

STUDIES OF SOME
TRANSITION METAL COMPLEXES WITH
OXYANIONS

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by

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ABSTRACT

In the first part of this thesis the preparation and properties of the copper complexes $Me_4N[Cu(RCOO)_2NCS]$, $R = CH_3$, or H are described. When $R = CH_3$, related ONO^- and Br^- complexes have also been isolated. (X-ray molecular structural determinations have shown that these complexes have dimeric structures related to that of cupric acetate monohydrate). The antiferromagnetism of these and similar complexes is discussed, particularly with respect to the metal-metal separations found in this type of complex and it is concluded that the antiferromagnetism observed in, for example, cupric acetate monohydrate is not solely the result of a direct metal metal interaction, the bridging ligands involved having considerable influence.

The preparation of some related dimeric $Cr(II)$ compounds is also described.

In the second part, the preparation and properties of a series of nitrite complexes of cobalt(II) and zinc with substituted pyridines and substituted ethylene diamines as the other ligands are described. Infrared and electronic spectra have been used to determine the structures of the complexes formed. These structures are discussed in relation to those established for nickel nitrite complexes, and some of the factors influencing the structures adopted are considered.

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Abbreviations

The following ligand abbreviations are used throughout

<u>Ligand</u>	<u>Abbreviation</u>
ethylenediamine	en
N-methylethylenediamine	men
N,N-dimethylethylenediamine	a-dimen
N,N-diethylethylenediamine	a-dieen
N,N'-diethylethylenediamine	s-dieen
N,N,N',N'-tetramethylethylenediamine	tetmen
pyridine	py
2-methylpyridine	2-mepy
3-methylpyridine	3-mepy
4-methylpyridine	4-mepy
Isoquinoline	I-quin
3-5 lutidine	3-5 lut.
o-xylylenebis-(triphenylphosphonium) ²⁺	o-cat ²⁺

In descriptions of electronic and infrared spectra the following abbreviations are used.

s - strong, m - medium, w - weak, vw - very weak.

sb - strong broad.

PART ONE

SOME ANIONIC, DIMERIC CUPRIC
COMPLEXES

CHAPTER 1

Introduction to Dimeric Copper(II) Carboxylate Complexes

Copper(II) complexes normally have magnetic moments slightly greater than the spin only value for one unpaired electron (1.73 B.M.) and the temperature variation of susceptibilities frequently follows Curie or Curie-Weiss behaviour (71 and references therein).

The unusually low magnetic susceptibility of copper acetate monohydrate was first reported in 1915¹; much later², the temperature variation of the molar susceptibility was examined. The susceptibility passes through a maximum (ca. 880×10^{-6} c.g.s.u) at about room temperature and then decreases so rapidly that it would apparently become zero at about 20°K. Because of this anomalous magnetic behaviour Bleaney and Bowers³ undertook an investigation of the magnetic properties of copper acetate monohydrate by means of electron spin resonance. It was shown that the paramagnetic resonance spectrum of copper acetate resembled that of an ion with a resultant spin $S = 1$, but the intensity of the spectrum decreased as the temperature was lowered.

To explain these results it was postulated that:

- (a) the crystalline field acting on each copper ion is similar to that in other cupric salts such as the Tutton salts, and
- (b) the lattice contains isolated pairs of copper ions which

interact strongly through exchange forces, each forming a lower spin-singlet state and an upper spin triplet state, the latter only being paramagnetic.

The second postulate (b) was verified when the crystal structure of copper acetate monohydrate was determined (Ref.4), see Fig.1a.

Isolated pairs of copper atoms are bridged by four acetate molecules, the terminal positions being occupied by water molecules. The most interesting feature of the structure is the close approach of the two copper atoms, the separation being 2.64 Å (cf. 2.56 Å in metallic copper).

The temperature variation of the susceptibility of the hydrate was also reported by Foex et al.⁵ and a further study, extended to higher temperatures was carried out by Figgis and Martin⁶. In the latter paper the magnetic behaviour of anhydrous copper acetate was also studied.

In general a singlet state with a triplet as the first excited state at an energy J above the singlet gives rise^{3,5,7} to a molar susceptibility.

$$\chi_m = \frac{g^2 N \beta^2}{3KT} \frac{1}{1 + \frac{1}{3} \exp J/KT} + N\alpha \quad \text{l.a.}$$

where

g = Landé factor

N α = Temperature

N = Avogadro's number

Independent Paramagnetic

β = Bohr Magneton

contribution per mole

K = Boltzman constant

of copper(II)

T = Temperature ⁰ Absolute

Cupric Acetate.

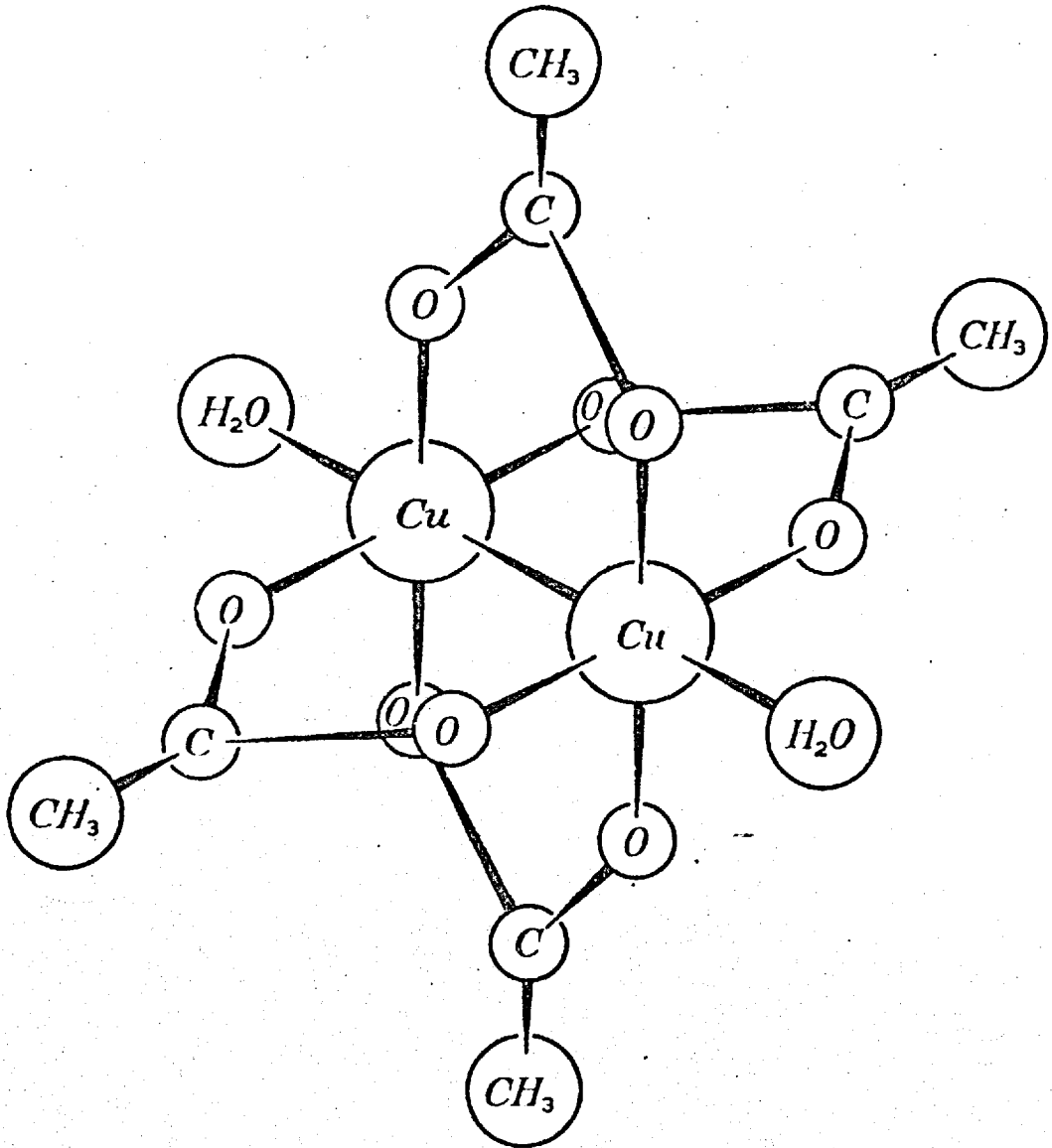


Fig. 1a.

J is a measure of the "exchange interaction" occurring in the compound concerned.

If J is of the same magnitude as KT , as the temperature is raised from absolute zero the triplet state becomes increasingly occupied, with a corresponding increase in susceptibility until a maximum value of χ_m is reached at a temperature usually denoted as T_c . This occurs when $T = 5/6 J$ (J in degrees absolute); at much higher temperatures than T_c the usual decrease in susceptibility with rise in temperature is observed. Susceptibility maxima were observed for anhydrous and hydrated cupric acetates at 270° and $255^\circ K$ leading to the values of 302 cm.^{-1} and 286 cm.^{-1} for the respective exchange interactions⁶. (These values were calculated by assuming $N\alpha = 60 \times 10^{-6}$ and that J is independent of temperature). A value of $259 \pm 26 \text{ cm.}^{-1}$ had previously been estimated from paramagnetic resonance experiments³. Taking these J values good agreement is obtained between experimental results and theoretical curves for the variation of magnetic susceptibility of the compounds with temperature.

Since the discovery of the magnetic properties and structure of cupric acetate, a great deal of experimental and theoretical work has been carried out with a view to understanding the exact mechanism of the magnetic interaction in this and many related compounds.

A number of complexes with other carboxylic acids have been prepared⁸ and in general have been found to have magnetic properties

similar to copper acetate (Table 1.1). The water molecules in the terminal positions in the dimeric unit in copper acetate have been replaced by other neutral molecules. X-ray crystal structure determinations have been carried out on the pyridine adduct of cupric acetate^{13,14} showing that it has a very similar structure to that of the monohydrate; complexes with urea¹⁵ and triphenylarsine oxide⁹ are assumed to be dimeric because of the general similarity of their properties to those of cupric acetate. In general the terminal groups appear to have little effect on the magnetic interactions between the copper ions with the notable exception of the aniline type adducts of copper butyrate¹² where the singlet-triplet interval is reduced by about 200 cm.^{-1} (i.e. 70%). Not all carboxylic acids form dimeric copper complexes. There is some correlation between the magnetic moments, and correspondingly, the structures of the compounds formed and the pKa of the acid (see Table 1.2).

Table 1.1

Magnetic Data for Dimeric Cu(II) Compounds

Acid ligand	Compound	T°K	$\chi_a \times 10^6$ c.g.s.u.	μ B.M.	J cm. ⁻¹	Ref.
Acetic acid	Cu(CH ₃ COO) ₂	295	869	1.39	300	6
	Cu(CH ₃ COO) ₂ ·2H ₂ O	290	875	1.43	284	6
	Cu(CH ₃ COO) ₂ (C ₆ H ₅) ₃ P·O	299	959	1.52		9
	Cu(CH ₃ COO) ₂ py	290	839	1.35	325	12
Propionic acid	Cu(C ₂ H ₅ ·COO) ₂	289	854	1.36	300	10
Valeric acid	Cu(C ₄ H ₉ COO) ₂	293	899	1.41		10
Stearic acid	Cu(C ₁₇ H ₃₅ COO) ₂	290	846	1.36	278	10
Monochloroacetic acid	Cu(ClCH ₂ ·COO) ₂	289	923	1.42		11
Butyric acid	Cu(C ₃ H ₇ COO) ₂	290	816	1.35	322	12
	Cu(C ₃ H ₇ COO) ₂ aniline	290	1326	1.73	119	12
	Cu(C ₃ H ₇ COO) ₂ p-toluidine	290.5	1326	1.73	101	12

Table 1.2

PKa values and Magnetic Moments

Acid	pKa	Compound	Room temp. Moment
CH ₃ COOH	4.6	Cu(CH ₃ COO) ₂	1.39
ClCH ₂ .COOH	2.6-2.9	Cu(ClCH ₂ .COO) ₂	1.42
Cl ₂ CH.COOH	1.25	Cu(Cl ₂ CH.COO) ₂	1.66
Cl ₃ C.COOH	0.66	Cu(Cl ₃ C.COO) ₂	1.77
F ₃ C.COOH	0.33	Cu(F ₃ C.COO) ₂	1.90

Copper Formate Complexes

No solid anhydrous or hydrated species of copper formate have been found to be dimeric²⁰ although in some compounds, particularly the tetrahydrate, appreciable magnetic interaction occurs²⁰ (see also Table 1.3). However by forming adducts with pyridine, α , β and γ picolines, dioxan²² and urea^{23,24} compounds having behaviour typical of dimeric structures can be prepared. These have significantly higher J values than the corresponding acetate complexes ($J \approx 600 \text{ cm.}^{-1}$ compared with 300 cm.^{-1} ²²).

Electronic Spectra of Dimeric Copper Carboxylate Compounds

The crystal spectrum of copper acetate monohydrate shows three major bands^{25,26} at $14,000 \text{ cm.}^{-1}$, $27,000 \text{ cm.}^{-1}$ and $40,000 \text{ cm.}^{-1}$. The band at $14,000 \text{ cm.}^{-1}$ (band I) resembles the band found in $\text{Cu(II)SO}_4 \cdot 5\text{H}_2\text{O}$ ²⁷. The second weaker band at $27,000 \text{ cm.}^{-1}$ (band II) is absent in all but a few monomeric copper compounds; the third band at $40,000 \text{ cm.}^{-1}$ is intense.

Reimann et al.²⁸ detected a shoulder at approximately $11,000 \text{ cm.}^{-1}$ on band I which becomes pronounced at liquid nitrogen temperatures. Otherwise the spectrum is essentially temperature independent, the only effect upon cooling being a slight blue shift. Band (II) occurs in a wide range of dimeric copper compounds and the presence of this band has often been used as evidence for the existence of dimeric copper species in solution^{29,30,31}.

Table 1.3

Magnetic Data for Cu(II) Formate Complexes

Terminal ligand	Ref. Formula of complex	T°K / a x10 ⁶ c.g.s.u	μ	J*cm. ⁻¹	
	20 Cu(HCOO) ₂ royal blue	296	1566	1.90	
	20 Cu(HCOO) ₂ turquoise	291	1357	1.75	
	20 Cu(HCOO) ₂ blue	289	1174	1.61	
	20 Cu(HCOO) ₂ · 2H ₂ O	291	1591	1.90	
	20 Cu(HCOO) ₂ · 4H ₂ O	290	1200	1.67	
	22 Cu(HCOO) ₂ · (C ₆ H ₅ NH ₂)	296	1489	1.85	
Pyridine	22 Cu(HCOO) ₂ · py	304	523	1.07	550
2 methylpyridine	22 Cu(HCOO) ₂ · 2mepy	297	530	1.06	540
3 methylpyridine	22 Cu(HCOO) ₂ · 3mepy	299	560	1.10	512
4 methylpyridine	22 Cu(HCOO) ₂ · 4mepy	296	527	1.06	546

* J value shown was estimated from data obtained at 350°C;

considerable variation in J with temperature was found using

a constant $g = 2.16$.

Although the polarisibilities of the bands have been measured^{25,28} and several theoretical treatments carried out^{25,26,34} the bands have not been satisfactorily assigned; it is not known whether band (II) is charge transfer in origin or a d-d transition; this is further discussed in Chapter 2.

The Bonding in Dimeric Copper Compounds

The small separation between copper atoms in copper acetate has led to much discussion as to the nature of the bonding (if any) between copper atoms, and the mechanism for the magnetic interaction which occurs in these compounds.

The earliest approach to the problem was the δ bond postulated by Figgis and Martin⁶ involving direct overlap of dx^2-y^2 orbitals. This orbital function, i.e. dx^2-y^2 is concentrated in the xy plane and overlap calculations indicated that the overlap involved was extremely small. It was stressed that the binuclear configuration of the molecule was maintained by the bridging acetate groups and not by the direct influence of metal-metal bonding.

A strong σ bond involving overlap of dz^2 orbitals has also been postulated³⁴.

The δ bonded model was strongly supported by Ross³².

In a more recent treatment³⁴ the weak nature of the spin interaction has been stressed in the coupled chromophore model, in which a molecular orbital method was used, all overlap integrals between

orbitals on different chromophores being neglected. Other authors^{3,20,35} have postulated that the magnetic interaction occurs via the bridging acetate groups by means of a superexchange mechanism, but no detailed description of such a mechanism has been given.

Chromous Acetate

The diamagnetism of chromous acetate was reported by King and Garner. A single crystal X-ray diffraction study^{37,38} showed that chromous acetate is also a binuclear molecule isostructural with copper acetate. A more recent investigation of the magnetic properties of hydrated and anhydrous chromous acetates³⁹ showed them both to be slightly paramagnetic ($\mu \approx 0.5$ B.H.) Chromium(II) compounds, which are normally high spin, generally exhibit magnetic moments corresponding to four unpaired electrons⁴⁰. Thus any consideration of the bonding in copper acetate type complexes also has to account for the almost complete spin pairing found in the corresponding chromium(II) compounds.

Molybdenum(II) and Rhodium(II) Acetates

More recent studies have shown that other compounds adopt a dimeric structure. An X-ray determination of the crystal and molecular structure of diamagnetic molybdenum(II) acetate shows that this compound has a structure very similar to that of copper(II) acetate; the Mo-Mo separation is 2.11 Å.

Rhodium(II) acetate also adopts the same structure as copper acetate. The Rh..Rh separation is 2.45 \AA and the compound is again diamagnetic. Adducts are readily formed with donor type ligands such as triphenylphosphine, ammonia etc^{44,45}. The addition is frequently reversible and the adducts are presumably analogous to those formed with copper acetate, i.e. the basic dimeric unit is retained whilst various ligands occupy the terminal positions.

The work described in the first chapters of this thesis was undertaken with a view to furthering the understanding of the bonding in dimeric molecules of the cupric acetate type. Among the particular aspects to be studied were the influence of both terminal ligands on the magnetic interactions occurring in dimeric copper compounds, and the general correlation of metal-metal separations with the interactions in dimeric compounds.

CHAPTER 2

A range of compounds have been described in the literature in which the terminal water molecules in cupric acetate monohydrate have been replaced by neutral ligands, such as pyridine⁸. Here the preparation and properties of a series of new compounds, $R_4N[Cu(CH_3COO)_2X]$ where $X = NCS, NO_2$ or Br are reported. In these compounds the water molecules have been replaced by anions. $Me_4N.NCS$ has also been found to induce the dimerisation of cupric formate and the preparation and properties of the dimeric compound $Me_4N[Cu(HCOO)_2NCS]$ are also reported. X-ray crystallographic structural determinations have been carried out, in the crystallography department^{46, 47} on the pair of compounds $Me_4N[Cu(RCOO)_2NCS]$, $R = CH_3$ or H .

Acetate Complexes (R = CH₃)

The compound where $X = NCS$ precipitated immediately when ethanolic solutions of cupric acetate monohydrate and tetramethylammonium thiocyanate were mixed. However the analogous complexes formed by tetramethylammonium nitrite and tetraethylammonium bromide are much more soluble in this solvent and were obtained in the solid state only by the addition of diethyl ether to the concentrated solutions. Despite this method of preparation, X-ray powder

photographs showed that they were true compounds and not mixtures of the quaternary ammonium salts and cupric acetate. A crystalline specimen of the thiocyanate complex was obtained from 2-methoxyethanol.

Me₄N[Cu(HCOO)₂NCS]

This compound precipitated when methanolic solutions of cupric formate tetrahydrate and tetramethyl ammonium thiocyanate were mixed at room temperature. (At higher temperatures, or in the presence of excess tetramethyl ammonium thiocyanate, some reduction of Cu(II) to Cu(I) occurred). Crystalline specimens of this compound were also obtained using 2-methoxyethanol as solvent.

Infrared Spectra of Compounds

The manner of coordination of the ions NCS⁻ and NO₂⁻ in these compounds can be inferred from their infrared spectra (Table 2.1).

Table 2.1

Infrared data (frequencies in cm.⁻¹)

Compound	ν_{C-N}	ν_{C-S}	
Me ₄ N[Cu(CH ₃ COO) ₂ NCS]	2070	784w	
Me ₄ N[Cu(H ₃ COO) ₂ NCS]	2070	790w	
	$\nu_{N=O}$	ν_{N-O}	δ_{NO_2}
Me ₄ N[Cu(CH ₃ COO) ₂ ONO]	1347	1165	810

The values of the C-N and C-S stretches found for the complexes $\text{Me}_4\text{N}[\text{Cu}(\text{R}_2\text{COO})_2\text{NCS}]$ ($\text{R} = \text{H}$ or CH_3) are within the ranges expected for the coordination of the NCS group through the nitrogen atom⁴⁸; this was subsequently confirmed by the X-ray structural determinations.

The spectrum of the nitrite complex has bands due to the coordinated nitrite (O-N-O) group assignable as follows 1347 cm.^{-1} ($\nu_{\text{N=O}}$) 1165 cm.^{-1} ($\nu_{\text{N-O}}$) and 810 cm.^{-1} NO_2 deformation. (The terminology used here is discussed in Chapter 6). These results, particularly the frequency of $\nu_{(\text{N-O})}$ are in accord with the presence of nitrito groups^{49,50}. This mode of coordination is perhaps somewhat surprising since here there do not seem to be any steric or kinetic factors operating to prevent the formation of the more usual M- NO_2 linkages. It is shown later however (Chapters 8 and 10) that M-ONO linkages occur in cases where crystal field stabilisation energy considerations are not important; this would be the case here, the terminal ligand appearing to have little influence on the electronic structure of the dimer unit.

The positions of the C-O stretching frequencies in the infrared spectrum of the formate compound are of interest as symmetrically bridged formate groups are not well characterised.

In a series of compounds containing bridging acetate groups the stretching frequencies show a regular shift from the free ion positions (Table 2.2), both bands being shifted to higher frequencies,

Table 2.2

COO Stretching frequencies in symmetrical coordination

Compound	Frequencies (cm. ⁻¹)		Ref.
	ν_{as}	ν_s	
Cr(CH ₃ COO) ₂ ·H ₂ O	1575	1420	51*
Cu(CH ₃ COO) ₂ ·H ₂ O	1605	1425	"
Be ₄ O(CH ₃ COO) ₆	1603	1447	"
Zn ₄ O(CH ₃ COO) ₆	1639	1489	"
Me ₄ N[Cu(HCOO) ₂ NCS]	1626	1366	a
Me ₄ N[Cu(CH ₃ COO) ₂ NCS]	1610	1425	a
Me ₄ N[Cu ₃ COO) ₂ ONO]	1606	1423	a
Et ₄ N[Cu(CH ₃ COO) ₂ Br]	1617	1413	a
Free ion values			
Na ₂ OOC·CH ₃	1578	1414	52 ^o
Na ₂ OOC·H	1567	1366	"

a this work

* spectra measured in KBr discs

^o measured using thin film of solid.

a pattern which is also shown in the anionic complexes. In solid sodium formate the C-O stretching frequencies occur at 1567 cm.^{-1} and 1366 cm.^{-1} . Unfortunately another strong band assigned by Itoh and Bernstein as a COO rocking mode occurs at 1377 cm.^{-1} . $\nu_{\text{as}}(\text{COO})$ can readily be assigned in the dimeric formate complex to the strong band which occurs at 1626 cm.^{-1} . A split strong band occurs at $1366, 1351 \text{ cm.}^{-1}$. The band at 1366 cm.^{-1} is assigned as $\nu_{\text{s}}(\text{COO})$ on the basis that a similar pattern of frequency shifts might be expected as that which occurs in the acetate complexes.

