12), 221(14), 123(100), 122(100).

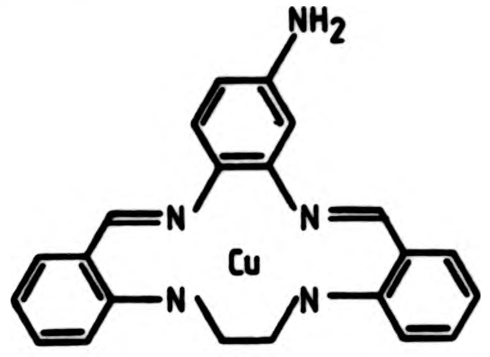
{(17,18,19,20-tetrahydro-9-aminotribenzo[e,i,m][1,4,8,11]tetraazacyclotetradecine-N^6,N^9,N^{15},N^{18})copper(II)}perchlorate.



[Cu(H_2cyphNH$_2$)](ClO_4)$_2$ 8.VIIIB

H_2cyphNH$_2$ (8.VIII) (0.2 g, 0.56 mmol) was added to a refluxing solution of copper(II) perchlorate (0.23 g, 0.61 mmol) in methanol (30 cm^3) under nitrogen. After 10 min the solution was cooled and filtered to give brown crystals of [(17,18,19,20-tetrahydro-9-aminotribenzo[e,i,m][1,4,8,11]tetraazacyclotetradecine-N^6,N^9,N^{15},N^{18})copper(II)]perchlorate (8.VIIIB) (0.22 g, 0.35 mmol, 63 % yield), mp >360°C, (found C, 43.0; H, 3.6; N, 11.0. $CuC_{22}H_{21}N_5Cl_2O_8$ requires: C, 42.8; H, 5.4; N, 11.3 %). ν_{max}/cm: 3380, 1620, 1600, 1575, 1550, 1330, 1275, 1230, 1190, 1170, 1100 b, 975, 930, 770, 629.

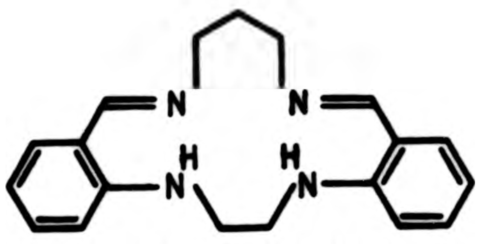
{(17,18,19,20-Tetrahydro-9-aminotribenzo[e,i,m][1,4,8,11]tetraazacyclotetradecinato(2-)-N^6,N^9,N^{15},N^{18})copper(II)}.



[Cu(cyphNH$_2$)] 8.VIIIA

4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (8.I) (1.0 g, 3.7 mmol) was heated in refluxing methanol (60 cm^3) under nitrogen and TAB3HCL (8.VII) (1.0 g, 4.3 mmol) was added in ten approximately equal aliquots over a period of 10 min. After each addition a deep red colour was produced which was discharged in each case by the dropwise addition of sodium methoxide (2.0 mol dm^{-3}) until a yellow/orange colour was produced (total 6 cm^3, 12 mmol). Addition of copper(II) acetate (0.8 g, 4.1 mmol) as a solution in methanol (20 cm^3) followed by refluxing for 4 h, and filtering the mixture gave dark brown coloured crystals of {(17,18,19,20-tetrahydro-9-aminotribenzo[*e*,*i*,*m*]-[1,4,8,11]tetraazacyclotetradecinato(2-)-N^6,N^9,N^{15},N^{18})copper(II)} (8.VIIIA) (1 g, 2.4 mmol, 65 % yield), mp 225°C(d), (found: C, 63.2; H, 4.6; N, 16.8. $CuC_{22}H_{19}N_5$ requires: C, 63.4; H, 4.6; N, 18.8 %). ν_{max}/cm: 3460, 3400, 1617, 1580, 1520, 1560, 1330, 1187, 1161, 990, 970, 750.

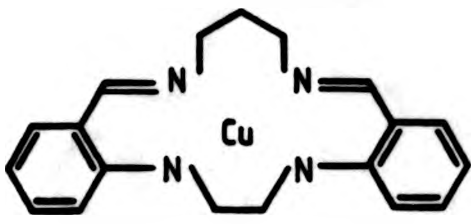
8,9,16,17,18,19-Hexahydro-7H-dibenzo[e,n][1,4,8,12]tetraazacyclopentadecine.



H_2cypr 8.IX

1,3-Diaminopropane (0.4 g, 5.4 mmol) was added to a refluxing solution of 4,7-Diaza-2,3:8,9-dibenzodecane-1,10-dione (8.I) (1.34 g, 5 mmol) in methanol/chloroform (1:1 , 50 cm^3). After 72 h of refluxing the solution was evaporated down at 50°C under reduced pressure to 20 cm^3 volume. Cooling and filtering gave a white crystalline material of 8,9,16,17,18,19-hexahydro-7H-dibenzo[e,n][1,4,8,12]tetraazacyclopentadecine (8.IX) (0.75 g, 2.45 mmol, 49.0 % yield), mp 175°C, (found: C, 74.3; H, 7.5; N, 18.2. $C_{19}H_{22}N_4$ requires: C, 74.5; H, 7.2; N, 18.3 %). ν_{max}/cm: 3208, 3168, 3140, 3088, 3022, 3000, 2922, 2900, 2878, 2840, 2816, 1627, 1594, 1576, 1134, 1064, 1042, 974, 965, 928, 918, 890, 873, 830, 747, 739, 732, 721, 696, 634, 587, 554, 480.

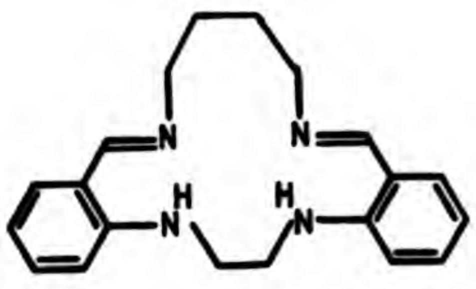
{(8,9,16,17,18,19-Hexahydro-7H-dibenzo[e,n][1,4,8,12]tetraazacyclopentadecinato(2-)-N,^{6},N^{10},N^{16},N^{19})copper(II)}.



[Cu(cypr)] 8.IXA

1,3-Diaminopropane (0.37 g, 5 mmol) in methanol was added to a refluxing suspension of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (8.I) (0.67 g, 2.5 mmol) and copper(II) acetate (0.5 g, 5 mmol) in methanol (100 cm^3). After refluxing for 18 h, cooling and filtering gave a deep brown powder of {(8,9,16,17,18,19-hexahydro-7H-dibenzo[e,n][1,4,8,12]tetraazacyclopentadecinato(2-)-N,^{6},N^{10},N^{16},N^{19})copper(II)} (8.IXA) (0.49 g, 1.33 mmol, 53 % yield), mp 205°C, (found: C, 62.1; H, 5.0; N, 14.8. $CuC_{19}H_{20}N_4$ requires: C, 62.0; H, 5.5; N, 15.2 %). ν_{max}/cm: 3020, 2940, 2920, 2876, 2816, 1610, 1524, 1510, 1478, 1432, 1402, 1392, 1362, 1352, 1340, 1252, 1200, 1165, 1135, 1100, 1072, 1040, 1032, 953, 935, 908, 863, 740, 722, 617, 480, 473, 442, 427.

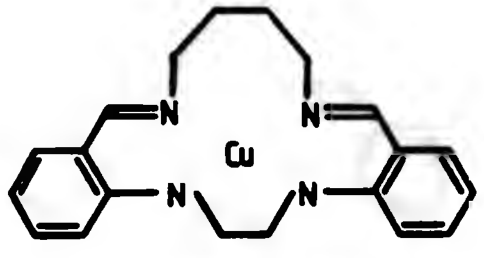
7,8,9,10,17,18,19,20-Octahydrodibenzo[e,o][1,4,8,13]tetraazacyclohexadecine.



H$_2$cybn 8.X

1,4-Diaminobutane (0.60 g, 6.8 mmol) in chloroform (25 cm^3) was added to a refluxing solution of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (8.I) (1.34 g, 5 mmol) in methanol/chloroform (2:1 , 150 cm^3). After 48 h at reflux the volume was reduced at 50°C and low pressure to approximately 30 cm^3. Cooling and filtering gave a white powder of 7,8,9,10,17,18,19,20-octahydrodibenzo[e,o][1,4,8,13]tetraazacyclohexadecine (8.X) (1.3 g, 4 mmol, 80 % yield) (found: C, 75.2; H, 7.1; N, 17.3. $C_{20}H_{24}N_4$ requires C, 75.0; H, 7.5; N, 17.5 %). ν_{max}/cm: 3230 b, 3085, 2950,2820, 1638, 1620, 1597, 1586, 1532, 1447, 1345, 1288, 1213, 1280, 1162, 1088, 1080, 1052, 1002, 986, 973, 927, 920, 838, 745, 734, 658, 644, 614, 581, 550, 510, 480, 431, 431.

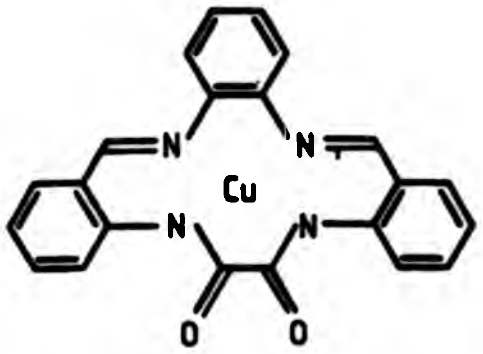
{(7,8,9,10,18,19-Hexahydrodibenzo[e,o][1,4,8,13]tetraazacyclosexadecinato(2-)-N^6,N^{11},N^{17},N^{20})copper(II)}.



[Cu(cybn)] 8.XA

1,2-Diaminobutane (0.25 g, 2.5 mmol) in methanol (50 cm^3) was added to a refuxing suspension of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (8.I) (0.34 g, 1.25 mmol) and copper(II) acetate (0.25 g, 1.25 mmol) in methanol (50 cm^3). After refluxing for 18 h, cooling and filtering gave a dark brown powder of {(7,8,9,10,18,19-hexahydrodibenzo[e,o][1,4,8,13]tetraazacyclosexadecinato(2-)-N^6,N^{11},N^{17},N^{20})copper(II)} (8.XA) (0.15 g, 0.4 mmol, 32 % yield), mp 250°C, (found: C, 61.7; H, 5.8; N,14.0. $CuC_{20}H_{22}N_4$ requires: C, 62.9; H, 5.8; N, 14.7 %). ν_{max}/cm 3072, 3027, 2980, 2930, 2890, 2865, 2820, 1604, 1524, 1454, 1440, 1401, 1364, 1350, 1439, 1257, 1214, 1204, 1194, 1172, 1164, 1132, 1094, 1074, 1042, 1035, 1008, 1000, 970, 942, 929, 859, 742, 733, 725, 638, 532, 471, 458, 437.

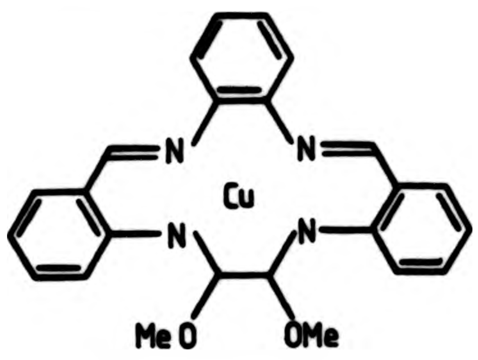
{(18,19-Dioxotribenzeo[e,i,m][1,4,8,11]tetradecinato(2-)-N^{5},N^{11},N^{17},N^{20}-)copper(II).



[Cu(cyphX)] 8.XI

Cucyph (8.IVA) (0.1 g,0.25 mmol) was added to dimethylacetamide (30 cm^{3}) and dissolved by refluxing for 10 sec. Cooling and leaving to stand for 14 days gave burgandy coloured crystals of 18,19-dioxotribenzeo[*e*,*i*,*m*][1,4,8,11]tetradecinato(2-)$\underline{N}^{5}$,$\underline{N}^{11}$,$\underline{N}^{17}$,$\underline{N}^{20}$)copper(II) (8.XI) (0.05 g, 0.12 mmol, 47 % yield), mp 350°C, (found: C, 60.9; H, 3.4; N, 13.4. $CuC_{22}H_{14}N_{4}O_{2}$ requires: C, 61.5; H, 3.28; N, 13.0 %). ν_{max}/cm: 1658, 1620, 1600, 1583, 1578, 1547, 1524, 1494, 1458, 1444, 1430, 1412, 1397, 1389, 1369, 1360, 1228, 1245, 1190, 1180, 1168, 1156, 1134, 1055, 1035, 985, 970, 948, 920, 825, 745, 735, 725, 700, 620, 554, 503.

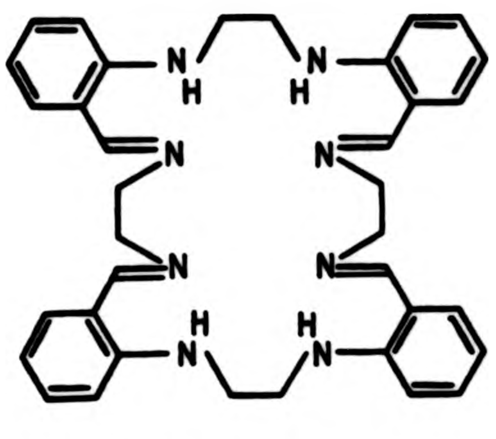
{(18,19-Dihydro-18,19-dimethoxytribenzo[e,i,m][1,4,8,11]tetraazacyclotetradecinato(2-)-N^6,N^{11},N^{17},N^{20})copper(II)}.



[(Cucyph(OMe)$_2$)] 8.XII

H_2cyph (8.IV) (0.3 g, 0.88 mmol) was added to a refluxing solution of copper(II) acetate (0.2 g, 10 mmol) in thf/methanol (5:1 ,60 cm^3). After 1 min the hot mixture was filtered, and recrystallisation of the isolated material from dmf (20 cm^3) gave [Cu(cyph)] (8.IVA) (0.18 g, 0.44 mmol 50 % yield). The filtrate on standing for 20 h at room temperature yielded fine gold needles of {(18,19-dihydro-18,19-dimethoxytribenzo[e,i,m][1,4,8,11]tetraazacyclotetradecinato(2-)-$\underline{N}^6$,$\underline{N}^{11}$,$\underline{N}^{17}$,$\underline{N}^{20}$)copper(II)} (8.XII) (0.09 g, 0.19 mmol, 22 % yield), mp 200°C(d), (found: Cu, 14.0; C, 62.2, H, 4.8; N, 12.1. $CuC_{22}H_{24}N_4O_2$ requires: Cu, 13.8; C, 62.4, H, 4.8; N, 12.1 %). Electronic Spectra (chloroform) (ε) λ_{max}/nm: 275 (3619), 315 (1844), 336 (1567), 354 (1521), 420 (1498), 480 (1106), 510 (1286). ν_{max}/cm: 3103, 3076, 3026, 2922, 2898, 2872, 2816, 1606, 1580, 1521, 1460, 1392, 1373, 1340, 1189, 1056, 1035, 912, 740, 725, 553. Mass Spectrum m/e: 461(M*), 429, 415, 399.

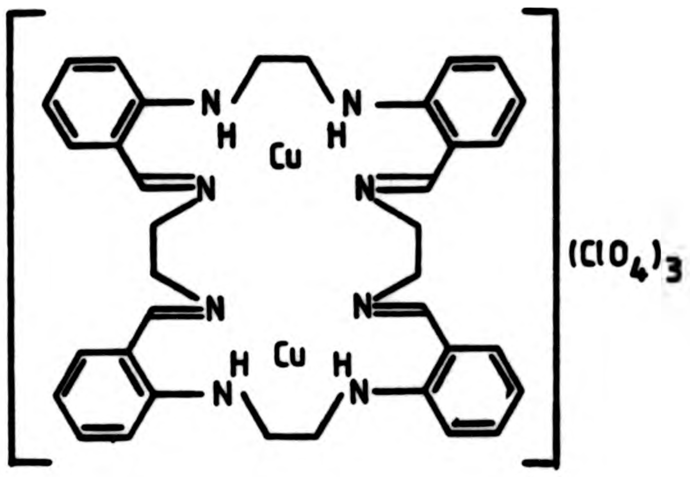
5,6,7,8,15,16,23,24,25,26,33,34-Dodecahydrotetrabenzo[e,m,s,a'][1,4,8-,11,15,18,22,25]octaazacyclooctacosine.



H_4cyendimer 8.XIII

4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (8.I) (9.58 g, 35.7 mmol) and 1,2-diaminoethane (2.4 g, 40 mmol) was heated in refluxing methanol (600 cm^3) for 5 h. Addition of chloroform (90 cm^3) and further refluxing for 18 h gave a white powder on filtration. Recrystallisation from dmf (500 cm^3) gave fine white needles of 5,6,7,8,15,16,23,-24,25,26,33,34-dodecahydrotetrabenzo[e,m,s,a'][1,4,8,11,15,18,22,25-]-octaazacyclooctacosine (8.XIII) (8.47 g, 29 mmol, 81 % yield), mp 278°C, (found: C, 73.4; H, 6.9; N, 18.9. $C_{36}H_{40}N_4$ requires: C, 73.9; H, 6.9; N, 19.2 %). Electronic Spectrum (dmf) λ/nm (ϵ): 272 (2385), 365 (2190). ν_{max}/cm: 3240, 3163, 3088, 3054, 3006, 3003, 2963, 2914, 2888, 2848, 2828, 1633, 1626, 1606, 1585, 1582, 1526, 1484, 1469, 1458, 1441, 1332, 1213, 1164, 1151, 1136, 1114, 1012, 964, 743, 617, 594, 549. Mass Spectrum m/e: 584(M^{*}=42 %), 464(16), 421(10), 408(18), 318(25), 305(37), 293(60), 292(88), 291(100), 280(22), 279(100), 234(21), 176(100), 174(31), 159(25), 145(31), 133(48), 132(62), 131(100), 130(64), 118(100), 117(57), 91(34).

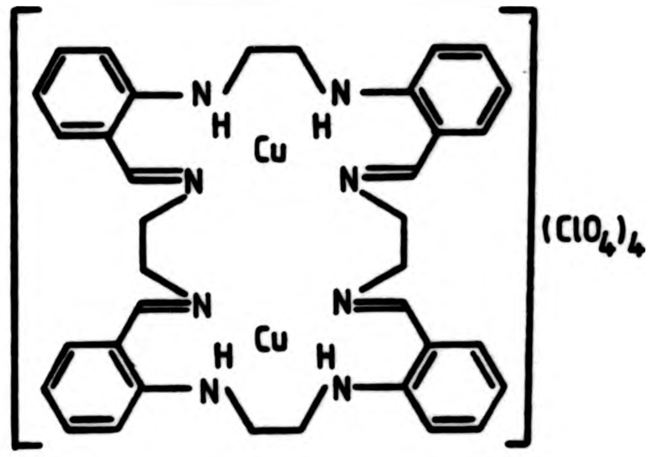
{(5,6,7,8,15,16,23,24,25,26,33,34-Dodecahydrotribenzo[e,m,s,a'][1,4,-8,11,15,18,22,25]octaazacyclooctacosine-N^{5},N^{8},N^{14},N^{35}:N^{17},N^{23},N^{26},N^{32}-dicopper}triperchlorate.



[Cu$_2$(H$_4$cyendimer)](ClO$_4$)$_3$ 8.XIIIB1

Copper(II) perchlorate (0.2 g, 0.55 mmol) in methanol (12 cm^3) was added to a suspension of H$_4$cyendimer (8.XIII) (0.1 g, 0.17 mmol) in refluxing THF (60 cm^3). After 1 min the translucent green solution was filtered, and left to cool. After 18 h, filtering gave green prisms of {(5,6,7,8,15,16,23,24,25,-26,33,34-dodecahhydrotribenzo[e,-m,s,a'][1,4,8,11,15,18,22,25]octaazacyclooctacosine-N^{5},N^{8},N^{14},N^{35}:N^{17}-,N^{23},N^{26},N^{32})dicopper}triperchlorate (8.XIIIB1) mp 198-200°C, (found: Cu, 12.3; C, 42.2; H, 4.00; N, 10.88. $Cu_2C_{36}H_{40}N_8Cl_3O_{12}$ requires: Cu, 12.6; C, 42.8; H, 4.0; N, 10.9 %). Electronic Spectrum (CH$_3$OH/THF 1:5) λ_{max}/nm (ε): 346 (1641), 450 (1978). ν_{max}/cm: 3578 b, 3258, 3058, 2943, 2878, 1617, 1600, 1576, 1502, 1426, 1407, 1365, 1248, 1210, 1202, 1164, 1075 b, 970, 930, 902, 882, 864, 790, 760, 624, 381. Crytal density 1.5 gcm^{-3}.

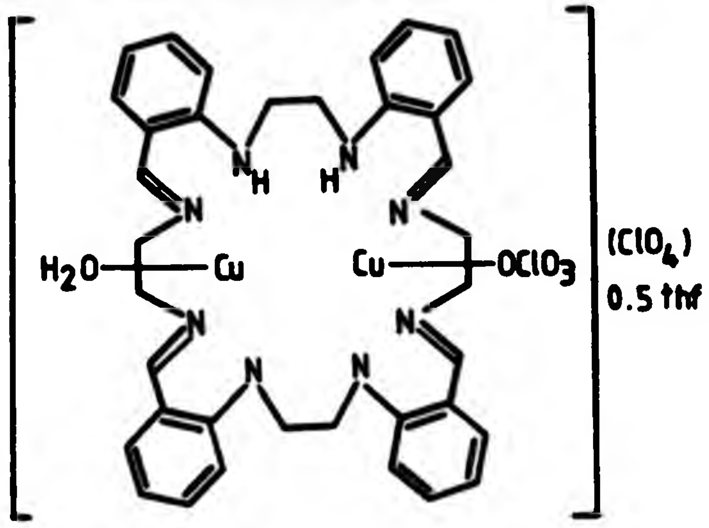
{(5,6,7,8,15,16,23,24,25,26,33,34-Dodecahydrotribenzo[e,m,s,a'][1,4,8,11,15,18,22,25]octaazacyclooctacosine-N^5,N^8,N^{14},N^{35}:N^{17},N^{23},N^{26},N^{32})copper(II)}tetraperchlorate.



[Cu_2(H_4cyendimer)](ClO_4)$_4$ 8.XIIIB2

H_4cyendimer (8.XIIIB2) (0.6 g, 1 mmol) and copper(II) perchlorate (0.9 g, 2.4 mmol) was dissolved in chloroform/methanol (8:3 , 220 cm^3) at room temperature. Addition of petrol (40:60 , 100 cm^3) and filtration gave a light green powder of {(5,6,7,8,15,16,23,24,25,26,33,34-dodecahydrotribenzo[*e*,*m*,*s*,*a*'][1,4,8,11,15,18,22,25]octaazacyclooctacosine-N^5,N^8,N^{14},N^{35}:N^{17},N^{23},N^{26},N^{32})copper(II)}tetraperchlorate (8.XIIIB2) (0.86 g, 0.78 mmol, 78 % yield). mp 220°C, (found: C, 39.5; H, 3.7; N, 10.0. $Cu_2C_{36}H_{40}N_8Cl_4O_{16}$ requires: C, 39.0; H, 3.6; N, 10.1 %). ν_{max}/cm: 3280, 3200, 3100, 1640, 1605, 1581, 1499, 1324, 1299, 1238, 1220, 1204, 1100 b, 970, 881, 807, 807, 765, 737, 651, 628, 556.

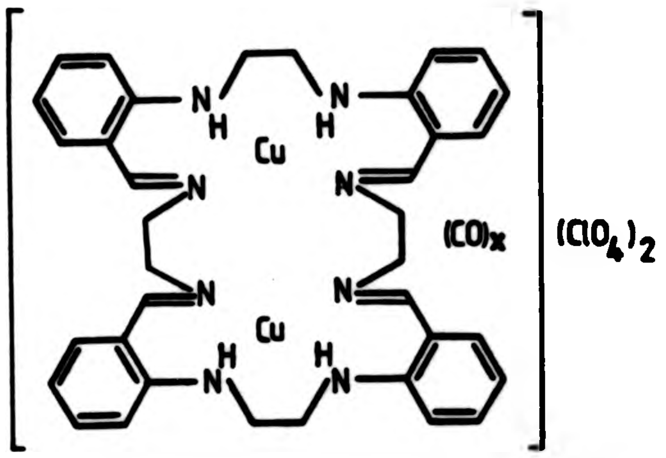
{(6,7,15,16,23,24,25,26,33,34-Decahydrotribenzo[e,m,s,a'][1,4,8,11,15,18,22,25]octaazacyclooctacosine-N^5,N^{35},N^{32},N^{26}:N^8,N^{14},N^{17},N^{23})dicopper(II)}diperchlorate.hydrate.tetrahydrofuran.



[Cu_2(H_2cyendimer)(ClO_4)(H_2O)](ClO_4).0.5thf 8.XIIIB3

$Cu(CH_3CN)_4(ClO_4)$ (0.55 g, 1.7 mmol) in degassed methanol (10 cm^{-3}) was added to a suspension of H_4cyendimer (0.4 g, 0.7 mmol) in thf (50 cm^{-3}). The mixture was diffused with nitrogen, and brown-green crystals of {(6,7,15,16,23,24,25,26,33,34-decahydrotribenzo[e,m,s,a']-[1,4,8,11,15,18,22,25]octaazacyclooctacosine-N^5,N^{35},N^{32},N^{26}:N^8,N^{14},N^{17}-N^{23})dicopper(II) }diperchlorate.hydrate.tetrahydrofuran (8.XIIIB3) were scraped from the side of the flask (0.9 g, 0.94 mmol, 13 % yield). (found: C, 48.8; H, 4.6; N, 11.5. $Cu_2C_{40}H_{48}N_8Cl_2O_{10}$ requires C, 49.5; H, 4.9; N, 11.3 %). ν_{max}/cm: 3500 b, 1660, 1632, 1601, 1532, 1409, 1344, 1305, 1198, 1187, 1090 b.

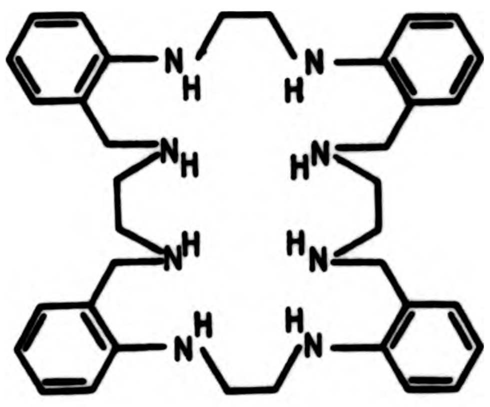
{(5,6,7,8,15,16,23,24,25,26,33,34-Dodecahydrotribenzo[e,m,s,a'][1,4,8,11,15,18,22,25]octaazacyclooctacosinedicopper(I)(carbonmonoxide))-diperchlorate.



$[Cu_2(H_4cyendimer)(CO)_x](ClO_4)_2$ **8.XIIIB4**

In an argon atmosphere, H_4cyendimer (0.25 g, 0.43 mmol) was added to thf (50 cm^{-3}) which had been distilled from $LiAlH_4$. For twenty minutes carbon monoxide was slowly diffused through the above suspension and also during the addition and reaction of $Cu(CH_3CN)_4(ClO_4)$ (0.58 g, 1.8 mmol). After one hour of the diffusion of carbon monoxide at room temperature, filtration and washing with diethyl ether (dried) followed by 20 min suction in the argon/CO atmosphere gave a white powder of {(5,6,7,8,15,16,23,24,25,26,33,34-dodecahydrotribenzo[e,m,s,a'][1,4,8,11,15,18,22,25]octaazacyclooctacosinedicopper(I)(carbon monoxide))diperchlorate (8.XIIIB4) (0.37 g, 0.38 mmol, 88 % yield). (found: Cu, 13.4; C, 46.6; H, 4.1; N, 11.2; Cl, 7.2. $Cu_2C_{38}H_{40}N_8Cl_2O_{10}$ requires: Cu, 13.1; C, 47.2; H, 4.2; N, 11.6; Cl, 7.3 %). ν_{max}/cm: 3400 b, 3270, 3250, 2088, 1627, 1602, 1588, 1502, 1309, 1205, 1100, 970, 787, 752.

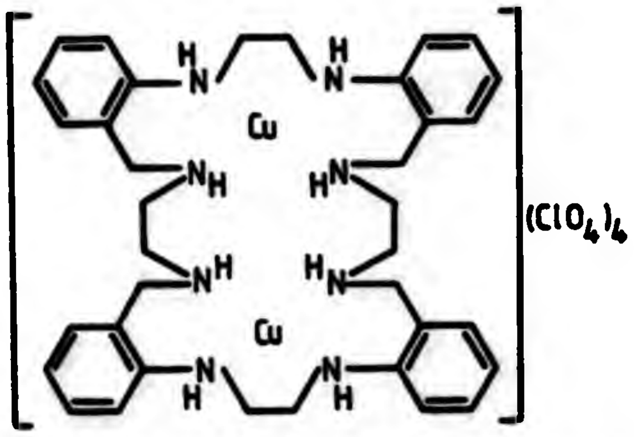
5,6,7,8,13,14,15,16,17,18,23,24,25,26,31,32,33,34,35,36-Eicosahydrotetrabenzo[e,m,s,a'][1,4,8,11,15,18,22,25]octaazacyclooctacosine.



H_{12}cyendimer 8.XIV

BH_3/thf (35 cm^3, 1 mol dm^{-3} solution, 35 mmol) was added in 5 cm^3 portions over a 20 min period, under nitrogen to H_4cyendimer (8.XIII) (0.69 g, 1.16 mmol). After refluxing for 1 h, distilled water (35 cm^3) was added, and the mixture evoporated to a volume of 30 cm^3 under reduced pressure at 50°C. Filtering and recrystallisation from dmf (20 cm^3) gave colourless granular crystals of 5,6,7,8,13,14,15,16,17,18,-23,24,25,26,31,32,33,34,35,36-eicosahydrotetrabenzo[e,m,s,a'][1,4,8,11,15,18,22,25]octaazacyclooctacosine (8.XIV) (0.59 g, 0.99 mmol, 86 % yield), mpt 228-230°C, (found: C, 73.0; H, 8.1; N, 18.9. $C_{36}H_{48}N_8$ requires: C, 72.9; H, 8.2; N, 18.9 %). Electronic Spectrum (dmf) λ_{max}/nm (ϵ): 268 (1066), 300 (710). ν_{max}/cm 3317, 3271, 3210, 3170, 3108, 3070, 3042, 3018, 2947, 2935, 2905, 2890, 2846, 1605, 1584, 1563, 1505, 1454, 1441, 1355, 1347, 1343, 1326, 1305, 1235, 1228, 1225, 1129, 1113, 1105, 1085, 1042, 1017, 932, 902, 864, 807, 772, 746, 726, 615, 606, 465, 415. Mass Spectrum m/e: 592(M^*=55 %), 457(15), 431(15), 426(10), 414(28), 402(12), 342(10), 332(13), 311(18), 309(63), 298(18), 297(72), 296(84), 295(100), 235(49), 225(31), 201(15), 161(57), 149(90), 147(100), 132(97), 132(97), 130(100), 121(67), 120(100), 118(100), 106(99), 91(9), 77(16).

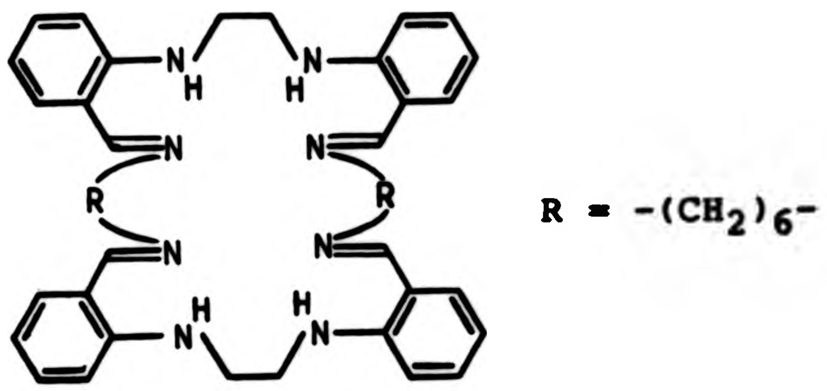
⟨(5,6,7,8,13,14,15,16,17,18,23,24,25,26,31,32,33,34,35,36-Eicosahydrotetrabenzo[e,m,s,a'][1,4,8,11,15,18,22,25]octaazacyclooctacosine-N^5,N^8,-N^{14},N^{35}:N^{17},N^{23},N^{26},N^{32})dicopper(II)⟩perchlorate.



[Cu$_2$(H$_{12}$cyendimer)](ClO$_4$)$_4$ 8.XIVB.

Copper(II) perchlorate (0.15 g, 0.4 mmol) in methanol (15 cm^3) was added to a suspension of H$_{12}$cyendimer (8.XIV) (0.1 g, 0.17 mmol) in chloroform (15 cm^3). The mixture was refluxed for 1 min which resulted in a red-brown solution, and addition of petrol (40:60 , 40 cm^3) induced crystallisation to give a light brown powder after filtration of ⟨(5,6,7,8,13,14,15,16,17,18,23,24,25,26,31,32,33,34,35,-36-eicosahydrotetrabenzo[*e*,*m*,*s*,*a*'][1,4,8,11,15,18,22,25]octaazacyclooctacosine-N^5,N^8,N^{14},N^{35}:N^{17},N^{23},N^{26},N^{32})dicopper(II)⟩perchlorate (8.XIVB) (0.18 g, 0.15 mmol, 89 % yield), mp 220°C(e), (found: Cu, 11.2; C, 37.9; H, 4.3; N, 10.0. $Cu_2C_{36}H_{48}N_8Cl_4O_{16}$ requires: Cu, 11.4; C, 38.7; H, 4.3; N, 10.0 %). Electronic Spectrum (methanol) λ_{max}/nm (ϵ): 328 (2250), 375 (1618). ν_{max}/cm: 3560,3260, 2970, 2900, 1635, 1620, 1595, 1502, 1470, 1420, 1370, 1219, 1080 b, 867, 828, 765, 719, 619.

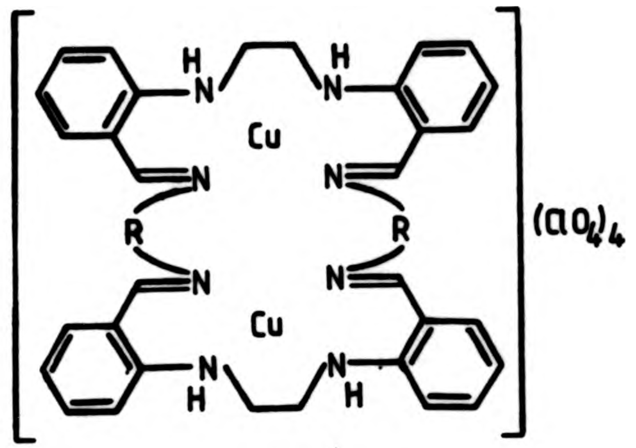
5,6,7,8,15,16,17,18,19,20,27,28,29,30,37,38,39,40,41,42-Eicosahydrotetrabenzo[e,q,w,i'][1,4,8,15,19,22,26,33]octaazacyclohexatriacontine.



H_4Cyhexdimer 8.XV

4,7-Diaza-2,3:8,9-dibenzodecane-1,10-dione (8.I) (1.34 g, 5 mmol) and 1,6-diaminohexane (0.67 g, 5.8 mmol) was heated in refluxing ethanol (100 cm^3) under nitrogen for 5 h. Acetic acid (0.003 g, 0.05 mmol) was added and refluxing continued for a further 48 h. Cooling, filtering, and recrystallisation from dichloromethane (40 cm^3) gave fine white needles of 5,6,7,8,15,16,17,18,19,20,27,28,29,30,37,38,39,-40,41,42-eicosahydrotetrabenzo[e,q,w,i'][1,4,8,15,19,22,26,33]octaazacyclohexatriacontine (8.XV) (1.42 g, 2.0 mmol, 82 % yield), (found: C, 75.3; H, 8.1; N, 15.8. $C_{44}H_{56}N_8$ requires: C, 75.8; H, 8.1; N, 16.8 %). ν_{max}/cm: 3250, 3175, 3100, 3030, 2938, 2895, 2860, 2840, 1640, 1621, 1595, 1530, 1370, 1333, 1284, 1212, 1167, 1150, 1104, 987, 972, 880, 750, 668, 636, 614, 510, 468.

{(5,6,7,8,15,16,17,18,19,20,27,28,29,30,37,38,39,40,41,42-Eicosahydrotetrabenzo[e,q,w,i'][1,4,8,15,19,22,26,33]octaazacyclohexatriacontine-N^5,N^8,N^{14},N^{21},N^{27},N^{30},N^{36},N^{43})dicopper(II)perchlorate.

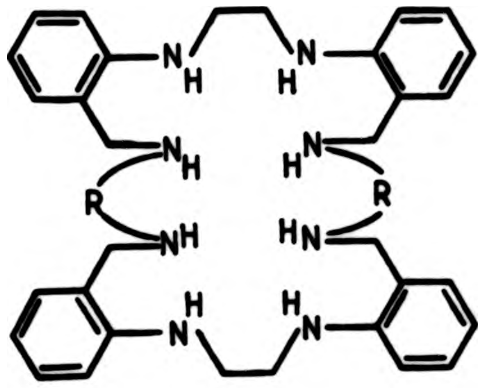


R = $-(CH_2)_6-$

$[Cu_2(H_4Cyhexdimer)](ClO_4)_4$ **8.XVB**

Copper(II) perchlorate (0.24 g, 0.65 mmol) in TEOF (10 cm^3) was added to a refluxing solution of H_4cyhexdimer (8.XV) (0.2 g, 0.28 mmol) in TEOF (50 cm^3). Cooling and filtering gave a red powder of 5,6,7,8,15,16,17,18,19,20,27,28,29,30,37,38,39,40,41,42-eicosahydrotetetrabenzo[e,q,w,i'][1,4,8,15,19,22,26,33]octaazacyclohexatriacontine-N^5,N^8,N^{14},N^{21},N^{27},N^{30},N^{36},N^{43})dicopper(II)perchlorate (8.XVB) (0.3 g, 0.25 mmol, 88 % yield), (found: C, 42.3; H, 4.5; N, 8.6. $Cu_2C_{44}H_{56}N_8$-Cl_4O_{16} requires: C, 43.3; H, 4.6; N, 9.2 %). ν_{max}/cm: 3500 b, 3370 b, 3180 b, 2940 b, 2870, 1680, 1648, 1640, 1611, 1586, 1503, 1315, 1240, 1220, 1100 b, 935, 769, 631.

5,6,7,8,13,14,15,16,17,18,19,20,21,22,27,28,29,30,35,36,37,38,39,40,-41,42,43,44-Octacosahydrotetrabenzo[e,q,w,i'][1,4,8,15,19,22,26,33]octaazacyclohexatriacontine.

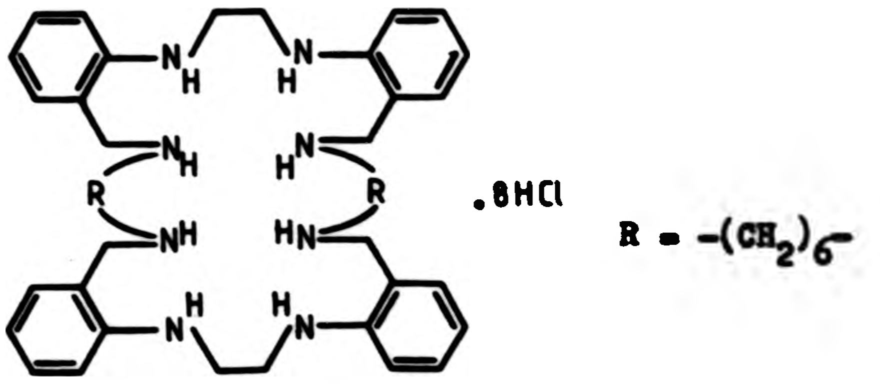


R = $-(CH_2)_6-$

H_{12}Cyhexdimer 8.XVI

BH_3/thf (20 cm^3, 1 mol dm^{-3}, 0.5 mmol) was added to H_4cyhexdimer (8.XV) (0.35 g, 0.5 mmol) under nitrogen. After refluxing for 18 h, distilled water (1 cm^3) was added followed by sodium hydroxide solution (2.5 cm^3, 2 mol dm^{-3}). The organic layer was separated and mixed with the same amount of alkali solution as previously used, shaken well and then evaporation of the organic phase to 5 cm^3 over a period of 7 days at room temperature gave white crystals of 5,6,7,8,-13,14,15,16,17,18,19,20,21,22,27,28,29,30,35,36,37,38,39,40,41,42,43,-44-octacosahydrotetrabenzo[e,q,w,i'][1,4,8,15,19,22,26,33]octaazacyclohexatriacontine. (8.XVI) (0.32 g, 0.46 mmol, 91 % yield), (found: C, 74.2; H, 9.5; N, 15.8. $C_{44}H_{64}N_8$ requires: C, 74.9; H, 9.2; N, 15.9 %). ν_{max}/cm: 3405, 3390, 1613, 1593, 1525, 1348, 1319, 1295, 1277, 1232, 1222, 1199, 1170, 1151, 1077, 1059, 1010, 925, 758, 484.

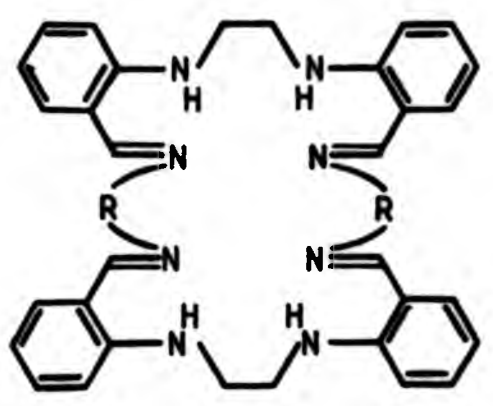
5,6,7,8,13,14,15,16,17,18,19,20,21,22,27,28,29,30,35,36,37,38,39,40,41,42,43,44-Octacosahydrotetrabenzo[e,q,w,i'][1,4,8,15,19,22,26,33]octa(azahydrochloride)cyclohexatriacontine.



H_{12}CyhexdimerCl$_8$ 8.XVIC

BH_3/thf (20 cm^3, 1 mol dm^{-3}, 0.5 mmol) was added to H_4cyhexdimer (8.XV) (0.35 g, 0.5 mmol) under nitrogen. After refluxing for 24 h, distilled water (2 cm^3) and concentrated hydrochloric acid (15 cm^3) was added, and refluxing continued for 3 days. The volume was then reduced to 5 cm^3 at 60°C at low pressure, followed by the addition of concentrated hydrochloric acid (10 cm^3)and further evaporation to 5 cm^3. Filtering and washing with methanol (2 cm^3) gave a white powder of 5,6,7,8,13,14,15,16,17,18,19,20,21,22,27,28,29,30,35,36,37,38,39,40,41,42,43,44-octacosahydrotetrabenzo[e,q,w,i'][1,4,8,15,19,22,26,33]octa(azahydrochloride)cyclohexatriacontine (8.XVIC) (0.32 g, 0.32 mmol, 65 % yield), (found: C, 54.7; H, 7.3; N, 10.4; Cl, 30.1. $C_{44}H_{72}N_8Cl_8$ requires: C, 53.0; H, 7.2; N, 11.2; Cl, 28.5 %). ν_{max}/cm: 3400-2400, 1615, 1594, 1530, 1475, 1450, 1385, 1320, 1288, 1233, 1172, 1120, 1098, 1060, 1011, 968, 925, 800, 755, 615, 498, 472.

5,6,7,8,15,17,24,25,26,27,34,36-Dodecahydro-16,35-dihydroxytetrabenzo-[e,n,t,c'][1,4,8,12,16,19,23,27]octaazacyclotriacontine.

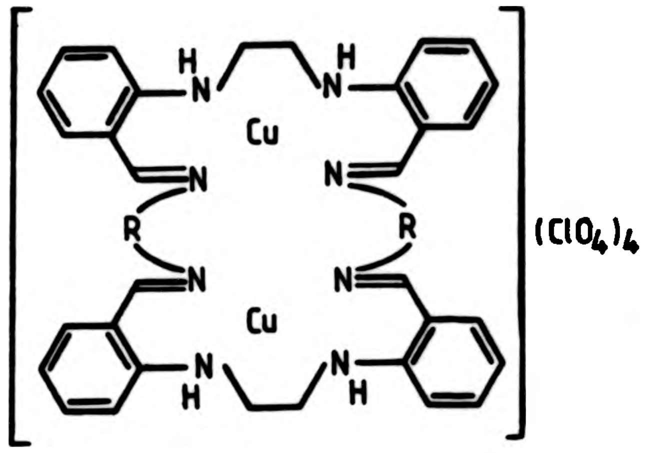


R = $-CH_2CHOHCH_2-$

H_4Cyprodimer 8.XVII

1,3-Diaminopropan-2-ol (0.48 g, 5.28 mmol) in methanol (20 cm^3) was added to a refluxing solution of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (8.I) (1.34 g, 5 mmol) in chloroform (50 cm^3) under nitrogen. After 25 h, acetic acid (0.003 g, 0.05 mmol) was added, and refluxing continued for 24 h. The solution was cooled and filtered, and the product recrystallised from dichloromethane to give white microcrystals of 5,6,7,8,15,17,24,25,26,27,34,36-dodecahydro-16,35-dihydroxytetrabenzo[e,n,t,c'][1,4,8,12,16,19,23,27]octaazacyclotriacontine (8.XVII) (1.03 g, 1.6 mmol, 64 % yield), (found: C, 71.2; H, 6.8; N, 17.9. $C_{38}H_{44}N_8O_2$ requires C, 70.8; H, 6.8; N, 17.8 %).ν_{max} 3500, 3210, 3090, 3025, 2923, 2880, 2857, 1630, 1600, 1578, 1518, 1463, 1453, 1327, 1320, 1630, 1600, 1578, 1518, 1463, 1453, 1327, 1320, 1200, 1155, 1135, 1091, 1050, 1042, 1033, 972, 873, 747, 600 cm^{-1}.

{(5,6,7,8,15,17,24,25,26,27,34,36-Dodecahydro-16,35-dihydroxytetrabenzo[*e*,*n*,*t*,*c'*][1,4,8,12,16,19,23,27]octaazacyclotriacontine-N^5,N^8,N^{14},-N^{37}:N^{18},N^{24},N^{27},N^{33})dicopper}perchlorate.

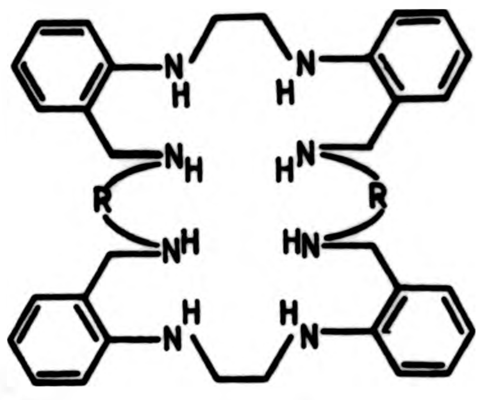


R = $-CH_2CHOHCH_2-$

$[Cu_2(H_4cyprodimer)](ClO_4)_4$ **8.XVIIB**

A solution fo copper(II) perchlorate (0.26 g, 0.70 mmol) in triethylorthoformate (5 cm^3) was added to a refluxing solution of H_4cyprodimer (8.XVII) (0.2 g, 0.31 mmol) in triethylorthoformate (240 cm^3). Cooling and filtering gave a dark red powder of 5,6,7,8,-15,17,24,25,26,27,34,36-dodecahydro-16,35-dihydroxytetrabenzo-[*e*,*n*,*t*,-*c'*][1,4,8,12,16,19,23,27]octaazacyclotriacontine-N^5,N^8,N^{14},N^{37}:N^{18},-N^{24},N^{27},N^{33})dicopper}perchlorate (8.XVIIB) (0.33 g, 0.28 mmol, 91 % yield), (found: C, 39.5; H, 3.6; N, 9.8. $Cu_2C_{38}H_{44}N_8Cl_4O_{16}$ requires: C, 39.2; H, 3.8; N, 9.6 %). ν_{max}/cm: 3250 b, 2980, 2940, 1650, 1612, 1590, 1500, 1100 b, 935, 768, 705, 630.

5,6,7,8,13,14,15,17,18,19,24,25,26,27,32,33,34,36,37,38-Eicosahydro-16,35-dihydroxytetrabenzo-[e,n,t,c'][1,4,8,12,16,19,23,27]octa(azahydrochloride)cyclotriacontine.

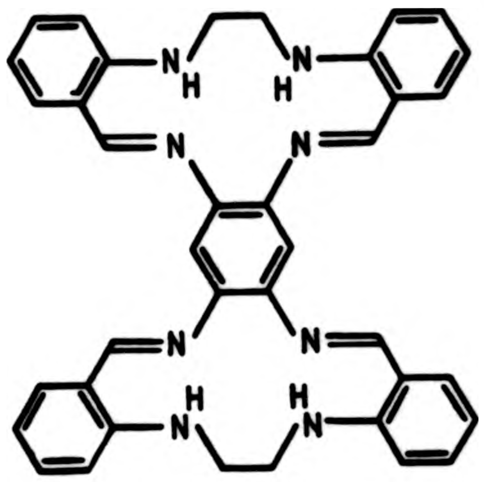


R = $-CH_2CHOHCH_2-$

$\underline{H}_{12}$**cyprodimerCl$_{\underline{8}}$ 8.XVIIIC**

BH_3/thf (20 cm^3, 1 mol dm^{-3} solution, 20 mmol) was added in 5 cm^3 portions over a 20 min period, under nitrogen to H_4cyprodimer (8.XVII) (0.3 g, 0.48 mmol). After refluxing for 24 h, distilled water (2 cm^3) and concentrated hydrochloric acid was added, and refluxing continued for 3 days. The volume was then reduced to 5 cm^3 at 60°C under reduced pressure, followed by the further addition of concentrated hydrochloric acid (5 cm^3) and evaporation to 5 cm^3. Filtering and washing with methanol (5 cm^3) gave a white powder of 5,6,7,8,13,14,15,17,18,19,24,25,26,27,32,33,34,36,37,38-eicosahydro-16,35-dihydroxytetrabenzo-[e,n,t,c'][1,4,8,12,16,19,23,27]octa(azahydrochloride)cyclotriacontine (8.XVIIIC) (0.28 g, 0.30 mmol, 62 % yield). ν_{max}/cm: 3400-2400, 1617, 1597, 1537, 1515, 1472, 1386, 1324, 1270, 1154, 1130, 1097, 1084, 1060, 983, 765, 731, 625, 480, 450.

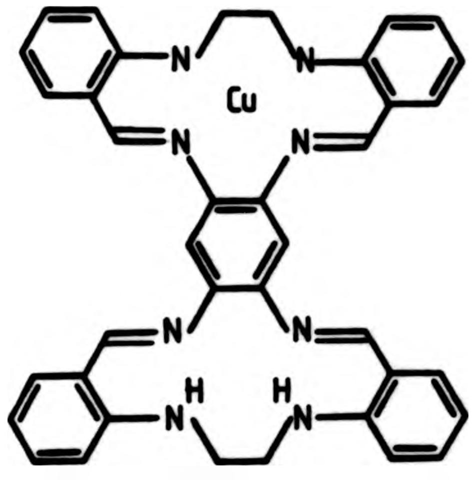
5,6,7,8,22,23,24,25-Octahydrotetrabenzo[f,f',1,1']benzo[1,2-b:4,5-b']-bis[1,4,8,11]tetraazacyclotetradecane.



H_4bicyphen 8.XIX

4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (8.I) (3.2 g, 12.0 mmol) was heated in refluxing ethanol (500 cm^3) under nitrogen. 1,2,4,5-tetraaminobenzene tetrahydrochloride (2.0 g, 7 mmol) was added in 15 approximately equal amounts over a period of 30 min. After each addition a deep red colour was produced which was discharged in each case by the dropwise addition of sodium methoxide solution (0.52 mol dm^{-3}) until a yellow/orange colour was obtained. (Total 45 cm^{-3}, 23.4 mmol). Refluxing was continued for 24 h and the mixture filtered hot. Recrystallisation from pyridine (230 cm^3) gave yellow plates of 5,6,7,8,22,23,24,25-octahydrotetrabenzo[f,f',1,1']benzo[1,2-b:4,5-b']-bis[1,4,8,11]tetraazacyclotetradecane (8.XIX) (2.75 g, 4.57 mmol, 76 % yield), mp 330°C(d), (found: C, 75.2; H, 6.0; N, 18.3. $C_{38}H_{34}N_8$ requires: C, 75.7; H, 5.7; N, 18.6 %). Electronic Spectrum (dmf) λ_{max}/nm (ε): 270 (1896), 320 (1069), 440 (1974). ν_{max}/cm: 3170, 3095, 3070, 3030, 2960, 2890, 2830, 1618, 1598, 1572, 1535, 1522, 1488, 1368, 1338, 1332, 1209, 1162, 1146, 749, 741, 720, 701. Mass Spectrum Field Desorption M^*=602.

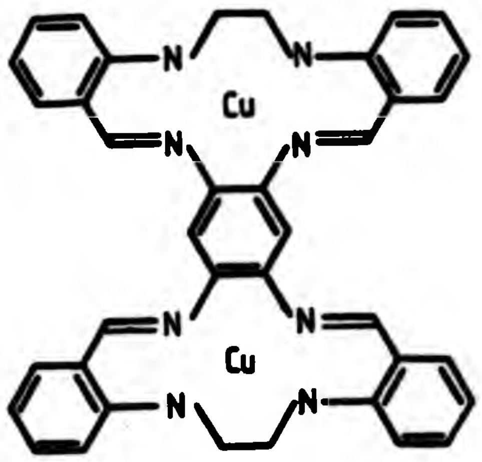
{(6,7,22,23,24,25-Hexahydrotetrabenzo[*f*,*f*',*1*,*1*']benzo[1,2-*b*:4,5-*b*'][1,-[1,4,8,11,1',4',8',11']octaazadicyclotetradecinato(2-)-*N*^{5},*N*^{8},*N*^{14},*N*^{33})-copper(II)}.



[Cu(H$_2$bicyphen)] 8.XIXA1

Copper(II) acetate (0.16 g, 0.8 mmol) in pyridine (20 cm^3) was added to a refluxing solution of H$_4$bicyphen (8.XIX) (0.2 g, 0.33 mmol) in pyridine (150 cm^3) under nitrogen. After 10 min the solution was cooled and left for 20 h before filtering to give purple microcrystals with a green sheen of {(6,7,22,23,24,25-hexahydrotetrabenzo[*f*,*f*',*1*,*1*'-]benzo[1,2*b*:4,5*b*'][1,[1,4,8,11,1',4',8',11']octaazadicyclotetradecinato(2-)-*N*^{5},*N*^{8},*N*^{14},*N*^{33})copper(II)} (8.XIXA1) (0.20 g, 0.31 mmol, 95 % yield), mp >360°C, (found: Cu, 9.4; C, 66.7; H, 4.5; N, 16.2. $CuC_{38}H_{32}N_8$ requires: Cu, 9.6; C, 68.7; H, 4.9; N, 16.9 %). Electonic Spectrum (pyridine 60°C) λ_{max}/nm (ϵ) 350 (492), 510 (526), 650 (240). ν_{max}/cm: 2940, 2860, 1611, 1580, 1516, 1478, 1448, 1391, 1361, 1254, 1220, 1173, 1140, 1035, 956, 944, 847, 835, 741, 629, 617, 585, 556, 545, 496. Laser Raman ν_{max}/cm: 1206, 1293, 1373, 1395, 1460, 1561, 1600.

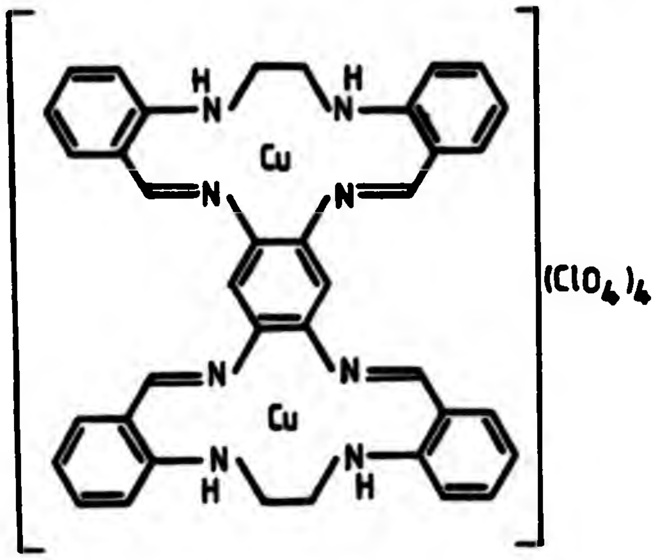
{(6,7,23,24-Tetrahydrotetrabenzo[f,f',1,1']benzo[1,2-b:4,5-b']bis([1,4,8,11]tetraazacyclotetradecinato)(4-)-N^5,N^8,N^{14},N^{33},N^{16},N^{22},N^{25},N^{31})-copper(II)}.



[Cu_2(bicyphen)] 8.XIXA2

A solution of copper(II) perchlorate (0.06 g, 0.15 mmol) in pyridine (10 cm^3) was added to a suspension of [Cu(H_2bicyphen)] (8.XIXA1) (0.1 g, 0.15 mmol) in refluxing pyridine. After 24 h the solution was cooled and filtered to give purple microcrystals with a green sheen of {(6,7,23,24-tetrahydrotetrabenzo[*f*,*f*',*1*,*1*']benzo[1,2-*b*:4,5-*b*']bis[1,4,8,11]tetraazacyclotetradecinato(4-)-N^5,N^8,N^{14},N^{33},N^{16},N^{22},N^{25},N^{31})copper(II)} (8.XIXA2) (0.08 g, 0.11 mmol, 74 % yield), mp >360°C, (found: Cu, 16.8; C, 62.1; H, 4.1 N, 15.3. $Cu_2C_{38}H_{30}N_8$ requires: Cu, 17.5; C, 62.9; H, 4.2; N, 15.4 %). Electronic Spectrum (pyridine) λ_{max}/nm (ε): 355 (823), 510 (769), 630 (491). ν_{max}/cm: 2940, 2860, 1611, 1580, 1516, 1478, 1448, 1391, 1361, 1254, 1220, 1173, 1140, 1035, 956, 944, 847, 835, 741, 629, 617, 585, 556, 545, 496. Laser Raman/cm: 1206, 1293, 1373, 1395, 1460, 1561, 1600.

{(6,7,23,24-Octahydrotetrabenzo[f,f',1,1']benzo[1,2-b:4,5-b']bis([1,4,8,11]tetraazacyclotetradecine)-N^5,N^8,N^{14},N^{33}:N^{16},N^{22},N^{25},N^{31})dicopper(II)}perchlorate.



