STUDIES OF TRANSITION METAL COMPLEXES INVOLVING PYRIMIDINE AND RELATED BASES.

a thesis presented by

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ABSTRACT.

Metal complexes of various substituted pyrimidine and purine bases have been prepared in an investigation of the co-ordination behaviour of these biochemically important ligands. The subjects of study were: 5-methyl- and 4-methyl-pyrimidine, 2-aminopyrimidine, 4,6-dimethylpyrimidine, 2,4,6-trimethylpyrimidine, adenine, guanine, xanthine and purine.

For the pyrimidine bases, complexes of divalent cobalt, nickel, copper and zinc are described, whereas for the purine bases most attention has been devoted to a study of the copper complexes.

An X-ray crystal structure determination on $Cu(adenine)_2 Cl_2 \cdot 3H_2O$ has shown it to possess a dimeric structure similar to that of the copper adenine inner complex isolated by Weiss. The antiferromagnetism of this complex and of related compounds has been investigated and the results are discussed with reference to dimeric cupric acetate monohydrate.

In general, the co-ordination geometries of the complexes have been studied using electronic spectroscopy, vibrational spectroscopy (including the low energy region) and magnetic susceptibility measurements. The copper complexes have also been examined by electron spin resonance spectroscopy.

ACKNOWLEDGEMENTS.

CONTENTS.

ABBREVIATIONS.

The following ligand abbreviations are used throughout the text.

5-methylpyrimidine	5Mepyr
4-methylpyrimidine	4Mepyr
2-aminopyrimidine	$2NH_2pyr$
4,6-dimethylpyrimidine	dmp
2,4,6-trimethylpyrimidine	tmp
pyridine	py
picoline	pic
imidazole	im
purine	pu
adenine	adH
guanine	gu
xanthine	xa
theophylline	theo

In descriptions of electronic and infra-red spectra the following abbreviations are used.

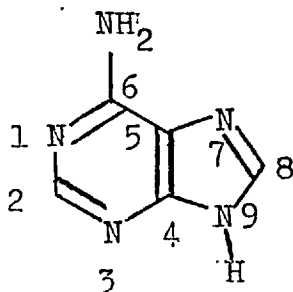S - strong m - medium w-weak sh-shoulder.

INTRODUCTION.

In recent years, there has been a rapidly expanding interest in the living cell, the relationship of the nucleus to the functioning of the cell, and, in particular, the role of the nucleic acids. A detailed study has only been possible since the development of such modern techniques as X-ray crystallography, chromatography and electron microscopy.

Two distinct types of nucleic acid have been isolated from the cell, deoxyribonucleic acid (DNA) which is found in the nucleus, and ribonucleic acid (RNA) which occurs in the surrounding cytoplasm[1,2]. DNA controls the production of RNA which, in turn, acts as a template for protein synthesis. The type of protein produced depends on the amino acid sequence and this is determined by the code the DNA transmits. It is now known that this code is contained in the sequence of bases in DNA.

Various molecular weight determinations[3] have established that nucleic acids are, in fact, high molecular weight polymers. The monomeric unit is a nucleotide, which is a base directly linked to a pentose sugar in the form of it's monophosphate ester. RNA contains the purine bases, adenine and guanine, and the pyrimidine bases, cytosine and

uracil. Each of these bases is linked to the pentose,
ribose. DNA contains adenine, guanine, cytosine and
thymine, each of the bases being linked to a 2-deoxyribose
pentose. The point of attachment of the bases to the sugar
groups has been firmly established[3]. The pyrimidine bases
are linked via N(3) and the purine bases via N(9).

Adenine.
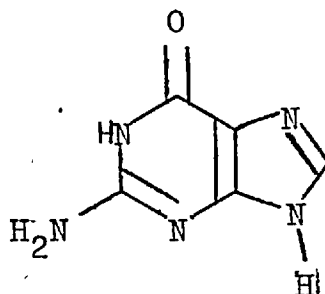
Guanine.
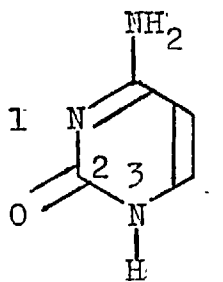
Thymine.

Cytosine.
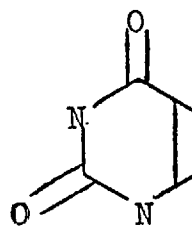
Uracil.
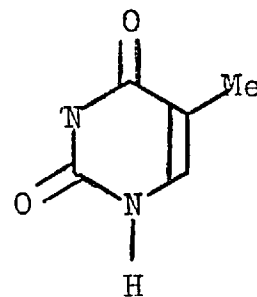
The celebrated work of Watson and Crick[4] completed
the picture of the DNA structure by providing a model that
satisfactorily explained the results of X-ray diffraction
studies[5-7]. There are two poly-nucleotide chains wound as
spirals round a common axis and heading in different directions.
The secondary helical structure is maintained by hydrogen
bonding between the bases of the two strands and these

bases are specific to one another. Adenine bonds only to thymine and guanine only to cytosine. In recent years, molecular interactions between aromatic molecules have been studied and it has been suggested[8] that base stacking may be more important than hydrogen-bonded interactions in maintaining a double-stranded helical structure.

The role of metal ions in the structure and function of nucleic acids has received increasing attention since the model for DNA was proposed[9-24]. Vallee[14] has reported reproducible findings of metals in RNA isolated from widely ranging sources and has suggested[14,16] that they may play a role in maintaining configuration, perhaps by linking purine and pyrimidine bases. It must be pointed out that while DNA has a firmly established helical structure, the nature of the secondary structure of RNA is less well-defined[25]. There is good evidence that the single polynucleotide chain is doubled back on itself so that pairs of bases may become linked by hydrogen bonds. Vallee's observations are consistent with such a model, and his suggestion that transition metal ions may act as cross-linking devices seems a valid one.

It is well known that metal ions interact with DNA[9,13,19,20,23]. Whereas most metals stabilise the structure, with respect to thermal denaturation, copper ions exhibit a marked destabilising influence[19,23]. The denaturation at

relatively low temperatures, induced by copper ions, has been shown by Eichhorn and Clark[19] to be reversible. They interpret their data by assuming that metal ions are interposed between complimentary strands of DNA by co-ordination to bases, in such a manner that hydrogen bonds are broken and the secondary structure of each strand is destroyed. However, in view of the ready renaturation of the denatured DNA, it is suggested that the copper ions must somehow keep the bases in register, even in the denatured state. Eichhorn has confirmed the possibility of base-metal interaction by investigating the bonding of copper ions to denatured DNA[20]. Adenine, guanine and cytosine base moities provide binding sites but thymine base seems to be unaffected.

There have been other studies on the destabilisation of the secondary structure of DNA which substantiate the theory of copper combination with helical bases[26,27]. It must be borne in mind that conditions under which such copper-DNA interactions have been demonstrated are relatively unphysiological, in that they involve heat denaturation or high levels of copper ions.

Frieden and Bryan[22] have made a more complete study of the key factors influencing the ability of copper to complex with DNA and produce changes in its conformation. They provide evidence of interactions in the room temperature

range and suggest that the time of exposure to copper ions, in this range, may be critical. One possible explanation of their data is the assumption that there is a purine specificity and that the purine nucleotides bind to copper ions in a 1:1 complex.

The mechanism of binding is not known. Frieden and Bryan propose that distortion of the secondary structure could result from interference with the base stacking and that there is not, necessarily, an unwinding of helices or strand separation.

The question of the possible physiological significance of copper-DNA complexes has not been answered. It does seem significant that copper ions can influence denaturation, when the relationship between denaturation and replication is considered. If the replication of DNA follows a mechanism in which the double helix unwinds, and each polynucleotide chain acts as a template for the synthesis of DNA[28], then any information on the forces which hold the two polynucleotide chains in register, and factors affecting these forces is vital to the understanding of this mechanism.

The influence of cupric ions on DNA has stimulated

interest in the type of bonding between these metal ions and the nucleotide bases[13,15,20,21]. A 2:1 copper cytosine complex has been isolated[29] and a crystal structure determination[30] has established that the metal ion is bonded to the N(1) atoms of the cytosine molecules. This nitrogen is a site of hydrogen bonding in the double helix and the isolation of this complex presents the possibility of copper-DNA interactions involving copper-cytosine-copper cross links. Since cytosine is hydrogen bonded to guanine, it is of interest to investigate the type of complexes this purine base will form, especially in view of the fact that copper destabilisation is greater for DNA rich in cytosine and guanine[27].

In this work, adenine has been studied as well as guanine because there is evidence of copper interaction with adenine nucleotide[20]. The compounds prepared have been examined by various physical methods to determine the structural aspects. Many of these compounds have been previously reported by Weiss[31,32], who has performed a largely preparative study of copper complexation by these bases.

For comparative purposes, this study has included purine, the parent ring system, and xanthine, a product of nucleic acid catabolism.

Apart from the pyrimidine bases that exist as independent entities within nucleic acids, the pyrimidine ring occurs, in the purine bases,fused to an imidazole ring. There has been no systematic investigation of the ligand capacity of pyrimidine molecules, although copper complexes of some simple pyrimidines[33,34,35] have been reported as well as metal complexation by pyrimidine acids[36,37]. In contrast, imidazole and substituted imidazoles have received considerable attention and their complexes are well documented[38-43]. The pyrimidine ring occurs in other metabolically active structures and a review of the literature on pyrimidine co-enzymes and their function has been made by Rossi[44].

In this work, a series of substituted pyrimidine molecules have been selected for study. These are 4-methyl-pyrimidine, 5-methylpyrimidine, 4,6-dimethylpyrimidine, 2,4,6-trimethylpyrimidine and 2-aminopyrimidine. This latter was included because of the difficulty experienced with the synthesis of the 2-methyl derivative.

Pyrimidine is a very weak base as compared with pyridine (pKa pyrimidine = 1.3, pKa pyridine = 5.2)[45]. The introduction of electron donor substituents increases the

basicity(pKa 4-methylpyrimidine = 2.0, pKa 2-aminopyrimidine = 3.5)[45] but can alter the steric requirements as a ligand. In the 4-methyl derivative, the effect of the substituent is to increase the basicity of the ortho-nitrogen, N(3), and make it the preferred donor site. There is equal basicity of the ring nitrogen atoms in the other derivatives.