The compounds $\text{Cu}(\text{HCOO})_2 \cdot \text{L}$, where L = py, 2-mepy, 3-mepy or 4-mepy all show a strong band between 1625 and 1630 cm.^{-1} which can also be assigned to $\nu_{\text{as}}(\text{COO})$ but in these ^{complexes} ligand modes make the assignment of ν_{sym} more difficult. The COO deformation mode at 775 cm.^{-1} in $\text{Me}_4\text{N}[\text{Cu}(\text{HCOO})_2\text{NCS}]$ shows a negligible shift from the free ion value.

A shoulder at 1567 cm.^{-1} of low and varying intensity occurred in the infrared spectrum of samples of $\text{Me}_4\text{N}[\text{Cu}(\text{HCOO})_2\text{NCS}]$. This can be assigned to small quantities of monomeric impurities. The concentrations of this are deduced below from susceptibility and electron spin resonance studies.

Visible and Near Infrared Spectra

These were obtained as reflectance spectra from the solid compounds (Table 2.3, Fig.2a).

The main features of the spectra of the anionic compounds are similar to those of the uncharged adducts of cupric acetate. The energy of band I is known to vary somewhat on changing the terminal ligand. With the anionic complexes studied here this band is shifted to low energies relative to cupric acetate monohydrate and the pyridine adduct⁵³. It has been suggested that the position of band I can be correlated with the "donor"⁵⁴ or "ligand field"⁵³ strength of the terminal group L in $\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{L}$. This does not seem to be the case for these anionic complexes in the solid state. The variation in the position of band I on replacing NCS^- by ONO^- or Br^- is quite small, and although the bromide ion lies well below N-bonded thiocyanate in the spectrochemical series, band I for the bromo complex is at lower energy than that of its isothiocyanato analogue.

The spectrum of the bromo complex showed a small shoulder at $\sim 19,000 \text{ cm.}^{-1}$ on the high energy side of band I. This may be due to the presence of a small amount of the compound $(\text{Et}_4\text{N})_2\text{CuBr}_4$, which is known⁵⁵ to contain a very strong band at $19,000 \text{ cm.}^{-1}$ (ϵ molar ~ 2200). However the powder photograph of the bromo complex of cupric acetate contained no lines attributable to tetraethylammonium

Table 2.3

Reflectance Spectra of Compounds (cm.⁻¹)

<u>Compound</u>	<u>Band II</u>	<u>Band I</u>	<u>Temp.</u>
Me ₄ N[Cu(CH ₃ COO) ₂ NCS]	≈ 26,000br	13,300	RT
	≈ 26,000br	13,800 ≈ 8500sh	≈ 95°K
Me ₄ N[Cu(CH ₃ COO) ₂ ONO]	≈ 26,200br	~ 23,500sh 13,400	RT
MEtN[Cu(CH ₃ COO) ₂ Br]	≈ 26,000br	≈ 19,000sh* 13,100	RT
Me ₄ N[Cu(HCOO) ₂ NCS]	≈ 25,400br	12,900	RT
	≈ 25,700br	13,300, 8,850sh	≈ 95°K

br broad

sh shoulder

RT room temperature

* Possibly due to Et₄NCuBr₄ impurity

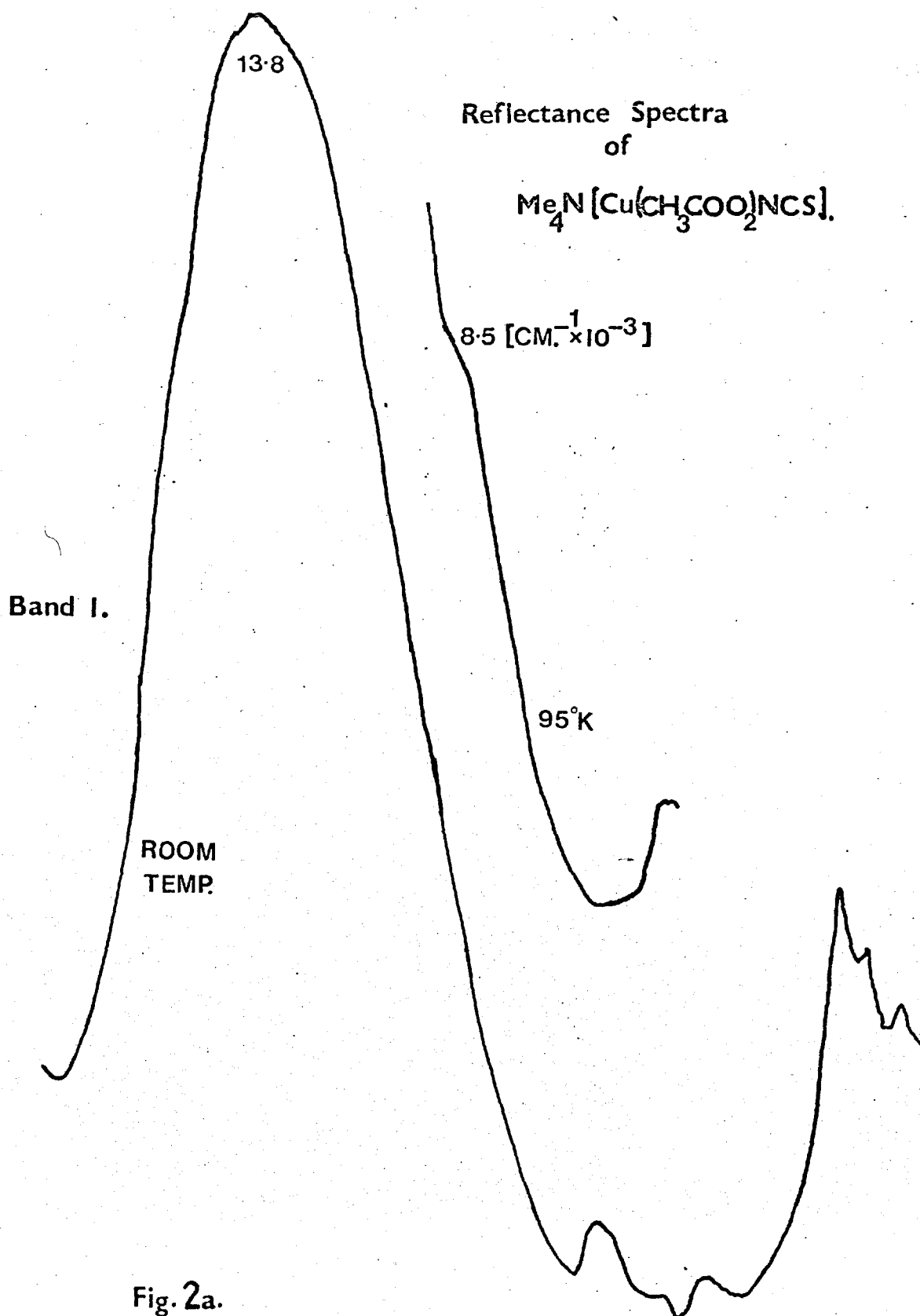


Fig. 2a.

tetrabromocuprate(II), so that if this is present, it is only in a small amount. A small shoulder is also present in the spectrum of the nitrito compound at $\sim 23,500 \text{ cm.}^{-1}$ on the low energy side of band II. No comparable absorption has been found for the neutral dimeric copper(II) carboxylates, though band (II) is usually quite broad.

In the formate complex, band I is again shifted to lower energy relative to its position in cupric acetate monohydrate. Low temperature spectra of all the complexes show a shoulder on the low energy side of band I, Fig.2a, as has been previously observed in the spectrum of copper acetate²⁸.

The bands in the electronic spectrum of copper acetate have not been unambiguously assigned. The assignment of band II has caused most debate. Originally Tsuchida and Yamada^{31,62}, from single crystal spectral studies suggested that the band was a diagnostic property of this type of dimeric Cu-Cu unit. The association of the band with the binuclear structure was confirmed by cryoscopic and magnetic measurements^{29,30}. Forster and Ballhausen²⁶ and Boudreaux⁵⁶ assigned band II as an electron transition between Cu-Cu molecular orbitals. More recently Hansen and Ballhausen³⁴ using the weakly coupled chromophore model assigned band II as a double electron excitation $3dz^2 \rightarrow 3dx^2-y^2$. In contrast Kokoszka et al.⁵⁷ have favoured the single electron

excitation $3dz^2 \rightarrow 3dx^2-y^2$ within the monomer components of the binuclear structure. Band II has also been assigned as a charge transfer band³⁸ characteristic of the bridging π system rather than of the binuclear structure.

Treatments^{26,56} which have considered a strong σ bond formed by dz^2 overlap can now be considered invalid in view of e.s.r. evidence³⁷ that the unpaired electrons occupy a dx^2-y^2 orbital, and also in view of the structural and magnetic evidence presented in this thesis, that the interaction between the copper atoms is not a strong bonding one. Otherwise however the rather insensitive nature of the band positions to changes in terminal ligands and bridging groups makes assignments difficult and unfortunately the reflectance spectra reported here add little to the understanding of the origins of the bands.

It is of interest to note the occurrence of charge transfer bands in approximately the position of band II in monomeric complexes with substituted acetylacetonate ligands^{39, 60, 61}.

Magnetic Susceptibility Measurements

The room temperature magnetic moments of the compounds are listed in Table 2.4. As has been found for other dimeric formate and acetate complexes the formate has an appreciably lower room temperature moment.

Table 2.4

Room Temperature Magnetic Moments of Compounds

Compound	Temp. °K	$10^6 \chi_{\text{Cu}}$ c.g.s.u.	μ (B.M.)*
$\text{Me}_4\text{N}[\text{Cu}(\text{CH}_3\text{COO})_2\text{NCS}]$	292	880	1.44
$\text{Me}_4\text{N}[\text{Cu}(\text{CH}_3\text{COO})_2(\text{ONO})]$	295	872	1.44
$\text{Et}_4\text{N}[\text{Cu}(\text{CH}_3\text{COO})_2\text{Br}]$	295	860	1.43
$\text{Me}_4\text{N}[\text{Cu}(\text{H.COO})_2\text{NCS}]$	296	519	1.11

* calculated from Curie Law

Table 2.5

Temperature-dependence of χ_{Cu} for $\text{Me}_4\text{N}[\text{Cu}(\text{CH}_3\text{COO})_2\text{NCS}]$

Temp.°K	292	272	247	218	188	160	152	135	130
$10^6 \chi_{\text{Cu}}$ *	820	816	803	765	680	579	500	435	350

* corrected for $N\alpha = 60 \times 10^{-6}$ c.g.s.u.

Diamagnetic correction for ligands (from Pascals constants)

 163×10^{-6} c.g.s.u.Temperature dependence of χ_{Cu} for $\text{Me}_4\text{N}[\text{Cu}(\text{HCOO})_2\text{NCS}]$

Temp.°K	296	264	245	225	197	177	153	126	98	86
$10^6 \chi_{\text{Cu}}$ *	459	390	383	365	304	204	149	103	48	38

* Corrected for $N\alpha = 60 \times 10^{-6}$ c.g.s.u.

Diamagnetic correction for ligands (from Pascals constants)

 145×10^{-6} c.g.s.u.

The temperature variation of the susceptibilities for the isothiocyanate complexes is shown in Fig.2(b) and Table 2.5. The theoretical curves plotted are calculated from the usual expression for the temperature variation of the magnetic susceptibility (eqn 1a) taking a value of 60 c.g.s.u. for the T.I.P. contribution per mole of copper. The g values used in the calculations are those obtained from the e.s.r. studies described in Chapter 3.

The formate complex could not be prepared totally free of a monomeric impurity. Because of the very low susceptibility of the formate small traces of this impurity have a large influence on the temperature variation of susceptibility. Thus some powder samples had susceptibilities of approximately 200 c.g.s.u. at $\approx 90^\circ\text{K}$. The temperature variation of susceptibility for these could be fitted to an expression.

$$\chi_{\text{exp}} = \frac{Ng^2\beta^2}{3KT} \left[1 + \frac{1}{3} \exp J/KT \right]^{-1} (1 - X) + X \frac{(0.448)}{T} + N\alpha$$

derived by assuming that the impurity is a monomeric Cu(II) species with a normal magnetic moment, i.e. 1.9 B.M.'s, and that it obeys the Curie Law; X being the mole fraction of monomer.

With a J value of the order found for the formate, at the lowest temperature the susceptibility will be entirely from the

Temperature Dependence
of Susceptibility

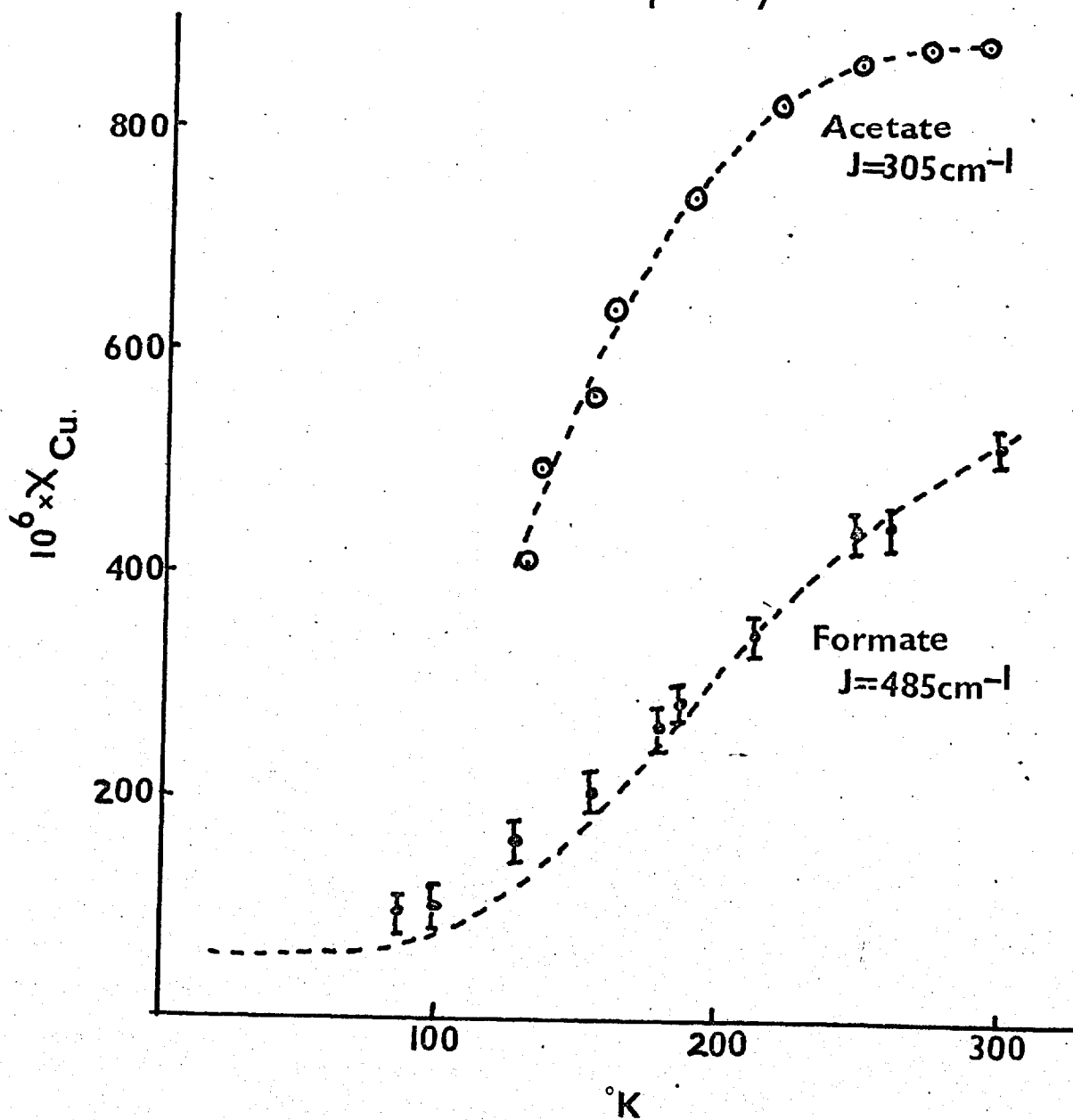


Fig.2b.

monomer plus the contribution from the temperature independent paramagnetism of copper, i.e.

$$\chi_{\text{exp}} = \frac{\chi_{\text{monomer}}(0.448)}{T} + N\alpha$$

Thus a susceptibility of 200 c.g.s.u. at 80°A corresponds to a 0.025 mole fraction of monomer if a value of 60 c.g.s.u. is assumed for the T.I.P. component.

Previous magnetic measurements on dimeric formate complexes have suggested that the susceptibility measured at low temperatures for these compounds is a direct measure of the T.I.P. contribution²²; values ranging from 120 - 160 c.g.s.u. were obtained. E.s.r. measurements carried out on samples of these compounds indicate that they also contain monomeric impurities, so that in fact no direct measure of the T.I.P. contribution can be made from susceptibility measurements without an independent method of checking for the absence of S = 1/2 impurities.

Crystalline samples of the formate and acetate compounds could be prepared in only small yield so that sufficient material could not be obtained for Gouy measurements of the magnetic susceptibility. X-ray powder patterns indicated that the powder and crystalline samples had the same structure. Magnetic moments were obtained for a series of crystalline and powder samples using a Faraday

balance, which requires only a small amount of material.* The crystalline samples of the formate and acetate were found to have the same room temperature moments as the powder samples of the same compounds.

The very low susceptibility of the formate complex led to considerable errors in the susceptibility data but calculations from the data for the two compounds show that for the acetate $J = 305 \pm 10 \text{ cm.}^{-1}$ and for the formate $J = 485 \pm 30 \text{ cm.}^{-1}$. Similar values have been found previously for related dimeric formate and acetate complexes²². In all cases so far studied appreciably greater spin exchange occurs in the formate complex compared with the acetate analogue.

X-ray Crystal Structures of the Compounds

Determinations of the crystal and molecular structures of $\text{Me}_4\text{N}[\text{Cu}(\text{CH}_3\text{COO})_2\text{NCS}]$ and $\text{Me}_4\text{N}[\text{Cu}(\text{HCOO})_2\text{NCS}]$ were carried out by single crystal X-ray methods, in the crystallographic department^{46,47}. Because the structures are of great importance when discussing the bonding and magnetic interactions which occur in these compounds,

* I would like to thank Dr D.M.L. Goodgame for carrying out these measurements and also Dr G.J. Hill of the Electrical Research Associates Laboratories, Leatherhead, for the use of the Faraday balance employed.

they are quoted in some detail here.

The compounds formed green tetragonal crystals with the following unit cell dimensions: $\text{Me}_4\text{N}[\text{Cu}(\text{HCOO})_2\text{NCS}]$ $a = 8.917$, $c = 15.800 \text{ \AA}$, $U = 1256.3 \text{ \AA}^3$, $Z = 2$; $\text{Me}_4\text{N}[\text{Cu}(\text{CH}_3\text{COO})_2\text{NCS}]$ $a = 8.873$, $c = 18.087 \text{ \AA}$, $U = 1424 \text{ \AA}^3$, $Z = 2$.

The main bond distances and bond angles of the two dimeric anions are shown in Fig. 2(c) and 2(d), in each case two of the bridging groups have been omitted for clarity. In both cases the copper atoms and the thiocyanate ligands lie on fourfold axes. In the acetate the Cu...Cu separation of 2.638 \AA ($\delta = 0.003 \text{ \AA}$) is typical of dimeric cupric acetate complexes. In the formate the Cu...Cu separation is 2.716 \AA ($\sigma = 0.002 \text{ \AA}$). Thus the longer Cu...Cu separation occurs in the compound with the greater spin exchange. The significance of this is discussed fully in Chapter 5.

Experimental

Preparation of the Compounds

The complex $(\text{Me}_4\text{N})[\text{Cu}(\text{CH}_3\text{COO})_2\text{NCS}]$. A solution of tetramethyl ammonium thiocyanate (1.8 g) in warm $\sim 40^\circ$ ethanol (70 ml) was added slowly and with stirring to an ethanolic solution of cupric acetate monohydrate (3 gm in 80 ml). The pale green complex precipitated immediately and was filtered, washed with ethanol and dried in vacuo (67% yield).

Found: C, 34.5: H, 5.6: Cu, 20.4: $C_9H_{18}CuN_2O_4S$ requires
C, 34.4: H, 5.9: Cu 20.2%.

The complex $(Me_4N)[Cu(CH_3COO)_2ONO]$. A solution of tetramethyl ammonium nitrite (2.4 gm) in methanol (100 ml) was added to an ethanolic solution of cupric acetate monohydrate (4 g in 120 ml). The solution was concentrated to approximately 25 ml by evaporation under reduced pressure. Slow addition of diethyl ether to this solution resulted in the precipitation of the pale green complex which was filtered off, washed with diethyl ether and dried in vacuo 49% yield.

Found: C, 32.1: H, 5.9: Cu, 20.4: $C_8H_{18}CuN_2O_6$ requires
C, 31.8: H, 6.0: Cu, 21.05%.

The complex $(Et_4N)Cu(CH_3COO)_2Br$. An ethanolic solution of tetraethylammonium bromide (2.1 gm in 50 ml) was shaken vigorously for 15 min. with solid cupric acetate monohydrate (2 gm). Treatment of the resulting solution by the procedure described for the previous compound gave a green complex (possibly contaminated with a small amount of tetraethylammonium tetrabromocuprate(II)).

Found: C, 36.6: H, 7.0: Br, 21.0: Cu 15.7: $C_{12}H_{26}BrCuNO_4$
requires C, 36.8: H, 6.7: Br, 20.4: Cu 16.2: N, 3.6%. The compound is slightly hygroscopic.

Crystals of $\text{Me}_2\text{N}[\text{Cu}(\text{CH}_3\text{COO})_2\text{NCS}]$ for X-ray crystallographic studies were prepared using 2-methoxyethanol as solvent. A saturated solution of tetramethylammonium thiocyanate in 2-methoxy ethanol was added dropwise to a saturated solution of cupric acetate monohydrate in warm (60°) 2-methoxyethanol until the solution became apple green coloured (addition of more $\text{Me}_2\text{N}\cdot\text{NCS}$ solution results in the solution becoming brown coloured and some reduction to copper(I) occurs). The solution was cooled in a fridge for a few hours; green crystals were deposited in low yield. The crystals were filtered off, washed with 2-methoxyethanol and ether and dried in vacuo.

The complex $\text{Me}_4\text{N}[\text{Cu}(\text{HCOO})_2\text{NCS}]$. A solution of $\text{Me}_4\text{N}\cdot\text{NCS}$ (1.3 gm 0.01M) in methanol (25 ml) was added dropwise to a vigorously stirred solution of cupric formate tetrahydrate (2.2 gm 0.01M) in methanol (100 ml). Both solutions were at room temperature. A green finely divided precipitate formed rapidly which was filtered off, washed with methanol and ether and dried in vacuo. Yield 30%.

Analysis

Found C, 29.37; H, 4.96; N, 9.66; $\text{C}_7\text{H}_{14}\text{CuN}_2\text{O}_4\text{S}$ requires
C, 29.41; H, 4.94; N, 9.80.

If hot solutions are mixed, or if the precipitation of the complex takes place over a long period a white crystalline cuprous complex is formed.

The cupric formate tetrahydrate used in the above preparation was prepared by reacting Merck's puriss. copper carbonate with excess dilute AnalaR formic acid and crystallising the tetrahydrate from solution.

Crystalline specimens of $\text{Me}_4\text{NCu}(\text{HCOO})_2\text{NCS}$ were obtained by adding a warm (60°C) solution of $\text{Me}_4\text{N}_2\text{NCS}$ in 2-methoxy ethanol to a saturated solution of copper formate tetrahydrate in warm (60°) 2-methoxy ethanol. The solution was cooled in a fridge for a few hours. The bright green crystals which formed in small yield were filtered off, washed with 2-methoxy ethanol and then ether and dried in vacuo.

Analysis found C, 29.10: H, 4.93: N, 9.80. $\text{C}_7\text{H}_{14}\text{CuN}_2\text{O}_4\text{S}$ requires C, 29.41: H, 4.94: N, 9.80.