$[Cu_2(H_4bicyph)](ClO_4)_4$ 8.XIXB

Method A

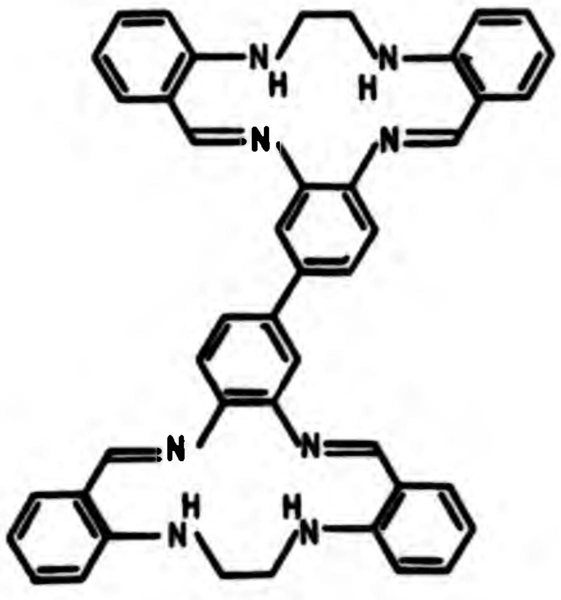
H_4bicyphen (8.XIX) (0.1 g, 0.17 mmol) was extracted from a Soxhlet thimble into a refluxing solution of copper(II) perchlorate (0.15 g, 0.39 mmol) over a period of 24 h under nitrogen. Cooling and filtering gave brown crystals of {(6,7,23,24octahydrotetrabenzo[*f*,*f*',*1*,*1*']benzo[1,2-*b*:4,5-*b*']bis([1,4,8,11]tetraazacyclotetradecine)N^5,N^8,N^{14},N^{33}:N^{16},N^{22},N^{25},N^{31})dicopper(II)dicopper}perchlorate (8.XIXB)(0.1 g, 0.09 mmol, 52 % yield), mp 200°C(d), (found: Cu, 11.0; C, 41.2; H, 3.4; N, 9.9. $Cu_2C_{38}H_{34}N_8Cl_4O_{16}$ requires: Cu, 11.3; C, 40.5; H, 3.0; N, 9.9 %). Electronic Spectrum (pyridine)λ_{max}/nm: 270, 320, 450, 600. ν_{max}/cm: 1612, 1598, 1542, 1536, 1517, 1485, 1362, 1336, 1320, 1314, 1218, 1158, 1100 b, 927, 756, 744, 719, 697, 622, 434.

Method B

A solution of copper(II) perchlorate (0.15 g, 0.4 mmol) in pyridine (5 cm^{-3}) was added to a solution of H_4bicyphen (0.1 g, 0.17

mmol) in refluxing pyridine (25 cm^{-3}). After 1 h the solution was cooled, and the addition of benzene (25 cm^{-3}) gave brown microcrystals of [Cu_2(H_4bicyph)](ClO_4)$_4$ (8.XIXB) (0.15 g, 1.4 mmol, 76 % yield).

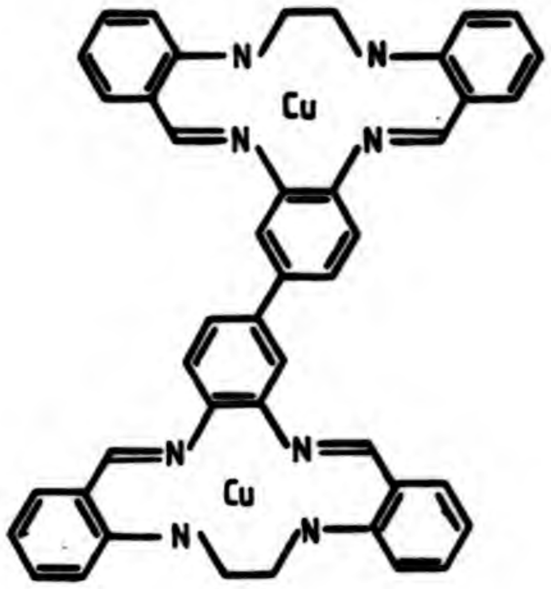
5,6,7,8,24,25,26,27-Octahydrotetrabenzo[f,f',1,1']benzidine[3,4-b:3',5'-b']bis[1,4,8,11]tetraazacyclotetradecane.



H_4bicybenz (8.XX)

4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (8.I) (2.2 g, 8.0 mmol), 4,4'-diaminobenzidine (0.86 g, 4 mmol) and zinc(II) acetate (1.76 g, 9.6 mmol) was heated in refluxing methanol (250 cm^3) for 48 h. Cooling and filtering, followed by recrystallisation from pyridine/methanol (2:5 , 70 cm^3) gave yellow crystals of H_4bicyph (8.XX) (2.0 g, 2.95 mmol, 74 % yield). (found: C, 77.4; H, 5.4; N, 16.1. $C_{44}H_{38}N_8$ requires: C, 77.9; H, 5.6; N, 16.5 %). Electronic Spectrum (chloroform)λ_{max}/nm (ε): 256 (7706), 400 (4155). ν_{max}/cm: 3170, 3095, 3070, 3030, 2960, 2890, 2830, 1618, 1598, 1572, 1338, 1162.

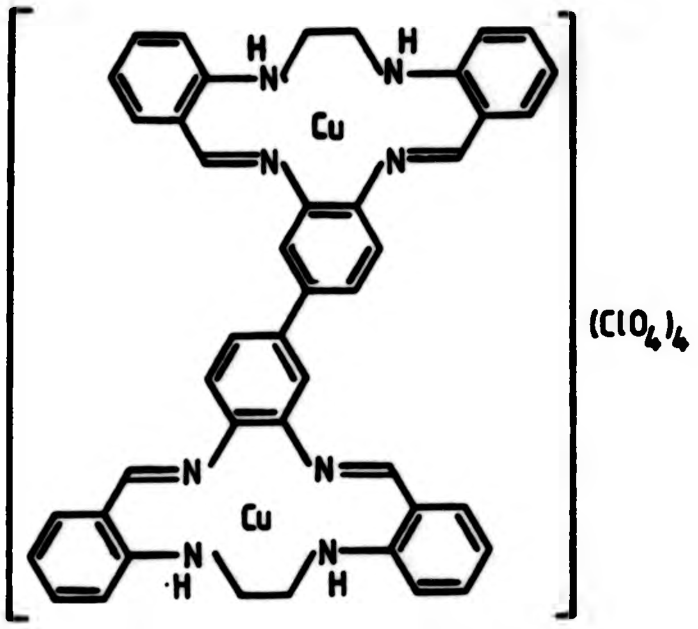
{(6,7.25,26-Tetrahydrotetrabenzo[f,f',1,1']benzidine[3,4-b:3,4-b']bis-[1,4.8.11]tetraazacyclotetradecinato)(4-)-N^5,N^8,N^{14},N^{37},N^{18},N^{24},N^{27},-N^{33})copper(II)}.



[Cu_2(bicybenz)] 8.XXA

H_4bicybenz (0.4 g, 0.59 mmol) was extracted from a Soxhlet thimble into a refluxing solution of copper(II) acetate (0.28 g, 1.4 mmol) in methanol/thf (4:3 , 70 cm ^{3}) for 48 h. Cooling and filtering gave a black powder of {(6,7,25,26-tetrahydrotetrabenzo[f,f',1,1']benzidine[3,4-b:3,4-b']bis([1,4,8,11]tetraazacyclotetradecinato)(4-)-N^5,-N^8,N^{14},N^{37},N^{18},N^{24},N^{27},N^{33})copper(II)} (8.XXA) (0.33 g, 0.41 mmol, 69 % yield), (found: Cu, 15.2; C, 65.2; H, 3.9; N, 13.6. $Cu_2C_{44}H_{34}N_8Cl_4O_{16}$ requires: Cu, 15.8; C, 65.9; H, 4.3; N, 14.0 %). Electronic Spectrum (dmf)λ_{max}/nm (ϵ): 270 (1958), 328 (1246), 440 (1079), 520 (1001), 600 (734).ν_{max}/cm: 3050, 2850, 1614, 1577, 1520, 1362, 1190, 1143, 748.

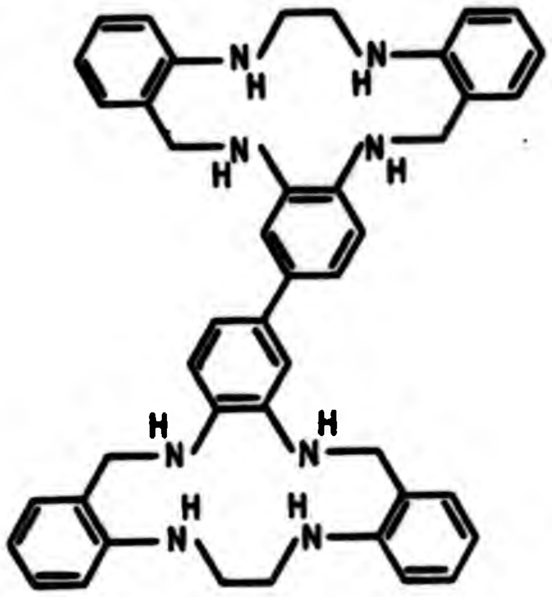
{(6,7,25,26-Tetrahydrotetrabenzo[f,f',1,1']benzidine[3,4-b:3,4-b']bis-[1,4,8,11]tetraazacyclotetradecine)-N^{5},N^{8},N^{14},N^{37},N^{18},N^{24},N^{27},N^{33})dicopper(II)}perchlorate.



[Cu$_2$(H$_4$bicybenz)](ClO$_4$)$_4$ 8.XXB

A solution of copper(II) perchlorate (0.6 g, 1.6 mmol) in methanol (10 cm^{-3}) was added to a warmed solution of H$_4$bicybenz (0.53 g, 0.73 mmol) in dmf (20 cm^{-3}). After 24 h the mixture was filtered to give dark brown micro crystals of {(6,7,25,26-tetrahydrotetrabenzo[f,-f',1,1']benzidine[3,4-b:3,4-b']bis[1,4,8,11]tetraazacyclotetradecine)-N^{5},N^{8},N^{14},N^{37},N^{18},N^{24},N^{27},N^{33})dicopper(II)}perchlorate (8.XXB) (0.62 g, 0.5 mmol, 71 % yield), (found: Cu 10.1; C, 44.1; H, 3.0; N, 9.6. $Cu_2C_{44}H_{38}N_8Cl_4O_{16}$ requires: Cu, 10.6; C, 43.9; H, 3.2; N, 9.3 %). Electronic Spectrum (dmf)λ_{max}/nm (ε): 270 (6019), 308 (3760), 330 (3700), 440 (3310), 470 (3310) 520 (2295), 650 (169). ν_{max}/cm: 1620, 1551, 1420, 1385, 1300, 1230, 1192, 1168, 1100, 760, 628.

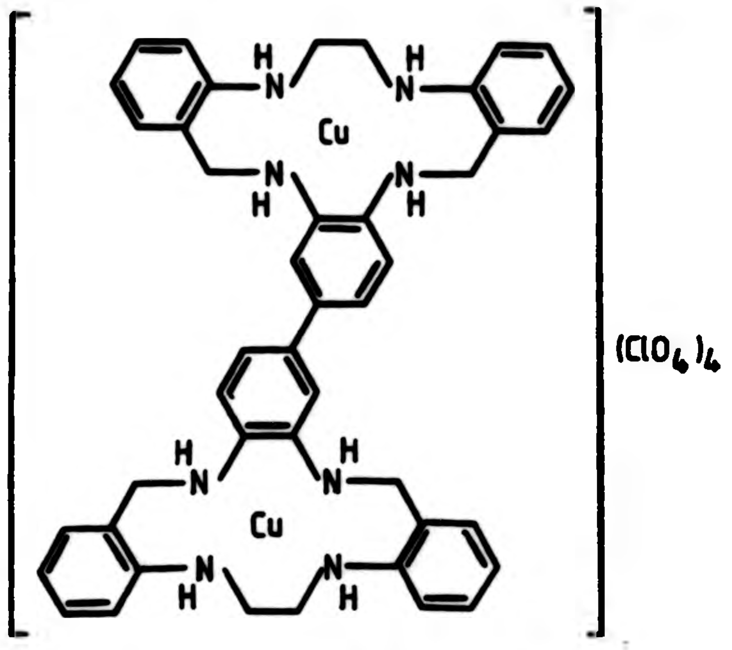
5,6,7,8,13,14,18,19,24,25,26,27,32,33,37,38-Hexadecahydrotetrabenzo[f,f',1,1']benzidine[3,4-b:3',5'-b']bis[1,4,8,11]tetraazacyclotetradecane.



H_{12}bicybenz 8.XXI

BH_3/thf (40 cm^3, 0.2 mol dm^{-3}, 8 mmol) was added to H_4bicyph (8.XXV) (0.5 g, 0.74 mmol) under nitrogen. After refluxing for 2 h the solution containing a small amount of dark coloured impurity was filtered and then quenched with thf/water (5:2 , 70 cm^3). Addition of sodium hydroxide solution (10 cm^3, 2 mol dm^{-3}, 20 mmol) and sodium chloride (3 g) and evaporation of the organic layer under reduced pressure at 50°C to 20 cm^3, followed by addition of a methanolic solution of hydrochloric acid (10:1 , 55 cm^3) gave a clear solution. Addition of sodium hydroxide solution to approx pH 7 (20 cm^3, 2 mol dm^{-3}, 40 mmol) gave a white precipitate. Filtering gave a white powder of 5,6,7,8,13,14,18,19,24,25,26,27,32,33,37,38-hexadecahydrotetrabenzo[f,f',1,1']benzidine[3,4-b:3',5'-b']bis[1,4,8,11]tetraazacyclotetradecane (0.4 g, 0.58 mmol, 79 % yield), (found: C, 76.2; H, 6.6; N, 16.0. $C_{44}H_{46}N_8$ requires: C, 76.9; H, 6.8; N, 16.3 %). Electronic Spectrum (chloroform)λ_{max}/nm (ε):260 (2776), 300 (2719). ν_{max}/cm: 3370, 3320, 1607, 1585, 1516, 1506, 1321, 1306, 1259, 1246, 1136, 1046, 1021, 754.

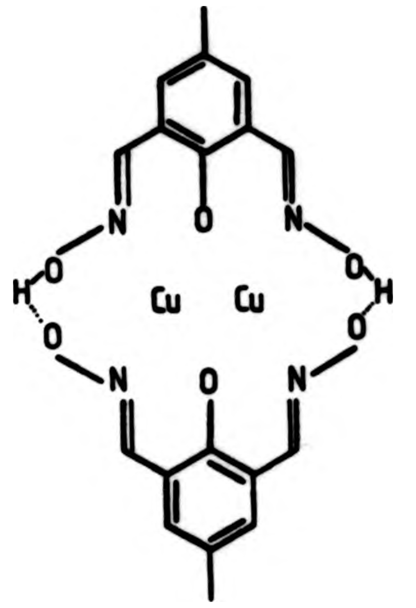
{(5,6,7,8,13,14,18,19,24,25,26,27,32,33,37,38-Hexadecahydrotetrabenzo-[f,f',1,1']benzidine[3,4-b:3,4-b']bis[1,4,8,11]tetraazacyclotetradecine)-N^5,N^8,N^{14},N^{37},N^{18},N^{24},N^{27},N^{33})dicopper(II)}perchlorate.



$[Cu_2(H_{12}bicybenz)](ClO_4)_4$ **8.XXIB**

A solution of copper(II) perchlorate (0.36 g, 0.97 mmol) in methanol (10 cm^{-3}) was added to a suspension of H_{12}bicybenz (0.3 g, 0.43 mmol) in heated thf (20 cm^{-3}). After 24 h the mixture was filtered to give black micro crystals of {(5,6,7,8,13,14,18,19,24,25,-26,27,32,33,37,38-hexadecahydrobenzo[f,f',1,1']benzidine[3,4-b:3,4-b'-]bis[1,4,8,11]tetraazacyclotetradecine)-N^5,N^8,N^{14},N^{37},N^{18},N^{24},N^{27},N^{33}-)dicopper(II)}perchlorate (8.XXIB) (0.45 g, 0.37 mmol, 86 % yield), (found: C, 44.3; H, 3.5; N, 9.2. $Cu_2C_{44}H_{46}N_8Cl_4O_{16}$ requires: C, 44.0; H, 3.9; N, 9.3 %). Electronic Spectrum (dmf)λ_{max}/nm (ε): 268 (5005), 320 (3337), 400 (1902), 440 (2369), 464 (2420) 526 (2169), 646 (267). ν_{max}/cm: 3550, 3200, 1610, 1555, 1495, 1420, 1305, 1100, 770.

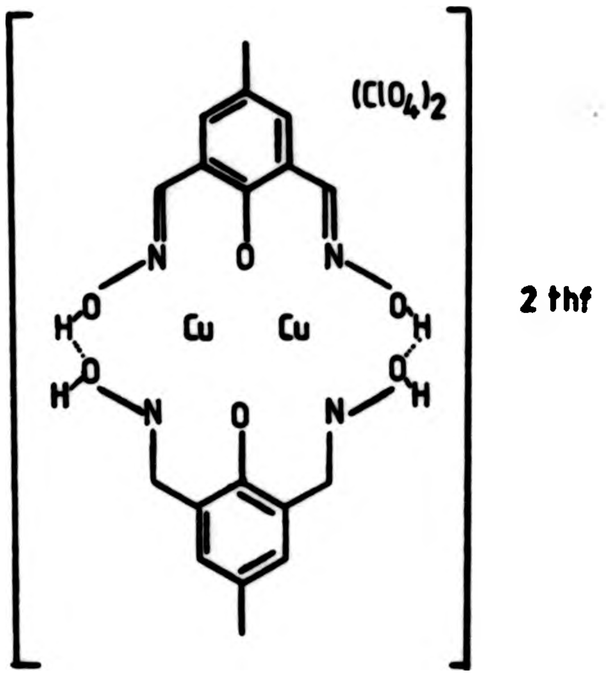
[Cu_2(HDFMP)$_2$] 8.XXIIA



[Cu_2(HDFMP)$_2$] 8.XXIIA

A solution of 1,6-diformaldoxime-4-methylphenol (0.1 g, 0.52 mmol) in dmf (50 cm^3) was added to a solution of copper(II) acetate (0.24 g, 1.2 mmol) in dmf (25 cm^3) which produced a light coloured green powdery suspension. The mixture was filtered and dried to give green microcrystals of [Cu_2(HDFMP)$_2$] (8.XXIIA) (0.13 g, 0.25 mmol, 97 % yield), (found: C, 41.8; H, 3.4; N, 10.9. $Cu_2C_{18}H_{18}N_4O_6$ requires: C, 42.1; H, 3.5; N, 10.9 %). ν_{max}/cm: 3450, 3025, 3005, 2930, 1620, 1600, 1588, 1402, 1350, 1302, 1237, 1190, 1098, 1070, 110, 960, 930, 906, 865, 822, 762, 707, 686, 582, 568, 519, 504, 477, 430.

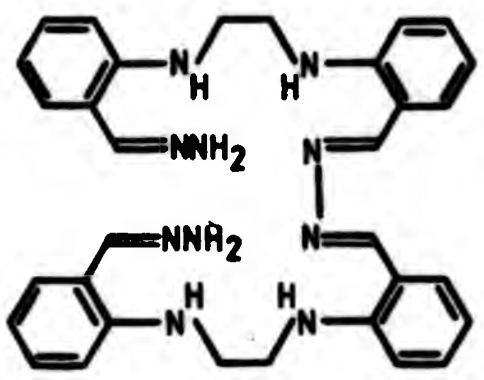
$[Cu_2(H_2DFMP)_2(ClO_4)_2]$.2thf **8.XXIIB**



$[Cu_2(H_2DFMP)_2(ClO_4)_2]$.2thf **8.XXIIB**

A solution of 1,6-diformaldoxime-4-methylphenol (0.1 g, 0.52 mmol) in thf (100 cm^3) was cooled in liquid nitrogen to a temperature just above the freezing point of the mixture. With fast stirring a solution of copper(II) perchlorate (0.5 g, 1.35 mmol) in methanol (25 cm^3) was added which produced a translucent green solution. On warming the mixture to room temperature, green crystals of $[Cu_2(H_2DFMP)_2(ClO_4)_2]$.2thf (8.XXIIB) were deposited (0.09 g, 0.11 mmol, 40 % yield), (found: C, 34.3; H, 3.6; N, 6.6. $Cu_2C_{26}H_{34}N_4Cl_2O_{16}$ requires: C, 34.5; H, 4.00; N, 6.5 %). ν_{max}/cm: 3260, 1642, 1628, 1612, 1572, 1370, 1350, 1313, 1268, 1243, 1200, 1100 b, 1003, 972, 956, 922, 882, 820, 762, 708, 682, 564, 514.

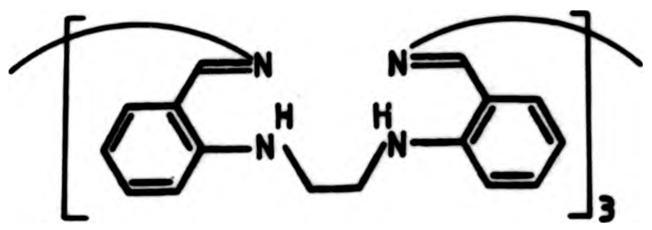
The [3+2] condensation product (Hydrazine:C_2dialdehyde) 8.XXIII



[3+2] product 8.XXIII

Hydrazine hydrate (5 g, 100 mmol) was added to a refluxing suspension of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (8.I) (1.5 g, 5.6 mmol). After refluxing for 2 h the solution was cooled and filtered to give the [3+2] product (8.XXIII) (1.43 g, 2.55 mmol, 91 % yield), (found: C, 68.1; H, 6.4; N, 24.5. $C_{32}H_{36}N_{10}$ requires: C, 68.6; H, 6.5; N, 25.0 %). ν_{max}/cm: 3416, 3300, 1605, 1530, 1488, 1400, 1343, 1331, 1313, 1234, 1202, 1167, 1141, 1085, 1048, 91, 930, 894, 767.

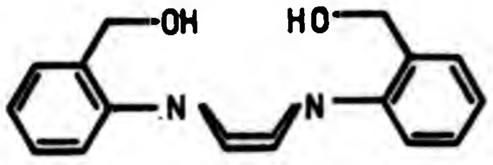
The [3+3] condensation product (Hydrazine:C_2dialdehyde) 8.XXIV



[3+3] product 8.XXIV

The [3+2] product (8.XXIII) (0.2 g, 0.36 mmol) and 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (8.I) (0.1 g, 0.37 mmol). was heated in refluxing methanol (70 cm^3) for 24 h. After cooling and standing for 3 days the solution was filtered and recrystallised from chloroform/methanol (5:1 , 100 cm^3) to give the [3+3] product (8.XXIV) (0.18 g, 0.23 mmol, 64 % yield), (found: C, 72.2; H, 6.2; N, 21.3. $C_{48}H_{48}N_8$ requires: C, 72.7; H, 6.1; N, 21.2 %). ν_{max}/cm: 3260, 1620, 1588, 1521, 1320, 1200, 1163, 1141, 1100, 1080, 1048, 928, 914, 863, 701, 686, 652, 597, 577, 541, 462.

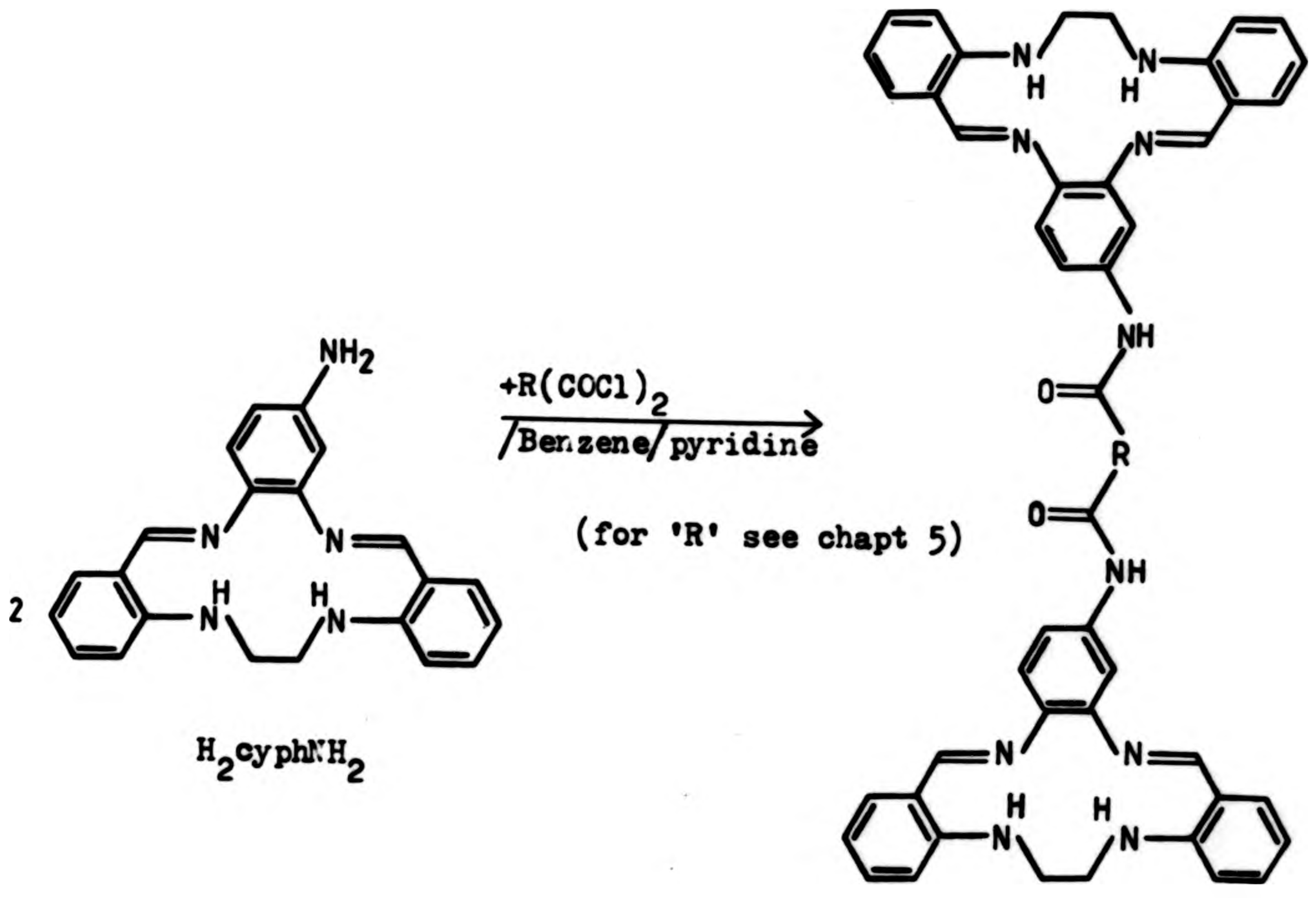
N.'N-di(o-benzylalcohol) piperazine $(C_2)_2$-dialcohol



$(C_2)_2$-dialcohol **8.XXV**

Type 'A' MnO_2 (see chapter 2) (400 g) was placed in a flask and flushed with nitrogen for twenty minutes. The MnO_2 was stirred as tetrahydrofuran (thf) (400 cm^3) was added slowly. C_2-dialcohol (see chapter 2) (30 g, 110 mmol) was added as a solution in thf (50 cm^3), followed by refluxing for 6 h. The product was extracted with hot thf (5 x 200 cm^3), and evaporation of the resulting mixture gave white crystals of N,'N-di(o-benzylalcohol) piperazine ($(C_2)_2$-dialcohol) (8.XXV) (29.5 g, 99 mmol, 90 % yield), (found: C, 72.1; H, 7.3; N, 9.2. $C_{18}H_{22}N_2O_2$ requires C, 72.5; H, 7.4; N, 9.4 %). ^1H nmr Spectrum δ/ppm: 2.98, s, $NC\underline{H}_2$-, 8H; 4.57, d, $-C\underline{H}_2OH$, 4H; 5.08, t, $-C\underline{H}$, 2H; 6.9-7.4, m, aryl protons, 8H. ν_{max}/cm^{-1}: 3300, 3220 b, 1605, 1580, 1500, 1402, 1326, 1292, 1284, 1230, 1222, 1187, 1013. Mass Spectrum m/e: 298(M* = 100%), 163(36), 162(64), 150(51), 149(30), 148(31), 144(40), 136(53), 106(91), 91(35).

General methods for the reaction of H_2cyphNH$_2$ (8.VIII) with acid chlorides and dichlorides.



Acetyl chloride (0.045 g, 0.57 mmol) in benzene (1 cm^3) was added to a solution of H_2cyphNH$_2$ (0.2 g, 0.56 mmol) in pyridine (10 cm^3). The solution was filtered to remove any insoluble component (only found for certain acid chlorides, see chapter 5), and to the filtrate was added methanol (~10 cm^3) which gave a yellow precipitate of the product (for the reaction between acetyl chloride and H_2cyphNH$_2$ a yield of 48 % was recorded, see chapter 5 for analytical data).

To produce the hydrochloride salt of the product, the solvent pyridine was replaced with benzene.

References

1 Green,M., Smith,J., Tasker,P.A. Inorg. Chim. Acta. 1971, 5 17.

2 Peters,R. Ph.d thesis. The Polytechnic of North London. 1982.

3 Original method described by Fleischer,E.B., Sklar,L., Kendall-Torry,A., Tasker,P.A., Taylor,F.B. Inorg. Nucl. Chem. Lett. 1973, 9, 1061.

Appendix

Appendix 1 X-ray crystallographic data.

7.1 $[Cu_2(H_4cyendimer)](ClO_4)_3$ A1

7.2 $[Cu_2(H2cyendimer)(H_2O)(ClO_4)](ClO_4).(.5thf)$ A18

7.3 $[Cu_2(H_2DFMP)_2(ClO_4)_2].2thf$ A31

7.4 $H_{12}cyendimer$ A39

7.5 [Cu(cyphX)] A47

Appendix 2 X-ray structure factors.

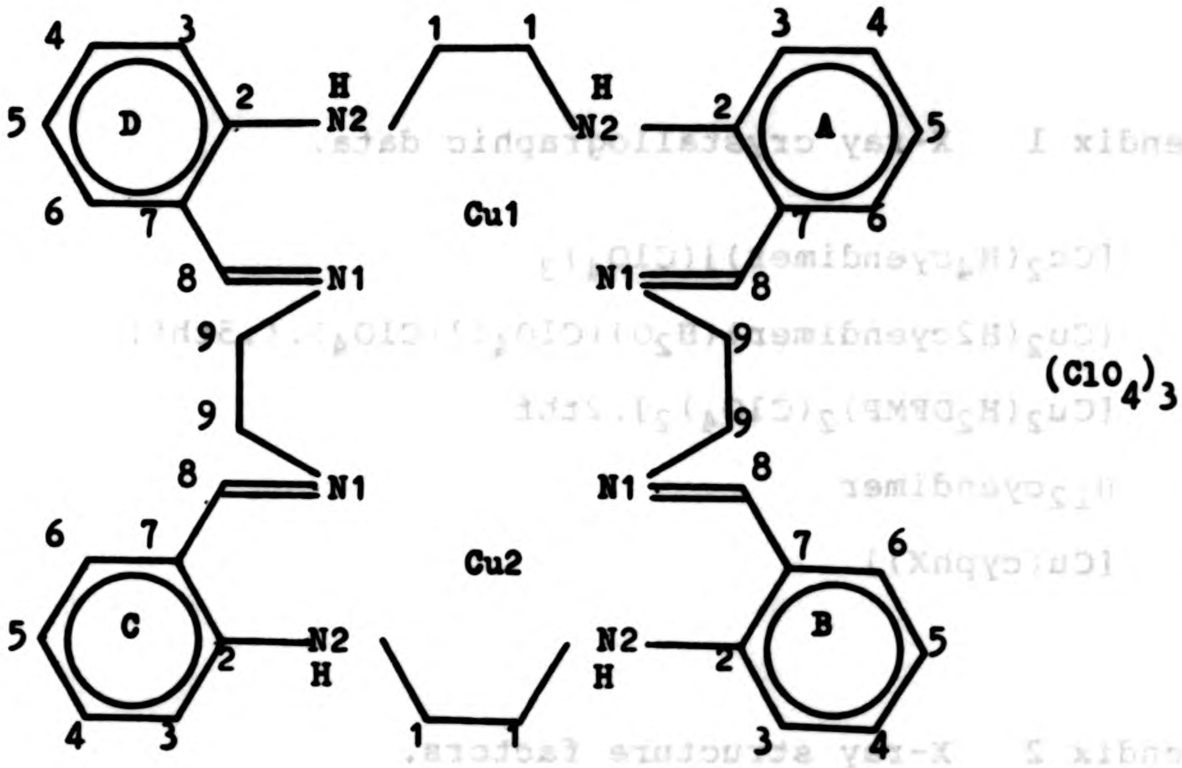
7.1 $[Cu_2(H_4cyendimer)](ClO_4)_3$ A55

7.2 $[Cu_2(H2cyendimer)(H_2O)(ClO_4)](ClO_4).(.5thf)$ A66

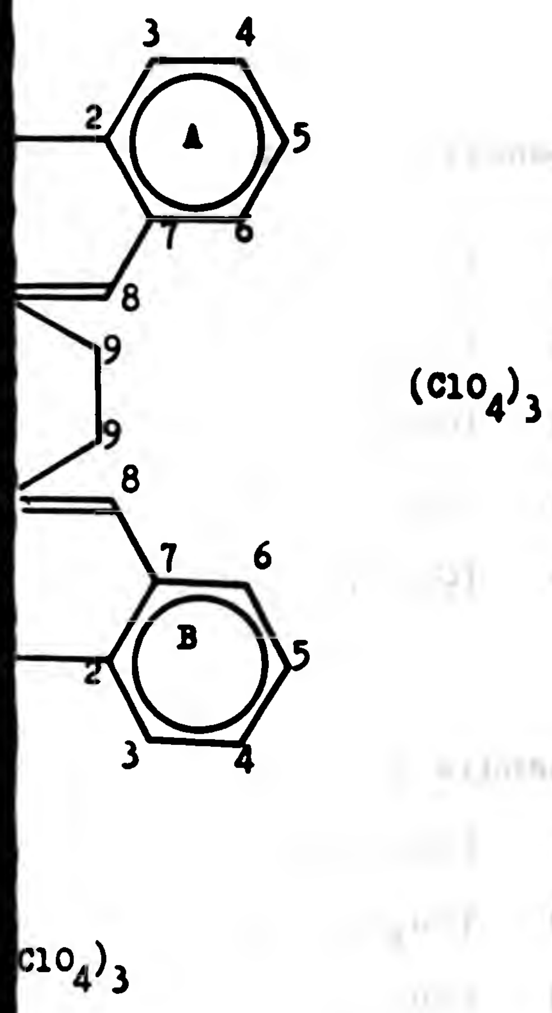
7.3 $[Cu_2(H_2DFMP)_2(ClO_4)_2].2thf$ A81

7.4 $H_{12}cyendimer$ A86

7.5 [Cu(cyphX)] A91



$[Cu_2(H_4cyendimer)](ClO_4)_3$



The X-ray crystallographic data for $[Cu_2H_4cyendimer](ClO_4)_3$ (see section 7.1) schematic diagram facing page.

TABLE 1 Fractional atomic coordinates and thermal parameters (Å^2)

Atom	x	y	z	Uiso or Ueq
Cu(1)	0.00000	0.23977(26)	0.25000	0.0521(16)
Cu(2)	0.1145(2)	0.1725(3)	0.2832(2)	0.052(2)
Cl(1)	0.1583(4)	0.0932(7)	0.6224(4)	0.087(5)
Cl(3)	0.4573(4)	-0.0817(7)	0.8794(4)	0.084(5)
O(11)	0.14178	-0.01857	0.59379	0.1336(60)
O(12)	0.18635	0.17017	0.59429	0.1336(60)
O(13)	0.11094	0.15167	0.64344	0.1336(60)
O(14)	0.21457	0.05146	0.68766	0.1336(60)
O(15)	0.13864	0.90215	0.17750	0.1336(60)
O(16)	0.09869	0.98128	0.05121	0.1336(60)
O(17)	0.18297	1.04202	0.13818	0.1336(60)
O(18)	0.20151	0.96613	0.09900	0.1336(60)
O(31)	0.49306	0.02235	0.91056	0.1336(60)
O(32)	0.42451	-0.15589	0.90865	0.1336(60)
O(33)	0.47273	-0.13512	0.82716	0.1336(60)
O(34)	0.40173	-0.00965	0.84476	0.1336(60)
O(35)	-0.02945	0.67129	0.44980	0.1336(60)
O(36)	0.02587	0.54251	0.43988	0.1336(60)
O(37)	-0.04669	0.44610	0.38109	0.1336(60)
O(38)	-0.10421	0.64864	0.34479	0.1336(60)
O(39)	-0.00396	0.62967	0.39527	0.1336(60)
O(40)	0.02632	0.63861	0.45680	0.1336(60)
Cl(2)	0.2928(4)	0.3797(7)	0.5064(4)	0.073(2)
O(21)	0.2719(12)	0.4392(22)	0.4367(13)	0.120(8)

O(22)	0.2783(15)	0.2602(29)	0.4966(17)	0.165(11)
O(23)	0.3611(13)	0.3970(24)	0.5579(14)	0.130(8)
O(24)	0.2453(17)	0.4319(28)	0.5276(18)	0.174(11)
N(2c)	0.1815(9)	0.0218(17)	0.3090(10)	0.058(5)
N(1c)	0.1211(8)	0.1689(16)	0.3797(9)	0.040(4)
N(2b)	0.2021(10)	0.2803(17)	0.2974(11)	0.064(6)
N(1b)	0.0727(9)	0.1752(17)	0.1789(9)	0.051(5)
N(1d)	0.0477(9)	0.3866(17)	0.2906(10)	0.051(5)
N(2a)	-0.0744(9)	0.2518(18)	0.2864(10)	0.056(5)
N(1a)	-0.0173(9)	0.0692(17)	0.2301(10)	0.054(5)
N(2d)	-0.0763(9)	0.3368(17)	0.1548(10)	0.054(5)
C(1a)	-0.1389(14)	0.2747(25)	0.2184(15)	0.076(8)
C(2a)	-0.0755(11)	0.1497(21)	0.3297(13)	0.056(6)
C(3a)	-0.0896(14)	0.1720(31)	0.3868(16)	0.091(9)
C(4a)	-0.0945(15)	0.0739(28)	0.4270(18)	0.093(9)
C(5a)	-0.0823(15)	-0.0444(30)	0.4147(18)	0.094(9)
C(6a)	-0.0637(14)	-0.0592(28)	0.3579(15)	0.081(8)
C(7a)	-0.0603(12)	0.0355(22)	0.3199(14)	0.063(7)
C(8a)	-0.0397(14)	-0.0021(28)	0.2619(16)	0.084(8)
C(9a)	0.0032(12)	0.0063(23)	0.1829(13)	0.062(7)
C(9b)	0.0173(12)	0.0916(21)	0.1358(13)	0.058(6)
C(8b)	0.0884(11)	0.2508(23)	0.1419(13)	0.060(6)
C(7b)	0.1340(12)	0.3533(22)	0.1663(13)	0.060(7)
C(6b)	0.1281(15)	0.4406(28)	0.1142(17)	0.088(9)
C(5b)	0.1640(16)	0.5399(30)	0.1328(19)	0.097(10)
C(4b)	0.2089(18)	0.5597(32)	0.2015(19)	0.110(11)
C(3b)	0.2244(14)	0.4761(25)	0.2624(16)	0.079(8)
C(2b)	0.1864(11)	0.3720(21)	0.2423(12)	0.052(6)
C(1b)	0.2503(13)	0.1847(22)	0.3018(14)	0.063(7)

O(22)	0.2783(15)	0.2602(29)	0.4966(17)	0.165(11)
O(23)	0.3611(13)	0.3970(24)	0.5579(14)	0.130(8)
O(24)	0.2453(17)	0.4319(28)	0.5276(18)	0.174(11)
N(2c)	0.1815(9)	0.0218(17)	0.3090(10)	0.058(5)
N(1c)	0.1211(8)	0.1689(16)	0.3797(9)	0.040(4)
N(2b)	0.2021(10)	0.2803(17)	0.2974(11)	0.064(6)
N(1b)	0.0727(9)	0.1752(17)	0.1789(9)	0.051(5)
N(1d)	0.0477(9)	0.3866(17)	0.2906(10)	0.051(5)
N(2a)	-0.0744(9)	0.2518(18)	0.2864(10)	0.056(5)
N(1a)	-0.0173(9)	0.0692(17)	0.2301(10)	0.054(5)
N(2d)	-0.0763(9)	0.3368(17)	0.1548(10)	0.054(5)
C(1a)	-0.1389(14)	0.2747(25)	0.2184(15)	0.076(8)
C(2a)	-0.0755(11)	0.1497(21)	0.3297(13)	0.056(6)
C(3a)	-0.0896(14)	0.1720(31)	0.3868(16)	0.091(9)
C(4a)	-0.0945(15)	0.0739(28)	0.4270(18)	0.093(9)
C(5a)	-0.0823(15)	-0.0444(30)	0.4147(18)	0.094(9)
C(6a)	-0.0637(14)	-0.0592(28)	0.3579(15)	0.081(8)
C(7a)	-0.0603(12)	0.0355(22)	0.3199(14)	0.063(7)
C(8a)	-0.0397(14)	-0.0021(28)	0.2619(16)	0.084(8)
C(9a)	0.0032(12)	0.0063(23)	0.1829(13)	0.062(7)
C(9b)	0.0173(12)	0.0916(21)	0.1358(13)	0.058(6)
C(8b)	0.0884(11)	0.2508(23)	0.1419(13)	0.060(6)
C(7b)	0.1340(12)	0.3533(22)	0.1663(13)	0.060(7)
C(6b)	0.1281(15)	0.4406(28)	0.1142(17)	0.088(9)
C(5b)	0.1640(16)	0.5399(30)	0.1328(19)	0.097(10)
C(4b)	0.2089(18)	0.5597(32)	0.2015(19)	0.110(11)
C(3b)	0.2244(14)	0.4761(25)	0.2624(16)	0.079(8)
C(2b)	0.1864(11)	0.3720(21)	0.2423(12)	0.052(6)
C(1b)	0.2503(13)	0.1847(22)	0.3018(14)	0.063(7)

C(1c)	0.2494(12)	0.0744(22)	0.3443(14)	0.060(7)
C(2c)	0.1767(11)	-0.0736(21)	0.3505(12)	0.054(6)
C(3c)	0.1911(13)	-0.1887(25)	0.3406(15)	0.078(8)
C(4c)	0.1880(17)	-0.2904(33)	0.3837(19)	0.110(11)
C(5c)	0.1635(16)	-0.2622(32)	0.4304(18)	0.103(10)
C(6c)	0.1539(20)	-0.1476(36)	0.4481(24)	0.132(13)
C(7c)	0.1572(15)	-0.0454(28)	0.4055(17)	0.092(9)
C(8c)	0.1379(13)	0.0721(25)	0.4196(15)	0.078(8)
C(9c)	0.1046(13)	0.2764(21)	0.4090(13)	0.062(7)
C(9d)	0.1006(12)	0.3890(22)	0.3729(13)	0.060(6)
C(8d)	0.0413(12)	0.4873(26)	0.2595(14)	0.064(7)
C(7d)	0.0013(11)	0.5079(23)	0.1794(13)	0.059(7)
C(6d)	0.0159(16)	0.6107(31)	0.1522(18)	0.098(10)
C(5d)	-0.0117(16)	0.6414(32)	0.0778(19)	0.105(11)
C(4d)	-0.0610(18)	0.5561(32)	0.0323(21)	0.115(12)
C(3d)	-0.0834(14)	0.4587(25)	0.0576(16)	0.080(8)
C(2d)	-0.0513(13)	0.4327(23)	0.1308(14)	0.060(7)
C(1d)	-0.1285(13)	0.3718(23)	0.1726(15)	0.072(7)

TABLE 2 **Fractional atomic coordinates for the hydrogen atoms**

Atom	x	y	z
HN(2c)	0.1684	-0.0168	0.2661
HN(2b)	0.2183	0.3271	0.3382
HN(2a)	-0.0645	0.3122	0.3189
HN(2d)	-0.0939	0.2888	0.1150
H(1a1)	-0.1535	0.2018	0.1907
H(1a2)	-0.1724	0.3008	0.2306
H(3a)	-0.0961	0.2528	0.3982
H(4a)	-0.1066	0.0894	0.4640

H(5a)	-0.0857	-0.1109	0.4417
H(6a)	-0.0542	-0.1382	0.3472
H(8a)	-0.0443	-0.0854	0.2486
H(9a1)	0.0432	-0.0387	0.2125
H(9a2)	-0.0320	-0.0477	0.1523
H(9b1)	-0.0225	0.1376	0.1068
H(9b2)	0.0288	0.0458	0.1049
H(8b)	0.0663	0.2367	0.0907
H(6b)	0.0973	0.4261	0.0641
H(5b)	0.1574	0.5985	0.0966
H(4b)	0.2334	0.6339	0.2127
H(3b)	0.2576	0.4930	0.3114
H(1b1)	0.2386	0.1599	0.2536
H(1b2)	0.2947	0.2179	0.3249
H(1c1)	0.2613	0.0979	0.3927
H(1c2)	0.2809	0.0160	0.3456
H(3c)	0.2037	-0.2042	0.3042
H(4c)	0.2020	-0.3701	0.3797
H(5c)	0.1523	-0.3280	0.4520
H(6c)	0.1452	-0.1345	0.4877
H(8c)	0.1376	0.0797	0.4647
H(9c1)	0.1385	0.2845	0.4587
H(9c2)	0.0620	0.2628	0.4065
H(9d1)	0.0885	0.4513	0.3960
H(9d2)	0.1437	0.4065	0.3776
H(8d)	0.0641	0.5551	0.2894
H(6d)	0.0479	0.6654	0.1869
H(5d)	0.0011	0.7109	0.0605
H(4d)	-0.0805	0.5665	-0.0191

H(3d)	-0.1205	0.4103	0.0244
H(1d1)	-0.1151	0.4450	0.2001
H(1d2)	-0.1697	0.3848	0.1287

TABLE 3 Anisotropic thermal parameters (Å^{2})

Atom	U11	U22	U33	U23	U13	U12
Cu(1)	0.051(1)	0.062(2)	0.043(1)	-0.005(2)	0.026(1)	-0.003(2)
Cu(2)	0.051(2)	0.072(2)	0.031(1)	-0.004(2)	0.022(1)	-0.002(2)
Cl(1)	0.112(6)	0.086(5)	0.063(4)	-0.006(4)	0.058(4)	-0.019(5)
Cl(3)	0.086(5)	0.086(5)	0.082(5)	-0.001(4)	0.051(4)	-0.010(4)

TABLE 4 Bond lengths (Å)

Cu(1) -Cu(2)	2.444(4)	Cu(1) -N(1d)	1.0(19)
Cu(1) -N(2a)	2.156(18)	Cu(1) -N(1a)	1.923(19)
Cu(1) -N(2d)	2.181(18)	Cu(2) -N(2c)	2.133(18)
Cu(2) -N(1c)	1.950(16)	Cu(2) -N(2b)	2.199(19)
Cu(2) -N(1b)	1.911(17)	Cl(1) -O(11)	1.340(7)
Cl(1) -O(12)	1.351(7)	Cl(1) -O(13)	1.486(8)
Cl(1) -O(14)	1.417(8)	Cl(3) -O(31)	1.371(7)
Cl(3) -O(32)	1.424(7)	Cl(3) -O(33)	1.425(8)
Cl(3) -O(34)	1.359(8)	Cl(2) -O(21)	1.453(24)
Cl(2) -O(22)	1.35(3)	Cl(2) -O(23)	1.402(24)
Cl(2) -O(24)	1.46(3)	N(2c) -C(1c)	1.46(3)
N(2c) -C(2c)	1.40(3)	N(1c) -C(8c)	1.29(3)
N(1c) -C(9c)	1.46(3)	N(2b) -C(2b)	1.44(3)
N(2b) -C(1b)	1.49(3)	N(1b) -C(9b)	1.46(3)
N(1b) -C(8b)	1.30(3)	N(1d) -C(9d)	1.55(3)
N(1d) -C(8d)	1.26(3)	N(2a) -C(1a)	1.48(3)

N(2a) -C(2a)	1.45(3)	N(1a) -C(8a)	1.28(3)
N(1a) -C(9a)	1.45(3)	N(2d) -C(2d)	1.40(3)
N(2d) -C(1d)	1.45(3)	C(1a) -C(1d)	1.53(4)
C(2a) -C(3a)	1.40(4)	C(2a) -C(7a)	1.34(3)
C(3a) -C(4a)	1.41(4)	C(4a) -C(5a)	1.38(4)
C(5a) -C(6a)	1.45(4)	C(6a) -C(7a)	1.34(3)
C(7a) -C(8a)	1.55(4)	C(9a) -C(9b)	1.50(3)
C(8b) -C(7b)	1.44(3)	C(7b) -C(6b)	1.41(3)
C(7b) -C(2b)	1.47(3)	C(6b) -C(5b)	1.30(4)
C(5b) -C(4b)	1.31(4)	C(4b) -C(3b)	1.47(4)
C(3b) -C(2b)	1.37(3)	C(1b) -C(1c)	1.51(3)
C(2c) -C(3c)	1.35(3)	C(2c) -C(7c)	1.45(4)
C(3c) -C(4c)	1.46(4)	C(4c) -C(5c)	1.37(4)
C(5c) -C(6c)	1.36(4)	C(6c) -C(7c)	1.46(4)
C(7c) -C(8c)	1.44(4)	C(9c) -C(9d)	1.43(3)
C(8d) -C(7d)	1.48(3)	C(7d) -C(6d)	1.38(4)
C(7d) -C(2d)	1.40(3)	C(6d) -C(5d)	1.41(4)
C(5d) -C(4d)	1.41(4)	C(4d) -C(3d)	1.39(4)
C(3d) -C(2d)	1.37(3)		

<u>TABLE 5</u> <u>Bond angles (°)</u>

N(1d) -Cu(1) -Cu(2)	80.7(5)	N(2a) -Cu(1) -Cu(2)	144.6(5)
N(2a) -Cu(1) -N(1d)	99.2(7)	N(1a) -Cu(1) -Cu(2)	80.8(6)
N(1a) -Cu(1) -N(1d)	160.1(7)	N(1a) -Cu(1) -N(2a)	91.5(8)
N(2d) -Cu(1) -Cu(2)	131.9(5)	N(2d) -Cu(1) -N(1d)	91.0(8)
N(2d) -Cu(1) -N(2a)	83.5(7)	N(2d) -Cu(1) -N(1a)	107.1(8)
N(2c) -Cu(2) -Cu(1)	146.2(5)	N(1c) -Cu(2) -Cu(1)	80.8(5)
N(1c) -Cu(2) -N(2c)	91.9(7)	N(2b) -Cu(2) -Cu(1)	129.2(5)
N(2b) -Cu(2) -N(2c)	84.5(7)	N(2b) -Cu(2) -N(1c)	104.9(7)

N(1b) -Cu(2) -Cu(1)	78.5(5)	N(1b) -Cu(2) -N(2c)	101.5(8)
N(1b) -Cu(2) -N(1c)	158.2(7)	N(1b) -Cu(2) -N(2b)	93.5(8)
O(22) -Cl(2) -O(21)	111(2)	O(23) -Cl(2) -O(21)	114(2)
O(23) -Cl(2) -O(22)	110(2)	O(24) -Cl(2) -O(21)	101(2)
O(24) -Cl(2) -O(22)	106(2)	O(24) -Cl(2) -O(23)	114(2)
C(1c) -N(2c) -Cu(2)	105(1)	C(2c) -N(2c) -Cu(2)	119(1)
C(2c) -N(2c) -C(1c)	111(2)	C(8c) -N(1c) -Cu(2)	122(2)
C(9c) -N(1c) -Cu(2)	121(1)	C(9c) -N(1c) -C(8c)	117(2)
C(2b) -N(2b) -Cu(2)	114(1)	C(1b) -N(2b) -Cu(2)	102(1)
C(1b) -N(2b) -C(2b)	116(2)	C(9b) -N(1b) -Cu(2)	120(1)
C(8b) -N(1b) -Cu(2)	124(2)	C(8b) -N(1b) -C(9b)	116(2)
C(9d) -N(1d) -Cu(1)	118(1)	C(8d) -N(1d) -Cu(1)	128(2)
C(8d) -N(1d) -C(9d)	113(2)	C(1a) -N(2a) -Cu(1)	104(1)
C(2a) -N(2a) -Cu(1)	115(1)	C(2a) -N(2a) -C(1a)	115(2)
C(8a) -N(1a) -Cu(1)	125(2)	C(9a) -N(1a) -Cu(1)	121(2)
C(9a) -N(1a) -C(8a)	113(2)	C(2d) -N(2d) -Cu(1)	115(1)
C(1d) -N(2d) -Cu(1)	106(1)	C(1d) -N(2d) -C(2d)	114(2)
C(1d) -C(1a) -N(2a)	110(2)	C(3a) -C(2a) -N(2a)	118(2)
C(7a) -C(2a) -N(2a)	123(2)	C(7a) -C(2a) -C(3a)	118(2)
C(4a) -C(3a) -C(2a)	119(3)	C(5a) -C(4a) -C(3a)	122(3)
C(6a) -C(5a) -C(4a)	115(3)	C(7a) -C(6a) -C(5a)	122(3)
C(6a) -C(7a) -C(2a)	123(2)	C(8a) -C(7a) -C(2a)	124(2)
C(8a) -C(7a) -C(6a)	112(2)	C(7a) -C(8a) -N(1a)	126(3)
C(9b) -C(9a) -N(1a)	113(2)	C(9a) -C(9b) -N(1b)	112(2)
C(7b) -C(8b) -N(1b)	130(2)	C(6b) -C(7b) -C(8b)	118(2)
C(2b) -C(7b) -C(8b)	124(2)	C(2b) -C(7b) -C(6b)	118(2)
C(5b) -C(6b) -C(7b)	122(3)	C(4b) -C(5b) -C(6b)	120(4)
C(3b) -C(4b) -C(5b)	125(3)	C(2b) -C(3b) -C(4b)	114(3)
C(7b) -C(2b) -N(2b)	122(2)	C(3b) -C(2b) -N(2b)	118(2)

C(3b) -C(2b) -C(7b)	120(2)	C(1c) -C(1b) -N(2b)	113(2)
C(1b) -C(1c) -N(2c)	109(2)	C(3c) -C(2c) -N(2c)	121(2)
C(7c) -C(2c) -N(2c)	118(2)	C(7c) -C(2c) -C(3c)	121(2)
C(4c) -C(3c) -C(2c)	123(3)	C(5c) -C(4c) -C(3c)	115(3)
C(6c) -C(5c) -C(4c)	125(4)	C(7c) -C(6c) -C(5c)	119(4)
C(6c) -C(7c) -C(2c)	116(3)	C(8c) -C(7c) -C(2c)	126(3)
C(8c) -C(7c) -C(6c)	117(3)	C(7c) -C(8c) -N(1c)	129(3)
C(9d) -C(9c) -N(1c)	116(2)	C(9c) -C(9d) -N(1d)	113(2)
C(7d) -C(8d) -N(1d)	125(2)	C(6d) -C(7d) -C(8d)	117(2)
C(2d) -C(7d) -C(8d)	124(2)	C(2d) -C(7d) -C(6d)	118(2)
C(5d) -C(6d) -C(7d)	126(3)	C(4d) -C(5d) -C(6d)	111(3)
C(3d) -C(4d) -C(5d)	125(4)	C(2d) -C(3d) -C(4d)	119(3)
C(7d) -C(2d) -N(2d)	122(2)	C(3d) -C(2d) -N(2d)	118(2)
C(3d) -C(2d) -C(7d)	119(2)	C(1a) -C(1d) -N(2d)	111(2)

TABLE 6 Intermolecular distances (Å)

O(15) ...Cl(1)	1.42	2	0.0	1.0	-1.0
O(16) ...Cl(1)	1.66	2	0.0	1.0	-1.0
O(17) ...Cl(1)	1.57	2	0.0	1.0	-1.0
O(18) ...Cl(1)	1.44	2	0.0	1.0	-1.0
O(15) ...O(11)	2.20	2	0.0	1.0	-1.0
O(16) ...O(11)	1.03	2	0.0	1.0	-1.0
O(17) ...O(11)	.98	2	0.0	1.0	-1.0
O(18) ...O(11)	1.42	2	0.0	1.0	-1.0
H(9b2)...O(11)	2.69	2	0.0	0.0	-1.0
H(8b) ...O(11)	2.93	2	0.0	0.0	-1.0
O(15) ...O(12)	2.58	2	0.0	1.0	-1.0
O(16) ...O(12)	2.41	2	0.0	1.0	-1.0
O(17) ...O(12)	2.53	2	0.0	1.0	-1.0

O(18) ...O(12)	1.53	2	0.0	1.0	-1.0
H(5b) ...O(12)	2.64	2	0.0	1.0	-1.0
O(15) ...O(13)	.91	2	0.0	1.0	-1.0
O(16) ...O(13)	2.33	2	0.0	1.0	-1.0
O(17) ...O(13)	2.72	2	0.0	1.0	-1.0
O(18) ...O(13)	2.93	2	0.0	1.0	-1.0
HN(2c)...O(13)	2.69	2	0.0	0.0	-1.0
H(9a1)...O(13)	2.85	2	0.0	0.0	-1.0
H(9b2)...O(13)	2.72	2	0.0	0.0	-1.0
H(6d) ...O(13)	2.86	2	0.0	1.0	-1.0
H(5d) ...O(13)	2.70	2	0.0	1.0	-1.0
O(15) ...O(14)	1.70	2	0.0	1.0	-1.0
O(16) ...O(14)	2.81	2	0.0	1.0	-1.0
O(17) ...O(14)	1.39	2	0.0	1.0	-1.0
O(18) ...O(14)	1.74	2	0.0	1.0	-1.0
HN(2c)...O(14)	2.36	2	0.0	0.0	-1.0
H(1b1)...O(14)	2.63	2	0.0	0.0	-1.0
H(1c2)...O(14)	2.99	2	0.0	0.0	-1.0
H(1a2)...O(14)	2.78	2	-0.5	0.5	-1.0
N(2c) ...O(15)	2.77	1	0.0	-1.0	0.0
HN(2c)...O(15)	1.86	1	0.0	-1.0	0.0
H(9a1)...O(15)	2.67	1	0.0	-1.0	0.0
H(9b2)...O(15)	2.70	1	0.0	-1.0	0.0
H(3c) ...O(15)	2.60	1	0.0	-1.0	0.0
H(9b2)...O(16)	2.44	1	0.0	-1.0	0.0
H(6c) ...O(16)	2.66	2	0.0	1.0	0.0
H(8c) ...O(16)	2.46	2	0.0	1.0	0.0
HN(2c)...O(17)	2.92	1	0.0	-1.0	0.0
H(1b1)...O(17)	2.48	1	0.0	-1.0	0.0

H(6c) ...O(18)	2.76	2	0.0	1.0	0.0
H(8c) ...O(18)	2.51	2	0.0	1.0	0.0
H(1d2)...O(18)	2.81	1	-0.5	-0.5	0.0
O(35) ...Cl(3)	1.67	2	-0.5	0.5	-1.0
O(36) ...Cl(3)	1.51	2	-0.5	0.5	-1.0
O(37) ...Cl(3)	1.50	2	-0.5	0.5	-1.0
O(38) ...Cl(3)	1.42	2	-0.5	0.5	-1.0
O(39) ...Cl(3)	.94	2	-0.5	0.5	-1.0
O(40) ...Cl(3)	1.73	2	-0.5	0.5	-1.0
H(4d) ...O(31)	2.74	1	-0.5	0.5	-1.0
O(35) ...O(31)	2.43	2	-0.5	0.5	-1.0
O(36) ...O(31)	1.00	2	-0.5	0.5	-1.0
O(37) ...O(31)	.88	2	-0.5	0.5	-1.0
O(38) ...O(31)	2.71	2	-0.5	0.5	-1.0
O(39) ...O(31)	1.71	2	-0.5	0.5	-1.0
O(40) ...O(31)	1.98	2	-0.5	0.5	-1.0
HN(2a)...O(31)	2.50	2	-0.5	0.5	-1.0
H(9c2)...O(31)	2.86	2	-0.5	0.5	-1.0
H(9d1)...O(31)	2.34	2	-0.5	0.5	-1.0
H(1b2)...O(32)	2.68	2	0.0	0.0	-1.0
H(4d) ...O(32)	2.91	1	-0.5	0.5	-1.0
O(35) ...O(32)	.99	2	-0.5	0.5	-1.0
O(36) ...O(32)	2.40	2	-0.5	0.5	-1.0
O(37) ...O(32)	2.54	2	-0.5	0.5	-1.0
O(38) ...O(32)	1.17	2	-0.5	0.5	-1.0
O(39) ...O(32)	1.79	2	-0.5	0.5	-1.0
O(40) ...O(32)	2.02	2	-0.5	0.5	-1.0
H(5a) ...O(32)	2.70	2	-0.5	-0.5	-1.0
H(6a) ...O(32)	2.76	2	-0.5	-0.5	-1.0