The presence of two potential donor atoms admits the possibility that pyrimidine molecules may act as bridging ligands forming complexes similar to those isolated with pyrazine[46-49], quinoxaline[50-52] and the 1,2-dipyridyl-ethylene isomers[53,54].

CHAPTER 1.

5-Methylpyrimidine Complexes.

The complexes prepared and studied in this work are listed in Table 1.1. In addition, manganese compounds, $Mn(5Mepyr)X_2$ (X=Cl,Br) and zinc compounds, $Zn(5Mepyr)_n X_2$ (n=1,2; X=Cl,Br,I) were made for comparison of their low frequency spectra.

5-Methylpyrimidine forms two series of compounds of stoichiometry $M(5Mepyr)X_2$ and $M(5Mepyr)_2X_2$, as do pyridine, 2- and 3-picoline[55-58]. Unlike pyridine it does not form an extensive series of compounds of the type $M(5Mepyr)_4X_2$, the only examples being the hydrated cobalt iodide and copper perchlorate complexes.

The pyrimidine system (1,3-diazine) might be expected to show a strong resemblance to the pyrazine (1,4-diazine) system. Although pyrazine compounds of the type NiL_4Cl_2 (L = pyrazine, substituted pyrazine) have been isolated[46], these readily lose ligand giving the 1:1 compounds and the most extensive sets of pyrazine compounds are those of 2:1 and 1:1 stoichiometries.
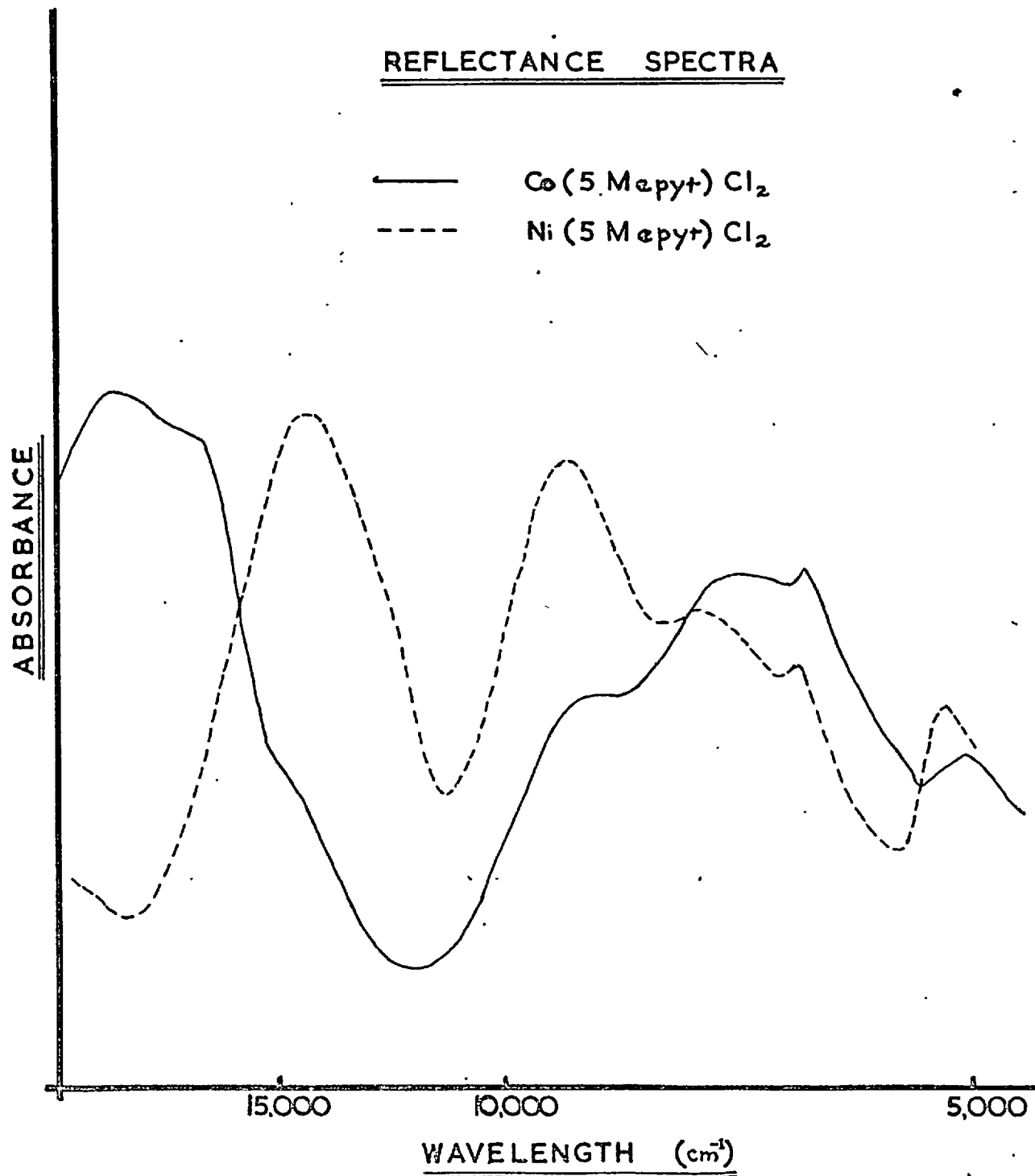
For 5-substituted pyrimidine the steric effect of the substituent is expected to be minimal and the ligand

character is dominated by a bridging tendency.

Electronic Spectra and Magnetic Properties. (Table 1.1, 1.3)

All the 1:1 metal halogen complexes can be assigned polymeric structures with metal-halogen chains and bridging pyrimidine molecules in axial positions. The symmetry of these compounds could be as high as D_{2h} but from structural studies on analogous Mpy_2X_2 systems[59,57,60] it is likely to be low (Ci). It is possible to interpret the spectra on the basis that the co-ordination sphere of each metal ion approximates to D_{4h} symmetry.

The near infra-red spectrum of $Fe(5Mepyr)Cl_2$ shows two clearly resolved electronic bands which are the transitions from $^5T_{2g}$ to the $^5A_{1g}$ and $^5B_{1g}$ levels arising from ^5E_g. It has been shown[61] that an application of the McClure theory to six co-ordinate ferrous complexes, predicts that the band splitting is solely a function of the difference in the σ-antibonding contributions of the ligands. The $\delta\sigma$ value calculated for this compound (+1200) compares closely with that of $Fe(3,5dichloropy)_2Cl_2$[61] (+1150) and is smaller than that of $Fepy_2Cl_2$[61] (+1500). This suggests that the extent of σ bonding increases in an order which parallels that of the pKa values for the three ligands (3,5-dichloropy 0.67; 5-Mepyr 1.8; pyr 5.2)[45].

FIG. I.

REFLECTANCE   SPECTRA

——————   Co (5 Mepyt) Cl₂
- - - - -   Ni (5 Mepyt) Cl₂

ABSORBANCE

WAVELENGTH (cm⁻¹)

15,000   10,000   5,000

The splittings of the ν_1 bands of Co(5Mepyr)X_2 and Ni(5Mepyr)X_2 are similar in magnitude and in sign (see Figure 1). The nickel compounds will be discussed in greater detail. In D_{4h} symmetry, the $^3T_{2g}$ and $^3T_{1g}$(F) levels of an octahedral nickel complex are split into $^3B_{2g} + ^3E_g$ and $^3A_{2g} + ^3E_g$ levels. The lower energy bands of Ni(5Mepyr)X_2 are assigned as the transitions to the components of $^3T_{2g}$, the stronger band at higher energy being the transition to the orbital doublet. This gives a splitting (Table 1.2) which is comparable in sign and magnitude to that found for trans-octahedral NiL_2X_2 systems (L=py, 3Mepy). There is also a similar, small splitting of the $^3T_{1g}$ level, the spectrum of Ni(5Mepyr)Cl_2 showing a single band with a low energy shoulder. By analogy with the pyridine system[56], this shoulder is assigned as the ^3E_g component.

If a Δ value is calculated using a weighted mean of the components of $^3T_{2g}$ as a measure of the energy of the unsplit band, it is found to be larger than that of Ni(3Mepy)$_2Cl_2$. Since $\delta\sigma$ is correspondingly smaller (Table 1.2), there must be increased metal-ligand π-bonding in the pyrimidine complex.

In Ni(5Mepyr)X_2, there is only a small decrease in Δ as X changes from Cl to Br, as compared with the reduction in Ni(3Mepyr)$_2X_2$. It is likely that as the contribution to the

ligand field from X decreases, there is a compensating effect due to increased π-bonding. This is expected since the ease of donation of d-electrons by the metal depends on the nature of the attached groups and, as the electronegativity of X decreases, the metal's ability to donate electrons will increase.