Attempts to prepare other anionic dimeric compounds

Attempts to make other compounds of this type with various anions, using methods essentially similar to those employed for the compounds described above, were unsuccessful; iodide, cyanide or selenocyanate ions reduced the Cu(II) under these conditions. Tetraethylammonium cyanate gave a green compound with cupric acetate the I.R. spectrum

of which contained a band at 2190 cm.^{-1} assignable as the CN stretch of a NCO group⁶³ and also bands due to the tetraethylammonium ion and acetate. However satisfactory analyses could not be obtained for this compound.

CHAPTER 3

Electron Spin Resonance (E.s.r.) Studies on Dimeric Copper(II)Carboxylate Complexes

Most magnetic studies carried out on dimeric copper(II) carboxylate complexes have been measurements of magnetic susceptibilities⁸. In fitting theoretical curves to temperature variation of susceptibility data, using the usual expression for the susceptibility, i.e.

$$\chi = \frac{Ng^2\beta^2}{3KT} \left[1 + \frac{1}{3} \exp(J/KT) \right]^{-1} + N\alpha,$$

three parameters, g , J , and $N\alpha$ can be varied. $N\alpha$ is usually assumed to be 60 cgs units, but this still leaves two variable parameters g and J . E.s.r. studies of the complexes $\text{Me}_4\text{N}[(\text{R.COO})_2\text{NCS}]$, $\text{R} = \text{CH}_3$ or H , were carried out as an independent means of determining the g values for these complexes. The average g values obtained for the complexes was then used to calculate J values from the temperature variation of susceptibility data reported above.

E.s.r. studies of dimeric complexes are relatively few^{16, 37, 65-69, 109} largely because only recently⁷⁰ has the possibility of obtaining the e.s.r. parameters from the spectra of powder samples been realised. The e.s.r. spectrum of copper acetate is anomalous^{3, 33, 64} giving a spectrum for a species with resultant spin $S = 1$. The spin

Hamiltonian for the triplet state of dimeric copper compounds is given by³:

$$\mathcal{H} = \beta H g_s + D S_z^2 + E(S_x^2 - S_y^2) - \frac{2}{3}D$$

where D and E are the zero field splitting parameters, β is the Bohr magneton and x, y and z are a principal axes coordinate system fixed with respect to the Cu-Cu bond.

In a study of the e.s.r. spectra of the triplet states of randomly orientated molecules Wasserman, Snyder and Yager⁷⁰ found that although absorption occurred over a range of several thousand gauss, the shape of the derivative curve gives special prominence to the resonant fields in which the external field lies along one of the principal magnetic axes of the triplet. These are the orientations most useful for the derivation of the zero field parameters.

When the magnetic field is along respectively the x, y and z directions the six $\Delta M = \pm 1$ resonance fields:

$$H_{x_1}^2 = \left(\frac{g_e}{g_x}\right)^2 [(H_0 - D' + E')(H_0 + 2E')]$$

$$H_{x_2}^2 = \left(\frac{g_e}{g_x}\right)^2 [(H_0 + D' - E')(H_0 - 2E')]$$

$$H_{y_1}^2 = \left(\frac{g_e}{g_y}\right)^2 [(H_0 - D' + E')(H_0 - 2E')]$$

$$H_{y_2}^2 = \left(\frac{g_e}{g_y}\right)^2 [(H_0 + D' + E')(H_0 + 2E')]$$

$$H_{z_1}^2 = \left(\frac{g_e}{g_z}\right)^2 [(H_0 - D')^2 - E'^2]$$

$$H_{z_2}^2 = \left(\frac{g_e}{g_z}\right)^2 [(H_0 + D')^2 - E'^2]$$

are obtained⁷⁰ where $H_0 = \frac{h\nu}{g_e\beta}$, $D' = \frac{D}{g_e\beta}$ and $E' = E/g_e\beta$. H_{x_1} and H_{x_2} are, for example, the two $\Delta M = \pm 1$ resonance fields when the magnetic field is along the x direction and g_e is the free electron g value. In addition to the six lines given by the equations above if $D < h\nu$ an additional line corresponding to the $\Delta M = \pm 2$ transition may be observed⁷⁰. This is quite isotropic and thus would appear as one additional line in the powder spectrum. Using X-band radiation ($h\nu \approx 0.3 \text{ cm.}^{-1}$) the D values which have been observed in copper dimers are usually greater than $h\nu$.

The room temperature e.s.r. spectrum obtained for a powdered sample of $\text{Me}_4\text{N}[\text{Cu}(\text{CH}_3\text{COO})_2\text{NCS}]$ is shown in Fig.3(a). Using the nomenclature from the above equations and assuming $D > h\nu$ the low and high field peaks are assigned as H_{z_1} and H_{z_2} respectively. As no splitting of the midfield peak is observed at liquid nitrogen temperatures $E \approx 0$, under these conditions the observed resonance occurs at fields given by

Room Temp. E.s.r. Spectrum of $\text{Me}_4\text{N}[\text{Cu}(\text{CH}_3\text{COO})_2\text{NCS}]$.

(Field Values in gauss).

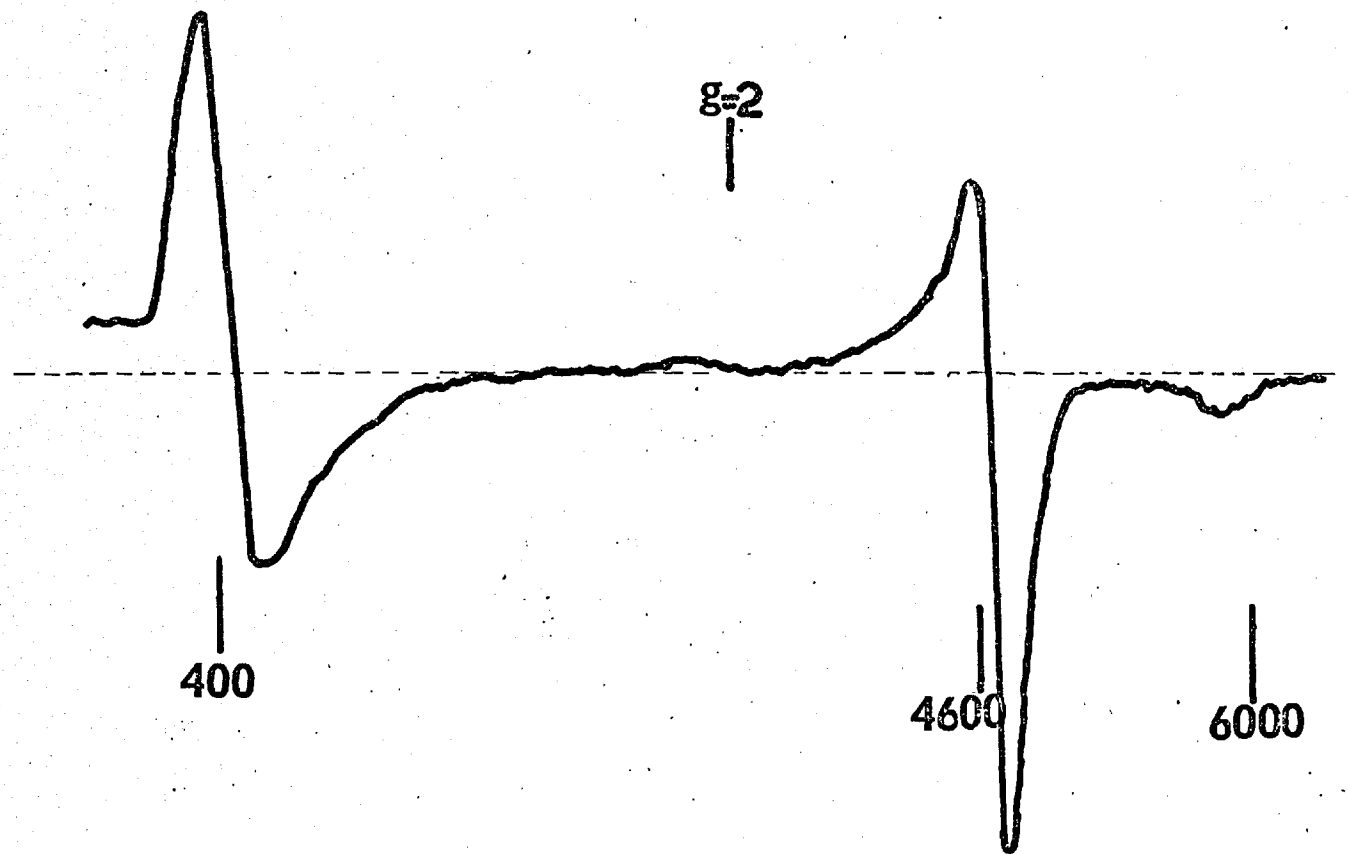


Fig.3a.

$$H_{12}^2 = \left(\frac{g_e}{g_1}\right)^2 [H_0(H_0 + D')] \quad (x \text{ and } y \text{ are now equivalent and denoted by } \perp)$$

$$H_{z1} = -\left(\frac{g_e}{g_z}\right) (H_0 - D')$$

$$H_{z2} = \left(\frac{g_e}{g_z}\right) (H_0 + D')$$

Substitution in these equations leads to values of $g_z = 2.36$, $g_{\perp} = 2.07$, $D = 0.34$, which are similar to those found for cupric acetate monohydrate (see below). At low temperatures (-160°C) hyperfine splittings are observed on both H_{z1} and H_{z2} (see Fig.3(b)). This seven line pattern is typical of dimeric copper compounds^{3, 66, 70}, showing interaction with both copper nuclei. In this compound the observed splitting is 65 gauss. The midfield absorption ($H_{\perp 2}$) becomes much narrower at low temperature but remains unsplit indicating that $E \approx 0$.

The value of the method for obtaining approximate e.s.r. parameters is confirmed by comparing the values obtained for copper acetate monohydrate, i.e. $g_z = 2.35$, $g_{\perp} = 2.08$, $D = 0.34 \text{ cm.}^{-1}$ with those obtained from more accurate single crystal data³³ $g_z = 2.344 \pm 0.01$, $g_x = 2.053 \pm 0.005$, $g_y = 2.093 \pm 0.005$, $D = 345 \text{ cm.}^{-1}$. (There is some discrepancy in the literature regarding the g values for cupric acetate. The original work of Bleaney and Bowers³ quotes $g_z = 2.42 \pm 0.03$, $g_{\perp} = 2.08 \pm 0.03$.

Subsequent determinations, also from single crystal studies⁵⁷ agree with the data from Abe and Shimada³³ quoted above.

E is significantly large in cupric acetate for H_{\perp} to be split at low temperatures, for the calculations here the resonance was assumed to occur at the mid point of the split line, i.e. $E = 0$.

In the e.s.r. spectrum of $Me_4N[Cu(HCOO)_2NCS]$ the resonances occur at higher fields and the calculated parameters i.e. $g_z = 2.40$, $g_{\perp} = 2.09$, $D = 0.44$ show that both the g values and the zero field splitting parameter D are significantly greater for the formate than the acetate. No hyperfine splitting was observed on the spectrum of the formate, and the midfield peak was unsplit at low temperatures, which again indicates that $E \approx 0$. The higher g values observed for the formate reflect the higher value of the spin orbit coupling constant to be expected in this compound, because of the decreased covalency in the metal ligand interaction relative to that in the acetate.^{57,111,112,113}

The room temperature X-band spectrum of the formate included a small peak at ≈ 3200 gauss. The hyperfine structure observed on this peak at low temperatures (Fig.3(c)) and the fact that the intensity of the line increased with decreasing temperature indicates it was due to the presence of an $S = \frac{1}{2}$ impurity. Qualitative measurements indicated that this was present in small quantity, less than 5% in agreement with the magnetic susceptibility data quoted above. The

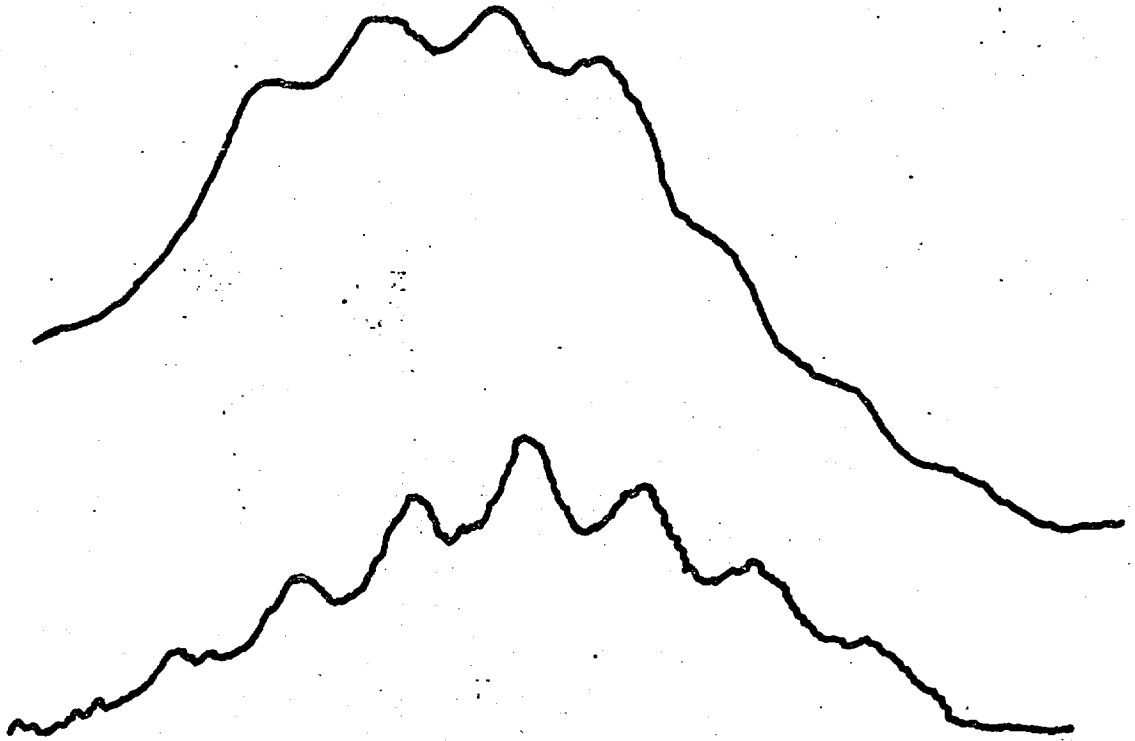


Fig-3b

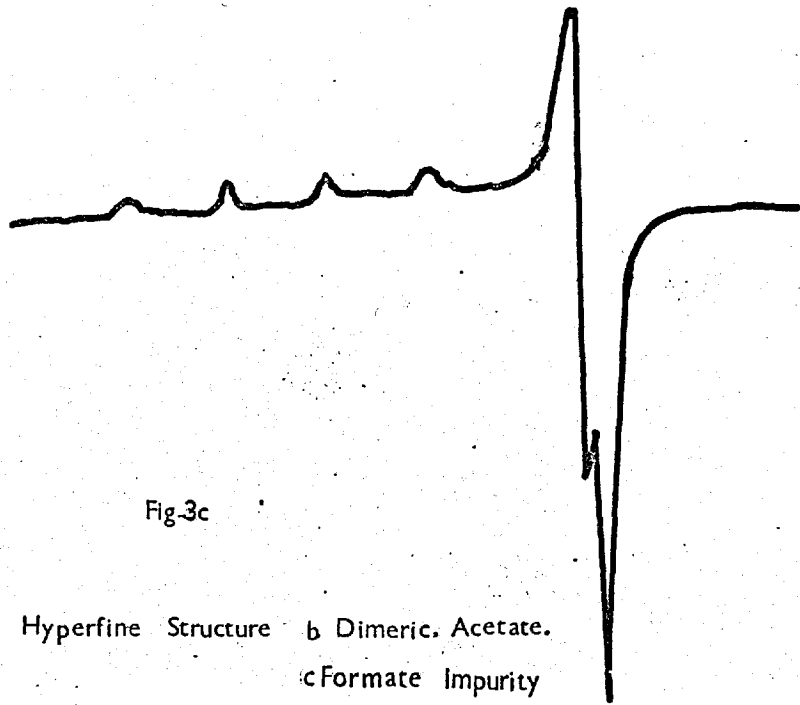


Fig-3c

Hyperfine Structure b Dimeric. Acetate.
 c Formate Impurity

spectrum of the acetate isothiocyanate complexes showed only traces of $S=1$ impurity in this compound. The e.s.r. spectra of powder and crystalline samples of $Me_4N[Cu(HCOO)_2NCS]$ were identical.

Calculated parameters determined by the method described above are listed in Table 3.1.

Table 3.1

E.s.r. Parameters: Dimeric Carboxylate Compounds

	g_2	g_1	D
$Me_4N[Cu(CH_3COO)_2ONO]$	2.36	2.07	0.34
$Et_4N[Cu(CH_3COO)_2Br]$	2.36	2.08	0.35
$Me_4N[Cu(CH_3COO)_2NCS]$	2.36	2.07	0.34
$Me_4N[Cu(HCOO)_2NCS]$	2.41	2.09	0.44

The e.s.r. spectra of copper butyrate and its aniline adduct are also of interest. The spectrum of the butyrate is typical of a dimeric compound, although the bands are broader than usual. The aniline adduct, which has been reported to have a much lower J value, gives an extremely broad absorption centred at approximately $g = 2$, which is not resolved at low

temperatures. Similarly results have been reported for other complexes with low J values, when it was postulated that the broadening and averaging effects could be due to magnetic dipole interactions between clusters of dimer units in the triplet state. E.s.r. spectra thus do not provide unambiguous evidence as to whether or not a copper compound is dimeric.

Preparation of Compounds

The preparation of the compounds mentioned in this chapter have all been previously described, either in this thesis, or in the references given below.

$\text{Cu}(\text{C}_3\text{H}_7\text{COO})_2$ and $\text{Cu}(\text{C}_2\text{H}_7\text{COO})_2$ aniline reference 12.

CHAPTER 4

Chromium(II) Complexes

Chromium acetate is a dimeric complex with a very similar crystal structure* to that of cupric acetate³⁸. However, the interactions in this molecule are such as to lead to almost complete spin pairing; a magnetic moment of 0.53 B.M. has been reported³⁹ for chromous acetate monohydrate. Some exploratory work was carried out to determine whether chromium(II) complexes analogous to the Cu(II) complexes reported above occur, and secondly if these could be obtained as crystalline samples suitable for X-ray structural determination.

The complex $\text{Me}_4\text{N}[\text{Cr}(\text{CH}_3\text{COO})_2\text{NCS}]$ was isolated as a purple solid; powder patterns indicated that it was isomorphous with the cupric analogue. Like chromous acetate it has a magnetic moment of ≈ 0.6 B.M. The C-N and C-S stretching frequencies are within the range expected for isothiocyanate groups at 2075 and 781 cm.^{-1} respectively.

The reflectance spectrum of the solid shows a strong broad band at 19,050 cm.^{-1} , with a weaker band at 24,600 cm.^{-1} . This is very similar to the reported solution spectrum of chromous acetate monohydrate⁵⁸, although both bands were not resolved in this case, the band at $\approx 25,000$ cm.^{-1} being filled by a gaussian

* The Cr...Cr separation in chromous acetate is sometimes quoted¹¹⁹ as being 2.46 Å. In fact in the structural determination referred to it was concluded that this distance is 2.64 Å, as in cupric acetate.

analysis of the spectrum obtained. Small traces of Cr(III) impurities also give rise to a band at $\approx 25,000 \text{ cm.}^{-1}$, and this band is particularly difficult to eliminate from the reflectance spectra of Cr(II) complexes¹⁰⁷, but the band observed appears to be too intense to be entirely due to surface impurities.

Attempts to obtain a crystalline sample of the above complex were unsuccessful, when chromous acetate was precipitated from water in the presence of $\text{Me}_4\text{N.NCS}$, pale blue crystals were obtained together with the red acetate. A sample of this complex was isolated and was found to be $(\text{Me}_4\text{N})_4[\text{Cr}(\text{NCS})_6]$. The infrared spectrum of this complex suggests the presence of isothiocyanate groups, the C-N stretching frequency occurs at 2075 cm.^{-1} and the C-S stretch as a split band at 807 and 793 cm.^{-1} .

Although chromous formate was found to react with ethanolic solutions of tetramethyl ammonium thiocyanate to give a purple solid a pure sample of this compound was not isolated.

Preparation of the Complexes

The preparation of the complexes was carried out in a glove box. A nitrogen atmosphere was obtained inside the box by inflating a polythene bag, with nitrogen, inside the box. (The nitrogen used was passed through wash bottles containing chromous chloride solutions over amalgamated zinc). When the polythene bag completely filled the box, the valves through which the air from inside the box had

3

been displaced were closed and the contents of the bag spilled into the box. This procedure was then repeated.

The preparations were carried out in an apparatus similar to that described by Holah¹¹⁶, a constant stream of nitrogen was passed through the apparatus throughout the reaction. All solvents used in the glove box were boiled and purged with nitrogen before being introduced into the box.

Chromous chloride solutions were prepared using the method of Lux and his co-workers^{117,118}. When very pure chromium metal* is reacted with dilute hydrochloric acid, in an inert atmosphere, a very pure chromous chloride solution is obtained. This technique does not introduce impurities, as the reduction of Cr(III) with zinc amalgam does and is much more convenient than electrolytic reduction procedures.

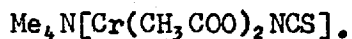
Chromous Acetate

Excess chromium metal (1.5 gm) was reacted with dilute hydrochloric acid (10 ml. 4N). The deep blue solution was filtered into a saturated aqueous solution (20 ml.) of sodium acetate. The brick red precipitate was washed with distilled water, ethanol and then ether and dried in vacuo.

Analysis Cr(II) found 27.3% required 27.65%. Cr(II) determined

* Electrolytic chromium obtained from Murex Limited, Rainham, Essex.

by titration with iodine (as KI_2 solution).

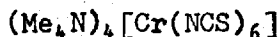


Finely powdered chromous acetate (0.6 gm) was added to an ethanolic solution (30 ml.) of $Me_4N.NCS$ (0.6 gm). A purple solid formed immediately. The reaction mixture was stirred for approximately fifteen minutes. The solid was then filtered off, washed with ethanol and ether and dried in vacuo.

Analysis Cr(II) found 17.0%, required 17.20%.

Chromous formate monohydrate

Although the magnetic properties of this compound have been described²¹ preparative details were not given. It was prepared using a method basically the same as that described above for chromous acetate. It is more soluble than chromous acetate and it was found that the addition of approximately 10 ml. of ethanol speeded up the precipitation of the blood red complex. This was filtered off, washed with ethanol and ether and dried in vacuo.



An aqueous solution of chromous chloride was prepared as described above (see prep. of chromous acetate). One millilitre of this solution was added to a rapidly stirred aqueous solution (10 ml) of $Me_4N.NCS$ (2.4 gm). The pale blue precipitate which formed was filtered off, washed with ethanol, then ether and dried in vacuo.

Analysis NCS^- found 49.5%, required 50.00%.

CHAPTER 5

Discussion of Dimeric Copper Compounds

The behaviour of the magnetic susceptibility with temperature for numerous dimeric Copper(II) compounds has been accounted for in terms of a spin singlet-spin triplet equilibrium*. The origin of the interaction leading to this singlet-triplet separation has been the subject of much debate.

The close approach of the copper ions in cupric acetate monohydrate⁴ led immediately^{4,6} to the proposition that a direct metal-metal bond was involved. Theoretical treatments have considered this bonding, regarding it as a weak δ bond⁶, a strong σ bond^{26,56} or a weak interaction³⁴.

Although X-ray crystal structural determinations have been carried out on a number of dimeric copper(II) compounds with structures related to that of copper acetate (Table 5.1), the copper-copper separations are all very similar; with the exception of the separation in a copper formate complex⁸¹ the structure of which was published during the course of this work. It has not previously been possible to attempt to correlate the spin interaction

* The singlet triplet separation is sometimes defined as J (e.g. 6) and sometimes as $2J$ (e.g. 66, 75). Throughout this work the singlet triplet separation is taken to be J , and where necessary for comparison, literature values will be adjusted.