H(6c) ...O(18)	2.76	2	0.0	1.0	0.0
H(8c) ...O(18)	2.51	2	0.0	1.0	0.0
H(1d2)...O(18)	2.81	1	-0.5	-0.5	0.0
O(35) ...Cl(3)	1.67	2	-0.5	0.5	-1.0
O(36) ...Cl(3)	1.51	2	-0.5	0.5	-1.0
O(37) ...Cl(3)	1.50	2	-0.5	0.5	-1.0
O(38) ...Cl(3)	1.42	2	-0.5	0.5	-1.0
O(39) ...Cl(3)	.94	2	-0.5	0.5	-1.0
O(40) ...Cl(3)	1.73	2	-0.5	0.5	-1.0
H(4d) ...O(31)	2.74	1	-0.5	0.5	-1.0
O(35) ...O(31)	2.43	2	-0.5	0.5	-1.0
O(36) ...O(31)	1.00	2	-0.5	0.5	-1.0
O(37) ...O(31)	.88	2	-0.5	0.5	-1.0
O(38) ...O(31)	2.71	2	-0.5	0.5	-1.0
O(39) ...O(31)	1.71	2	-0.5	0.5	-1.0
O(40) ...O(31)	1.98	2	-0.5	0.5	-1.0
HN(2a)...O(31)	2.50	2	-0.5	0.5	-1.0
H(9c2)...O(31)	2.86	2	-0.5	0.5	-1.0
H(9d1)...O(31)	2.34	2	-0.5	0.5	-1.0
H(1b2)...O(32)	2.68	2	0.0	0.0	-1.0
H(4d) ...O(32)	2.91	1	-0.5	0.5	-1.0
O(35) ...O(32)	.99	2	-0.5	0.5	-1.0
O(36) ...O(32)	2.40	2	-0.5	0.5	-1.0
O(37) ...O(32)	2.54	2	-0.5	0.5	-1.0
O(38) ...O(32)	1.17	2	-0.5	0.5	-1.0
O(39) ...O(32)	1.79	2	-0.5	0.5	-1.0
O(40) ...O(32)	2.02	2	-0.5	0.5	-1.0
H(5a) ...O(32)	2.70	2	-0.5	-0.5	-1.0
H(6a) ...O(32)	2.76	2	-0.5	-0.5	-1.0

O(35) ...O(33)	2.62	2	-0.5	0.5	-1.0
O(36) ...O(33)	2.30	2	-0.5	0.5	-1.0
O(37) ...O(33)	2.51	2	-0.5	0.5	-1.0
O(38) ...O(33)	1.95	2	-0.5	0.5	-1.0
O(39) ...O(33)	1.26	2	-0.5	0.5	-1.0
O(40) ...O(33)	2.37	2	-0.5	0.5	-1.0
H(6a) ...O(33)	2.65	2	-0.5	-0.5	-1.0
H(8d) ...O(33)	2.69	2	-0.5	0.5	-1.0
H(1c2)...O(34)	2.74	2	0.0	0.0	-1.0
H(4d) ...O(34)	2.81	1	-0.5	0.5	-1.0
O(35) ...O(34)	2.66	2	-0.5	0.5	-1.0
O(36) ...O(34)	2.56	2	-0.5	0.5	-1.0
O(37) ...O(34)	1.25	2	-0.5	0.5	-1.0
O(38) ...O(34)	1.54	2	-0.5	0.5	-1.0
O(39) ...O(34)	2.28	2	-0.5	0.5	-1.0
HN(2a)...O(34)	2.45	2	-0.5	0.5	-1.0
H(1d1)...O(34)	2.95	2	-0.5	0.5	-1.0
H(5a) ...O(35)	2.68	1	0.0	-1.0	0.0
H(6a) ...O(35)	2.86	1	0.0	-1.0	0.0
H(8b) ...O(35)	2.87	2	0.0	1.0	-1.0
H(6b) ...O(35)	2.90	2	0.0	1.0	-1.0
H(6b) ...O(36)	2.33	2	0.0	1.0	-1.0
H(4d) ...O(37)	2.55	2	0.0	1.0	-1.0
H(6a) ...O(38)	2.59	1	0.0	-1.0	0.0
C(1b) ...O(38)	2.98	1	0.5	-0.5	0.0
H(1b2)...O(38)	2.25	1	0.5	-0.5	0.0
H(1c2)...O(38)	2.99	1	0.5	-0.5	0.0
H(6a) ...O(39)	2.78	1	0.0	-1.0	0.0
H(5c) ...O(40)	2.92	1	0.0	-1.0	0.0

H(8b) ...O(40)	2.84	2	0.0	1.0	-1.0
H(6b) ...O(40)	2.15	2	0.0	1.0	-1.0
H(4c) ...O(21)	2.55	1	0.0	-1.0	0.0
HN(2d)...O(22)	2.80	2	-0.5	0.5	-1.0
H(3d) ...O(22)	2.79	2	-0.5	0.5	-1.0
H(1d2)...O(22)	2.90	2	-0.5	0.5	-1.0
HN(2d)...O(23)	2.34	2	-0.5	0.5	-1.0
H(9a2)...O(23)	2.81	2	-0.5	0.5	-1.0
H(9b1)...O(23)	2.35	2	-0.5	0.5	-1.0
H(5b) ...O(24)	2.98	2	0.0	1.0	-1.0

TABLE 7 Intramolecular distances (Å)

N(1c) ...Cu(1)	2.87	N(1b) ...Cu(1)	2.79
HN(2a)...Cu(1)	2.62	HN(2d)...Cu(1)	2.64
C(1a) ...Cu(1)	2.90	C(8a) ...Cu(1)	2.86
C(9a) ...Cu(1)	2.95	H(9c2)...Cu(1)	2.88
C(9d) ...Cu(1)	2.97	C(8d) ...Cu(1)	2.86
C(1d) ...Cu(1)	2.93	HN(2c)...Cu(2)	2.53
HN(2b)...Cu(2)	2.67	N(1d) ...Cu(2)	2.84
N(1a) ...Cu(2)	2.86	C(9a) ...Cu(2)	2.99
H(9a1)...Cu(2)	2.81	C(9b) ...Cu(2)	2.93
C(8b) ...Cu(2)	2.85	C(1b) ...Cu(2)	2.90
C(1c) ...Cu(2)	2.88	C(8c) ...Cu(2)	2.86
C(9c) ...Cu(2)	2.97	O(12) ...O(11)	2.31
O(13) ...O(11)	2.40	H(6c) ...O(11)	2.59
H(8c) ...O(11)	2.87	O(13) ...O(12)	2.39
O(14) ...O(12)	2.17	H(8c) ...O(12)	2.58
H(9c1)...O(12)	2.80	O(14) ...O(13)	2.34
O(16) ...O(15)	2.50	O(17) ...O(15)	2.20

H(8b) ...O(40)	2.84	2	0.0	1.0	-1.0
H(6b) ...O(40)	2.15	2	0.0	1.0	-1.0
H(4c) ...O(21)	2.55	1	0.0	-1.0	0.0
HN(2d)...O(22)	2.80	2	-0.5	0.5	-1.0
H(3d) ...O(22)	2.79	2	-0.5	0.5	-1.0
H(1d2)...O(22)	2.90	2	-0.5	0.5	-1.0
HN(2d)...O(23)	2.34	2	-0.5	0.5	-1.0
H(9a2)...O(23)	2.81	2	-0.5	0.5	-1.0
H(9b1)...O(23)	2.35	2	-0.5	0.5	-1.0
H(5b) ...O(24)	2.98	2	0.0	1.0	-1.0

TABLE 7 Intramolecular distances (Å)

N(1c) ...Cu(1)	2.87	N(1b) ...Cu(1)	2.79
HN(2a)...Cu(1)	2.62	HN(2d)...Cu(1)	2.64
C(1a) ...Cu(1)	2.90	C(8a) ...Cu(1)	2.86
C(9a) ...Cu(1)	2.95	H(9c2)...Cu(1)	2.88
C(9d) ...Cu(1)	2.97	C(8d) ...Cu(1)	2.86
C(1d) ...Cu(1)	2.93	HN(2c)...Cu(2)	2.53
HN(2b)...Cu(2)	2.67	N(1d) ...Cu(2)	2.84
N(1a) ...Cu(2)	2.86	C(9a) ...Cu(2)	2.99
H(9a1)...Cu(2)	2.81	C(9b) ...Cu(2)	2.93
C(8b) ...Cu(2)	2.85	C(1b) ...Cu(2)	2.90
C(1c) ...Cu(2)	2.88	C(8c) ...Cu(2)	2.86
C(9c) ...Cu(2)	2.97	O(12) ...O(11)	2.31
O(13) ...O(11)	2.40	H(6c) ...O(11)	2.59
H(8c) ...O(11)	2.87	O(13) ...O(12)	2.39
O(14) ...O(12)	2.17	H(8c) ...O(12)	2.58
H(9c1)...O(12)	2.80	O(14) ...O(13)	2.34
O(16) ...O(15)	2.50	O(17) ...O(15)	2.20

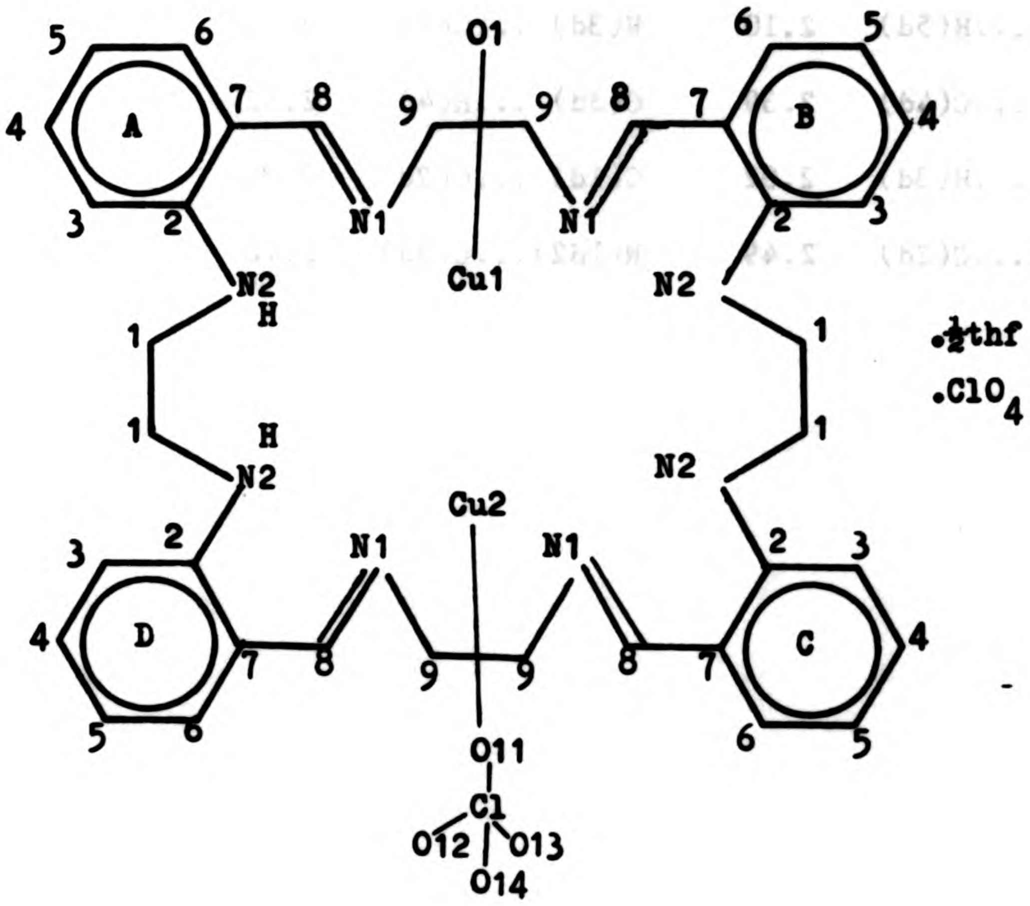
O(18) ...O(15)	2.73	O(32) ...O(31)	2.49
O(33) ...O(31)	2.34	O(33) ...O(32)	2.44
O(34) ...O(33)	2.28	O(37) ...O(35)	2.80
O(38) ...O(36)	2.88	H(9d1)...O(36)	2.26
O(38) ...O(37)	2.51	O(39) ...O(37)	2.20
O(40) ...O(37)	2.68	N(2a) ...O(37)	2.78
HN(2a)...O(37)	1.88	H(3a) ...O(37)	2.51
H(9d1)...O(37)	2.91	O(40) ...O(38)	2.74
H(9d1)...O(39)	2.86	O(22) ...O(21)	2.30
O(23) ...O(21)	2.40	O(24) ...O(21)	2.25
HN(2b)...O(21)	2.19	H(3b) ...O(21)	2.55
H(9d2)...O(21)	2.56	O(23) ...O(22)	2.26
O(24) ...O(22)	2.24	H(1c1)...O(22)	2.69
H(9c1)...O(22)	2.87	O(24) ...O(23)	2.40
H(9c1)...O(24)	2.68	H(9d2)...O(24)	2.87
N(1c) ...N(2c)	2.94	N(2b) ...N(2c)	2.91
H(9a1)...N(2c)	2.86	C(1b) ...N(2c)	2.42
H(1b1)...N(2c)	2.60	H(1c1)...N(2c)	1.99
H(1c2)...N(2c)	1.99	C(3c) ...N(2c)	2.39
H(3c) ...N(2c)	2.55	C(7c) ...N(2c)	2.45
C(8c) ...N(2c)	2.97	N(1b) ...HN(2c)	2.94
C(1b) ...HN(2c)	2.75	C(1c) ...HN(2c)	2.03
C(3c) ...HN(2c)	2.35	N(1d) ...N(1c)	3.00
C(7c) ...N(1c)	2.47	H(8c) ...N(1c)	1.90
H(9c1)...N(1c)	1.97	H(9c2)...N(1c)	1.97
C(9d) ...N(1c)	2.46	H(9d2)...N(1c)	2.67
N(1b) ...N(2b)	3.00	C(7b) ...N(2b)	2.54
C(3b) ...N(2b)	2.41	H(3b) ...N(2b)	2.61
H(1b1)...N(2b)	2.00	H(1b2)...N(2b)	2.00

C(1c) ...N(2b)	2.50	H(1c1)...N(2b)	2.69
H(9d2)...N(2b)	2.94	C(3b) ...HN(2b)	2.33
C(2b) ...HN(2b)	1.84	C(1b) ...HN(2b)	2.02
C(1c) ...HN(2b)	2.86	N(1a) ...N(1b)	2.96
C(9a) ...N(1b)	2.46	H(9a1)...N(1b)	2.63
H(9b1)...N(1b)	1.98	H(9b2)...N(1b)	1.98
H(8b) ...N(1b)	1.90	C(7b) ...N(1b)	2.49
HN(2a)...N(1d)	2.98	N(2d) ...N(1d)	2.92
C(9c) ...N(1d)	2.48	H(9c2)...N(1d)	2.66
H(9d1)...N(1d)	2.06	H(9d2)...N(1d)	2.06
H(8d) ...N(1d)	1.90	C(7d) ...N(1d)	2.44
N(1a) ...N(2a)	2.93	N(2d) ...N(2a)	2.89
H(1a1)...N(2a)	2.01	H(1a2)...N(2a)	2.01
C(3a) ...N(2a)	2.45	H(3a) ...N(2a)	2.61
C(7a) ...N(2a)	2.46	H(9c2)...N(2a)	2.88
C(1d) ...N(2a)	2.47	H(1d1)...N(2a)	2.65
C(1a) ...HN(2a)	2.00	C(2a) ...HN(2a)	1.84
C(3a) ...HN(2a)	2.35	C(1d) ...HN(2a)	2.76
C(7a) ...N(1a)	2.52	H(8a) ...N(1a)	1.91
H(9a1)...N(1a)	1.97	H(9a2)...N(1a)	1.97
C(9b) ...N(1a)	2.46	H(9b1)...N(1a)	2.63
C(1a) ...N(2d)	2.46	H(1a1)...N(2d)	2.66
H(9b1)...N(2d)	2.91	C(8d) ...N(2d)	2.99
C(7d) ...N(2d)	2.45	C(3d) ...N(2d)	2.38
H(3d) ...N(2d)	2.54	H(1d1)...N(2d)	1.97
H(1d2)...N(2d)	1.98	C(1a) ...HN(2d)	2.80
C(3d) ...HN(2d)	2.30	C(1d) ...HN(2d)	1.95
C(2a) ...C(1a)	2.48	H(1d1)...C(1a)	2.04
H(1d2)...C(1a)	2.05	C(2a) ...H(1a1)	2.63

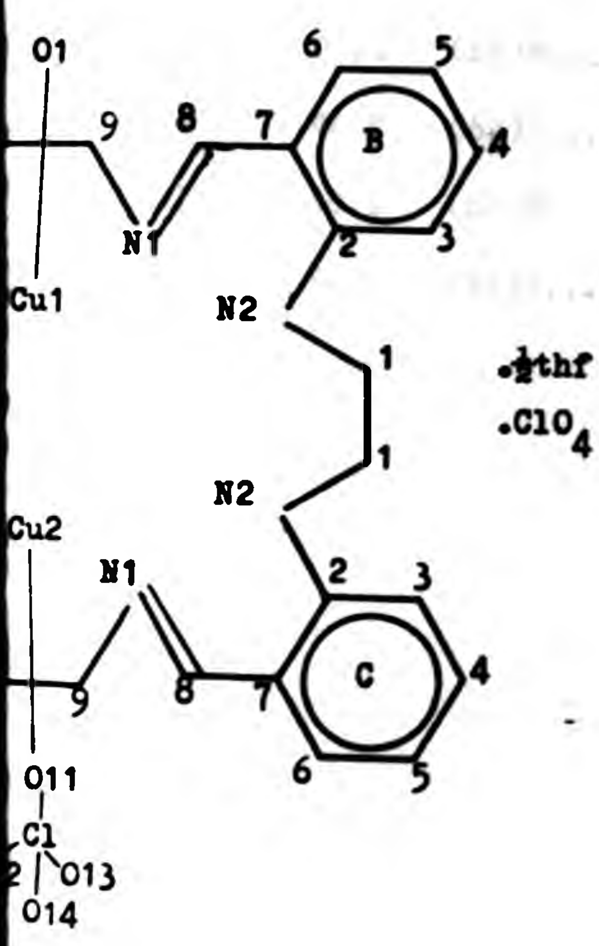
C(1d) ...H(1a1)	2.04	C(2a) ...H(1a2)	2.73
C(1d) ...H(1a2)	2.05	H(3a) ...C(2a)	2.05
C(4a) ...C(2a)	2.42	C(5a) ...C(2a)	2.83
C(6a) ...C(2a)	2.36	C(8a) ...C(2a)	2.56
H(9c2)...C(2a)	2.99	H(4a) ...C(3a)	2.04
C(5a) ...C(3a)	2.44	C(6a) ...C(3a)	2.75
C(7a) ...C(3a)	2.36	C(4a) ...H(3a)	2.06
H(5a) ...C(4a)	2.05	C(6a) ...C(4a)	2.39
C(7a) ...C(4a)	2.73	C(5a) ...H(4a)	2.02
H(6a) ...C(5a)	2.08	C(7a) ...C(5a)	2.43
C(6a) ...H(5a)	2.12	C(8a) ...C(6a)	2.40
H(8a) ...C(6a)	2.54	C(7a) ...H(6a)	1.98
C(8a) ...H(6a)	2.47	H(8a) ...C(7a)	2.16
C(9a) ...C(8a)	2.28	H(9a1)...C(8a)	2.57
H(9a2)...C(8a)	2.43	C(9a) ...H(8a)	2.34
H(9b1)...C(9a)	2.02	H(9b2)...C(9a)	2.02
C(9b) ...H(9a1)	2.02	C(9b) ...H(9a2)	2.02
C(8b) ...C(9b)	2.34	H(8b) ...C(9b)	2.38
C(8b) ...H(9b1)	2.56	C(8b) ...H(9b2)	2.55
C(6b) ...C(8b)	2.45	H(6b) ...C(8b)	2.59
C(2b) ...C(8b)	2.57	C(7b) ...H(8b)	2.03
C(6b) ...H(8b)	2.56	H(6b) ...C(7b)	2.04
C(5b) ...C(7b)	2.37	C(4b) ...C(7b)	2.72
C(3b) ...C(7b)	2.46	H(5b) ...C(6b)	1.96
C(4b) ...C(6b)	2.27	C(3b) ...C(6b)	2.82
C(2b) ...C(6b)	2.46	C(5b) ...H(6b)	1.95
H(4b) ...C(5b)	1.95	C(3b) ...C(5b)	2.47
C(2b) ...C(5b)	2.79	C(4b) ...H(5b)	1.97
H(3b) ...C(4b)	2.14	C(2b) ...C(4b)	2.38

C(3b) ...H(4b)	2.09	C(2b) ...H(3b)	2.05
C(1b) ...C(2b)	2.48	H(1b1)...C(2b)	2.57
H(1b2)...C(2b)	2.78	H(1c1)...C(1b)	2.03
H(1c2)...C(1b)	2.04	C(1c) ...H(1b1)	2.02
C(1c) ...H(1b2)	2.03	C(2c) ...C(1c)	2.36
C(2c) ...H(1c1)	2.52	C(7c) ...H(1c1)	2.95
C(2c) ...H(1c2)	2.60	C(3c) ...H(1c2)	3.00
H(3c) ...C(2c)	1.99	C(4c) ...C(2c)	2.47
C(5c) ...C(2c)	2.77	C(6c) ...C(2c)	2.47
C(8c) ...C(2c)	2.58	H(4c) ...C(3c)	2.13
C(5c) ...C(3c)	2.39	C(6c) ...C(3c)	2.79
C(7c) ...C(3c)	2.43	C(4c) ...H(3c)	2.09
H(5c) ...C(4c)	1.99	C(6c) ...C(4c)	2.43
C(7c) ...C(4c)	2.88	C(5c) ...H(4c)	2.04
H(6c) ...C(5c)	2.02	C(7c) ...C(5c)	2.43
C(6c) ...H(5c)	1.99	C(8c) ...C(6c)	2.48
H(8c) ...C(6c)	2.58	C(7c) ...H(6c)	2.11
C(8c) ...H(6c)	2.65	H(8c) ...C(7c)	2.04
C(9c) ...C(8c)	2.35	H(9c1)...C(8c)	2.48
H(9c2)...C(8c)	2.64	C(9c) ...H(8c)	2.40
H(9d1)...C(9c)	1.95	H(9d2)...C(9c)	1.95
C(9d) ...H(9c1)	1.95	C(9d) ...H(9c2)	1.94
C(8d) ...C(9d)	2.35	H(8d) ...C(9d)	2.38
C(8d) ...H(9d1)	2.55	C(8d) ...H(9d2)	2.59
C(6d) ...C(8d)	2.44	H(6d) ...C(8d)	2.53
C(2d) ...C(8d)	2.55	C(7d) ...H(8d)	2.10
C(6d) ...H(8d)	2.60	H(6d) ...C(7d)	2.00
C(5d) ...C(7d)	2.48	C(4d) ...C(7d)	2.74
C(3d) ...C(7d)	2.39	H(1d1)...C(7d)	2.95

H(5d) ...C(6d)	2.09	C(4d) ...C(6d)	2.33
C(3d) ...C(6d)	2.73	C(2d) ...C(6d)	2.39
C(5d) ...H(6d)	2.03	H(4d) ...C(5d)	2.04
C(3d) ...C(5d)	2.49	C(2d) ...C(5d)	2.88
C(4d) ...H(5d)	2.10	H(3d) ...C(4d)	2.05
C(2d) ...C(4d)	2.39	C(3d) ...H(4d)	2.02
C(2d) ...H(3d)	2.02	C(1d) ...C(2d)	2.39
H(1d1)...C(2d)	2.49	H(1d2)...C(2d)	2.70



$[Cu_2(H_2cyendimer)(H_2O)(ClO_4)](ClO_4)\cdot\frac{1}{2}thf$



r)$(H_2O)(ClO_4)](ClO_4)$.½thf

The X-ray crystallographic data for $[Cu_2H_2$cyendimer$(H_2O)(ClO_4)]$-(ClO_4)thf (see section 7.2) schematic diagram facing page.

TABLE 1 Fractional atomic coordinates and thermal parameters (Å^2)

Atom	x	y	z	Uiso or Ueq
Cu(1)	0.00000	0.14474(9)	0.25000	0.0444(8)
Cu(2)	0.12483(9)	0.38292(9)	0.33461(17)	0.0517(9)
C(9c)	0.1327(8)	0.5424(11)	0.2533(21)	0.119(16)
C(9d)	0.1643(12)	0.5007(12)	0.1957(21)	0.145(19)
O(1)	-0.0938(5)	0.1178(8)	0.3052(10)	0.100(9)
Cl(1)	0.2720(2)	0.4547(3)	0.5106(4)	0.098(3)
Cl(2)	-0.0014(2)	0.2286(2)	0.8017(4)	0.078(3)
C(1a)	0.0305(6)	0.2966(7)	0.1515(11)	0.049(3)
N(2a)	-0.0060(4)	0.2723(5)	0.2274(8)	0.042(2)
C(2a)	-0.0716(5)	0.2961(7)	0.1883(10)	0.042(3)
C(3a)	-0.0942(6)	0.3607(8)	0.2372(12)	0.056(3)
C(4a)	-0.1585(7)	0.3883(10)	0.1945(13)	0.073(4)
C(5a)	-0.1941(6)	0.3487(9)	0.1066(12)	0.061(4)
C(6a)	-0.1719(6)	0.2839(9)	0.0609(12)	0.064(4)
C(7a)	-0.1101(5)	0.2543(7)	0.0985(10)	0.043(3)
C(8a)	-0.0903(6)	0.1834(8)	0.0484(12)	0.059(4)
N(1a)	-0.0437(5)	0.1384(6)	0.0986(9)	0.054(3)
C(9a)	-0.0290(6)	0.0648(8)	0.0439(11)	0.059(4)
C(9b)	-0.0183(6)	-0.0025(9)	0.1302(12)	0.068(4)
N(1b)	0.0211(5)	0.0310(6)	0.2322(9)	0.050(3)
C(8b)	0.0624(6)	-0.0122(8)	0.2939(11)	0.053(3)
C(7b)	0.0984(5)	0.0116(7)	0.4017(10)	0.047(3)

C(6b)	0.1395(6)	-0.0492(8)	0.4585(12)	0.060(4)
C(5b)	0.1721(7)	-0.0367(8)	0.5585(12)	0.063(4)
C(4b)	0.1643(7)	0.0324(8)	0.6117(12)	0.064(4)
C(3b)	0.1260(6)	0.0965(7)	0.5622(11)	0.052(3)
C(2b)	0.0912(5)	0.0882(7)	0.4514(10)	0.041(3)
N(2b)	0.0529(4)	0.1494(6)	0.4026(8)	0.042(2)
C(1b)	0.0376(6)	0.2148(7)	0.4716(11)	0.052(3)
C(1c)	0.0878(5)	0.2813(7)	0.5028(10)	0.044(3)
N(2c)	0.0731(4)	0.3586(6)	0.4379(8)	0.048(2)
C(2c)	0.0306(5)	0.4096(7)	0.4640(10)	0.044(3)
C(3c)	-0.0050(6)	0.3866(8)	0.5419(12)	0.062(4)
C(4c)	-0.0526(7)	0.4351(9)	0.5631(13)	0.076(4)
C(5c)	-0.0645(7)	0.5119(10)	0.5106(13)	0.073(4)
C(6c)	-0.0299(7)	0.5362(9)	0.4457(12)	0.066(4)
C(7c)	0.0185(6)	0.4894(8)	0.4197(11)	0.053(3)
C(8c)	0.0514(6)	0.5251(9)	0.3500(12)	0.062(4)
N(1c)	0.0970(5)	0.4954(7)	0.3155(11)	0.067(3)
N(1d)	0.1793(6)	0.4143(8)	0.2404(11)	0.077(4)
C(8d)	0.2273(8)	0.3738(9)	0.2264(14)	0.076(5)
C(7d)	0.2389(6)	0.2900(8)	0.2590(12)	0.058(3)
C(6d)	0.2996(8)	0.2567(10)	0.2608(14)	0.082(5)
C(5d)	0.3133(8)	0.1781(9)	0.2873(14)	0.076(4)
C(4d)	0.2745(7)	0.1271(9)	0.3202(13)	0.069(4)
C(3d)	0.2131(6)	0.1578(8)	0.3200(11)	0.055(3)
C(2d)	0.1972(6)	0.2357(8)	0.2900(11)	0.055(3)
N(2d)	0.1324(4)	0.2644(5)	0.2840(8)	0.044(2)
C(1d)	0.0943(6)	0.2558(8)	0.1714(11)	0.053(3)
O(11)	0.2280(7)	0.3868(9)	0.4906(13)	0.124(5)
O(12)	0.3109(7)	0.4500(8)	0.6186(13)	0.124(5)

O(13)	0.3093(8)	0.4512(9)	0.4347(14)	0.141(5)
O(14)	0.2342(6)	0.5292(8)	0.5017(12)	0.120(4)
O(21)	0.0460(6)	0.2174(8)	0.7432(11)	0.100
O(22)	-0.0379(7)	0.2991(10)	0.7577(19)	0.100
O(23)	-0.0398(11)	0.1573(12)	0.7925(20)	0.100
O(24)	0.0306(9)	0.2476(13)	0.9090(18)	0.100
O(25)	-0.03580	0.27660	0.86200	0.1000
O(27)	-0.02310	0.16560	0.72580	0.1000
O(28)	0.05080	0.27510	0.76630	0.1000
O(29)	-0.01080	0.15750	0.85410	0.1000
O(30)	0.04280	0.19180	0.90290	0.1000
O(31)	-0.05810	0.23770	0.71030	0.1000
O(32)	-0.03450	0.30290	0.81370	0.1000
O(41)	0.3258(14)	0.2840(18)	0.8735(27)	0.129(10)
C(42)	0.2632(17)	0.2970(23)	0.8190(31)	0.097(11)
C(43)	0.2246(22)	0.2360(28)	0.8477(42)	0.125(15)
C(44)	0.2629(22)	0.2206(27)	0.9656(39)	0.129(15)
C(45)	0.3315(24)	0.2468(33)	0.9751(48)	0.146(17)
HN(2a)	-0.00420	0.30670	0.28320	0.0500
HN(2d)	0.12300	0.22310	0.30220	0.0500

TABLE 2 Fractional atomic coordinates for the hydrogen atoms

Atom	x	y	z
H(1a1)	0.0045	0.2811	0.0706
H(1a2)	0.0373	0.3621	0.1576
H(3a1)	-0.0646	0.3904	0.3068
H(4a1)	-0.1772	0.4393	0.2310
H(5a1)	-0.2414	0.3694	0.0730
H(6a1)	-0.2025	0.2534	-0.0069

H(8a1)	-0.1150	0.1673	-0.0331
H(9a1)	-0.0678	0.0485	-0.0224
H(9a2)	0.0124	0.0743	0.0136
H(9b1)	0.0058	-0.0534	0.1036
H(9b2)	-0.0626	-0.0232	0.1432
H(8b1)	0.0719	-0.0718	0.2646
H(6b1)	0.1441	-0.1069	0.4195
H(5b1)	0.2053	-0.0821	0.5985
H(4b1)	0.1885	0.0391	0.6959
H(5b1)	0.1221	0.1520	0.6064
H(1b1)	-0.0055	0.2437	0.4289
H(1b2)	0.0309	0.1873	0.5454
H(1c1)	0.1313	0.2570	0.4901
H(1c2)	0.0934	0.2959	0.5875
H(3c1)	0.0059	0.3296	0.5855
H(4c1)	-0.0797	0.4153	0.6190
H(5c1)	-0.1020	0.5504	0.5235
H(6c1)	-0.0394	0.5959	0.4087
H(8c1)	0.0363	0.5856	0.3207
H(8d1)	0.2602	0.4045	0.1887
H(6d1)	0.3350	0.2956	0.2408
H(5d1)	0.3583	0.1545	0.2812
H(4d1)	0.2885	0.0655	0.3462
H(3d1)	0.1792	0.1181	0.3433
H(1d1)	0.1199	0.2827	0.1172
H(1d2)	0.0874	0.1913	0.1539

TABLE 3 Anisotropic thermal parameters (Å^2)

Atom	U11	U22	U33	U23	U13	U12
Cu(1)	0.045(1)	0.046(1)	0.042(1)	0.003(1)	0.007(1)	0.007(1)
Cu(2)	0.050(1)	0.054(1)	0.051(1)	0.010(1)	0.012(1)	0.000(1)
C(9c)	0.086(12)	0.075(12)	0.195(25)	0.061(14)	0.077(15)	0.028(10)
C(9d)	0.191(22)	0.062(11)	0.182(25)	0.046(14)	0.109(21)	0.001(14)
O(1)	0.067(7)	0.139(10)	0.094(9)	0.012(8)	0.027(7)	-0.017(7)
Cl(1)	0.082(3)	0.139(4)	0.073(3)	-0.009(3)	0.019(3)	0.037(3)
Cl(2)	0.101(3)	0.063(2)	0.069(3)	0.006(2)	0.039(2)	0.011(2)

TABLE 4 Bond lengths (Å)

Cu(1) -N(2a)	2.102(9)	Cu(1) -N(1a)	1.938(11)
Cu(1) -N(1b)	1.940(10)	Cu(1) -N(2b)	2.010(9)
Cu(1) -O(1)	2.369(12)	Cu(2) -N(2c)	1.968(12)
Cu(2) -N(1c)	1.932(12)	Cu(2) -N(1d)	1.951(15)
Cu(2) -N(2d)	2.059(9)	C(1a) -N(2a)	1.447(18)
C(1a) -C(1d)	1.519(17)	N(2a) -C(2a)	1.461(14)
N(2a) -HN(2a)	.899(9)	C(2a) -C(3a)	1.375(19)
C(2a) -C(7a)	1.421(16)	C(3a) -C(4a)	1.461(19)
C(4a) -C(5a)	1.363(20)	C(5a) -C(6a)	1.353(21)
C(6a) -C(7a)	1.412(17)	C(7a) -C(8a)	1.437(19)
C(8a) -N(1a)	1.298(16)	N(1a) -C(9a)	1.461(18)
C(9a) -C(9b)	1.530(20)	C(9b) -N(1b)	1.481(17)
N(1b) -C(8b)	1.264(15)	C(8b) -C(7b)	1.460(17)
C(7b) -C(6b)	1.418(17)	C(7b) -C(2b)	1.428(17)
C(6b) -C(5b)	1.317(20)	C(5b) -C(4b)	1.347(21)
C(4b) -C(3b)	1.396(18)	C(3b) -C(2b)	1.439(17)
C(2b) -N(2b)	1.358(14)	N(2b) -C(1b)	1.470(17)

C(1b) -C(1c)	1.531(16)	C(1c) -N(2c)	1.501(15)
N(2c) -C(2c)	1.351(16)	C(2c) -C(3c)	1.449(21)
C(2c) -C(7c)	1.419(18)	C(3c) -C(4c)	1.387(22)
C(4c) -C(5c)	1.415(22)	C(5c) -C(6c)	1.308(24)
C(6c) -C(7c)	1.409(21)	C(7c) -C(8c)	1.397(22)
C(8c) -N(1c)	1.279(20)	N(1c) -C(9c)	1.46(3)
C(9c) -C(9d)	1.31(4)	C(9d) -N(1d)	1.528(24)
N(1d) -C(8d)	1.291(22)	C(8d) -C(7d)	1.434(20)
C(7d) -C(6d)	1.436(22)	C(7d) -C(2d)	1.396(20)
C(6d) -C(5d)	1.343(22)	C(5d) -C(4d)	1.328(24)
C(4d) -C(3d)	1.438(21)	C(3d) -C(2d)	1.350(18)
C(2d) -N(2d)	1.483(16)	N(2d) -C(1d)	1.482(16)
N(2d) -HN(2d)	.757(9)	Cl(1) -O(11)	1.453(16)
Cl(1) -O(12)	1.436(15)	Cl(1) -O(13)	1.407(20)
Cl(1) -O(14)	1.463(15)	O(41) -C(42)	1.40(4)
O(41) -C(45)	1.41(7)	C(42) -C(43)	1.41(6)
C(43) -C(44)	1.55(6)	C(44) -C(45)	1.54(7)

TABLE 5 Bond angles (°)

N(1a) -Cu(1) -N(2a)	85.2(4)	N(1b) -Cu(1) -N(2a)	160.2(5)
N(1b) -Cu(1) -N(1a)	84.8(4)	N(2b) -Cu(1) -N(2a)	95.6(4)
N(2b) -Cu(1) -N(1a)	174.6(5)	N(2b) -Cu(1) -N(1b)	92.8(4)
O(1) -Cu(1) -N(2a)	101.2(4)	O(1) -Cu(1) -N(1a)	91.3(4)
O(1) -Cu(1) -N(1b)	96.1(5)	O(1) -Cu(1) -N(2b)	93.8(4)
N(1c) -Cu(2) -N(2c)	93.4(5)	N(1d) -Cu(2) -N(2c)	175.2(5)
N(1d) -Cu(2) -N(1c)	84.0(6)	N(2d) -Cu(2) -N(2c)	96.9(4)
N(2d) -Cu(2) -N(1c)	154.3(5)	N(2d) -Cu(2) -N(1d)	87.0(5)
C(1d) -C(1a) -N(2a)	114(1)	C(1a) -N(2a) -Cu(1)	109.7(7)
C(2a) -N(2a) -Cu(1)	109.5(7)	C(2a) -N(2a) -C(1a)	111.0(9)

HN(2a)-N(2a) -Cu(1)	121.5(8)	HN(2a)-N(2a) -C(1a)	115.2(9)
HN(2a)-N(2a) -C(2a)	87.5(8)	C(3a) -C(2a) -N(2a)	119(1)
C(7a) -C(2a) -N(2a)	120(1)	C(7a) -C(2a) -C(3a)	121(1)
C(4a) -C(3a) -C(2a)	119(1)	C(5a) -C(4a) -C(3a)	118(1)
C(6a) -C(5a) -C(4a)	122(1)	C(7a) -C(6a) -C(5a)	123(1)
C(6a) -C(7a) -C(2a)	117(1)	C(8a) -C(7a) -C(2a)	124(1)
C(8a) -C(7a) -C(6a)	119(1)	N(1a) -C(8a) -C(7a)	122(1)
C(8a) -N(1a) -Cu(1)	127(1)	C(9a) -N(1a) -Cu(1)	113.7(8)
C(9a) -N(1a) -C(8a)	118(1)	C(9b) -C(9a) -N(1a)	105(1)
N(1b) -C(9b) -C(9a)	109(1)	C(9b) -N(1b) -Cu(1)	110.5(8)
C(8b) -N(1b) -Cu(1)	128.1(9)	C(8b) -N(1b) -C(9b)	121(1)
C(7b) -C(8b) -N(1b)	126(1)	C(6b) -C(7b) -C(8b)	115(1)
C(2b) -C(7b) -C(8b)	124(1)	C(2b) -C(7b) -C(6b)	121(1)
C(5b) -C(6b) -C(7b)	121(1)	C(4b) -C(5b) -C(6b)	121(1)
C(3b) -C(4b) -C(5b)	122(1)	C(2b) -C(3b) -C(4b)	120(1)
C(3b) -C(2b) -C(7b)	115(1)	N(2b) -C(2b) -C(7b)	124(1)
N(2b) -C(2b) -C(3b)	120(1)	C(2b) -N(2b) -Cu(1)	124.5(8)
C(1b) -N(2b) -Cu(1)	116.2(7)	C(1b) -N(2b) -C(2b)	118(1)
C(1c) -C(1b) -N(2b)	115(1)	N(2c) -C(1c) -C(1b)	114.0(9)
C(1c) -N(2c) -Cu(2)	116.9(8)	C(2c) -N(2c) -Cu(2)	125.6(8)
C(2c) -N(2c) -C(1c)	117(1)	C(3c) -C(2c) -N(2c)	122(1)
C(7c) -C(2c) -N(2c)	123(1)	C(7c) -C(2c) -C(3c)	115(1)
C(4c) -C(3c) -C(2c)	122(1)	C(5c) -C(4c) -C(3c)	119(2)
C(6c) -C(5c) -C(4c)	120(1)	C(7c) -C(6c) -C(5c)	124(1)
C(6c) -C(7c) -C(2c)	119(1)	C(8c) -C(7c) -C(2c)	124(1)
C(8c) -C(7c) -C(6c)	117(1)	N(1c) -C(8c) -C(7c)	129(1)
C(8c) -N(1c) -Cu(2)	125(1)	C(9c) -N(1c) -Cu(2)	112(1)
C(9c) -N(1c) -C(8c)	123(1)	C(9d) -C(9c) -N(1c)	117(2)
N(1d) -C(9d) -C(9c)	112(2)	C(9d) -N(1d) -Cu(2)	111(1)

C(8d) -N(1d) -Cu(2)	126(1)	C(8d) -N(1d) -C(9d)	122(2)
C(7d) -C(8d) -N(1d)	123(2)	C(6d) -C(7d) -C(8d)	118(1)
C(2d) -C(7d) -C(8d)	127(1)	C(2d) -C(7d) -C(6d)	115(1)
C(5d) -C(6d) -C(7d)	121(2)	C(4d) -C(5d) -C(6d)	124(2)
C(3d) -C(4d) -C(5d)	117(1)	C(2d) -C(3d) -C(4d)	120(1)
C(3d) -C(2d) -C(7d)	122(1)	N(2d) -C(2d) -C(7d)	118(1)
N(2d) -C(2d) -C(3d)	119(1)	C(2d) -N(2d) -Cu(2)	115.4(7)
C(1d) -N(2d) -Cu(2)	108.7(7)	C(1d) -N(2d) -C(2d)	110(1)
HN(2d)-N(2d) -Cu(2)	134(1)	HN(2d)-N(2d) -C(2d)	91.9(9)
HN(2d)-N(2d) -C(1d)	94.5(9)	N(2d) -C(1d) -C(1a)	114(1)
O(12) -Cl(1) -O(11)	110.3(9)	O(13) -Cl(1) -O(11)	109(1)
O(13) -Cl(1) -O(12)	110(1)	O(14) -Cl(1) -O(11)	106.1(9)
O(14) -Cl(1) -O(12)	108.4(9)	O(14) -Cl(1) -O(13)	113.2(9)

TABLE 6 Intermolecular distances (Å)

H(5c1)...C(4a)	2.92	2	0.0	1.0	0.0
H(5c1)...C(5a)	2.99	2	0.0	1.0	0.0
C(4b) ...H(5a1)	2.75	2	0.5	0.5	0.0
C(3b) ...H(5a1)	2.94	2	0.5	0.5	0.0
C(6d) ...H(6a1)	2.97	2	0.5	0.5	0.0
C(5d) ...H(6a1)	2.94	2	0.5	0.5	0.0
C(4d) ...H(6a1)	2.89	2	0.5	0.5	0.0
C(3d) ...H(6a1)	2.91	2	0.5	0.5	0.0
C(2d) ...H(6a1)	2.97	2	0.5	0.5	0.0
O(11) ...H(6a1)	2.75	2	0.5	0.5	0.0
O(13) ...H(8a1)	2.52	2	0.5	0.5	0.0
O(13) ...H(9a1)	2.62	2	0.5	0.5	0.0
C(7b) ...H(9a2)	2.97	2	0.0	0.0	0.0
C(3b) ...H(9b1)	2.90	2	0.0	0.0	0.0

O(12) ...H(9b2)	2.97	2	0.5	0.5	0.0
C(4d) ...H(5b1)	2.96	2	0.0	0.0	-1.0
O(12) ...H(8d1)	2.85	2	0.0	1.0	0.0
O(14) ...H(8d1)	2.55	2	0.0	1.0	0.0
O(12) ...O(1)	2.98	2	0.5	0.5	0.0
O(41) ...O(1)	2.68	2	0.5	0.5	0.0

TABLE 7 Intramolecular distances (Å)

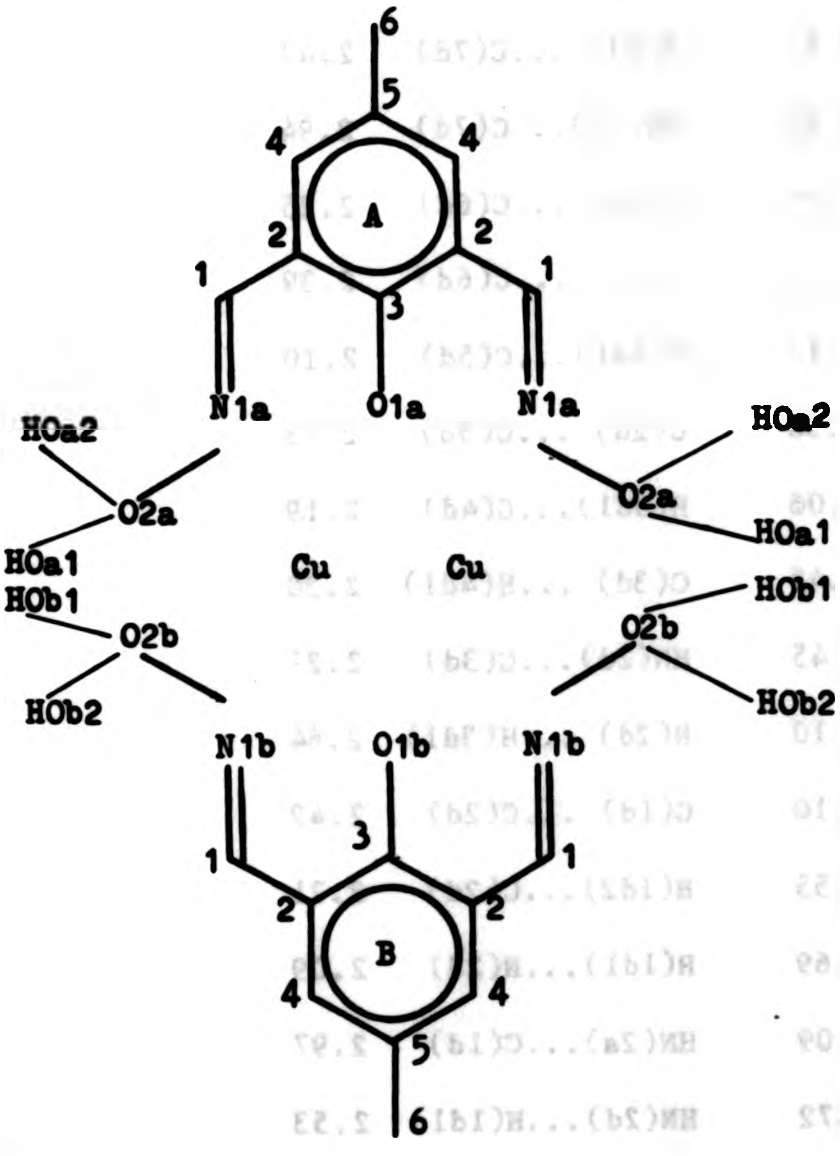
C(1a) ...Cu(1)	2.93	C(2a) ...Cu(1)	2.93
C(8a) ...Cu(1)	2.91	C(9a) ...Cu(1)	2.86
C(9b) ...Cu(1)	2.82	C(8b) ...Cu(1)	2.90
C(2b) ...Cu(1)	3.00	C(1b) ...Cu(1)	2.97
H(1b1)...Cu(1)	2.81	H(1d2)...Cu(1)	2.62
HN(2a)...Cu(1)	2.68	HN(2d)...Cu(1)	2.92
H(1a2)...Cu(2)	2.61	C(1c) ...Cu(2)	2.97
H(1c1)...Cu(2)	2.83	C(2c) ...Cu(2)	2.97
C(8c) ...Cu(2)	2.86	C(9c) ...Cu(2)	2.82
C(9d) ...Cu(2)	2.88	C(8d) ...Cu(2)	2.91
C(1d) ...Cu(2)	2.90	O(11) ...Cu(2)	2.63
HN(2d)...Cu(2)	2.64	C(2a) ...C(1a)	2.40
N(2d) ...C(1a)	2.52	H(1d1)...C(1a)	2.12
H(1d2)...C(1a)	2.12	HN(2a)...C(1a)	2.00
HN(2d)...C(1a)	2.72	N(2a) ...H(1a1)	2.06
C(2a) ...H(1a1)	2.50	C(7a) ...H(1a1)	2.66
C(8a) ...H(1a1)	2.59	N(1a) ...H(1a1)	2.62
C(1d) ...H(1a1)	2.12	N(2a) ...H(1a2)	2.06
C(2a) ...H(1a2)	2.73	N(2d) ...H(1a2)	2.81
C(1d) ...H(1a2)	2.12	HN(2a)...H(1a2)	2.21
C(3a) ...N(2a)	2.44	H(3a1)...N(2a)	2.65

C(7a) ...N(2a)	2.49	C(8a) ...N(2a)	2.95
N(1a) ...N(2a)	2.74	H(1b1)...N(2a)	2.60
N(2d) ...N(2a)	2.96	C(1d) ...N(2a)	2.49
H(1d2)...N(2a)	2.78	HN(2d)...N(2a)	2.88
H(3a1)...C(2a)	2.13	C(4a) ...C(2a)	2.45
C(5a) ...C(2a)	2.78	C(6a) ...C(2a)	2.41
C(8a) ...C(2a)	2.52	N(1a) ...C(2a)	2.94
HN(2a)...C(2a)	1.68	H(4a1)...C(3a)	2.22
C(5a) ...C(3a)	2.43	C(6a) ...C(3a)	2.77
C(7a) ...C(3a)	2.44	HN(2a)...C(3a)	2.12
C(4a) ...H(3a1)	2.21	C(2c) ...H(3a1)	2.54
C(3c) ...H(3a1)	2.96	C(6c) ...H(3a1)	2.95
C(7c) ...H(3a1)	2.60	HN(2a)...H(3a1)	1.98
H(5a1)...C(4a)	2.11	C(6a) ...C(4a)	2.37
C(7a) ...C(4a)	2.83	C(5a) ...H(4a1)	2.13
H(6a1)...C(5a)	2.10	C(7a) ...C(5a)	2.43
C(6a) ...H(5a1)	2.10	C(8a) ...C(6a)	2.46
H(8a1)...C(6a)	2.71	C(7a) ...H(6a1)	2.15
C(8a) ...H(6a1)	2.66	H(8a1)...C(7a)	2.18
N(1a) ...C(7a)	2.39	C(9a) ...C(8a)	2.37
H(9a1)...C(8a)	2.47	H(9a2)...C(8a)	2.99
N(1a) ...H(8a1)	2.06	C(9a) ...H(8a1)	2.54
H(9a1)...N(1a)	2.10	H(9a2)...N(1a)	2.10
C(9b) ...N(1a)	2.38	H(9b2)...N(1a)	2.75
N(1b) ...N(1a)	2.61	H(1d2)...N(1a)	2.93
H(9b1)...C(9a)	2.15	H(9b2)...C(9a)	2.16
N(1b) ...C(9a)	2.45	C(9b) ...H(9a1)	2.15
C(9b) ...H(9a2)	2.17	N(1b) ...H(9a2)	2.83
C(8b) ...C(9b)	2.40	H(8b1)...C(9b)	2.55

N(1b) ...H(9b1)	2.10	C(8b) ...H(9b1)	2.53
N(1b) ...H(9b2)	2.11	C(8b) ...H(9b2)	2.96
H(8b1)...N(1b)	2.00	C(7b) ...N(1b)	2.43
C(2b) ...N(1b)	2.99	N(2b) ...N(1b)	2.86
C(6b) ...C(8b)	2.43	H(6b1)...C(8b)	2.61
C(2b) ...C(8b)	2.55	C(7b) ...H(8b1)	2.18
C(6b) ...H(8b1)	2.58	H(6b1)...C(7b)	2.17
C(5b) ...C(7b)	2.38	C(4b) ...C(7b)	2.74
C(3b) ...C(7b)	2.42	N(2b) ...C(7b)	2.46
H(3d1)...C(7b)	2.71	H(5b1)...C(6b)	2.08
C(4b) ...C(6b)	2.31	C(3b) ...C(6b)	2.77
C(2b) ...C(6b)	2.47	C(5b) ...H(6b1)	2.07
H(4b1)...C(5b)	2.10	C(3b) ...C(5b)	2.40
C(2b) ...C(5b)	2.83	C(4b) ...H(5b1)	2.10
H(5b1)...C(4b)	2.16	C(2b) ...C(4b)	2.45
C(3b) ...H(4b1)	2.13	N(2b) ...C(3b)	2.43
C(1b) ...C(3b)	2.79	H(1b2)...C(3b)	2.53
H(1c1)...C(3b)	2.79	C(2b) ...H(5b1)	2.19
N(2b) ...H(5b1)	2.67	C(1b) ...H(5b1)	2.43
C(1c) ...H(5b1)	2.51	O(21) ...H(5b1)	2.89
C(1b) ...C(2b)	2.42	H(1b2)...C(2b)	2.56
H(1c1)...C(2b)	2.90	H(3d1)...C(2b)	2.67
H(1b1)...N(2b)	2.08	H(1b2)...N(2b)	2.08
C(1c) ...N(2b)	2.53	H(1c1)...N(2b)	2.53
HN(2d)...N(2b)	2.53	H(1c1)...C(1b)	2.13
H(1c2)...C(1b)	2.14	N(2c) ...C(1b)	2.54
H(3c1)...C(1b)	2.56	HN(2a)...C(1b)	2.79
C(1c) ...H(1b1)	2.13	N(2c) ...H(1b1)	2.53
C(2c) ...H(1b1)	2.83	C(3c) ...H(1b1)	2.74

HN(2a)...H(1b1)	2.12	C(1c) ...H(1b2)	2.13
C(2c) ...C(1c)	2.43	C(3c) ...C(1c)	2.80
H(3c1)...C(1c)	2.42	HN(2d)...C(1c)	2.99
N(2c) ...H(1c1)	2.10	N(2d) ...H(1c1)	2.63
O(11) ...H(1c1)	3.00	HN(2d)...H(1c1)	2.41
N(2c) ...H(1c2)	2.11	C(2c) ...H(1c2)	2.60
C(3c) ...H(1c2)	2.57	C(3c) ...N(2c)	2.44
H(3c1)...N(2c)	2.69	C(7c) ...N(2c)	2.43
C(8c) ...N(2c)	2.93	N(1c) ...N(2c)	2.84
HN(2a)...N(2c)	2.42	H(3c1)...C(2c)	2.19
C(4c) ...C(2c)	2.49	C(5c) ...C(2c)	2.84
C(6c) ...C(2c)	2.44	C(8c) ...C(2c)	2.49
N(1c) ...C(2c)	2.99	HN(2a)...C(2c)	2.80
H(4c1)...C(3c)	2.15	C(5c) ...C(3c)	2.41
C(6c) ...C(3c)	2.73	C(7c) ...C(3c)	2.42
C(4c) ...H(3c1)	2.13	O(21) ...H(3c1)	2.70
H(5c1)...C(4c)	2.17	C(6c) ...C(4c)	2.35
C(7c) ...C(4c)	2.81	C(5c) ...H(4c1)	2.17
H(6c1)...C(5c)	2.05	C(7c) ...C(5c)	2.40
C(6c) ...H(5c1)	2.07	C(8c) ...C(6c)	2.39
H(8c1)...C(6c)	2.52	C(7c) ...H(6c1)	2.14
C(8c) ...H(6c1)	2.56	H(8c1)...C(7c)	2.11
N(1c) ...C(7c)	2.41	C(9c) ...C(8c)	2.41
N(1c) ...H(8c1)	2.00	C(9c) ...H(8c1)	2.56
C(9d) ...N(1c)	2.36	N(1d) ...N(1c)	2.60
N(1d) ...C(9c)	2.35	C(8d) ...C(9d)	2.47
H(8d1)...C(9d)	2.65	H(8d1)...N(1d)	2.04
C(7d) ...N(1d)	2.39	C(2d) ...N(1d)	2.99
N(2d) ...N(1d)	2.76	H(1d1)...N(1d)	2.79

C(6d) ...C(8d)	2.46	H(6d1)...C(8d)	2.66
C(2d) ...C(8d)	2.53	N(2d) ...C(8d)	2.97
H(1d1)...C(8d)	2.85	C(7d) ...H(8d1)	2.17
C(6d) ...H(8d1)	2.65	H(6d1)...C(7d)	2.18
C(5d) ...C(7d)	2.42	C(4d) ...C(7d)	2.83
C(3d) ...C(7d)	2.41	N(2d) ...C(7d)	2.47
H(1d1)...C(7d)	2.80	HN(2d)...C(7d)	2.94
H(5d1)...C(6d)	2.09	C(4d) ...C(6d)	2.35
C(3d) ...C(6d)	2.73	C(2d) ...C(6d)	2.39
C(5d) ...H(6d1)	2.10	H(4d1)...C(5d)	2.10
C(3d) ...C(5d)	2.36	C(2d) ...C(5d)	2.73
C(4d) ...H(5d1)	2.06	H(3d1)...C(4d)	2.19
C(2d) ...C(4d)	2.42	C(3d) ...H(4d1)	2.20
N(2d) ...C(3d)	2.45	HN(2d)...C(3d)	2.21
C(2d) ...H(3d1)	2.10	N(2d) ...H(3d1)	2.64
HN(2d)...H(3d1)	2.10	C(1d) ...C(2d)	2.42
H(1d1)...C(2d)	2.55	H(1d2)...C(2d)	2.71
HN(2d)...C(2d)	1.69	H(1d1)...N(2d)	2.09
H(1d2)...N(2d)	2.09	HN(2a)...C(1d)	2.97
HN(2d)...C(1d)	1.72	HN(2d)...H(1d1)	2.53
HN(2d)...H(1d2)	1.93	O(12) ...O(11)	2.37
O(13) ...O(11)	2.32	O(14) ...O(11)	2.33
O(13) ...O(12)	2.33	O(14) ...O(12)	2.35
O(14) ...O(13)	2.40		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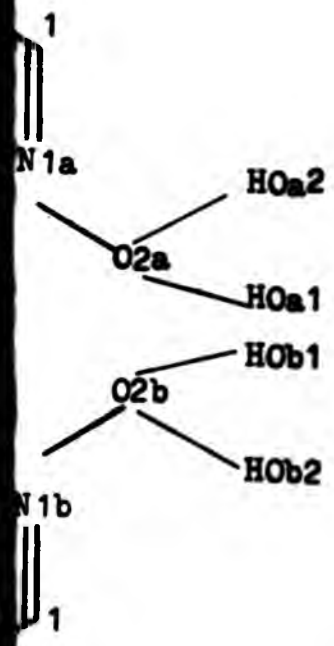


The X-ray crystallographic data for $[Cu_2(H_2DFMP)_2(ClO_4)_2].thf$ (see section 7.3) schematic diagram facing page.