In the Cu(5Mepyr)X$_2$ compounds, the tetragonal distortion is such that the three predicted transitions[62] are unresolved and the visible spectrum consists of a single, broad, low intensity band. The energy of absorption is close to that of structurally similar compounds involving pyrazine[33], quinoxaline[52] and 1,2 di(4-pyridyl) ethylene[53].
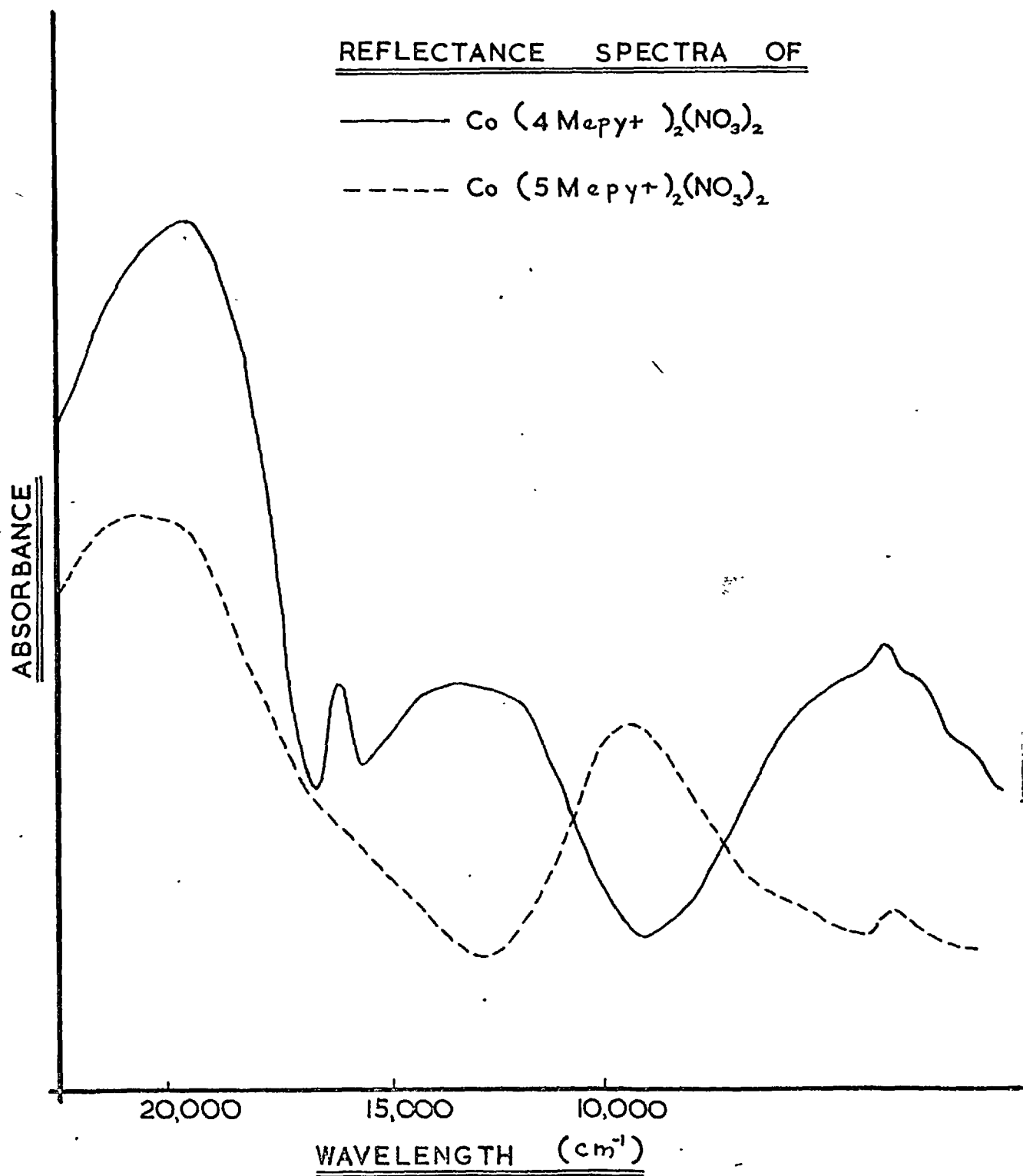
All other copper complexes of this ligand have asymmetric bands characteristic of tetragonal environments. The 2:1 copper halogen compounds can be assigned polymeric halogen-bridged structures analogous to that of Cupy$_2$X$_2$[63]. The bands are at lower energies than those observed for the pyridine complexes[62] and there is a greater difference in energy between the chloro and bromo compounds. Also the band in Cu(5Mepyr)$_2$Cl$_2$ contains a low energy shoulder.

The copper nitrite complexes absorb at higher energies and at positions consistent with the presence of nitrite or other O-bonded groups. For comparison, Cu(NH$_3$)$_2$(ONO)$_2$[64],

which contains nitrite groups and is believed to have a rhombic structure, absorbs intensely at $16,700 cm^{-1}$, whereas the corresponding nitro complex, $Cu(NH_3)_2(NO_2)_2$[64], has a band maximum at $18,200 cm^{-1}$. Both $Cu(5Mepyr)_2(NO_2)_2$ and $Cu(5Mepyr)_2(NO_3)_2$ absorb at slightly higher energies than the 1:1 compounds and the bands show low energy shoulders (unresolved in the case of the nitrite). A temperature range magnetic study has been made for the nitrite complexes; $Cu(5Mepyr)(NO_2)_2$ is found to exhibit pronounced anti-ferro-magnetic exchange.

The carboxylate complexes, $Cu(CH_3COO)_2(5Mepyr)_{0.5}$ and $Cu(HCOO)_2(5Mepyr)$ will be discussed in a later chapter together with analogous compounds formed by other substituted pyrimidine molecules.

The hydrated complexes of cobalt and nickel bromide have the spectra of distorted octahedra and can be formulated as $M(5Mepyr)_2Br_2.2H_2O$ or $\left[M(5Mepyr)_2(OH_2)_2\right]Br_2$. The sign of the distortion is the reverse of that observed for $M(5Mepyr)Br_2$ (M=Co,Ni) and indicates an in-plane environment of nitrogen atoms. Thus the structure may be visualised as a pyrimidine-bridged polymer with either water molecules or bromine atoms in axial positions.

FIG. 2.

REFLECTANCE   SPECTRA   OF

——— Co (4 Mepy+)₂(NO₃)₂

----- Co (5 Mepy+)₂(NO₃)₂

ABSORBANCE

20,000   15,000   10,000

WAVELENGTH   (cm⁻¹)

Both compounds obey the Curie Weiss law down to $90^{\circ}K$ and have negative Θ values of 24(Ni) and 42(Co). These values confirm that the structures are not monomeric but do involve bridging molecules which enable anti-ferromagnetic interactions between the metal ions.

When the spectral parameters of the nickel compound (Table 1.2) are compared with those of NiL_4Br_2 (L=py, 3Mepy) it can be seen that Dt is smaller than that usually observed for a NiN_4Br_2 unit. It is of the same order as the splitting parameter of $Ni(im)_4Br_2 \cdot 2H_2O$[41] which is believed to contain co-ordinated water molecules. On this basis, it is tempting to infer that the compound involves bonded water.

A similar Dt value (220) is observed for the corresponding cobalt complex.

It is not possible to decide if the hydrated nickel nitrate complex, $Ni(5Mepyr)(NO_3)_2 \cdot 3H_2O$, contains bonded water. The spectrum is that of an octahedral complex and the bands show no evidence of splitting.

Either of two possibilities for the co-ordination sphere of cobalt in $Co(5Mepyr)_2(NO_3)_2$ would explain the observed spectrum (Figure 2). It could be formed by four nitrogen atoms and two oxygen atoms (i.e. a polymeric

TABLE 1.1.

Diffuse Reflectance Spectra (cm^{-1}.)

Fe(5Mepyr)Cl$_2$	6560(m) 9710(m)
Co(5Mepyr)Cl$_2$	6560 ca.8660 ca.14800(sh,w) 16950 18690
Co(5Mepyr)Br$_2$	6020 8400 ca.13330(sh,w) 16120 18450
Co(5Mepyr)$_2$(NO$_3$)$_2$	9520(m) ca.19690(m) 20400(m)
Co(5Mepyr)$_2$(NCS)$_2$	9620(s) 19610(s) 20410(s)
Co(5Mepyr)$_2$I$_2$	ca.5990(s,sh) 6710(s) 8780(s) 14800(vs) 24100(vs)
Co(5Mepyr)$_2$Br$_2$2H$_2$O	ca.6410 8330 ca.17860(sh) 18520 19230
Co(5Mepyr)$_3$(ClO$_4$)$_2$.H$_2$O	8850(m) ca.19050(m,sh) 20080(m) 21370(m)
Co(5Mepyr)$_4$I$_2$.4H$_2$O	8620 ca.12050(w,sh) ca.22200(m) 26300(m)
Ni(5Mepyr)Cl$_2$	ca.6670 8500 ca.12350(sh) 14490 ca.20620(sh) 24150
Ni(5Mepyr)Br$_2$	ca.6500 8400 13900 ca.19610(sh) 23260
Ni(5Mepyr)(NO$_3$)$_2$.3H$_2$O	9170(m) 16130(m) ca.21980(sh,w) 26110(s)
Ni(5Mepyr)$_2$Br$_2$.2H$_2$O	8330 10420 14930 21280(sh) 24880
Cu(5Mepyr)Cl$_2$	14180
Cu(5Mepyr)Br$_2$	14080
Cu(5Mepyr)(NO$_2$)	15870
Cu(5Mepyr)(NO$_3$)$_2$	14950
Cu(5Mepyr)$_2$Cl$_2$	ca.9760(sh) 13610

Table 1.1 continued.

$Cu(5Mepyr)_2Br_2$ 14300

$Cu(5Mepyr)_2(NO_2)_2$ <u>ca.</u>10000(sh) 16130

$Cu(5Mepyr)_2(NO_3)_2$ <u>ca.</u>11240 15150

$Cu(5Mepyr)_4(ClO_4)_2.2H_2O$ 16390

$Cu(5Mepyr)(HCO_2)_2$ <u>ca.</u>8400(sh) 14490

$Cu(5Mepyr)(CH_3CO_2)_2$ 14490

TABLE 1.2.

	Δ	Δ_{xy}	Δ_z	Dt	Ds	$\delta\sigma$
A.						
Ni(5Mepyr)Cl$_2$	7840	650	1050	-210	-400	990
Ni(5Mepyr)Br$_2$	7730	640	1040	-220		
Ni(5Mepyr)$_2$Br$_2$.2H$_2$O	9030	1040	630	240		
Ni(2NH$_2$pyr)$_2$Cl$_2$.2H$_2$O	8300	950	590	210	260	
Ni(2NH$_2$pyr)$_2$Br$_2$.3H$_2$O	7750	990	350	370	360	
B.						
Nipy$_2$Cl$_2$	7600	600	1080	-275	-340	
Nipy$_2$Br$_2$	7250	580	1020	-250	-400	
Ni(3Mepy)$_2$Cl$_2$	7730	620	1075	-260	-360	1030
Ni(3Mepy)$_2$Br$_2$	7300	590	1010	-240	-400	
Ni(3Mepy)$_4$Br$_2$	9100	1130	465	380	500	
Ni(4Mepy)$_4$Br$_2$	8930	1130	410	410	530	
Ni(3Mepy)$_4$Cl$_2$	9130	1040	660	220	310	
Ni(4Mepy)$_4$Cl$_2$	9370	1110	590	300	410	

A : this work.

B : data from reference 56.