Table 5.1

Metal-Metal separations in Complexes with structures related to the
Copper Acetate Structure.

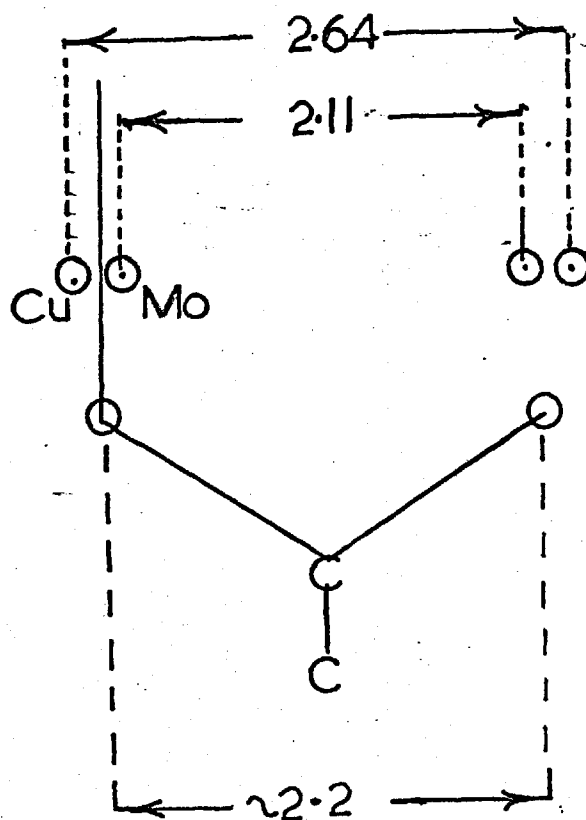
Compound	Metal-metal separation Å	Reference
$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	2.64	4
$\text{Cu}(\text{CH}_3\text{COO})_2 \text{ py}$	2.63 monoclinic	13
$\text{Cu}(\text{CH}_3\text{COO})_2 \text{ py}$	2.64 orthorhombic	14
$\text{Cu}(\text{C}_3\text{H}_7\text{COO})_2$	2.65	76
$\text{Cu}(\text{CH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O}$	2.61	95
$\text{Me}_4\text{N}[\text{Cu}(\text{CH}_3\text{COO})_2\text{NCS}]$	2.64	46, 47
$\text{Me}_4\text{N}[\text{Cu}(\text{HCOO})_2\text{NCS}]$	2.72	46, 47
$\text{Cu}(\text{HCOO})_2 \cdot \frac{1}{2} \text{ dioxan}$	2.58	81
$\text{Cu}(\text{I})$ (diazaminobenzene)	2.45	80
$\text{Ni}(\text{II})$ (diazaminobenzene)	2.38	79
$\text{Mo}(\text{CH}_3\text{COO})_2$	2.11	41
$\text{Rh}(\text{CH}_3\text{COO})_2$	2.45	42
$\text{Ru}_2(\text{C}_2\text{H}_7\text{COO})_4 \text{ Cl}$	2.28	77
$\text{Re}(\text{C}_6\text{H}_6\text{COO})_2 \cdot \text{Cl}$	2.235	78
$\text{Cu}(\text{C}_5\text{H}_5\text{N}_5)_2 \cdot 4\text{H}_2\text{O}$ ($\text{C}_5\text{H}_5\text{N}_5$ adenine)	2.947	92

with copper-copper separation.

The pair of compounds $\text{Me}_4\text{N}[\text{Cu}(\text{RCOO})_2\text{NCS}]$; $\text{R} = \text{H}$ or CH_3 , have widely differing singlet-triplet separations. Crystal structural determinations have been carried out on both compounds^{46,47} and the copper-copper separations differ very significantly. The surprising feature is that the greater exchange interaction occurs in the complex with the longer metal metal separation.

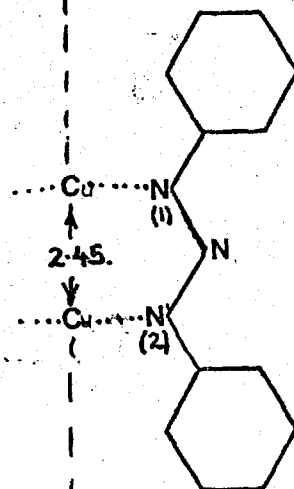
Since the publication of the structure of copper acetate monohydrate, many other X-ray structural determinations have been carried out and it has become apparent that mere proximity of metal atoms in a compound is not a good criterion for metal metal bonding⁸³. For example $\text{Cu}(\text{I})$ forms a dimeric complex with the anion of diazoaminobenzene (Fig.5a, ref.80), here the Cu-Cu separation is only 2.45 \AA , but as the authors point out the close approach is presumably a consequence of the overall molecular geometry rather than the result of any metal-metal bonding interaction. Indeed for linear N-Cu-N coordination the Cu-Cu separation would be the same as that between the nitrogen atoms N_1 and N_2 (see diag.) i.e. 2.19 \AA ; considerably less than the observed separation. In this respect the structure of cupric acetate monohydrate is in marked contrast to that of molybdenum acetate (Fig.5b). In the latter compound the molybdenum ions are inside the plane of four oxygen atoms suggesting a strong attractive or bonding force between the molybdenum ions;

5b



5a

Structure of
Copper(I) Diazoaminobenzene



the copper ions in cupric acetate are well outside the plane of the oxygen atoms suggesting an overall repulsion between them. This effect is marked in the structure of $\text{Me}_4\text{N}[\text{Cu}(\text{HCOO})_2\text{NCS}]$ described here. Thus the structure of copper acetate presents no strong evidence for metal metal bonding.

Although a bonding model involving a strong σ bond between the copper ions has been postulated, this is not compatible with e.s.r. measurements on zinc doped copper acetate monohydrate⁵⁷ which have shown that g_x and g_y lie nearly along the oxygen-copper-oxygen bond axes confirming that the single unpaired electron centred on each copper atom occupies a $d_{x^2-y^2}$ orbital; therefore only the δ bonded model involving overlap of the $d_{x^2-y^2}$ orbitals will be considered. Direct overlap of $d_{x^2-y^2}$ orbitals will decrease exponentially as the metal-metal separation increases^{6,84} which would lead to a rapid fall off in the exchange interaction as the metal metal separation increases. [This assumes, of course, that no large differences in the radii of the d orbital functions occurs, in the two compounds discussed the d orbitals would be expected to have a smaller radius in the formate complex (see below)]. The fact that greater interaction occurs in the molecule with the longer metal-metal separation indicates that the bridging ligands play an important role in the exchange interaction in dimeric copper complexes. The possibility that the interaction involves the

bridging groups has often been discussed but direct evidence of their influence has not previously been presented.

Metal-metal interactions often occur in transition metal complexes when the paramagnetic centres are separated by distances such that direct bonding between them is not possible, the interaction taking place via the intervening diamagnetic groups. Such 'super exchange' interactions are also postulated to occur in a range of dimeric copper compounds where the metal metal separations are not much greater than that found in copper acetate. Typical of these is $\text{di-}\mu(\text{pyridineoxide})\text{bis}(\text{dichlorocopperII})$. The copper has a distorted square planar configuration in a dimeric molecule, the copper copper separation being 3.25 \AA . The magnetic moment at room temperature is 0.85 B.M. ⁸⁶⁻⁸⁹. A related structure occurs in acetylacetonone mono(o-hydroxyanil)copper(II). Here the copper-copper separation is 3.0 \AA and the room temperature moment is 1.37 B.M. ⁸⁵. In fact the magnetic behaviour of the latter compound closely parallels that of copper acetate. Values of J and g calculated from temperature variation of susceptibility data being 298 cm.^{-1} and 2.09 respectively. In contrast to the magnetic behaviour of these compounds other compounds in which copper(II) ions approach closely have normal magnetic behaviour. For example, the CsCuCl_3 structure consists of distorted hexagonally close packed layers of caesium ions and chlorine atoms with the copper atoms

occupying all the octahedral holes, which have six chlorine nearest neighbours. The Cu-Cu separation is 3.062 \AA but the magnetic moment is normal down to 80°K ⁹¹. Discussing the possibility of metal metal bonding in this compound Schlueter et al.⁹¹ deduce from overlap calculations that "for metals at the right of the first transition series the single bond length for $d_{z^2} \cdot d_{z^2}$ σ bonding is so extremely short that such metal metal bonding cannot possibly occur unless there are gross changes in the orbital exponent of the combined metal". Obviously these calculations would rule out any direct metal-metal bonding in copper acetate and related compounds. However the calculations can give only an approximate value of the overlap because of the uncertainty in the orbital exponents for the isolated atoms and also the change of exponent in considering a complexed ion. Thus Figgis and Martin⁶ were able to quote overlap calculations supporting the δ bonded model.

Interactions in compounds with polyatomic bridging groups are not so well characterised. A super exchange mechanism has been postulated to account for the antiferromagnetism of copper(II) formate tetrahydrate. In this compound although the Cu...Cu separation is 5.80 \AA ¹⁹ the room temperature moment is 1.64 B.M.s. More recently⁹³ a super exchange mechanism has been postulated to account for the antiferromagnetic behaviour of the adenine complex $\text{Cu}(\text{C}_5\text{H}_4\text{N}_5)_2 \cdot 4\text{H}_2\text{O}$. This is a dimeric copper complex with a copper copper separation of 2.947 \AA ⁹².

The theory of super exchange mechanisms has been developed comparatively recently^{84,97,98,99}. Early models⁹⁹ stressed the contribution of excited paramagnetic forms of the bridging ligands. In the more recent theory of Anderson however the distinction between direct and indirect exchange becomes ill defined. In super exchange the exchange is described as taking place between orbitals which are expanded by overlap with suitable orbitals from the diamagnetic ligand. Spin pairing then occurs as this then allows delocalisation of the electrons into non-orthogonal orbitals. The existence of a π -bonding system extending over the copper acetate molecule has previously been discussed. The results presented here suggest that the formate group provides a better pathway for the exchange than the acetate group and that the exchange occurring in copper acetate and related compounds is not only a result of direct d orbital overlap.

The suggestion that the spin spin interaction in copper acetate is caused by a super exchange interaction is not intended to exclude direct metal-metal bonding in the other compounds listed in Table 5.1. A graduation in interactions between 1st and 2nd transition series elements has been observed in the structures of the $\text{Cr}_2\text{Cl}_9^{3-}$ ¹⁰³ and $\text{W}_2\text{Cl}_9^{3-}$ ¹⁰⁴ ions. The Re...Re separation observed in dichlorotetrabenzotodirhenium(III) is identical within experimental error

with the separation observed in the ReCl_8^{2-} ¹⁰¹ ion and $\text{Re}_2\text{Cl}_6[\text{P}(\text{C}_2\text{H}_5)_3]_2$ ¹⁰² where "unsupported" metal metal bonds occur. Similarly the Mo...Mo 2.11 Å separation in $\text{Mo}(\text{CH}_3\text{COO})_2$ ⁴¹ is very similar to that occurring in $\text{Mo}_2\text{Cl}_8^{2-}$ (2.14 Å), where again an unsupported metal metal bond occurs. In all these complexes multiple metal-metal bonds are proposed ⁸³.

The role of tetramethylammonium thiocyanate in 'conditioning' the copper formate to adopt a dimeric structure closely parallels that of pyridine. It has been proposed that acids with low PKa values will be correspondingly poorer donors of σ electron density. In the complexes that copper forms with these acids there will be a considerable residual positive charge on the copper atoms leading to instability of the dimeric forms. Suitable ligands in the terminal positions will be effective in reducing this positive charge leading to stability of the dimer. This has been found to occur with acids with PKa's less than ≈ 4.2 ^{66, 74, 75}. The radii of the d orbitals will be sensitive to the positive nuclear charge and would be expected to be correspondingly smaller for the formate.

Unlike acetates ⁵¹ the two crystal structural determinations which have been carried out on dimeric formates show very significant differences in the metal metal separations. This reflects the greater flexibility of the formate group which can adjust to compensate

for packing factors and residual charges on the copper atoms. It is of interest that the magnetic behaviour of the two formate complexes (Ref.22 and this work) is very similar, in keeping with a super exchange rather than direct interaction. Unfortunately, although the results described here illustrate the importance of the bridging groups in the mechanism of the spin interaction, the presence of some direct interaction cannot be disproved. The literature on copper acetate and related compounds will continue to grow.

Dimeric Compounds

1. J. Lifshutz and E. Rosenblum, *Z. Elektrochem.*, 1915, 21, 499.
2. B.C. Guha, *Proc. Roy. Soc.*, 1951, A206, 353.
3. B. Bleaney and K.D. Bowers, *Proc. Roy. Soc.*, 192, A214, 451.
4. J.N. Van Niekerk and F.R.L. Schoening, *Acta Cryst.*, 1953, 6, 227.
5. Foex, Karantassis and Perakis, *Compt. Rend.*, 1953, 237, 982.
6. B.N. Figgis and R.L. Martin, *J. Chem. Soc.*, 1956, 3837.
7. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, 1962, 147.
8. M. Kato, H.B. Jonassen and J.C. Fanning, *Chem. Rev.*, 1964, 64, 99.
(this is a comprehensive review of dimeric copper compounds).
9. D.M.L. Goodgame and F.A. Cotton, *J. Chem. Soc.*, 1961, 2298.
10. R.L. Martin and H. Waterman, *J. Chem. Soc.*, 1957, 2545.
11. M. Kondo and M. Kubo, *J. Phys. Chem.*, 1958, 62, 1558.
12. E. Kokot and R.L. Martin, *Inorg. Chem.*, 1964, 3, 1306.
13. G.A. Barclay, C.H.L. Kennard, *J. Chem. Soc.*, 1961, 5244.
14. F. Hanic, D.V. Stempelova and K. Hanicova, *Chem. Zvest.*, 1961, 15, 102 and F. Hanic, D.V. Stempelova and K. Hanicova, *Acta Cryst.*, 1964, 17, 633.
15. M. Kishita, *J. Chem. Soc., Japan Pure Chem. Sect.*, 1962, 83, 264.
16. G.F. Kokoszka, M. Linzer and G. Gordon, *Inorg. Chem.*, 1968, 7, 1730.
17. R. Tsuchida, S. Yamada and H. Nakamura, *Nature*, 1958, 181, 479.
18. G.A. Barclay and C.H.L. Kennard, *J. Chem. Soc.*, 1961, 3289.
19. R. Kiriyaama, H. Ibamato and K. Matsuo, *Acta Cryst.*, 1954, 7, 482.

20. R.L. Martin and Hanneke Waterman, *J. Chem. Soc.*, 1959, 1359.
21. A. Earnshaw, L.F. Larkworthy and K.S. Patel, *Proc. Chem. Soc.*, 1963, 281.
22. R.L. Martin and Hanneke Waterman, *J. Chem. Soc.*, 1959, 2960.
23. M. Kishita and M. Kubo, *Naturwissenschaften*, 1962, 49, 230.
24. M. Kishita, M. Inoue and M. Kubo, *Inorg. Chem.*, 1964, 3, 237.
25. M. Tonnet, S. Yamada and I. Ross, *Trans. Faraday Soc.*, 1964, 60, 840.
26. L. Forster and C. Ballhausen, *Acta Chem. Scand.*, 1964, 8, 1275.
27. O. Holmes and D. McClure, *J. Chem. Phys.*, 1957, 26, 1686.
28. C. Reimann, G. Kokoszka and G. Gordon, *Inorg. Chem.*, 1965, 4, 1082.
29. R.L. Martin and A. Whitley, *J. Chem. Soc.*, 1958, 1394.
30. M. Kondo and M. Kubo, *J. Chem. Phys.*, 1958, 62, 468.
31. R. Tsuchida and S. Yamada, *Nature*, 1955, 176, 1171.
32. I.G. Ross, *Trans. Faraday Soc.*, 1959, 55, 1057.
33. H. Abe and J. Shimada, *Phys. Rev.*, 1953, 90, 316.
34. A.E. Hansen and C.J. Ballhausen, *Trans. Faraday Soc.*, 1964, 631.
35. T. Watanabe, *J. Phys. Soc. Japan*, 1961, 16, 1677.
36. W.R. King and G.S. Garner, *J. Chem. Phys.*, 1950, 18, 689.
37. J.N. Van Niekerk and F.R.L. Schoening, *Nature*, 1953, 171, 36.
38. J.N. Van Niekerk, F.R.L. Schoening and de Wet, *Acta Cryst.*, 1953, 6, 501.
39. Herzog and Kalies, *Z. Anorg. Chem.*, 1964, 83, 329.

40. A. Earnshaw, L.F. Larkworthy and K.S. Patel, *J. Chem. Soc.*, 1965, 3267.
41. D. Lawton and R. Mason, *J. Amer. Chem. Soc.*, 1965, 87, 921.
42. M.A. Porai-Koshits and A.S. Antsyshkina, *Dokl. Akad. Nauk. S.S.S.R.*, 1962, 146, 1102.
43. T.A. Stephenson, E. Bannister and G. Wilkinson, *J. Chem. Soc.*, 1964, 2538.
44. S.A. Johnson, H.R. Hunt and H.M. Neumann, *Inorg. Chem.*, 1963, 2, 961.
45. T.A. Stephenson et al., *J. Chem. Soc.*, 1965, 3632.
46. D.M.L. Goodgame, M. Hill, D. Marsham, A. Skapski, P. Troughton, M. Smart, *Chem. Comm.*, 1969, 629.
47. A. Skapski, P. Troughton, M. Smart, to be published.
48. J. Lewis, R.S. Nyholm and P.W. Smith, *J. Chem. Soc.*, 1961, 4590.
49. D.M.L. Goodgame and M.A. Hitchman, *Inorg. Chem.*, 1964, 3, 1389.
50. D.M.L. Goodgame and M.A. Hitchman, *Inorg. Chem.*, 1965, 4, 721.
51. K. Nakamoto, Y. Morimoto and A.E. Martell, *J. Amer. Chem. Soc.*, 1961, 83, 4528.
52. K. Itoh and H.J. Bernstein, *Can. J. Chem.*, 1956, 34, 170.
53. L. Dubicki, C.M. Harris, E. Kakot and R.L. Martin, *Inorg. Chem.*, 1966, 5, 93.
54. B.J. Edmondson and A.B.P. Lever, *Inorg. Chem.*, 1965, 4, 1608.
55. C. Furlani and G. Morpurgo, *Theoret. chim. Acta*, 1963, 1, 102.
56. E.A. Boudreaux, *Inorg. Chem.*, 1964, 3, 506.
57. G.F. Kokoszka, H.C. Allen Jr. and G. Gordon, *J. Chem. Phys.*, 1965, 42, 3693.

58. L. Dubicki and R.L. Martin, *Inorg. Chem.*, 1966, 5, 2203.
59. G. Basu, R.L. Belford and R.E. Dickerson, *Inorg. Chem.*, 1962, 1, 438.
60. D.P. Graddon, *J. Inorg. Nucl. Chem.*, 1960, 14, 161.
61. A.B.P. Lever, J. Lewis and R.S. Nyholm, *J. Chem. Soc.*, 1962, 5262.
62. R. Tsuchida, H. Nakamura and S. Yamada, *Nature*, 1956, 178, 1192.
63. D. Forster and D.M.L. Goodgame, *J. Chem. Soc.*, 1965, 262.
64. Kumagai, H. Abe and J. Shimada, *Phys. Rev.*, 1952, 87, 385.
65. G.F. Kokoszka, H. Allen and G. Gordon, *J. Chem. Phys.*, 1967, 47, 10.
66. J. Lewis, F.E. Mobbs, L.K. Royston and W.R. Smail, *J. Chem. Soc.(A)*, 1969, 291.
67. A.V. Ablov, Yu. V. Yablokov and L.N. Milkova, *Dokl. Akad. Nauk. S.S.R.*, 1966, 171 (3) 593.
68. H. Abe and H. Shirai, *J. Phys. Soc. Japan*, 1961, 16, 118.
69. J.R. Wasson, Chin-I. Shyr and C. Trapp, *Inorg. Chem.*, 1968, 7, 469.
70. E. Wasserman, L.C. Snyder and W.A. Yager, *J. Chem. Phys.*, 1964, 41, 1763.
71. B.N. Figgis and J. Lewis, *Progress in Inorganic Chemistry*, Vol. 6, p.37, Interscience, 1964.
72. K.D. Bowers and J. Owen, *Reports on Progress in Physics*, Vol. XVIII, p.304, 1955.
73. W.E. Hatfield and C.S. Fountain, *Inorg. Chem.*, 1965, 4, 1368.
74. J. Lewis and R.C. Thompson, *Nature*, 1963, 200, 468.
75. J. Lewis, Y.C. Lin, L.K. Royston and R.B. Thompson, *J. Chem. Soc.*, 1965, 6464.

76. A.V. Ablov, Yu. A. Simnov and T.I. Maleninovskii, Summaries of reports to the Eighth Scientific-Technical Conference on Applications of X-rays in Research on Materials, Leningrad, 1964, p.101.
77. M.J. Bennett, K.G. Coulton and F.A. Cotton, Inorg. Chem., 1969, 8, 1.
78. M.J. Bennett, W.K. Bratton, F.A. Cotton and W.R. Robinson, Inorg. Chem., 1968, 7, 1570.
79. M.D. Corbett and B.F. Hoskins, Chem. Comm., 1968, 24, 1602.
80. I.D. Brown and J.D. Dunitz, Acta Cryst., 1961, 14, 480.
81. M. Bukowska-Strzyzewska Roczniki Chem., 1966, 40, 567.
82. J.W. Tracy, N.W. Gregory, J.M. Stewart, E.C. Lingafelter, Acta Cryst., 1962, 15, 460.
83. F.A. Cotton, Reviews of Pure and Applied Chemistry, 1967, 17, 25.
84. R.L. Martin, New Pathways in Inorganic Chemistry, Eds. E.A.V. Ebsworth, A.G. Maddock and A.G. Sharpe, Cambridge University Press, 1968, p.175.
85. G.A. Barclay, C.M. Harris, B.F. Hoskins and E. Kokot. Proc. Chem. Soc., 1961, p.264.
86. H.L. Schäfer, J.C. Morrow and H.M. Smith, J. Chem. Phys., 1965, 42, 504.
87. R.S. Sager, R.J. Williams and W.H. Watson, Inorg. Chem., 1967, 6, 951.
88. W.E. Hatfield, Y. Muto, H.B. Jonassen and J.S. Paschal, Inorg. Chem., 1965, 4, 97.

89. M.R. Kidd, R.S. Sager and W.H. Watson, *Inorg. Chem.*, 1967, 6, 946.
90. A.W. Schleuter, R.A. Jacobson and R.E. Rundle, *Inorg. Chem.*, 1966, 277.
91. B.N. Figgis and C.M. Harris, *J. Chem. Soc.*, 1959, 855.
92. E. Sletten, *Chem. Comm.*, 1967, 1119.
93. D.M.L. Goodgame and K. Angela Price, *Nature*, 1968, 220, 783.
94. R.W. Duerst, S.J. Baum, G.F. Kokoszka, *Nature*, 1969, 222, 665.
95. B.H. O'Connor and E.W. Maslen, *Acta Cryst.*, 1966, 20, 824.
96. H. Koizumi, K. Osaki and T. Watanabe, *J. Phys. Soc. Japan*, 1965, 18, 117.
97. J.P. Goodenough, *Magnetism and the Chemical Bond*, New York Interscience Publishers 1963.
98. P.W. Anderson, *Magnetism* (ed. G.T. Rado and H. Suhl), Vol. I, p.25, New York, Academic Press Inc. 1963.
99. P.W. Anderson, *Phys. Rev.*, 1950, 79, 350.
100. P.W. Anderson, *Phys. Rev.*, 1959, 115, 2.
101. F.A. Cotton and C.B. Harris, *Inorg. Chem.*, 1965, 4, 330.
102. M.J. Bennett, F.A. Cotton, B.M. Foxman and P.F. Stokely, *J. Amer. Chem. Soc.*, 1967, 89, 2759.
103. G.J. Wessel and D.J.W. Ijdo, *Acta Cryst.*, 1957, 10, 466.
104. J. Waser and W.H. Watson, *Acta Cryst.*, 1958, 11, 689.
105. J.V. Brencic and F.A. Cotton, *Inorg. Chem.*, 1969, 8, 7.
106. K.E. Hyde, G. Gordon, G.F. Kokoszka, *J. Inorg. Chem.*, 1968, 30, 2155, 2161.