TABLE 1 Fractional atomic coordinates and thermal parameters (Å^2)

Atom	x	y	z	Uiso or Ueq
Cu	0.51711(11)	0.18051(10)	0.12873(21)	0.0624(14)
Cl	0.5144(3)	0.2273(2)	-0.1008(4)	0.073(4)
O(1b)	0.5763(8)	0.2500	0.1250	0.069(5)
(C3b)	0.6374(12)	0.2500	0.1250	0.054(7)
C(2b)	0.6696(8)	0.1964(8)	0.1378(13)	0.056(5)
C(4b)	0.7364(9)	0.1956(9)	0.1418(13)	0.068(6)
(C5b)	0.7697(14)	0.2500	0.1250	0.083(9)
C(6b)	0.8400(16)	0.2500	0.1250	0.110(12)
C(2b)	0.6410(10)	0.1321(10)	0.1557(13)	0.076(7)
N(1b)	0.5858(8)	0.1217(8)	0.1554(10)	0.063(5)
O(2b)	0.5725(8)	0.0607(8)	0.1821(10)	0.094(5)
O(1a)	0.4597(7)	0.2500	0.1250	0.051(4)
C(3a)	0.3973(11)	0.2500	0.1250	0.048(6)
C(2a)	0.3646(8)	0.1944(8)	0.1217(14)	0.056(5)
C(1a)	0.3901(8)	0.1332(9)	0.1130(14)	0.062(5)
C(4a)	0.2995(9)	0.1960(10)	0.1203(17)	0.074(6)
C(5a)	0.2665(14)	0.2500	0.1250	0.085(9)
C(6a)	0.1922(17)	0.2500	0.1250	0.115(13)
N(1a)	0.4485(7)	0.1225(8)	0.1148(13)	0.064(5)
O(2a)	0.4656(7)	0.0598(7)	0.1012(10)	0.090(5)
O(31)	0.5193(9)	0.2882(8)	-0.0598(10)	0.098(5)
O(32)	0.5349(8)	0.1807(9)	-0.0392(11)	0.111(5)
O(33)	0.4541(9)	0.2170(8)	-0.1333(15)	0.130(6)

O(34)	0.5557(9)	0.2261(9)	-0.1769(13)	0.130(7)
C(1)	0.3674(26)	-0.0483(24)	-0.1430(39)	0.101(16)
C(2)	0.40618	-0.03529	-0.06861	0.1567(41)
C(3)	0.3304(58)	-0.0377(55)	-0.1027(83)	0.092(35)
C(4)	0.3798(52)	0.0621(49)	-0.0946(69)	0.106(35)
C(5)	0.3300(39)	-0.0068(37)	-0.1353(57)	0.075(24)
C(6)	0.4220(19)	0.0179(19)	-0.0318(24)	0.074(11)
C(7)	0.3913(19)	0.0227(22)	-0.0285(27)	0.085(12)
C(8)	0.3895(18)	0.0090(21)	-0.1773(24)	0.136(14)
C(9)	0.4175(26)	0.0493(23)	-0.1088(40)	0.134(18)
C(10)	0.3665(19)	-0.0368(18)	-0.0388(27)	0.136(13)
HO(b2)	0.59007	0.03444	0.23837	0.1000
HO(a2)	0.44543	0.03271	0.04435	0.1000
HO(b1)	0.54050	0.04970	0.12800	0.1000
HO(a1)	0.50229	0.03769	0.14746	0.1000

TABLE 2 Fractional atomic coordinates for the hydrogen atoms

Atom	x	y	z
H(13)	0.7609	0.1531	0.1571
H(16)	0.6722	0.0938	0.1686
H(26)	0.3587	0.0945	0.1046
H(23)	0.2744	0.1527	0.1152

TABLE 3 Anisotropic thermal parameters (Å^2)

Atom	U11	U22	U33	U23	U13	U12
Cu	0.059(1)	0.031(1)	0.097(2)	0.000(1)	-0.007(2)	-0.002(1)
Cl	0.066(3)	0.073(3)	0.080(4)	-0.002(3)	0.006(3)	-0.001(3)

TABLE 4 Bond lengths (Å)

Cu	-O(1b)	1.965(12)	Cu	-N(1b)	1.985(18)
Cu	-O(1a)	1.941(10)	Cu	-N(1a)	1.945(16)
Cu	-O(32)	2.508(17)	Cu	-Cu	2.994(4)
O(1b)	-(C3b)	1.32(3)	(C3b)	-C(2b)	1.359(21)
C(2b)	-C(4b)	1.44(3)	C(2b)	-C(2b)	1.54(3)
C(4b)	-(C5b)	1.394(24)	(C5b)	-C(6b)	1.51(5)
C(2b)	-N(1b)	1.21(3)	C(2b)	-O(2b)	2.16(3)
N(1b)	-O(2b)	1.401(24)	O(2b)	-HO(b2)	1.074(16)
O(2b)	-HO(b1)	1.081(16)	O(2b)	-HO(a1)	1.671(17)
O(1a)	-C(3a)	1.34(3)	C(3a)	-C(2a)	1.389(20)
C(2a)	-C(1a)	1.43(3)	C(2a)	-C(4a)	1.402(25)
C(1a)	-N(1a)	1.279(24)	C(4a)	-C(5a)	1.37(3)
C(5a)	-C(6a)	1.60(5)	N(1a)	-O(2a)	1.414(22)
O(2a)	-HO(a2)	1.110(15)	O(2a)	-HO(b1)	1.675(14)
O(2a)	-HO(a1)	1.148(15)	Cl	-O(31)	1.449(17)
Cl	-O(32)	1.423(19)	Cl	-O(33)	1.402(20)
Cl	-O(34)	1.433(20)	C(1)	-C(2)	1.41(6)
HO(b1)-HO(a1)		.909(1)			

TABLE 5 Bond angles (°)

N(1b)	-Cu	-O(1b)	90.5(7)	O(1a)	-Cu	-O(1b)	79.9(5)
O(1a)	-Cu	-N(1b)	166.1(6)	N(1a)	-Cu	-O(1b)	167.9(6)
N(1a)	-Cu	-N(1b)	100.2(7)	N(1a)	-Cu	-O(1a)	90.5(6)
O(32)	-Cu	-O(1b)	82.7(4)	O(32)	-Cu	-N(1b)	94.8(6)
O(32)	-Cu	-O(1a)	93.9(4)	O(32)	-Cu	-N(1a)	90.7(7)
Cu	-O(1b)	-Cu	99.2(8)	Cu	-O(1a)	-Cu	100.9(7)
(C3b)	-O(1b)	-Cu	130.4(4)	C(2b)	-(C3b)	-O(1b)	121(1)
C(4b)	-C(2b)	-(C3b)	122(2)	C(2b)	-C(2b)	-(C3b)	126(2)
C(2b)	-C(2b)	-C(4b)	112(2)	C(2b)	-(C3b)	-C(2b)	119(2)

(C5b) -C(4b) -C(2b)	120(2)	C(4b) -(C5b) -C(4b)	118(3)
C(6b) -(C5b) -C(4b)	121(1)	N(1b) -C(2b) -C(2b)	124(2)
O(2b) -C(2b) -C(2b)	160(2)	O(2b) -C(2b) -N(1b)	37(1)
C(2b) -N(1b) -Cu	128(2)	O(2b) -N(1b) -Cu	120(1)
O(2b) -N(1b) -C(2b)	112(2)	N(1b) -O(2b) -C(2b)	31(1)
HO(b2)-O(2b) -C(2b)	106(1)	HO(b2)-O(2b) -N(1b)	130(2)
HO(b1)-O(2b) -C(2b)	117(1)	HO(b1)-O(2b) -N(1b)	97(1)
HO(b1)-O(2b) -HO(b2)	133(2)	HO(a1)-O(2b) -C(2b)	140(1)
HO(a1)-O(2b) -N(1b)	112(1)	HO(a1)-O(2b) -HO(b2)	113(1)
HO(a1)-O(2b) -HO(b1)	29.8(5)	C(3a) -O(1a) -Cu	129.5(3)
C(2a) -C(3a) -O(1a)	120(1)	C(1a) -C(2a) -C(3a)	127(2)
C(4a) -C(2a) -C(3a)	119(2)	C(4a) -C(2a) -C(1a)	114(2)
C(2a) -C(3a) -C(2a)	119(2)	N(1a) -C(1a) -C(2a)	123(2)
C(5a) -C(4a) -C(2a)	123(2)	C(4a) -C(5a) -C(4a)	117(3)
C(6a) -C(5a) -C(4a)	121(1)	C(1a) -N(1a) -Cu	129(1)
O(2a) -N(1a) -Cu	115(1)	O(2a) -N(1a) -C(1a)	115(2)
HO(a2)-O(2a) -N(1a)	120(1)	HO(b1)-O(2a) -N(1a)	110(1)
HO(b1)-O(2a) -HO(a2)	119(1)	HO(a1)-O(2a) -N(1a)	119(1)
HO(a1)-O(2a) -HO(a2)	120(1)	HO(a1)-O(2a) -HO(b1)	31.0(4)
O(32) -Cl -O(31)	110(1)	O(33) -Cl -O(31)	111(1)
O(33) -Cl -O(32)	113(1)	O(34) -Cl -O(31)	107(1)
O(34) -Cl -O(32)	107(1)	O(34) -Cl -O(33)	108(1)
Cl -O(32) -Cu	126(1)		

<u>TABLE 6 Intermolecular distances (Å)</u>

O(1b) ...Cu	1.97	3	0.0	0.0	0.0
(C3b) ...Cu	2.99	3	0.0	0.0	0.0
O(1a) ...Cu	1.94	3	0.0	0.0	0.0
C(3a) ...Cu	2.98	3	0.0	0.0	0.0

O(31) ...Cu	2.76	3	0.0	0.0	0.0
HO(b2)...Cu	2.98	6	0.5	0.5	0.5
C(2b) ...C(2b)	2.34	3	0.0	0.0	0.0
C(4b) ...C(2b)	2.77	3	0.0	0.0	0.0
(C5b) ...C(2b)	2.45	3	0.0	0.0	0.0
C(4b) ...C(4b)	2.39	3	0.0	0.0	0.0
(C5b) ...C(4b)	1.39	3	0.0	0.0	0.0
C(6b) ...C(4b)	2.53	3	0.0	0.0	0.0
(C5b) ...H(13)	2.15	3	0.0	0.0	0.0
C(6b) ...H(13)	2.73	3	0.0	0.0	0.0
O(33) ...H(13)	2.43	8	0.5	0.5	-0.5
O(31) ...H(16)	2.60	8	0.5	0.5	-0.5
O(33) ...H(16)	2.71	8	0.5	0.5	-0.5
O(2a) ...O(2b)	2.97	2	1.0	0.0	0.0
HO(a2)...O(2b)	2.89	2	1.0	0.0	0.0
HO(a1)...O(2b)	2.71	2	1.0	0.0	0.0
HO(a1)...O(2b)	2.96	5	0.5	-0.5	0.5
HO(b2)...O(2b)	2.66	6	0.5	0.5	0.5
C(2a) ...C(2a)	2.40	3	0.0	0.0	0.0
C(4a) ...C(2a)	2.75	3	0.0	0.0	0.0
C(5a) ...C(2a)	2.43	3	0.0	0.0	0.0
HO(b2)...C(1a)	2.88	6	0.5	0.5	0.5
O(31) ...H(26)	2.55	4	0.5	-0.5	-0.5
C(4a) ...C(4a)	2.33	3	0.0	0.0	0.0
C(5a) ...C(4a)	1.37	3	0.0	0.0	0.0
C(6a) ...C(4a)	2.59	3	0.0	0.0	0.0
C(5a) ...H(23)	2.11	3	0.0	0.0	0.0
C(6a) ...H(23)	2.75	3	0.0	0.0	0.0
O(34) ...H(23)	2.41	4	0.5	-0.5	-0.5

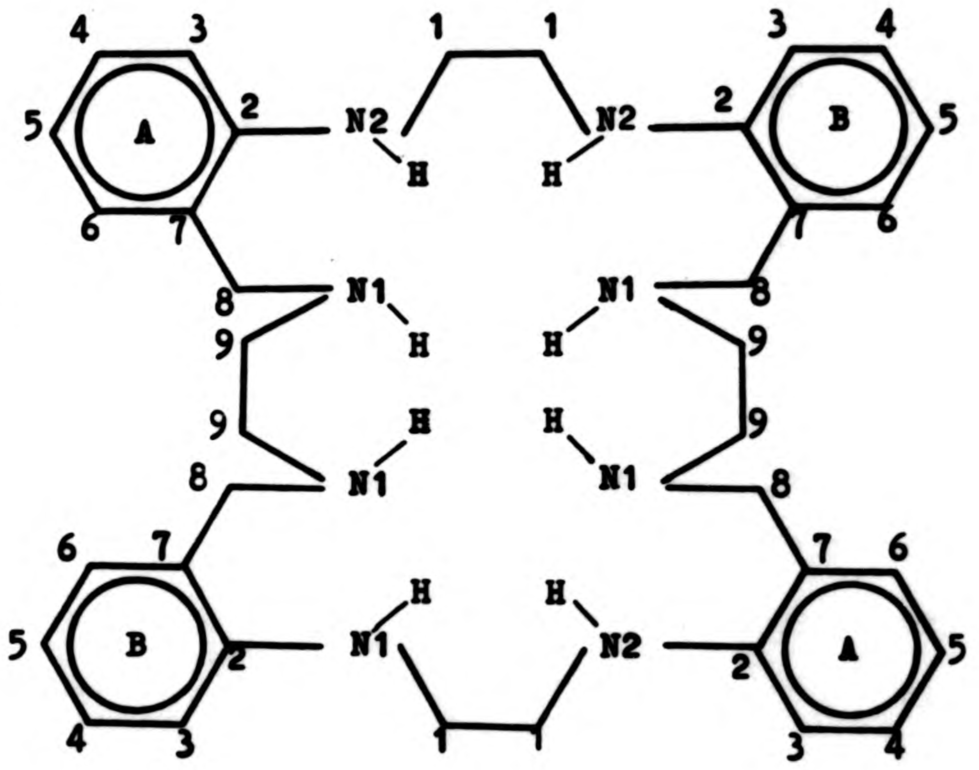
HO(b2)...N(1a)	2.31	6	0.5	0.5	0.5
O(2a) ...O(2a)	2.97	2	1.0	0.0	0.0
HO(a2)...O(2a)	2.89	2	1.0	0.0	0.0
HO(b1)...O(2a)	2.39	2	1.0	0.0	0.0
HO(b2)...O(2a)	2.31	2	1.0	0.0	0.0
HO(b2)...O(2a)	2.46	6	0.5	0.5	0.5
HO(b2)...O(31)	2.95	8	1.0	0.0	0.0
HO(b1)...C(6)	2.89	2	1.0	0.0	0.0
HO(a1)...HO(b2)	2.18	5	0.5	-0.5	0.5
HO(b1)...HO(a2)	2.18	2	1.0	0.0	0.0
HO(a1)...HO(a2)	2.43	2	1.0	0.0	0.0
HO(a1)...HO(b1)	2.11	2	1.0	0.0	0.0
HO(a1)...HO(b2)	1.63	2	1.0	0.0	0.0

TABLE 7 Intramolecular distances (Å)

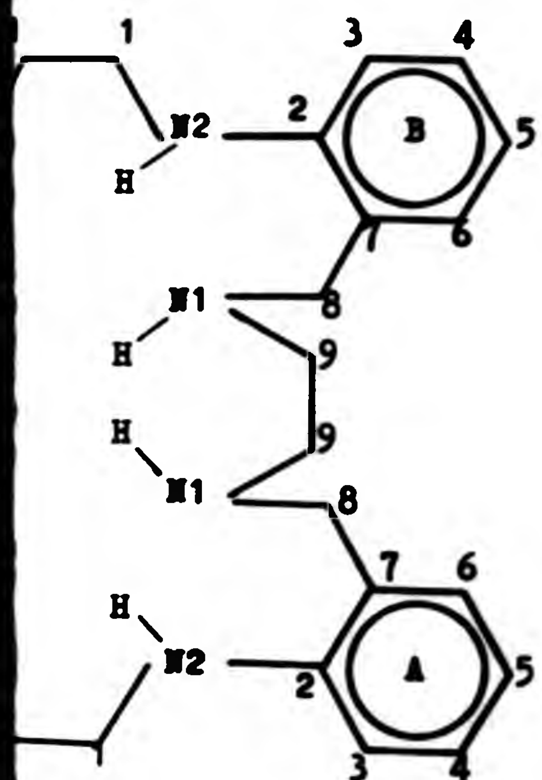
(C3b) ...Cu	2.99	C(2b) ...Cu	2.89
O(2b) ...Cu	2.95	C(3a) ...Cu	2.98
C(1a) ...Cu	2.93	O(2a) ...Cu	2.85
HO(b1)...Cu	2.86	C(2b) ...O(1b)	2.32
C(2b) ...O(1b)	2.93	N(1b) ...O(1b)	2.81
O(1a) ...O(1b)	2.51	O(32) ...O(1b)	2.98
C(4b) ...(C3b)	2.44	(C5b) ...(C3b)	2.85
C(2b) ...(C3b)	2.58	H(13) ...C(2b)	2.19
(C5b) ...C(2b)	2.45	H(16) ...C(2b)	2.26
N(1b) ...C(2b)	2.43	C(6b) ...C(4b)	2.53
C(2b) ...C(4b)	2.48	H(16) ...C(4b)	2.62
(C5b) ...H(13)	2.15	C(6b) ...H(13)	2.73
C(2b) ...H(13)	2.62	HO(b2)...C(2b)	2.67
HO(b1)...C(2b)	2.83	N(1b) ...H(16)	1.96

O(2b) ...H(16)	2.27	HO(b2)...H(16)	2.41
HO(b2)...N(1b)	2.25	HO(b1)...N(1b)	1.88
HO(a1)...N(1b)	2.55	O(2a) ...O(2b)	2.59
C(2a) ...O(1a)	2.37	C(1a) ...O(1a)	2.93
N(1a) ...O(1a)	2.76	C(1a) ...C(3a)	2.52
C(4a) ...C(3a)	2.41	C(5a) ...C(3a)	2.82
N(1a) ...C(3a)	2.96	H(26) ...C(2a)	2.17
H(23) ...C(2a)	2.14	C(5a) ...C(2a)	2.43
N(1a) ...C(2a)	2.38	C(4a) ...C(1a)	2.37
H(23) ...C(1a)	2.52	O(2a) ...C(1a)	2.27
HO(a2)...C(1a)	2.67	C(4a) ...H(26)	2.54
N(1a) ...H(26)	2.03	O(2a) ...H(26)	2.42
C(6) ...H(26)	2.94	C(7) ...H(26)	2.60
HO(a2)...H(26)	2.46	C(6a) ...C(4a)	2.59
C(5a) ...H(23)	2.11	C(6a) ...H(23)	2.75
HO(a2)...N(1a)	2.20	HO(b1)...N(1a)	2.53
HO(a1)...N(1a)	2.22	C(6) ...O(2a)	2.35
C(7) ...O(2a)	2.62	O(32) ...O(31)	2.36
O(33) ...O(31)	2.35	O(34) ...O(31)	2.32
O(33) ...O(32)	2.36	O(34) ...O(32)	2.30
O(34) ...O(33)	2.29	C(4) ...C(1)	2.50
C(6) ...C(1)	2.47	C(7) ...C(1)	2.34
C(9) ...C(1)	2.41	HO(a2)...C(2)	2.37
C(4) ...C(3)	2.40	C(6) ...C(3)	2.53
C(9) ...C(3)	2.65	C(10) ...C(4)	2.30
HO(a2)...C(4)	2.57	C(6) ...C(5)	2.56
C(9) ...C(5)	2.27	C(8) ...C(6)	2.27
C(10) ...C(8)	2.32	C(10) ...C(9)	2.39
HO(a2)...C(9)	2.37	HO(a2)...C(10)	2.58

HO(b1)...HO(b2)	1.97	HO(a1)...HO(b2)	2.32
HO(b1)...HO(a2)	2.42	HO(a1)...HO(a2)	1.96



H_{12}cyendimer



dimer

The X-ray crystallographic data for H_{12}cyendimer (see section 7.4)

TABLE 1 Fractional atomic coordinates and thermal parameters (Å²)

Atom	x	y	z	Uiso or Ueq
N(2a)	0.4464(6)	0.1386(9)	-0.2225(8)	0.050(6)
N(1a)	0.5178(6)	0.1768(9)	0.0208(8)	0.056(7)
N(1b)	0.5746(7)	0.3025(9)	0.2540(7)	0.048(6)
N(2b)	0.4680(7)	0.0898(9)	0.3516(8)	0.053(7)
N(2b')	0.5320(7)	-0.0898(9)	-0.3516(8)	0.000
C(1a)	0.4854(6)	0.1492(10)	-0.3334(9)	0.061(3)
C(2a)	0.3797(7)	0.2333(10)	-0.1971(9)	0.048(3)
C(3a)	0.3295(6)	0.3087(10)	-0.2861(9)	0.060(3)
C(4a)	0.2652(7)	0.3989(11)	-0.2557(10)	0.067(3)
C(5a)	0.2503(7)	0.4167(12)	-0.1434(10)	0.073(4)
C(6a)	0.2986(7)	0.3417(10)	-0.0530(11)	0.069(3)
C(7a)	0.3644(6)	0.2493(10)	-0.0798(9)	0.049(3)
C(8a)	0.4161(7)	0.1695(11)	0.0194(9)	0.063(3)
C(9a)	0.5562(6)	0.3168(10)	0.0415(9)	0.057(3)
C(9b)	0.5365(6)	0.3838(10)	0.1528(9)	0.053(3)
C(8b)	0.5459(6)	0.3536(10)	0.3637(9)	0.058(3)
C(7b)	0.4457(7)	0.3305(11)	0.3681(9)	0.056(3)
C(6b)	0.3852(7)	0.4378(12)	0.3775(9)	0.071(4)
C(5b)	0.2934(8)	0.4144(13)	0.3849(10)	0.083(4)
C(4b)	0.2587(8)	0.2897(12)	0.3772(9)	0.077(4)
C(3b)	0.3134(7)	0.1755(12)	0.3647(9)	0.069(3)
C(2b)	0.4074(7)	0.2002(11)	0.3593(9)	0.052(3)
C(1b)	0.5627(7)	0.0508(10)	-0.3395(10)	0.064(3)

TABLE 2 Fractional atomic coordinates for the hydrogen atoms

Atom	x	y	z	
HN(2a)	0.4919(46)	0.1289(75)	-0.1649(62)	0.014(27)
HN(1a)	0.5418(50)	0.1375(73)	0.0829(65)	0.018(28)
HN(1b)	0.6367(68)	0.3135(**)	0.2725(92)	0.096(49)
HN(2b)	0.5151(51)	0.1175(82)	0.3184(70)	0.035(32)
H(1a1)	0.4381	0.1305	-0.3961	
H(1a2)	0.5076	0.2390	-0.3412	
H(3a)	0.3396	0.2976	-0.3658	
H(4a)	0.2301	0.4504	-0.3155	
H(5a)	0.2061	0.4816	-0.1254	
H(6a)	0.2868	0.3533	0.0260	
H(8a1)	0.3976	0.0771	0.0116	
H(8a2)	0.4008	0.2044	0.0918	
H(9a1)	0.6213	0.3117	0.0435	
H(9a2)	0.5313	0.3720	-0.0227	
H(9b1)	0.4716	0.3910	0.1523	
H(9b2)	0.5632	0.4719	0.1583	
H(8b1)	0.5800	0.3078	0.4280	
H(8b2)	0.5582	0.4483	0.3697	
H(6b)	0.4077	0.5284	0.3787	
H(5b)	0.2541	0.4889	0.3958	
H(4b)	0.1944	0.2779	0.3802	
H(3b)	0.2884	0.0862	0.3602	
H(1b1)	0.6046	0.0590	-0.2694	
H(1b2)	0.5934	0.0732	-0.4053	

TABLE 3 Anisotropic thermal parameters (Å^2)

Atom	U11	U22	U33	U23	U13	U12
N(2a)	0.059(7)	0.052(7)	0.039(6)	-0.006(6)	-0.007(6)	-0.007(5)
N(1a)	0.087(8)	0.043(6)	0.038(6)	-0.004(6)	-0.006(6)	0.020(6)
N(1b)	0.054(7)	0.040(6)	0.050(6)	-0.002(5)	-0.001(5)	0.004(5)
N(2b)	0.064(7)	0.049(6)	0.046(6)	-0.002(5)	0.009(5)	-0.019(6)

TABLE 4 Bond lengths (Å)

C(1a) -N(2a)	1.461(12)	C(1a) -C(1b)	1.496(11)
N(2a) -HN(2a)	.88(6)	N(2a) -C(2a)	1.404(11)
C(2a) -C(3a)	1.393(12)	C(2a) -C(7a)	1.399(13)
C(3a) -C(4a)	1.369(12)	C(4a) -C(5a)	1.344(13)
C(5a) -C(6a)	1.390(13)	C(6a) -C(7a)	1.386(12)
C(7a) -C(8a)	1.505(11)	C(8a) -N(1a)	1.485(11)
N(1a) -HN(1a)	.85(7)	N(1a) -C(9a)	1.495(12)
C(9a) -C(9b)	1.496(12)	C(9b) -N(1b)	1.460(11)
N(1b) -HN(1b)	.91(9)	N(1b) -C(8b)	1.463(12)
C(8b) -C(7b)	1.488(12)	C(7b) -C(6b)	1.389(13)
C(7b) -C(2b)	1.398(13)	C(6b) -C(5b)	1.373(12)
C(5b) -C(4b)	1.327(14)	C(4b) -C(3b)	1.397(13)
C(3b) -C(2b)	1.404(12)	C(2b) -N(2b)	1.411(12)
N(2b) -HN(2b)	.87(7)	C(1b) -N(2b')	1.456(12)

TABLE 5 Bond angles (°)

C(1b) -C(1a) -N(2a)	112.0(9)	HN(2a)-N(2a) -C(1a)	109(5)
C(2a) -N(2a) -C(1a)	119.3(9)	C(2a) -N(2a) -HN(2a)	113(5)
C(3a) -C(2a) -N(2a)	121(1)	C(7a) -C(2a) -N(2a)	118.2(9)
C(7a) -C(2a) -C(3a)	121(1)	C(4a) -C(3a) -C(2a)	118(1)
C(5a) -C(4a) -C(3a)	122(1)	C(6a) -C(5a) -C(4a)	121(1)

C(7a) -C(6a) -C(5a)	119(1)	C(6a) -C(7a) -C(2a)	119(1)
C(8a) -C(7a) -C(2a)	122.8(9)	C(8a) -C(7a) -C(6a)	118(1)
N(1a) -C(8a) -C(7a)	112.8(9)	HN(1a)-N(1a) -C(8a)	107(5)
C(9a) -N(1a) -C(8a)	113.6(8)	C(9a) -N(1a) -HN(1a)	100(5)
C(9b) -C(9a) -N(1a)	115.7(9)	N(1b) -C(9b) -C(9a)	109.9(8)
HN(1b)-N(1b) -C(9b)	113(7)	C(8b) -N(1b) -C(9b)	111.8(8)
C(8b) -N(1b) -HN(1b)	98(7)	C(7b) -C(8b) -N(1b)	111.5(9)
C(6b) -C(7b) -C(8b)	122(1)	C(2b) -C(7b) -C(8b)	122(1)
C(2b) -C(7b) -C(6b)	117(1)	C(5b) -C(6b) -C(7b)	121(1)
C(4b) -C(5b) -C(6b)	121(1)	C(3b) -C(4b) -C(5b)	122(1)
C(2b) -C(3b) -C(4b)	116(1)	C(3b) -C(2b) -C(7b)	123(1)
N(2b) -C(2b) -C(7b)	117.6(9)	N(2b) -C(2b) -C(3b)	119(1)
HN(2b)-N(2b) -C(2b)	109(6)	N(2b')-C(1b) -C(1a)	113.3(8)

TABLE 6 Intermolecular distances (Å)

N(2b) ...C(1a)	2.47	-1	1.0	0.0	0.0
HN(2b)...C(1a)	2.63	-1	1.0	0.0	0.0
C(2b) ...H(1a1)	2.87	1	0.0	0.0	1.0
N(2b) ...H(1a1)	2.58	-1	1.0	0.0	0.0
HN(2b)...H(1a1)	2.66	-1	1.0	0.0	0.0
HN(2b)...N(2a)	2.84	-1	1.0	0.0	0.0
H(9b2)...C(3a)	2.95	-1	1.0	1.0	0.0
H(9b2)...C(4a)	2.90	-1	1.0	1.0	0.0
HN(1b)...C(4a)	2.85	2	0.0	0.0	0.0
H(9b2)...C(5a)	2.96	-1	1.0	1.0	0.0
HN(1b)...C(5a)	2.90	2	0.0	0.0	0.0
N(1a) ...H(8a1)	2.83	-1	1.0	0.0	0.0
HN(1a)...H(8a1)	2.58	-1	1.0	0.0	0.0
C(9b) ...H(9a2)	2.93	-1	1.0	1.0	0.0

N(2b')...N(1b)	2.92	-1	1.0	0.0	0.0
N(2b')...C(8b)	2.83	-1	1.0	0.0	0.0
N(2b')...H(8b1)	2.77	-1	1.0	0.0	0.0
N(2b')...C(7b)	2.40	-1	1.0	0.0	0.0
C(1b) ...C(3b)	2.91	-1	1.0	0.0	0.0
H(1b1)...C(3b)	2.88	-1	1.0	0.0	0.0
H(1b2)...C(3b)	2.81	-1	1.0	0.0	0.0
N(2b')...C(3b)	2.43	-1	1.0	0.0	0.0
C(1b) ...H(3b)	2.59	-1	1.0	0.0	0.0
N(2b')...H(3b)	2.64	-1	1.0	0.0	0.0
C(1b) ...C(2b)	2.53	-1	1.0	0.0	0.0
H(1b1)...C(2b)	2.75	-1	1.0	0.0	0.0
H(1b2)...C(2b)	2.74	-1	1.0	0.0	0.0
N(2b')...C(2b)	1.41	-1	1.0	0.0	0.0
C(1b) ...N(2b)	1.46	-1	1.0	0.0	0.0
H(1b1)...N(2b)	1.98	-1	1.0	0.0	0.0
H(1b2)...N(2b)	1.97	-1	1.0	0.0	0.0
C(1b) ...HN(2b)	2.04	-1	1.0	0.0	0.0
H(1b1)...HN(2b)	2.48	-1	1.0	0.0	0.0
N(2b')...HN(2b)	.87	-1	1.0	0.0	0.0

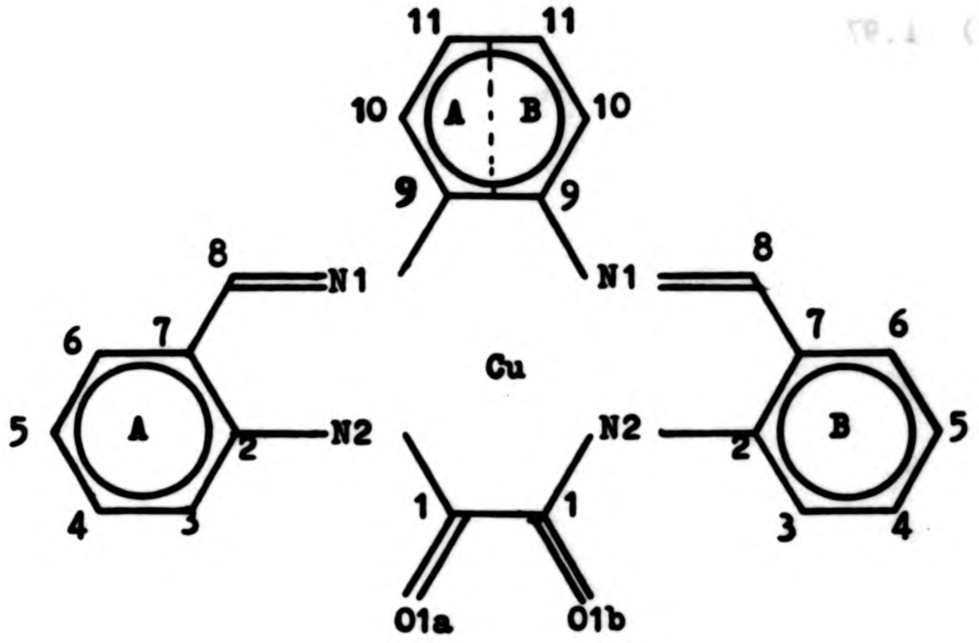
TABLE 7 Intramolecular distances (Å)

HN(2a)...C(1a)	1.93	C(2a) ...C(1a)	2.47
C(3a) ...C(1a)	2.87	H(3a) ...C(1a)	2.57
H(1b1)...C(1a)	2.01	H(1b2)...C(1a)	2.01
N(2b')...C(1a)	2.47	N(2a) ...H(1a1)	1.98
C(2a) ...H(1a1)	2.73	C(3a) ...H(1a1)	2.77
C(1b) ...H(1a1)	2.01	N(2b')...H(1a1)	2.58
N(2a) ...H(1a2)	1.98	HN(2a)...H(1a2)	2.33

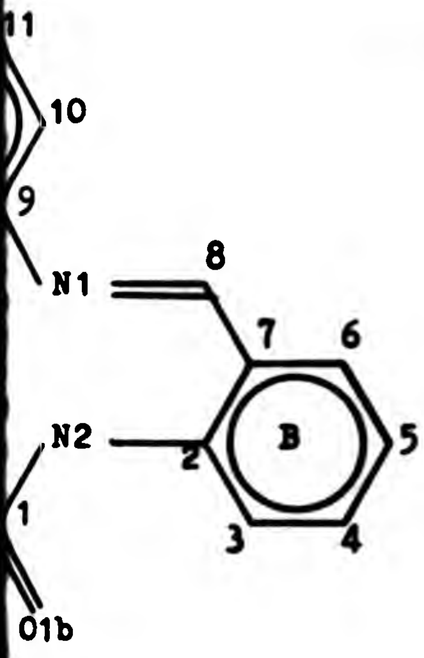
C(2a) ...H(1a2)	2.65	C(3a) ...H(1a2)	2.84
C(1b) ...H(1a2)	2.02	C(3a) ...N(2a)	2.44
H(3a) ...N(2a)	2.63	C(7a) ...N(2a)	2.41
C(8a) ...N(2a)	2.88	H(8a1)...N(2a)	2.93
N(1a) ...N(2a)	2.88	C(1b) ...N(2a)	2.45
H(1b1)...N(2a)	2.56	C(2a) ...HN(2a)	1.93
C(7a) ...HN(2a)	2.51	C(8a) ...HN(2a)	2.54
H(8a1)...HN(2a)	2.64	N(1a) ...HN(2a)	2.17
C(1b) ...HN(2a)	2.49	H(1b1)...HN(2a)	2.26
H(3a) ...C(2a)	2.05	C(4a) ...C(2a)	2.37
C(5a) ...C(2a)	2.74	C(6a) ...C(2a)	2.40
C(8a) ...C(2a)	2.55	H(8a1)...C(2a)	2.83
H(4a) ...C(3a)	2.01	C(5a) ...C(3a)	2.37
C(6a) ...C(3a)	2.78	C(7a) ...C(3a)	2.43
C(4a) ...H(3a)	2.03	H(5a) ...C(4a)	1.99
C(6a) ...C(4a)	2.38	C(7a) ...C(4a)	2.76
C(5a) ...H(4a)	1.99	H(6a) ...C(5a)	2.04
C(7a) ...C(5a)	2.39	C(6a) ...H(5a)	2.03
C(8a) ...C(6a)	2.48	H(8a2)...C(6a)	2.49
C(7a) ...H(6a)	2.04	C(8a) ...H(6a)	2.62
H(8a1)...C(7a)	2.02	H(8a2)...C(7a)	2.02
N(1a) ...C(7a)	2.49	H(9a2)...C(7a)	2.72
HN(1a)...C(8a)	1.91	C(9a) ...C(8a)	2.49
H(9a2)...C(8a)	2.69	H(9b1)...C(8a)	2.72
N(1a) ...H(8a1)	2.00	HN(1a)...H(8a1)	2.24
N(1a) ...H(8a2)	2.00	HN(1a)...H(8a2)	2.18
C(9a) ...H(8a2)	2.65	C(9b) ...H(8a2)	2.68
H(9a1)...N(1a)	2.00	H(9a2)...N(1a)	2.00
C(9b) ...N(1a)	2.53	H(9b1)...N(1a)	2.73

N(1b) ...N(1a)	2.97	C(9a) ...HN(1a)	1.85
H(9a1)...HN(1a)	2.15	H(9a2)...HN(1a)	2.60
C(9b) ...HN(1a)	2.56	N(1b) ...HN(1a)	2.55
H(9b1)...C(9a)	2.02	H(9b2)...C(9a)	2.02
N(1b) ...C(9a)	2.42	HN(1b)...C(9a)	2.76
C(9b) ...H(9a1)	2.00	N(1b) ...H(9a1)	2.59
HN(1b)...H(9a1)	2.60	C(9b) ...H(9a2)	2.01
HN(1b)...C(9b)	2.00	C(8b) ...C(9b)	2.42
H(8b2)...C(9b)	2.55	C(7b) ...C(9b)	2.99
N(1b) ...H(9b1)	1.99	C(8b) ...H(9b1)	2.55
C(7b) ...H(9b1)	2.62	N(1b) ...H(9b2)	1.99
HN(1b)...H(9b2)	2.22	C(8b) ...H(9b2)	2.67
H(8b1)...N(1b)	1.99	H(8b2)...N(1b)	1.99
C(7b) ...N(1b)	2.44	N(2b) ...N(1b)	2.92
HN(2b)...N(1b)	2.19	C(8b) ...HN(1b)	1.83
H(8b1)...HN(1b)	2.06	H(8b2)...HN(1b)	2.15
C(6b) ...C(8b)	2.51	H(6b) ...C(8b)	2.67
C(2b) ...C(8b)	2.52	N(2b) ...C(8b)	2.83
HN(2b)...C(8b)	2.41	C(7b) ...H(8b1)	2.01
C(2b) ...H(8b1)	2.76	N(2b) ...H(8b1)	2.77
HN(2b)...H(8b1)	2.38	C(7b) ...H(8b2)	2.01
C(6b) ...H(8b2)	2.54	H(6b) ...C(7b)	2.03
C(5b) ...C(7b)	2.40	C(4b) ...C(7b)	2.78
C(3b) ...C(7b)	2.46	N(2b) ...C(7b)	2.40
HN(2b)...C(7b)	2.43	H(5b) ...C(6b)	2.02
C(4b) ...C(6b)	2.35	C(3b) ...C(6b)	2.78
C(2b) ...C(6b)	2.37	C(5b) ...H(6b)	2.02
H(4b) ...C(5b)	1.97	C(3b) ...C(5b)	2.38
C(2b) ...C(5b)	2.72	C(4b) ...H(5b)	1.97

H(3b) ...C(4b)	2.06	C(2b) ...C(4b)	2.38
C(3b) ...H(4b)	2.03	N(2b) ...C(3b)	2.43
C(2b) ...H(3b)	2.07	N(2b) ...H(3b)	2.64
HN(2b)...C(2b)	1.88	N(2b')...H(1b1)	1.98
N(2b')...H(1b2)	1.97		



[Cu(cyphX)]



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The X-ray crystallographic data of [Cu(cyphX)] (see section 7.5)

TABLE 1 Fractional atomic coordinates and thermal parameters (Å^2)

Atom	x	y	z	Uiso or Ueq
Cu	0.47163(4)	-0.06659(4)	0.17723(9)	0.0417(4)
N(2a)	0.5726(3)	-0.0022(3)	0.2858(6)	0.043(3)
N(1a)	0.3855(3)	0.0221(3)	0.2047(6)	0.046(3)
N(2b)	0.5537(3)	-0.1582(3)	0.1543(6)	0.043(3)
N(1b)	0.3666(3)	-0.1286(3)	0.0733(6)	0.044(3)
C(1a)	0.6471(3)	-0.0513(4)	0.3097(9)	0.052(4)
C(2a)	0.5735(4)	0.0791(3)	0.3489(7)	0.046(3)
C(3a)	0.6518(4)	0.1212(4)	0.4259(9)	0.056(4)
C(4a)	0.6499(5)	0.2012(4)	0.4919(9)	0.068(4)
C(5a)	0.5706(5)	0.2458(4)	0.4873(10)	0.068(4)
C(6a)	0.4940(4)	0.2095(4)	0.4106(9)	0.061(4)
C(7a)	0.4922(4)	0.1252(3)	0.3407(8)	0.050(3)
C(8a)	0.4051(4)	0.0961(4)	0.2713(9)	0.051(3)
C(9a)	0.2962(4)	-0.0013(4)	0.1398(8)	0.051(3)
C(10a)	0.2194(5)	0.0484(4)	0.1466(12)	0.081(5)
C(11a)	0.1392(4)	0.0190(5)	0.0727(14)	0.094(6)
C(11b)	0.1297(4)	-0.0604(5)	-0.0022(12)	0.084(5)
C(10b)	0.2025(4)	-0.1109(4)	-0.0068(10)	0.064(4)
C(9b)	0.2860(3)	-0.0825(3)	0.0666(8)	0.047(3)
C(8b)	0.3660(4)	-0.2057(4)	0.0189(8)	0.048(3)
C(7b)	0.4423(4)	-0.2591(3)	0.0181(8)	0.046(3)
C(6b)	0.4209(4)	-0.3391(3)	-0.0591(9)	0.058(4)
C(5b)	0.4861(5)	-0.3965(4)	-0.0800(10)	0.068(4)
C(4b)	0.5756(5)	-0.3755(4)	-0.0245(11)	0.072(5)

C(3b)	0.5969(4)	-0.2985(4)	0.0514(10)	0.062(4)
C(2b)	0.5329(4)	-0.2370(3)	0.0789(8)	0.045(3)
C(1b)	0.6347(4)	-0.1419(3)	0.2517(9)	0.052(4)
O(1a)	0.7195(5)	-0.0349(4)	0.3867(12)	0.144(6)
O(1b)	0.6946(3)	-0.1909(3)	0.3031(8)	0.088(3)

TABLE 2 Fractional atomic coordinates for the hydrogen atoms

Atom	x	y	z
H(3a)	0.7151	0.0920	0.4504
H(4a)	0.7183	0.2269	0.5559
H(5a)	0.5816	0.3059	0.5244
H(6a)	0.4198	0.2405	0.4053
H(8a)	0.3480	0.1407	0.2662
H(10a)	0.2260	0.1047	0.1817
H(11a)	0.0793	0.0540	0.0950
H(11b)	0.0651	-0.0813	-0.0905
H(10b)	0.1929	-0.1783	-0.0654
H(8b)	0.3038	-0.2351	-0.0219
H(6b)	0.3354	-0.3559	-0.1286
H(5b)	0.4781	-0.4570	-0.1639
H(4b)	0.6209	-0.4207	-0.0698
H(3b)	0.6592	-0.2856	0.0758

TABLE 3 **Anisotropic thermal parameters ($\mathring{A}^2$)**

Atom	U11	U22	U33	U23	U13	U12
Cu	0.378(3)	0.0399(3)	0.0474(4)	0.0039(4)	0.0027(3)	0.0005(3)
N(2a)	0.038(2)	0.043(3)	0.048(3)	0.001(2)	0.004(2)	-0.002(2)
N(1a)	0.042(3)	0.045(3)	0.051(3)	0.008(2)	0.007(2)	0.003(2)
N(2b)	0.040(2)	0.041(2)	0.048(3)	0.006(2)	0.004(2)	0.003(2)
N(1b)	0.037(2)	0.046(3)	0.049(3)	0.011(2)	0.002(2)	0.003(2)
C(1a)	0.029(3)	0.071(4)	0.057(4)	-0.001(3)	-0.003(3)	-0.011(3)
C(2a)	0.054(3)	0.049(4)	0.035(3)	0.004(3)	0.009(2)	-0.009(3)
C(3a)	0.056(4)	0.057(4)	0.055(4)	0.001(3)	0.007(3)	-0.011(3)
C(4a)	0.077(5)	0.065(4)	0.063(4)	-0.006(4)	0.012(4)	-0.024(4)
C(5a)	0.096(5)	0.045(4)	0.062(4)	-0.005(3)	0.013(4)	-0.018(4)
C(6a)	0.081(4)	0.044(3)	0.057(4)	0.001(3)	0.016(4)	0.002(3)
C(7a)	0.066(4)	0.036(3)	0.047(4)	0.003(3)	0.014(3)	-0.007(3)
C(8a)	0.058(4)	0.043(3)	0.053(4)	0.004(3)	0.009(3)	0.002(3)
C(9a)	0.045(3)	0.051(3)	0.057(4)	0.010(3)	0.004(3)	0.007(3)
C(10a)	0.060(4)	0.049(4)	0.134(7)	0.005(4)	0.003(4)	0.017(3)
C(11a)	0.039(4)	0.081(5)	0.161(8)	0.006(6)	-0.004(4)	0.021(4)
C(11b)	0.039(3)	0.076(5)	0.136(7)	0.009(5)	-0.013(4)	0.005(4)
C(10b)	0.048(3)	0.055(4)	0.088(5)	0.004(4)	-0.009(3)	0.000(3)
C(9b)	0.039(3)	0.050(4)	0.052(4)	0.013(3)	0.004(3)	0.003(2)
C(8b)	0.052(3)	0.044(3)	0.047(4)	0.004(3)	0.001(3)	-0.008(3)
C(7b)	0.046(3)	0.043(3)	0.051(4)	0.002(3)	0.000(3)	0.005(3)
C(6b)	0.069(4)	0.040(3)	0.066(4)	0.001(3)	-0.002(3)	0.001(3)
C(5b)	0.095(5)	0.043(3)	0.065(4)	-0.008(3)	-0.004(4)	0.013(4)
C(4b)	0.074(5)	0.052(4)	0.089(5)	-0.016(4)	-0.007(4)	0.022(4)
C(3b)	0.046(3)	0.061(4)	0.080(5)	-0.002(4)	0.001(3)	0.014(3)

C(2b)	0.047(3)	0.041(3)	0.047(3)	0.004(3)	0.004(3)	0.006(3)
C(1b)	0.039(3)	0.045(3)	0.072(4)	0.001(3)	-0.003(3)	0.001(3)
O(1a)	0.120(5)	0.116(5)	0.189(7)	-0.030(5)	-0.004(5)	0.007(4)
O(1b)	0.051(3)	0.061(3)	0.152(5)	-0.004(3)	-0.032(3)	0.011(2)

TABLE 4 Bond lengths (Å)

Cu -N(2a)	1.928(4)	Cu -N(1a)	1.952(4)
Cu -N(2b)	1.940(4)	Cu -N(1b)	1.945(4)
Cu -C(1a)	2.719(5)	Cu -C(1b)	2.737(5)
N(2a) -C(1a)	1.368(7)	N(2a) -C(2a)	1.380(7)
N(1a) -C(8a)	1.301(7)	N(1a) -C(9a)	1.423(7)
N(2b) -C(2b)	1.397(7)	N(2b) -C(1b)	1.361(7)
N(1b) -C(9b)	1.419(7)	N(1b) -C(8b)	1.297(7)
C(1a) -C(1b)	1.516(8)	C(1a) -O(1a)	1.195(9)
C(2a) -C(3a)	1.416(8)	C(2a) -C(7a)	1.428(8)
C(3a) -C(4a)	1.368(10)	C(4a) -C(5a)	1.391(10)
C(5a) -C(6a)	1.353(10)	C(6a) -C(7a)	1.441(8)
C(7a) -C(8a)	1.428(8)	C(9a) -C(10a)	1.412(9)
C(9a) -C(9b)	1.406(8)	C(10a)-C(11a)	1.349(10)
C(11a)-C(11b)	1.382(11)	C(11b)-C(10b)	1.369(9)
C(10b)-C(9b)	1.385(8)	C(8b) -C(7b)	1.435(8)
C(7b) -C(6b)	1.419(8)	C(7b) -C(2b)	1.431(8)
C(6b) -C(5b)	1.369(9)	C(5b) -C(4b)	1.404(10)
C(4b) -C(3b)	1.372(9)	C(3b) -C(2b)	1.410(8)
C(1b) -O(1b)	1.223(7)		

TABLE 5 Bond angles (°)

N(1a) -Cu	-N(2a)	94.2(2)	N(2b) -Cu	-N(2a)	87.5(2)
N(2b) -Cu	-N(1a)	177.5(2)	N(1b) -Cu	-N(2a)	177.6(2)

N(1b) -Cu -N(1a)	83.6(2)	N(1b) -Cu -N(2b)	94.6(2)
C(1a) -Cu -N(2a)	28.2(2)	C(1a) -Cu -N(1a)	122.2(2)
C(1a) -Cu -N(2b)	59.5(2)	C(1a) -Cu -N(1b)	153.8(2)
C(1b) -Cu -N(2a)	60.4(2)	C(1b) -Cu -N(1a)	153.6(2)
C(1b) -Cu -N(2b)	27.7(2)	C(1b) -Cu -N(1b)	121.6(2)
C(1b) -Cu -C(1a)	32.3(2)	C(1a) -N(2a) -Cu	110.1(4)
C(2a) -N(2a) -Cu	128.0(3)	C(2a) -N(2a) -C(1a)	121.7(4)
C(8a) -N(1a) -Cu	125.1(4)	C(9a) -N(1a) -Cu	113.0(4)
C(9a) -N(1a) -C(8a)	121.8(5)	C(2b) -N(2b) -Cu	126.9(3)
C(1b) -N(2b) -Cu	110.8(3)	C(1b) -N(2b) -C(2b)	121.4(4)
C(9b) -N(1b) -Cu	113.8(3)	C(8b) -N(1b) -Cu	125.4(4)
C(8b) -N(1b) -C(9b)	120.7(4)	N(2a) -C(1a) -Cu	41.8(2)
C(1b) -C(1a) -Cu	74.5(3)	C(1b) -C(1a) -N(2a)	116.3(5)
O(1a) -C(1a) -Cu	169.3(6)	O(1a) -C(1a) -N(2a)	128.8(6)
O(1a) -C(1a) -C(1b)	114.5(6)	C(3a) -C(2a) -N(2a)	123.8(5)
C(7a) -C(2a) -N(2a)	119.9(5)	C(7a) -C(2a) -C(3a)	116.3(5)
C(4a) -C(3a) -C(2a)	122.2(6)	C(5a) -C(4a) -C(3a)	121.8(6)
C(6a) -C(5a) -C(4a)	118.6(6)	C(7a) -C(6a) -C(5a)	121.8(6)
C(6a) -C(7a) -C(2a)	119.3(5)	C(8a) -C(7a) -C(2a)	126.7(5)
C(8a) -C(7a) -C(6a)	114.1(5)	C(7a) -C(8a) -N(1a)	126.0(5)
C(10a)-C(9a) -N(1a)	126.1(5)	C(9b) -C(9a) -N(1a)	115.1(5)
C(9b) -C(9a) -C(10a)	118.7(5)	C(11a)-C(10a)-C(9a)	119.4(6)
C(11b)-C(11a)-C(10a)	121.6(6)	C(10b)-C(11b)-C(11a)	120.4(6)
C(9b) -C(10b)-C(11b)	119.6(6)	C(9a) -C(9b) -N(1b)	114.4(4)
C(10b)-C(9b) -N(1b)	125.5(5)	C(10b)-C(9b) -C(9a)	120.2(5)
C(7b) -C(8b) -N(1b)	126.4(5)	C(6b) -C(7b) -C(8b)	113.3(5)
C(2b) -C(7b) -C(8b)	126.1(5)	C(2b) -C(7b) -C(6b)	120.6(5)
C(5b) -C(6b) -C(7b)	121.1(6)	C(4b) -C(5b) -C(6b)	119.2(6)
C(3b) -C(4b) -C(5b)	120.1(6)	C(2b) -C(3b) -C(4b)	123.5(5)

C(7b) -C(2b) -N(2b)	120.4(5)	C(3b) -C(2b) -N(2b)	124.1(5)
C(3b) -C(2b) -C(7b)	115.5(5)	N(2b) -C(1b) -Cu	41.5(2)
C(1a) -C(1b) -Cu	73.2(3)	C(1a) -C(1b) -N(2b)	113.6(5)
O(1b) -C(1b) -Cu	163.6(5)	O(1b) -C(1b) -N(2b)	128.3(5)
O(1b) -C(1b) -C(1a)	118.0(5)		

TABLE 6 Intermolecular distances (Å)

H(3b) ...C(4a)	2.98	2	1.0	-1.0	0.0
H(5a) ...C(11a)	2.95	-2	1.0	1.0	1.0
H(5b) ...C(5b)	2.94	-1	1.0	-1.0	0.0
H(10b)...C(3b)	2.98	-2	0.0	0.0	0.0
H(6b) ...O(1a)	2.49	-2	0.0	0.0	0.0
H(6a) ...O(1b)	2.97	-1	1.0	0.0	1.0
H(10b)...O(1b)	2.30	-2	0.0	0.0	0.0
H(8b) ...O(1b)	2.28	-2	0.0	0.0	0.0
H(6b) ...O(1b)	2.25	-2	0.0	0.0	0.0

TABLE 7 Intramolecular distances (Å)

C(2a) ...Cu	2.98	C(8a) ...Cu	2.90
C(9a) ...Cu	2.83	C(9b) ...Cu	2.83
C(8b) ...Cu	2.90	C(2b) ...Cu	3.00
N(1a) ...N(2a)	2.84	N(2b) ...N(2a)	2.68
C(3a) ...N(2a)	2.47	C(7a) ...N(2a)	2.43
C(8a) ...N(2a)	2.97	C(1b) ...N(2a)	2.45
O(1a) ...N(2a)	2.31	H(3a) ...N(2a)	2.78
N(1b) ...N(1a)	2.60	C(7a) ...N(1a)	2.43
C(10a)...N(1a)	2.53	C(9b) ...N(1a)	2.39
H(8a) ...N(1a)	2.05	H(10a)...N(1a)	2.74
N(1b) ...N(2b)	2.86	C(1a) ...N(2b)	2.41

C(8b) ...N(2b)	2.99	C(7b) ...N(2b)	2.45
C(3b) ...N(2b)	2.48	O(1b) ...N(2b)	2.33
H(3b) ...N(2b)	2.69	C(9a) ...N(1b)	2.37
C(10b)...N(1b)	2.49	C(7b) ...N(1b)	2.44
H(10b)...N(1b)	2.81	H(8b) ...N(1b)	2.03
C(2a) ...C(1a)	2.40	C(3a) ...C(1a)	2.89
O(1b) ...C(1a)	2.35	H(3a) ...C(1a)	2.67
C(4a) ...C(2a)	2.44	C(5a) ...C(2a)	2.85
C(6a) ...C(2a)	2.48	C(8a) ...C(2a)	2.55
O(1a) ...C(2a)	2.85	H(3a) ...C(2a)	2.19
C(5a) ...C(3a)	2.41	C(6a) ...C(3a)	2.76
C(7a) ...C(3a)	2.42	O(1a) ...C(3a)	2.73
H(4a) ...C(3a)	2.13	C(6a) ...C(4a)	2.36
C(7a) ...C(4a)	2.78	H(3a) ...C(4a)	2.05
H(5a) ...C(4a)	2.00	C(7a) ...C(5a)	2.44
H(4a) ...C(5a)	2.25	H(6a) ...C(5a)	2.28
C(8a) ...C(6a)	2.41	H(5a) ...C(6a)	2.13
H(8a) ...C(6a)	2.57	H(6a) ...C(7a)	2.22
H(8a) ...C(7a)	2.19	C(9a) ...C(8a)	2.38
C(10a)...C(8a)	2.94	H(6a) ...C(8a)	2.51
H(10a)...C(8a)	2.71	C(11a)...C(9a)	2.38
C(11b)...C(9a)	2.77	C(10b)...C(9a)	2.42
H(8a) ...C(9a)	2.54	H(10a)...C(9a)	2.04
C(11b)...C(10a)	2.38	C(10b)...C(10a)	2.78
C(9b) ...C(10a)	2.43	H(8a) ...C(10a)	2.51
H(11a)...C(10a)	2.10	C(10b)...C(11a)	2.39
C(9b) ...C(11a)	2.75	H(10a)...C(11a)	2.00
H(11b)...C(11a)	2.22	C(9b) ...C(11b)	2.38
H(11a)...C(11b)	2.13	H(10b)...C(11b)	2.19

C(8b) ...C(10b)	2.89	H(11b)...C(10b)	2.14
H(8b) ...C(10b)	2.52	C(8b) ...C(9b)	2.36
H(10b)...C(9b)	2.22	H(8b) ...C(9b)	2.55
C(6b) ...C(8b)	2.38	C(2b) ...C(8b)	2.56
H(10b)...C(8b)	2.65	H(6b) ...C(8b)	2.65
C(5b) ...C(7b)	2.43	C(4b) ...C(7b)	2.79
C(3b) ...C(7b)	2.40	H(8b) ...C(7b)	2.11
H(6b) ...C(7b)	2.39	C(4b) ...C(6b)	2.39
C(3b) ...C(6b)	2.76	C(2b) ...C(6b)	2.47
H(8b) ...C(6b)	2.47	H(5b) ...C(6b)	2.24
C(3b) ...C(5b)	2.41	C(2b) ...C(5b)	2.85
H(6b) ...C(5b)	2.35	H(4b) ...C(5b)	2.06
C(2b) ...C(4b)	2.45	H(5b) ...C(4b)	2.13
H(3b) ...C(4b)	1.99	C(1b) ...C(3b)	2.92
O(1b) ...C(3b)	2.79	H(4b) ...C(3b)	2.19
C(1b) ...C(2b)	2.41	O(1b) ...C(2b)	2.86
H(3b) ...C(2b)	2.06	O(1a) ...C(1b)	2.29
H(3b) ...C(1b)	2.67	O(1b) ...O(1a)	2.59
H(3a) ...O(1a)	2.09	H(3b) ...O(1b)	2.25

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.1

H	K	L	10FO	10FC
-20	0	0	285	267
-18	0	0	423	424
-16	0	0	889	814
-14	0	0	416	398
-12	0	0	933	895
-10	0	0	1064	1083
-8	0	0	1142	1085
-6	0	0	2415	2447
-4	0	0	3479	4250
4	0	0	3444	4244
6	0	0	2345	2412
8	0	0	1116	1192
10	0	0	994	1077
12	0	0	846	894
14	0	0	410	410
16	0	0	775	800
18	0	0	426	441
20	0	0	238	260
-15	1	0	416	366
-13	1	0	313	325
-9	1	0	516	506
-7	1	0	543	514
-5	1	0	1238	1336
-3	1	0	2808	3056
3	1	0	3087	3083
5	1	0	1247	1361
7	1	0	519	547
9	1	0	466	535
13	1	0	323	305
15	1	0	412	373
-16	2	0	538	506
-14	2	0	513	499
-12	2	0	559	530
-10	2	0	1334	1373
-8	2	0	1038	1058
-4	2	0	1761	1619
-2	2	0	560	628
2	2	0	582	730
4	2	0	1875	1666
8	2	0	1072	1004
10	2	0	1325	1354
12	2	0	530	544
14	2	0	521	488
16	2	0	529	500
-15	3	0	363	362
-13	3	0	358	307
-11	3	0	303	300
-9	3	0	1116	1146
-7	3	0	867	872
-5	3	0	881	823
-3	3	0	1535	1442
-1	3	0	907	853
1	3	0	898	902
3	3	0	1517	1448
5	3	0	889	767
7	3	0	898	841
9	3	0	1125	1171
11	3	0	310	300
13	3	0	303	305
15	3	0	338	366
19	3	0	268	344
-22	4	0	256	228
-18	4	0	296	267
-16	4	0	364	284
-14	4	0	418	442
-12	4	0	807	838
-10	4	0	484	542
-8	4	0	332	343
-6	4	0	977	943
-4	4	0	1325	1321
-2	4	0	701	701
0	4	0	288	282
2	4	0	698	713
4	4	0	1334	1306
6	4	0	1011	983
8	4	0	308	313
10	4	0	534	549
12	4	0	788	855
14	4	0	419	442
16	4	0	332	293
18	4	0	238	263
-17	5	0	393	361
-13	5	0	406	401
-11	5	0	447	455
-9	5	0	430	454
-7	5	0	689	738
-5	5	0	490	477
-3	5	0	660	694
-1	5	0	849	859
1	5	0	820	880
3	5	0	659	672
5	5	0	490	470
7	5	0	650	710
9	5	0	440	404
11	5	0	432	466
13	5	0	379	402
17	5	0	391	378
-14	6	0	496	499
-12	6	0	510	424
-10	6	0	584	567
-6	6	0	716	749
-4	6	0	1072	1019
-2	6	0	609	665
0	6	0	405	441
2	6	0	598	634
4	6	0	1046	1017
6	6	0	671	720
10	6	0	580	540
12	6	0	494	432
14	6	0	508	533
-13	7	0	391	359
-11	7	0	354	343
-7	7	0	642	633
-5	7	0	484	438
-3	7	0	416	400
3	7	0	437	399
5	7	0	406	447
7	7	0	582	637
11	7	0	325	335
13	7	0	369	350
-14	8	0	414	372
-10	8	0	383	389
-8	8	0	332	272
-6	8	0	622	623
-4	8	0	646	660
-2	8	0	461	437
2	8	0	449	444
4	8	0	666	706
6	8	0	590	622
8	8	0	285	272
10	8	0	416	398
14	8	0	352	378
-13	9	0	330	268
-5	9	0	498	450
-3	9	0	403	376
-1	9	0	454	483
1	9	0	442	472
3	9	0	375	373
5	9	0	471	427
13	9	0	357	273
0	10	0	271	247
2	10	0	221	223
-3	11	0	317	327
3	11	0	367	334
0	12	0	317	284
2	12	0	265	262
-17	1	1	521	544
-15	1	1	742	660
-11	1	1	1203	1208
-9	1	1	1857	1847
-7	1	1	1578	1690
-5	1	1	1657	1853
-3	1	1	994	491
3	1	1	1046	977
5	1	1	1700	1428
7	1	1	1055	1084
9	1	1	1299	1399
11	1	1	968	982
13	1	1	371	401
15	1	1	844	872
17	1	1	575	574
-18	2	1	301	290
-16	2	1	385	353
-14	2	1	454	515
-12	2	1	250	196
-10	2	1	1238	1170
-8	2	1	1142	1204
-6	2	1	1003	1033
-4	2	1	1848	1851
-2	2	1	2154	2144
0	2	1	924	1030
2	2	1	1116	1094
4	2	1	2441	2370
6	2	1	1247	1176
8	2	1	1229	1242
14	2	1	479	474
18	2	1	279	244
-19	3	1	398	403
-17	3	1	274	288
-13	3	1	839	816