Note: $\delta\sigma$ was calculated from the relationship developed by Rowley and Drago[65] in a crystal field analysis of the spectra of tetragonal nickel (II) pyridine complexes.

TABLE 1.3.

Room Temperature Magnetic Moments (BM).

$Mn(5Mepyr)Cl_2$	5.66	$Cu(5Mepyr)Cl_2$	2.00
$Mn(5Mepyr)Br_2$	5.70	$Cu(5Mepyr)Br_2$	1.93
$Fe(5Mepyr)Cl_2$	5.58	$Cu(5Mepyr)(NO_2)_2$	1.86(θ=-96)
$Co(5Mepyr)Cl_2$	5.06	$Cu(5Mepyr)(NO_3)_2$	1.82
$Co(5Mepyr)Br_2$	4.76	$Cu(5Mepyr)_2Cl_2$	1.79
$Co(5Mepyr)_2(NCS)_2$	4.70	$Cu(5Mepyr)_2Br_2$	1.95
$Co(5Mepyr)_2I_2$	4.50	$Cu(5Mepyr)_2(NO_2)_2$	1.86 (θ=0)
$Co(5Mepyr)_2Br_2.2H_2O$	5.07(θ=-42)	$Cu(5Mepyr)_2(NO_3)_2$	1.84
$Co(5Mepyr)_3(ClO_4)_2.H_2O$	4.59	$Cu(5Mepyr)_4(ClO_4)_2.2H_2O$	1.83
$Co(5Mepyr)_4I_2.4H_2O$	4.73	$Cu(5Mepyr)(HCO_2)_2$	1.26
$Ni(5Mepyr)Cl_2$	3.18	$Cu(5Mepyr)_{0.5}(CH_3CO_2)_2$	1.50
$Ni(5Mepyr)Br_2$	3.20		
$Ni(5Mepyr)_2Br_2.2H_2O$	3.10(θ=-24)		

pyrimidine-bridged structure or by four oxygen atoms and two nitrogen atoms (a monomeric structure with bidentate nitrate anions). Each of these structures has symmetry less than octahedral and a small splitting of the ν_1 band is observed. The absorption energy is similar to that found for $CoL_4(ONO)_2$ (L=4Mepy, isoquinoline; ν_1 = 9300cm^{-1}, 9800cm^{-1} respectively)[66] and greater than that of $Co(py)_4(ONO)_2$ .2py (ν_1 = 9170cm^{-1})[66]. This could be taken as evidence in

favour of a pyrimidine-bridged arrangement. Also, $CoL_2(NO_3)_2$ compounds that are known to contain (L=Me$_3$PO)[67], or, thought to contain (L=4Mepy, im, 2Meim)[41] chelating nitrates produce spectra more similar to those of pseudo-tetrahedral complexes. However, the presence of chelating anions is not inconsistent with the observed infra-red spectrum. The compound also has a magnetic moment well below the usual range for six co-ordinate cobalt (II) and more like those of the postulated chelating nitrate complexes. As there appears to be a small ligand field distortion this would be best explained as arising from magnetic exchange in a bridged structure.

There is no detectable splitting of the ν_1 band in Co(5Mepyr)$_2$(NCS)$_2$ which suggests that there is an almost regular arrangement of nitrogen atoms about the cobalt atom. In fact, the band energies are close to those of Co(im)$_6$(NO$_3$)$_2$[41] which does have this type of cobalt environment. The vibrational spectra do not clearly indicate the nature of the co-ordinated anion, and it is possible that the pyrimidine molecules are acting as bridging ligands. The nature and intensity of the electronic bands produced by Co(5Mepyr)$_2$I$_2$ indicate an approximately tetrahedral geometry and this is confirmed by the magnetic moment (4.5BM). The low intensity spectrum of Co(5Mepyr)$_4$I$_2$.4H$_2$O does not allow unambiguous assignment. The band at 8660cm^{-1} may represent the complete ν_1 transition. However, there is unusually

strong absorption around $5880cm^{-1}$ where ligand vibrations occur, and it is possible that there may be a low energy component of ν_1. The magnetic moment (4.73BM) is somewhat lower than expected for octahedrally co-ordinated cobalt (II) with an orbital triplet ground state. Structurally, the complex may be visualised as monomeric, possibly with water molecules completing the co-ordination sphere.

There appears to be little departure from octahedral symmetry in the geometry of $Co(5Mepyr)_3(ClO_4)_2 \cdot H_2O$. ν_1 is unsplit but does show slight asymmetry to the low energy side. The room temperature magnetic moment (4.59 BM) is compatible with a structure formed by a network of pyrimidine bridges. The electronic band lies at lower energy than that of $Co(5Mepyr)_2(NCS)_2$, and makes it unlikely that there is a CoN_6 chromophore.

A nickel iodide complex has been made which analyses for the formula $Ni(5Mepyr)_{1.5}I_2$. It has a low magnetic moment and a spectrum very like that of planar $Ni(4Mepyr)_2I_2$ (Chapter 2). These observations can be explained, if the material is, in fact, $Ni(5Mepyr)_2I_2$ with a high level (ca. 10%) of tetrahedral impurity. The shoulder observed at about $10,000cm^{-1}$ could be the ν_2 band of a tetrahedral nickel species. Also, no shoulder can be detected in the corresponding 4-methylpyrimidine complex.

Vibrational Spectra. (Table 1.4)

Ring vibrations that occur at $1405 cm^{-1}$ (s) and $1435 cm^{-1}$ (m,br) shift to $1425 cm^{-1}$ (s) and $1450 cm^{-1}$ (m.br) on co-ordination, and complicate bond assignments in that region.

The $\nu_3(NO_3)$ bands of $Cu(5Mepyr)(NO_3)_2$ are consistent with the presence of bidentate nitrate groups[68] whereas the lower energy of ν_3 in $Cu(5Mepyr)_2(NO_3)_2$ could suggest monodentate nitrate groups (Table 1.4). For comparison, $Cu(pyridine)_2(NO_3)_2$ which produces bands in the regions $1477-1468 cm^{-1}$ and $1282-1268 cm^{-1}$[69] is now known to contain bridging and bidentate nitrate groups[70].

The $\nu_3(NO_3)$ bands of $Co(5Mepyr)_2(NO_3)_2$ are concordant with bidentate nitrate groups. However, it has been noted[71,72] that infra-red data, alone, is often inconclusive as to the nature of nitrate co-ordination and, for this compound, the electronic data strongly suggest monodentate groups.

There is a large number of nitrite bands in $Cu(5Mepyr)(NO_2)_2$ (Table 1.4). The strong band at $1030 cm^{-1}$ is lower than $\nu_{sym.}$ for most types of co-ordinated nitrite and close to the range defined for an O-bridged nitrite[73]. However, the high energy band ($1439 cm^{-1}$) is somewhat lower

TABLE 1.4.

Nitrate group frequencies (cm^{-1}).

	ν_3				ν_1	ν_2	
$Cu(5Mepyr)_2(NO_3)_2$	1408(m)	1351(s)	1307(m)		1031(s)	820(w)	
$Cu(5Mepyr)(NO_3)_2$	1449(m)	1355(s)	1307(s)	1290(sh)	1031(s)	820(m)	
$Co(5Mepyr)_2(NO_3)_2$	1470(s)	1295(s)	1274(s)		1022(s)	813(m)	810(s)

ν_4 obscured by ligand vibrations.

Nitrite group frequencies (cm^{-1}).

	$\nu(N-O)$					$\delta(ONO)$
$Cu(5Mepyr)_2(NO_2)_2$	1374(s)	1176(m)	1120(s)			820(m)
$Cu(5Mepyr)(NO_2)_2$	1439(m)	1395(m)	1295(s)	1124(m)	1031(s,br)	830(m)

than expected for $\nu_{asy.}$ of a single O-bridge. The bands
at 1395cm^{-1} and 1124cm^{-1} suggest the existence of nitrito
groups, while the band at 1295cm^{-1} falls close to $\nu_{asym.}$
for symmetrically chelating nitrites. There does not appear
to be any absorption in the $\nu_{sym.}$ region of the chelating
anion. It seems fair to conclude that this compound
contains two or more different types of O-bonded nitrites

There are fewer nitrite bands in $Cu(5Mepyr)_2(NO_2)_2$.
The bands at 1374cm^{-1} and 1120cm^{-1} lie within the ranges of
N-O stretches of nitrito groups[73]. It is difficult to
explain the presence of a band at 1170cm^{-1} but interesting
to note that the compound $\left[Cubipy_2(ONO)\right]NO_3$[74], which contains
a chelating nitrite, produces absorptions at 1360cm^{-1} and
1150cm^{-1}.

The band at 2100cm^{-1} (s), in $Co(5Mepyr)_2(NCS)_2$, can
be assigned as $\nu(C-N)$. No vibrational mode could be
distinguished around 800cm^{-1} that could be assigned as $\nu(C-S)$.

Vibrational Spectra (400cm^{-1} - 90cm^{-1}) Table 1.5.

In the free ligand, there is an out-of-plane ring
deformation which occurs at 345cm^{-1}. On co-ordination this
band moves to higher frequency. In the polymeric octahedral
complexes, the magnitude of the shift is dependent on the

metallic radius Mn($\underline{ca}$.352cm^{-1}); Fe(360cm^{-1}); Co($\underline{ca}$.370cm^{-1}); Ni($\underline{ca}$.378cm^{-1}); Cu($\underline{ca}$.378cm^{-1}). In the polymeric tetrahedral complex, Co(5Mepyr)Br$_2$, the band is doubled.

Polymeric octahedral Compounds.

In recent years, interest has been shown in the far infra-red spectra of Cupy$_2$X$_2$ and similar polymeric copper compounds[75-78]. Often, two halogen sensitive bands are observed in the normal copper-halogen stretching region and there has been controversy as to the origin of the second band[79,80].

In Cu(5Mepyr)$_2$X$_2$, there is only one definite halogen dependent absorption above 200cm^{-1} with the copper-chlorine band containing a resolvable shoulder. Below 200cm^{-1}, there is a second halogen-sensitive absorption that could be due to the copper-halogen in-plane band of the distorted $\left[CuX_4 \right]_n$ chain.