107. J.P. Fackler and D.G. Holah, *Inorg. Chem.*, 1965, 4, 954.
108. G. Polder, *Physica*, 1942, 9, 709.
109. G.F. Kokoszka and H.C. Allen, *J. Chem. Phys.*, 1967, 46, 3013.
110. K.E. Hyde, G. Gordon and G.F. Kokoszka, *J. Inorg. Nucl. Chem.*, 1968, 30, 2155.
111. H.R. Gersman and J.D. Swalen, *J. Chem. Phys.*, 1962, 36, 322.
112. A.H. Maki and B.R. McGarvey, *J. Chem. Phys.*, 1958, 29, pp.31, 35.
113. D. Kivelson and R. Nieman, *J. Chem. Phys.*, 1961, 35, pp. 149, 156, 162.
114. J. Lewis and R. Nyholm, *Science Progress*, 1964, 52, 557.
115. Y. Kuroda, A. Sasano and M. Kubo, *Bull. Chem. Soc. Japan*, 1966, 39, 1002.
116. D.G. Holah, *J. Chem. Ed.*, 1965, 561.
117. H. Lux and G. Illman, *Chem. Ber.*, 1958, 91, 2143.
118. H. Lux, L. Eberle and D. Sarre, *Chem. Ber.*, 1964, 97, 503.
119. *Advanced Inorganic Chemistry*, F.A. Cotton and G. Wilkinson, Interscience Publishers, 2nd Edition, p.821.

PART TWO

SOME NITRITE COMPLEXES OF COBALT(II)

AND ZINC

CHAPTER 6

Introduction to the Chemistry of Nitrite Complexes

One of the interesting features of the chemistry of the nitrite ion is its versatility as a ligand, the ion can coordinate to metal ions in a variety of ways. In a study of nitrite complexes of nickel¹ complexes containing the nitrite group coordinated in the following ways were isolated:

- (a) Nitro complexes containing the nitrite group bonded to the transition metal through the nitrogen atom.
- (b) Nitrito complexes containing the nitrite group bonded to the transition metal through an oxygen atom.
- (c) Compounds containing chelating nitrite groups were isolated. These contain nitrite groups bonded to one transition metal atom by both oxygen atoms. This coordination ranges from symmetrically chelating nitrite groups where the two metal oxygen distances are equal through to the extreme of nitrito groups where one of the oxygens is no longer bonded to the metal. Where the bonding lies between these extremes the nitrite groups will be described as "unsymmetrically chelating".
- (d) The nitrite group bridges two metal atoms, bonding to one through a nitrogen atom and to the other with an oxygen atom. This mode of bridging is referred to as bridging(NO).

(e) To explain some infrared data a form of bonding was postulated¹ in which a nitrite group bridges two metal atoms bonding to them both with the same oxygen atom. This will be referred to as bridging('O').

These modes of coordination are diagrammatically represented in Fig.(6a) and some compounds in which the particular modes of coordination are found are listed in Table 6.1.

Methods of Determining the Mode of Nitrite Bonding

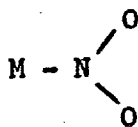
(a) Infrared spectroscopy.

The uncoordinated nitrite ion belongs to the C_{2v} point group and has three non-degenerate infrared active fundamental vibrations (Fig.6b). These are ν_s and ν_{as} the symmetric and antisymmetric nitrogen oxygen stretches and δ_{NO_2} the NO_2 deformation.

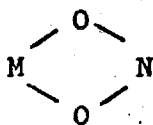
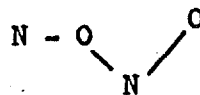
Free ion values

Many workers have studied the infrared and Raman spectra of sodium nitrite, both in the solid state and aqueous solution¹³⁻¹⁷. Although there is not complete agreement bands have been reported at $828 \pm 3 \text{ cm.}^{-1}$ (medium sharp), 1250 ± 30 (very strong, broad) and $1326 \pm 2 \text{ cm.}^{-1}$ (weak sharp). On the basis of Raman polarisability measurements on an aqueous solution¹³ and on single crystals^{14,17} the band at 1326 cm.^{-1} has been assigned as ν_s . This leaves ν_{as} as the broad intense absorption centred at $\sim 1250 \text{ cm.}^{-1}$. It is apparent that the nitrite ion is unusual in having ν_s higher than ν_{as} .

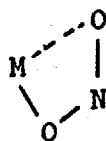
NITRO



NITRITO

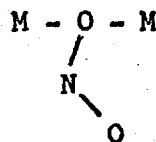
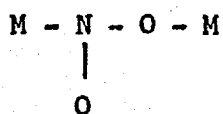


Chelating



Unsymmetrically chelating

Bridging (NO)



Bridging 'O'

Fig. 6(a)

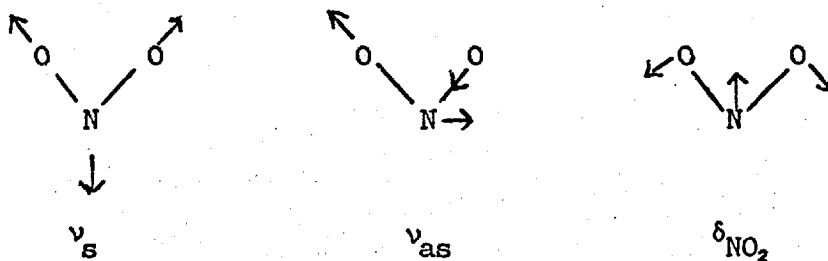
Table 6.1

Typical compounds illustrating modes of bonding of the nitrite ion

Modes of bonding	Complexes
Nitro	$\text{Ni}(\text{NH}_3)_4(\text{NO}_2)_2$ (2*)
	$\text{K}_2\text{BaCo}(\text{NO}_2)_6$ (3*)
	$\text{Cu}(\text{NH}_3)_4(\text{NO}_2)_2$ (12*)
Nitrito	$[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ (4,5,6)
	$\text{Ni}(\text{py})_4(\text{ONO})_2$ (1)
	$\text{Ni}(\text{adimen})_2(\text{ONO})_2$ (7*)
Chelating	$\text{Co}(\text{AsO})_2(\text{NO}_2)_2$ (1)
	$\text{Ni}(\text{tetmen})(\text{NO}_2)_2$ (9*)
	$[\text{K}_2\text{Hg}(\text{NO}_2)_4]\text{NO}_3$ (8*)
Bridging (NO)	$[\text{Ni}(\text{en})_2(\text{NO}_2)\text{ClO}_4]; [\text{Ni}(\text{en})_2\text{NO}_2]\text{BF}_4$ (10*11*)
	$[(\text{NH}_3)_4\text{Co} \begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{NO}_2 \end{array} \text{Co}(\text{NH}_3)_4]\text{Cl}_4$ (20)
Bridging ('O') ?	$\text{Ni}(\text{Mepy})_2(\text{NO}_2)_2 \cdot \frac{1}{3}\text{C}_6\text{H}_6$ (1)

* Indicates that reference given is to an X-ray Crystallographic Structural determination.

Fundamental vibrations of the Nitrite Ion



Vibrations Associated with an M-NO₂ group

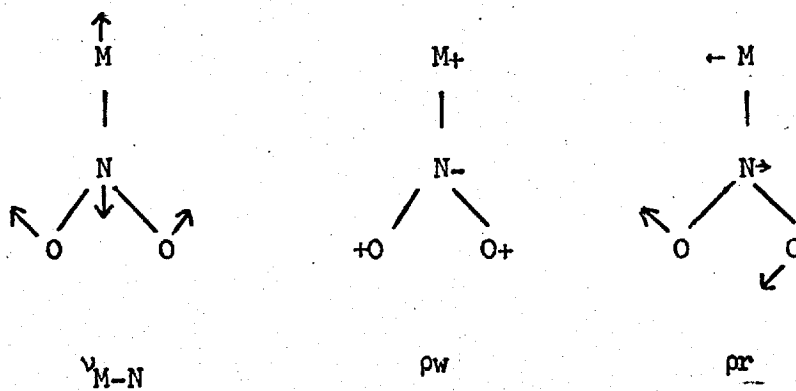


Fig. 6b

Coordinated Nitrite Groups

The nitrite group is of sufficiently low symmetry for all the normal modes to be both infrared and Raman active in the free ion; on coordination of the nitrite group however the positions and intensities of the infrared absorptions vary in a manner which is characteristic of the mode of bonding adopted by the nitrite group (Table 6.2).

Nitro complexes

Mathieu et al.^{18,19} have shown from Raman polarisability data and symmetry considerations that in the nitro complexes of Co(III) and Pt(II) ν_{as} is raised to $\sim 1400 \text{ cm.}^{-1}$ while ν_g remains unaltered from its free ion value at $\approx 1330 \text{ cm.}^{-1}$. It appears that in nitro complexes of bivalent, first series, transition metals, although ν_{as} is raised from the free ion value it remains less than ν_g . (Unfortunately some confusion arises in the literature because some authors²⁰⁻²⁵ have reversed the free ion assignments of ν_{as} and ν_{sym}).

Nitro coordination can also be characterised by considering the vibrations associated directly with the metal nitrite bond. If the planar group $M\text{-NO}_2$ is considered in isolation it has six normal vibrations modes. Three of these approximate to ν_g , ν_{as} and δ_{NO_2} of the uncoordinated NO_2^- ion. The other three are illustrated (Fig. 6b). Nakamoto et al.²¹ found that the nitro complexes $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{++}$, $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$, and similar compounds could

Table 6.2

Infrared frequencies of NO_2^- *

Type of bonding	Metal Ion	ν_{as}	ν_{sym}	Ref
Ionic	$\text{Na}^{\text{I}} \text{K}^{\text{I}}$	1225 - 1270vs br	1325-1335w vw	13-17
	Ba^{II}			27
Nitro	Ni^{II}	1300 - 1335vs	1320-1350w vw	1,18,21
	$\text{Co}^{\text{II}} \text{Cu}^{\text{II}}$	1280 - 1335vs	1335-1395m-vw	1,28,29
	$\text{Co}^{\text{III}} \text{Rh}^{\text{III}}$	1375 - 1420s vs	1330-1350s	18, 28
		$\nu_{\text{N=O}}$	$\nu_{\text{N-O}}$	
Nitrito	Ni(II)	1400 - 1340ms-s	1220-1114s vs	1
	$\text{Co(III)} \text{Rh(III)}$	1470 - 1460s	1070-1060s vs	18,30,31
Chelating	$\text{Ni(II)} \text{Co(II)}$	1315 - 1265vw-m	1205-1175vs	1
	Mn(II)	1300vw	1240-1205vs br	1
	$\text{Cd(II)} \text{Hg(II)}$	a	1270-1200vs br	1,18,32
Unsymmetrically chelating	$\text{Co(II)} \text{Cu(II)}$	1390 - 1370ms	1205-1195vs	1
Bridging (NO)	Ni(II)	1440 - 1410s	1255-1200s vs	1
	Co(III)	1515 - 1485s	1200-1180s	21,23
Bridging (O)	Ni(II)	1490 - 1460s	1025-1005s	1

(a) this frequency has not been assigned with certainty.

* Information for this table was drawn mainly from Ref.1.

be distinguished from the nitrito complex $[\text{Cr}(\text{NH}_3)_5\text{ONO}]^+$; the M-N wagging mode occurred at approximately 600 cm.^{-1} in the former complexes and was not present in the spectrum of the latter.

Nitrito Coordination

As is the case of nitro coordination six vibrational modes are expected; these are approximately two nitrogen oxygen stretches $\nu_{\text{N=O}}$ and $\nu_{\text{N-O}}$ and an ONO deformation δ_{ONO} , a metal ligand stretch $\nu_{\text{M-O}}$, a metal oxygen bend δ_{MONO} , and an out of plane deformation ρ_w . There is little available information in the literature on the positions of the last three modes. The nitrogen oxygen stretching frequencies in nitrito complexes have been shown to occur as two strong bands occurring in nickel complexes at $1400 - 1340 \text{ cm.}^{-1}$ ($\nu_{\text{N=O}}$) and $1220 - 1114 \text{ cm.}^{-1}$ ($\nu_{\text{N-O}}$).

In all other modes of coordination the N-O stretching frequencies will be described as $\nu_{\text{N=O}}$ and $\nu_{\text{N-O}}$, $\nu_{\text{N=O}}$ being taken as the band occurring at higher energy.

Chelating Nitrite Groups

The infrared spectra of these complexes contain a strong broad band assigned to $\nu_{\text{N-O}}$ which occurs at $1205 - 1175 \text{ cm.}^{-1}$ in Ni^{II} complexes; $\nu_{\text{N=O}}$ is seen as a very weak band occurring at slightly higher energy. δ_s also frequently occurs at higher energy than in the free ion. As the coordination becomes more unsymmetrical the infrared spectrum become similar to those observed in nitrito complexes(1).

Bridging (NO)

An X-ray structural determination has been carried out on only one compound containing bridging (NO) groups¹¹ but it has been postulated^{1,20} that several compounds contain this group. Two strong bands from N-O stretching modes are observed in the infrared spectrum.

Bridging (O)

No conclusive evidence for the occurrence of this mode of bonding, i.e. no complete X-ray crystallographic structural determination is available. It has been postulated¹ as the most logical method of explaining the position of the NO stretching frequencies in a group of compounds¹, the coordination number of the metal ions present indicates that the nitrite groups must be bridging.

Electronic spectra

The 'd-d' electronic transitions also provide information as to the mode of bonding of the nitrite group. In the case of nitro and nitrito coordination the two modes of coordination are well separated in the spectrochemical series²⁶, the nitro group is a 'strong' ligand; the nitrito group is fairly weak.

Indirect evidence of the mode of bonding can also often be obtained from the electronic spectrum. The coordination number of the metal atom, which can usually be deduced from the electronic spectrum together with magnetic susceptibility data, often indicates

whether the nitrite group is acting as a mono-dentate or bi-dentate ligand. In the case of chelating nitrite groups more direct use of electronic spectra can be made since the electronic spectra of complexes containing chelating nitrite groups are often very similar to those containing chelating nitrate groups and a direct comparison is useful if the latter form of coordination is well established.

X-ray studies

Several X-ray crystallographic structural determinations have now been carried out on complexes containing nitrite groups (Table 6.1) with several different modes of coordination providing confirmation for conclusions which have been drawn from other evidence. This means that predictions of coordination type can confidently be made using evidence for the sort outlined above.

Occurrence of Different Bonding Modes

Nitro and Nitrito

Prior to the work described in Ref.1 nitrito coordination was found in only a few compounds in which an unusual reaction mechanism led to the formation of unstable nitrito complexes with a few kinetically inert metal ions^{5,6,31}. In a series of nickel complexes with substituted ethylene diamines^{1,33} it was found that nitro complexes were found in $\text{Ni(en)}_2(\text{NO}_2)_2$, $\text{Ni(men)}_2(\text{NO}_2)_2$, and $\text{Ni(o-phenylene diamine)}_2(\text{NO}_2)_2$; with increasing substitution of the ethylene diamine nitrito complexes were formed. Similarly $\text{Ni(NH}_3)_2(\text{NO}_2)_2$ contains nitro groups whereas $\text{Ni(py)}_2(\text{NO}_2)_2$ contains nitrito groups. These

results led to the conclusion that steric factors were also important in determining the mode of bonding of the unidentate nitrite group. The influence of these is shown clearly in the structure of $\text{Ni}(\text{en}_2(\text{NO}_2)_2)$ where interactions between the nitrite group and the amines lead to significant differences in bond lengths compared with $\text{Ni}(\text{NH}_3)_4(\text{NCS})_2$.² However when kinetic and steric factors are not important nitro coordination occurs in most complexes of $\text{Ni}(\text{II})$, $\text{Pt}(\text{II})$, $\text{Pd}(\text{II})$, $\text{Co}(\text{III})$, $\text{Rh}(\text{II})$, $\text{Ir}(\text{III})$ and $\text{Pt}(\text{IV})$.

Chelating

Chelating nitrite groups occur in several complexes of the type $\text{ML}_2(\text{NO}_2)_2$ [$\text{M} = \text{Co}^{\text{II}}$ and Ni^{II} , $\text{L} = \text{a monodentate ligand, e.g. } \beta_3\text{PO}$]. Steric factors presumably prevent the nitrite groups bridging, chelation of the nitrite groups will then be favoured as the coordination of the metal ion is increased from four to six. In tetranitrite complexes of Co^{II} and Cu^{II} ¹ the chelation apparently becomes very unsymmetrical since symmetrical coordination would presumably cause too much steric interaction around the metal ion.

Bridging [NO] and bridging [O]

The latter mode of coordination has not been confirmed.

Bridging [NO] nitrite groups occur in several complexes of $\text{Ni}(\text{II})$ and $\text{Co}(\text{III})$ but factors influencing these modes of bonding have not been elucidated.

The studies described in the following chapters have extended the range of nitrite studies to include two other first series transition metals, Co(II) and Zn(II); with a view to furthering the understanding of the factors influencing the mode of bonding of nitrite groups. Although information on the stereochemistry of zinc complexes is difficult to obtain this metal was chosen because the influence of crystal field stabilisation energies could then be studied.

Magnetic studies on a series of nitrite complexes containing bridging nitrite groups have also been carried out.

CHAPTER 7

Cobalt(II) Nitrite Complexes

Complexes of trivalent cobalt containing ionic or coordinated nitrite ions have been known for many years and the classic example of nitro-nitrito isomerism, $\text{Co}(\text{NH}_3)_5(\text{NO}_2)^{2+}$ and $\text{Co}(\text{NH}_3)_5(\text{ONO})^{2+}$ was found in this group of complexes^{5,6}; Co(II) nitrite complexes however are not well characterised^{6,34-38}. In this chapter the preparation, infrared, electronic spectra and magnetic moments of a range of cobalt(II) nitrite complexes with amine ligands are reported. In all cases the corresponding nickel analogues have already been prepared¹ so that direct comparisons are possible. The compounds reported are $[\text{Co}(\text{py})_4(\text{ONO})_2](\text{pyridine})_2$, $\text{CoL}_4(\text{ONO})_2$ (L = isoquinoline or 4-methyl pyridine), $\text{CoL}_3(\text{NO}_2)_2$ (L = isoquinoline, pyridine or β picoline), $\text{CoL}_2(\text{NO}_2)_2$ (L = py, 1-quin, 3-mepy or 4-mepy), $\text{Co}(\text{a-dimen})_2(\text{NO}_2)_2$, $\text{Co}(\text{tetmen})(\text{NO}_2)_2$ and $\text{Co}(\text{s-dien})_2(\text{ONO})_2$.

Many of the compounds described here were prepared by the method employed by Babaeva and his co-workers for the preparation of $\text{Co}(\text{py})_6(\text{NO}_2)_2$. In this procedure sodium cobaltinitrite was heated with the pure liquid amine, prolonged interaction (2-3 months) at room temperature was reported³⁶ to form $\text{Co}^{\text{III}}(\text{py})_3(\text{NO}_2)_3$, whereas after three hours at 50-60°C mainly $\text{Co}(\text{py})_6(\text{NO}_2)_2$ was obtained³.

Here reduction to cobalt(II) was affected by heating the reactants on the steam bath for 1 - 3 days. A similar procedure using $K_4Ni(NO_2)_6 \cdot H_2O$ ³⁹ as starting material provides a very convenient way of preparing nickel nitrito complexes such as $Ni(py)_4(ONO)_2$. In that case the reaction occurs quite rapidly on warming.

The stoichiometries of the initial products obtained from sodium cobaltinitrite depended on the identity of the amine ligand. Thus pyridine gives first a 6:1 compound which rapidly loses pyridine to give a 3:1 complex. Isoquinoline and γ -picoline, however, formed 4:1 compounds as the reaction products, whereas with 3-methylpyridine the highest amine to metal ratio was 3:1. With the diamines *N,N*-dimethylethylenediamine and *N,N'*-diethylethylenediamine 2:1 complexes were obtained, but *N,N,N',N'*-tetramethylethylenediamine gave only a 1:1 compound. Complexes with fewer heterocyclic amine molecules than the maxima indicated above could be obtained by mild thermal or other methods.

The mode of bonding of the anions can be deduced from their infrared (i.r.) spectra (Table 7.1) employing the criteria discussed in Chapter 6. The results for the complexes with heterocyclic amines will be considered first.

4:1 Complexes The i.r. spectra of these compounds show that they are nitrito-complexes. Bands due to the two N-O stretches occur at ~ 1400 and ~ 1115 cm^{-1} , corresponding to those observed for

Ni(pyridine)₄(ONO)₂ and related complexes^{1,24}. Moreover, X-ray powder patterns show that Co(4-methylpyridine)₄(ONO)₂ is isomorphous with its nickel(II) analogue. The relatively simple nature of Co(isoquinoline)₄(ONO)₂ contrasts with the 4:1 isoquinoline complex with nickel nitrite which appears to contain both N- and O-bonded nitrite groups¹.

A 4:1 complex with pyridine could not be isolated. The hexakis compound loses pyridine readily but the loss of amine does not stop at a 4:1 stoichiometry. However the properties of the hexakis complex immediately after isolation, or when kept in an atmosphere of pyridine suggest that its true formulation is [Co(py)₄(ONO)₂](pyridine)₂ as has been found⁴¹ with some other hexakis pyridine complexes, rather than [Co(pyridine)₆](NO₂)₂. The i.r. spectrum of a sample mullied in a mixture of nujol and pyridine (Table 7.1) was characteristic of the presence of nitrito-coordination and not ionic nitrite. Mulls in dry nujol alone showed a medium intensity band at ~ 1220 cm.⁻¹ and a weak band at 850 cm.⁻¹ in addition to those observed for [Co(pyridine)₄(ONO)₂](pyridine)₂, indicating that without extra pyridine some of the 3:1 complex (see below) is formed on grinding. Cobalt(II) nitrate also forms a hexakis-pyridine complex⁴³ which, in contrast to the behaviour of the cobalt(II) nitrite-pyridine system, was obtained⁴³ by the ready uptake of 3 moles of pyridine by the compound Co(pyridine)₃(NO₃)₂, and was formulated as [Co(pyridine)₃(NO₃)₂](pyridine)₃.

Table 7.1Nitrite infrared frequencies (cm.^{-1}) of the complexes

Complex		$\nu(\text{N-O})$	$\delta(\text{NO}_2)$
[Co _{py} ₄ (ONO) ₂].2py	a	1405 _s 1109 _s	824 _w
	b	1405 _m , ~1220 _m , 1109 _m	850 _w , 824 _w
Co _{py} ₃ (NO ₂) ₂		1304 _w , 1228 _s	852 _m
Co _{py} ₂ (NO ₂) ₂		1330 _m , 1180 _s	854 _m
Co(1-quin) ₄ (ONO) ₂		1406 _m , 1116 _s	c
Co(1-quin) ₃ (NO ₂) ₂		1425 _m , 1212 _{ms} , 1092 _m	c
Co(1-quin) ₂ (NO ₂) ₂		1315 _w , 1195 _s	c
Co(4-Mepy) ₄ (ONO) ₂		1410 _m , 1115 _s	c
Co(4-Mepy) ₄ (NO ₂) ₂		1329 _m , 1180 _s	850 _m
Co(3-Mepy) ₃ (NO ₂) ₂		1302 _{vw} , 1228 _s	855 _m
Co(3-Mepy) ₂ (NO ₂) ₂		1334 _w , 1195 _s	852 _m
Co(adimen) ₂ (ONO) ₂		1396 _s , 1120 _s	806 _m
Co(sdien) ₂ (ONO) ₂		1380 ^d _m , 1210 _s	815 _m
Co(tetmen)(NO ₂) ₂		1290 ^d , 1207 _{vs}	850 _m

a Mulled in nujol + pyridine.

b Mulled in nujol only.

c Obscured by ligand bands

d Assignment uncertain due to amine bands in same region.