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.1

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-11	3	1	808	769	-5	5	1	1465	1379	4	8	1	744	753	-5	1	2	1055	969	5	3	2	933	1136
-9	3	1	562	522	-3	5	1	1072	1047	6	8	1	428	411	-3	1	2	473	559	7	3	2	807	757
-7	3	1	228	282	-1	5	1	506	517	10	8	1	350	314	1	1	2	881	803	9	3	2	787	820
-5	3	1	907	969	1	5	1	787	724	12	8	1	301	295	3	1	2	2511	2455	11	3	2	474	460
-3	3	1	742	757	3	5	1	1500	1647	-5	9	1	453	427	5	1	2	1308	1317	13	3	2	262	274
1	3	1	3017	2922	5	5	1	924	909	-3	9	1	488	428	7	1	2	1264	1225	17	3	2	338	283
3	3	1	707	565	7	5	1	521	549	-1	9	1	301	294	9	1	2	636	618	-14	4	2	795	795
5	3	1	1099	1099	9	5	1	296	318	1	9	1	442	402	11	1	2	414	440	-12	4	2	439	442
7	3	1	703	753	11	5	1	666	733	3	9	1	348	229	17	1	2	303	298	-10	4	2	589	540
9	3	1	548	498	13	5	1	474	488	5	9	1	348	313	-20	2	2	358	321	-8	4	2	673	717
11	3	1	383	357	15	5	1	379	378	-12	10	1	317	261	-16	2	2	449	412	-6	4	2	1413	1416
13	3	1	378	427	-18	6	1	248	224	-6	10	1	596	557	-14	2	2	416	430	-4	4	2	994	1067
15	3	1	325	379	-10	6	1	248	287	-4	10	1	395	320	-12	2	2	753	748	-2	4	2	773	681
-18	4	1	381	306	-8	6	1	405	375	0	10	1	385	392	-10	2	2	1386	1345	0	4	2	1325	1262
-16	4	1	391	410	-2	6	1	615	595	-9	11	1	338	284	-8	2	2	1447	1477	2	4	2	1299	1281
-14	4	1	369	307	0	6	1	403	406	-18	0	2	719	640	-6	2	2	1064	1191	4	4	2	1430	1403
-12	4	1	332	312	2	6	1	469	470	-16	0	2	872	726	-4	2	2	1072	1080	6	4	2	753	761
-10	4	1	502	463	4	6	1	432	476	-14	0	2	658	626	-2	2	2	2354	2124	10	4	2	698	655
-8	4	1	793	795	6	6	1	361	340	-12	0	2	1046	1096	0	2	2	1474	1529	12	4	2	279	307
-6	4	1	865	766	-15	7	1	460	353	-10	0	2	1360	1321	2	2	2	659	663	14	4	2	541	547
-4	4	1	924	943	-13	7	1	341	293	-8	0	2	1439	1332	8	2	2	942	933	-19	5	2	323	258
-2	4	1	1160	1148	-11	7	1	526	438	-6	0	2	3357	2976	10	2	2	703	795	-13	5	2	391	359
0	4	1	1011	1210	-7	7	1	559	581	-4	0	2	1814	1366	12	2	2	418	370	-9	5	2	498	478
2	4	1	857	763	-5	7	1	950	887	2	0	2	3226	3632	14	2	2	447	506	-7	5	2	451	532
4	4	1	779	797	-3	7	1	538	590	4	0	2	2590	2245	16	2	2	507	470	-5	5	2	463	464
6	4	1	881	855	-1	7	1	373	393	6	0	2	1918	1913	-17	3	2	437	391	-3	5	2	587	568
8	4	1	437	426	1	7	1	534	485	8	0	2	1796	1945	-15	3	2	476	476	-1	5	2	898	996
10	4	1	600	620	3	7	1	656	693	10	0	2	824	857	-13	3	2	279	286	1	5	2	933	864
12	4	1	271	331	5	7	1	677	745	14	0	2	968	1007	-11	3	2	770	809	3	5	2	601	568
16	4	1	391	400	7	7	1	514	535	16	0	2	807	878	-9	3	2	1535	1429	5	5	2	548	557
18	4	1	320	319	9	7	1	437	399	18	0	2	369	317	-7	3	2	1238	1313	7	5	2	345	340
-15	5	1	354	355	13	7	1	484	517	-17	1	2	439	393	-5	3	2	1177	1187	9	5	2	325	306
-13	5	1	620	601	-10	8	1	285	281	-15	1	2	602	590	-3	3	2	731	829	15	5	2	345	330
-11	5	1	354	379	-4	8	1	440	440	-11	1	2	898	908	-1	3	2	1011	960	-14	6	2	530	484
-9	5	1	440	478	-2	8	1	490	459	-9	1	2	872	847	1	3	2	1081	1162	-12	6	2	541	525
-7	5	1	618	595	2	8	1	456	445	-7	1	2	1003	1005	3	3	2	959	937	-8	6	2	375	320

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.1

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-6	6	2	907	967	-19	1	3	437	481	-9	3	3	824	918	3	5	3	1186	1267	12	8	3	403	322
-4	6	2	968	1056	-17	1	3	496	468	-7	3	3	609	603	5	5	3	786	849	-13	9	3	262	266
-2	6	2	638	699	-15	1	3	373	334	-5	3	3	924	884	7	5	3	265	299	-11	9	3	268	234
0	6	2	364	415	-13	1	3	655	657	-3	3	3	1282	1379	9	5	3	317	360	-7	9	3	398	464
2	6	2	898	915	-11	1	3	1133	1137	-1	3	3	543	415	11	5	3	401	415	1	9	3	330	369
4	6	2	881	899	-9	1	3	1822	1900	1	3	3	1133	950	13	5	3	632	674	5	9	3	442	418
6	6	2	793	772	-7	1	3	710	737	3	3	3	1229	1318	-16	6	3	308	315	-4	10	3	325	256
10	6	2	486	492	-5	1	3	2084	1842	5	3	3	933	847	-12	6	3	350	354	2	10	3	529	453
12	6	2	549	524	-3	1	3	1665	1569	7	3	3	898	965	-10	6	3	514	558	-20	0	4	364	280
14	6	2	430	363	-1	1	3	3121	3183	9	3	3	933	974	-6	6	3	244	255	-18	0	4	513	548
-5	7	2	565	594	1	1	3	3200	2432	11	3	3	317	315	-4	6	3	528	438	-16	0	4	950	1002
-3	7	2	231	195	3	1	3	1657	1416	13	3	3	500	459	-2	6	3	704	691	-12	0	4	620	604
-1	7	2	241	286	5	1	3	1692	1903	15	3	3	383	392	0	6	3	710	728	-10	0	4	1648	1648
1	7	2	305	368	7	1	3	1125	1149	-20	4	3	352	335	2	6	3	449	409	-8	0	4	539	532
3	7	2	282	273	9	1	3	530	560	-14	4	3	624	634	6	6	3	348	363	-6	0	4	1910	1586
-8	8	2	330	382	15	1	3	657	675	-10	4	3	706	735	8	6	3	310	332	-4	0	4	3697	3559
-6	8	2	674	651	17	1	3	500	520	-8	4	3	1317	1381	12	6	3	214	170	-2	0	4	550	718
-4	8	2	574	556	19	1	3	330	270	-6	4	3	568	529	-15	7	3	361	350	0	0	4	1971	1558
-2	8	2	516	548	-18	2	3	521	471	-4	4	3	1439	1377	-13	7	3	618	589	2	0	4	1264	1629
0	8	2	330	377	-16	2	3	486	470	-2	4	3	681	665	-11	7	3	330	253	4	0	4	2799	2933
2	8	2	647	646	-12	2	3	868	865	0	4	3	643	567	-9	7	3	248	295	6	0	4	692	681
4	8	2	416	392	-10	2	3	759	729	2	4	3	898	995	-7	7	3	907	948	8	0	4	1343	1338
6	8	2	293	364	-8	2	3	1081	1048	4	4	3	327	353	-5	7	3	797	812	10	0	4	597	603
12	8	2	323	341	-6	2	3	2197	2347	8	4	3	479	439	-3	7	3	804	755	12	0	4	539	615
-13	9	2	320	261	-4	2	3	2049	1962	10	4	3	772	806	1	7	3	534	635	14	0	4	813	850
-9	9	2	323	278	-2	2	3	2799	2669	12	4	3	473	436	3	7	3	587	584	16	0	4	646	608
-7	9	2	357	384	0	2	3	2973	2679	16	4	3	395	367	5	7	3	602	544	-13	1	4	557	568
-5	9	2	606	575	2	2	3	716	704	-15	5	3	466	409	11	7	3	440	427	-11	1	4	463	439
-3	9	2	565	516	4	2	3	803	726	-13	5	3	582	508	13	7	3	337	307	-9	1	4	609	644
-1	9	2	474	517	6	2	3	1683	1891	-11	5	3	412	382	-14	8	3	317	312	-7	1	4	1962	2108
1	9	2	405	435	8	2	3	451	464	-9	5	3	293	259	-8	8	3	298	245	-5	1	4	1168	1203
3	9	2	367	365	16	2	3	345	298	-7	5	3	1142	1080	-6	8	3	305	307	-3	1	4	1474	1287
-8	10	2	358	313	-17	3	3	474	390	-5	5	3	1325	1375	-4	8	3	330	372	-1	1	4	2433	2353
-3	11	2	290	209	-15	3	3	854	768	-3	5	3	806	696	4	8	3	385	310	1	1	4	1439	1302
3	11	2	260	282	-13	3	3	352	320	-1	5	3	290	298	6	8	3	250	251	3	1	4	861	968
-21	1	3	381	341	-11	3	3	1038	1097	1	5	3	968	980	10	8	3	285	360	5	1	4	657	596

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.1

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
7	1	4	664	794	11	3	4	410	457	0	6	4	381	422	-3	1	5	942	702	9	3	5	613	628
9	1	4	760	703	-16	4	4	473	484	2	6	4	861	877	-1	1	5	2965	2258	11	3	5	735	747
11	1	4	367	380	-14	4	4	405	411	4	6	4	707	678	1	1	5	519	697	13	3	5	282	280
13	1	4	604	615	-12	4	4	552	562	6	6	4	369	393	3	1	5	907	1026	15	3	5	305	378
-20	2	4	405	430	-10	4	4	474	444	10	6	4	569	566	5	1	5	1369	1281	-14	4	5	337	311
-18	2	4	449	437	-8	4	4	1168	1159	12	6	4	480	476	7	1	5	1386	1240	-12	4	5	698	751
-16	2	4	447	495	-6	4	4	942	871	14	6	4	395	354	9	1	5	465	497	-10	4	5	814	899
-12	2	4	718	758	-4	4	4	408	455	-5	7	4	410	442	15	1	5	426	390	-8	4	5	889	937
-10	2	4	985	1068	-2	4	4	1116	1202	-3	7	4	487	552	17	1	5	296	348	-6	4	5	1343	1248
-8	2	4	1003	1080	0	4	4	1343	1294	-1	7	4	317	312	-16	2	5	679	623	-4	4	5	832	833
-6	2	4	1796	2053	2	4	4	1360	1370	1	7	4	231	239	-14	2	5	350	392	-2	4	5	565	617
-4	2	4	1700	1606	4	4	4	1413	1381	3	7	4	453	488	-12	2	5	350	384	0	4	5	662	665
-2	2	4	1369	1098	6	4	4	500	462	-16	8	4	279	252	-10	2	5	523	607	2	4	5	358	382
0	2	4	1578	1873	8	4	4	474	513	-14	8	4	218	185	-8	2	5	1447	1663	6	4	5	682	664
2	2	4	722	670	12	4	4	428	424	-8	8	4	580	596	-6	2	5	486	486	8	4	5	733	771
4	2	4	649	628	-17	5	4	416	325	-6	8	4	442	423	-4	2	5	985	960	-17	5	5	330	334
6	2	4	1229	1176	-15	5	4	332	314	-4	8	4	616	587	0	2	5	1177	1111	-15	5	5	677	704
8	2	4	1020	1149	-13	5	4	369	376	-2	8	4	305	307	2	2	5	699	815	-13	5	5	809	875
10	2	4	519	533	-11	5	4	545	640	0	8	4	626	645	4	2	5	1343	1324	-11	5	5	358	303
12	2	4	276	301	-7	5	4	290	259	2	8	4	423	376	6	2	5	659	687	-9	5	5	606	570
14	2	4	449	467	-5	5	4	626	646	4	8	4	458	470	8	2	5	994	1048	-7	5	5	1142	1224
16	2	4	338	330	-3	5	4	296	314	12	8	4	262	195	10	2	5	373	355	-5	5	5	860	878
-19	3	4	303	319	-1	5	4	668	740	-5	9	4	344	318	12	2	5	410	405	-3	5	5	363	418
-17	3	4	316	349	1	5	4	1177	1212	1	9	4	367	343	14	2	5	293	292	-1	5	5	1072	1041
-15	3	4	419	439	3	5	4	381	363	11	9	4	334	304	-17	3	5	373	364	1	5	5	856	865
-13	3	4	439	509	5	5	4	423	369	-10	10	4	250	252	-15	3	5	490	531	3	5	5	1229	1161
-11	3	4	643	684	7	5	4	723	777	-4	10	4	288	196	-13	3	5	446	448	5	5	5	620	663
-9	3	4	1186	1312	9	5	4	308	280	-5	11	4	248	226	-9	3	5	1133	1184	7	5	5	290	246
-7	3	4	637	614	-16	6	4	480	472	-21	1	5	397	446	-7	3	5	1064	1011	11	5	5	480	420
-5	3	4	1099	1043	-14	6	4	1090	1110	-19	1	5	541	514	-5	3	5	538	485	-8	6	5	391	396
-3	3	4	1168	1267	-12	6	4	565	588	-17	1	5	701	586	-3	3	5	1500	1604	-4	6	5	711	792
-1	3	4	907	856	-10	6	4	613	659	-13	1	5	453	400	-1	3	5	480	435	-2	6	5	469	524
1	3	4	749	687	-8	6	4	725	765	-11	1	5	1543	1773	1	3	5	405	378	0	6	5	317	359
5	3	4	703	680	-6	6	4	759	787	-9	1	5	1430	1464	3	3	5	813	772	2	6	5	298	338
7	3	4	406	412	-4	6	4	849	852	-7	1	5	837	765	5	3	5	741	777	4	6	5	218	173
9	3	4	889	867	-2	6	4	950	965	-5	1	5	1439	1294	7	3	5	301	314	6	6	5	430	476

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.1

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-15	7	5	480	517	4	0	6	1020	1189	-13	3	6	308	306	-14	6	6	814	849	-11	1	7	1474	1412
-13	7	5	241	229	6	0	6	1247	1303	-11	3	6	593	568	-12	6	6	657	653	-9	1	7	1630	1816
-9	7	5	507	472	8	0	6	471	456	-9	3	6	858	819	-10	6	6	262	312	-7	1	7	611	735
-7	7	5	666	654	14	0	6	419	421	-7	3	6	775	703	-8	6	6	1195	1174	-5	1	7	428	344
-5	7	5	831	902	-21	1	6	308	286	-5	3	6	749	887	-6	6	6	1046	1012	-3	1	7	1971	1856
-3	7	5	773	832	-15	1	6	423	483	-3	3	6	1177	1176	-4	6	6	525	480	-1	1	7	1936	1497
-1	7	5	256	303	-13	1	6	433	500	-1	3	6	1081	1134	-2	6	6	582	610	1	1	7	1343	1173
1	7	5	776	764	-7	1	6	580	594	1	3	6	1055	999	0	6	6	650	658	3	1	7	371	412
3	7	5	673	700	-5	1	6	2337	2215	3	3	6	611	698	2	6	6	740	790	5	1	7	950	926
13	7	5	391	385	-3	1	6	673	718	5	3	6	305	339	4	6	6	218	234	7	1	7	1290	1277
-14	8	5	308	224	-1	1	6	1395	1258	7	3	6	933	959	10	6	6	330	315	9	1	7	656	714
-12	8	5	406	368	1	1	6	617	628	9	3	6	435	466	12	6	6	477	477	11	1	7	218	180
-6	8	5	679	603	3	1	6	461	512	11	3	6	389	382	-15	7	6	316	291	13	1	7	345	351
-4	8	5	550	456	5	1	6	543	533	13	3	6	271	275	-13	7	6	317	329	-18	2	7	439	434
-2	8	5	279	183	7	1	6	748	786	-16	4	6	369	315	-9	7	6	332	335	-16	2	7	288	270
0	8	5	602	551	9	1	6	218	255	-14	4	6	636	638	-5	7	6	371	448	-12	2	7	395	410
2	8	5	348	258	13	1	6	310	344	-12	4	6	310	269	1	7	6	271	339	-10	2	7	1046	1039
-9	9	5	460	420	-20	2	6	414	453	-8	4	6	768	778	3	7	6	334	321	-8	2	7	671	683
-5	9	5	345	369	-18	2	6	435	472	-6	4	6	512	489	-16	8	6	332	325	-6	2	7	303	433
-3	9	5	290	288	-16	2	6	584	652	-2	4	6	512	385	-10	8	6	214	203	-4	2	7	609	561
3	9	5	381	379	-12	2	6	1099	1160	0	4	6	1168	1225	-8	8	6	293	219	-2	2	7	1212	1069
5	9	5	308	307	-10	2	6	1508	1540	2	4	6	950	984	-6	8	6	458	515	0	2	7	469	431
-2	10	5	271	257	-8	2	6	437	478	4	4	6	796	823	-4	8	6	421	427	2	2	7	534	573
4	10	5	383	377	-6	2	6	1160	1210	6	4	6	521	488	2	8	6	444	452	4	2	7	618	657
-22	0	6	425	384	-4	2	6	768	630	8	4	6	446	513	4	8	6	395	455	6	2	7	487	478
-20	0	6	560	564	-2	2	6	791	851	10	4	6	484	450	6	8	6	262	219	10	2	7	670	630
-18	0	6	620	617	0	2	6	1168	1069	-15	5	6	387	429	8	8	6	317	309	12	2	7	437	466
-16	0	6	310	285	2	2	6	889	823	-13	5	6	403	437	3	9	6	433	378	-21	3	7	432	453
-12	0	6	968	1072	4	2	6	850	803	-11	5	6	437	460	5	9	6	235	204	-19	3	7	310	271
-10	0	6	1299	1214	6	2	6	1203	1254	-7	5	6	352	407	-4	10	6	271	270	-15	3	7	354	278
-8	0	6	2808	2643	8	2	6	994	924	-5	5	6	553	638	-7	11	6	332	243	-13	3	7	595	626
-6	0	6	977	991	10	2	6	433	434	-3	5	6	352	323	-21	1	7	395	342	-11	3	7	1003	1015
-4	0	6	371	333	12	2	6	248	320	5	5	6	410	416	-19	1	7	502	485	-7	3	7	752	794
-2	0	6	5066	4334	16	2	6	378	378	7	5	6	225	219	-17	1	7	630	606	-5	3	7	282	303
0	0	6	1517	1329	-17	3	6	433	434	9	5	6	398	377	-15	1	7	395	446	-3	3	7	649	684
2	0	6	736	773	-15	3	6	371	342	-16	6	6	521	533	-13	1	7	582	698	-1	3	7	1421	1436

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.1

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
1	3	7	534	576	-4	6	7	305	366	4	0	8	1038	844	-17	3	8	469	447	-18	6	8	282	315
3	3	7	430	385	2	6	7	244	267	6	0	8	1866	1817	-15	3	8	235	296	-16	6	8	664	666
5	3	7	692	657	4	6	7	361	390	8	0	8	458	496	-13	3	8	486	486	-14	6	8	463	514
7	3	7	539	525	-17	7	7	378	393	-19	1	8	460	419	-11	3	8	235	151	-12	6	8	397	355
9	3	7	325	316	-15	7	7	467	433	-17	1	8	361	267	-9	3	8	686	740	-8	6	8	832	714
13	3	7	320	346	-13	7	7	327	338	-13	1	8	308	330	-7	3	8	1360	1312	-6	6	8	1247	1245
-20	4	7	323	329	-7	7	7	650	597	-11	1	8	833	896	-5	3	8	565	550	-4	6	8	747	752
-18	4	7	371	373	-5	7	7	435	418	-9	1	8	492	430	-3	3	8	977	813	-2	6	8	345	356
-14	4	7	405	390	-3	7	7	442	508	-7	1	8	225	245	-1	3	8	924	1027	0	6	8	1038	1061
-12	4	7	621	660	1	7	7	782	778	-5	1	8	916	861	1	3	8	276	313	2	6	8	898	977
-10	4	7	611	625	3	7	7	555	497	-3	1	8	1630	1389	3	3	8	793	711	4	6	8	488	565
-8	4	7	471	414	5	7	7	337	317	-1	1	8	337	328	5	3	8	572	601	8	6	8	317	350
-6	4	7	451	487	7	7	7	241	182	1	1	8	453	389	7	3	8	671	748	10	6	8	330	366
-4	4	7	456	397	11	7	7	456	462	3	1	8	568	568	9	3	8	569	583	12	6	8	316	341
-2	4	7	500	459	-14	8	7	367	265	5	1	8	487	491	-22	4	8	296	290	-15	7	8	361	264
0	4	7	977	921	-8	8	7	235	208	7	1	8	548	493	-16	4	8	430	402	-11	7	8	510	527
2	4	7	532	484	-6	8	7	317	294	9	1	8	567	553	-14	4	8	469	491	-9	7	8	332	299
4	4	7	488	465	-4	8	7	664	618	-22	2	8	419	393	-12	4	8	712	778	-7	7	8	590	545
6	4	7	652	598	2	8	7	458	499	-20	2	8	364	340	-10	4	8	303	260	-5	7	8	397	416
8	4	7	748	703	-5	9	7	423	380	-18	2	8	262	290	-8	4	8	510	598	-1	7	8	430	372
-23	5	7	260	228	1	9	7	313	280	-16	2	8	393	392	-6	4	8	354	453	-14	8	8	369	335
-17	5	7	361	384	-14	10	7	296	265	-14	2	8	479	497	-4	4	8	303	251	-8	8	8	348	374
-15	5	7	907	981	-8	10	7	367	280	-12	2	8	1195	1230	-2	4	8	898	873	-6	8	8	391	338
-13	5	7	649	642	5	11	7	238	272	-10	2	8	2075	2098	2	4	8	710	696	4	8	8	487	506
-11	5	7	479	512	-22	0	8	348	381	-8	2	8	942	952	4	4	8	870	845	-9	9	8	320	323
-9	5	7	713	676	-20	0	8	800	808	-6	2	8	1212	1103	8	4	8	633	598	-5	9	8	348	373
-7	5	7	699	660	-18	0	8	666	624	-4	2	8	1587	1564	-21	5	8	354	327	-3	9	8	225	274
-5	5	7	557	549	-16	0	8	536	491	-2	2	8	1395	1257	-15	5	8	334	310	1	9	8	432	451
-3	5	7	325	289	-14	0	8	800	788	0	2	8	698	658	-11	5	8	498	493	3	9	8	341	361
-1	5	7	611	666	-12	0	8	775	777	2	2	8	276	182	-9	5	8	622	578	5	9	8	310	195
1	5	7	670	710	-10	0	8	1910	1908	4	2	8	555	586	-7	5	8	612	667	-4	10	8	330	262
3	5	7	907	925	-8	0	8	587	527	6	2	8	806	817	-3	5	8	683	709	-21	1	9	521	521
5	5	7	454	418	-4	0	8	2136	1620	8	2	8	733	736	-1	5	8	624	657	-19	1	9	401	416
9	5	7	506	561	-2	0	8	1753	1595	10	2	8	381	441	3	5	8	323	293	-17	1	9	378	396
-10	6	7	456	471	0	0	8	2555	2250	14	2	8	419	393	5	5	8	338	441	-13	1	9	597	688
-6	6	7	460	514	2	0	8	950	900	-19	3	8	456	483	7	5	8	354	366	-11	1	9	1552	1572

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.1

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-9	1	9	977	954	11	3	9	238	196	-1	7	9	442	477	-7	1	10	564	546	-12	4	10	592	604
-7	1	9	567	454	-18	4	9	316	256	1	7	9	378	435	-5	1	10	933	888	-10	4	10	585	573
-5	1	9	1456	1424	-16	4	9	401	377	3	7	9	490	524	-3	1	10	808	818	-8	4	10	788	883
-3	1	9	1822	1631	-14	4	9	361	430	9	7	9	418	394	1	1	10	601	536	-6	4	10	660	699
-1	1	9	2232	1982	-10	4	9	916	1013	11	7	9	262	305	7	1	10	385	315	-4	4	10	381	382
1	1	9	750	720	-8	4	9	601	660	-16	8	9	298	286	-22	2	10	385	354	0	4	10	474	484
3	1	9	620	655	-6	4	9	722	751	-14	8	9	371	305	-20	2	10	338	350	2	4	10	632	628
5	1	9	1195	1204	-2	4	9	620	625	-10	8	9	446	436	-18	2	10	317	346	4	4	10	838	857
7	1	9	571	636	0	4	9	727	699	0	8	9	350	357	-14	2	10	562	525	10	4	10	301	214
9	1	9	395	361	2	4	9	634	595	2	8	9	395	465	-12	2	10	916	1029	-19	5	10	421	435
13	1	9	369	381	4	4	9	606	588	4	8	9	379	433	-10	2	10	869	846	-15	5	10	398	434
17	1	9	271	199	6	4	9	406	416	1	9	9	338	307	-8	2	10	1064	1010	-13	5	10	369	333
-20	2	9	548	504	8	4	9	357	363	3	9	9	313	267	-6	2	10	803	868	-9	5	10	467	484
-18	2	9	332	353	-17	5	9	293	234	0	10	9	381	378	-4	2	10	646	647	-7	5	10	461	456
-14	2	9	652	647	-15	5	9	379	372	-22	0	10	543	484	-2	2	10	1229	1244	-3	5	10	588	598
-12	2	9	344	352	-13	5	9	776	761	-20	0	10	480	484	0	2	10	708	605	-1	5	10	907	944
-8	2	9	305	422	-11	5	9	325	335	-18	0	10	677	628	4	2	10	698	711	1	5	10	550	513
-4	2	9	1421	1404	-9	5	9	959	886	-16	0	10	296	275	6	2	10	868	903	3	5	10	303	278
-2	2	9	1038	1108	-7	5	9	1317	1257	-14	0	10	759	721	-19	3	10	354	412	5	5	10	530	552
0	2	9	636	622	-5	5	9	574	586	-12	0	10	1866	1879	-17	3	10	453	519	7	5	10	235	302
2	2	9	872	828	-3	5	9	395	396	-10	0	10	1378	1094	-15	3	10	626	628	-18	6	10	379	382
4	2	9	868	812	-1	5	9	587	662	-8	0	10	854	881	-13	3	10	378	415	-16	6	10	607	658
6	2	9	361	466	1	5	9	844	796	-6	0	10	1238	1299	-11	3	10	549	614	-12	6	10	592	545
8	2	9	492	458	3	5	9	748	759	-4	0	10	2014	1561	-9	3	10	671	673	-10	6	10	401	384
-19	3	9	296	362	5	5	9	609	629	-2	0	10	2476	2166	-7	3	10	835	848	-8	6	10	790	775
-17	3	9	678	704	7	5	9	276	369	0	0	10	432	340	-5	3	10	814	922	-6	6	10	695	713
-13	3	9	783	783	9	5	9	352	362	2	0	10	395	391	-3	3	10	686	713	-4	6	10	313	359
-11	3	9	711	731	-16	6	9	256	186	4	0	10	687	657	-1	3	10	574	503	-2	6	10	361	414
-7	3	9	593	569	-12	6	9	552	536	6	0	10	713	712	1	3	10	572	587	0	6	10	854	856
-5	3	9	444	515	-10	6	9	320	347	8	0	10	791	770	3	3	10	461	466	2	6	10	872	878
-3	3	9	560	640	-4	6	9	432	386	12	0	10	421	420	5	3	10	325	388	4	6	10	444	497
-1	3	9	872	741	0	6	9	256	287	14	0	10	378	326	7	3	10	449	507	8	6	10	467	516
1	3	9	835	851	-15	7	9	607	562	-17	1	10	345	319	9	3	10	290	231	10	6	10	352	350
3	3	9	630	693	-9	7	9	602	553	-13	1	10	248	232	-24	4	10	332	317	-15	7	10	363	364
5	3	9	555	548	-7	7	9	799	809	-11	1	10	406	412	-18	4	10	373	365	-9	7	10	406	380
7	3	9	868	851	-5	7	9	350	378	-9	1	10	1125	1148	-14	4	10	492	497	-5	7	10	588	540

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.1

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-9	1	9	977	954	11	3	9	238	196	-1	7	9	442	477	-7	1	10	564	546	-12	4	10	592	604
-7	1	9	567	454	-18	4	9	316	256	1	7	9	378	435	-5	1	10	933	888	-10	4	10	585	573
-5	1	9	1456	1424	-16	4	9	401	377	3	7	9	490	524	-3	1	10	808	818	-8	4	10	788	883
-3	1	9	1822	1631	-14	4	9	361	430	9	7	9	418	394	1	1	10	601	536	-6	4	10	660	699
-1	1	9	2232	1982	-10	4	9	916	1013	11	7	9	262	305	7	1	10	385	315	-4	4	10	381	382
1	1	9	750	720	-8	4	9	601	660	-16	8	9	298	286	-22	2	10	385	354	0	4	10	474	484
3	1	9	620	655	-6	4	9	722	751	-14	8	9	371	305	-20	2	10	338	350	2	4	10	632	628
5	1	9	1195	1204	-2	4	9	620	625	-10	8	9	446	436	-18	2	10	317	346	4	4	10	838	857
7	1	9	571	636	0	4	9	727	699	0	8	9	350	357	-14	2	10	562	525	10	4	10	301	214
9	1	9	395	361	2	4	9	634	595	2	8	9	395	465	-12	2	10	916	1029	-19	5	10	421	435
13	1	9	369	381	4	4	9	606	588	4	8	9	379	433	-10	2	10	869	846	-15	5	10	398	434
17	1	9	271	199	6	4	9	406	416	1	9	9	338	307	-8	2	10	1064	1010	-13	5	10	369	333
-20	2	9	548	504	8	4	9	357	363	3	9	9	313	267	-6	2	10	803	868	-9	5	10	467	484
-18	2	9	332	353	-17	5	9	293	234	0	10	9	381	378	-4	2	10	646	647	-7	5	10	461	456
-14	2	9	652	647	-15	5	9	379	372	-22	0	10	543	484	-2	2	10	1229	1244	-3	5	10	588	598
-12	2	9	344	352	-13	5	9	776	761	-20	0	10	480	484	0	2	10	708	605	-1	5	10	907	944
-8	2	9	305	422	-11	5	9	325	335	-18	0	10	677	628	4	2	10	698	711	1	5	10	550	513
-4	2	9	1421	1404	-9	5	9	959	886	-16	0	10	296	275	6	2	10	868	903	3	5	10	303	278
-2	2	9	1038	1108	-7	5	9	1317	1257	-14	0	10	759	721	-19	3	10	354	412	5	5	10	530	552
0	2	9	636	622	-5	5	9	574	586	-12	0	10	1866	1879	-17	3	10	453	519	7	5	10	235	302
2	2	9	872	828	-3	5	9	395	396	-10	0	10	1378	1094	-15	3	10	626	628	-18	6	10	379	382
4	2	9	868	812	-1	5	9	587	662	-8	0	10	854	881	-13	3	10	378	415	-16	6	10	607	658
6	2	9	361	466	1	5	9	844	796	-6	0	10	1238	1299	-11	3	10	549	614	-12	6	10	592	545
8	2	9	492	458	3	5	9	748	759	-4	0	10	2014	1561	-9	3	10	671	673	-10	6	10	401	384
-19	3	9	296	362	5	5	9	609	629	-2	0	10	2476	2166	-7	3	10	835	848	-8	6	10	790	775
-17	3	9	678	704	7	5	9	276	369	0	0	10	432	340	-5	3	10	814	922	-6	6	10	695	713
-13	3	9	783	783	9	5	9	352	362	2	0	10	395	391	-3	3	10	686	713	-4	6	10	313	359
-11	3	9	711	731	-16	6	9	256	186	4	0	10	687	657	-1	3	10	574	503	-2	6	10	361	414
-7	3	9	593	569	-12	6	9	552	536	6	0	10	713	712	1	3	10	572	587	0	6	10	854	856
-5	3	9	444	515	-10	6	9	320	347	8	0	10	791	770	3	3	10	461	466	2	6	10	872	878
-3	3	9	560	640	-4	6	9	432	386	12	0	10	421	420	5	3	10	325	388	4	6	10	444	497
-1	3	9	872	741	0	6	9	256	287	14	0	10	378	326	7	3	10	449	507	8	6	10	467	516
1	3	9	835	851	-15	7	9	607	562	-17	1	10	345	319	9	3	10	290	231	10	6	10	352	350
3	3	9	630	693	-9	7	9	602	553	-13	1	10	248	232	-24	4	10	332	317	-15	7	10	363	364
5	3	9	555	548	-7	7	9	799	809	-11	1	10	406	412	-18	4	10	373	365	-9	7	10	406	380
7	3	9	868	851	-5	7	9	350	378	-9	1	10	1125	1148	-14	4	10	492	497	-5	7	10	588	540

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.1

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
1	7	10	414	445	-11	3	11	994	1080	-9	7	11	496	566	-5	1	12	385	286	-2	4	12	575	543
-8	8	10	567	596	-9	3	11	694	713	-7	7	11	762	835	-3	1	12	444	461	0	4	12	521	560
-6	8	10	412	391	-7	3	11	471	435	-5	7	11	674	617	-1	1	12	609	595	2	4	12	1038	959
-4	8	10	293	257	-5	3	11	344	376	-1	7	11	348	400	1	1	12	231	148	4	4	12	418	407
2	8	10	466	468	-3	3	11	519	529	1	7	11	534	613	3	1	12	352	369	8	4	12	381	344
-7	9	10	308	311	-1	3	11	541	534	7	7	11	310	302	5	1	12	369	362	-13	5	12	504	491
1	9	10	317	376	1	3	11	358	334	-10	8	11	389	374	-20	2	12	305	374	-11	5	12	726	641
-21	1	11	530	562	3	3	11	1151	1115	-8	8	11	541	472	-18	2	12	423	428	-9	5	12	620	656
-19	1	11	580	557	5	3	11	559	588	-4	8	11	383	361	-14	2	12	683	687	-7	5	12	486	501
-15	1	11	449	487	9	3	11	345	344	-2	8	11	332	384	-12	2	12	706	710	-5	5	12	615	586
-13	1	11	1107	1114	-16	4	11	363	383	0	8	11	405	436	-10	2	12	486	521	-3	5	12	301	338
-11	1	11	650	692	-14	4	11	473	431	-15	9	11	274	234	-6	2	12	628	516	7	5	12	444	447
-9	1	11	959	898	-12	4	11	463	495	-9	9	11	323	334	-4	2	12	674	703	-18	6	12	383	340
-7	1	11	508	452	-10	4	11	862	869	-22	0	12	473	428	-2	2	12	810	717	-16	6	12	425	441
-5	1	11	1064	883	-8	4	11	1177	1080	-20	0	12	698	668	0	2	12	290	242	-14	6	12	418	401
-3	1	11	1875	1652	-6	4	11	541	512	-18	0	12	369	402	4	2	12	572	612	-10	6	12	773	831
-1	1	11	548	584	-4	4	11	1229	1161	-16	0	12	367	358	6	2	12	486	537	-8	6	12	1299	1239
3	1	11	718	686	-2	4	11	1011	981	-14	0	12	1238	1249	-17	3	12	308	360	-4	6	12	466	447
5	1	11	640	754	0	4	11	643	615	-12	0	12	942	875	-13	3	12	525	521	-2	6	12	559	585
7	1	11	526	554	2	4	11	344	434	-10	0	12	1439	1413	-11	3	12	824	837	4	6	12	244	296
13	1	11	345	359	4	4	11	451	478	-8	0	12	642	618	-9	3	12	598	628	6	6	12	221	192
-20	2	11	412	452	6	4	11	218	341	-6	0	12	834	765	-7	3	12	977	966	10	6	12	290	253
-18	2	11	678	679	-19	5	11	410	394	-4	0	12	1927	1778	-5	3	12	968	982	-7	7	12	231	263
-16	2	11	439	507	-17	5	11	320	329	-2	0	12	1160	1043	-3	3	12	679	701	1	7	12	363	308
-14	2	11	496	593	-13	5	11	375	403	0	0	12	383	349	-1	3	12	788	812	-10	8	12	334	302
-12	2	11	664	681	-9	5	11	1072	1055	2	0	12	859	887	1	3	12	604	590	-8	8	12	480	450
-10	2	11	699	706	-7	5	11	1299	1225	4	0	12	698	693	3	3	12	320	332	-6	8	12	435	451
-8	2	11	381	292	-5	5	11	460	496	6	0	12	576	608	5	3	12	637	687	0	8	12	437	463
-6	2	11	933	911	-1	5	11	898	888	8	0	12	435	424	7	3	12	350	312	2	8	12	348	344
-4	2	11	1107	858	1	5	11	689	633	12	0	12	330	391	-20	4	12	502	485	-9	9	12	325	331
-2	2	11	703	657	3	5	11	617	625	14	0	12	330	326	-18	4	12	612	619	-7	9	12	320	278
0	2	11	653	637	-10	6	11	412	400	-21	1	12	303	333	-12	4	12	381	355	-23	1	13	330	305
6	2	11	711	660	-8	6	11	337	316	-17	1	12	408	348	-10	4	12	437	452	-21	1	13	439	471
-19	3	11	260	293	-6	6	11	231	295	-11	1	12	373	392	-8	4	12	860	897	-19	1	13	476	456
-17	3	11	684	716	-4	6	11	344	347	-9	1	12	419	371	-6	4	12	670	775	-15	1	13	768	810
-15	3	11	454	485	-2	6	11	395	415	-7	1	12	898	901	-4	4	12	303	282	-13	1	13	933	876

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.1

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-11	1	13	1046	1053	-6	4	13	425	410	-6	0	14	1317	1230	-12	4	14	282	326	-5	1	15	813	796
-9	1	13	308	262	-4	4	13	317	331	-4	0	14	1020	898	-10	4	14	657	676	-3	1	15	907	874
-5	1	13	1264	1191	-2	4	13	729	718	-2	0	14	959	864	-8	4	14	433	478	-1	1	15	348	282
-3	1	13	985	1004	4	4	13	449	498	2	0	14	387	417	-6	4	14	334	289	1	1	15	296	304
-1	1	13	385	334	6	4	13	449	484	4	0	14	738	761	-4	4	14	786	682	3	1	15	416	450
1	1	13	305	256	-19	5	13	408	434	6	0	14	465	471	-2	4	14	373	372	5	1	15	492	478
3	1	13	449	394	-17	5	13	715	753	10	0	14	228	183	0	4	14	545	555	-22	2	15	375	419
5	1	13	541	558	-11	5	13	412	464	-21	1	14	369	346	2	4	14	361	418	-12	2	15	350	354
7	1	13	408	459	-9	5	13	889	891	-15	1	14	628	568	6	4	14	344	341	-10	2	15	582	595
11	1	13	265	260	-7	5	13	508	553	-13	1	14	779	740	-17	5	14	274	228	-8	2	15	403	368
-16	2	13	363	305	-5	5	13	348	283	-9	1	14	525	540	-11	5	14	506	510	-6	2	15	490	477
-14	2	13	375	391	-3	5	13	378	344	-5	1	14	285	258	-9	5	14	397	385	-4	2	15	752	681
-12	2	13	850	888	-1	5	13	440	452	1	1	14	486	356	-7	5	14	350	389	-2	2	15	444	426
-10	2	13	437	515	1	5	13	488	548	3	1	14	285	284	-5	5	14	449	462	0	2	15	361	307
-8	2	13	950	923	3	5	13	308	340	-14	2	14	465	486	-3	5	14	383	408	2	2	15	516	512
-6	2	13	659	636	-16	6	13	418	390	-12	2	14	806	817	1	5	14	440	418	-21	3	15	260	273
-4	2	13	841	810	-14	6	13	293	361	-10	2	14	467	458	-18	6	14	256	372	-19	3	15	418	397
-2	2	13	574	549	-8	6	13	248	265	-8	2	14	271	270	-16	6	14	369	323	-15	3	15	430	442
0	2	13	361	312	-4	6	13	456	380	-6	2	14	559	511	-14	6	14	256	221	-11	3	15	731	680
2	2	13	288	306	-17	7	13	391	412	-4	2	14	942	888	-10	6	14	471	514	-7	3	15	801	764
4	2	13	337	327	-11	7	13	389	383	-2	2	14	461	491	-8	6	14	898	941	-5	3	15	622	568
-21	3	13	279	260	-9	7	13	473	524	2	2	14	276	283	-6	6	14	564	532	-3	3	15	615	609
-19	3	13	271	259	-7	7	13	463	478	6	2	14	405	376	-2	6	14	526	571	-1	3	15	552	530
-13	3	13	695	649	-5	7	13	274	267	-17	3	14	332	316	-3	7	14	250	234	5	3	15	357	377
-11	3	13	469	460	-3	7	13	352	342	-15	3	14	250	295	-10	8	14	317	326	-14	4	15	439	463
-9	3	13	546	617	1	7	13	357	327	-13	3	14	593	634	-8	8	14	345	350	-12	4	15	430	520
-7	3	13	788	862	-6	8	13	327	325	-11	3	14	530	509	2	8	14	337	299	-8	4	15	521	438
-3	3	13	1046	1023	-2	8	13	316	289	-9	3	14	560	582	-7	9	14	296	329	4	4	15	305	333
-1	3	13	350	399	-7	9	13	369	307	-7	3	14	549	472	-23	1	15	325	375	-19	5	15	298	306
1	3	13	301	237	-22	0	14	549	550	-5	3	14	325	384	-21	1	15	361	404	-17	5	15	526	548
3	3	13	416	442	-20	0	14	557	567	-3	3	14	596	549	-17	1	15	395	408	-11	5	15	473	506
5	3	13	375	414	-16	0	14	959	870	-1	3	14	381	420	-15	1	15	726	694	-9	5	15	398	494
-16	4	13	432	470	-14	0	14	977	932	1	3	14	221	244	-13	1	15	1072	1059	-6	6	15	358	301
-14	4	13	618	619	-12	0	14	1465	1294	3	3	14	446	475	-11	1	15	658	667	0	6	15	305	287
-12	4	13	580	511	-10	0	14	405	397	-18	4	14	649	616	-9	1	15	344	322	-17	7	15	469	466
-8	4	13	381	400	-8	0	14	428	470	-16	4	14	279	350	-7	1	15	758	724	-11	7	15	248	312

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.1

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-9	7	15	576	600	-1	3	16	334	294	-17	3	17	494	457	-14	4	18	358	311	-7	5	19	254	303
-7	7	15	408	381	-16	4	16	521	516	-9	3	17	338	248	-10	4	18	256	249	-1	5	19	403	411
-24	0	16	268	361	-12	4	16	357	356	-5	3	17	440	471	-8	4	18	412	431	-24	0	20	305	350
-22	0	16	476	482	-10	4	16	555	567	-3	3	17	437	426	-6	4	18	323	341	-16	0	20	354	401
-20	0	16	466	473	-8	4	16	397	391	1	3	17	303	328	0	4	18	416	422	-14	0	20	707	739
-18	0	16	453	385	-6	4	16	316	392	-10	4	17	543	511	-15	5	18	285	335	-10	0	20	325	255
-16	0	16	808	744	-4	4	16	397	438	-6	4	17	313	366	-13	5	18	423	408	-8	0	20	344	453
-14	0	16	1221	1155	-2	4	16	550	572	-4	4	17	538	543	-11	5	18	308	303	-4	0	20	453	469
-12	0	16	541	553	-21	5	16	268	251	-17	5	17	305	351	-18	6	18	367	409	-11	1	20	316	319
-10	0	16	767	698	-15	5	16	296	258	-9	5	17	305	391	-12	6	18	310	339	-16	2	20	369	395
-8	0	16	643	585	-9	5	16	317	260	-7	5	17	408	393	-10	6	18	416	436	-14	2	20	454	460
-6	0	16	807	806	-3	5	16	323	379	-3	5	17	410	444	-2	6	18	256	295	-6	2	20	435	433
-4	0	16	1186	1041	-18	6	16	437	492	-1	5	17	397	423	0	6	18	303	287	-4	2	20	487	496
-2	0	16	317	341	-8	6	16	296	260	-10	6	17	241	249	-15	1	19	419	399	2	2	20	254	301
0	0	16	357	308	-6	6	16	341	373	-9	7	17	363	427	-13	1	19	555	581	-11	3	20	375	397
2	0	16	521	439	0	6	16	410	402	-7	7	17	348	367	-7	1	19	516	543	-5	3	20	480	472
4	0	16	486	519	0	8	16	262	257	-1	7	17	358	376	-5	1	19	476	576	-1	3	20	250	242
6	0	16	383	393	-21	1	17	378	416	-22	0	18	492	526	-3	1	19	265	282	-12	4	20	293	311
-13	1	16	590	580	-17	1	17	327	363	-20	0	18	313	295	3	1	19	344	350	-13	5	20	265	335
-11	1	16	393	411	-15	1	17	760	743	-16	0	18	813	766	-16	2	19	440	359	-7	5	20	303	353
-7	1	16	465	481	-13	1	17	579	580	-14	0	18	500	501	-14	2	19	484	443	-10	6	20	430	479
-5	1	16	395	380	-11	1	17	727	665	-12	0	18	791	748	-10	2	19	643	543	-8	6	20	378	366
-20	2	16	282	239	-9	1	17	325	296	-10	0	18	244	251	-8	2	19	710	643	-4	6	20	320	370
-14	2	16	397	456	-7	1	17	477	481	-6	0	18	942	857	-6	2	19	357	380	-2	6	20	363	317
-12	2	16	916	845	-5	1	17	835	816	-4	0	18	579	660	-15	3	19	425	433	-15	1	21	553	551
-10	2	16	435	448	-3	1	17	387	420	2	0	18	439	441	-13	3	19	332	260	-5	1	21	538	551
-8	2	16	517	480	5	1	17	354	427	-9	1	18	282	249	-11	3	19	496	478	-6	2	21	398	427
-6	2	16	494	453	-20	2	17	256	276	-7	1	18	317	300	-5	3	19	373	371	-13	3	21	375	329
-4	2	16	585	647	-18	2	17	345	315	-3	1	18	367	309	1	3	19	265	201	-9	3	21	389	353
-2	2	16	325	300	-16	2	17	348	356	-14	2	18	461	484	-12	4	19	371	305	-7	3	21	403	379
-17	3	16	430	434	-14	2	17	428	513	-12	2	18	548	604	-6	4	19	308	345	-10	4	21	308	296
-15	3	16	298	322	-12	2	17	344	308	-8	2	18	555	503	-4	4	19	410	467	-19	5	21	344	310
-13	3	16	643	588	-8	2	17	449	456	-6	2	18	447	451	-19	5	19	358	381	-11	5	21	371	389
-11	3	16	487	459	-6	2	17	327	319	-4	2	18	419	452	-17	5	19	288	288	-16	0	22	494	486
-9	3	16	395	361	-2	2	17	453	395	-7	3	18	387	388	-11	5	19	358	336	-14	0	22	577	519
-7	3	16	454	471	4	2	17	363	384	-5	3	18	425	447	-9	5	19	383	379	-12	0	22	453	420

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.1

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-9	7	15	576	600	-1	3	16	334	294	-17	3	17	494	457	-14	4	18	358	311	-7	5	19	254	303
-7	7	15	408	381	-16	4	16	521	516	-9	3	17	338	248	-10	4	18	256	249	-1	5	19	403	411
-24	0	16	268	361	-12	4	16	357	356	-5	3	17	440	471	-8	4	18	412	431	-24	0	20	305	350
-22	0	16	476	482	-10	4	16	555	567	-3	3	17	437	426	-6	4	18	323	341	-16	0	20	354	401
-20	0	16	466	473	-8	4	16	397	391	1	3	17	303	328	0	4	18	416	422	-14	0	20	707	739
-18	0	16	453	385	-6	4	16	316	392	-10	4	17	543	511	-15	5	18	285	335	-10	0	20	325	255
-16	0	16	808	744	-4	4	16	397	438	-6	4	17	313	366	-13	5	18	423	408	-8	0	20	344	453
-14	0	16	1221	1155	-2	4	16	550	572	-4	4	17	538	543	-11	5	18	308	303	-4	0	20	453	469
-12	0	16	541	553	-21	5	16	268	251	-17	5	17	305	351	-18	6	18	367	409	-11	1	20	316	319
-10	0	16	767	698	-15	5	16	296	258	-9	5	17	305	391	-12	6	18	310	339	-16	2	20	369	395
-8	0	16	643	585	-9	5	16	317	260	-7	5	17	408	393	-10	6	18	416	436	-14	2	20	454	460
-6	0	16	807	806	-3	5	16	323	379	-3	5	17	410	444	-2	6	18	256	295	-6	2	20	435	433
-4	0	16	1186	1041	-18	6	16	437	492	-1	5	17	397	423	0	6	18	303	287	-4	2	20	487	496
-2	0	16	317	341	-8	6	16	296	260	-10	6	17	241	249	-15	1	19	419	399	2	2	20	254	301
0	0	16	357	308	-6	6	16	341	373	-9	7	17	363	427	-13	1	19	555	581	-11	3	20	375	397
2	0	16	521	439	0	6	16	410	402	-7	7	17	348	367	-7	1	19	516	543	-5	3	20	480	472
4	0	16	486	519	0	8	16	262	257	-1	7	17	358	376	-5	1	19	476	576	-1	3	20	250	242
6	0	16	383	393	-21	1	17	378	416	-22	0	18	492	526	-3	1	19	265	282	-12	4	20	293	311
-13	1	16	590	580	-17	1	17	327	363	-20	0	18	313	295	3	1	19	344	350	-13	5	20	265	335
-11	1	16	393	411	-15	1	17	760	743	-16	0	18	813	766	-16	2	19	440	359	-7	5	20	303	353
-7	1	16	465	481	-13	1	17	579	580	-14	0	18	500	501	-14	2	19	484	443	-10	6	20	430	479
-5	1	16	395	380	-11	1	17	727	665	-12	0	18	791	748	-10	2	19	643	543	-8	6	20	378	366
-20	2	16	282	239	-9	1	17	325	296	-10	0	18	244	251	-8	2	19	710	643	-4	6	20	320	370
-14	2	16	397	456	-7	1	17	477	481	-6	0	18	942	857	-6	2	19	357	380	-2	6	20	363	317
-12	2	16	916	845	-5	1	17	835	816	-4	0	18	579	660	-15	3	19	425	433	-15	1	21	553	551
-10	2	16	435	448	-3	1	17	387	420	2	0	18	439	441	-13	3	19	332	260	-5	1	21	538	551
-8	2	16	517	480	5	1	17	354	427	-9	1	18	282	249	-11	3	19	496	478	-6	2	21	398	427
-6	2	16	494	453	-20	2	17	256	276	-7	1	18	317	300	-5	3	19	373	371	-13	3	21	375	329
-4	2	16	585	647	-18	2	17	345	315	-3	1	18	367	309	1	3	19	265	201	-9	3	21	389	353
-2	2	16	325	300	-16	2	17	348	356	-14	2	18	461	484	-12	4	19	371	305	-7	3	21	403	379
-17	3	16	430	434	-14	2	17	428	513	-12	2	18	548	604	-6	4	19	308	345	-10	4	21	308	296
-15	3	16	298	322	-12	2	17	344	308	-8	2	18	555	503	-4	4	19	410	467	-19	5	21	344	310
-13	3	16	643	588	-8	2	17	449	456	-6	2	18	447	451	-19	5	19	358	381	-11	5	21	371	389
-11	3	16	487	459	-6	2	17	327	319	-4	2	18	419	452	-17	5	19	288	288	-16	0	22	494	486
-9	3	16	395	361	-2	2	17	453	395	-7	3	18	387	388	-11	5	19	358	336	-14	0	22	577	519
-7	3	16	454	471	4	2	17	363	384	-5	3	18	425	447	-9	5	19	383	379	-12	0	22	453	420

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.1

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-10	0	22	613	477	-4	0	22	344	345	-14	2	22	373	375	-9	3	22	325	286	-13	1	23	288	307
-8	0	22	432	457	-9	1	22	334	317	-6	2	22	401	387	-17	1	23	487	496	-7	1	23	352	347
-6	0	22	557	565	-16	2	22	463	475	-13	3	22	296	304	-15	1	23	567	549	-5	1	23	290	321

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.2

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
4	0	0	2707	2469	13	3	0	326	334	14	6	0	381	388	2	10	0	439	433	2	14	0	611	633
6	0	0	2228	2128	15	3	0	307	300	18	6	0	260	248	4	10	0	840	814	4	14	0	605	643
8	0	0	1468	1425	17	3	0	186	206	20	6	0	307	352	6	10	0	552	587	6	14	0	251	238
10	0	0	1771	1606	19	3	0	651	629	22	6	0	204	173	8	10	0	295	250	10	14	0	302	238
12	0	0	375	342	21	3	0	386	422	1	7	0	617	579	10	10	0	571	581	12	14	0	378	369
14	0	0	605	587	23	3	0	266	240	3	7	0	1639	1540	12	10	0	359	311	14	14	0	202	206
16	0	0	657	608	0	4	0	863	754	5	7	0	571	557	14	10	0	360	385	3	15	0	194	163
18	0	0	451	455	2	4	0	211	187	7	7	0	538	505	16	10	0	294	308	7	15	0	216	234
22	0	0	557	539	4	4	0	954	973	9	7	0	340	347	18	10	0	269	264	2	16	0	184	190
24	0	0	298	309	6	4	0	479	415	11	7	0	487	485	20	10	0	324	320	4	16	0	368	355
3	1	0	1097	1201	8	4	0	1091	1041	13	7	0	386	383	1	11	0	566	541	6	16	0	302	315
5	1	0	1371	1348	10	4	0	651	660	15	7	0	234	217	3	11	0	628	607	1	17	0	312	334
7	1	0	851	834	12	4	0	347	348	17	7	0	239	228	5	11	0	1171	1173	3	17	0	218	227
9	1	0	623	680	14	4	0	737	765	19	7	0	342	371	7	11	0	640	601	7	17	0	326	347
11	1	0	1125	1049	16	4	0	568	588	21	7	0	222	190	9	11	0	148	113	9	17	0	290	264
13	1	0	543	531	18	4	0	617	603	23	7	0	198	172	11	11	0	271	308	6	18	0	180	176
15	1	0	201	158	20	4	0	238	195	0	8	0	1965	1925	13	11	0	344	323	-23	1	1	205	218
17	1	0	166	156	22	4	0	367	345	2	8	0	1274	1319	15	11	0	159	164	-17	1	1	471	461
19	1	0	374	393	24	4	0	307	317	4	8	0	306	283	17	11	0	239	224	-15	1	1	485	525
21	1	0	381	397	1	5	0	559	610	6	8	0	264	290	19	11	0	248	223	-13	1	1	414	422
2	2	0	1559	1631	3	5	0	794	780	8	8	0	1108	1087	0	12	0	605	617	-11	1	1	1331	1250
4	2	0	1234	1025	5	5	0	467	443	10	8	0	828	753	2	12	0	174	186	-9	1	1	1177	1166
6	2	0	1034	1096	7	5	0	571	562	12	8	0	155	120	6	12	0	404	369	-7	1	1	466	398
8	2	0	521	491	9	5	0	419	430	14	8	0	485	489	8	12	0	352	359	-5	1	1	783	732
10	2	0	845	833	11	5	0	558	555	16	8	0	462	432	10	12	0	347	363	-3	1	1	404	309
12	2	0	458	377	13	5	0	413	438	18	8	0	400	397	14	12	0	313	295	3	1	1	2308	2058
14	2	0	247	226	15	5	0	439	473	1	9	0	1097	1044	1	13	0	754	728	5	1	1	1142	1102
16	2	0	300	287	17	5	0	271	259	3	9	0	657	697	3	13	0	447	388	7	1	1	611	691
20	2	0	366	344	19	5	0	231	197	5	9	0	524	502	5	13	0	266	302	9	1	1	1371	1306
24	2	0	236	206	21	5	0	225	211	7	9	0	515	525	7	13	0	617	566	11	1	1	368	415
1	3	0	817	744	2	6	0	948	889	9	9	0	634	631	9	13	0	447	443	13	1	1	577	626
3	3	0	3004	2801	4	6	0	777	729	11	9	0	543	497	11	13	0	182	222	15	1	1	499	525
5	3	0	548	576	6	6	0	368	346	13	9	0	200	204	13	13	0	279	266	17	1	1	371	417
7	3	0	982	971	8	6	0	371	346	17	9	0	319	331	15	13	0	360	360	21	1	1	318	300
9	3	0	446	369	10	6	0	270	299	19	9	0	165	155	17	13	0	254	235	23	1	1	262	256
11	3	0	525	540	12	6	0	446	433	0	10	0	487	548	0	14	0	335	310	-22	2	1	539	464