The 1:1 compounds have essentially identical spectra to the corresponding 2:1 compounds as may be expected from their closely related structures. All four compounds show bands at, or near, 255cm^{-1} and 190cm^{-1}. It can be assumed that these are associated with copper-nitrogen vibrations as they are unaffected by changes of halogen.

The hydrated compounds $M(5Mepyr)_2Br_2.2H_2O$ (M=Co,Ni) have similar spectra in the region 400-200cm^{-1}. There is a medium, strong, broad band system centred at 230cm^{-1} that is in the expected range for the metal-nitrogen stretching mode. A few tentative assignments have been made for the remaining $M(5Mepyr)X_2$ compounds (Table 1.5). In the chloro complexes, when two definite bands are apparent above 200cm^{-1}, the band at higher energy has been assigned as the metal-chlorine stretching mode. Assuming that the ratio ν(M-Br):ν(M-Cl) is of the same order as that observed for the copper compounds (ca. 0.8), most metal-bromine stretching modes are expected below 200cm^{-1}. In general, broad, medium-intensity bands are observed in that region and no assignments are possible.

$Co(5Mepyr)Br_2$ has a spectrum with two sharp bands at 236cm^{-1} and 215cm^{-1}. A similar spectrum is observed for $Ni(5Mepyr)Br_2$ with the bands at 250cm^{-1} and 227cm^{-1}. In each case, the bands have been treated as a split metal-nitrogen stretching mode.

The spectrum of $Co(5Mepyr)_2(NCS)_2$ does not exclude the possibility that the thiocyanate group may be bridging. Although the bridging anion in $Copy_2(NCS)_2$[81] produces bands at 472cm^{-1} and 468cm^{-1}, the more widely separated pair of bands (482cm^{-1} and 432cm^{-1}) observed for $Co(5Mepyr)_2(NCS)_2$ could have the same origin. Absorption at 302cm^{-1} and

$252 cm^{-1}$ may be attributed to the M-N modes of bonded iso-thiocyanate and bonded pyrimidine.

Tetrahedral Species (Table 1.5).

On the basis of their vibrational spectra, $Zn(5Mepyr)_2X_2$ and $Zn(5Mepyr)X_2$ may be assigned tetrahedral configurations. Metal-halogen vibrations occur in similar positions in the spectra of $Znpy_2X_2$[82,83].

$Co(5Mepyr)_2I_2$ shows absorption from about $260 cm^{-1}$ to $170 cm^{-1}$ that is resolved into broad components centred at $220 cm^{-1}$ and $195 cm^{-1}$. This band system is the envelope of the M-N and M-I vibrational modes.

Nitrate complexes.

The bands between $260 cm^{-1}$ and $350 cm^{-1}$ can be attributed to metal-oxygen vibrations, while the bands around $240 cm^{-1}$ are predominantly the result of metal-nitrogen vibrations. For comparison, the compounds $M(2\text{-pic})_2(NO_3)_2$ $(M=Co,Ni,Cu)$[84] give rise to metal-oxygen vibrations at 280, $306 cm^{-1}$ (Co); 286, $312 cm^{-1}$ (Ni) and 282, $326 cm^{-1}$ (Cu) and have been assigned bidentate nitrate groups.

Nitrite Complexes.

Cu(5Mepyr)(NO$_2$)$_2$ and Cu(5Mepyr)$_2$(NO$_2$)$_2$ each show medium-strong band systems between 350cm^{-1} and 400cm^{-1} that probably contain components of the expected M-O stretching mode. It is likely that the ligand vibration contributes to the absorption at 380cm^{-1}.

TABLE 1.5.

Vibrational Spectra (400-90cm^{-1}).

Distorted octahedral.

$Cu(5Mepyr)_2Cl_2$	302(s) 287(s) 252(ms) 192(m) 167(m) 137(w) 103(ms)
$Cu(5Mepyr)_2Br_2$	255(ms) 236(s) 190(ms) 180(s) 153(w) 128(ms) 90(m)
$Co(5Mepyr)_2Br_2.2H_2O$	294(m,br) 228(s) 215(s) 177(m,br) 136(m)
$Ni(5Mepyr)_2Br_2.2H_2O$	365(w) 295(m,br) 252(sh) 235(s) 220(ms) 176(m) 160(m)
$Co(5Mepyr)_2(NCS)_2$	482(m) 432(m) 362(m) 302(ms) 250(ms)
$Mn(5Mepyr)Cl_2$	352(w) 238(s) ca.208(s) ca.157(m,br) ca.137(m)
$Mn(5Mepyr)Br_2$	355(w) 210(s) ca.150(m,br)
$Fe(5Mepyr)Cl_2$	360(w) 241(s) 215(m)
$Co(5Mepyr)Cl_2$	368(w) 248(s) 220(s) ca.200(s) 165(s,br)
$Co(5Mepyr)Br_2$	371(w) 355(w) 236(s) 215(s) ca.170(m,br) 136(m)
$Ni(5Mepyr)Cl_2$	377(w) 260(s) ca.200(s,br)
$Ni(5Mepyr)Br_2$	380(w) 250(s) 227(s) 187(s,br) 160(s)
$Cu(5Mepyr)Cl_2$	378(w) 300(s) 260(w) 244(w) 193(s) 165(ms) 137(m) 107(m)
$Cu(5Mepyr)Br_2$	253(m) 234(ms) 190(ms) 181(s) 153(m) 127(m)
$Ni(5Mepyr)_{1.5}I_2$	268(m) 248(m) 232(m) 173(w) 152(m) 130(w)

Table 1.5 continued.

Nitrates.

$Co(5Mepyr)_2(NO_3)_2$	380(w) 345(w) 295(sh,m) 272(s) 235(s) 185(m) 152(m)
$Cu(5Mepyr)(NO_3)_2$	370(w) 298(s) 248(ms) 228(ms) 180(m) 130(m,br)
$Cu(5Mepyr)_2(NO_3)_2$	368(m) 300(m) 270(s) 248(s) 210(ms) 183(m) 128(m,br)
$Ni(5Mepyr)(NO_3)_2 \cdot 3H_2O$	<u>ca</u>.260(w) 232(m)

Nitrites.

$Cu(5Mepyr)_2(NO_2)_2$	380(ms) 356(m) 342(ms) <u>ca</u>.300(w) 236(m) 173(s) 125(m,br)
$Cu(5Mepyr)(NO_2)_2$	382(m) 358(ms) 294(m) 260(w) 224(mw)

Tetrahedral.

	ν(M-X)	ν(M-N)	Other bands
$Zn(5Mepyr)_2Cl_2$	335(s) 285(s)	205(ms) 192(ms)	307(ms) 110(m,br)
$Zn(5Mepyr)_2Br_2$	259(s) 222(s)[∓]	207(w,sh)	177(w)
$Zn(5Mepyr)_2I_2$	210(s)	198(s)	180(w) 138(m)
$Zn(5Mepyr)Cl_2$	342(s) 308(s)	223(ms) 210(ms)	187(m) 158(m) 110(m,br)
$Zn(5Mepyr)Br_2$	262(s)	228(s)	184(m) 160(m) 87(m)
$Zn(5Mepyr)I_2$	208(m)	230(s) 195(s)	168(ms) 140(m)

Tentative assignments for polymeric octahedral complexes.

	ν(M-X)	ν(M-N)	
$Cu(5Mepyr)_2Cl_2$	287(s)	252(ms)	
$Cu(5Mepyr)_2Br_2$	236(s)	255(ms)	∓ may be M-N or M-X.
$Cu(5Mepyr)Cl_2$	300(s)	252(w)av.	

Table 1.5 continued.

	$\nu(M-X)$	$\nu(M-N)$
Cu(5Mepyr)Br$_2$	234(ms)	253(m)
Ni(5Mepyr)Br$_2$		238(s)av.
Co(5Mepyr)Br$_2$		225(s)av.
Co(5Mepyr)Cl$_2$	248(s)	220(s)
Mn(5Mepyr)Cl$_2$	238(s)	208(s)
Mn(5Mepyr)Br$_2$		210(s)
Fe(5Mepyr)Cl$_2$	241(s)	215(m)

38.

These assignments are, in general, consistent with those postulated for a series of pyrimidine complexes which have been reported during the course of this work[85].

CHAPTER 2.

4-Methylpyrimidine Complexes.

The most extensive series of compounds of this
ligand have the general formula $M(4Mepyr)_2X_2$. The steric
effect of a methyl group in the 4-position tends to destabilise
a polymeric structure involving pyrimidine and halogen bridges
and 1:1 compounds of this type are formed less readily than
for 5-methylpyrimidine.

Electronic spectra and magnetics. (Tables 2.1 and 2.3)

The compounds $M(4Mepyr)_2X_2$ (M=Co,Ni,X=Cl; M=Ni,X=Br)
and $Co(4Mepyr)_2Br_2.2H_2O$ have spectra characteristic of
distorted octahedral complexes in which the axial field is
stronger than the in-plane field and have been formulated as
halogen-bridged polymers.

The Δ values calculated for $Ni(4Mepyr)_2X_2$ are very
similar to those of $Ni(3pic)_2X_2$ but are smaller than those of
$Ni(5Mepyr)X_2$ (Tables 1.2 and 2.2). In 4-methylpyrimidine, there
is a preferred donor site, $N(3)$, which is ortho to the
substituent and, consequently, more basic than $N(1)$. If the
ligand bonds via $N(3)$, then it would be expected to provide a
greater contribution to the overall ligand field than would
5-methylpyrimidine. However, there would be steric inter-

action involving the methyl group which would cause a lenthening of the metal- N(3) bond and a reduction in the axial field strength. It would be possible that Δ decreased despite the increased basicity of the ligand.

On the basis of the Δ values this type of bonding could be postulated but when the extent of the band splitting is considered, it becomes unlikely. A steric effect which lengthened Ni-N(3) would weaken the axial field to a similar value to the in-plane field and produce a spectrum indicating a smaller deviation from octahedral symmetry. This effect has been observed for $Ni(2Meim)_2Cl_2$[41] which is a polymeric octahedral complex with no detectable band splitting, even at $95^{\circ}K$.

The compounds $Ni(4Mepyr)_2X_2$ (X=Cl,Br) have comparable Dt values to $Ni(5Mepyr)X_2$ and there is an increase in the Dt:Ds ratio which indicates greater covalency. This is good evidence that the pyrimidine molecules do not bond through the more basic nitrogen atom but link via N(1) because of steric considerations.