Despite the formal D_{4h} symmetry of the CoN_4O_2 coordination sphere in $Co(isoquinoline)_4(ONO)_2$ the electronic band corresponding to the ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$ transition in O_h symmetry remains unsplit (Figure 7a) and this is also true for the 4:1 complex with 4-methylpyridine and the hexakis-pyridine compound (Table 7.2). The weak shoulder between 18,000 and 19,000 $cm.^{-1}$ may be the ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transition, as this is expected⁴⁴ in this region for ligand fields of $Dq \approx 1000 cm.^{-1}$. The electronic spectra in acetone solution suggest that lower complexes are formed (see later).

The magnetic moments (Table 7.2) fall within the usual range for six coordinate cobalt(II). The value quoted for the hexakis-pyridine compound is less accurate than those of the other compounds because of the need to avoid the use of the powdered specimens usually employed in the Gouy method.

2:1 Complexes Several coordination geometries are possible for the purple 2:1 compounds. Coordination of the anions through nitrogen is ruled out on the basis of the i.r. results (also the high ligand field strength of nitro-groups would almost certainly have led to a square, low-spin CoN_4 system, whereas the complexes are high spin). Nor are the i.r. spectra consistent with the presence of bridging nitrites^{21,23}. Two other likely configurations are four coordination with nitrito-linkages or six coordination with chelating anions. The i.r. data indicate very strongly that the anions are, in fact, chelating in these compounds. The relative

intensities and frequencies of the $\nu(\text{N-O})$ bands are consistent with this mode of coordination²⁵, and the values of $\delta(\text{NO}_2)$ are raised well above the free ion value which is not the case for simple nitrito-coordination.^{1,22,24}

The reflectance spectra show a small splitting of the ${}^4\text{T}_{2g}$ level, as well as the expected bathochromic band shift with respect to the band energies of the 4:1 compounds. The increased ligand field distortion implied by the former observation is also demonstrated by the lower magnetic moments (Table 7.2). In contrast to the behaviour of the 4:1 compounds the electronic spectra of the 2:1 complexes in acetone are essentially the same as those of the solids, except that the small splittings of the first spin-allowed bands are not resolved in the solution spectra. The relatively high extinction coefficients (120 - 190) observed for the main band in the visible region suggest that the complexes have cis-configurations, as in the bidentate nitrate-complex $\text{Co}(\text{Me}_3\text{PO})_2(\text{NO}_3)_2$ ^{45,46}. The spectra are also similar to that of the compound $\text{Co}(2\text{-methylpyridine})_2(\text{NO}_3)_2$ for which an essentially cis-arrangement of bidentate nitrate groups has been proposed.⁴⁷

3:1 Complexes In view of the various ways in which the nitrite ions can coordinate the natures of the 3:1 complexes present an interesting problem. Infrared evidence suggests that all the amine

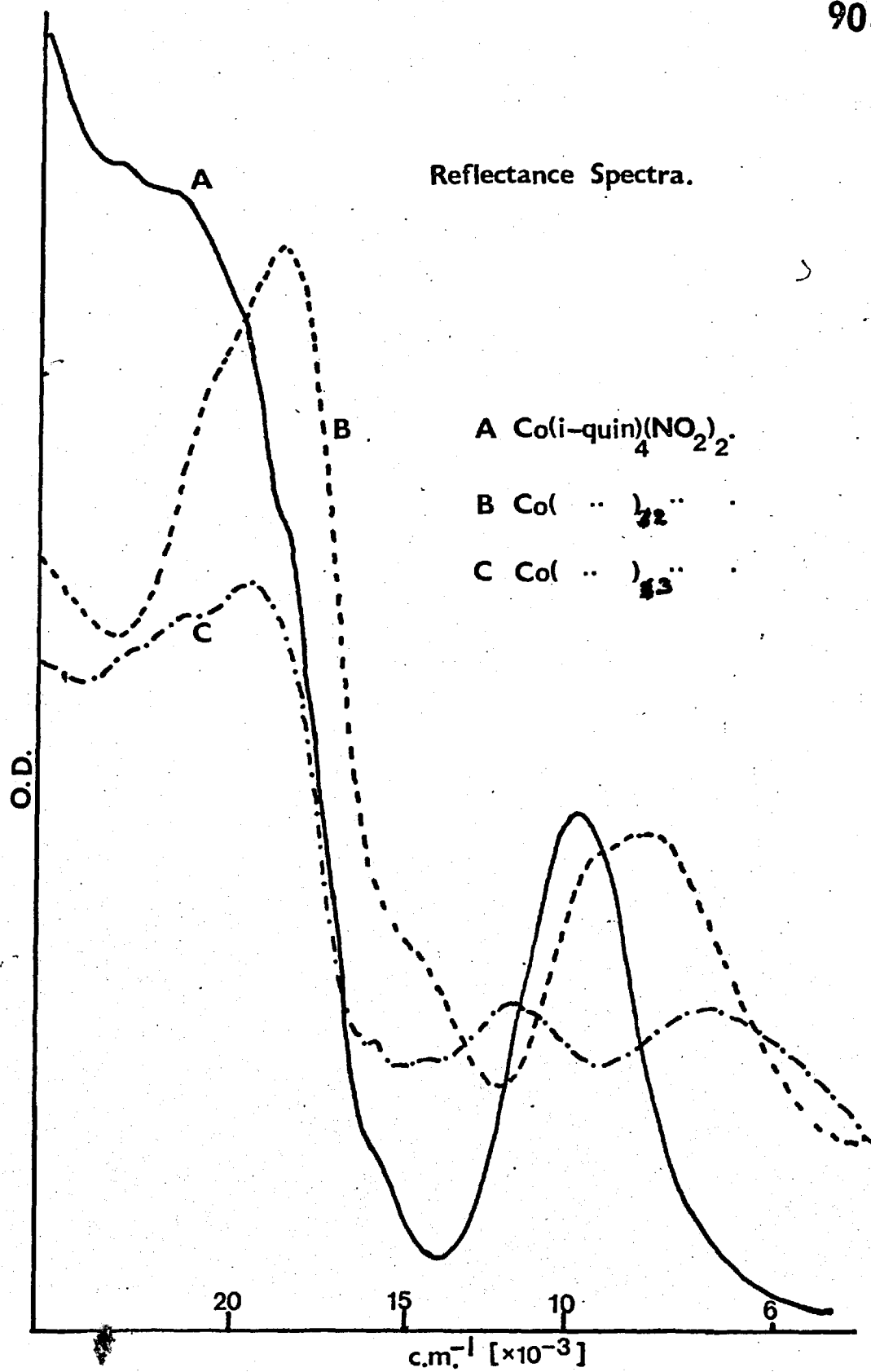


Fig.7a.

I.R. SPECTRA.

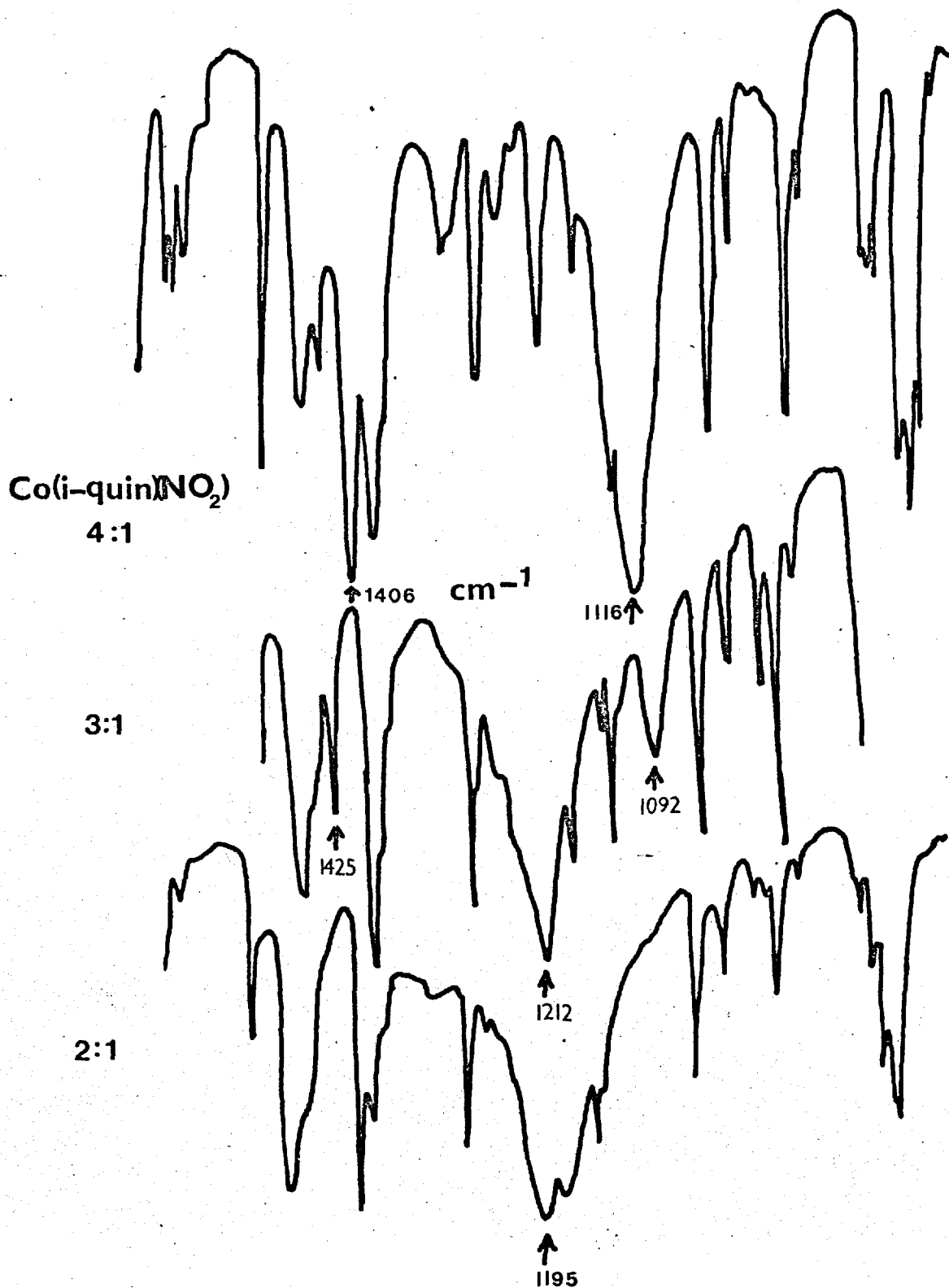


Fig.7b.

molecules are coordinated. It has been shown⁴⁸ for 3-methylpyridine that in the region 2000 - 200 cm.^{-1} four bands (at 1227, 630, 454 and 337 cm.^{-1}) are shifted to higher frequency upon coordination. In the complex $\text{Co}(3\text{-methylpyridine})_3(\text{NO}_2)_2$ the 1220 cm.^{-1} region is obscured by $\nu(\text{N-O})$ but no bands assignable to free amine occur in the other regions. Also there is no evidence for uncoordinated pyridine in $\text{Co}(\text{pyridine})_3(\text{NO}_2)_2$ as there is no band at 603 cm.^{-1} , but only one due to coordinated pyridine⁴⁹ at 629 cm.^{-1} . The 504 cm.^{-1} band of isoquinoline which disappears on coordination⁴² is absent from the spectrum of $\text{Co}(\text{isoquinoline})_3(\text{NO}_2)_2$.

The i.r. spectrum of $\text{Co}(\text{isoquinoline})_3(\text{NO}_2)_2$ shows that there are two types of nitrite coordination present (Fig. 7b). Three $\nu(\text{N-O})$ bands were observed (Table 1) at frequencies consistent with nitrito- (1425 and 1092 cm.^{-1}) and chelating-nitrite (1212 cm.^{-1} *) coordination (the $\delta(\text{NO}_2)$ region was obscured by isoquinoline bands). On this basis, this compound can be formulated as having a CoN_3O_3 coordination sphere, made up of the three amine ligands, one nitrito-group, and one chelating nitrite. A similar environment for the cobalt(II) ion has been postulated⁴³ for the compound $\text{Co}(\text{pyridine})_3(\text{NO}_2)_2$.

In contrast to the above, the i.r. spectra of the 3:1 complexes with pyridine and 3-methylpyridine each contained only one pair of

* The weak band expected⁶ in the 1300 cm.^{-1} region was not resolved.

Table 7.2

Room temperature magnetic moments and electronic band energies of the complexes

Complex ^a	μ_{eff} (B.M.)	Phase ^b	ν cm. ⁻¹ (ϵ_{molar} for solns.)
[CoPy ₄ (ONO) ₂].2py	4.9 ^c	R	9170, ~18,500sh, 20,800
		A	8600(10), 14,400sh, 18,850(125), 20,600sh
CoPy ₃ (NO ₂) ₂	4.47	R	6850, 11,760, ~13,800sh, 16,800vw, 19,420, 20,600sh.
CoPy ₂ (NO ₂) ₂	4.36	R	8300sh, 9500, ~14,800wsh, 18,900, ~20,400sh.
		A	8600(15), 14,300wsh, 18,800(120), 20,500sh.
Co(i-quin) ₄ (ONO) ₂	4.80	R	9800, ~18,690sh, 21,280
		A	8700(17), 14,400wsh, 18,900(190), 20,500sh.
Co(i-quin) ₃ (NO ₂) ₂	4.48	R	6990, 11,760, 16,000vw, 19,420, ~21,050sh, ~22,400sh.
		A	8600(22), 14,300wsh, 18,900(190), 20,600sh.
Co(i-quin) ₂ (NO ₂) ₂	4.53	R	8130, ~9090sh, ~14,800sh, 18,690, ~20,400wsh.
		A	8700(18), 14,300wsh, 19,000(190), 20,800sh.
Co(4-Mepy) ₄ (ONO) ₂	4.93	R	9300, ~18,500sh, ~19,600sh, 20,800
		A	8600(15), 14,400sh, 18,750(165), 20,600sh.
Co(4-Mepy) ₂ (NO ₂) ₂	4.48	R	8200, ~14,900sh, 18,690, ~20,400sh
		A	8700(17), 14,300wsh, 18,900(185), 20,700sh.

Table 7.2 (continued)

Complex ^a	μ_{eff} (B.M.)	Phase ^b	ν cm. ⁻¹ (ϵ_{molar} for solns.)
Co(3-Mepy) ₃ (NO ₂) ₂	4.43	R	7040, 12,050 ^d , 16,000vw, 19,420, ~21,300sh.
		A	8500(17), 14,300wsh, 18,900(160), 20,700sh.
Co(3-Mepy) ₂ (NO ₂) ₂	4.44	R	7870, ~9500sh, 14,400wsh, 18,870, ~20,650wsh.
		A	8600(16), ~14,300wsh, 18,900(140), 20,700sh.
Co(adimen) ₂ (ONO) ₂	4.78	R	8900, 16,100vw, 20,400
Co(sdieen) ₂ (ONO) ₂	4.75	R	7875, 10,000, ~18,200wsh, 20,120
Co(tetmen)(NO ₂) ₂	4.77	R	9400, 14,700vw, 18,900, 24,400vw

a Ligand abbreviations as in Table 7.1.

b R = solid, by reflectance; A = acetone solution

c Approximate value (see text)

d Asymmetric to higher energy.

$\nu(\text{N-O})$ bands, a strong one at 1228 cm.^{-1} and a weak one at $\sim 1300 \text{ cm.}^{-1}$. This implies that in these compounds both nitrite groups are bonded in a similar fashion, more specifically as essentially chelating groups. The presence of at least one such group is confirmed by the high value of $\delta(\text{NO}_2)$, $\sim 855 \text{ cm.}^{-1}$. In the case of the pyridine complex the presence of only one type of nitrite coordination is supported by the observation of only one $\delta(\text{NO}_2)$ band, but we cannot be sure that there is only one such band for the 3-methylpyridine complex because of amine absorption at $\sim 800 \text{ cm.}^{-1}$.

Three coordinated amines and two bidentate nitrites require distorted seven-fold coordination for the metal ion in these compounds. Distorted eight-coordination is known for $\text{Co}(\text{NO}_3)_4^{2-}$ ⁵⁰, $\text{Zn}(\text{NO}_2)_4^{2-}$ ⁵¹, $\text{Cd}(\text{NO}_2)_4^{2-}$ ⁵¹, and $\text{Hg}(\text{NO}_2)_4^{2-}$ ⁸, and has been suggested on similarity of spectral evidence⁵² for $\text{Mn}(\text{NO}_2)_4^{2-}$ and $\text{Co}(\text{NO}_2)_4^{2-}$. It appears that these oxy-anions, and especially the nitrite ion, may be particularly liable to produce complexes with high coordination numbers by employing their chelating ability. On this basis it is reasonable to postulate a CoN_3O_4 coordination sphere for the 3:1 complexes with pyridine and 3-methylpyridine. Inspection of the geometry of the $\text{Zn}(\text{NO}_2)_4^{2-}$ ion⁵¹ shows that there would be no steric problem in replacing two of the chelating nitrite groups by three of these amine molecules. The reflectance spectra are quite

different from those of their 2:1 analogues with a very pronounced splitting of the ${}^4T_{2g}$ level indicative of appreciable distortion of the ligand field. (Fig.7a).

The 3:1 complex with 3-methylpyridine was obtained as well-formed, monoclinic crystals. In view of the possibly unusual coordination geometry these were examined by X-ray diffraction by Professor D. Rogers and Mr T. Sundaesan of this Department. Unfortunately, detailed study of the structure has had to be suspended, partly because of high thermal attenuation, but more significantly because the crystals decomposed within 20 hours' exposure to X-radiation (even with FeK radiation) although the compound is apparently quite air-stable in the absence of X-radiation.

No 3:1 complex could be isolated with 4-methylpyridine. On treating the 4:1 compound with ether the amine was gradually removed but the products were mixtures of the 4:1 and 2:1 species.

Solution Spectra All the $\text{Co(amine)}_n(\text{NO}_2)_2$ complexes dissolve in acetone. The electronic spectra of solutions of the compounds where $n > 2$ are virtually identical to those of the analogous 2:1 compounds, and it appears that dissolution is accompanied by removal of amine ligands from the 4:1 and 3:1 compounds leaving $\text{Co(amine)}_2(\text{NO}_2)_2$, with chelating anions, as the predominant solute species. A similar dissociation occurs for $\text{Ni(pyridine)}_4(\text{ONO})_2$ and related compounds on solution in benzene¹, and for $\text{Ni(pyridine)}_3(\text{NO}_3)_2$ in dichloromethane.⁵³

The acetone solutions of the cobalt complexes were unstable and changed colour from purple to red-brown within ca. ten minutes. This change was accompanied by a decrease in the intensities of the d-d bands and an increase in the absorption in the ultraviolet region. Addition of free amine also decreased the intensities of the d-d bands, but quantitative studies of the solution equilibria have not been made.

Complexes with diamines The solid complexes with the three N-substituted ethylenediamines listed in Table 7.1 are quite analogous to the corresponding nickel compounds. N,N-dimethylethylenediamine and N,N'-diethylethylenediamine give nitrito-complexes of the type $\text{Co}(\text{diamine})_2(\text{ONO})_2$, but with the more heavily substituted ligand N,N,N',N'-tetramethylethylenediamine only one diamine molecule coordinates and the metal ion achieves six coordination by means of chelating nitrite groups.

Previous work had shown⁵⁴ that diamines offering little steric hindrance perpendicular to the Ni-N_4 plane produced nitrocomplexes with nickel nitrite. However attempts to prepare the analogous cobalt(II) complexes, using ethylenediamine, its N-methyl and -ethyl derivatives, or racemic-1,2-diphenylethylenediamine have been unsuccessful. This is further discussed in Chapter 10. Also, solutions of the solid nickel nitrito-complexes with N,N-dimethyl- and N,N'-diethylethylenediamine in various organic solvents showed²⁵ an equilibrium between nitro- and nitrito-isomers. However,

solutions of the corresponding cobalt complexes, even in dry, oxygen-free solvents, rapidly produced brown, flocculent precipitates and gave dark red solutions having no discernable d-d bands but with intense absorption in the near ultraviolet region.

A similar phenomenon was encountered when attempts were made to prepare compounds analogous to those nickel complexes which have been postulated to contain bridged (O) nitrite groups¹. The preparation of $\text{Ni}(4\text{-Mepy})_2(\text{NO}_2)_2 \cdot \text{C}_6\text{H}_6$ for example involves dissolving $\text{Ni}(4\text{-mepy})_4(\text{ONO})_2$ in boiling benzene. When $\text{Co}(4\text{-mepy})_4(\text{NO}_2)_2$ was dissolved in boiling benzene a mauve coloured solution was formed but even when air free benzene was used this solution rapidly became reddish brown and deposited an orange deposit. It is of interest in this respect that the purple complex $\text{Co}(\text{py})_2(\text{NO}_2)_2$ is unstable even in dry air becoming orange-brown coloured over a period of weeks. The decomposition products formed in these reactions have not been investigated but they are probably Co(III) species.

Experimental

Preparation of Complexes Unless stated otherwise the general method of preparation was to react sodium cobaltinitrite (A.R. grade) with an excess of the amine in a stoppered flask on the steam bath. The mixture was filtered hot and the desired complex separated on cooling, often as large, well-formed crystals.

$[\text{Co}(\text{pyridine})_4(\text{ONO})_2] \cdot (\text{pyridine})_2$ Sodium cobaltinitrite and pyridine were heated for 24 hrs. Orange crystals separated from

the filtrate on cooling. The compound loses pyridine rapidly on exposure to the atmosphere. [Found: NO_2^- , 14.4. Calc. for $\text{C}_{30}\text{H}_{30}\text{CoN}_8\text{O}_4$: NO_2^- , 14.7%].

$\text{Co}(4\text{-methylpyridine})_4(\text{ONO})_2$ Orange crystals, recrystallized from methanol containing ~ 10% 4-methylpyridine. [Found: C, 55.0; H, 5.2; N, 16.2. $\text{C}_{24}\text{H}_{23}\text{CoN}_6\text{O}_4$ requires C, 55.1; H, 5.4; N, 16.05%].

$\text{Co}(\text{isoquinoline})_4(\text{ONO})_2$ Orange crystals, recrystallized from methanol/isoquinoline. [Found: C, 64.5; H, 4.5; N, 12.75; NO_2^- , 13.4. $\text{C}_{36}\text{H}_{28}\text{CoN}_6\text{O}_4$ requires C, 64.8; H, 4.2; N, 12.6; NO_2^- , 13.8%].

$\text{Co}(\text{isoquinoline})_3(\text{NO}_2)_2$ This complex was obtained as large, dark brown crystals on recrystallising the previous compound from acetone (1 g in ~ 5 ml.). [Found: C, 60.2; H, 4.0; N, 13.15; NO_2^- , 17.4. $\text{C}_{27}\text{H}_{21}\text{CoN}_5\text{O}_4$ requires C, 60.2; H, 3.9; N, 13.0; NO_2^- , 17.1%].