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.2

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-20	2	1	474	502	15	3	1	258	240	7	5	1	524	562	-11	7	1	518	477	-19	9	1	292	313
-18	2	1	400	400	17	3	1	266	263	9	5	1	1005	1050	-9	7	1	442	526	-17	9	1	243	205
-16	2	1	440	441	19	3	1	399	375	11	5	1	583	503	-7	7	1	528	468	-15	9	1	225	255
-14	2	1	731	736	21	3	1	271	254	13	5	1	788	785	-5	7	1	1411	1466	-13	9	1	221	289
-12	2	1	851	842	-20	4	1	326	274	15	5	1	794	780	-3	7	1	994	1018	-11	9	1	476	450
-10	2	1	1097	1090	-16	4	1	300	312	17	5	1	380	406	-1	7	1	874	797	-9	9	1	697	690
-8	2	1	657	642	-12	4	1	504	499	19	5	1	443	392	1	7	1	1479	1529	-7	9	1	788	759
-6	2	1	1599	1484	-10	4	1	577	530	21	5	1	202	197	3	7	1	1354	1388	-5	9	1	297	334
-4	2	1	2416	2369	-8	4	1	651	648	-22	6	1	200	256	5	7	1	731	658	-3	9	1	462	446
-2	2	1	1188	1193	-6	4	1	737	721	-20	6	1	521	507	7	7	1	863	977	-1	9	1	1177	1133
2	2	1	2056	1981	-4	4	1	874	975	-18	6	1	356	412	9	7	1	536	557	1	9	1	731	667
4	2	1	1497	1401	-2	4	1	1239	1252	-16	6	1	212	254	11	7	1	483	491	3	9	1	354	382
6	2	1	628	601	0	4	1	1194	1278	-14	6	1	605	608	13	7	1	559	544	5	9	1	368	321
8	2	1	419	438	2	4	1	388	336	-12	6	1	1194	1205	15	7	1	346	387	7	9	1	516	501
10	2	1	1177	1064	4	4	1	994	991	-10	6	1	760	772	17	7	1	214	242	9	9	1	697	695
12	2	1	805	842	6	4	1	942	968	-8	6	1	885	915	19	7	1	220	244	11	9	1	404	376
14	2	1	394	355	8	4	1	720	689	-6	6	1	914	885	-18	8	1	299	303	13	9	1	347	352
18	2	1	634	615	10	4	1	356	356	-4	6	1	1913	1995	-16	8	1	332	359	15	9	1	408	431
20	2	1	594	618	12	4	1	316	288	-2	6	1	657	587	-14	8	1	531	470	17	9	1	246	264
22	2	1	173	208	14	4	1	333	314	0	6	1	368	365	-10	8	1	800	744	-20	10	1	179	153
-19	3	1	376	340	18	4	1	323	313	2	6	1	1971	1984	-8	8	1	823	774	-16	10	1	300	329
-17	3	1	264	302	-23	5	1	237	256	4	6	1	1314	1218	-6	8	1	1091	1108	-14	10	1	419	342
-15	3	1	468	504	-21	5	1	244	223	6	6	1	908	944	-4	8	1	550	527	-12	10	1	157	136
-11	3	1	697	703	-19	5	1	528	518	8	6	1	300	233	-2	8	1	1234	1245	-10	10	1	214	246
-9	3	1	891	948	-17	5	1	559	602	10	6	1	1034	1079	0	8	1	1685	1769	-8	10	1	538	520
-7	3	1	811	871	-15	5	1	537	521	12	6	1	800	813	2	8	1	937	909	-6	10	1	498	511
-5	3	1	1771	1694	-13	5	1	577	577	14	6	1	611	594	4	8	1	1017	1090	-4	10	1	423	399
-3	3	1	600	546	-11	5	1	264	243	16	6	1	285	302	6	8	1	765	755	-2	10	1	657	687
-1	3	1	2959	2799	-9	5	1	857	868	18	6	1	551	530	8	8	1	1137	1170	0	10	1	651	691
1	3	1	1011	935	-7	5	1	651	647	20	6	1	251	313	10	8	1	519	538	2	10	1	553	568
3	3	1	948	918	-5	5	1	823	802	22	6	1	243	226	12	8	1	422	412	4	10	1	544	544
5	3	1	783	797	-3	5	1	1377	1477	-23	7	1	186	170	14	8	1	398	365	6	10	1	399	394
7	3	1	651	737	-1	5	1	1999	1887	-19	7	1	327	340	16	8	1	588	608	8	10	1	518	457
9	3	1	851	805	1	5	1	2033	2004	-17	7	1	266	269	18	8	1	318	301	10	10	1	556	590
11	3	1	437	405	3	5	1	514	542	-15	7	1	354	396	22	8	1	188	195	12	10	1	282	315
13	3	1	235	267	5	5	1	674	753	-13	7	1	800	795	-21	9	1	198	221	18	10	1	165	193

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.2

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-21	11	1	285	275	11	13	1	183	194	2	18	1	206	264	-7	1	2	1074	1013	-15	3	2	554	531
-19	11	1	237	250	13	13	1	211	193	-5	19	1	286	279	-5	1	2	2559	2444	-13	3	2	851	840
-13	11	1	317	352	15	13	1	182	193	-3	19	1	292	281	-3	1	2	2753	2698	-11	3	2	1085	1079
-11	11	1	382	401	-12	14	1	275	269	1	19	1	211	229	-1	1	2	908	999	-9	3	2	1000	984
-9	11	1	229	160	-10	14	1	300	284	3	19	1	245	266	1	1	2	1154	1140	-7	3	2	1228	1378
-7	11	1	640	609	-6	14	1	389	430	-24	0	2	316	304	3	1	2	3861	3688	-5	3	2	2913	2718
-5	11	1	623	622	-4	14	1	399	335	-22	0	2	234	220	5	1	2	1188	1257	-3	3	2	450	399
-3	11	1	312	307	-2	14	1	307	279	-20	0	2	475	495	7	1	2	424	400	-1	3	2	857	906
-1	11	1	175	208	0	14	1	287	332	-18	0	2	680	707	9	1	2	486	517	1	3	2	1137	1138
1	11	1	371	376	2	14	1	314	299	-16	0	2	1171	1175	11	1	2	743	819	3	3	2	1879	1827
3	11	1	691	691	4	14	1	264	270	-14	0	2	731	731	13	1	2	521	497	5	3	2	1085	1046
5	11	1	418	400	10	14	1	256	286	-12	0	2	552	555	15	1	2	334	326	9	3	2	1200	1136
7	11	1	244	220	-15	15	1	314	304	-10	0	2	1919	1976	17	1	2	379	373	11	3	2	960	945
9	11	1	731	746	-13	15	1	349	323	-8	0	2	1497	1419	19	1	2	540	534	13	3	2	617	630
11	11	1	505	483	-11	15	1	256	254	-6	0	2	2039	2000	-18	2	2	245	250	15	3	2	295	270
19	11	1	258	293	-7	15	1	350	344	-4	0	2	2148	1878	-16	2	2	296	324	17	3	2	583	565
-12	12	1	211	226	-5	15	1	588	622	-2	0	2	3850	3815	-14	2	2	342	375	19	3	2	462	479
-10	12	1	252	276	-3	15	1	486	473	0	0	2	2690	2536	-12	2	2	223	215	21	3	2	213	206
-8	12	1	459	477	-1	15	1	238	252	2	0	2	1257	1315	-10	2	2	279	188	-20	4	2	395	348
-6	12	1	451	465	3	15	1	190	191	4	0	2	1257	1104	-8	2	2	720	804	-18	4	2	510	513
-4	12	1	215	210	5	15	1	287	282	6	0	2	1696	1792	-6	2	2	2479	2329	-14	4	2	356	392
-2	12	1	351	340	11	15	1	317	338	8	0	2	1405	1429	-4	2	2	2428	2267	-12	4	2	528	522
0	12	1	357	285	13	15	1	251	249	10	0	2	805	749	-2	2	2	255	120	-10	4	2	645	635
2	12	1	186	188	-10	16	1	285	299	12	0	2	891	941	0	2	2	2599	2801	-8	4	2	1034	1017
10	12	1	248	255	-8	16	1	481	534	14	0	2	1222	1205	2	2	2	1257	1140	-6	4	2	148	184
14	12	1	299	302	-6	16	1	258	302	16	0	2	771	728	4	2	2	2639	2619	-4	4	2	925	817
16	12	1	279	304	-2	16	1	414	435	18	0	2	261	267	6	2	2	406	436	-2	4	2	714	794
-15	13	1	201	203	0	16	1	412	423	20	0	2	288	273	8	2	2	519	464	0	4	2	908	872
-9	13	1	231	229	2	16	1	226	243	-23	1	2	228	126	10	2	2	512	475	2	4	2	1457	1496
-7	13	1	246	242	4	16	1	166	114	-21	1	2	212	278	12	2	2	208	169	4	4	2	1565	1581
-5	13	1	381	459	6	16	1	423	455	-19	1	2	228	257	14	2	2	471	439	6	4	2	977	988
-3	13	1	211	212	8	16	1	344	351	-17	1	2	187	170	16	2	2	265	248	8	4	2	708	693
-1	13	1	332	365	1	17	1	163	170	-15	1	2	805	811	22	2	2	188	188	10	4	2	304	337
1	13	1	296	298	-8	18	1	211	240	-13	1	2	680	673	-23	3	2	262	327	12	4	2	430	434
3	13	1	288	297	-2	18	1	214	234	-11	1	2	748	711	-21	3	2	286	333	14	4	2	583	562
7	13	1	209	215	0	18	1	271	266	-9	1	2	319	325	-19	3	2	457	448	16	4	2	243	291

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.2

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
18	4	2	301	261	10	6	2	440	447	14	8	2	557	560	12	10	2	439	428	-19	13	2	215	174
20	4	2	231	226	12	6	2	253	258	16	8	2	244	260	14	10	2	525	521	-17	13	2	246	233
22	4	2	374	371	18	6	2	257	215	22	8	2	215	225	16	10	2	188	191	-15	13	2	219	200
-21	5	2	294	277	-21	7	2	248	260	-21	9	2	211	133	18	10	2	191	184	-11	13	2	271	225
-19	5	2	294	293	-15	7	2	410	400	-19	9	2	321	303	20	10	2	240	227	-9	13	2	391	403
-17	5	2	296	301	-13	7	2	492	474	-17	9	2	230	247	-15	11	2	223	223	-7	13	2	210	178
-15	5	2	289	280	-9	7	2	449	448	-15	9	2	291	314	-11	11	2	811	806	-3	13	2	487	486
-13	5	2	403	443	-7	7	2	840	855	-13	9	2	577	541	-9	11	2	611	633	-1	13	2	868	850
-11	5	2	902	907	-5	7	2	1177	1184	-11	9	2	743	766	-7	11	2	475	469	1	13	2	483	422
-9	5	2	765	787	-3	7	2	788	766	-9	9	2	446	496	-5	11	2	645	645	5	13	2	455	471
-7	5	2	628	646	-1	7	2	1177	1112	-7	9	2	555	542	-3	11	2	470	438	7	13	2	324	328
-5	5	2	623	542	1	7	2	1091	1120	-5	9	2	680	752	-1	11	2	400	400	9	13	2	303	319
-3	5	2	1160	1115	3	7	2	1268	1192	-3	9	2	435	481	1	11	2	651	639	13	13	2	331	300
-1	5	2	743	730	5	7	2	651	633	-1	9	2	674	650	3	11	2	623	582	15	13	2	320	333
1	5	2	897	843	7	7	2	360	334	1	9	2	645	716	5	11	2	438	439	17	13	2	298	266
3	5	2	1342	1167	9	7	2	482	474	3	9	2	483	483	7	11	2	227	232	-14	14	2	312	337
5	5	2	406	362	11	7	2	588	581	5	9	2	550	555	9	11	2	188	178	-12	14	2	434	444
7	5	2	472	511	13	7	2	611	543	7	9	2	708	681	11	11	2	605	604	-10	14	2	231	206
9	5	2	415	458	15	7	2	328	370	9	9	2	358	360	13	11	2	289	310	-8	14	2	384	401
11	5	2	617	627	17	7	2	416	407	11	9	2	426	440	15	11	2	278	251	-6	14	2	571	555
13	5	2	364	387	-20	8	2	223	271	13	9	2	240	247	19	11	2	188	213	-4	14	2	645	602
15	5	2	398	360	-18	8	2	356	352	15	9	2	302	289	-16	12	2	237	257	-2	14	2	269	275
17	5	2	398	410	-16	8	2	249	254	-20	10	2	206	227	-14	12	2	240	301	0	14	2	357	319
-22	6	2	212	210	-14	8	2	500	458	-14	10	2	246	241	-12	12	2	318	325	2	14	2	268	276
-18	6	2	261	292	-12	8	2	390	415	-12	10	2	245	238	-10	12	2	386	299	4	14	2	340	366
-16	6	2	249	239	-10	8	2	925	983	-10	10	2	777	804	-8	12	2	403	413	8	14	2	249	293
-14	6	2	302	246	-8	8	2	914	906	-8	10	2	577	605	-6	12	2	358	455	10	14	2	448	446
-12	6	2	282	261	-6	8	2	228	246	-6	10	2	937	934	-4	12	2	321	321	12	14	2	281	294
-6	6	2	805	798	-4	8	2	465	459	-4	10	2	535	576	-2	12	2	386	426	16	14	2	220	199
-4	6	2	1171	1037	-2	8	2	1080	1112	-2	10	2	577	566	0	12	2	186	147	-9	15	2	182	182
-2	6	2	611	639	0	8	2	1622	1624	0	10	2	308	306	4	12	2	336	369	-3	15	2	224	234
0	6	2	557	577	2	8	2	731	722	2	10	2	800	805	6	12	2	279	281	9	15	2	176	201
2	6	2	697	642	4	8	2	368	396	4	10	2	668	650	8	12	2	427	454	-6	16	2	343	395
4	6	2	211	243	6	8	2	823	751	6	10	2	437	420	10	12	2	338	298	-4	16	2	424	426
6	6	2	481	434	8	8	2	623	645	8	10	2	456	486	12	12	2	246	229	-2	16	2	311	310
8	6	2	771	776	12	8	2	236	267	10	10	2	674	676	14	12	2	251	246	2	16	2	337	348

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.2

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
4	16	2	285	303	-14	2	3	840	883	17	3	3	208	196	15	5	3	362	307	9	7	3	588	580
10	16	2	188	203	-12	2	3	794	838	-18	4	3	250	246	17	5	3	376	345	11	7	3	313	318
12	16	2	195	176	-10	2	3	419	448	-14	4	3	206	211	21	5	3	276	257	13	7	3	805	746
-9	17	2	301	339	-8	2	3	2108	2017	-12	4	3	343	257	-22	6	3	275	305	15	7	3	272	241
-7	17	2	195	191	-6	2	3	2211	2218	-10	4	3	1377	1304	-20	6	3	376	383	-20	8	3	191	250
-3	17	2	314	343	-4	2	3	645	713	-8	4	3	765	825	-16	6	3	242	284	-18	8	3	249	303
-1	17	2	286	275	-2	2	3	1422	1393	-6	4	3	485	521	-14	6	3	874	898	-16	8	3	438	432
5	17	2	229	228	0	2	3	1062	1055	-4	4	3	908	823	-12	6	3	725	722	-14	8	3	308	288
7	17	2	351	348	2	2	3	1434	1486	-2	4	3	371	339	-10	6	3	617	635	-12	8	3	571	608
-8	18	2	210	150	4	2	3	1999	1939	0	4	3	281	248	-8	6	3	342	336	-10	8	3	691	682
-6	18	2	233	183	6	2	3	403	399	2	4	3	383	337	-6	6	3	1451	1521	-8	8	3	948	950
-21	1	3	304	272	8	2	3	725	658	4	4	3	645	684	-4	6	3	1080	1071	-6	8	3	594	591
-19	1	3	412	435	10	2	3	1325	1324	6	4	3	743	660	-2	6	3	187	172	-4	8	3	1120	1068
-17	1	3	685	628	12	2	3	600	642	8	4	3	714	658	0	6	3	1057	1054	-2	8	3	1074	1065
-15	1	3	476	422	14	2	3	324	339	10	4	3	135	229	2	6	3	1497	1482	0	8	3	965	969
-13	1	3	516	547	16	2	3	527	492	12	4	3	313	356	4	6	3	1302	1276	2	8	3	115	175
-11	1	3	1302	1291	18	2	3	454	439	16	4	3	226	228	6	6	3	902	820	4	8	3	577	574
-9	1	3	1651	1584	-25	3	3	248	218	18	4	3	174	182	8	6	3	788	784	6	8	3	1045	1062
-7	1	3	1245	1155	-19	3	3	426	420	-23	5	3	185	193	10	6	3	663	647	8	8	3	525	510
-5	1	3	931	802	-17	3	3	410	414	-19	5	3	556	526	12	6	3	760	769	10	8	3	561	531
-3	1	3	651	688	-15	3	3	264	203	-17	5	3	284	346	16	6	3	507	522	12	8	3	645	669
-1	1	3	2679	2324	-13	3	3	151	171	-15	5	3	431	438	18	6	3	169	256	14	8	3	817	757
1	1	3	634	613	-11	3	3	697	773	-13	5	3	466	489	-19	7	3	311	283	16	8	3	279	329
3	1	3	2216	2173	-9	3	3	623	718	-11	5	3	1228	1259	-17	7	3	215	200	-13	9	3	400	397
5	1	3	1828	1795	-7	3	3	488	491	-9	5	3	1479	1503	-15	7	3	714	675	-11	9	3	760	753
7	1	3	1165	1060	-5	3	3	594	602	-7	5	3	1022	879	-13	7	3	628	664	-9	9	3	823	785
9	1	3	720	717	-3	3	3	937	1045	-5	5	3	1405	1383	-11	7	3	420	431	-7	9	3	577	591
11	1	3	260	279	-1	3	3	2410	2398	-3	5	3	1074	1099	-9	7	3	547	498	-5	9	3	304	330
13	1	3	1194	1184	1	3	3	737	832	-1	5	3	1342	1373	-7	7	3	565	581	-3	9	3	788	771
15	1	3	697	677	3	3	3	566	557	1	5	3	274	258	-5	7	3	651	733	-1	9	3	908	916
21	1	3	212	174	5	3	3	1502	1575	3	5	3	232	333	-3	7	3	194	212	1	9	3	306	326
-24	2	3	228	192	7	3	3	937	912	5	5	3	369	337	-1	7	3	459	419	3	9	3	680	735
-22	2	3	231	248	9	3	3	908	934	7	5	3	1000	1036	1	7	3	221	264	5	9	3	851	827
-20	2	3	192	216	11	3	3	246	296	9	5	3	811	779	3	7	3	857	788	7	9	3	720	699
-18	2	3	281	238	13	3	3	310	305	11	5	3	546	530	5	7	3	857	901	9	9	3	344	344
-16	2	3	1040	1003	15	3	3	312	302	13	5	3	714	700	7	7	3	295	319	11	9	3	153	188

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.2

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
13	9	3	332	309	-10	12	3	468	462	7	15	3	173	193	16	0	4	541	527	6	2	4	851	878
15	9	3	212	196	-6	12	3	366	384	9	15	3	396	403	18	0	4	165	194	10	2	4	440	393
19	9	3	228	201	-4	12	3	479	404	11	15	3	263	268	20	0	4	231	174	12	2	4	434	408
-16	10	3	467	470	-2	12	3	416	409	-14	16	3	177	136	22	0	4	414	431	20	2	4	196	162
-14	10	3	201	231	2	12	3	284	257	-12	16	3	256	231	-21	1	4	268	251	-23	3	4	256	195
-12	10	3	317	268	4	12	3	224	221	-10	16	3	356	372	-19	1	4	206	221	-21	3	4	324	342
-10	10	3	462	433	6	12	3	388	383	-8	16	3	318	347	-17	1	4	588	605	-19	3	4	220	182
-8	10	3	588	577	8	12	3	280	264	-4	16	3	366	367	-15	1	4	456	506	-17	3	4	176	223
-6	10	3	520	515	10	12	3	304	342	-2	16	3	423	446	-13	1	4	557	536	-15	3	4	851	840
-4	10	3	303	320	12	12	3	315	356	0	16	3	269	224	-11	1	4	522	522	-13	3	4	395	439
-2	10	3	410	400	14	12	3	282	302	4	16	3	324	311	-9	1	4	674	713	-11	3	4	880	952
0	10	3	429	405	-11	13	3	262	279	6	16	3	430	424	-7	1	4	1776	1747	-9	3	4	357	376
2	10	3	449	401	-9	13	3	356	376	8	16	3	223	223	-5	1	4	1045	1087	-7	3	4	1239	1212
6	10	3	306	340	-7	13	3	247	209	12	16	3	183	206	-3	1	4	988	956	-5	3	4	645	655
8	10	3	374	354	-3	13	3	338	329	0	18	3	290	229	-1	1	4	851	768	-3	3	4	617	620
10	10	3	552	543	-1	13	3	226	197	-26	0	4	339	298	1	1	4	777	769	-1	3	4	685	706
12	10	3	379	388	7	13	3	156	170	-24	0	4	224	285	3	1	4	2439	2395	1	3	4	1017	1069
-17	11	3	211	220	9	13	3	312	339	-22	0	4	241	221	5	1	4	407	422	3	3	4	1160	1226
-15	11	3	279	286	11	13	3	296	266	-20	0	4	460	502	7	1	4	210	243	5	3	4	553	550
-13	11	3	196	218	13	13	3	216	261	-18	0	4	720	790	9	1	4	1062	1037	7	3	4	1177	1202
-11	11	3	155	216	-12	14	3	330	297	-16	0	4	691	678	11	1	4	456	480	9	3	4	783	820
-9	11	3	326	284	-10	14	3	195	175	-14	0	4	153	108	13	1	4	255	242	11	3	4	680	634
-7	11	3	748	768	-4	14	3	246	232	-12	0	4	1000	1001	15	1	4	444	425	13	3	4	216	248
-5	11	3	811	754	-2	14	3	167	191	-10	0	4	1091	1144	17	1	4	224	215	15	3	4	307	283
-3	11	3	351	313	2	14	3	362	393	-8	0	4	1177	1214	-20	2	4	342	317	17	3	4	462	425
-1	11	3	276	303	4	14	3	284	324	-6	0	4	1120	1176	-16	2	4	640	656	19	3	4	259	269
1	11	3	390	366	-15	15	3	254	249	-4	0	4	1051	1287	-14	2	4	169	218	-20	4	4	441	484
3	11	3	600	675	-13	15	3	284	280	-2	0	4	499	552	-12	2	4	475	524	-18	4	4	530	464
5	11	3	390	376	-11	15	3	176	187	0	0	4	2953	3074	-10	2	4	885	901	-16	4	4	249	207
7	11	3	200	202	-9	15	3	162	220	2	0	4	811	694	-8	2	4	891	926	-14	4	4	560	555
9	11	3	403	386	-7	15	3	330	317	4	0	4	3027	2999	-6	2	4	1485	1418	-12	4	4	1325	1371
11	11	3	346	309	-5	15	3	427	480	6	0	4	1691	1649	-4	2	4	196	184	-10	4	4	1599	1585
17	11	3	217	205	-3	15	3	308	308	8	0	4	1160	1206	-2	2	4	588	618	-8	4	4	1268	1148
-16	12	3	266	249	-1	15	3	277	266	10	0	4	336	298	0	2	4	731	777	-6	4	4	954	990
-14	12	3	159	179	1	15	3	342	373	12	0	4	1097	1121	2	2	4	931	1045	-2	4	4	1245	1173
-12	12	3	444	465	3	15	3	340	334	14	0	4	1205	1176	4	2	4	508	563	0	4	4	617	577

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.2

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
13	9	3	332	309	-10	12	3	468	462	-7	15	3	173	193	16	0	4	541	527	6	2	4	851	878
15	9	3	212	196	-6	12	3	366	384	9	15	3	396	403	18	0	4	165	194	10	2	4	440	393
19	9	3	228	201	-4	12	3	479	404	11	15	3	263	268	20	0	4	231	174	12	2	4	434	408
-16	10	3	467	470	-2	12	3	416	409	-14	16	3	177	136	22	0	4	414	431	20	2	4	196	162
-14	10	3	201	231	2	12	3	284	257	-12	16	3	256	231	-21	1	4	268	251	-23	3	4	256	195
-12	10	3	317	268	4	12	3	224	221	-10	16	3	356	372	-19	1	4	206	221	-21	3	4	324	342
-10	10	3	462	433	6	12	3	388	383	-8	16	3	318	347	-17	1	4	588	605	-19	3	4	220	182
-8	10	3	588	577	8	12	3	280	264	-4	16	3	366	367	-15	1	4	456	506	-17	3	4	176	223
-6	10	3	520	515	10	12	3	304	342	-2	16	3	423	446	-13	1	4	557	536	-15	3	4	851	840
-4	10	3	303	320	12	12	3	315	356	0	16	3	269	224	-11	1	4	522	522	-13	3	4	395	439
-2	10	3	410	400	14	12	3	282	302	4	16	3	324	311	-9	1	4	674	713	-11	3	4	880	952
0	10	3	429	405	-11	13	3	262	279	6	16	3	430	424	-7	1	4	1776	1747	-9	3	4	357	376
2	10	3	449	401	-9	13	3	356	376	8	16	3	223	223	-5	1	4	1045	1087	-7	3	4	1239	1212
6	10	3	306	340	-7	13	3	247	209	12	16	3	183	206	-3	1	4	988	956	-5	3	4	645	655
8	10	3	374	354	-3	13	3	338	329	0	18	3	290	229	-1	1	4	851	768	-3	3	4	617	620
10	10	3	552	543	-1	13	3	226	197	-26	0	4	339	298	1	1	4	777	769	-1	3	4	685	706
12	10	3	379	388	7	13	3	156	170	-24	0	4	224	285	3	1	4	2439	2395	1	3	4	1017	1069
-17	11	3	211	220	9	13	3	312	339	-22	0	4	241	221	5	1	4	407	422	3	3	4	1160	1226
-15	11	3	279	286	11	13	3	296	266	-20	0	4	460	502	7	1	4	210	243	5	3	4	553	550
-13	11	3	196	218	13	13	3	216	261	-18	0	4	720	790	9	1	4	1062	1037	7	3	4	1177	1202
-11	11	3	155	216	-12	14	3	330	297	-16	0	4	691	678	11	1	4	456	480	9	3	4	783	820
-9	11	3	326	284	-10	14	3	195	175	-14	0	4	153	108	13	1	4	255	242	11	3	4	680	634
-7	11	3	748	768	-4	14	3	246	232	-12	0	4	1000	1001	15	1	4	444	425	13	3	4	216	248
-5	11	3	811	754	-2	14	3	167	191	-10	0	4	1091	1144	17	1	4	224	215	15	3	4	307	283
-3	11	3	351	313	2	14	3	362	393	-8	0	4	1177	1214	-20	2	4	342	317	17	3	4	462	425
-1	11	3	276	303	4	14	3	284	324	-6	0	4	1120	1176	-16	2	4	640	656	19	3	4	259	269
1	11	3	390	366	-15	15	3	254	249	-4	0	4	1051	1287	-14	2	4	169	218	-20	4	4	441	484
3	11	3	600	675	-13	15	3	284	280	-2	0	4	499	552	-12	2	4	475	524	-18	4	4	530	464
5	11	3	390	376	-11	15	3	176	187	0	0	4	2953	3074	-10	2	4	885	901	-16	4	4	249	207
7	11	3	200	202	-9	15	3	162	220	2	0	4	811	694	-8	2	4	891	926	-14	4	4	560	555
9	11	3	403	386	-7	15	3	330	317	4	0	4	3027	2999	-6	2	4	1485	1418	-12	4	4	1325	1371
11	11	3	346	309	-5	15	3	427	480	6	0	4	1691	1649	-4	2	4	196	184	-10	4	4	1599	1585
17	11	3	217	205	-3	15	3	308	308	8	0	4	1160	1206	-2	2	4	588	618	-8	4	4	1268	1148
-16	12	3	266	249	-1	15	3	277	266	10	0	4	336	298	0	2	4	731	777	-6	4	4	954	990
-14	12	3	159	179	1	15	3	342	373	12	0	4	1097	1121	2	2	4	931	1045	-2	4	4	1245	1173
-12	12	3	444	465	3	15	3	340	334	14	0	4	1205	1176	4	2	4	508	563	0	4	4	617	577

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.2

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
2	4	4	628	564	-2	6	4	296	271	-2	8	4	743	721	8	10	4	583	601	3	13	4	196	164
4	4	4	1125	1243	0	6	4	268	188	0	8	4	531	515	10	10	4	397	438	5	13	4	462	565
6	4	4	1674	1712	2	6	4	743	740	2	8	4	376	413	18	10	4	221	195	7	13	4	342	337
8	4	4	535	471	4	6	4	248	241	4	8	4	731	741	-15	11	4	258	275	11	13	4	228	220
10	4	4	210	218	6	6	4	240	251	6	8	4	817	827	-13	11	4	348	325	13	13	4	287	288
12	4	4	794	811	8	6	4	674	678	8	8	4	432	434	-11	11	4	297	314	15	13	4	344	321
14	4	4	377	366	10	6	4	492	431	12	8	4	490	551	-9	11	4	243	260	-16	14	4	230	257
18	4	4	248	235	12	6	4	191	185	14	8	4	617	599	-7	11	4	273	264	-14	14	4	271	244
20	4	4	224	216	16	6	4	316	282	20	8	4	291	232	-5	11	4	640	622	-12	14	4	277	268
-23	5	4	216	160	18	6	4	282	344	-15	9	4	352	363	-3	11	4	312	299	-6	14	4	242	155
-21	5	4	198	208	-23	7	4	222	195	-13	9	4	547	597	-1	11	4	419	437	-4	14	4	271	291
-19	5	4	230	190	-19	7	4	245	202	-11	9	4	431	425	1	11	4	436	378	0	14	4	352	388
-17	5	4	318	291	-17	7	4	588	573	-9	9	4	611	589	3	11	4	605	609	2	14	4	494	518
-15	5	4	548	559	-15	7	4	902	901	-7	9	4	503	449	5	11	4	515	510	4	14	4	220	171
-13	5	4	246	220	-13	7	4	394	375	-5	9	4	415	418	7	11	4	411	436	6	14	4	274	205
-11	5	4	154	92	-11	7	4	383	368	-3	9	4	611	678	9	11	4	674	680	8	14	4	442	506
-9	5	4	397	463	-9	7	4	891	863	-1	9	4	445	463	11	11	4	435	479	10	14	4	291	282
-7	5	4	857	770	-7	7	4	914	867	1	9	4	163	247	-18	12	4	235	209	-7	15	4	298	277
-5	5	4	748	780	-5	7	4	925	1053	3	9	4	583	615	-12	12	4	246	269	-5	15	4	250	222
-3	5	4	577	652	-3	7	4	340	346	5	9	4	834	824	-8	12	4	344	353	-6	16	4	226	213
-1	5	4	564	578	-1	7	4	492	517	7	9	4	281	259	-6	12	4	366	424	0	16	4	254	289
1	5	4	628	624	1	7	4	379	432	9	9	4	179	192	-4	12	4	448	458	2	16	4	247	243
5	5	4	1228	1300	3	7	4	569	575	11	9	4	256	325	-2	12	4	394	384	-11	17	4	281	290
7	5	4	1160	1209	5	7	4	259	281	13	9	4	500	492	0	12	4	219	202	-9	17	4	223	243
9	5	4	708	639	7	7	4	874	822	-16	10	4	404	392	2	12	4	317	272	-5	17	4	247	243
11	5	4	233	187	9	7	4	623	638	-14	10	4	640	646	4	12	4	264	258	-3	17	4	328	372
13	5	4	235	236	11	7	4	674	690	-12	10	4	445	455	6	12	4	211	217	-1	17	4	228	275
15	5	4	414	350	13	7	4	335	324	-10	10	4	339	370	-19	13	4	263	235	3	17	4	216	225
17	5	4	279	260	15	7	4	183	176	-8	10	4	960	924	-17	13	4	251	274	5	17	4	417	416
-16	6	4	487	459	-18	8	4	257	309	-6	10	4	908	908	-11	13	4	342	437	7	17	4	315	234
-14	6	4	553	562	-16	8	4	547	494	-4	10	4	331	396	-9	13	4	429	444	-8	18	4	258	225
-12	6	4	338	332	-12	8	4	498	528	-2	10	4	188	222	-7	13	4	367	302	0	18	4	295	203
-10	6	4	315	352	-10	8	4	811	769	0	10	4	496	481	-5	13	4	229	286	-21	1	5	284	241
-8	6	4	583	628	-8	8	4	487	521	2	10	4	628	627	-3	13	4	611	551	-19	1	5	367	340
-6	6	4	452	406	-6	8	4	415	387	4	10	4	600	604	-1	13	4	499	466	-17	1	5	507	495
-4	6	4	444	474	-4	8	4	680	691	6	10	4	219	263	1	13	4	291	254	-15	1	5	175	255

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.2

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-13	1	5	1154	1120	-17	3	5	568	550	-17	5	5	264	249	16	6	5	524	465	-15	9	5	332	365
-11	1	5	1125	1154	-15	3	5	512	542	-15	5	5	368	358	18	6	5	246	250	-13	9	5	422	443
-9	1	5	982	990	-13	3	5	760	746	-13	5	5	737	790	-17	7	5	283	225	-11	9	5	379	404
-7	1	5	783	771	-11	3	5	1028	1049	-11	5	5	794	813	-15	7	5	478	473	-9	9	5	336	326
-5	1	5	1371	1366	-9	3	5	925	899	-9	5	5	640	690	-13	7	5	232	235	-5	9	5	403	392
-3	1	5	885	888	-7	3	5	1468	1486	-7	5	5	394	363	-11	7	5	242	280	-3	9	5	469	478
-1	1	5	805	833	-5	3	5	731	717	-5	5	5	308	339	-9	7	5	440	482	-1	9	5	528	506
1	1	5	126	271	-3	3	5	657	705	-3	5	5	748	786	-7	7	5	304	306	1	9	5	583	578
3	1	5	1502	1511	-1	3	5	385	462	-1	5	5	811	893	-5	7	5	571	610	3	9	5	942	936
5	1	5	937	905	1	3	5	299	298	1	5	5	388	437	-3	7	5	254	264	5	9	5	748	775
7	1	5	468	458	3	3	5	1154	1194	3	5	5	691	710	-1	7	5	754	763	7	9	5	538	588
11	1	5	651	690	5	3	5	948	999	5	5	5	874	938	1	7	5	583	577	9	9	5	252	186
13	1	5	891	851	7	3	5	942	1004	7	5	5	284	316	3	7	5	611	620	11	9	5	183	176
21	1	5	310	301	9	3	5	422	422	9	5	5	495	458	5	7	5	588	557	13	9	5	427	498
-24	2	5	207	258	11	3	5	449	453	11	5	5	458	458	7	7	5	386	403	15	9	5	214	238
-22	2	5	261	292	13	3	5	524	526	13	5	5	410	401	9	7	5	524	535	-18	10	5	199	179
-18	2	5	313	315	15	3	5	486	423	15	5	5	335	330	11	7	5	490	457	-16	10	5	247	226
-16	2	5	714	709	-20	4	5	334	293	19	5	5	214	169	17	7	5	233	289	-12	10	5	180	230
-14	2	5	657	640	-18	4	5	246	119	-22	6	5	246	300	19	7	5	276	232	-10	10	5	383	428
-12	2	5	160	83	-16	4	5	219	282	-20	6	5	276	271	-18	8	5	318	327	-8	10	5	605	593
-10	2	5	567	594	-12	4	5	483	471	-18	6	5	279	290	-16	8	5	354	378	-6	10	5	605	648
-8	2	5	1474	1386	-10	4	5	466	501	-16	6	5	1057	1100	-14	8	5	282	276	-4	10	5	440	459
-6	2	5	1656	1650	-8	4	5	355	384	-14	6	5	645	652	-12	8	5	300	306	-2	10	5	600	596
-4	2	5	386	338	-6	4	5	691	734	-12	6	5	691	734	-10	8	5	628	616	0	10	5	505	441
-2	2	5	823	801	-4	4	5	183	138	-10	6	5	430	441	-8	8	5	244	253	2	10	5	583	621
0	2	5	1125	1127	-2	4	5	495	544	-8	6	5	1022	1075	-6	8	5	805	752	6	10	5	384	354
2	2	5	2171	2107	0	4	5	188	219	-6	6	5	885	906	-4	8	5	651	605	8	10	5	427	372
4	2	5	563	546	2	4	5	227	238	-4	6	5	335	251	-2	8	5	385	366	12	10	5	244	233
6	2	5	931	957	4	4	5	413	385	-2	6	5	385	325	0	8	5	511	505	-17	11	5	252	269
8	2	5	1291	1317	6	4	5	332	417	0	6	5	657	692	2	8	5	230	265	-15	11	5	343	414
10	2	5	668	686	8	4	5	464	466	2	6	5	617	642	4	8	5	811	803	-13	11	5	332	327
12	2	5	402	375	10	4	5	319	331	4	6	5	600	632	6	8	5	720	753	-9	11	5	378	433
14	2	5	244	249	14	4	5	228	242	6	6	5	777.	757	8	8	5	657	703	-7	11	5	645	630
16	2	5	415	431	16	4	5	197	128	8	6	5	737	733	12	8	5	478	480	-5	11	5	503	522
18	2	5	209	255	-21	5	5	358	368	10	6	5	891	863	-19	9	5	355	304	-3	11	5	304	313
-19	3	5	492	424	-19	5	5	390	410	14	6	5	282	318	-17	9	5	326	355	-1	11	5	460	431

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.2

H	K	L	10FO	10FC
1	11	5	605	642
3	11	5	298	362
7	11	5	395	434
9	11	5	332	312
-14	12	5	256	229
-12	12	5	367	357
-10	12	5	244	203
-6	12	5	383	431
-4	12	5	552	498
-2	12	5	460	479
2	12	5	232	228
4	12	5	588	596
6	12	5	296	270
8	12	5	203	195
12	12	5	209	144
14	12	5	219	137
-13	13	5	277	302
-11	13	5	251	252
-9	13	5	212	303
-5	13	5	223	239
-3	13	5	252	274
-1	13	5	223	228
7	13	5	231	287
9	13	5	229	230
-14	14	5	225	216
-12	14	5	251	302
-10	14	5	239	197
-6	14	5	213	169
0	14	5	289	261
2	14	5	319	310
-15	15	5	282	285
-9	15	5	261	257
-7	15	5	399	308
-5	15	5	225	208
-3	15	5	307	287
-1	15	5	471	494
1	15	5	495	556
7	15	5	328	366
9	15	5	283	282
-4	16	5	215	160
-2	16	5	270	268
4	16	5	382	357
6	16	5	262	275
-4	18	5	244	168
-2	18	5	200	202
-20	0	6	600	545
-18	0	6	405	367
-16	0	6	507	488
-14	0	6	651	612
-12	0	6	507	516
-10	0	6	948	955
-8	0	6	428	421
-6	0	6	1468	1413
-4	0	6	1491	1425
-2	0	6	1794	1846
0	0	6	965	940
2	0	6	1160	1151
4	0	6	708	748
6	0	6	1451	1413
10	0	6	494	523
12	0	6	971	908
14	0	6	324	367
18	0	6	231	227
20	0	6	439	377
-21	1	6	194	246
-17	1	6	304	358
-15	1	6	569	596
-13	1	6	379	393
-9	1	6	925	880
-7	1	6	931	908
-5	1	6	309	300
-3	1	6	783	761
-1	1	6	1217	1256
1	1	6	1445	1415
3	1	6	434	465
7	1	6	840	800
9	1	6	320	336
11	1	6	379	372
15	1	6	239	268
17	1	6	282	260
-18	2	6	339	376
-16	2	6	338	408
-14	2	6	354	363
-12	2	6	176	151
-10	2	6	335	344
-8	2	6	487	441
-6	2	6	350	381
-4	2	6	360	343
-2	2	6	325	322
0	2	6	628	653
2	2	6	531	503
4	2	6	552	614
6	2	6	241	210
8	2	6	367	379
12	2	6	437	402
14	2	6	311	257
-25	3	6	238	192
-23	3	6	326	316
-17	3	6	570	591
-15	3	6	500	521
-13	3	6	416	455
-11	3	6	257	226
-9	3	6	383	426
-7	3	6	805	825
-5	3	6	605	595
-3	3	6	400	368
-1	3	6	851	815
1	3	6	657	720
3	3	6	1194	1193
5	3	6	645	621
7	3	6	743	789
9	3	6	863	891
11	3	6	448	420
15	3	6	432	426
17	3	6	262	288
-22	4	6	316	344
-20	4	6	538	520
-18	4	6	354	339
-16	4	6	199	228
-14	4	6	914	948
-12	4	6	1171	1187
-10	4	6	714	751
-8	4	6	362	362
-6	4	6	708	745
-4	4	6	1040	1133
-2	4	6	524	554
0	4	6	378	363
2	4	6	1051	1028
4	4	6	771	856
8	4	6	490	522
10	4	6	556	613
12	4	6	491	504
14	4	6	229	209
18	4	6	281	287
20	4	6	251	239
-23	5	6	306	270
-21	5	6	255	220
-17	5	6	651	644
-15	5	6	393	398
-13	5	6	290	319
-11	5	6	369	343
-9	5	6	794	816
-7	5	6	720	759
-5	5	6	212	220
-3	5	6	691	715
-1	5	6	354	370
1	5	6	384	365
5	5	6	600	621
7	5	6	897	895
9	5	6	525	545
11	5	6	406	396
13	5	6	352	368
15	5	6	350	311
-20	6	6	323	322
-16	6	6	211	200
-14	6	6	190	190
-12	6	6	316	297
-10	6	6	350	330
-8	6	6	169	181
-6	6	6	199	190
-4	6	6	368	392
-2	6	6	506	528
0	6	6	472	501
2	6	6	645	645
4	6	6	452	439
6	6	6	559	525
8	6	6	685	713
10	6	6	344	372
12	6	6	320	325
-23	7	6	210	168
-19	7	6	330	389
-17	7	6	685	723
-15	7	6	218	258
-13	7	6	190	160
-11	7	6	501	527
-9	7	6	559	593
-7	7	6	897	923
-5	7	6	531	515
-1	7	6	851	880
1	7	6	760	784

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.2

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
3	7	6	668	663	9	9	6	184	225	-11	13	6	375	367	13	1	7	226	301	5	3	7	396	446
5	7	6	691	674	11	9	6	434	441	-9	13	6	319	372	15	1	7	205	214	7	3	7	306	299
7	7	6	525	551	-18	10	6	243	240	-5	13	6	199	209	17	1	7	249	243	11	3	7	417	372
9	7	6	375	405	-16	10	6	408	487	-3	13	6	368	343	19	1	7	310	275	13	3	7	375	339
11	7	6	191	203	-14	10	6	284	265	-1	13	6	326	305	-24	2	7	302	311	-22	4	7	228	219
13	7	6	332	325	-10	10	6	417	433	3	13	6	419	447	-20	2	7	188	86	-18	4	7	200	215
15	7	6	358	322	-8	10	6	336	258	5	13	6	330	358	-18	2	7	403	406	-14	4	7	487	419
17	7	6	304	331	-6	10	6	317	340	-8	14	6	284	332	-16	2	7	668	689	-12	4	7	343	321
-20	8	6	251	265	-4	10	6	299	289	-6	14	6	247	211	-14	2	7	259	207	-10	4	7	520	569
-18	8	6	300	258	-2	10	6	697	617	-4	14	6	283	254	-12	2	7	229	262	-8	4	7	231	255
-12	8	6	427	417	0	10	6	754	765	-2	14	6	315	335	-10	2	7	680	679	-6	4	7	605	643
-10	8	6	482	467	2	10	6	547	602	0	14	6	394	421	-8	2	7	1034	1089	-4	4	7	526	549
-8	8	6	235	232	4	10	6	310	311	2	14	6	276	226	-6	2	7	535	535	-2	4	7	407	455
-6	8	6	697	710	6	10	6	500	512	8	14	6	238	231	-4	2	7	657	648	0	4	7	251	250
-4	8	6	640	600	8	10	6	309	306	-6	16	6	207	177	-2	2	7	1508	1567	2	4	7	550	565
-2	8	6	691	692	-15	11	6	261	233	-7	17	6	291	253	0	2	7	1011	1043	4	4	7	458	493
0	8	6	270	261	-11	11	6	344	334	-5	17	6	328	303	2	2	7	634	659	8	4	7	388	394
2	8	6	490	522	-9	11	6	226	278	-3	17	6	288	313	6	2	7	982	992	10	4	7	345	334
4	8	6	908	849	-7	11	6	337	337	3	17	6	351	363	8	2	7	714	734	12	4	7	419	394
6	8	6	331	355	-5	11	6	372	425	-21	1	7	417	442	10	2	7	545	548	18	4	7	255	185
10	8	6	334	385	-1	11	6	202	219	-19	1	7	294	338	14	2	7	518	514	-23	5	7	190	177
12	8	6	286	313	1	11	6	370	390	-17	1	7	588	542	16	2	7	462	465	-21	5	7	287	297
14	8	6	218	256	3	11	6	412	426	-15	1	7	422	471	18	2	7	226	210	-19	5	7	278	325
-21	9	6	196	192	5	11	6	236	305	-13	1	7	765	727	-21	3	7	327	272	-13	5	7	377	404
-19	9	6	194	210	7	11	6	266	281	-11	1	7	714	767	-19	3	7	309	295	-11	5	7	777	755
-15	9	6	296	287	-14	12	6	236	232	-9	1	7	402	404	-17	3	7	367	371	-7	5	7	286	269
-13	9	6	498	518	-8	12	6	214	277	-7	1	7	1148	1164	-15	3	7	216	219	-5	5	7	1085	1076
-11	9	6	605	574	-6	12	6	184	209	-5	1	7	1102	1160	-13	3	7	271	301	-3	5	7	788	763
-7	9	6	478	530	-2	12	6	235	203	-3	1	7	1114	1133	-11	3	7	547	519	-1	5	7	640	614
-5	9	6	994	976	0	12	6	258	291	-1	1	7	411	389	-9	3	7	617	642	1	5	7	511	521
-3	9	6	668	717	2	12	6	200	190	1	1	7	617	621	-7	3	7	473	469	3	5	7	851	807
-1	9	6	189	148	4	12	6	250	317	3	1	7	737	732	-5	3	7	788	742	5	5	7	424	408
1	9	6	674	692	6	12	6	216	202	5	1	7	657	711	-3	3	7	777	762	7	5	7	368	344
3	9	6	805	827	8	12	6	264	238	7	1	7	267	265	-1	3	7	691	743	9	5	7	312	323
5	9	6	490	544	12	12	6	212	229	9	1	7	514	510	1	3	7	765	734	11	5	7	521	516
7	9	6	233	280	-13	13	6	337	281	11	1	7	605	657	3	3	7	544	523	13	5	7	384	341

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.2

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
17	5	7	211	214	-2	8	7	256	260	-15	11	7	282	290	2	16	7	283	276	13	1	8	419	379
-18	6	7	478	530	0	8	7	436	438	-13	11	7	253	217	4	16	7	219	232	15	1	8	350	310
-16	6	7	355	328	2	8	7	754	753	-11	11	7	219	234	-22	0	8	444	436	-18	2	8	244	296
-14	6	7	192	282	4	8	7	544	523	-9	11	7	253	253	-20	0	8	462	416	-16	2	8	191	140
-12	6	7	366	371	6	8	7	293	302	-7	11	7	172	162	-16	0	8	215	146	-14	2	8	270	249
-10	6	7	546	531	10	8	7	290	262	-3	11	7	253	264	-14	0	8	216	289	-12	2	8	283	186
-8	6	7	788	853	12	8	7	239	248	-1	11	7	550	587	-12	0	8	634	650	-10	2	8	232	233
-6	6	7	472	504	-21	9	7	258	276	1	11	7	317	306	-10	0	8	561	483	-8	2	8	158	186
-4	6	7	267	247	-13	9	7	246	235	5	11	7	215	238	-8	0	8	708	678	-6	2	8	312	263
-2	6	7	845	829	-11	9	7	283	289	7	11	7	359	386	-6	0	8	628	685	-4	2	8	319	303
0	6	7	925	889	-9	9	7	222	234	9	11	7	224	268	-4	0	8	1291	1335	-2	2	8	600	617
2	6	7	611	598	-7	9	7	427	439	-16	12	7	246	177	-2	0	8	634	601	0	2	8	278	247
4	6	7	311	299	-5	9	7	516	525	-14	12	7	299	324	0	0	8	311	331	2	2	8	200	263
6	6	7	187	256	-3	9	7	868	854	-12	12	7	394	472	2	0	8	351	445	10	2	8	212	186
8	6	7	376	415	-1	9	7	651	663	-10	12	7	206	204	4	0	8	994	951	-19	3	8	319	319
10	6	7	354	393	1	9	7	708	751	-8	12	7	325	329	6	0	8	170	212	-17	3	8	521	581
14	6	7	211	254	3	9	7	663	693	-6	12	7	600	678	8	0	8	298	317	-15	3	8	546	592
16	6	7	346	311	5	9	7	362	358	-4	12	7	435	462	10	0	8	540	511	-13	3	8	218	171
-13	7	7	372	376	9	9	7	218	272	-2	12	7	309	266	12	0	8	308	320	-11	3	8	400	376
-11	7	7	506	553	11	9	7	206	258	0	12	7	224	190	14	0	8	288	220	-9	3	8	374	397
-7	7	7	480	470	13	9	7	198	206	2	12	7	459	443	18	0	8	238	291	-7	3	8	657	645
-5	7	7	294	265	-18	10	7	210	124	4	12	7	340	360	-19	1	8	267	236	-5	3	8	238	242
-3	7	7	454	479	-16	10	7	254	278	10	12	7	283	244	-17	1	8	344	316	-3	3	8	408	468
-1	7	7	366	296	-14	10	7	215	110	12	12	7	222	250	-15	1	8	318	294	-1	3	8	547	533
1	7	7	467	438	-12	10	7	212	224	-7	13	7	214	197	-13	1	8	211	282	1	3	8	348	336
3	7	7	541	521	-10	10	7	311	298	-5	13	7	303	252	-11	1	8	411	455	3	3	8	285	283
5	7	7	261	277	-8	10	7	412	373	1	13	7	195	182	-9	1	8	640	605	5	3	8	343	321
7	7	7	301	277	-6	10	7	180	193	-10	14	7	212	174	-7	1	8	327	299	7	3	8	395	431
9	7	7	445	449	-4	10	7	325	345	2	14	7	247	186	-5	1	8	259	312	9	3	8	331	321
-22	8	7	251	223	-2	10	7	499	462	6	14	7	204	153	-3	1	8	1194	1194	13	3	8	308	293
-20	8	7	266	305	0	10	7	425	434	-11	15	7	228	220	-1	1	8	1005	988	15	3	8	326	400
-12	8	7	320	261	4	10	7	227	216	-9	15	7	380	354	1	1	8	355	361	17	3	8	207	214
-10	8	7	260	215	6	10	7	390	446	-7	15	7	282	231	3	1	8	188	181	-22	4	8	301	338
-8	8	7	403	401	8	10	7	289	335	-1	15	7	422	370	5	1	8	605	628	-20	4	8	350	376
-6	8	7	208	142	10	10	7	223	202	1	15	7	225	229	7	1	8	457	475	-16	4	8	231	231
-4	8	7	477	448	-17	11	7	277	288	7	15	7	246	227	9	1	8	270	278	-14	4	8	505	479

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.2

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-12	4	8	565	558	0	6	8	421	472	-5	9	8	480	418	-23	1	9	309	331	-19	3	9	240	285
-8	4	8	536	545	2	6	8	484	401	-3	9	8	411	402	-21	1	9	346	338	-17	3	9	263	239
-6	4	8	1279	1299	6	6	8	358	353	-1	9	8	214	222	-17	1	9	311	285	-11	3	9	600	573
-4	4	8	868	868	8	6	8	275	278	1	9	8	384	403	-15	1	9	291	269	-9	3	9	207	217
-2	4	8	281	243	-19	7	8	219	159	3	9	8	466	454	-13	1	9	551	537	-7	3	9	213	205
0	4	8	748	727	-17	7	8	280	223	7	9	8	259	201	-11	1	9	394	374	-5	3	9	663	640
2	4	8	1040	1023	-15	7	8	256	223	9	9	8	308	299	-9	1	9	657	664	-3	3	9	680	655
4	4	8	515	561	-13	7	8	338	315	-18	10	8	232	183	-7	1	9	914	876	-1	3	9	462	444
6	4	8	342	294	-11	7	8	521	486	-16	10	8	208	161	-5	1	9	897	941	1	3	9	577	625
8	4	8	196	270	-9	7	8	908	946	-12	10	8	386	413	-3	1	9	496	484	3	3	9	512	510
10	4	8	628	643	-7	7	8	594	625	-10	10	8	274	396	-1	1	9	583	535	7	3	9	315	294
12	4	8	513	534	-5	7	8	640	621	-8	10	8	380	350	1	1	9	486	489	9	3	9	362	352
16	4	8	219	206	-3	7	8	971	1005	-4	10	8	339	347	3	1	9	663	646	11	3	9	374	348
-19	5	8	384	417	-1	7	8	977	972	-2	10	8	502	498	5	1	9	268	293	-16	4	9	192	230
-17	5	8	348	383	1	7	8	680	644	0	10	8	399	387	7	1	9	277	296	-12	4	9	203	213
-13	5	8	246	217	3	7	8	203	175	6	10	8	318	289	9	1	9	475	466	-8	4	9	311	284
-11	5	8	548	561	5	7	8	351	404	8	10	8	332	331	11	1	9	231	269	-6	4	9	399	376
-9	5	8	760	783	7	7	8	583	626	-9	11	8	236	180	13	1	9	202	194	-4	4	9	480	500
-7	5	8	332	369	9	7	8	301	316	-5	11	8	237	240	-20	2	9	220	219	-2	4	9	204	226
-3	5	8	506	536	11	7	8	300	338	1	11	8	270	308	-18	2	9	499	511	2	4	9	533	511
-1	5	8	446	431	13	7	8	281	293	-10	12	8	248	190	-16	2	9	392	372	6	4	9	197	224
1	5	8	329	310	15	7	8	220	243	-2	12	8	222	246	-14	2	9	182	151	10	4	9	288	275
3	5	8	287	276	-20	8	8	262	241	0	12	8	218	259	-12	2	9	385	372	12	4	9	204	172
5	5	8	192	185	-14	8	8	300	302	2	12	8	219	231	-10	2	9	828	793	-15	5	9	271	246
7	5	8	288	212	-12	8	8	470	461	4	12	8	276	236	-8	2	9	663	655	-13	5	9	386	428
9	5	8	259	272	-8	8	8	202	245	6	12	8	224	249	-6	2	9	407	435	-11	5	9	221	260
11	5	8	402	419	-6	8	8	494	454	-11	13	8	265	275	-4	2	9	737	794	-9	5	9	302	261
13	5	8	243	279	-4	8	8	617	599	-5	13	8	302	291	-2	2	9	914	934	-7	5	9	731	745
-16	6	8	214	194	-2	8	8	471	522	-3	13	8	276	280	0	2	9	605	584	-5	5	9	416	425
-14	6	8	243	241	0	8	8	322	284	3	13	8	271	311	2	2	9	179	140	-3	5	9	422	444
-12	6	8	276	256	2	8	8	378	310	5	13	8	285	316	4	2	9	539	522	-1	5	9	338	349
-10	6	8	496	453	8	8	8	214	214	-10	14	8	252	257	6	2	9	645	621	1	5	9	577	602
-8	6	8	567	533	10	8	8	233	240	-8	14	8	244	274	8	2	9	279	288	3	5	9	362	343
-6	6	8	537	510	-15	9	8	344	357	-2	14	8	386	356	12	2	9	462	462	5	5	9	215	141
-4	6	8	571	526	-13	9	8	475	447	0	14	8	272	257	14	2	9	426	404	9	5	9	326	303
-2	6	8	623	676	-7	9	8	463	452	-1	15	8	314	256	16	2	9	330	309	11	5	9	322	277

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.2

H	K	L	10FO	10FC
-18	6	9	271	227
-16	6	9	273	331
-12	6	9	302	325
-10	6	9	411	439
-8	6	9	600	601
-6	6	9	210	162
-4	6	9	564	535
-2	6	9	451	409
0	6	9	480	481
2	6	9	234	240
4	6	9	218	193
6	6	9	474	455
12	6	9	228	238
14	6	9	294	276
-21	7	9	228	186
-19	7	9	216	179
-15	7	9	253	298
-13	7	9	324	291
-9	7	9	217	224
-7	7	9	432	465
-5	7	9	396	406
-1	7	9	634	622
1	7	9	418	378
5	7	9	300	266
7	7	9	308	310
-14	8	9	264	276
-8	8	9	251	309
-6	8	9	219	246
-4	8	9	374	454
-2	8	9	217	249
0	8	9	231	267
8	8	9	200	242
10	8	9	187	157
12	8	9	218	230
-15	9	9	264	244
-13	9	9	444	452
-11	9	9	271	281
-9	9	9	244	173
-7	9	9	340	326
-5	9	9	273	302
-3	9	9	467	480
-1	9	9	277	258
1	9	9	212	235
3	9	9	298	262
5	9	9	259	304
9	9	9	336	323
11	9	9	215	218
-18	10	9	218	197
-10	10	9	354	291
-8	10	9	229	210
-6	10	9	223	213
-4	10	9	420	386
-2	10	9	510	556
0	10	9	240	230
4	10	9	263	265
6	10	9	272	294
-17	11	9	205	222
-11	11	9	399	433
-9	11	9	319	323
-3	11	9	361	398
-1	11	9	384	419
5	11	9	286	287
7	11	9	244	288
-14	12	9	235	171
-8	12	9	424	400
-6	12	9	474	476
-4	12	9	294	340
0	12	9	251	251
2	12	9	308	327
4	12	9	230	215
8	12	9	274	243
-5	13	9	307	290
-8	14	9	311	243
-6	14	9	248	218
2	14	9	273	257
4	14	9	239	235
-3	15	9	264	249
-22	0	10	264	261
-20	0	10	333	298
-18	0	10	351	360
-16	0	10	294	248
-14	0	10	284	294
-12	0	10	234	209
-10	0	10	503	542
-8	0	10	493	568
-6	0	10	737	762
-2	0	10	473	473
0	0	10	530	579
2	0	10	691	715
6	0	10	186	244
8	0	10	506	508
14	0	10	213	127
-19	1	10	217	207
-17	1	10	338	268
-13	1	10	311	329
-11	1	10	513	528
-7	1	10	194	255
-5	1	10	506	494
-3	1	10	391	374
-1	1	10	320	333
1	1	10	306	306
3	1	10	278	338
5	1	10	354	365
7	1	10	295	327
-12	2	10	186	291
-6	2	10	393	389
-4	2	10	280	308
-2	2	10	187	198
0	2	10	382	384
2	2	10	186	196
4	2	10	193	177
-19	3	10	254	228
-17	3	10	270	285
-13	3	10	244	268
-11	3	10	290	308
-9	3	10	432	437
-3	3	10	408	437
-1	3	10	445	406
5	3	10	399	387
7	3	10	188	220
11	3	10	333	268
13	3	10	276	252
-22	4	10	223	230
-16	4	10	475	450
-14	4	10	674	667
-12	4	10	461	476
-10	4	10	387	391
-8	4	10	754	731
-6	4	10	657	614
-4	4	10	466	461
-2	4	10	245	227
0	4	10	765	763
2	4	10	891	859
4	4	10	345	327
8	4	10	491	447
10	4	10	488	499
-19	5	10	219	233
-17	5	10	253	221
-9	5	10	484	468
-7	5	10	218	223
-5	5	10	338	357
-3	5	10	371	422
-1	5	10	200	236
3	5	10	212	232
5	5	10	418	413
7	5	10	219	166
13	5	10	220	157
-20	6	10	196	178
-12	6	10	299	336
-10	6	10	251	206
-8	6	10	394	385
-6	6	10	252	275
-4	6	10	371	343
-2	6	10	327	267
2	6	10	313	352
4	6	10	337	304
6	6	10	322	346
10	6	10	213	236
-17	7	10	407	406
-15	7	10	190	213
-13	7	10	334	339
-11	7	10	532	507
-9	7	10	494	513
-7	7	10	364	387
-5	7	10	628	618
-3	7	10	551	506
-1	7	10	406	348
3	7	10	227	265
5	7	10	645	617
7	7	10	391	417
-16	8	10	310	281
-14	8	10	331	278
-8	8	10	311	314
-6	8	10	280	320
-2	8	10	231	280
0	8	10	231	282
10	8	10	260	237
-15	9	10	311	259
-13	9	10	232	219
-9	9	10	349	384