It is interesting that neither $Ni(4Mepyr)_2Br_2$ nor $Co(4Mepyr)_2Br_2 \cdot 2H_2O$ adopts the pyrimidine bridged structure of $M(5Mepyr)_2Br_2 \cdot 2H_2O$ (M=Ni,Co) which would accommodate the

methyl group more easily[x] than a halogen-bridged structure with axial M-N(3) bands. The fact that this arrangement is not found confirms that N(1) is the probable donor site in the Ni(4Mepyr)$_2$X$_2$ compounds and the similar band splittings of the cobalt halide compounds prompts a similar assertion.

The 1:1 compound, Ni(4Mepyr)Cl$_2$, (Table 2.2) has markedly smaller band splitting than Ni(5Mepyr)Cl$_2$, although the nature of the splitting confirms that there is a similar metal environment in each. This reduction is expected because the ligand is acting as a bridge and steric intereaction can be minimised only by a lengthening of metal-ligand bonds, which will reduce the axial field strength.

In contrast to Ni(4Mepyr)Cl$_2$, the only 1:1 cobalt halide complex, Co(4Mepyr)Br$_2$, adopts a pseudo-tetrahedral structure. The compound can be formulated as a dimer with bromine bridges or a polymer with pyrimidine molecules linking successive pseudo-tetrahedral units. In either situation the symmetry about each cobalt atom will be less

_ _

[x]In the pyrimidine bridged structure the distance between 4-methyl hydrogen and neighbouring C$_6$ hydrogen is _ca._ 1.28 Å and interaction would be small.

than tetrahedral. It will be very approximately C_{3v} in the dimer and C_{2v} in the polymer.

The near infra-red spectrum shows two bands of separation ca.2000cm^{-1}, that at higher energy (6780cm^{-1}) being slightly more intense and broader than the other band (4760cm^{-1}). When this spectrum is compared with those of other distorted tetrahedral cobalt complexes, in the same region, a close resemblance to the C_{3v} species, Co(benzimidazole)Br$_3$$^-$ [86], can be seen (bands at 6900cm^{-1} and 4900cm^{-1}). This suggests that an analogous band assignment may be made.

In C_{3v} symmetry, the ν_2 band of tetrahedral cobalt is split into two components which are the transitions to the $^4A_2$ and ^4E upper states derived from the original $^4T_1(F)$ level. Since the higher energy band of Co(4Mepyr)Br$_2$ is broader, and somewhat more intense, it can be taken as the transition to the E component.

On the basis of spectral evidence, the compound is assigned the dimeric structure. A similar assignment is preferred for Co(methylpyrazine)Br$_2$[47], largely on the basis of infra-red data.

The band system of Co(4Mepyr)$_2$(NO$_3$)$_2$ indicates a more

distorted cobalt environment than that in $Co(5Mepyr)_2(NO_3)_2$ (Figure 2). The 4-methyl group will introduce steric interaction in a pyrimidine bridged arrangement and although this is expected to be small it is possible that this structure will become less favourable than one formed by chelating nitrate groups. The spectrum does bear overall resemblance to that of $Co(Me_3PO)_2(NO_3)_2$[71] which is known to contain cis-bidentate nitrate groups.

$Co(4Mepyr)_2(NCS)_2 \cdot 2H_2O$ has a broader, more asymmetric ν_1 band than $Co(5Mepyr)_2(NCS)_2$ and it occurs at lower energy. This is consistent with a thiocyanate-bridged polymer and $N(3)$ bonded pyrimidine molecules. It is improbable that the water molecules are bonded to the metal ion as the vibrational spectra support the assignment of bridging anions.

The compound $Co(4Mepyr)_2(ClO_4)_2 \cdot 4H_2O$ has a spectrum resembling that of $Co(5Mepyr)_3(ClO_4)_2 \cdot H_2O$ and a similar low value magnetic moment $(\mu = 4.55)$. It provides a definite example of bridging by the 4-substituted pyrimidine molecule.

The 2:1 cobalt iodide complex is pseudo-tetrahedral as evinced by its magnetic moment and electronic band energies. The splitting of the ν_2 band is larger than that found for $Co(5Mepyr)_2I_2$ and indicates an increase in distortion.

Ni(4Mepyr)$_2$I$_2$ is diamagnetic and has a spectrum like that of Ni(quinoline)$_2$I$_2$[87]; band assignments have been made by comparison with this compound and are given in Table 2.2. It is interesting that this compound adopts a planar arrangement and not a tetrahedral one as do NiL$_2$I$_2$ (L=py, 3-pic, 4-pic)[57]. The structural differences are probably related to varying contributions of σ and π bonding. Since the pyrimidine molecule is a better π acceptor than pyridine, adoption of a planar arrangement would maximise back-donation.

The 2:1 copper complexes have similar bond energies to their 5-methylpyrimidine counterparts and can be assumed to have the same co-ordination geometry, whereas the 1:1 compounds have spectra which reflect marked structural differences from Cu(5Mepyr)X$_2$.

A pseudo-tetrahedral structure would account for the position of the absorption band in Cu(4Mepyr)Cl$_2$ and it has already been noted that one other 1:1 compound, Cu(4Mepyr)Br$_2$, has this type of structure. However, most copper complexes with distorted tetrahedral environments give rise to a very intense pair of near infra-red bands[88].

A very large increase in tetragonal distortion would account for the shift in band energy from ca.14000cm^{-1} in

TABLE 2.1.

Electronic Spectra (cm^{-1}).

$Co(4Mepyr)Br_2$	4760(s) 6780(s) 14930(s)
$Co(4Mepyr)_2Cl_2$	ca.6210(m) 8550(m) ca.14800(sh) 16390(m,sp) 18350 19050(ms) ca.20200(sh)
$Co(4Mepyr)_2Br_2.2H_2O$	ca.5810(m) 8620(m,w) 15430(m,sp) ca.17390(m,sh) 18520(ms) ca.19610(m,sh)
$Co(4Mepyr)_2I_2$	ca.5680(s,sh) ca.6410(s) 8620(s) 15150(s)
$Co(4Mepyr)_2(NO_3)_2$	ca.6210(m) ca.13100(m,br) 16130(m,sp) 19610(s)
$Co(4Mepyr)_2(NCS)_2.2H_2O$	8330(m) ca.9520(sh) 15630(m,sp) 19690(ms) ca.20620(ms,sh)
$Co(4Mepyr)_2(ClO_4)_2.4H_2O$	8850(m) ca.16390(sh) 19230(ms) 20410(ms) 21980(ms)
$Ni(4Mepyr)Cl_2$	ca.6900(m) 7940(m) ca.12500(m,sh) 13510(m) ca.18870(sh) 23260(ms)
$Ni(4Mepyr)_2Cl_2$	ca.6140(m) 8480(m) ca.12500(m,sh) 14080(m) 24390(ms)
$Ni(4Mepyr)_2Br_2$	ca.5950(m) 8200(m) ca.11630(m,sh) 13790(m) ca.19610(m) 23360(ms)
$Ni(4Mepyr)_2I_2$	14290(s) 23810(vs)
$Cu(4Mepyr)Cl_2$	12990(s)
$Cu(4Mepyr)Br_2$	18520(s)
$Cu(4Mepyr)_2Cl_2$	14290(s)
$Cu(4Mepyr)_2Br_2$	14080(s)
$Cu(4Mepyr)_3(ClO_4)_2.2H_2O$	7870(ms) 16130(ms)

Cu(5Mepyr)Br$_2$ to <u>ca.</u>1800cm^{-1} in Cu(4Mepyr)Br$_2$.

Cu(4Mepyr)$_3$(ClO$_4$)$_2$.2H$_2$O has an electronic spectrum which is unusual in that it contains a low energy band (7870cm^{-1}) together with one at 16000cm^{-1}. Unfortunately, no crystalline material could be obtained for a more detailed study.

<u>TABLE 2.2.</u>

<u>Parameters for Ni(II) Compounds.</u>

	Δ	Dt	Ds	Δ_{xy}	Δ_z
Ni(4Mepyr)Cl$_2$	7590	−120		690	900
Ni(4Mepyr)$_2$Cl$_2$	7700	−270	−320	610	1080
Ni(4Mepyr)$_2$Br$_2$	7450	−260	−390	600	1060

Band assignments for Ni(4Mepyr)$_2$I$_2$

$^1A_g \longrightarrow {}^1A_g$ (cm^{-1})	$^1A_g \longrightarrow {}^1B_{2g}$ (cm^{-1})
23,810	14,290.

<u>TABLE 2.3.</u>

<u>Room Temperature Magnetic Moments (B.M.)</u>

Mn(4Mepyr)Cl$_2$	5.71	Ni(4Mepyr)Cl$_2$	3.14
Mn(4Mepyr)Br$_2$	5.74	Ni(4Mepyr)$_2$Cl$_2$	3.50
Co(4Mepyr)$_2$Cl$_2$	5.02	Ni(4Mepyr)$_2$Br$_2$	3.30
Co(4Mepyr)$_2$Br$_2$.2H$_2$O	5.15	Ni(4Mepyr)$_2$I$_2$	diamagnetic
Co(4Mepyr)$_2$(NO$_3$)$_2$	4.54	Cu(4Mepyr)Cl$_2$	1.88
Co(4Mepyr)$_2$(NCS)$_2$.2H$_2$O	4.74	Cu(4Mepyr)$_2$Cl$_2$	1.81
Co(4Mepyr)$_2$(ClO$_4$)$_2$.4H$_2$O	4.55	Cu(4Mepyr)Br$_2$	1.82
		Cu(4Mepyr)$_2$Br$_2$	1.83.

Vibrational Spectra.

4-Methylpyrimidine produces strong vibrations across the region 1500-1300cm^{-1} which partially obscure the $\nu_3(NO_3)$ bands of Co(4Mepyr)$_2$(NO$_3$)$_2$. The spectrum shows absorption bands at 1475cm^{-1} and 1290cm^{-1} which seem to be the result of ν_3 (NO$_3$) vibrations. The electronic spectrum does indicate the existence of chelating anions which would also be compatible with the ν_3 (NO$_3$) quoted here.