$\text{Co}(3\text{-methylpyridine})_3(\text{NO}_2)_2$ Sodium cobaltinitrite and 3-methylpyridine were heated for 48 hrs. The dark brown crystals which separated from the filtrate on cooling were recrystallised from 4:1 methanol/3-methylpyridine. [Found: C, 49.6; H, 4.8; N, 16.1. $\text{C}_{18}\text{H}_{21}\text{CoN}_5\text{O}_4$ requires C, 50.2; H, 4.9; N, 16.3%].

$\text{Co}(\text{pyridine})_3(\text{NO}_2)_2$ The hexakis-pyridine complex was stirred with anhydrous ether until the solid showed no i.r. bands due to the starting material. Prolonged washing with ether caused the partial

formation of the 2:1 compound. [Found: C, 46.5; H, 3.8; N, 18.1.

$C_{15}H_{15}CoN_5O_4$ requires C, 46.4; H, 3.9; N, 18.0%].

$CoL_2(NO_2)_2$, (L = isoquinoline, 4-, or 3-methylpyridine) The 4:1

complex (for isoquinoline and 4-methylpyridine) or $Co(3\text{-methyl-}$

$pyridine)_3(NO_2)_2$ was heated in vacuo until a homogeneous purple

solid had formed (~ 4 hrs). (The 3-methylpyridine compound formed

as a purple oil which solidified on triturating with anhydrous

ether). (L = isoquinoline: Found: C, 53.2; H, 3.9; N, 13.6.

$C_{13}H_{14}CoN_4O_4$ requires C, 52.8; H, 3.45; N, 13.7%. L = 3-methyl-

pyridine: Found: NO_2^- , 26.9; $C_{12}H_{14}CoN_4O_4$ requires $NO_2^- = 27.4\%$.

L = 4-methylpyridine: Found: C, 43.6; H, 4.1; N, 16.6.

$C_{12}H_{14}CoN_4O$ requires C, 42.7; H, 4.2; N, 16.6%].

$Co(pyridine)_2(NO_2)_2$ This purple compound was obtained by storing

the hexakis-complex in vacuo over H_2SO_4 for 6 hrs. It is very

hygroscopic, and it decomposes slowly on keeping. [Found: C, 38.7;

H, 3.85; N, 18.0. $C_{10}H_{10}CoN_4O_4$ requires C, 38.8; H, 3.2; N, 18.1%].

$Co(N,N\text{-dimethylethylenediamine})_2(ONO)_2$ A solution of cobalt(II)

nitrite was prepared by adding anhydrous cobalt bromide in ethanol

to solid silver nitrite and shaking in a nitrogen atmosphere.

The solution was then filtered into an excess of the diamine in

ethanol to give a pink-brown solid. The complex was recrystallised

from ethanol. [Found: C, 28.7; H, 7.5; N, 25.6; O, 19.95.

$C_8H_{14}CoN_6O_4$ requires C, 29.4; H, 7.4; N, 25.7; O, 19.55%].

Co(N,N,N',N'-tetramethylethylenediamine)(NO₂)₂ Sodium cobalti-
nitrite and the diamine were heated for 3 days. Addition of
ethanol to the filtrate and cooling to ~ 0° overnight gave mauve
crystals. [Found: C, 26.8; H, 5.7; N, 21.4. C₆H₁₆CoN₄O₄
requires C, 27.0; H, 6.0; N, 21.0%].

Co(N,N'-diethylethylenediamine)₂(ONO)₂ On heating sodium cobalti-
nitrite and the diamine large purple crystals were formed. No
suitable solvent could be found for separating the complex from
unreacted starting material, so the large crystals were hand-picked
and washed with ether (these operations were carried out in a dry-box
as the compound is hygroscopic). [Found: C, 38.2; H, 8.3;
N, 22.1. C₁₂H₃₂CoN₆O₄ requires C, 37.6; H, 8.4; N, 21.9%].

CHAPTER 8

Zinc Nitrite Complexes

Zinc has less tendency to form octahedral complexes than either nickel or cobalt, also there are no crystal field stabilisation energy (C.F.S.E.) effects involved in complex formation with this metal. A series of zinc nitrite complexes has been prepared to investigate the effects of these properties on the coordination of the nitrite groups. The major disadvantage in working with zinc is the relatively few physical techniques which can be used to determine the structures of the complexes formed. However, as infrared spectroscopy is the main technique for determining the mode of coordination of nitrite ions considerable structural information can be obtained for the complexes reported here. (No C.F.S.E. occurs with manganese complexes and more techniques are available for studying the complexes formed. Preliminary experiments with manganese indicated that although complexes of the type $Mn(py)_4(ONO)_2$ could be prepared complexes with substituted ethylenediamines as ligands could not readily be obtained because of oxidation and hydrolysis).

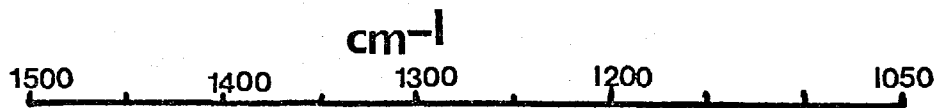
The infrared spectra ($2000 - 650 \text{ cm.}^{-1}$) of the complexes are listed in Table 8.1. For reference purposes the positions of the nitrite infrared bands in various nickel complexes are summarised diagrammatically in Table 8.2.

Table 8.1

Complex	$\nu_{N=O}$	ν_{N-O}	δ_{NO_2}
Zn(py) ₂ (NO ₂) ₂	1351(m)	1171(sb)	850(m)
Zn(2-mepy) ₂ (NO ₂) ₂	1370(s)	1131(sb)	839(m)
Zn(3-mepy) ₂ (NO ₂) ₂	1342(s)	1166(sb)	853(m)
Zn(4-mepy) ₂ (NO ₂) ₂	1346(m)	1163(sb)	865(m)
Zn(3,5lut) ₂ (NO ₂) ₂	*	1185(sb)	*
Zn(1-quin) ₂ (NO ₂) ₂	1370(m)	1160(sb)	*
Zn(en) ₂ (NO ₂) ₂	*	1230(sb)	850m
Zn(men) ₂ (NO ₂) ₂	*	1215(sb)	*
Zn(ophen) ₂ (NO ₂) ₂	*	1170(s)	826
Zn(a-dimen) ₂ (NO ₂) ₂	1380(s)	1145(s)	812(a)
Zn(S-dieen) ₂ (NO ₂) ₂	1380(m)	1215(s)	815
Zn tetmen(NO ₂) ₂	1316(m)	1183(s)	850(m)

* bands obscured by ligand modes

(a) position uncertain because of presence of ligand modes.



Free Ion

w vs

Nitro

w-vw
vs

Nitrito

ms-s s-vs

Chelating

vw-m vs

Bridging N-O s

s-vs

Table 8[2]

Nickel Nitrite Complexes:

Posns. of N-O Stretching Frequencies.

Prior to the commencement of this work no structural information on zinc nitrites was available. The molecular structure of $\text{Cs}_2\text{Zn}(\text{NO}_2)_4$ has recently been determined by X-ray crystallography⁵¹ and this is pertinent to the discussion of the structures of the complexes prepared here. Each zinc ion is surrounded by four nitrite groups disposed in a similar manner to that reported⁸ for the complex $\text{K}_3\text{Hg}(\text{NO}_2)_4\text{NO}_3$, i.e. there are four unsymmetrically chelating nitrite groups surrounding each zinc ion. The unsymmetrical nature of the bonding is demonstrated by the Zn-O bond lengths; 2.49 and 2.10 Å respectively for one nitrite group. (The corresponding distances in a symmetrically chelating nitrite group, e.g. $\text{Ni}(\text{tetmen})(\text{NO}_2)_2$ ⁹ are 2.06 and 2.12 Å). The infrared spectrum of the tetranitrite complex is in fact much more typical of a nitrito complex with $\nu_{\text{N=O}}$ occurring as a strong band at 1381 cm.^{-1} , $\nu_{\text{N-O}}$ a strong broad band at 1167 cm.^{-1} and δ_{NO_2} as a sharp medium intensity band at 847 cm.^{-1} . (This is in contrast to the spectrum of $\text{Ni}(\text{tetmen})(\text{NO}_2)_2$ where the corresponding bands occur at 1289 $\text{cm.}^{-1}(\text{m})$, 1200 $\text{cm.}^{-1}(\text{vs})$ and 863 $\text{cm.}^{-1}(\text{m})$). Thus the band lengths and the infrared spectrum both suggest that the interaction with one of the oxygen atoms is very weak.

The complexes $\text{ZnL}_2(\text{NO}_2)_2$ where L is py, 2, 3 or 4 mepy. or I-quin. all have infrared spectra typical of nitrito complexes.

It seems probable that the structures are closely related to that of the $\text{Zn}(\text{NO}_2)_4^{2-}$ ion; two of the asymmetrically coordinated nitrite ions being replaced by pyridine or substituted pyridine molecules. The infrared spectrum of $\text{Zn tetmen}(\text{NO}_2)_2$ suggests that the coordination of the nitrite group is much more asymmetric in this molecule than the nickel analogue and X-ray powder patterns confirm that they are structurally different.

$\text{Zn}(\text{s-dieen})_2(\text{NO}_2)_2$ and $\text{Co}(\text{s-dieen})_2(\text{NO}_2)_2$ have identical infrared spectra, as has been described in Chapter 7, the cobalt complex (and thus also the zinc complex) contains nitrito groups. $\text{Zn}(\text{a-dimen})_2(\text{NO}_2)_2$ has a very similar spectrum to $\text{Ni}(\text{a-dimen})_2(\text{NO}_2)_2$, a preliminary X-ray structural investigation indicated that it has a very similar molecular structure, i.e. nitrito groups again occur.

It has been shown in the case of nickel complexes that as the substitution of the ethylenediamine groups decreases there is a transition from nitrito to nitro groups. Perhaps the most interesting zinc complexes are those with ligands which in the case of nickel form nitro complexes. These are $\text{Zn}(\text{en})_2(\text{NO}_2)_2$, $\text{Zn}(\text{men})_2(\text{NO}_2)_2$ and $\text{Zn}(\text{ophen})_2(\text{NO}_2)_2$. Unfortunately in all these complexes only one of the N-O stretching modes can be assigned with certainty. Although this means that the mode coordination of the nitrite groups cannot be unambiguously identified, nitro coordination can almost certainly be eliminated.

The infrared spectra of $\text{Zn}(\text{ophen})_2(\text{NO}_2)_2$ and $\text{Ni}(\text{ophen})_2(\text{NO}_2)_2$ are illustrated in Fig.8(a). The i.r. bands of this ligand change considerably on going from one model compound to another which makes assignment of the nitrite bands difficult. In the nickel complex the band at 1280 cm.^{-1} has been tentatively assigned to the nitrite groups. In the spectrum of the zinc complex this is replaced by a strong broad band at 1170 cm.^{-1} ; typical of nitrito coordination.

The spectra of $\text{Zn}(\text{men})_2(\text{NO}_2)_2$ and $\text{Zn}(\text{en})_2(\text{NO}_2)_2$ contain strong bands at 1215 cm.^{-1} and 1230 cm.^{-1} respectively. This lowering of a band from the free ion positions is typical of oxygen coordination. The position of the band in these complexes coupled with the weak nature of the other NO stretching mode is more typical of chelating than nitrito coordination, suggesting some interaction with both oxygen atoms of the nitrite group. The exact nature of these interactions cannot be determined without further evidence. (The stretching modes in $\text{Zn}(\text{en})_2(\text{NO}_2)_2$ do not differ greatly from those observed in the free ion. However $\text{Zn}(\text{en})_2(\text{NO}_2)_2$ like $\text{Zn}(\text{py})_2(\text{ONO})_2$ behaves as a non-electrolyte in nitrobenzene).

Far infrared spectra ($500 - 200 \text{ cm.}^{-1}$)

There is little information available on the far infrared spectra of oxygen coordinated nitrite groups.

I.R. SPECTRA.

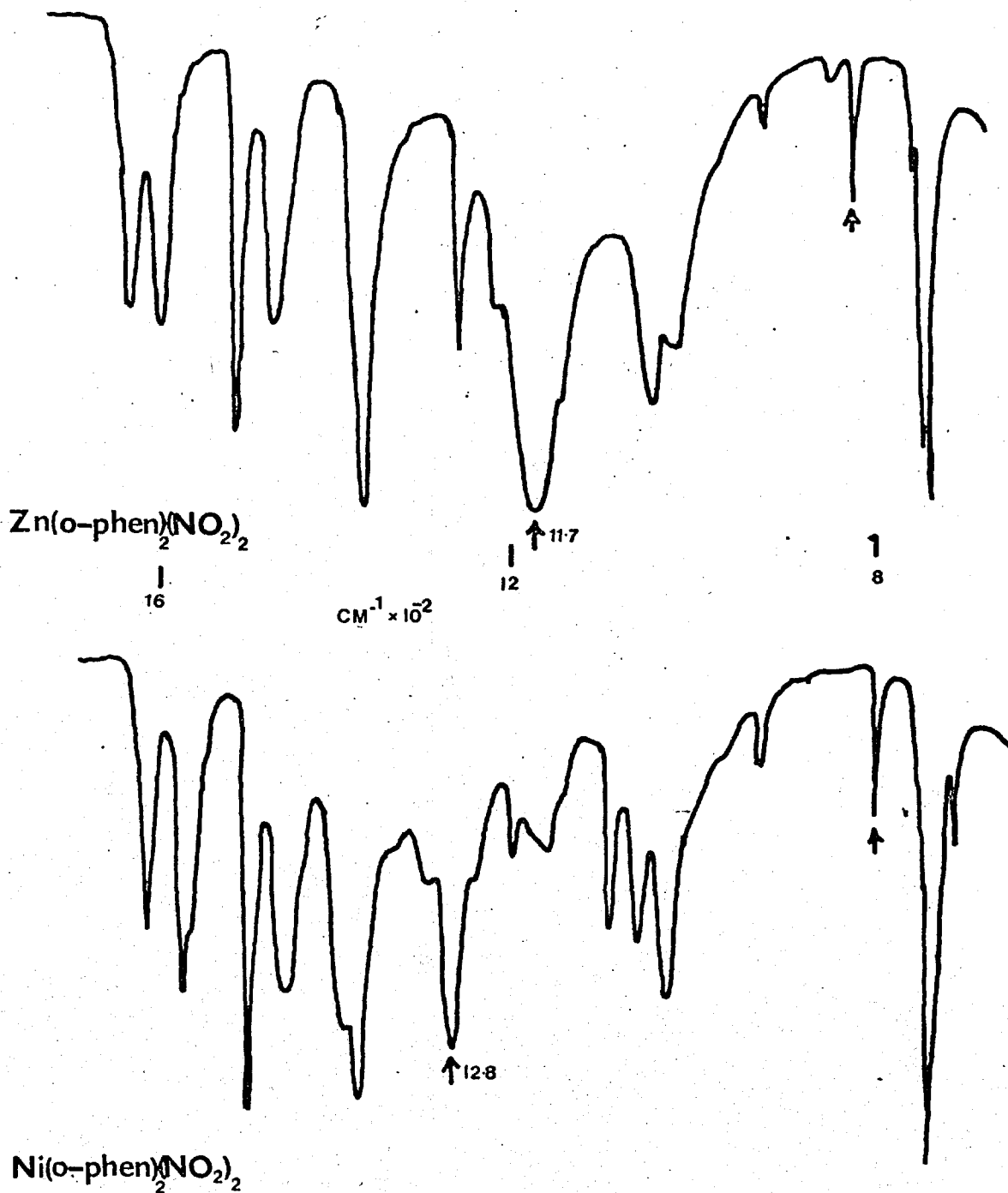


Fig. 8a.

The bands expected in the far infrared region are the metal ligand stretch ν_{M-O} , a metal oxygen bonding mode δ_{M-ONO} and an out of plane deformation ρ_w . The metal ligand stretch has been assigned⁵⁹ at 340, 355 and 345 cm.^{-1} in the series of complexes $[M(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$. $M = \text{Rh, Ir and Cr respectively}$. (The assignment in these complexes was aided by the fact that the nitrito isomers are unstable for the Rh and Ir complexes and the bands reported gradually change to 352 and 374 cm.^{-1} respectively as isomerisation occurs. The bending and wagging modes were not located and were presumed to be at low energy. The far infrared spectrum of the $\text{Zn}(\text{NO}_2)_4^{=}$ ion has been reported.¹ In the spectrum of $(\text{ocat}^{2+})\text{Zn}(\text{NO}_2)_4$, a single band occurs at 308 cm.^{-1} which was assigned as ν_{M-O} , however in the compound $\text{Cs}_2\text{Zn}(\text{NO}_2)_4$, a broad band occurs at $\approx 310 \text{ cm.}^{-1}$ which is split into two components at 328 cm.^{-1} and 290 cm.^{-1} . Again no other modes were observed.

The far infrared spectra of $\text{ZnL}_2(\text{NO}_2)_2$ ($L = \text{py, 2-mepy, 3-mepy}$ or 4-mepy) are all very similar; a very broad absorption occurs between 380 and 260 cm.^{-1} . In the spectrum of $\text{Zn}(3\text{-mepy})_2(\text{NO}_2)_2$ this is resolved into three peaks at 338 cm.^{-1} , 318 cm.^{-1} and 294 cm.^{-1} and similarly in the spectrum of $\text{Zn}(2\text{-mepy})_2(\text{NO}_2)_2$ three peaks are observed at 348 cm.^{-1} , 330 cm.^{-1} and 300 cm.^{-1} . In view of the probable similarity in the coordination of the nitrite groups in these complexes to that occurring in the $\text{Zn}(\text{NO}_2)_4^{=}$ ion this group

of bands are probably all components of the M-O stretching mode, the splitting occurring as a result of the low symmetry of the complex and solid state effects. Metal oxygen stretching frequencies have been observed⁶⁰ at 285 cm.^{-1} and 305 cm.^{-1} in the corresponding nitrate complex $\text{Zn(py)}_2(\text{NO}_3)_2$.

Preparation of Compounds

A methanolic solution of zinc nitrite was prepared by reacting a solution of zinc sulphate with a solution of sodium nitrite. A solution of sodium nitrite (2.76 gm 0.02M) in boiling methanol (90 ml) was added to a solution of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (5.74 gm 0.02M) in cold methanol (50 ml). The mixed solutions were reheated to boiling point and were filtered hot as the precipitated sodium sulphate is less soluble in hot methanol than in cold.

The general procedure for preparing zinc nitrite complexes was to add the ligand to the methanolic solution. The methanol was then taken off under vacuum and the residual solid was recrystallised from a suitable solvent.

Analytical results for the complexes are listed in Table 8.

$\text{Zn(py)}_2(\text{NO}_2)_2$

Pyridine (2 ml > 0.02M) was added to a methanolic solution (50 ml) of zinc nitrite (0.75 gm 0.005M). The methanol was taken off under vacuum and the product recrystallised from absolute alcohol. Yield 1.8 gm.

Zn(3-mepy)₂(NO₂)₂

Prep. as for pyridine complex. Yield 1.3 gm.

Zn(2-mepy)₂(NO₂)₂

Prep. as for pyridine complex. Yield 1.2 gm.

Zn(4-mepy)₂(NO₂)₂

Prep. as for pyridine complex. Yield 0.9 gm.

Zn(1-quin)₂(NO₂)₂

Excess isoquinoline was added to a methanolic zinc nitrite solution. On standing a flocculant white precipitate formed which was recrystallised from ethanol.

Zn(3-5 lut)₂(NO₂)₂

3-5Lutidine was added in excess to a solution of zinc nitrite in methanol. A crystalline precipitate rapidly formed in good yield. This precipitate was recrystallised from ethanol.

Zn(tetmen)(NO₂)₂

Excess tetmen was added to a methanolic solution of zinc nitrite. A white crystalline precipitate slowly formed. The product was recrystallised from methanol.

The compounds listed below were all prepared using a 2:1 mole ratio of ligand to metal. The hygroscopic complexes were handled in a dry box.

Zn(en)₂(NO₂)₂

Methanol taken off under vacuum. Product recrystallised from a mixture of ethanol and ether.

Zn(men)₂(NO₂)₂

Prep. as for Zn(en)₂(NO₂)₂. Compound was hygroscopic.

Zn(a-dimen)₂(NO₂)₂

Prep. as for Zn(en)₂(NO₂)₂ - hygroscopic.

Zn(s-dieen)₂(NO₂)₂

Prep. as for Zn(en)₂(NO₂)₂ - hygroscopic.

Zn(σ-phen)₂(NO₂)₂

A saturated methanolic solution of o-phenylenediamine (2 gm 0.1M) was added to a methanolic solution (30 ml) of zinc nitrite (1.5 gm 0.01M). A crystalline precipitate formed rapidly. The product was recrystallised from methanol. Yield 1.5 gm.

In all cases, the corresponding halide complexes which were prepared for purposes of comparison when assigning the infrared bands of the nitrite groups, could be prepared as crystalline solids by mixed ethanolic solutions of the zinc salt and the ligand.

Analytical Results

<u>Complex</u>	<u>Required</u>				<u>Found</u>			
	C	H	N	NO ₂ ⁻	C	H	N	NO ₂ ⁻
Zn(py) ₂ (NO ₂) ₂	38.06	3.19	17.75	29.2	38.53	3.26	17.86	29.0
Zn(2-mepy) ₂ (NO ₂) ₂	41.95	4.08	16.30	26.8	42.03	4.31	16.31	26.5
Zn(3-mepy) ₂ (NO ₂) ₂	41.95	4.08	16.30		41.7	4.2	16.7	26.3
Zn(4-mepy) ₂ (NO ₂) ₂	41.95	4.08	16.30		41.75	4.35	16.4	26.7
Zn(3-5 Lut) ₂ (NO ₂) ₂	45.3	4.90	15.05		44.9	4.8	15.0	
Zn(I-quin) ₂ (NO ₂) ₂	52.01	3.39	13.48	22.2	52.15	3.51	13.57	22.0
Zn(en) ₂ (NO ₂) ₂	17.3	5.85	30.4	-	17.03	6.40	29.8	
Zn(men) ₂ (NO ₂) ₂	23.7	6.7	27.6		22.3	6.07	26.2	
Zn(ophen) ₂ (NO ₂) ₂	38.7	4.31	22.5		38.92	4.54	22.15	
Zn(a-dimen) ₂ (NO ₂) ₂	28.78	7.25	25.18		28.69	7.78	25.47	
Zn(s-dieen) ₂ (NO ₂) ₂	37.0	8.28	21.6		36.8	8.3	21.3	
Zn(tetmen)(NO ₂) ₂	26.34	5.89	23.89		26.43	5.71	23.5	

Chapter 9

Magnetic Studies on Compounds containing Bridging Nitrite
Groups

Studies of nickel nitrite complexes¹ led to the isolation of a number of complexes postulated to contain bridging (NO) and bridging (O) nitrite groups. It was considered possible that both types of bridging would lead to magnetic interactions between the bridged nickel ions. To investigate these interactions the magnetic susceptibilities of a group of the compounds have been determined over a temperature range.

During the course of this work the data for $[\text{Ni}(\text{en})_2\text{NO}_2]\text{ClO}_4$ have been published⁵⁵. There is good agreement between the published results and those reported here.

The room temperature moments of the compounds are listed in Table 9.1. Temperature variation of susceptibility data is listed in Table 9.2 and representative behaviour of the compounds is shown in diagrams 9(a) and (b).

Structures of the Compounds

The structure of only one of the compounds studied here, i.e. $[\text{Ni}(\text{en})_2\text{NO}_2]\text{ClO}_4$, has been definitely established. The structure of the isomorphous fluoroborate complex(II) indicates that nickel atoms are linked in chains by bridging (NO) nitrite groups.

An X-ray crystallographic structural determination is being carried

out on $\text{Ni}(\text{3-mepy})_2(\text{NO}_2)_2 \cdot \frac{1}{3}\text{C}_6\text{H}_6$ but no details of the structure are so far available.