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.2

H	K	L	10FO	10FC
-7	9	10	444	409
-5	9	10	281	266
-1	9	10	368	304
1	9	10	315	313
3	9	10	262	226
-12	10	10	405	375
-2	10	10	372	348
4	10	10	267	248
6	10	10	230	233
3	11	10	187	119
-12	12	10	274	235
2	12	10	275	199
-7	13	10	241	265
-5	13	10	286	239
1	13	10	208	233
-17	1	11	442	331
-15	1	11	342	342
-13	1	11	476	485
-11	1	11	403	406
-9	1	11	454	428
-7	1	11	663	601
-5	1	11	261	225
-3	1	11	302	291
-1	1	11	307	353
1	1	11	493	489
3	1	11	280	288
7	1	11	290	320
-20	2	11	300	277
-18	2	11	348	317
-14	2	11	475	446
-12	2	11	561	532
-10	2	11	453	399
-8	2	11	207	228
-6	2	11	316	333
-4	2	11	600	595
-2	2	11	530	544
2	2	11	302	336
4	2	11	527	515
6	2	11	430	463
10	2	11	239	186
12	2	11	239	247
-15	3	11	277	272
-13	3	11	281	262
-5	3	11	252	276
-1	3	11	336	382
1	3	11	393	373
3	3	11	228	257
7	3	11	251	208
-16	4	11	238	218
-14	4	11	347	321
-10	4	11	388	365
-8	4	11	350	307
-6	4	11	542	520
-4	4	11	207	201
-2	4	11	295	244
8	4	11	218	239
-17	5	11	274	255
-15	5	11	265	300
-13	5	11	189	226
-9	5	11	299	337
-7	5	11	230	195
-5	5	11	238	296
-1	5	11	301	321
1	5	11	403	406
3	5	11	323	259
7	5	11	251	243
9	5	11	366	335
-18	6	11	292	232
-12	6	11	254	280
-10	6	11	356	402
-6	6	11	361	349
-4	6	11	412	494
-2	6	11	280	239
2	6	11	231	301
4	6	11	628	602
6	6	11	259	285
-15	7	11	231	229
-7	7	11	337	337
-1	7	11	202	188
1	7	11	212	227
3	7	11	193	214
5	7	11	263	225
-8	8	11	294	234
-2	8	11	228	220
0	8	11	300	332
2	8	11	312	276
6	8	11	272	255
-15	9	11	242	216
-13	9	11	253	257
-7	9	11	250	299
-1	9	11	256	207
1	9	11	379	382
3	9	11	303	278
-12	10	11	246	186
-10	10	11	240	228
-4	10	11	227	210
-2	10	11	235	223
4	10	11	218	195
-13	11	11	251	259
-9	11	11	268	206
-3	11	11	338	339
-1	11	11	237	195
-10	12	11	308	261
-8	12	11	434	379
-6	12	11	330	344
0	12	11	210	202
2	12	11	232	243
-7	13	11	202	171
-18	0	12	319	320
-16	0	12	328	310
-12	0	12	239	280
-10	0	12	270	327
-8	0	12	391	417
-6	0	12	302	282
-4	0	12	292	249
-2	0	12	412	421
0	0	12	463	433
2	0	12	207	208
6	0	12	263	281
8	0	12	318	342
10	0	12	258	229
-15	1	12	265	197
-13	1	12	346	318
-7	1	12	247	230
-5	1	12	292	289
-3	1	12	248	264
1	1	12	330	332
3	1	12	250	282
5	1	12	338	364
-14	2	12	228	213
-4	2	12	272	279
-15	3	12	285	307
-13	3	12	307	289
-11	3	12	298	289
-7	3	12	240	194
-5	3	12	414	355
-3	3	12	362	309
-1	3	12	219	196
1	3	12	215	161
3	3	12	384	351
5	3	12	365	354
7	3	12	206	200
-18	4	12	216	221
-16	4	12	440	450
-14	4	12	408	468
-8	4	12	312	275
-6	4	12	523	489
-4	4	12	309	275
-2	4	12	302	283
0	4	12	380	385
2	4	12	404	369
6	4	12	312	301
8	4	12	356	351
-13	5	12	278	280
-11	5	12	198	196
-7	5	12	292	283
-5	5	12	274	292
-3	5	12	362	362
3	5	12	358	331
5	5	12	264	248
-14	6	12	222	214
-6	6	12	243	220
-4	6	12	268	293
-2	6	12	212	188
0	6	12	243	200
2	6	12	262	279
4	6	12	277	275
6	6	12	243	242
-13	7	12	280	241
-11	7	12	354	345
-9	7	12	371	338
-7	7	12	193	161
-5	7	12	231	241
-3	7	12	251	186
-1	7	12	272	248
3	7	12	249	320
5	7	12	323	303
-16	8	12	206	142
-10	8	12	282	283
-8	8	12	251	228

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.2

H	K	L	10FO	10FC
-6	8	12	252	231
0	8	12	255	283
-9	9	12	340	267
1	9	12	280	263
-4	10	12	328	312
2	10	12	213	193
-17	1	13	340	319
-15	1	13	227	233
-9	1	13	310	321
-7	1	13	216	175
-1	1	13	334	353
1	1	13	261	269
5	1	13	234	222
7	1	13	277	251
-14	2	13	334	287
-12	2	13	242	183
-6	2	13	343	323
-4	2	13	392	361
-2	2	13	227	216
2	2	13	360	309
4	2	13	434	413
-17	3	13	204	190
-13	3	13	219	194
-11	3	13	296	319
-3	3	13	203	215
-1	3	13	248	225
-8	4	13	224	242
-2	4	13	225	216
-9	5	13	246	201
-7	5	13	290	296
-5	5	13	246	205
-3	5	13	271	214
1	5	13	282	276
-14	6	13	222	262
-12	6	13	328	292
-4	6	13	354	263
2	6	13	254	241
-11	7	13	212	174
-5	7	13	288	206
-4	8	13	239	251
-1	9	13	235	258
-12	0	14	221	203
-10	0	14	455	473
-2	0	14	363	336
0	0	14	259	264
3	1	14	244	227
-8	2	14	224	204
-6	2	14	212	200
-7	3	14	308	306
-5	3	14	275	319
-3	3	14	239	222
1	3	14	229	203
-10	4	14	320	240
-8	4	14	340	261
-4	4	14	298	233
-2	4	14	333	290
0	4	14	334	322
-11	5	14	207	131
-6	6	14	266	186
-5	7	14	237	203
-6	2	15	351	285

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.3

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
2	2	0	4381	4456	12	12	0	341	227	5	21	0	352	431	7	8	1	1773	1707	4	15	1	677	604
1	3	0	1311	1293	1	13	0	1773	1778	7	21	0	730	720	2	9	1	1685	1668	8	15	1	616	671
0	4	0	5487	5191	3	13	0	1099	1117	9	21	0	459	302	4	9	1	769	767	12	15	1	679	738
2	4	0	3677	3388	5	13	0	1135	1135	11	21	0	488	480	6	9	1	1135	972	14	15	1	364	438
4	4	0	1487	1477	9	13	0	1685	1681	13	21	0	506	547	8	9	1	669	750	1	16	1	1934	1599
1	5	0	1377	1477	11	13	0	289	264	15	21	0	313	288	1	10	1	302	550	3	16	1	850	716
3	5	0	1516	1447	0	14	0	1150	1265	2	22	0	695	792	3	10	1	930	834	5	16	1	361	501
0	6	0	1531	1487	2	14	0	762	849	4	22	0	518	562	5	10	1	1736	1564	11	16	1	539	466
2	6	0	2315	2072	4	14	0	676	761	6	22	0	387	377	7	10	1	1436	1453	15	16	1	620	610
4	6	0	996	909	6	14	0	641	719	8	22	0	679	650	9	10	1	611	581	0	17	1	585	556
6	6	0	2557	2272	8	14	0	438	490	3	23	0	339	285	0	11	1	682	791	4	17	1	305	265
1	7	0	1509	1617	10	14	0	317	287	5	23	0	314	281	2	11	1	335	386	6	17	1	448	398
3	7	0	1231	1321	1	15	0	1890	1832	7	23	0	292	242	4	11	1	449	475	10	17	1	335	268
5	7	0	1831	1680	7	15	0	399	471	9	23	0	389	408	6	11	1	674	701	14	17	1	396	422
0	8	0	268	172	9	15	0	231	270	0	24	0	453	460	10	11	1	484	435	1	18	1	703	735
2	8	0	2417	2255	13	15	0	762	793	4	24	0	305	304	1	12	1	1055	1058	3	18	1	541	405
4	8	0	1927	1807	0	16	0	1472	1256	6	24	0	377	380	3	12	1	1011	1034	7	18	1	558	617
6	8	0	615	578	2	16	0	791	676	0	26	0	422	350	5	12	1	813	917	15	18	1	320	319
8	8	0	1348	1288	4	16	0	409	374	2	28	0	388	401	7	12	1	820	861	2	19	1	445	376
1	9	0	2095	2039	1	17	0	1062	1123	1	2	1	2007	2444	9	12	1	901	827	6	19	1	307	267
3	9	0	938	926	3	17	0	311	207	0	3	1	1216	1264	11	12	1	298	285	8	19	1	396	343
5	9	0	777	769	15	17	0	502	537	1	4	1	820	732	2	13	1	586	600	10	19	1	443	480
7	9	0	1912	2020	0	18	0	401	516	3	4	1	2330	2173	4	13	1	516	511	14	19	1	365	316
0	10	0	256	219	2	18	0	723	667	0	5	1	1341	1153	6	13	1	755	669	1	20	1	540	561
4	10	0	695	740	4	18	0	515	375	2	5	1	2747	2780	8	13	1	604	583	3	20	1	635	634
6	10	0	1494	1421	1	19	0	835	785	4	5	1	1253	1227	10	13	1	974	851	5	20	1	386	358
10	10	0	505	485	3	19	0	730	703	1	6	1	1626	1572	12	13	1	469	489	7	20	1	326	459
1	11	0	740	866	9	19	0	442	576	3	6	1	1245	1195	1	14	1	1773	1788	9	20	1	434	450
3	11	0	305	375	11	19	0	442	452	5	6	1	2432	2175	3	14	1	1128	1117	11	20	1	247	216
5	11	0	813	752	15	19	0	557	512	0	7	1	1736	1741	5	14	1	930	889	15	20	1	345	226
7	11	0	740	792	0	20	0	791	887	2	7	1	703	738	7	14	1	1297	1228	0	21	1	274	196
9	11	0	945	933	2	20	0	730	744	4	7	1	1011	1035	9	14	1	740	782	4	21	1	385	304
4	12	0	864	773	4	20	0	603	678	6	7	1	2300	2264	11	14	1	505	428	6	21	1	318	374
6	12	0	637	517	6	20	0	559	588	1	8	1	2234	2215	13	14	1	486	475	8	21	1	682	627
8	12	0	230	225	10	20	0	295	336	3	8	1	1993	2094	0	15	1	401	340	10	21	1	409	362
10	12	0	328	359	1	21	0	377	422	5	8	1	2681	2646	2	15	1	496	535	12	21	1	517	517

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.3

H	K	L	10FO	10FC
1	22	1	389	487
3	22	1	416	510
5	22	1	469	506
7	22	1	492	512
9	22	1	325	367
6	23	1	394	419
8	23	1	271	289
10	23	1	336	384
5	24	1	338	249
5	28	1	382	233
1	1	2	813	798
0	2	2	2286	1991
1	3	2	360	397
3	3	2	1231	1185
0	4	2	3231	3083
2	4	2	4249	4029
1	5	2	344	368
3	5	2	457	478
5	5	2	1524	1431
0	6	2	784	851
2	6	2	1604	1597
4	6	2	2308	2328
1	7	2	491	593
3	7	2	407	478
7	7	2	2344	2282
0	8	2	1414	1408
2	8	2	490	513
4	8	2	1765	1541
6	8	2	3201	3037
1	9	2	319	115
3	9	2	740	679
5	9	2	2513	2412
7	9	2	392	271
9	9	2	1494	1500
0	10	2	223	91
2	10	2	502	410
4	10	2	618	643
8	10	2	1040	989
1	11	2	510	446
3	11	2	228	208
5	11	2	1026	1015
7	11	2	1165	1024
9	11	2	674	686
11	11	2	274	283
0	12	2	552	551
2	12	2	1092	1047
4	12	2	923	1007
6	12	2	312	228
8	12	2	813	812
1	13	2	864	810
3	13	2	555	604
5	13	2	544	546
7	13	2	1927	1826
9	13	2	278	320
11	13	2	1018	1051
13	13	2	1106	1137
0	14	2	1604	1738
2	14	2	1333	1353
4	14	2	1209	1142
6	14	2	974	1046
8	14	2	453	493
10	14	2	387	514
12	14	2	302	291
1	15	2	614	629
5	15	2	1055	1081
9	15	2	509	659
11	15	2	695	619
15	15	2	1421	1383
0	16	2	2535	2203
2	16	2	1187	1047
4	16	2	703	789
6	16	2	385	401
8	16	2	297	444
1	17	2	390	481
3	17	2	433	375
5	17	2	329	307
7	17	2	666	679
13	17	2	680	744
17	17	2	583	538
8	18	2	423	396
1	19	2	299	333
7	19	2	399	565
9	19	2	376	388
13	19	2	404	384
15	19	2	338	276
17	19	2	316	279
2	20	2	517	569
8	20	2	422	445
5	21	2	418	406
9	21	2	616	600
11	21	2	436	428
0	22	2	292	313
6	22	2	572	566
7	23	2	407	434
0	1	3	1824	2072
1	2	3	1846	1883
0	3	3	1092	1007
2	3	3	1289	1380
1	4	3	642	586
3	4	3	695	675
0	5	3	679	663
2	5	3	484	385
4	5	3	1157	1062
1	6	3	908	916
3	6	3	777	880
5	6	3	1421	1388
0	7	3	1216	1172
2	7	3	901	975
4	7	3	879	819
6	7	3	1868	1927
1	8	3	570	697
3	8	3	716	708
5	8	3	2630	2559
7	8	3	1333	1262
0	9	3	357	503
2	9	3	930	899
4	9	3	1062	1129
6	9	3	740	714
8	9	3	967	1012
1	10	3	289	254
3	10	3	599	580
5	10	3	1443	1370
7	10	3	1026	1069
9	10	3	676	560
0	11	3	431	528
2	11	3	661	574
4	11	3	410	363
6	11	3	703	725
8	11	3	478	523
10	11	3	322	244
1	12	3	364	274
3	12	3	1004	951
5	12	3	1062	1104
7	12	3	967	979
9	12	3	872	844
11	12	3	280	350
2	13	3	661	670
4	13	3	593	522
6	13	3	857	771
8	13	3	545	532
10	13	3	835	798
12	13	3	629	612
1	14	3	1509	1439
3	14	3	1128	1133
5	14	3	1223	1118
7	14	3	1201	1259
9	14	3	673	656
11	14	3	410	481
13	14	3	533	569
2	15	3	320	205
4	15	3	544	500
6	15	3	398	329
8	15	3	689	697
10	15	3	261	340
12	15	3	740	747
14	15	3	426	495
1	16	3	1597	1440
3	16	3	675	600
5	16	3	615	654
7	16	3	418	617
9	16	3	357	384
11	16	3	488	482
13	16	3	284	354
15	16	3	618	642
0	17	3	463	384
2	17	3	374	292
6	17	3	395	392
10	17	3	311	229
14	17	3	368	425
1	18	3	651	587
7	18	3	515	565
9	18	3	281	276
13	18	3	289	402
17	18	3	319	282
2	19	3	300	302
8	19	3	438	409
14	19	3	322	280
1	20	3	339	325
3	20	3	372	462
7	20	3	349	484

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.3 PAGE 3

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
9	20	3	451	412	7	9	4	1238	1298	12	16	4	319	257	1	2	5	2286	2308	3	12	5	574	638
4	21	3	346	318	2	10	4	536	524	1	17	4	857	848	0	3	5	1744	1737	5	12	5	228	235
6	21	3	317	342	4	10	4	620	616	3	17	4	337	330	2	3	5	1450	1484	7	12	5	423	413
8	21	3	522	482	6	10	4	1004	1007	9	17	4	336	174	1	4	5	850	917	9	12	5	828	788
10	21	3	327	322	8	10	4	305	276	15	17	4	486	496	3	4	5	1011	1068	0	13	5	376	423
12	21	3	298	400	10	10	4	316	299	0	18	4	412	368	0	5	5	1619	1557	2	13	5	670	606
1	22	3	299	414	1	11	4	415	396	2	18	4	522	484	2	5	5	1648	1736	4	13	5	348	422
3	22	3	310	410	3	11	4	371	324	4	18	4	283	210	4	5	5	703	733	6	13	5	574	533
5	22	3	354	388	5	11	4	619	539	6	18	4	294	229	1	6	5	835	922	8	13	5	299	345
7	22	3	437	400	7	11	4	791	801	1	19	4	703	630	3	6	5	557	511	10	13	5	762	706
4	23	3	262	103	9	11	4	473	496	3	19	4	610	567	5	6	5	1428	1287	1	14	5	1758	1672
6	23	3	364	380	0	12	4	264	407	7	19	4	320	215	0	7	5	2344	2359	3	14	5	716	669
10	23	3	368	302	4	12	4	740	718	9	19	4	369	452	2	7	5	330	386	5	14	5	639	621
0	0	4	16263	15492	6	12	4	552	606	11	19	4	357	377	4	7	5	930	906	7	14	5	740	703
0	2	4	1722	1600	10	12	4	251	340	15	19	4	451	442	6	7	5	1165	1097	9	14	5	553	602
2	2	4	2930	3246	1	13	4	1275	1202	0	20	4	506	512	1	8	5	1582	1649	11	14	5	314	335
0	4	4	2784	2786	3	13	4	1033	1010	2	20	4	509	536	3	8	5	967	1015	13	14	5	302	338
2	4	4	1553	1638	5	13	4	938	894	4	20	4	508	555	5	8	5	1648	1588	4	15	5	356	359
4	4	4	1978	1877	7	13	4	388	410	6	20	4	497	525	7	8	5	835	838	8	15	5	505	563
1	5	4	492	532	9	13	4	1113	1122	10	20	4	298	271	0	9	5	389	443	12	15	5	458	531
3	5	4	813	840	11	13	4	330	233	12	20	4	333	217	2	9	5	1700	1671	14	15	5	316	286
0	6	4	1062	1151	0	14	4	923	972	7	21	4	626	623	4	9	5	524	561	1	16	5	1245	1209
2	6	4	820	770	2	14	4	908	879	9	21	4	248	219	6	9	5	791	775	3	16	5	538	534
4	6	4	1121	1174	4	14	4	762	753	11	21	4	344	385	8	9	5	1077	1066	11	16	5	305	231
6	6	4	2220	2065	6	14	4	434	459	13	21	4	385	468	1	10	5	938	943	13	16	5	360	302
1	7	4	619	624	8	14	4	276	452	15	21	4	344	208	3	10	5	360	412	15	16	5	363	352
3	7	4	842	814	10	14	4	312	306	0	22	4	336	334	5	10	5	695	652	14	17	5	349	272
5	7	4	1407	1346	1	15	4	1341	1287	2	22	4	600	651	7	10	5	1231	1220	1	18	5	525	665
0	8	4	270	410	3	15	4	503	407	4	22	4	395	481	9	10	5	371	325	3	18	5	662	563
2	8	4	1436	1559	7	15	4	602	498	6	22	4	355	261	0	11	5	974	930	5	18	5	267	264
4	8	4	1150	1174	9	15	4	307	351	8	22	4	543	532	2	11	5	353	359	15	18	5	336	267
6	8	4	628	591	13	15	4	695	747	9	23	4	347	358	4	11	5	820	798	0	19	5	438	452
8	8	4	1245	1355	0	16	4	1209	1160	0	24	4	386	331	6	11	5	640	640	10	19	5	479	497
1	9	4	1033	962	2	16	4	565	481	4	24	4	328	252	8	11	5	284	294	1	20	5	574	590
3	9	4	703	722	4	16	4	320	332	6	24	4	410	363	10	11	5	459	482	3	20	5	536	571
5	9	4	264	237	8	16	4	315	326	0	1	5	4542	4747	1	12	5	1267	1274	5	20	5	367	339

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.3

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
9	20	3	451	412	7	9	4	1238	1298	12	16	4	319	257	1	2	5	2286	2308	3	12	5	574	638
4	21	3	346	318	2	10	4	536	524	1	17	4	857	848	0	3	5	1744	1737	5	12	5	228	235
6	21	3	317	342	4	10	4	620	616	3	17	4	337	330	2	3	5	1450	1484	7	12	5	423	413
8	21	3	522	482	6	10	4	1004	1007	9	17	4	336	174	1	4	5	850	917	9	12	5	828	788
10	21	3	327	322	8	10	4	305	276	15	17	4	486	496	3	4	5	1011	1068	0	13	5	376	423
12	21	3	298	400	10	10	4	316	299	0	18	4	412	368	0	5	5	1619	1557	2	13	5	670	606
1	22	3	299	414	1	11	4	415	396	2	18	4	522	484	2	5	5	1648	1736	4	13	5	348	422
3	22	3	310	410	3	11	4	371	324	4	18	4	283	210	4	5	5	703	733	6	13	5	574	533
5	22	3	354	388	5	11	4	619	539	6	18	4	294	229	1	6	5	835	922	8	13	5	299	345
7	22	3	437	400	7	11	4	791	801	1	19	4	703	630	3	6	5	557	511	10	13	5	762	706
4	23	3	262	103	9	11	4	473	496	3	19	4	610	567	5	6	5	1428	1287	1	14	5	1758	1672
6	23	3	364	380	0	12	4	264	407	7	19	4	320	215	0	7	5	2344	2359	3	14	5	716	669
10	23	3	368	302	4	12	4	740	718	9	19	4	369	452	2	7	5	330	386	5	14	5	639	621
0	0	4	16263	15492	6	12	4	552	606	11	19	4	357	377	4	7	5	930	906	7	14	5	740	703
0	2	4	1722	1600	10	12	4	251	340	15	19	4	451	442	6	7	5	1165	1097	9	14	5	553	602
2	2	4	2930	3246	1	13	4	1275	1202	0	20	4	506	512	1	8	5	1582	1649	11	14	5	314	335
0	4	4	2784	2786	3	13	4	1033	1010	2	20	4	509	536	3	8	5	967	1015	13	14	5	302	338
2	4	4	1553	1638	5	13	4	938	894	4	20	4	508	555	5	8	5	1648	1588	4	15	5	356	359
4	4	4	1978	1877	7	13	4	388	410	6	20	4	497	525	7	8	5	835	838	8	15	5	505	563
1	5	4	492	532	9	13	4	1113	1122	10	20	4	298	271	0	9	5	389	443	12	15	5	458	531
3	5	4	813	840	11	13	4	330	233	12	20	4	333	217	2	9	5	1700	1671	14	15	5	316	286
0	6	4	1062	1151	0	14	4	923	972	7	21	4	626	623	4	9	5	524	561	1	16	5	1245	1209
2	6	4	820	770	2	14	4	908	879	9	21	4	248	219	6	9	5	791	775	3	16	5	538	534
4	6	4	1121	1174	4	14	4	762	753	11	21	4	344	385	8	9	5	1077	1066	11	16	5	305	231
6	6	4	2220	2065	6	14	4	434	459	13	21	4	385	468	1	10	5	938	943	13	16	5	360	302
1	7	4	619	624	8	14	4	276	452	15	21	4	344	208	3	10	5	360	412	15	16	5	363	352
3	7	4	842	814	10	14	4	312	306	0	22	4	336	334	5	10	5	695	652	14	17	5	349	272
5	7	4	1407	1346	1	15	4	1341	1287	2	22	4	600	651	7	10	5	1231	1220	1	18	5	525	665
0	8	4	270	410	3	15	4	503	407	4	22	4	395	481	9	10	5	371	325	3	18	5	662	563
2	8	4	1436	1559	7	15	4	602	498	6	22	4	355	261	0	11	5	974	930	5	18	5	267	264
4	8	4	1150	1174	9	15	4	307	351	8	22	4	543	532	2	11	5	353	359	15	18	5	336	267
6	8	4	628	591	13	15	4	695	747	9	23	4	347	358	4	11	5	820	798	0	19	5	438	452
8	8	4	1245	1355	0	16	4	1209	1160	0	24	4	386	331	6	11	5	640	640	10	19	5	479	497
1	9	4	1033	962	2	16	4	565	481	4	24	4	328	252	8	11	5	284	294	1	20	5	574	590
3	9	4	703	722	4	16	4	320	332	6	24	4	410	363	10	11	5	459	482	3	20	5	536	571
5	9	4	264	237	8	16	4	315	326	0	1	5	4542	4747	1	12	5	1267	1274	5	20	5	367	339

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.3

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
7	20	5	313	398	9	9	6	1223	1213	2	16	6	583	515	6	9	7	443	437	7	16	7	391	467
4	21	5	316	240	0	10	6	298	299	4	16	6	565	593	8	9	7	813	768	13	16	7	325	290
6	21	5	362	284	4	10	6	505	420	6	16	6	401	366	1	10	7	267	323	15	16	7	376	421
8	21	5	465	491	8	10	6	730	728	7	17	6	473	476	3	10	7	674	597	6	17	7	319	330
10	21	5	394	307	1	11	6	490	455	13	17	6	501	500	5	10	7	740	749	12	17	7	280	248
12	21	5	397	422	3	11	6	429	432	0	18	6	329	289	7	10	7	850	869	1	18	7	423	385
14	21	5	335	263	5	11	6	505	535	2	18	6	305	162	9	10	7	519	504	7	18	7	344	285
1	22	5	429	449	7	11	6	1026	1059	7	19	6	344	415	2	11	7	385	357	13	18	7	323	265
3	22	5	385	403	9	11	6	561	525	2	20	6	480	516	4	11	7	320	301	3	20	7	292	309
5	22	5	385	410	11	11	6	406	425	4	20	6	328	217	6	11	7	536	526	7	20	7	325	295
7	22	5	297	387	0	12	6	675	653	8	20	6	320	308	8	11	7	281	212	4	21	7	298	255
9	22	5	298	332	2	12	6	562	599	5	21	6	359	326	1	12	7	264	272	6	23	7	314	246
6	23	5	349	312	4	12	6	557	533	9	21	6	404	414	3	12	7	813	789	0	0	8	4058	4575
1	1	6	872	796	6	12	6	321	292	11	21	6	281	294	5	12	7	652	650	0	2	8	952	1005
0	2	6	3275	3277	8	12	6	288	327	0	22	6	331	272	7	12	7	704	676	2	2	8	1179	1403
1	3	6	516	540	10	12	6	526	441	2	22	6	333	264	9	12	7	637	686	1	3	8	480	443
3	3	6	1099	1319	1	13	6	709	727	6	22	6	470	423	11	12	7	262	232	0	4	8	916	1023
0	4	6	673	712	3	13	6	494	423	0	1	7	1890	1963	2	13	7	462	370	2	4	8	703	691
2	4	6	401	476	5	13	6	470	522	1	2	7	894	873	6	13	7	719	691	4	4	8	503	573
1	5	6	689	695	7	13	6	1282	1268	0	3	7	974	1122	8	13	7	296	324	3	5	8	529	543
3	5	6	716	859	9	13	6	363	455	1	4	7	265	274	10	13	7	463	494	0	6	8	1121	1098
5	5	6	1187	1236	11	13	6	510	603	3	4	7	447	379	12	13	7	357	417	2	6	8	263	208
0	6	6	806	679	13	13	6	536	630	2	5	7	464	405	1	14	7	1223	1109	4	6	8	518	534
2	6	6	1729	1717	0	14	6	1018	984	4	5	7	1363	1444	3	14	7	681	675	6	6	8	1333	1272
4	6	6	1414	1386	2	14	6	1040	941	1	6	7	1194	1147	5	14	7	886	796	1	7	8	350	302
1	7	6	945	884	4	14	6	740	689	3	6	7	1055	1044	7	14	7	791	796	3	7	8	273	215
5	7	6	277	310	6	14	6	546	573	5	6	7	857	861	9	14	7	610	562	5	7	8	1033	1114
7	7	6	2124	2122	8	14	6	377	406	0	7	7	762	721	13	14	7	347	294	0	8	8	269	252
0	8	6	1385	1353	10	14	6	328	297	2	7	7	541	608	4	15	7	439	434	2	8	8	740	670
2	8	6	655	710	12	14	6	363	347	4	7	7	613	692	8	15	7	481	495	4	8	8	575	601
4	8	6	1289	1326	1	15	6	397	504	6	7	7	1370	1357	10	15	7	325	308	6	8	8	456	469
6	8	6	2220	2223	5	15	6	709	631	1	8	7	762	701	12	15	7	479	484	8	8	8	974	983
1	9	6	612	606	9	15	6	451	495	3	8	7	357	362	14	15	7	319	370	1	9	8	573	537
3	9	6	577	666	11	15	6	489	405	5	8	7	1780	1812	1	16	7	886	854	3	9	8	467	543
5	9	6	1428	1450	15	15	6	857	874	7	8	7	1070	1088	3	16	7	476	449	7	9	8	864	893
7	9	6	381	404	0	16	6	1370	1320	4	9	7	798	784	5	16	7	497	497	0	10	8	294	232

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.3

H	K	L	10FO	10FC
2	10	8	461	453
6	10	8	570	521
8	10	8	300	298
10	10	8	270	200
1	11	8	541	430
5	11	8	358	379
7	11	8	526	539
0	12	8	448	380
4	12	8	482	503
6	12	8	388	387
8	12	8	384	374
1	13	8	489	486
3	13	8	715	694
5	13	8	589	595
7	13	8	342	331
9	13	8	655	690
0	14	8	879	875
2	14	8	709	657
4	14	8	430	430
6	14	8	360	365
8	14	8	270	308
1	15	8	588	600
3	15	8	336	257
7	15	8	446	404
13	15	8	526	535
0	16	8	602	664
2	16	8	369	354
4	16	8	360	324
8	16	8	317	305
1	17	8	380	412
15	17	8	378	334
0	18	8	302	322
1	19	8	319	335
2	20	8	302	280
4	20	8	274	297
6	20	8	337	352
7	21	8	323	358
2	22	8	357	337
4	22	8	377	351
0	1	9	1099	1146
1	2	9	1363	1534
0	3	9	516	482
2	3	9	670	837
1	4	9	435	365
3	4	9	436	555
0	5	9	989	927
2	5	9	437	486
4	5	9	304	332
1	6	9	385	391
5	6	9	489	505
0	7	9	894	949
2	7	9	270	179
4	7	9	319	294
6	7	9	382	385
1	8	9	637	562
3	8	9	331	334
5	8	9	582	546
7	8	9	380	420
0	9	9	492	535
2	9	9	553	562
8	9	9	458	471
1	10	9	365	233
3	10	9	388	355
7	10	9	442	446
0	11	9	397	432
4	11	9	315	323
6	11	9	273	262
10	11	9	299	148
1	12	9	659	622
3	12	9	295	145
7	12	9	282	343
2	13	9	287	285
1	14	9	872	846
3	14	9	421	460
5	14	9	365	348
7	14	9	377	370
9	14	9	303	251
1	16	9	543	554
3	16	9	322	267
13	16	9	343	257
1	18	9	294	378
3	18	9	374	396
10	19	9	361	299
1	20	9	330	357
3	20	9	351	336
7	20	9	316	228
1	22	9	344	297
3	22	9	323	262
0	2	10	1648	1676
1	3	10	213	290
3	3	10	503	656
0	4	10	375	328
1	5	10	377	396
5	5	10	301	261
2	6	10	467	514
4	6	10	529	571
1	7	10	628	617
3	7	10	364	325
7	7	10	683	653
0	8	10	563	585
4	8	10	309	365
6	8	10	857	866
1	9	10	427	376
3	9	10	352	326
5	9	10	610	622
9	9	10	662	672
8	10	10	560	631
1	11	10	442	445
3	11	10	401	405
5	11	10	368	282
7	11	10	390	433
0	12	10	357	363
2	12	10	310	301
6	12	10	321	275
8	12	10	344	275
10	12	10	374	333
1	13	10	491	496
3	13	10	327	308
7	13	10	554	511
0	14	10	437	425
2	14	10	433	364
4	14	10	336	325
1	15	10	302	334
9	15	10	311	248
15	15	10	371	376
0	16	10	418	520
2	20	10	343	290
0	1	11	309	479
1	2	11	347	378
0	3	11	366	408
4	5	11	467	482
1	6	11	464	436
3	6	11	637	587
5	6	11	555	652
2	7	11	338	291
6	7	11	614	588
1	8	11	566	472
5	8	11	608	605
7	8	11	500	542
6	9	11	344	330
5	10	11	438	474
4	11	11	379	282
7	12	11	454	431
1	14	11	474	458
3	14	11	317	305
7	14	11	386	409
1	16	11	365	411
0	0	12	1560	1764
2	2	12	495	583
0	4	12	445	469
2	4	12	398	326
4	4	12	345	359
1	5	12	396	335
3	5	12	535	519
0	6	12	563	476
4	6	12	303	235
6	6	12	681	718
5	7	12	559	625
2	8	12	406	312
4	8	12	416	304
8	8	12	388	396
1	9	12	325	269
7	9	12	446	447
6	10	12	359	352
5	13	12	338	262
9	13	12	371	369
0	14	12	416	446
7	15	12	348	223
0	1	13	615	578
1	2	13	437	573
2	3	13	412	397
1	4	13	453	387
0	5	13	442	441
1	12	13	325	274
2	13	13	330	27
1	14	13	335	366
0	2	14	596	613

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.4

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
2	0	0	935	997	5	4	0	196	189	9	0	1	168	181	12	2	1	208	-202	10	4	1	157	187
4	0	0	569	578	7	4	0	276	-272	-10	1	1	98	97	-15	3	1	101	-30	11	4	1	114	96
6	0	0	510	-506	8	4	0	157	179	-9	1	1	164	-163	-13	3	1	86	-86	-10	5	1	110	104
8	0	0	191	-204	9	4	0	151	-184	-7	1	1	565	-593	-11	3	1	157	-179	-9	5	1	142	164
10	0	0	168	-156	10	4	0	77	62	-6	1	1	245	-253	-8	3	1	141	-128	-8	5	1	153	170
1	1	0	160	-195	11	4	0	89	-70	-5	1	1	449	-458	-7	3	1	212	206	-5	5	1	153	132
2	1	0	965	1004	12	4	0	77	48	-4	1	1	369	-396	-6	3	1	72	63	-4	5	1	195	203
3	1	0	485	-490	15	4	0	71	-10	-3	1	1	289	294	-5	3	1	347	328	-3	5	1	188	170
4	1	0	594	-594	1	5	0	103	82	-2	1	1	240	-269	-4	3	1	277	-285	-1	5	1	87	-93
6	1	0	98	-103	3	5	0	107	104	-1	1	1	222	226	-3	3	1	297	-280	0	5	1	180	174
7	1	0	139	-138	6	5	0	239	-229	0	1	1	70	-71	-1	3	1	150	153	1	5	1	109	-85
8	1	0	180	-165	8	5	0	92	69	1	1	1	423	445	0	3	1	86	-82	2	5	1	345	310
10	1	0	72	76	9	5	0	200	-190	2	1	1	236	233	1	3	1	169	171	4	5	1	121	133
11	1	0	97	-100	10	5	0	147	179	3	1	1	335	330	2	3	1	585	-586	5	5	1	131	115
0	2	0	1109	-1145	0	6	0	144	156	5	1	1	218	203	4	3	1	148	143	9	5	1	83	-39
1	2	0	411	409	2	6	0	260	260	6	1	1	112	128	5	3	1	71	-66	10	5	1	203	-229
2	2	0	257	-267	5	6	0	113	130	7	1	1	81	-78	6	3	1	83	87	-6	6	1	172	-169
3	2	0	1224	-1243	7	6	0	197	183	8	1	1	76	100	7	3	1	273	277	-5	6	1	164	-140
4	2	0	317	309	8	6	0	254	-249	-13	2	1	110	-82	9	3	1	106	125	-4	6	1	98	-65
5	2	0	280	-299	9	6	0	123	144	-8	2	1	75	-68	10	3	1	180	173	-3	6	1	205	-221
7	2	0	316	-325	10	6	0	75	39	-7	2	1	137	124	13	3	1	140	-147	-2	6	1	176	-168
8	2	0	67	63	4	7	0	106	-115	-5	2	1	207	-223	-12	4	1	110	-84	1	6	1	159	-143
1	3	0	74	69	10	7	0	92	-77	-4	2	1	289	-283	-10	4	1	104	87	6	6	1	151	-137
2	3	0	137	-152	13	7	0	95	-53	-3	2	1	576	565	-6	4	1	167	147	7	6	1	256	229
3	3	0	203	192	0	8	0	151	-185	-2	2	1	748	767	-5	4	1	413	397	-4	7	1	159	156
5	3	0	64	-50	3	8	0	89	125	-1	2	1	711	711	-4	4	1	141	-155	-3	7	1	98	-117
6	3	0	308	288	6	8	0	84	75	0	2	1	488	523	-2	4	1	267	-272	-2	7	1	172	212
7	3	0	263	263	8	8	0	89	84	1	2	1	244	251	-1	4	1	71	65	1	7	1	131	125
8	3	0	68	-55	9	9	0	87	12	2	2	1	1134	1147	0	4	1	168	-169	4	7	1	81	-128
9	3	0	216	229	-11	0	1	106	107	3	2	1	711	-674	2	4	1	84	-71	5	7	1	156	-134
11	3	0	151	159	-9	0	1	213	-251	4	2	1	185	200	3	4	1	126	112	6	7	1	143	-138
0	4	0	621	-644	-7	0	1	238	-259	5	2	1	107	74	4	4	1	487	-470	9	7	1	99	100
1	4	0	427	418	-5	0	1	160	-155	6	2	1	273	-262	5	4	1	321	-325	-2	8	1	85	95
2	4	0	387	-392	-3	0	1	266	-266	7	2	1	71	-63	6	4	1	248	225	-1	8	1	107	-100
3	4	0	441	435	3	0	1	77	93	8	2	1	262	-259	7	4	1	169	-164	0	8	1	108	100
4	4	0	615	-598	5	0	1	238	257	10	2	1	132	-158	8	4	1	138	-125	3	8	1	197	186

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.4

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
4	8	1	160	180	-3	2	2	192	-185	6	4	2	207	227	-7	0	3	137	118	10	2	3	113	-103
1	9	1	233	-225	-2	2	2	150	-164	10	4	2	93	-136	-1	0	3	675	-688	-10	3	3	180	-182
2	9	1	106	-102	-1	2	2	159	188	-11	5	2	92	-108	1	0	3	1893	-1959	-9	3	3	99	107
3	9	1	103	-104	0	2	2	107	-121	-9	5	2	121	131	3	0	3	264	-274	-8	3	3	188	-208
1	11	1	103	78	1	2	2	60	65	-8	5	2	129	144	5	0	3	462	-459	-7	3	3	72	52
-10	0	2	253	257	3	2	2	219	207	-7	5	2	86	50	7	0	3	308	326	-3	3	3	121	129
-6	0	2	440	406	4	2	2	297	-299	-5	5	2	124	137	9	0	3	164	160	-1	3	3	236	229
-4	0	2	207	203	5	2	2	93	79	-4	5	2	153	-157	-9	1	3	189	-196	1	3	3	254	271
-2	0	2	1109	1153	6	2	2	93	-88	-2	5	2	86	-94	-8	1	3	76	-62	2	3	3	320	-323
0	0	2	556	-556	7	2	2	131	115	-1	5	2	304	-302	-7	1	3	89	-84	3	3	3	175	-170
2	0	2	1134	-1150	8	2	2	75	-66	0	5	2	136	130	-6	1	3	81	-76	4	3	3	79	-80
4	0	2	326	-320	-13	3	2	127	112	3	5	2	78	-95	-5	1	3	71	83	6	3	3	172	-171
6	0	2	104	-115	-11	3	2	113	112	5	5	2	128	-143	-2	1	3	406	410	7	3	3	122	-125
8	0	2	96	106	-6	3	2	155	137	6	5	2	140	141	-1	1	3	941	960	8	3	3	134	-132
14	0	2	104	129	-5	3	2	309	-310	7	5	2	89	-48	0	1	3	349	341	10	3	3	153	-190
-8	1	2	229	245	-4	3	2	298	295	8	5	2	309	356	1	1	3	99	103	11	3	3	229	-234
-7	1	2	255	-258	-3	3	2	89	74	-11	6	2	101	-75	2	1	3	315	335	-8	4	3	169	-164
-6	1	2	96	-105	-2	3	2	151	-161	-3	6	2	101	108	3	1	3	226	244	-6	4	3	107	-123
-5	1	2	80	61	-1	3	2	222	223	0	6	2	178	171	4	1	3	429	428	-5	4	3	95	95
-3	1	2	283	-265	2	3	2	66	-53	2	6	2	146	142	5	1	3	124	112	-2	4	3	181	191
-2	1	2	379	-393	4	3	2	177	169	4	6	2	172	149	6	1	3	122	123	-1	4	3	139	132
-1	1	2	408	424	5	3	2	140	137	7	6	2	152	-139	7	1	3	156	-164	0	4	3	245	258
0	1	2	1019	1044	11	3	2	78	49	8	6	2	102	89	8	1	3	136	144	1	4	3	243	237
1	1	2	218	-223	-11	4	2	126	115	10	6	2	111	126	13	1	3	96	-126	2	4	3	144	-158
2	1	2	481	-501	-10	4	2	88	-81	-3	7	2	99	123	15	1	3	121	-95	4	4	3	224	-225
3	1	2	387	385	-7	4	2	101	-118	3	7	2	104	-115	-11	2	3	150	148	5	4	3	93	68
4	1	2	128	-131	-6	4	2	215	-233	8	7	2	174	-157	-8	2	3	73	79	8	4	3	110	109
6	1	2	369	-356	-4	4	2	218	213	-4	8	2	115	-121	-4	2	3	80	-63	9	4	3	104	87
7	1	2	173	160	-3	4	2	412	-411	-3	8	2	203	207	-2	2	3	185	-190	10	4	3	190	202
8	1	2	174	-199	-2	4	2	133	110	-2	8	2	144	-132	-1	2	3	139	144	-10	5	3	100	98
10	1	2	119	-124	-1	4	2	119	127	-1	8	2	165	154	1	2	3	272	280	-9	5	3	169	199
-11	2	2	154	-157	0	4	2	83	84	1	8	2	224	198	2	2	3	235	-215	-8	5	3	81	88
-7	2	2	359	-351	1	4	2	139	-135	4	9	2	134	-123	3	2	3	134	131	-3	5	3	169	-146
-6	2	2	111	133	3	4	2	385	-400	-3	10	2	99	-51	4	2	3	174	190	-1	5	3	302	-310
-5	2	2	169	-169	4	4	2	119	116	-11	0	3	135	-136	5	2	3	219	229	0	5	3	157	-151
-4	2	2	139	-140	5	4	2	342	-318	-9	0	3	110	-96	9	2	3	168	-155	4	5	3	218	-215

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.4

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
8	5	3	95	-104	-3	1	4	114	104	3	3	4	410	393	5	6	4	127	-128	-7	2	5	81	-79
10	5	3	178	158	-1	1	4	102	100	4	3	4	180	160	-3	7	4	163	-172	-6	2	5	157	-147
-11	6	3	118	-106	0	1	4	156	-175	9	3	4	131	-163	-1	7	4	183	-179	-4	2	5	321	-322
-1	6	3	206	-227	1	1	4	397	-375	11	3	4	175	-147	1	7	4	134	-140	-3	2	5	240	234
1	6	3	209	-195	2	1	4	583	-574	12	3	4	112	-90	2	7	4	89	-111	-2	2	5	238	-238
3	6	3	88	-106	3	1	4	197	-187	-12	4	4	100	-105	7	7	4	111	77	-1	2	5	359	348
-9	7	3	97	-115	4	1	4	83	-58	-6	4	4	104	118	9	7	4	103	109	0	2	5	245	-237
-5	7	3	141	-127	6	1	4	169	171	-5	4	4	180	-186	-2	8	4	92	-103	1	2	5	162	-154
-4	7	3	77	-49	7	1	4	76	-55	-4	4	4	140	150	-6	9	4	99	-88	3	2	5	80	86
-2	7	3	124	-150	9	1	4	90	73	-2	4	4	194	192	-4	9	4	97	-90	4	2	5	78	-52
-1	7	3	146	145	-13	2	4	154	-138	1	4	4	149	-141	2	9	4	131	125	5	2	5	96	-106
5	7	3	83	81	-11	2	4	127	-126	2	4	4	133	135	4	9	4	143	131	-12	3	5	119	-116
6	7	3	117	136	-9	2	4	109	-116	3	4	4	275	273	-7	0	5	101	126	-11	3	5	101	86
7	7	3	120	141	-7	2	4	300	-288	5	4	4	193	197	-5	0	5	130	-128	-10	3	5	119	-122
-1	8	3	127	130	-6	2	4	120	-105	8	4	4	104	-119	-3	0	5	421	-415	-7	3	5	165	175
0	8	3	86	-36	-5	2	4	207	204	11	4	4	140	-139	-1	0	5	1097	-1075	-5	3	5	147	-154
1	8	3	283	285	-2	2	4	357	-364	-9	5	4	98	-88	1	0	5	127	125	-4	3	5	189	181
2	8	3	103	101	-1	2	4	371	374	-8	5	4	95	-92	3	0	5	192	183	-3	3	5	74	-61
3	9	3	128	118	0	2	4	302	-303	-7	5	4	113	-108	5	0	5	264	257	-1	3	5	209	-199
5	9	3	90	-42	1	2	4	184	187	-6	5	4	83	-93	7	0	5	209	234	0	3	5	231	-221
-1	10	3	115	74	2	2	4	114	-110	-5	5	4	126	-110	9	0	5	144	-147	1	3	5	295	-286
-2	11	3	94	41	3	2	4	186	-193	-3	5	4	90	-99	-13	1	5	100	76	2	3	5	136	-127
0	11	3	98	50	6	2	4	159	168	-2	5	4	208	205	-12	1	5	98	70	3	3	5	210	-212
-14	0	4	104	106	7	2	4	153	158	-1	5	4	197	205	-8	1	5	133	181	6	3	5	87	-55
-12	0	4	93	112	8	2	4	186	178	0	5	4	100	98	-6	1	5	191	174	8	3	5	125	101
-10	0	4	79	70	9	2	4	105	113	3	5	4	201	-176	-4	1	5	221	230	-9	4	5	120	-147
-4	0	4	657	-645	11	2	4	115	124	8	5	4	92	-62	-3	1	5	315	324	-6	4	5	95	115
0	0	4	730	-714	-11	3	4	96	-85	10	5	4	95	-110	1	1	5	277	-255	-4	4	5	171	157
2	0	4	104	98	-10	3	4	127	111	-9	6	4	99	115	3	1	5	101	114	-3	4	5	92	-85
4	0	4	159	163	-6	3	4	165	-183	-8	6	4	97	80	4	1	5	212	-203	-2	4	5	152	148
8	0	4	93	-112	-4	3	4	248	-257	-6	6	4	97	84	5	1	5	216	-228	-1	4	5	118	141
-9	1	4	95	-99	-3	3	4	273	259	-5	6	4	115	125	6	1	5	119	-112	1	4	5	113	112
-7	1	4	88	59	-2	3	4	85	-67	-2	6	4	87	125	7	1	5	190	176	2	4	5	175	-179
-6	1	4	289	292	-1	3	4	134	-147	0	6	4	186	207	8	1	5	172	-166	3	4	5	147	125
-5	1	4	215	209	1	3	4	349	344	1	6	4	137	-153	9	1	5	93	107	4	4	5	269	290
-4	1	4	140	144	2	3	4	161	161	3	6	4	124	-119	-12	2	5	89	78	6	4	5	192	191

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.4

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
8	4	5	130	164	-9	1	6	98	-128	-2	5	6	169	167	-10	2	7	87	-33	-9	2	8	92	-105
-9	5	5	89	-101	-8	1	6	173	186	-1	5	6	87	-89	-8	2	7	128	151	-8	2	8	122	121
-8	5	5	96	-118	-7	1	6	122	135	1	5	6	156	-163	-6	2	7	138	118	-3	2	8	147	132
-7	5	5	160	-167	-6	1	6	110	110	-10	6	6	92	83	-5	2	7	148	137	4	2	8	108	-99
-4	5	5	265	-280	-5	1	6	75	-97	-6	6	6	133	149	0	2	7	139	-137	6	2	8	86	87
0	5	5	101	121	-4	1	6	288	-276	-5	6	6	110	-132	1	2	7	92	-80	-11	3	8	106	105
2	5	5	125	124	-2	1	6	78	-63	-4	6	6	77	38	2	2	7	81	-107	-3	3	8	206	-191
4	5	5	118	125	-1	1	6	332	-327	3	6	6	110	111	-7	3	7	157	-184	-2	3	8	138	-153
6	5	5	194	189	0	1	6	458	-442	5	6	6	96	96	-4	3	7	90	-99	5	3	8	92	96
7	5	5	112	-115	-11	2	6	207	224	-7	7	6	120	-110	-1	3	7	92	107	-4	4	8	97	73
9	5	5	93	-141	-10	2	6	189	-207	-2	7	6	180	-154	1	3	7	78	-92	-1	4	8	166	-206
-9	6	5	113	126	-9	2	6	116	165	-1	7	6	180	185	4	3	7	80	-71	0	4	8	93	-116
-1	6	5	119	-138	-7	2	6	130	146	0	7	6	165	-172	7	3	7	96	122	5	4	8	115	-106
0	6	5	130	117	-5	2	6	115	133	-3	8	6	100	-97	-7	4	7	129	166	7	4	8	99	-96
7	6	5	92	58	-4	2	6	112	-136	-2	8	6	130	105	-6	4	7	84	-73	-4	5	8	112	106
-3	7	5	116	138	0	2	6	88	89	0	9	6	128	139	-5	4	7	90	-111	-2	5	8	136	127
-1	7	5	166	156	1	2	6	200	-187	1	9	6	106	79	2	4	7	171	159	-4	6	8	142	-149
1	7	5	121	137	2	2	6	83	77	-13	0	7	98	-82	-7	5	7	103	115	-2	6	8	116	119
-7	8	5	104	80	-10	3	6	107	-85	-11	0	7	201	-239	-5	5	7	151	184	0	6	8	83	41
-3	8	5	135	131	-9	3	6	229	215	-7	0	7	134	-161	-4	5	7	194	211	-6	7	8	96	77
-2	8	5	99	-123	-8	3	6	192	-217	-1	0	7	259	249	-2	5	7	154	147	-4	7	8	93	-83
-1	8	5	96	99	-5	3	6	102	69	1	0	7	443	442	1	5	7	81	-63	-3	7	8	115	122
0	8	5	132	-117	-4	3	6	130	114	5	0	7	101	-85	4	5	7	133	130	-1	8	8	150	154
2	8	5	99	-101	-2	3	6	136	135	-14	1	7	96	79	-9	6	7	110	-96	-7	0	9	93	-92
3	8	5	99	-104	-1	3	6	106	102	-11	1	7	93	-134	-7	6	7	153	-154	-3	0	9	90	-75
-14	0	6	113	-146	1	3	6	177	186	-9	1	7	88	-94	-4	6	7	126	-101	-1	0	9	86	49
-8	0	6	121	109	-11	4	6	99	-88	-8	1	7	96	37	-10	7	7	94	27	1	0	9	156	-123
-6	0	6	82	101	-10	4	6	86	66	-6	1	7	80	-51	0	7	7	94	68	3	0	9	215	-241
-4	0	6	362	355	-6	4	6	115	-149	-5	1	7	74	-55	-4	0	8	158	178	5	0	9	98	157
-2	0	6	262	278	-4	4	6	93	-93	-4	1	7	157	-176	-2	0	8	121	100	-6	1	9	100	-117
0	0	6	267	280	-3	4	6	137	152	-2	1	7	182	-167	0	0	8	355	345	-3	1	9	160	152
2	0	6	543	529	-2	4	6	144	-130	-1	1	7	232	-206	6	0	8	254	-271	-1	1	9	278	261
4	0	6	107	122	0	4	6	143	-149	0	1	7	170	-179	-10	1	8	113	66	0	1	9	272	271
6	0	6	106	81	2	4	6	183	-165	1	1	7	185	168	-2	1	8	197	-175	1	1	9	391	392
-12	1	6	103	-124	11	4	6	106	-91	3	1	7	238	260	0	1	8	165	-148	2	1	9	166	152
-10	1	6	127	137	-5	5	6	107	106	5	1	7	94	73	2	1	8	165	-208	4	1	9	124	124

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.4

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
5	1	9	140	-120	4	3	9	114	-123	-7	7	9	107	-98	4	1	10	117	103	3	4	10	103	-103
-10	2	9	98	-91	-1	4	9	93	111	-8	0	10	114	90	-7	2	10	96	-101	1	0	11	119	-120
-7	2	9	124	119	4	4	9	83	-57	-6	0	10	144	158	-6	2	10	124	-111	-1	1	11	107	75
-1	2	9	104	-117	10	4	9	107	98	-4	0	10	86	-90	1	2	10	94	21	2	1	11	96	-81
2	2	9	136	141	-8	5	9	101	77	-2	0	10	103	-91	3	2	10	96	119	-5	2	11	91	-67
-5	3	9	90	95	-3	5	9	162	-160	0	0	10	218	-207	-1	3	10	127	130	7	2	11	92	8
-3	3	9	106	116	-1	5	9	97	-81	2	0	10	153	-110	7	3	10	107	-113	2	1	12	123	-106
0	3	9	175	-207	7	5	9	107	65	4	0	10	114	-158	2	4	10	98	58	-1	2	12	99	92
2	3	9	186	-178	-9	6	9	117	-91	2	1	10	102	81										

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.4

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
5	1	9	140	-120	4	3	9	114	-123	-7	7	9	107	-98	4	1	10	117	103	3	4	10	103	-103
-10	2	9	98	-91	-1	4	9	93	111	-8	0	10	114	90	-7	2	10	96	-101	1	0	11	119	-120
-7	2	9	124	119	4	4	9	83	-57	-6	0	10	144	158	-6	2	10	124	-111	-1	1	11	107	75
-1	2	9	104	-117	10	4	9	107	98	-4	0	10	86	-90	1	2	10	94	21	2	1	11	96	-81
2	2	9	136	141	-8	5	9	101	77	-2	0	10	103	-91	3	2	10	96	119	-5	2	11	91	-67
-5	3	9	90	95	-3	5	9	162	-160	0	0	10	218	-207	-1	3	10	127	130	7	2	11	92	8
-3	3	9	106	116	-1	5	9	97	-81	2	0	10	153	-110	7	3	10	107	-113	2	1	12	123	-106
0	3	9	175	-207	7	5	9	107	65	4	0	10	114	-158	2	4	10	98	58	-1	2	12	99	92
2	3	9	186	-178	-9	6	9	117	-91	2	1	10	102	81										

```
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  7.5

  H  K  L  10FO 10FC      H  K  L  10FO 10FC      H  K  L  10FO 10FC      H  K  L  10FO 10FC      H  K  L  10FO 10FC

  4  0  0    92  -91      5  3  0   168  137      3  6  0   523  498     13  8  0   134  142     10 11  0   154  155
  6  0  0   267  252      6  3  0  1016-1002      4  6  0   792 -795     14  8  0   229  237     12 11  0   283  290
 10  0  0    80  -71      7  3  0   719  656      5  6  0   257  236     16  8  0   230  234     14 11  0   133  151
 12  0  0   473 -448      8  3  0   650 -655      6  6  0   241 -219     18  8  0   129   96      1 12  0   125  -83
 14  0  0   140  120      9  3  0    68  -72      7  6  0   191  226      1  9  0   257  253      2 12  0   260  254
 16  0  0   185 -166     10  3  0   569 -580      8  6  0    83  -80      2  9  0   153  156      3 12  0   211 -223
 18  0  0   223 -237     11  3  0   210 -233      9  6  0   366  356      3  9  0   534  533      4 12  0   205  211
  2  1  0   227 -195     12  3  0   419 -393     10  6  0    77   70      4  9  0   259  245      5 12  0   205 -201
  3  1  0   259 -230     14  3  0   262 -278     11  6  0   191  196      5  9  0   377  343      6 12  0   247 -255
  4  1  0   255 -224     15  3  0   155  136     12  6  0   121  124      6  9  0   296  305      7 12  0   187 -181
  5  1  0   538 -528      0  4  0    94  -60     13  6  0   203  230      8  9  0   304  301      8 12  0   298 -303
  7  1  0   133 -140      2  4  0   171 -156     14  6  0   197  176      9  9  0   120 -133      9 12  0   220 -238
  8  1  0   364 -340      3  4  0   513  560     16  6  0   218  224     10  9  0   334  317     11 12  0   307 -286
 10  1  0   179 -160      5  4  0  1108 1071      1  7  0   633  618     11  9  0   121 -111     13 12  0   169 -172
 11  1  0   233  226      6  4  0   251 -252      2  7  0   274  257     12  9  0   101  113      1 13  0   348 -355
 12  1  0   107  108      7  4  0  1016  954      3  7  0   640  656     13  9  0   168 -174      2 13  0    98  101
 13  1  0   185  178      8  4  0   155 -141      4  7  0   146 -182     15  9  0   159 -139      3 13  0   311 -306
 14  1  0    96 -103      9  4  0   338  345      5  7  0   592  593      0 10  0   117 -137      4 13  0    93  114
 15  1  0   172  151     11  4  0   435  409      6  7  0    90  -88      1 10  0   103  -96      5 13  0   142 -165
 17  1  0   202  194     13  4  0   140  165      7  7  0   140  134      2 10  0   359 -356      6 13  0   151  156
  2  2  0   249 -224      1  5  0    82  104      8  7  0   102  -74      3 10  0   244 -269      7 13  0   162  177
  3  2  0   323  312      2  5  0   307 -283      9  7  0    83  -57      4 10  0   193 -191      8 13  0   154  175
  4  2  0   328  364      3  5  0   424  400     12  7  0   111 -129      5 10  0   428 -425     10 13  0   237  200
  7  2  0   358  374      4  5  0   699 -691     13  7  0   135 -121      7 10  0   340 -341     12 13  0   137  144
  8  2  0   273  268      5  5  0   270 -214     14  7  0   109 -116      9 10  0   395 -373      0 14  0   334  388
  9  2  0   398  393      6  5  0  1115-1055     15  7  0   222 -241     10 10  0   265  268      1 14  0   148 -154
 11  2  0   297  302      7  5  0   239  240     17  7  0   210 -227     11 10  0   304 -317      2 14  0   298  279
 12  2  0   212 -230      8  5  0   344 -359      0  8  0   296 -329     12 10  0   119  130      3 14  0   396 -397
 13  2  0   106   88     10  5  0   267 -283      1  8  0   739 -695     13 10  0   144 -140      4 14  0   125  119
 15  2  0   129  117     11  5  0    90  -88      2  8  0   226 -274     14 10  0    88   76      6 14  0   114  120
 16  2  0   166 -157     12  5  0   193 -174      3  8  0   253 -254      1 11  0    89  108      8 14  0   104   97
 20  2  0   133  -94     15  5  0   199 -187      4  8  0   484 -501      2 11  0   231  221      9 14  0   166 -150
  1  3  0    52  -54     17  5  0   127 -103      6  8  0   296 -299      3 11  0   125  123     12 14  0   116 -104
  2  3  0   166  170      0  6  0   759 -769      8  8  0   100 -106      4 11  0   461  465      1 15  0   407 -400
  3  3  0   526 -469      1  6  0   429 -378      9  8  0    95  -83      6 11  0   593  562      3 15  0   187 -195
  4  3  0   347 -362      2  6  0   851 -836     12  8  0   128  130      7 11  0   409  406      4 15  0    94   68
```