The bands at 2100cm^{-1} (s) and 790cm^{-1} (w) in Co(4Mepyr)$_2$(NCS)$_2$.2H$_2$O may be assigned as ν(C-N) and ν(C-S) respectively. Their positions are consistent with N-bonded thiocyanates. The ν(C-S) value is at the low end of the range for the N-bonded anion but is very similar to that observed for the polymeric octahedral compound Copy$_2$(NCS)$_2$[81] (ν(C-S) = 787cm^{-1}(w)).

Vibrational Spectra (400-90)cm^{-1}.

The ligand has absorption bands at 362cm^{-1} and 352cm^{-1} (sh) which move to higher energy on complexation.

Polymeric octahedral species. (Table 2.4)

In general, the far infra-red spectra of the poly-

meric complexes are even less well-defined than those of 5-methylpyrimidine. The chloro-compounds produce a single broad absorption band above $200 cm^{-1}$ and although there is evidence of higher energy shoulders there is no clear resolution into metal-pyrimidine and metal-chlorine stretches.

Comparison of the spectra of $Cu(4Mepyr)_2Cl_2$ and $Cu(5Mepyr)_2Cl_2$ suggest the assignment, $\nu(M-Cl) = 294 cm^{-1}$, $\nu(M-N) = 249 cm^{-1}$. As may be expected the metal-nitrogen band has a similar energy in each compound. However, the metal-chlorine band is shifted slightly to lower energy; a similar shift in the other chloro complexes might explain their broad unresolved spectra.

If $Cu(4Mepyr)Cl_2$ had a pseudo-tetrahedral structure, it would be expected to produce a spectrum similar to that of $Zn(4Mepyr)Cl_2$. In fact, there is only one metal-chlorine band and this has virtually the same energy as $\nu(M-Cl)$ for $Cu(4Mepyr)_2Cl_2$. However, the band does show an increased intensity with respect to the metal-nitrogen band. The latter is broader than $\nu(M-N)$ for $Cu(4Mepyr)_2Cl_2$ and can be resolved into two definite components. It seems noteworthy that the ligand modes experience a similar displacement in $Cu(4Mepyr)Cl_2$ and $Zn(4Mepyr)Cl_2$.

Despite the structural differences implied by their electronic band energies, the copper bromide complexes produce seemingly identical vibrational spectra. Each has a multi-component band between $280cm^{-1}$ and $200cm^{-1}$ which contains the metal-ligand and metal-bromine stretches. The only apparent difference is that the components at $230cm^{-1}$ and $205cm^{-1}$ show an increased intensity in $Cu(4Mepyr)Br_2$.

$Co(4Mepyr)_2(NCS)_2.2H_2O$ has a band at $463cm^{-1}$ that indicates bridging thiocyanate molecules. The metal-nitrogen vibrations of bonded thiocyanate and pyrimidine absorb at $280cm^{-1}$ and $208cm^{-1}$ respectively.

Tetrahedral species.

The postulated assignments are given in Table 2.4 $Co(4Mepyr)Br_2$ exhibits medium absorption from ca.$270cm^{-1}$ to $200cm^{-1}$ that can be resolved into three components. Those at higher energy are predominantly the result of metal-bromine vibrations.

Nitrates (400–$20cm^{-1}$).

The higher energy bands can be associated, mainly with metal-oxygen vibrations, while those at $235cm^{-1}$ (Co) and $258cm^{-1}$ (Cu) may be largely attributed to metal-ligand vibrations.

TABLE 2.4.

Vibrational Spectra (400-90cm^{-1})

Polymeric octahedral.

Mn(4Mepyr)Cl$_2$ 392(mw) 382(m) ca.248(m,sh) 237(s) ca.200(m) 130(m,br)

Co(4Mepyr)$_2$Cl$_2$ 395(w) 377(m) 366(mw) 235(ms,sh) 222(s)

Co(4Mepyr)$_2$Br$_2$ .2H$_2$O   380(mw) 372(mw) 362(mw) 237(mw,sh) 210(s) 152(ms) 130(ms)
                                                                                 96(m)

Ni(4Mepyr)Cl$_2$ 398(m) 265(ms) 215(s) 185(m)155 115(m)

Ni(4Mepyr)$_2$Cl$_2$ 383(m) 377(m) 250(m,sh) 230(s) 175 155 110(m)

Ni(4Mepyr)$_2$Br$_2$ 382(m) 367(mw) 262(mw) 226(s) 155(m,br) 125(m)

Cu(4Mepyr)Cl$_2$ 432(m,sh) 412(m) 385(m,sh) 298(s) 245(m) 220(m,w) 180(m,br)
                                                                               130(m) 103(m)

Cu(4Mepyr)Br$_2$ 392(w) 380(m) 370(w,sh) 272(w,sh) 250(m,sh) 242(m) 232(s)
                                                                       205(m) 188(ms) 128(w)

Cu(4Mepyr)$_2$Cl$_2$ 382(m) 367(m,w) 294(s) 276(m,sh) 249(ms) 173(ms) 85(m)

Cu(4Mepyr)$_2$Br$_2$ 392(w) 380(m) 370(w) 272(w,sh) 250(m,sh) 242(m) 230(m) 205(w)
                                                                                  188(ms) 128(w)

Co(4Mepyr)$_2$(NCS)$_2$ .2H$_2$O   480 463 380(m) 370(w) 322(m,br) 280(s) 208(ms)

Nitrates. (400-200cm^{-1})

Co(4Mepyr)$_2$(NO$_3$)$_2$ 389(w,sh) 381(m) 345(w) ca.297(m,sh) 270(ms) 235(s)

<u>Table 2.4 continued.</u>

<u>Tetrahedral.</u>

$Co(4Mepyr)Br_2$ 395(m) 375(m) 260(w,sh) 250(m) 240(m) 207(m) 152(ms,br)

	ν(M–X)	ν(M–N)	Other bands
$Zn(4Mepyr)_2Cl_2$	327(s) 293(s)	205(ms) 191(ms)	382(m) 367(w) 176(ms) 110(ms,br)
$Zn(4Mepyr)_2Br_2$	264(s) 210(s)	202(s)	165(w,sh) 132(w) 90(ms)
$Zn(4Mepyr)_2I_2$	223(m) 148(m)	194(s)	
$Zn(4Mepyr)Cl_2$	335(s) 304(s)	220(m)	402(m) 385(m) 265(w,sh) 183(ms) 137(ms) 110(ms,br)
$Zn(4Mepyr)Br_2$	252(s)	215(s) 203(ms)	395(m) 382(m) 177(ms)
$Co(4Mepyr)_2I_2$	<u>ca</u>.248(sh,m) 196(ms)	240(m) 215(m) 130(m)	

<u>Planar.</u>

$Ni(4Mepyr)_2I_2$ 247(m) 235(m) 207(w) 188(m) 127(w)

CHAPTER 3.

2-Aminopyrimidine Complexes.

The introduction of the 2-amino substituent increases
the basicity with respect to that of 4-methylpyrimidine (pKa
2-aminopyrimidine = 3.5, pKa 4-methylpyrimidine = 2.0) but
alters the steric requirements as a ligand.

The stoichiometries of the compounds isolated with
2-aminopyrimidine are listed in Table 3.1. There are few
examples of 1:1 polymeric systems but there is an extensive
series of 2:1 compounds. These often have structural
differences from the 5-methyl- and 4-methyl congeners.

Electronic Spectra (Table 3.1).

The ν_1 band is split to roughly the same extent in
$Co(2NH_2pyr)Cl_2$ and $Ni(2NH_2pyr)Cl_2$, the spectral parameters
of the nickel compound being similar to those observed for
$Ni(4Mepyr)Cl_2$. The band maximum of $Cu(2NH_2pyr)Cl_2$ reflects
greater tetragonal distortion than that found in $Cu(5Mepyr)Cl_2$;
there is no structural similarity to $Cu(4Mepyr)Cl_2$.

The reflectance spectra and magnetic moments clearly
indicate a basically tetrahedral structure for $Co(2NH_2pyr)_2X_2$
(X=Cl,Br,I,NCS). The complexes actually possess C_{2v} symmetry,

the reduction in symmetry giving rise to band splitting. In the near infra-red region, the ν_2^- band is split into three components of quite similar intensity, and the extent of the splitting, 2000-2800cm^{-1}, is comparable to that observed for analogous compounds containing quinoline[86], quinoxaline[50] and 2-substituted pyridines[89].

The parameters, Δ and B' have been calculated using the secular equations for tetrahedral cobalt and taking the centres of the split bands to be ν_2 and ν_3. It is found that the Δ values (Table 3.2) lie in the sequence I < Br < Cl < NCS, which is the same as that observed by Cotton et al. for CoX$_4$$^{2-}$ complexes[90]. Similarly, the values of B' increase in the order I < NCS < Br < Cl.

The spectrum of Co(2NH$_2$pyr)$_2$(NO$_3$)$_2$ resembles that of Co(5Mepyr)$_2$(NO$_3$)$_2$ but with the bands moved to lower energies. A consideration of the intermolecular distances and geometry concerned, rules out the possibility of pyrimidine bridging for the 2-amino compound, and it is assigned a bidentate nitrato structure. The difference in band energies between the two compounds would be expected if the co-ordination sphere is CoN$_4$O$_2$ in the 5-methyl compound (i.e. bridged pyrimidine structure) compared with CoN$_2$O$_4$ in the 2-amino compound. The distortion in Co(2NH$_2$pyr)$_2$(NO$_3$)$_2$ is less than that in

$Co(4Mepyr)_2(NO_3)_2$ which has been assigned a similar geometry.
In 2-aminopyrimidine, both nitrogen atoms have an ortho group
and the steric influence of this may well lengthen the cobalt-
nitrogen bond weakening the pyrimidine contribution to the
total ligand field and thus reducing the ligand field
asymmetry. In contrast, 4-methylpyrimidine has an available
donor site, $N(1)$, that involves little steric interaction.
It is also possible that the potentially hydrogen-bonding
group in the 2-position engages in inter- or intra- molecular
interactions with nitrates and that this modifies the geometry
about the metal ion.