Some information on the structure of the other complexes has been obtained from their infrared and electronic spectra¹. The infrared spectra of the complexes $\text{Me}_4\text{N.Ni}(\text{NO}_2)_2$, $\text{Ni en}(\text{NO}_2)_2$ and $\text{Ni men}(\text{NO}_2)_2$ suggest that only one type of nitrite coordination occurs in these complexes, i.e. NO bridging. The nickel atoms are all octahedrally coordinated.

The structures of the other complexes, i.e. $\text{Ni}(\text{iquin})_2(\text{NO}_2)_2$, $\text{Ni}(\text{3-mepy})_2(\text{NO}_2)_2 \cdot \frac{1}{3}\text{C}_6\text{H}_6$ and $\text{Ni}(\text{4-mepy})_2(\text{NO}_2)_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$ are more complex. Infrared data suggest that more than one type of nitrite coordination occurs and it is in these complexes that bridging by nitrite groups coordinated by a single oxygen atom has been postulated to account for the infrared spectra. The nickel atoms are again octahedrally coordinated.

Magnetic Behaviour of the Compounds

In keeping with the octahedral coordination of the nickel atoms the room temperature moments indicate a ${}^3\text{A}_{2g}$ ground state for all the complexes. For the perchlorate complex the room temperature moment is less than the spin only value indicating some magnetic interaction.

The temperature variation of susceptibility data for this compound, (Table 9.2 ~~diagram 9a~~) shows that it does not obey a Curie Weiss law.

Below 150°K antiferromagnetic behaviour is observed. Extrapolation of the linear portion of the graph gives a Weiss constant of 110°.

All the other compounds obey the Curie-Weiss law over the temperature range studied. The Weiss constants, ranging from 20 to 76°, indicate some magnetic interaction but unfortunately this cannot be correlated with the postulated structures of the compounds. There is no clear distinction between those compounds containing NO bridged nitrite groups only, and those with more complex structures.

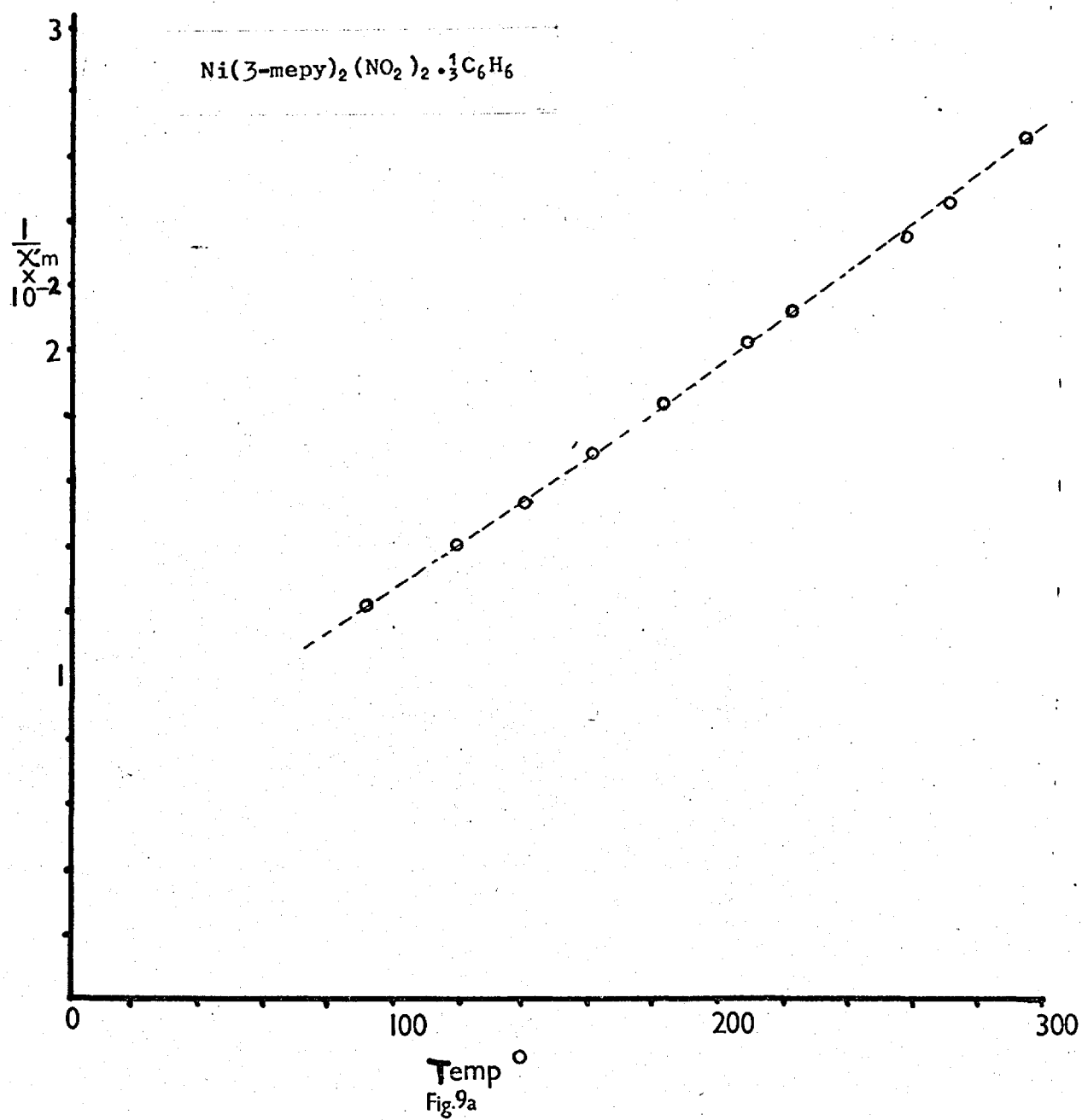
Table 9.1

Room Temperature Magnetic Moments of Compounds

<u>Compound</u>	<u>μ^*</u>	<u>T</u>	<u>θ^0</u>
Me ₄ N Ni(NO ₂) ₃	2.98	295	36
Ni en(NO ₂) ₂	3.16	297	20
Ni men(NO ₂) ₂	3.26	298	20
[Ni en ₂ (NO ₂)]ClO ₄	2.81	295	110°
Ni(iquin) ₂ (NO ₂) ₂	3.10	294	58
Ni(3-mepy) ₂ (NO ₂) ₂ · $\frac{1}{3}$ C ₆ H ₆	2.98	294	76
Ni(4-mepy) ₂ (NO ₂) ₂ ·C ₆ H ₆	3.15	296	60

* Calculated from Curie Law

° Obtained from temperature variation of susceptibility data.



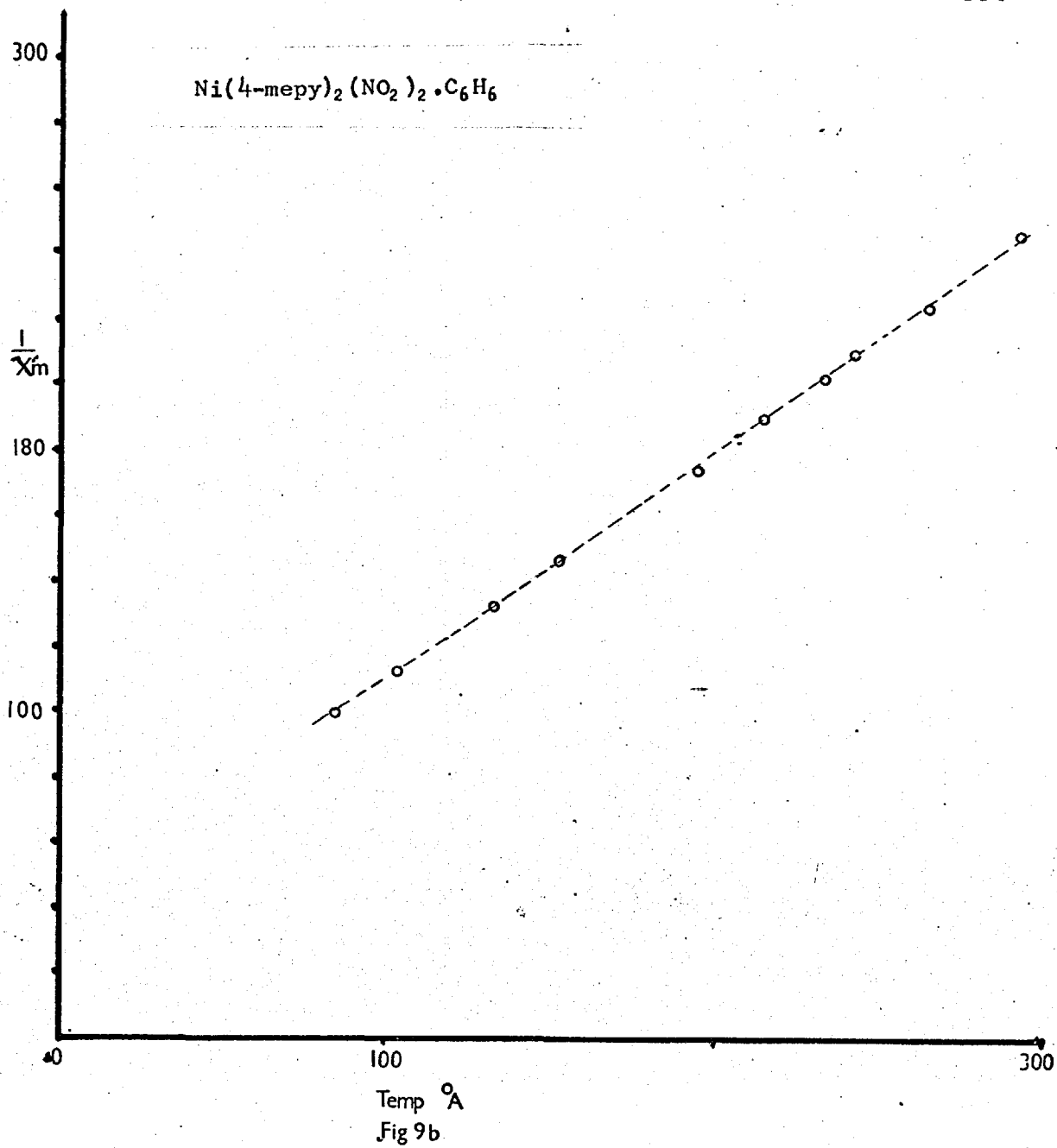


Table 9.2

Variation of Molar Susceptibility ($\times 10^{-6}$ c.g.s.u.) with Temperature ($^{\circ}\text{K}$)

Compound		Diamagnetic Correction for Ligands*							
<u>$[\text{Ni}(\text{en})_2\text{NO}_2]\text{ClO}_4$</u>		(D.C.) 137×10^{-6} c.g.s.u.							
χ'_M		3318	3648	3916	4215	4545	4969	5426	5708
T		295	263	239	212	185	156	138	110
χ'_M		6040							
T		95							
<u>$\text{Me}_4\text{N}, \text{Ni}(\text{NO}_2)_3$</u>		(D.C.) 121×10^{-6} c.g.s.u.							
χ'_M		4064	4365	4514	4765	4996	5297	5589	6280
T		295	275	262	248	234	220	206	179
χ'_M		7502	8437	9662	11270				
T		146	125	104	83				
<u>$\text{Ni}(\text{men})(\text{NO}_2)_2$</u>		(D.C.)* 94×10^{-6} c.g.s.u.							
χ'_M		4438	4833	5089	5528	5977	6533	7209	8015
T		298	273	260	238	220	196	176	159
χ'_M		9058	10440	13080					
T		135	113	81					

* From Pascal's constants

<u>Ni en(NO₂)₂</u>		(D.C.)* 82 x 10 ⁻⁶ c.g.s.u.										
χ'_M		4192	4617	5067	5698	6228	6879	7430	8151	9380	10600	12920
T		297	264	242	214	194	174	157	140	126	105	86

<u>Ni(iquin)₂(NO₂)₂</u>		(D.C.)* 146 x 10 ⁻⁶ c.g.s.u.										
χ'_M		4050	4354	4683	5112	5418	6028	6760	7550	8470	9325	
T		294	266	248	220	211	180	153	128	110	93	

<u>Ni(3-mepy)₂(NO₂)₂ $\frac{1}{3}$C₆H₆</u>		(D.C.) 184 x 10 ⁻⁶ c.g.s.u.										
χ'_M		3743	4042	4326	4705	4934	5449	5922	6492	7168	8210	
T		294	270	251	222	208	182	160	140	119	91	

<u>Ni(4-mepy)₂(NO₂)₂ C₆H₆</u>		(D.C.)* 220 x 10 ⁻⁶ c.g.s.u.										
χ'_M		4142	4458	4754	5252	5734	6288	6808	7530	8880	10026	
T		296	264	242	214	194	173	152	132	103	84	

Preparation of Compounds

The preparation of all the complexes studied here have been reported elsewhere^{1,57}.

Ni(men)(NO₂)₂

Prep. as in ref.1, p.95. Not recrystallised from methanol.

Analysis. Found 26.1% Ni. Theoretical 26.1% Ni.

[Ni(en)₂NO₂]₂ClO₄

Prep. ref.1, p.94.

Analysis. Found C, 15.0, H, 4.8, N, 21.5.

Required C, 14.81, H, 4.97, N, 21.60.

Ni(Iquin)₂(NO₂)₂

Prep. as in ref.1, p.105 (as a grey crystalline precipitate from a methanolic solution of nickel nitrite).

Analysis. Found C, 52.6, H, 3.52, NO₂⁻, 22.3.

Required C, 52.88, H, 3.45, NO₂⁻, 22.50.

Me₄N₂Ni(NO₂)₃

Prepared as in ref.1, p.147.

Analysis. Found 21.4% Ni,

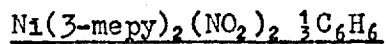
Required 21.67% Ni.

Ni en(NO₂)₂

Prepared as in ref.1, p.95.

Analysis. Found 27.4% Ni,

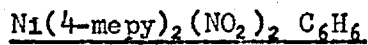
Required 27.85% Ni.



Prep. as in ref.1, p.107.

Analysis. Found C, 47.1, H, 4.39, N, 15.48.

Required C, 46.31, H, 4.44, N, 15.44.



Prep. as in ref.1, p.107.

Analysis. Found C, 51.98, H, 4.69, N, 13.28,

Required C, 52.1, H, 4.86, N, 13.50.

Chapter 10

Nitrite Complexes. A Summary

The results described here generally confirm the usefulness of infrared spectra for determining the structures of nitrite complexes. Not surprisingly, unambiguous structural assignments cannot always be made from infrared data alone; the infrared spectra of the free ion, a nitrito group and a chelating group can in particular be very similar. Usually other experimental evidence, e.g. electronic spectra, or conductivity measurements, gives clear information of which of these types of bonding is involved.

Rather surprisingly none of the new nitrite complexes described is a nitro compound; oxygen coordination, i.e. nitrito or chelating, is the predominant mode of bonding that has been found.

For the cobalt complexes the same factors are involved as have previously been discussed in relation to nickel nitrite complexes; steric factors favour the formation of the nitrito complex for most of the compounds described. In fact the cobalt complexes in general are very similar to the corresponding nickel complexes. However nickel complexes corresponding to the 3:1 cobalt(II) complexes with pyridine and substituted pyridines have not been isolated; and the 4:1 isoquinoline complexes differ in

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that the cobalt complex is a simple nitrito complex whereas the nickel analogue contains nitro groups as well as nitrito.

Cobalt(II) complexes with en, men, etc were not isolated. Only mixed products containing Co(III) species could be obtained. The combination of high ligand field strength and small steric hindrance involved with these ligands both favour the higher oxidation state, low spin d^6 system.

In the case of zinc the usual tendency of this metal to form complexes with a lower ligand to metal ratio than the corresponding nickel complexes is observed, thus pyridine forms $Zn(py)_2(NO_2)_2$, whereas with nickel $Ni(py)_4(NO_2)_2$ is obtained. With substituted ethylene diamine ligands octahedral complexes are formed as the substitution is decreased from tetmen.

With en, men, and o-phen, nitro complexes are not formed with zinc. A large number of factors are involved in determining the structure adopted by a particular complex, in this case it is conceivable that the steric hindrance to nitro bonding, in the case of nickel complexes, is more than balanced by the greater C.F.S.E. this mode of bonding would produce. Obviously this would not be the case for zinc, and oxygen coordination would thus be favoured.

Nitrite References

1. M.A. Hitchman, Ph.D. Thesis, London University, 1966.
2. M.A. Porai-Koshits and L.M. Dikareva, *Kristallografiya*; 1959, 4, 650.
3. J.A. Bertrand and D.A. Carpenter, *Inorg. Chem.*, 1966, 514.
4. S.M. Jørgensen, *Z. Anorg. Chem.*, 1894, 5, 169.
5. F. Basolo, R.G. Pearson, P.M. Henry and J.G. Bergman, *J. Amer. Chem. Soc.*, 1954, 76, 5920.
6. R.K. Murmann and H. Taube, *ibid.*, 1956, 78, 4886.
7. M.G. Drew, D.M.L. Goodgame, M.A. Hitchman and D. Rogers, *Proc. Chem. Soc.*, 1964, 363.
8. D. Hall and R.V. Holland, *Proc. Chem. Soc.*, 1963, 204.
9. M.G.B. Drew and D. Rogers, *Chem. Comm.*, 1965, 476.
10. M.G.B. Drew, Ph.D. Thesis, University of London, June 1966.
11. M.G.B. Drew, D.M.L. Goodgame, M.A. Hitchman and D. Rogers, *Chem. Comm.*, 1965, 20, 477.
12. M.A. Porai-Koshits and M. Bukovska, *Kristallografiya*, 1961, 6, 381.
13. A. Langseth and E. Walles, *Z. Phys. Chem.*, 1934, 27, 209.
14. R. Newman, *J. Chem. Phys.*, 1952, 20, 444.
15. R.E. Weston and T.F. Brodasky, *J. Chem. Phys.*, 1957, 27, 683.
16. J.W. Sidman, *J. Amer. Chem. Soc.*, 1957, 79, 2675.
17. A. Tramer, *Compt. Rend.*, 1959, 248, 3546.
18. M. le Postellec, J.P. Mathieu and H. Poulet, *J. Chim. Phys.*, 1963, 60, 1319.
19. M. le Postellec and J.P. Mathieu, *Compt. Rend.*, 1962, 254, 1800.
20. B.M. Gatehouse, *J. Inorg. Nucl. Chem.*, 1958, 8, 79.

21. K. Nakamoto, J. Fujita and H. Murata, *J. Amer. Chem. Soc.*, 1958, 80, 4817.
22. K. Nakamoto "Infrared spectra of Inorganic and Coordination Compounds", p.154, John Wiley and Sons Inc., 1963.
23. J. Chatt, L.A. Duncanson, B.M. Gatehouse, J. Lewis, R.S. Nyholm, M.L. Tobe, P.F. Todd and L.M. Venanzi, *J. Chem. Soc.*, 1959, 4073.
24. D.M.L. Goodgame and M.A. Hitchman, *Inorg. Chem.*, 1964, 3, 1389.
25. D.M.L. Goodgame and M.A. Hitchman, *Inorg. Chem.*, 1965, 4, 721.
26. C.K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon Press, 1962, p.109.
27. A. Tramer and J.P. Mathieu, *Compt. Rend.*, 1959, 247, 392.
28. Y. Puget and C. Duval, *Compt. Rend.*, 1960, 250, 4141.
29. H. Elliott, B.J. Hathaway and R.C. Slade, *Inorg. Chem.*, 1966, 5, 669.
30. F. Basolo and G.S. Hammaker, *J. Amer. Chem. Soc.*, 1960, 82, 1001.
31. F. Basolo and G.S. Hammaker, *Inorg. Chem.*, 1962, 1, 1.
32. J.I. Bullock and D.G. Tuck, *J. Chem. Soc.*, 1965, 1877.
33. D.M.L. Goodgame and M.A. Hitchman, *Inorg. Chem.*, 1964, 3, 1389.
34. Gmelin, 1961, 58.
35. L. Cambi and E. Paglia, *Atti Accad. Naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1956 [8], 21, 372.
36. A.V. Babaeva, I.B. Baranovskii and G.G. Afanas'eva, *Dokl. akad. Nauk, S.S.S.R.*, 1962, 143, 587.
37. A.V. Babaeva, G.J. Volkova and N.G. Grigor'eva, *Zhur. neorg. Khim.*, 1959, 4, 330.
38. L. El-Sayed and R.C. Ragsdale, *Inorg. Chem.*, 1967, 6, 1940.

39. D.M.L. Goodgame and M.A. Hitchman, *Inorg. Chem.*, 1967, 6, 813.
40. J.F. Duncan, R.M. Golding and K.F. Mok, *J. Inorg. Nucl. Chem.*, 1966, 28, 1114.
41. A.H. Norbury, E.A. Ryder and R.F. Williams, *J. Chem. Soc. (A)*, 1967, 1439.
42. C.D. Burbridge, Ph.D. Thesis, 1968, University of London.
43. R.V. Biagetti and H.M. Haendler, *Inorg. Chem.*, 1966, 5, 383.
44. A.D. Liehr, *J. Phys. Chem.*, 1963, 67, 1314.
45. F.A. Cotton and R.H. Soderberg, *J. Amer. Chem. Soc.*, 1963, 85, 2402.
46. F.A. Cotton, D.M.L. Goodgame and R.H. Soderberg, *Inorg. Chem.*, 1963, 2, 1162.
47. A.B.P. Lever, *Inorg. Chem.*, 1965, 4, 1042.
48. N.S. Gill and H.J. Kingdon, *Austral. J. Chem.*, 1966, 19, 2197.
49. N.S. Gill, R.H. Nuttall, D.E. Scaife and D.W.A. Sharp, *J. Inorg. Nucl. Chem.*, 1961, 18, 79.
50. F.A. Cotton and J.G. Bergman, *Inorg. Chem.*, 1966, 5, 1208.
51. P. Phavanantha, personal communication.
52. D.M.L. Goodgame and M.A. Hitchman, *J. Chem. Soc. (A)*, 1967, 612.
53. M.R. Rosenthal and R.S. Drago, *Inorg. Chem.*, 1965, 4, 840.
54. D.M.L. Goodgame and M. Hitchman, *Inorg. Chem.*, 1966, 5, 1303.
55. B.J. Hathaway and R.C. Slade, *J. Chem. Soc. (A)*, 1967, 952.
56. P. Phavanantha, personal communication.
57. F.J. Llewellyn and J.M. Waters, *J. Chem. Soc.*, 1962, 3845.

58. W.G. Palmer, *Experimental Inorganic Chemistry*, Cambridge University Press, 1954, p.559.
59. M.J. Cleare and W.P. Griffith, *J. Chem. Soc. (A)*, 1967, 1144.
60. R.H. Nuttall and D.W. Taylor, *Chem. Comms.*, 1968, 1417.
61. B.N. Figgis and R.S. Nyholm, *J. Chem. Soc.*, 1958, 4190.
62. A.I. Vogel, *"Quantitative Inorganic Analysis"*, Longmans 1961, p.497.
63. *Ibid.* p.322.

PHYSICAL TECHNIQUES

Electronic spectra were obtained by diffuse reflectance using a Beckman D.K.2. Solution spectra were obtained on a Perkin Elmer 350.

Magnetic measurements were made by the Gouy method, using an instrument constructed by Dr D. Forster. The field was calibrated using $\text{CoHg}(\text{SCN})_4$ ⁶¹.

E.s.r. spectra were obtained on a Varian V 4500-15 spectrometer.

Infrared spectra were recorded on a Grubb Parsons spectrometer (4000 - 400 cm.^{-1}) and D.M.4 Mark II (500 - 200 cm.^{-1}) instruments.

Analyses

Carbon, hydrogen and nitrogen analyses were performed by the Microanalytical Department. Nickel was determined gravimetrically by precipitation with dimethylglyoxime. Copper was determined by precipitation as cuprous thiocyanate⁶². Analysis for nitrite was carried out by the method in Vogel⁶³.