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.5

H	K	L	10FO	10FC
5	15	0	271	-259
7	15	0	148	-148
0	16	0	323	324
2	16	0	206	196
3	16	0	105	110
4	16	0	155	153
5	16	0	145	150
6	16	0	144	129
1	17	0	108	-121
2	17	0	110	-91
3	17	0	159	-169
4	17	0	113	-112
5	17	0	117	-116
6	17	0	125	-121
8	17	0	141	-146
10	17	0	94	-90
3	18	0	118	123
5	18	0	142	135
9	20	0	133	117
0	22	0	121	-121
-15	0	1	224	238
-13	0	1	579	550
-11	0	1	805	804
-9	0	1	666	634
-7	0	1	315	251
-5	0	1	602	607
-3	0	1	884	-870
-1	0	1	798	-815
1	0	1	641	-577
3	0	1	1056	-1017
5	0	1	236	-277
7	0	1	134	-219
9	0	1	533	-521
11	0	1	497	-512
17	0	1	92	97
-14	1	1	226	-217
-13	1	1	267	249
-12	1	1	976	-967
-10	1	1	611	-609
-8	1	1	319	-319
-7	1	1	75	-98
-6	1	1	156	-191
-5	1	1	311	-310
-4	1	1	454	-466
-3	1	1	468	462
-2	1	1	319	-219
-1	1	1	588	-628
0	1	1	518	448
1	1	1	213	-221
2	1	1	319	-249
4	1	1	616	584
5	1	1	400	-353
6	1	1	586	596
7	1	1	189	165
8	1	1	608	604
9	1	1	223	219
10	1	1	503	496
11	1	1	429	463
12	1	1	137	142
13	1	1	101	98
17	1	1	161	155
-20	2	1	123	-106
-18	2	1	155	-136
-13	2	1	232	208
-12	2	1	210	-204
-11	2	1	384	376
-10	2	1	100	81
-9	2	1	251	268
-7	2	1	297	294
-6	2	1	488	479
-5	2	1	265	-222
-4	2	1	460	463
-3	2	1	293	-286
-2	2	1	511	530
-1	2	1	798	755
0	2	1	910	912
1	2	1	378	-336
2	2	1	327	303
3	2	1	648	-666
4	2	1	321	286
5	2	1	811	-755
6	2	1	336	347
7	2	1	486	-450
8	2	1	86	-57
9	2	1	356	-374
10	2	1	486	-513
11	2	1	612	-616
12	2	1	377	-367
14	2	1	201	-190
16	2	1	111	-137
18	2	1	127	-141
-19	3	1	162	154
-17	3	1	177	173
-14	3	1	108	74
-12	3	1	103	-94
-9	3	1	332	-323
-8	3	1	158	-146
-7	3	1	530	-527
-6	3	1	151	-155
-5	3	1	858	-854
-3	3	1	534	-521
-2	3	1	181	202
-1	3	1	917	-924
0	3	1	943	843
2	3	1	447	451
3	3	1	239	-263
4	3	1	142	-109
5	3	1	363	-355
6	3	1	371	343
8	3	1	267	269
9	3	1	303	326
10	3	1	297	317
11	3	1	679	704
12	3	1	268	250
13	3	1	211	233
15	3	1	232	224
17	3	1	148	184
-18	4	1	191	-196
-16	4	1	240	-213
-12	4	1	102	-127
-8	4	1	495	496
-6	4	1	1154	1142
-5	4	1	526	-499
-4	4	1	871	875
-2	4	1	897	886
-1	4	1	472	425
0	4	1	332	365
1	4	1	184	194
2	4	1	699	674
3	4	1	119	99
4	4	1	613	597
7	4	1	78	66
10	4	1	320	-303
11	4	1	89	-74
12	4	1	111	-135
13	4	1	228	213
14	4	1	295	-279
16	4	1	216	-222
-17	5	1	217	209
-16	5	1	127	124
-15	5	1	214	197
-14	5	1	142	131
-12	5	1	198	198
-10	5	1	77	74
-9	5	1	258	-249
-8	5	1	273	280
-7	5	1	485	-453
-6	5	1	519	489
-5	5	1	943	-907
-4	5	1	105	110
-3	5	1	627	-603
-2	5	1	393	383
-1	5	1	660	-680
0	5	1	308	-297
1	5	1	579	-558
2	5	1	165	-166
3	5	1	444	-451
4	5	1	449	-489
5	5	1	446	-409
6	5	1	449	-427
7	5	1	106	108
8	5	1	172	-200
9	5	1	175	191
10	5	1	240	-229
11	5	1	212	199
12	5	1	92	-60
15	5	1	222	209
17	5	1	123	168
-18	6	1	158	-142
-16	6	1	105	-103
-15	6	1	206	-174
-13	6	1	226	-233
-11	6	1	316	-307
-10	6	1	115	103
-9	6	1	212	-228
-7	6	1	176	-181
-6	6	1	643	602
-5	6	1	160	-155
-4	6	1	307	324
-2	6	1	449	453

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.5

H	K	L	10FO	10FC
-1	6	1	119	-123
0	6	1	412	428
1	6	1	443	446
3	6	1	778	770
4	6	1	679	656
5	6	1	1042	1001
7	6	1	599	585
8	6	1	113	-126
9	6	1	217	226
10	6	1	148	-172
12	6	1	113	-120
14	6	1	181	-177
16	6	1	152	-167
-16	7	1	162	155
-14	7	1	205	203
-13	7	1	106	-108
-12	7	1	248	253
-10	7	1	383	358
-8	7	1	426	438
-6	7	1	375	374
-5	7	1	350	-320
-4	7	1	351	358
-3	7	1	109	-82
-1	7	1	426	-422
0	7	1	164	-178
1	7	1	453	-421
2	7	1	497	-507
3	7	1	98	61
4	7	1	924	-902
5	7	1	205	-164
6	7	1	444	-449
7	7	1	127	93
8	7	1	478	-483
10	7	1	260	-270
-15	8	1	193	-197
-13	8	1	234	-220
-11	8	1	226	-191
-9	8	1	404	-397
-7	8	1	362	-367
-6	8	1	111	-107
-5	8	1	416	-394
-4	8	1	323	-308
-1	8	1	170	182
0	8	1	165	154
2	8	1	93	72
3	8	1	532	555
5	8	1	612	638
6	8	1	221	-186
7	8	1	411	445
8	8	1	102	-119
9	8	1	430	413
11	8	1	206	216
12	8	1	144	130
13	8	1	116	106
-14	9	1	150	162
-13	9	1	124	-110
-12	9	1	137	112
-11	9	1	172	172
-10	9	1	222	198
-9	9	1	162	189
-8	9	1	293	289
-7	9	1	255	231
-6	9	1	204	219
-5	9	1	401	418
-4	9	1	160	148
-3	9	1	282	281
-2	9	1	465	-443
-1	9	1	314	288
0	9	1	360	-367
1	9	1	129	140
2	9	1	443	-425
3	9	1	146	136
4	9	1	590	-587
5	9	1	136	126
6	9	1	360	-397
7	9	1	105	-105
8	9	1	374	-369
9	9	1	90	-87
12	9	1	159	-189
13	9	1	175	-145
15	9	1	133	-168
-18	10	1	110	93
-13	10	1	176	-151
-10	10	1	140	-127
-9	10	1	212	-209
-8	10	1	237	-225
-7	10	1	185	-209
-6	10	1	548	-544
-5	10	1	150	-147
-4	10	1	346	-348
-3	10	1	181	172
-2	10	1	334	-350
-1	10	1	232	215
0	10	1	567	-552
1	10	1	169	156
2	10	1	484	-478
3	10	1	231	223
4	10	1	298	-308
5	10	1	324	343
7	10	1	212	213
10	10	1	121	100
11	10	1	115	78
12	10	1	234	221
14	10	1	170	200
-9	11	1	137	144
-7	11	1	292	279
-5	11	1	310	320
-4	11	1	160	148
-3	11	1	679	658
-2	11	1	136	-135
-1	11	1	679	691
1	11	1	508	494
3	11	1	258	257
5	11	1	229	235
7	11	1	127	108
9	11	1	96	-74
11	11	1	148	-148
13	11	1	189	-206
15	11	1	135	-173
-11	12	1	149	141
-8	12	1	251	-259
-6	12	1	267	-253
-5	12	1	392	-383
-3	12	1	164	-184
-2	12	1	415	-381
-1	12	1	77	-91
0	12	1	501	-519
1	12	1	179	-174
2	12	1	454	-443
4	12	1	110	-124
5	12	1	226	-219
10	12	1	192	195
12	12	1	205	237
14	12	1	159	188
-12	13	1	144	-149
-10	13	1	161	-163
-9	13	1	212	243
-8	13	1	98	-96
-7	13	1	173	178
-6	13	1	79	-50
-4	13	1	263	240
-3	13	1	213	208
-1	13	1	339	346
0	13	1	236	217
1	13	1	290	288
2	13	1	118	130
6	13	1	350	321
8	13	1	142	164
9	13	1	158	-154
10	13	1	143	136
11	13	1	152	-151
-13	14	1	147	157
-11	14	1	241	230
-9	14	1	182	199
-7	14	1	309	295
-6	14	1	156	-134
-4	14	1	161	-168
-2	14	1	218	-209
0	14	1	148	-123
1	14	1	128	-115
3	14	1	84	60
4	14	1	285	301
5	14	1	265	-265
7	14	1	233	-250
9	14	1	207	-213
11	14	1	129	-136
-12	15	1	162	-181
-10	15	1	251	-230
-8	15	1	208	-209
-6	15	1	235	-227
0	15	1	137	135
2	15	1	131	109
4	15	1	175	159
6	15	1	268	277
8	15	1	278	276
10	15	1	172	169
-11	16	1	166	144
-9	16	1	190	178
-7	16	1	184	161
-6	16	1	103	102

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.5

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-5	16	1	100	111	-2	0	2	1108	-1183	12	1	2	115	124	-14	3	2	122	-128	1	4	2	686	-758
-4	16	1	115	111	0	0	2	371	358	13	1	2	136	-163	-12	3	2	243	-223	2	4	2	241	210
-2	16	1	100	113	2	0	2	294	247	15	1	2	201	-193	-10	3	2	191	-183	3	4	2	548	-579
2	16	1	120	-109	4	0	2	706	-630	17	1	2	127	-150	-9	3	2	114	104	4	4	2	133	102
3	16	1	169	-160	6	0	2	232	209	-13	2	2	294	276	-8	3	2	319	-309	5	4	2	622	-604
5	16	1	221	-234	8	0	2	236	245	-12	2	2	173	-180	-7	3	2	634	619	6	4	2	222	210
7	16	1	208	-211	10	0	2	288	306	-11	2	2	270	253	-6	3	2	379	-361	7	4	2	416	-421
9	16	1	171	-176	12	0	2	189	187	-10	2	2	170	-160	-5	3	2	362	373	8	4	2	92	-92
-12	17	1	102	-96	14	0	2	261	251	-9	2	2	150	171	-4	3	2	74	-39	9	4	2	363	-401
-9	17	1	116	-91	16	0	2	211	235	-8	2	2	170	-197	-2	3	2	194	189	10	4	2	236	-241
-7	17	1	115	-117	-19	1	2	119	-118	-7	2	2	233	213	-1	3	2	578	556	11	4	2	148	-112
-5	17	1	153	-113	-15	1	2	140	149	-6	2	2	418	-403	0	3	2	420	351	17	4	2	110	100
-1	17	1	137	-139	-14	1	2	158	-154	-5	2	2	295	313	1	3	2	71	-95	19	4	2	131	116
1	17	1	132	-141	-13	1	2	100	-85	-4	2	2	431	-410	2	3	2	666	690	-18	5	2	164	-135
3	17	1	110	-120	-12	1	2	349	-345	-3	2	2	759	-737	3	3	2	183	-174	-16	5	2	173	-187
4	17	1	119	110	-11	1	2	325	333	-2	2	2	1491	-1527	4	3	2	617	639	-14	5	2	271	-276
6	17	1	154	134	-10	1	2	231	-260	-1	2	2	2533	-2514	5	3	2	584	-533	-12	5	2	225	-234
8	17	1	123	150	-9	1	2	406	411	0	2	2	1412	-1359	6	3	2	805	758	-10	5	2	325	-306
-6	18	1	96	99	-8	1	2	111	103	1	2	2	477	-463	7	3	2	185	146	-9	5	2	369	-376
-4	18	1	163	155	-7	1	2	358	401	2	2	2	303	-279	8	3	2	210	213	-8	5	2	539	-529
-2	18	1	117	133	-6	1	2	83	-88	3	2	2	534	-539	9	3	2	124	-131	-7	5	2	625	-611
0	18	1	135	139	-5	1	2	191	193	4	2	2	532	510	10	3	2	88	86	-6	5	2	104	-96
2	18	1	103	114	-3	1	2	608	563	5	2	2	1023	-951	11	3	2	278	-290	-5	5	2	511	-503
-5	19	1	117	-118	-2	1	2	1590	1616	6	2	2	686	614	14	3	2	151	-127	-4	5	2	306	291
-3	19	1	196	-178	-1	1	2	2672	2692	7	2	2	516	-477	-17	4	2	206	192	-3	5	2	482	-489
-1	19	1	137	-132	0	1	2	963	858	8	2	2	230	241	-15	4	2	237	225	-2	5	2	549	520
3	19	1	109	-94	1	1	2	280	221	9	2	2	190	-188	-13	4	2	305	295	-1	5	2	171	-163
-4	20	1	132	143	2	1	2	82	117	10	2	2	348	329	-11	4	2	255	258	0	5	2	243	236
-2	20	1	125	125	3	1	2	58	-21	11	2	2	87	72	-9	4	2	272	260	1	5	2	469	-447
2	20	1	112	110	4	1	2	412	372	12	2	2	143	186	-8	4	2	279	251	2	5	2	838	862
-14	0	2	172	189	5	1	2	466	-467	13	2	2	189	-202	-7	4	2	490	521	3	5	2	175	-200
-12	0	2	90	-89	6	1	2	412	399	14	2	2	182	140	-6	4	2	110	-104	4	5	2	609	613
-10	0	2	391	-368	7	1	2	331	-313	16	2	2	110	125	-5	4	2	228	-235	5	5	2	103	94
-8	0	2	323	-316	8	1	2	123	117	17	2	2	94	113	-3	4	2	151	-195	6	5	2	273	281
-6	0	2	485	-577	9	1	2	367	-347	-18	3	2	166	-147	-2	4	2	408	365	8	5	2	268	273
-4	0	2	317	-305	11	1	2	344	-361	-16	3	2	175	-177	-1	4	2	474	-470	9	5	2	317	310

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.5

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
10	5	2	381	365	-1	7	2	223	-238	-9	9	2	184	-176	10	10	2	174	-177	-12	13	2	170	161
11	5	2	127	99	0	7	2	454	-417	-8	9	2	142	128	12	10	2	145	-196	-8	13	2	169	-155
13	5	2	100	117	2	7	2	208	220	-7	9	2	552	-522	14	10	2	106	-94	-7	13	2	150	158
14	5	2	119	-122	3	7	2	119	-138	-5	9	2	459	-492	-18	11	2	104	88	-5	13	2	129	141
15	5	2	110	102	4	7	2	347	339	-4	9	2	185	199	-14	11	2	174	184	-4	13	2	146	138
-15	6	2	161	173	5	7	2	270	284	-3	9	2	216	-230	-12	11	2	302	293	-3	13	2	141	159
-13	6	2	170	155	7	7	2	267	251	-2	9	2	117	93	-11	11	2	102	96	-2	13	2	119	-139
-12	6	2	107	87	9	7	2	279	294	-1	9	2	288	-303	-10	11	2	355	348	-1	13	2	153	187
-11	6	2	158	175	11	7	2	195	214	0	9	2	393	-346	-8	11	2	352	370	0	13	2	305	-300
-10	6	2	123	141	13	7	2	294	293	1	9	2	245	-252	-5	11	2	81	94	1	13	2	203	187
-9	6	2	174	167	15	7	2	214	235	2	9	2	367	-382	-4	11	2	278	-267	2	13	2	367	-385
-8	6	2	520	526	-12	8	2	130	122	4	9	2	414	-398	-2	11	2	172	-185	4	13	2	336	-348
-7	6	2	288	259	-10	8	2	199	194	5	9	2	204	185	0	11	2	427	-407	5	13	2	217	-195
-6	6	2	512	481	-8	8	2	321	291	8	9	2	199	-185	2	11	2	505	-509	6	13	2	334	-343
-5	6	2	152	176	-6	8	2	588	581	9	9	2	232	242	4	11	2	337	-326	8	13	2	116	-110
-4	6	2	629	643	-5	8	2	72	86	10	9	2	147	-171	5	11	2	150	-184	11	13	2	152	-152
-3	6	2	375	-383	-4	8	2	673	670	11	9	2	280	304	6	11	2	90	-78	-7	14	2	117	112
-2	6	2	514	497	-2	8	2	398	387	13	9	2	180	225	7	11	2	163	-153	-6	14	2	252	-232
0	6	2	229	-196	-1	8	2	359	367	15	9	2	148	171	8	11	2	212	-214	-4	14	2	332	-324
3	6	2	627	-653	0	8	2	460	453	-17	10	2	110	-102	9	11	2	136	108	-2	14	2	337	-338
4	6	2	342	-304	2	8	2	288	257	-15	10	2	175	-170	10	11	2	182	-189	-1	14	2	135	142
5	6	2	569	-575	3	8	2	230	244	-14	10	2	100	67	-13	12	2	233	-240	0	14	2	218	-223
6	6	2	128	-115	4	8	2	123	107	-13	10	2	183	-184	-11	12	2	222	-216	2	14	2	96	-86
7	6	2	272	-257	5	8	2	236	233	-11	10	2	199	-195	-7	12	2	227	-209	5	14	2	181	187
8	6	2	174	-173	6	8	2	216	-232	-9	10	2	196	-207	-6	12	2	193	-206	6	14	2	148	165
9	6	2	119	-99	7	8	2	187	191	-8	10	2	400	386	-3	12	2	111	98	7	14	2	97	135
10	6	2	181	-180	8	8	2	521	-521	-7	10	2	257	-249	-1	12	2	255	267	8	14	2	207	210
14	6	2	203	-199	9	8	2	263	252	-6	10	2	244	245	0	12	2	179	-166	10	14	2	179	191
16	6	2	148	-169	10	8	2	344	-347	-4	10	2	225	220	1	12	2	488	473	12	14	2	99	105
-14	7	2	134	-142	12	8	2	310	-301	-1	10	2	121	131	3	12	2	359	401	-9	15	2	156	138
-11	7	2	177	-184	14	8	2	193	-209	0	10	2	164	172	4	12	2	130	123	-7	15	2	157	169
-9	7	2	223	-247	15	8	2	93	-71	1	10	2	413	433	5	12	2	369	381	-5	15	2	247	264
-7	7	2	556	-541	16	8	2	131	-136	3	10	2	535	542	6	12	2	164	167	-3	15	2	321	315
-5	7	2	719	-714	-16	9	2	108	103	5	10	2	180	161	7	12	2	171	174	-1	15	2	229	258
-3	7	2	586	-564	-13	9	2	88	-91	6	10	2	294	309	8	12	2	83	-69	7	15	2	169	-164
-2	7	2	329	309	-10	9	2	96	80	9	10	2	138	145	-14	13	2	117	109	-8	16	2	145	-146

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.5

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-6	16	2	234	-235	15	0	3	190	-209	-6	2	3	639	-673	5	3	3	366	-336	-8	5	3	112	84
-4	16	2	287	-299	17	0	3	193	-206	-5	2	3	312	339	6	3	3	148	-129	-7	5	3	581	605
-2	16	2	258	-265	-16	1	3	139	115	-3	2	3	365	378	7	3	3	331	-358	-6	5	3	78	77
8	16	2	107	127	-15	1	3	149	132	-2	2	3	201	-220	8	3	3	111	-127	-5	5	3	431	453
-7	17	2	93	80	-14	1	3	342	346	-1	2	3	584	551	9	3	3	658	-626	-4	5	3	78	126
-5	17	2	142	136	-13	1	3	292	304	0	2	3	92	67	10	3	3	366	-347	-3	5	3	474	490
-3	17	2	98	105	-12	1	3	324	310	1	2	3	427	458	11	3	3	234	-234	-2	5	3	118	82
-2	17	2	137	115	-11	1	3	220	248	2	2	3	218	230	12	3	3	123	94	1	5	3	169	-154
-1	17	2	129	136	-10	1	3	146	139	3	2	3	186	173	13	3	3	220	-221	2	5	3	408	415
0	17	2	212	179	-9	1	3	129	107	4	2	3	98	-94	15	3	3	131	-142	3	5	3	96	-111
2	17	2	107	125	-7	1	3	339	353	5	2	3	286	299	-15	4	3	113	70	4	5	3	378	363
4	17	2	206	207	-6	1	3	193	-176	6	2	3	191	209	-12	4	3	181	-183	5	5	3	336	-340
1	18	2	160	-164	-5	1	3	239	252	7	2	3	206	219	-10	4	3	319	-306	6	5	3	215	192
3	18	2	167	-159	-4	1	3	412	-438	8	2	3	362	354	-8	4	3	452	-456	7	5	3	346	-348
5	18	2	129	-134	-3	1	3	242	247	9	2	3	181	183	-7	4	3	161	157	9	5	3	422	-402
7	18	2	137	-135	-2	1	3	573	-577	10	2	3	395	414	-6	4	3	462	-429	10	5	3	259	-280
0	19	2	131	118	-1	1	3	156	175	12	2	3	225	231	-4	4	3	368	-397	11	5	3	144	-178
2	19	2	164	188	0	1	3	485	-469	13	2	3	224	-190	-2	4	3	503	-535	13	5	3	175	-154
4	19	2	185	159	2	1	3	585	-611	14	2	3	146	146	-1	4	3	64	86	15	5	3	94	-100
-4	20	2	129	86	4	1	3	636	-622	-13	3	3	219	205	0	4	3	140	135	-17	6	3	195	188
-1	20	2	94	-82	5	1	3	82	72	-12	3	3	212	224	2	4	3	140	127	-15	6	3	166	169
3	20	2	112	-105	6	1	3	153	-139	-11	3	3	236	235	3	4	3	96	-101	-14	6	3	92	-89
-15	0	3	215	-210	7	1	3	102	-102	-9	3	3	393	405	4	4	3	398	386	-13	6	3	160	169
-13	0	3	630	-633	8	1	3	78	-87	-8	3	3	192	-165	5	4	3	194	-205	-11	6	3	90	63
-11	0	3	295	-292	9	1	3	163	-158	-7	3	3	719	727	6	4	3	342	343	-10	6	3	234	-222
-9	0	3	73	-99	12	1	3	113	89	-6	3	3	484	-448	8	4	3	507	520	-8	6	3	325	-334
-7	0	3	179	188	13	1	3	125	-140	-5	3	3	457	454	9	4	3	251	260	-6	6	3	389	-390
-5	0	3	137	141	14	1	3	170	194	-4	3	3	373	-407	10	4	3	679	633	-5	6	3	192	-205
-3	0	3	225	318	16	1	3	235	224	-3	3	3	658	672	11	4	3	185	189	-4	6	3	195	-176
-1	0	3	533	513	-14	2	3	151	-130	-2	3	3	388	421	12	4	3	174	182	-3	6	3	197	-207
1	0	3	329	360	-13	2	3	364	-376	-1	3	3	151	137	14	4	3	135	114	-2	6	3	468	-461
3	0	3	772	771	-12	2	3	288	-293	0	3	3	188	-203	-14	5	3	170	-171	-1	6	3	241	-268
5	0	3	752	723	-11	2	3	167	-183	1	3	3	346	318	-13	5	3	132	122	0	6	3	314	-309
7	0	3	373	380	-10	2	3	307	-317	2	3	3	212	-221	-12	5	3	107	-100	1	6	3	431	-431
11	0	3	118	-96	-8	2	3	412	-366	3	3	3	87	-84	-11	5	3	239	222	3	6	3	536	-555
13	0	3	95	-86	-7	2	3	246	231	4	3	3	207	-180	-9	5	3	304	336	4	6	3	94	131

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.5

H	K	L	10FO	10FC
5	6	3	303	-296
6	6	3	289	291
7	6	3	267	-282
8	6	3	245	243
9	6	3	141	-128
10	6	3	110	102
-16	7	3	214	-206
-14	7	3	179	-172
-10	7	3	84	-77
-7	7	3	143	149
-6	7	3	178	194
-4	7	3	327	317
-2	7	3	432	446
-1	7	3	116	109
0	7	3	354	362
2	7	3	630	633
3	7	3	211	198
4	7	3	639	664
6	7	3	314	318
7	7	3	218	-218
8	7	3	179	157
14	7	3	133	-162
16	7	3	122	-96
-17	8	3	144	137
-15	8	3	160	159
-13	8	3	115	96
-11	8	3	108	95
-9	8	3	87	83
-8	8	3	98	69
-7	8	3	246	-267
-5	8	3	152	-124
-4	8	3	128	109
-3	8	3	439	-451
-2	8	3	113	120
-1	8	3	505	-511
1	8	3	600	-590
3	8	3	818	-849
4	8	3	140	-130
5	8	3	263	-266
6	8	3	164	-160
7	8	3	168	-176
8	8	3	152	-150
13	8	3	123	132
15	8	3	104	117
-16	9	3	102	-124
-14	9	3	119	-106
-12	9	3	139	-133
-11	9	3	126	-136
-10	9	3	109	-106
-9	9	3	175	-167
-7	9	3	321	-310
-5	9	3	303	-290
-4	9	3	358	345
-3	9	3	232	-237
-2	9	3	439	454
-1	9	3	174	-184
0	9	3	422	419
2	9	3	391	415
4	9	3	412	412
6	9	3	210	228
7	9	3	152	141
9	9	3	129	162
11	9	3	200	183
13	9	3	119	135
-12	10	3	148	140
-10	10	3	238	254
-8	10	3	300	278
-7	10	3	106	118
-6	10	3	131	130
-5	10	3	151	143
-4	10	3	216	196
-3	10	3	311	-295
-2	10	3	230	228
-1	10	3	290	-298
1	10	3	311	-319
3	10	3	254	-243
4	10	3	137	-136
5	10	3	125	-143
6	10	3	115	-135
7	10	3	114	-128
8	10	3	205	-214
10	10	3	214	-228
12	10	3	232	-204
-13	11	3	123	-74
-11	11	3	235	-239
-9	11	3	324	-336
-7	11	3	236	-243
-6	11	3	342	-348
-1	11	3	93	-81
3	11	3	172	154
5	11	3	273	302
7	11	3	241	229
8	11	3	132	-127
9	11	3	224	211
11	11	3	262	257
13	11	3	146	163
-12	12	3	109	100
-10	12	3	255	267
-8	12	3	334	324
-6	12	3	183	190
-5	12	3	111	97
-4	12	3	286	272
-2	12	3	208	230
-1	12	3	183	179
0	12	3	123	101
1	12	3	164	170
3	12	3	164	179
4	12	3	201	-215
5	12	3	100	101
6	12	3	129	-144
8	12	3	166	-143
10	12	3	205	-198
-12	13	3	156	155
-9	13	3	184	-184
-7	13	3	258	-249
-6	13	3	133	-127
-5	13	3	204	-213
-4	13	3	148	-154
-3	13	3	196	-184
-2	13	3	206	-218
-1	13	3	172	-178
0	13	3	284	-276
2	13	3	142	-153
4	13	3	259	-241
5	13	3	114	133
6	13	3	125	-140
7	13	3	161	154
9	13	3	138	118
-13	14	3	125	-124
-10	14	3	159	155
-8	14	3	118	119
-6	14	3	124	119
-5	14	3	189	181
-3	14	3	228	227
-2	14	3	153	146
-1	14	3	293	279
0	14	3	173	186
1	14	3	128	131
3	14	3	162	162
5	14	3	193	193
8	14	3	138	-126
-14	15	3	139	137
-4	15	3	176	-176
-2	15	3	217	-223
0	15	3	146	-139
3	15	3	142	138
4	15	3	195	-190
6	15	3	122	-146
-8	16	3	100	-117
-5	16	3	113	101
-3	16	3	165	162
-1	16	3	200	171
2	16	3	158	-166
5	16	3	111	101
8	16	3	100	66
-5	17	3	130	121
0	17	3	142	-119
4	17	3	115	-110
5	17	3	149	-130
7	17	3	148	-145
-8	18	3	124	-112
-6	18	3	113	-122
-4	18	3	115	-103
6	18	3	125	136
-7	19	3	109	94
-4	19	3	115	-88
7	19	3	138	-130
-16	0	4	125	129
-14	0	4	214	222
-12	0	4	391	395
-10	0	4	245	247
-8	0	4	369	350
-6	0	4	202	225
-4	0	4	67	-81
-2	0	4	136	139
2	0	4	424	-471
4	0	4	1029	-1004
6	0	4	586	-559
8	0	4	385	-369
10	0	4	250	-257

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.5

H	K	L	10FO	10FC
12	0	4	298	-274
-13	1	4	193	-225
-11	1	4	265	-269
-9	1	4	284	-266
-8	1	4	174	140
-7	1	4	435	-457
-6	1	4	110	109
-5	1	4	156	-174
-4	1	4	180	-154
-3	1	4	195	-190
-2	1	4	301	-321
-1	1	4	94	89
1	1	4	257	268
2	1	4	351	-376
3	1	4	425	427
4	1	4	366	-356
5	1	4	621	580
7	1	4	261	275
9	1	4	217	222
11	1	4	156	179
13	1	4	107	86
-15	2	4	158	-159
-12	2	4	100	104
-10	2	4	231	225
-8	2	4	371	408
-6	2	4	110	84
-5	2	4	177	177
-4	2	4	300	322
-3	2	4	778	798
-2	2	4	398	366
-1	2	4	226	185
0	2	4	333	-359
1	2	4	274	297
2	2	4	215	-191
3	2	4	476	494
4	2	4	389	-377
5	2	4	179	185
6	2	4	113	-124
8	2	4	265	-254
9	2	4	88	-101
10	2	4	138	-148
13	2	4	141	-174
15	2	4	156	-166
-18	3	4	117	113
-14	3	4	195	185
-11	3	4	97	-94
-9	3	4	104	-135
-6	3	4	265	-283
-4	3	4	785	-777
-3	3	4	673	-723
-2	3	4	1425	-1422
-1	3	4	391	-331
1	3	4	162	126
2	3	4	348	-359
3	3	4	200	212
4	3	4	280	-250
5	3	4	158	165
7	3	4	137	138
8	3	4	87	85
9	3	4	203	179
10	3	4	82	94
14	3	4	156	166
16	3	4	154	151
18	3	4	120	101
-19	4	4	131	-143
-17	4	4	118	-128
-15	4	4	120	-106
-7	4	4	199	188
-6	4	4	119	-116
-5	4	4	426	482
-3	4	4	811	799
-2	4	4	649	660
-1	4	4	611	591
0	4	4	122	113
1	4	4	472	484
3	4	4	212	218
5	4	4	223	244
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  7.5                                                                    PAGE  9

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  0 11  4  421  432      6 14  4  146 -142    -10  1  5  166  160      4  2  5  334 -319      4  4  5  328 -346
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.5

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.5

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 7.5

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6	8	6	207	-213
8	8	6	160	-169
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-9	9	6	121	-105
-8	9	6	146	-174
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1	9	6	239	249
3	9	6	164	171
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2	14	6	144	125
4	14	6	104	108
1	15	6	138	-134
0	16	6	140	122
2	16	6	143	142
4	16	6	142	140
-11	0	7	178	162
-9	0	7	266	302
-7	0	7	206	201
-5	0	7	173	144
9	0	7	115	-104
-12	1	7	107	-111
-10	1	7	179	-178
-8	1	7	214	-212
-6	1	7	154	-140
-4	1	7	90	-97
1	1	7	143	-151
6	1	7	115	139
-11	2	7	99	95
-9	2	7	125	128
-7	2	7	121	134
-5	2	7	129	136
-2	2	7	93	85
0	2	7	186	191
2	2	7	214	216
4	2	7	92	79
5	2	7	104	-101
-5	3	7	92	-76
-3	3	7	115	-104
-1	3	7	156	-137
1	3	7	224	-209
3	3	7	195	-207
5	3	7	166	-172
6	3	7	112	94
-16	4	7	126	-125
-14	4	7	109	-89
-4	4	7	121	125
-2	4	7	179	184
0	4	7	214	187
2	4	7	208	194
-5	5	7	121	-113
-3	5	7	203	-212
-1	5	7	220	-208
1	5	7	187	-179
6	5	7	133	-145
8	5	7	115	-109
-9	6	7	103	-91
-6	6	7	117	106
-5	6	7	205	-204
-3	6	7	98	-75
-2	6	7	146	111
0	6	7	142	136
5	6	7	110	102
7	6	7	216	207
-4	7	7	117	131
6	7	7	193	-194
8	7	7	221	-212
-11	8	7	135	-112
-8	8	7	113	-127
3	8	7	100	82
5	8	7	132	136
7	8	7	168	182
9	8	7	119	122
-10	9	7	113	113
-6	9	7	108	113
-1	9	7	128	109
1	9	7	148	166
4	9	7	106	-92
-4	10	7	104	-95
-2	10	7	91	-96
0	10	7	168	-165
2	10	7	144	-144
1	11	7	162	160
3	11	7	106	129
0	12	7	148	-118
2	12	7	131	-120
-6	0	8	179	-174
-4	0	8	179	-176
-2	0	8	175	-176
0	0	8	192	-180
-7	1	8	130	105
-5	1	8	141	135
-3	1	8	118	86
-1	1	8	136	139
1	1	8	129	135
-9	2	8	100	108
0	2	8	135	-119
1	2	8	135	-117
2	3	8	226	221
4	3	8	155	173
6	3	8	148	152
-7	4	8	121	107
3	4	8	119	-116
5	4	8	120	-124
7	4	8	111	-105
-10	5	8	113	-89
-6	6	8	171	176
-5	6	8	146	152
-4	6	8	245	250
-2	6	8	147	149
-5	7	8	168	-185
-3	7	8	218	-230
-1	7	8	168	-141
-6	8	8	90	23
-4	8	8	128	139
-2	8	8	128	118
2	11	8	142	-97
-1	0	9	113	111
4	7	9	114	90

Appendix 3 General experimental techniques

The infrared spectra was recorded on a Pye Unicam SP2000 spectrometer, in the range 4000-626 cm^{-1}. Nujol and hexachlorobutadiene mulls were made of the compounds and were supported between potassium bromide discs. The spectra were calibrated against the 1603 cm^{-1} band of polystyrene.

Mass spectra were obtained from MS9 and MS4 spectrometers. Field desorption mass spectra were obtained on a KRATOS MS50 spectrometer operated at 8-kv accelerating voltage with a potential difference of 10 kv between the emitter and extractor plate.

^1H nmr spectra were recorded on a Perkin Elmer R12B and a Bruker WP80.

Uv/vis spectra were recorded using a Pye Unicam SP1800 spectrometer.

X-ray crystallographic data were collected on a Philips PW1100 diffractometer with Mo-K_α radiation.

Isolation of a Stable Binuclear Copper Complex Containing a Copper–Copper Bonded Unit. *X*-Ray Structure Determination of {(7,8,15,16,17,18,25,26,33,34,35,36-Dodecahydrotetrabenzo[*e*,*m*,*s*,*a'*][1,4,8,11,15,18,22,25]octaazacyclo-octacosine)dicopper} Triperchlorate

By Keith P. Dancey and Peter A. Tasker*
(*Department of Chemistry, The Polytechnic of North London, Holloway, London* N7 8DB)
Raymond Price
(*I.C.I. Organics Division, Hexagon House, Blackley, Manchester* M9 3DA)
and William E. Hatfield* and Douglas C. Brower
(*Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina* 27514)

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Isolation of a Stable Binuclear Copper Complex Containing a Copper–Copper Bonded Unit. X-Ray Structure Determination of {(7,8,15,16,17,18,25,26,33,34,35,36-Dodecahydrotetrabenzo[*e,m,s,a′*][1,4,8,11,15,18,22,25]octa-azacyclo-octacosine)dicopper} Triperchlorate

By KEITH P. DANCEY and PETER A. TASKER*
(*Department of Chemistry, The Polytechnic of North London, Holloway, London* N7 8DB)

RAYMOND PRICE
(*I.C.I. Organics Division, Hexagon House, Blackley, Manchester* M9 3DA)

and WILLIAM E. HATFIELD* and DOUGLAS C. BROWER
(*Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina* 27514)

Summary The *X*-ray crystal structure of the title octa-azamacrocycle with a 28-membered ring shows that it is capable of incorporating a symmetrical copper–copper bonded unit which contains a short Cu–Cu bond [2·448(4) Å]; the compound is paramagnetic with μ_{eff} = 1·87 μ_B at 300 K, exhibiting a single line at g = 2·09 in the *X*-band e.s.r. spectra of solid samples or of frozen acetonitrile solutions (77 K).

A NUMBER of dinucleating ligands have been used[1,2] recently to bring two copper atoms into close proximity, thus providing models for the 'Type 3 Coppers' in the multi-copper oxidases.[3] These copper sites are characterised[3] by an ability to act as two-electron acceptor–donor systems and contain two Cu^{2+} ions which are strongly antiferromagnetically coupled. In most of these model systems the two copper atoms are separated by bridges

Containing a Copper–Copper
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riperchlorate

TASKER*
s, Holloway, London N7 8DB)

y, Manchester M9 8DA)

s C. BROWER
pel Hill, North Carolina 27514)

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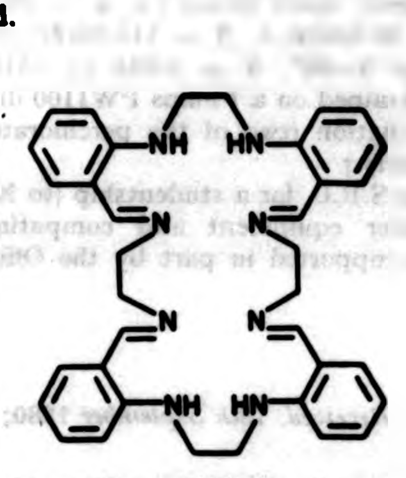
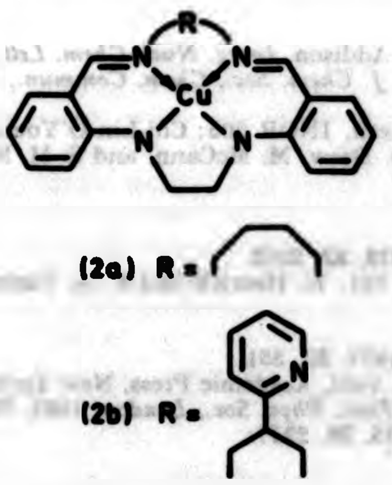
containing one[1] or more[2] atoms. We report here the preparation of a dinuclear complex which contains a direct Cu–Cu bond.



(1)



(2a) R =

(2b) R =

Treatment of a suspension of the octa-azamacrocycle (1)[4] in tetrahydrofuran with a methanolic solution of copper(II) perchlorate resulted in almost complete dissolution of (1). After filtration, the green solution slowly deposited green prisms of the title complex, $[Cu_2(1)](ClO_4)_3$. The presence of a tricationic complex was unexpected and could have arisen either (i) by the transfer of a single electron to the dicopper centre, (ii) by the loss of one of the anilino-protons from the ligand (a common form of co-ordination for related tetra-azamacrocycles),[5] (iii) by the reduction of the copper ions and simultaneous mono-oxidation of the macrocyclic ligand, or (iv) from a bonded pair of copper(II) ions with a reduced ligand. The second possibility can be excluded on the basis of an *X*-ray structure determination which shows that all four anilino-nitrogen atoms have approximately tetrahedral geometry (Figure), rather than a trigonal planar arrangement which has been found[6] for the deprotonated anilino-nitrogen atoms in the neutral complexes (2).

A magnetic-moment determination by the Faraday method on a solid sample at room temperature (300 K) yielded $\mu_{eff} = 1{\cdot}87\ \mu_B$, thus confirming the expected paramagnetism of the $[Cu_2(1)]^{3+}$ formulation.

The two copper atoms have very similar co-ordination geometries (Table) and the cation has approximate 2-fold symmetry about an axis which passes through the mid-point of the Cu–Cu bond and relates the ligand portion A to C and B to D (see the Figure). The similarity of the environments of Cu(1) and Cu(2) and the short bond [2·445(4) Å] between them suggest that the copper atoms should not be assigned the discrete formal oxidation states +1 and +2, but that the single unpaired electron is delocalised over both metal centres, or that the metal centres are identical and the unpaired electron resides on the ligand.

The e.s.r. spectra, at the *X*-band, of a powdered sample or of a frozen acetonitrile solution (77 K) exhibited one line at $g = 2{\cdot}09$ with a peak line width of 80—90 G. These data do not unambiguously support the immediate conclusions from the *X*-ray structural study that the copper ions are equivalent and that this is a 'type 3A' mixed-valence compound.[7] The single line could arise from exchange-narrowing between sites with life-times which are very short on the e.s.r. time-scale or from inherently narrow lines arising from isotropic, nuclear, hyperfine coupling-constants of the order of 40×10^{-4} cm^{-1}, as estimated from the line width. Such small coupling-constants are known for the 'blue' copper proteins[8] as well as a variety of typical co-ordination compounds of copper(II).[9] It is well established that a 4s and 4p orbital admixture in the ground state leads to small, hyperfine coupling-constants[9] and single line e.s.r. spectra. The magnetic susceptibility and e.s.r. data clearly indicate that the formulation of the compound as $[Cu_2L](ClO_4)_3$ is correct and the *X*-ray

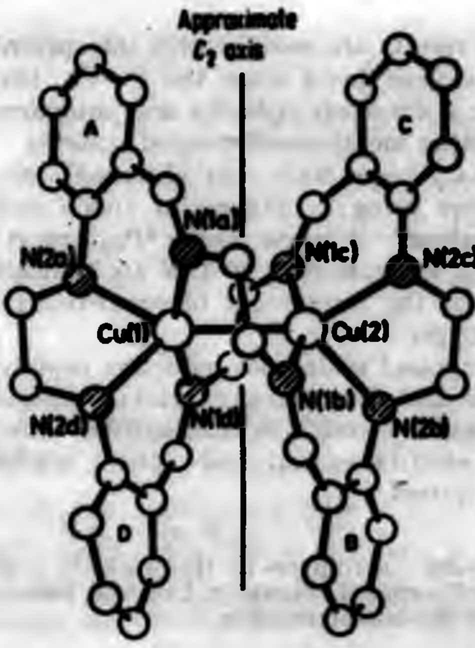


FIGURE.

TABLE. Geometry about the copper atoms Cu(1) and Cu(2).

	Cu(1)		Cu(2)	
	Part A	Part D	Part B	Part C
Bond-lengths/Å				
Cu–N(1)	1·95(2)	1·98(2)	1·91(2)	1·97(2)
Cu–N(2)	2·18(2)	2·20(2)	2·19(2)	2·15(2)
Angles/°				
N(1)–Cu–N(2)	91·8(9)	92·5(7)	93·7(9)	92.3(8)
N(1)–Cu–N(1)[a]	159·8(7)	—	158·0(9)	—
N(1)–Cu–N(2)[a]	106·1(7)	96·3(9)	101·2(9)	105·0(8)
N(2)–Cu–N(2)[a]	83·5(8)	—	84·6(8)	—
N(1)–Cu–Cu[b]	81·0(6)	80·6(7)	78·7(7)	80·5(6)
N(2)–Cu–Cu[b]	144·6(5)	131·8(7)	129·0(5)	146·4(6)

[a] Denotes an atom in the alternative quarter of the ligand which is co-ordinated to the same Cu atom. [b] Denotes the Cu atom in the other half of the complex.

structural results are most readily interpreted in terms of a copper–copper bond since the Cu–Cu distance is very short[10] for a dinuclear complex and compares with values found in other metal–metal bonded systems.

An E.S.C.A. spectrum was obtained with a PHI 548 spectrometer using a magnesium anode and a precision energy analyser. A single copper ${}^2P_{3/2}$ line at 935·6 eV and a ${}^2P_{3/2}$–${}^2P_{1/2}$ separation of 20·3 eV are compelling pieces of evidence for the assignment of equal oxidation states to the two copper ions.

The compound undergoes reduction rapidly in a variety of solvents including tetrahydrofuran–methanol solutions, but is relatively stable in acetonitrile, thus permitting a range of electrochemical and optical studies on a new chemical system.

Crystal data: $[Cu_2(1)](ClO_4)_2$, $C_{30}H_{40}Cl_2Cu_2N_8O_{12}$, M = 1010·2, monoclinic, space group Cc, a = 22·577(7), b = 11·016(4), c = 20·909(8) Å, β = 118·96(2)°, U = 4550·0, Z = 4, θ-range 3—35°, R = 0·060 for 1815 data with $I/\sigma(I) > 3{\cdot}0$ obtained on a Philips PW1100 diffractometer with Mo-K_α radiation (two of the perchlorate ions show extensive disorder).†

We thank the S.R.C. for a studentship (to K. P. D.) and for diffractometer equipment and computing facilities. This work was supported in part by the Office of Naval Research.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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m., 1975, 28, 2377.

Dinucleating Octaaza Macrocyclic Ligands from Simple Imine Condensations

Keith P. Dancey, Kim Henrick, Patricia M. Judd,
Philip G. Owston, Roger Peters, and Peter A. Tasker*

Department of Chemistry, The Polytechnic of North London
Holloway, London N7 8DB, United Kingdom

Anne Dell

Department of Biochemistry, Imperial College
London SW7 2AY, United Kingdom

Ralph W. Turner

I.C.I. Pharmaceuticals Division
Macclesfield, Cheshire SK10 4TG, United Kingdom

Received February 19, 1981

Macrocyclic ligands which are capable of incorporating two metal ions[1] offer the possibility of studying unusual electronic and chemical properties which depend upon proximity of two metal centers. An advantage of macrocyclic systems for this type of investigation is that variation of ring size or other geometric constraints should allow the separation and disposition of the two metal ions to be controlled in a systematic manner. In this paper we describe a series of such ligands which have been obtained in high yields from simple imine condensation reactions and have been characterized by field desorption mass spectrometry and X-ray structure determination.

We have reported[2] that under appropriate conditions the dialdehyde 1a can be condensed with a range of diamines 2 to give tetraaza macrocycles 3 with a wide range of ring sizes. These reactions proceed without addition of "metal-ion templates",[3] provided that reaction conditions and solvents are selected which allow the free ligands to separate from solution before they can undergo conversion to species which are less soluble or thermodynamically more stable. It was noted,[2] for example, that on prolonged heating in methanol, 3a is converted to a species of higher relative molecular mass (m_r). We have now characterized a number of the higher m_r materials obtained from condensations under conditions defined in Scheme I and shown them to be an

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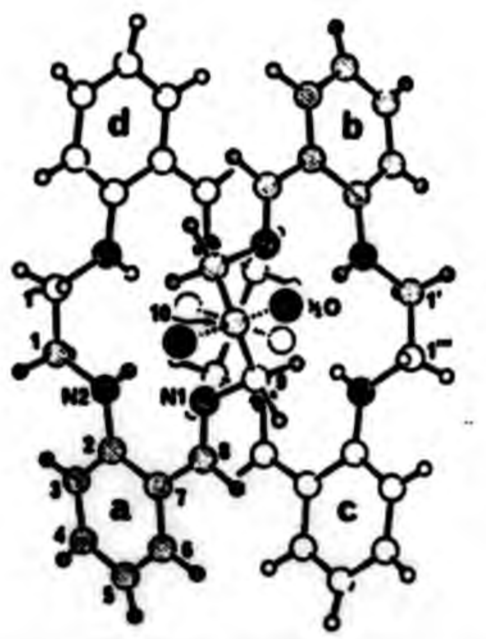


Figure 1. Tetraimine **5b**, showing the disorder of the hydroxyl groups about the 2-fold axis which passes through carbon atoms C(10). Another crystallographic C_2 axis passes through the midpoints of the C(1)–C(1) bonds. Shaded C and H atoms are in the half of the molecule nearer the viewer.

interesting new class of potentially octadentate macrocycles **5**.

These high m_r compounds, which were obtained (see Scheme I) from reactions of the diamines **2a–c**, are relatively insoluble and involatile, and cryoscopic methods and electron-impact mass spectrometry could not be used to determine their relative molecular masses. However, the samples showed simple field desorption (FD) mass spectra,[4] giving molecular ions compatible with the [2 + 2] condensation products:[5] **5a**, *m/e* 584; **5b**, *m/e* 645 $(M + 1)^+$; **5c**, *m/e* 697 $(M - 1)^+$. No fragmentation products were observed in the range *m/e* 400–800.

FDMS also proved useful in identifying compounds which were present when mixtures of products were obtained from similar condensation reactions. For example, a mixture (ca. 1:4) of the diimine **4** and the tetraimine **6** [*m/e* 307 $(M + 1)^+$ and *m/e* 613 $(M + 1)^+$, respectively] was obtained from the condensation of the trimethylene-bridged dialdehyde **1b** and 1,2-diaminoethane (1:1.1, 4 h in 15-cm^3 refluxing $CHCl_3$). These substrates have been used previously,[6] but under conditions of high dilution, to prepare the diimine **4**.

An X-ray structure determination[7] confirmed the presence of a 30-membered ring in **5b** (see Figure 1). The inner great ring has a configuration which effectively creates two "N_4" donor sets (from the *o*-iminoanilino units of a with d and b with c, see Figure 1), in the two halves of the molecule. Such an arrangement would cause close approximation of two metal ions in a dinculear complex, because the centroids of the two donor sets are separated by only 3.44 Å. A similar ligand geometry is found[8] in a dicopper complex of the smaller ring **5a** in which the two copper ions are forced to adopt a very short Cu–Cu bond [2.445 (5) Å].

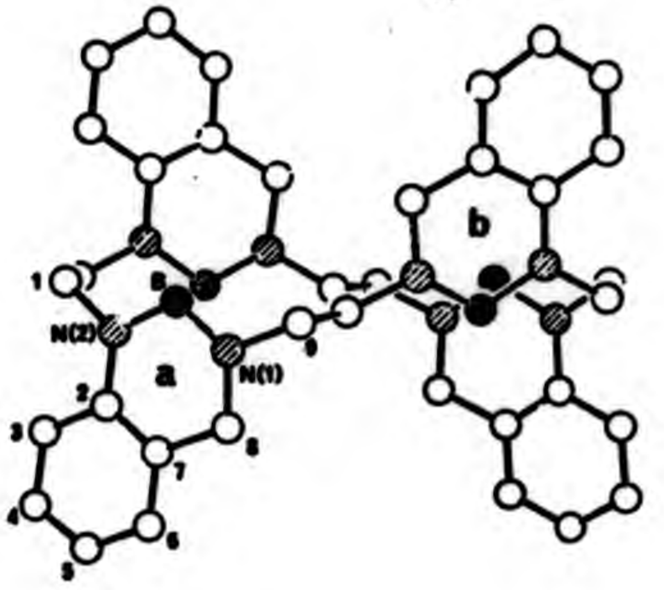
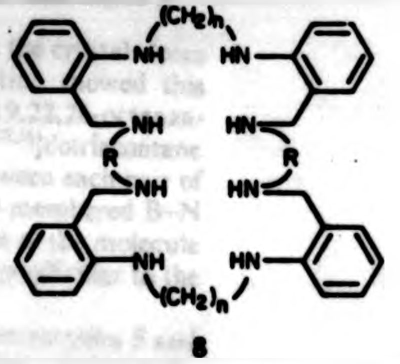


Figure 2. The 20-membered B–N heterocycle **7**.

A crystallographic 2-fold axis passes through the carbon atoms having the hydroxyl substituents, and the oxygen atoms are statistically disordered with half-occupancies of the sites shown in Figure 1. Consequently, the structure determination does not allow a distinction to be made between meso and racemic isomeric forms for **5b**.

We conclude that ease of isolation of the metal-free macrocycles **5** is dependent on the presence of strong *intra*molecular hydrogen bonding in the *o*-iminoanilino units. The geometry of the *o*-iminoanilino unit in **5b** is very similar to that found[2] in the related tetraaza macrocycles **3**. Reactions of 2,6-diacetylpyridine with certain diamines have also been observed[9] to give large ring ligands by [2 + 2] condensations,[1a] but for these systems the new chelate rings are of the α-diimine type and do not have the facility to form *intra*molecular H bonds. In these cases the free ligands have not been isolated, but an extensive range of mono- and binuclear complexes have been prepared[9] by carrying out transmetalation reactions on complexes prepared in the presence of certain metal ion templates.

The 28-membered ring structure for **5a** was indirectly confirmed by x-ray structure analysis[10] of an unusual borane adduct (**7**) which was obtained as an intermediate in the reduction with borane/THF to give the corresponding octaamine **8**. Crystals of **7** which separated from a suspension of **5a** in borane/THF gave a sharp infrared absorption band at 2510 cm^{-1}, a region in whcih B–H stretching modes are known to occur. They were found to be surprisingly stable to hydrolysis, and X-ray diffraction data were



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[4] Spectra were obtained on a KRATOS MS50 spectrometer, operated at 8-kV accelerating voltage and with a potential difference of 10 kV between the emitter and extractor plate. Spectra, recorded on oscillograph paper, were calibrated with the EI spectrum of Fomblin oil (Henning, J.; L.., H. *Vacuum* 1977, *27*, 171–175). High-temperature activated emitters were loaded by dipping into either a solution (**5c** and **4**/**6**) or a suspension (**5a**,**b**,**8a**) in CH_2Cl_2. Emitter heating currents in the range 15–21 mA were required to desorb these compounds.

[5] The hydrogenated octaaza macrocycle (**8**, R = $(CH_2)_2$, $n = 2$) and a related "N_4O_4" system (with phenoxo groups replacing the anilino units: Lindoy, L. F. et al., unpublished results) were also identified by FDMS measurements [*m/e* 592 $(M)^+$ and 597 $(M + 1)^+$, respectively].

[6] Black, D. St. C.; Hartshorn, A. J.; Horner, M.; Hunig, S. *Aust. J. Chem.* 1977, *30*, 2493–2514.

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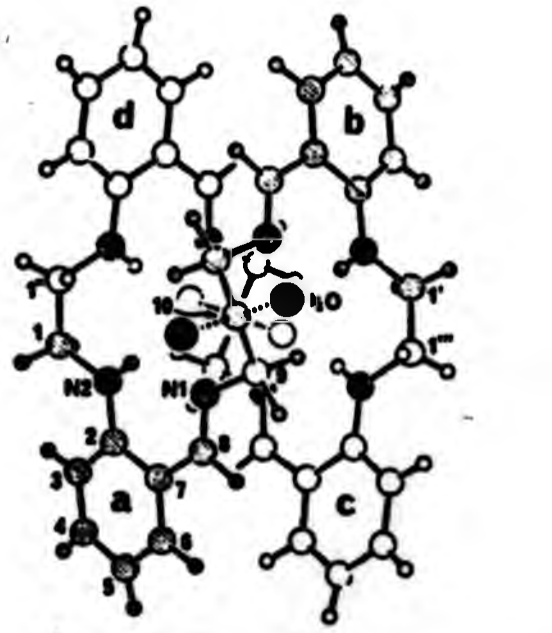

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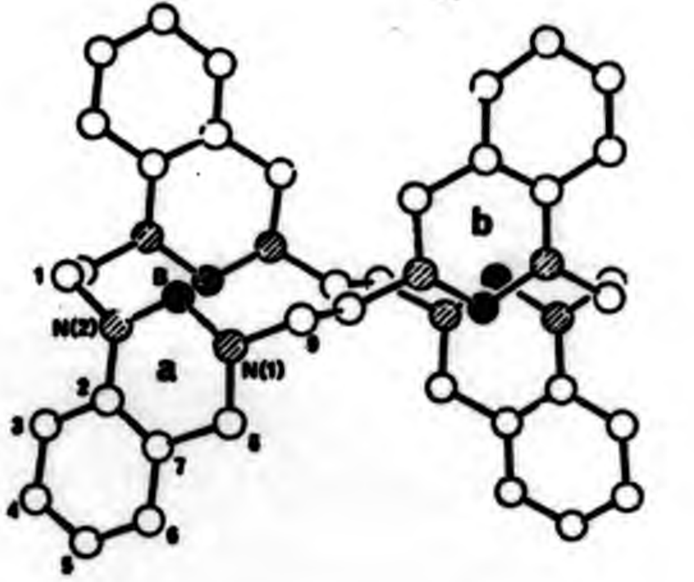

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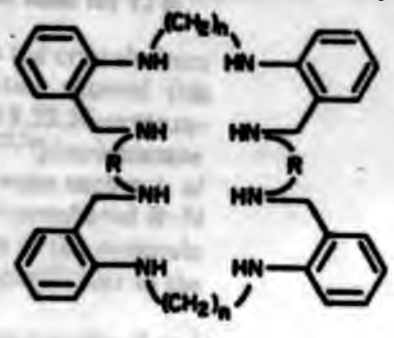

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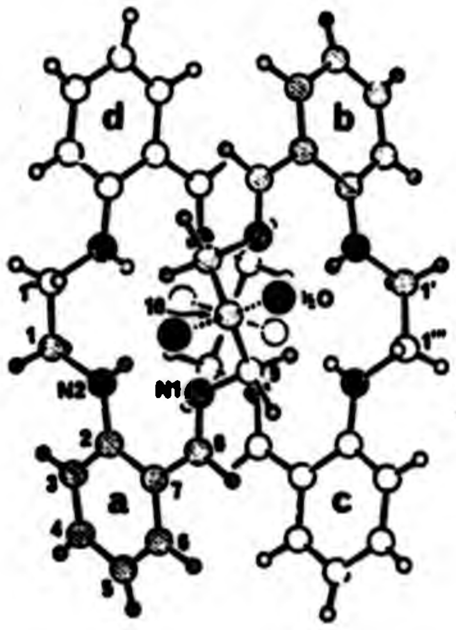

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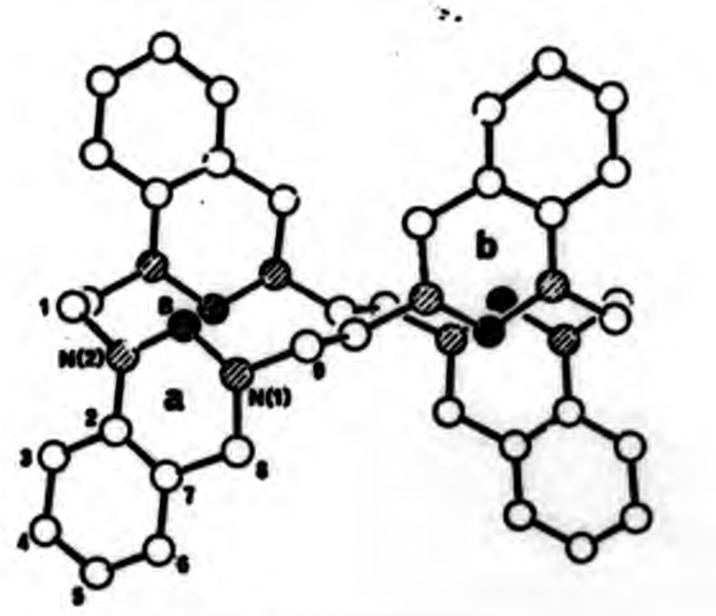

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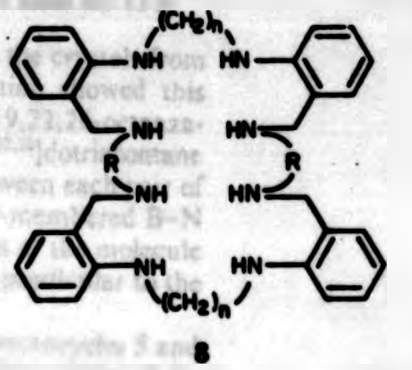

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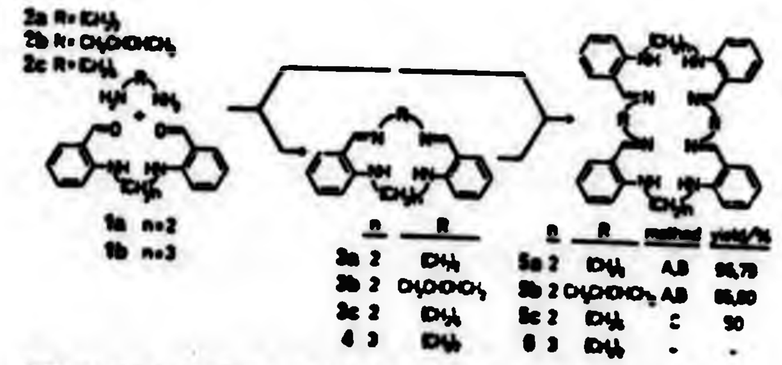
Scheme I[a]



[a] Reaction conditions are (A) 1a (2 mmol) + 2 (2.2 mmol) in MeOH (40–50 cm^3) refluxed 6 h and a further 24 h after addition of $CHCl_3$ (5 cm^3); (B) 3 heated 24 h in refluxing MeOH containing acetic acid (1 mol %); (C) 1a (10 mmol) + 2c (11.5 mmol) in EtOH (50 cm^3) refluxed for 1.5 h, filtered, and set aside for 12 h.

collected without special precautions to protect the crystals from atmospheric moisture. Structure determination showed this material to be tetrabenz[*a*,*g*,*o*,*u*]-1,5,8,12,15,19,22,26-octaaza-29,30,31,32-tetraborapentacyclo[$1^{1,5}.1^{8,12}.1^{15,19}.1^{22,26}$]dotriacontane in which a B–H unit has been incorporated between each pair of *o*-iminoanilino nitrogen to give the unusual 20-membered B–N heterocycle shown in Figure 2. The two halves of the molecule are related by a crystallographic 2-fold axis perpendicular to the best plane through the inner great ring.

The isolation of the potentially octadentate macrocycles 5 and 8 presents the interesting possibility of preparing a series of dinuclear complexes in which the separation and disposition of the two metal ions is controlled by ring sizes and other geometric constraints in the ligands.

Acknowledgment. We thank the Science Research Council (U.K.) for studentships (to R.P., P.M.J., and K.P.D.) and diffractometer equipment and computing facilities. P.A.T. thanks the Regents of the University of California for support during a period of leave spent at the Irvine Campus.

Supplementary Material Available: Fractional coordinates, thermal parameters, bond distances, bond angles and observed and calculated structure factors for compounds 5b and 7 (7 pages). Ordering information is given on any current masthead page.

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