The pink thiocyanate complex $Co(2NH_2pyr)_2(NCS)_2.3H_2O$
has an octahedral symmetry. Since removal of the water
molecules produces the dark blue pseudo-tetrahedral compound,
$Co(2NH_2pyr)_2(NCS)_2$, it can be inferred that in the octahedral
complex water molecules form part of the co-ordination sphere.
Surprisingly, there is no detectable splitting of the ν_1 band.

The nature of the absorption produced by $Ni(2NH_2pyr)_2X_2$
$.nH_2O$ is indicative of a strong in-plane field. It is not
possible to visualise a NiN_4X_2 co-ordination sphere because
this would imply a bridging pyrimidine system which is
sterically unfavourable. The spectral parameters appear to
support this inference. Although the splitting is comparable
to that in substituted pyridine complexes (see p.25) of formula

TABLE 3.1.

Electronic Spectra (cm^{-1}).

$Co(2NH_2pyr)Cl_2$ ca.6620 ca.7690 ca.12660(sh) 16950 17860 18870 19610 .

$Co(2NH_2pyr)_2Cl_2$ 6250(s) 6900(s) 8620(vs) 16000(vs) 17090(vs,sh) 19230(sh)

$Co(2NH_2pyr)_2Br_2$ 6370(s) 7020(s) 8330(s) 16000(vs) 16950(vs,sh)

$Co(2NH_2pyr)_2I_2$ 5680(s) 6850(vs) 8480(vs) 15150(vs) 18520(sh)

$Co(2NH_2pyr)_2(NCS)_2$ 7140(s) 8260(s) 9520(s) 16260(s) 17540(s,sh)

$Co(2NH_2pyr)_2(NCS)_2.3H_2O$ 8930 20330 21320(sh)

$Co(2NH_2pyr)_2(NO_3)_2$ ca.7810(m) 8550(m) 16130(m,sh) 19420(ms) 20620(s,sh)

$Ni(2NH_2pyr)Cl_2$ ca.6670(m) 7750(m) ca.12350(m,sh) 13160(m) ca.19230(sh)
ca.21740(sh) 23260(m)

$Ni(2NH_2pyr)_2Cl_2.2H_2O$ ca.7690(m) 9520(m) ca.12990(sh) 14290(m) ca.20000(sh)
25000(s)

$Ni(2NH_2pyr)_2Br_2.3H_2O$ ca.6670(m) 9900(m) ca.12820(sh) 14490(m) ca.20000(sh)
22470(sh) 24390(s)

$Ni(2NH_2pyr)_2I_2$ 10200(w) 15870(s) 23360(vs)

$Ni(2NH_2pyr)_2(NO_3)_2.H_2O$ 9090(m) 15040(s) 21050(sh) 25000(s)

$Cu(2NH_2pyr)Cl_2$ 14990(s)

$Cu(2NH_2pyr)_2Br_2$ ca.15630(s,sh) 16810(s)

$Cu(2NH_2pyr)_2(NO_3)_2$ 10990(s,sh) 14710(s)

$Cu(2NH_2pyr)_2(NO_2)_2$ ca.15380(s,sh) ca.18620(s,sh)

TABLE 3.2.

Parameters for tetrahedral cobalt complexes.

	Observed (cm^{-1})		Calculated (cm^{-1})	
	ν_2	ν_3	Δ	B'
Co(2NH$_2$pyr)$_2$Cl$_2$	7260	16550	4250	740
Co(2NH$_2$pyr)$_2$Br$_2$	7240	16480	4200	740
Co(2NH$_2$pyr)$_2$I$_2$	7000	15150	4100	660
Co(2NH$_2$pyr)$_2$(NCS)$_2$	8310	16900	4900	700

NiL$_4$X$_2$, the mean Δ value is smaller, which is unexpected as pyrimidine molecules appear to provide a stronger field. On this evidence it is proposed that the compounds contain bonded water molecules. Consideration of molecular models suggests that there could be hydrogen bonding between the amino groups and water molecules in a trans arrangement of these ligands. Ni(2NH$_2$pyr)$_2$(NO$_3$)$_2$.H$_2$O has the characteristic spectrum of an octahedral complex; there is no detectable splitting of the bands.

The tetragonal distortion in Cu(2NH$_2$pyr)$_2$Br$_2$ is comparable to that in the analogous dimethylpyrimidine compound (see page 68). A similar tentative assignment is presented. The bands at 16,810cm^{-1} and 15,380cm^{-1} could represent the $^2B_1 \longrightarrow ^2B_2$ and $^2B_1 \longrightarrow ^2E$ transitions while the $^2B_1 \longrightarrow ^2A_1$ transition remains obscured by a charge transfer band.

Whereas the electron transition energies of $Cu(2NH_2pyr)_2(NO_3)_2$ and $Cu(5Mepyr)_2(NO_3)_2$ are alike, there is a considerable difference in the energies of the corresponding nitrites. Since the vibrational spectrum of $Cu(2NH_2pyr)_2(NO_2)_2$ does not indicate the presence of N-bonded anions, the band positions must point to a larger distortion in this compound. It is possible that, in this case, the $^2B_1 \longrightarrow ^2A_1$ transition lies at $18620 cm^{-1}$.

Vibrational Spectra (Table 3.3)

The positions of the nitrate bands would indicate the presence of bidentate groups.

There is a diversity of nitrite bands in $Cu(2NH_2pyr)_2$ $(NO_2)_2$. The pair of bands, $1340 cm^{-1}(ms)$ and $1175 cm^{-1}(s)$, compare closely with those produced by $Znpy_2(NO_2)_2$ for which asymmetrically chelating nitrite groups have been proposed[91]. The pair of bands at $1475 cm^{-1}(ms)$ and $1120 cm^{-1}(s)$ could result from an O-bridged nitrite group.

TABLE 3.3.

Nitrate Group Frequencies (cm^{-1}).

	ν_3			ν_1
$Co(2NH_2pyr)_2(NO_3)_2$	1500(s)	1470(s)	1275(s)	1035(m)
$Ni(2NH_2pyr)_2(NO_3)_2 \cdot H_2O$	1490(s)	1447(s)	1300(s)	1037(m)
$Cu(2NH_2pyr)_2(NO_3)_2$	1500(s)	1465(s)	1290(s)	1040(m)

Nitrite Group Frequencies (cm^{-1}).

	$\nu(NO)$			
$Cu(2NH_2pyr)_2(NO_2)_2$	1475(ms)	1340(ms)	1175(s)	1120(s)

Vibrational Spectra. (400-90cm^{-1}) Table 3.4.

The ligand has an absorption band at 400cm^{-1} (shoulder at ca. 390cm^{-1}). Most of the complexes and, in particular, those with a basically octahedral geometry show a medium broad absorption from 400cm^{-1} tailing down to about 280cm^{-1}. Bands in this region are superimposed on this background absorption.

The assignments for the tetrahedral species are given in the Table 3.4. A few inferences may be drawn from the remaining spectra. The compounds $M(2NH_2pyr)_2(NO_3)_2 \cdot nH_2O$ (M=Mn(II), Co(II)) produce a medium broad band from ca. 270

to $210cm^{-1}$ (Mn) and ca.290 to $210cm^{-1}$ (Co). Although there is evidence of components, these are not clearly resolved and it would appear that there is extensive coupling of M-O and M-pyrimidine vibrations in these compounds. The remaining nitrates show well-defined bands and it is considered likely that M-O vibrations are responsible for the absorption at 327 and $280cm^{-1}$ (Cu); $276cm^{-1}$ (Ni); 270 and ca.$245cm^{-1}$ (Zn).

The halogen sensitive bands of $Cu(2NH_2pyr)Cl_2$ and $Cu(2NH_2pyr)_2Br_2$, $320cm^{-1}$ and $240cm^{-1}$, respectively, occur at higher energies than those of analogous 5-methylpyrimidine compounds. The band at $260cm^{-1}$ (Cl) and at $263cm^{-1}$ (Br) can be attributed to a metal-pyrimidine vibration.

$Cu(2NH_2pyr)_2(NO_2)_2$ has a spectrum not unlike that of $Cu(5Mepyr)(NO_2)_2$.

The planar compound $Ni(2NH_2pyr)_2I_2$ is assigned a trans structure on the basis of the observed electronic spectrum. One M-N and one M-I vibrational mode are expected in the region $400-200cm^{-1}$, while bending modes are likely to be at lower frequencies.

Nickel-nitrogen modes have been observed in the range $300-400 \text{cm}^{-1}$ for the diamagnetic square complex cations NiL_4^{2+} (L=im, 2Meim, 1,2-diMeim)[42] and this suggests that the 388cm^{-1} band in $Ni(2NH_2pyr)_2I_2$ is the asymmetric nickel-nitrogen stretch. A comparison with the square-planar complexes reported by Shabaraki and Nakamoto[92] suggests that the band at 257cm^{-1} is the nickel-iodine stretching mode. It is possible that the medium band at 223cm^{-1} is a bending mode.

TABLE 3.4.

Vibrational Spectra (400–180cm^{-1}).

Octahedral Species.

$Mn(2NH_2pyr)_2Cl_2$	240(m) $\underline{ca}$.205(ms)
$Mn(2NH_2pyr)_2Br_2$	$\underline{ca}$.215(m,sh) $\underline{ca}$.185(m)
$Co(2NH_2pyr)Cl_2$	$\underline{ca}$.225(m,sh) 207(m)
$Ni(2NH_2pyr)Cl_2$	$\underline{ca}$.250(m,sh) 240(m)
$Ni(2NH_2pyr)_2Cl_2.2H_2O$	247(m) 229(m)
$Ni(2NH_2pyr)_2Br_2.3H_2O$	245(m) 227(m)
$Cu(2NH_2pyr)Cl_2$	320(ms) 260(m)
$Cu(2NH_2pyr)_2Br_2$	265(s) 240(s)

Nitrates.

$Ni(2NH_2pyr)_2(NO_3)_2.H_2O$	276(m) 240(m) $\underline{ca}$.220(w,sh)
$Cu(2NH_2pyr)_2(NO_3)_2$	327(m,br) 280(m) $\underline{ca}$.245(w,sh) 210(w)
$Zn(2NH_2pyr)_2(NO_3)_2.H_2O$	270(m) $\underline{ca}$.245(w,sh) 208(w,sh)

Tetrahedral. (400cm^{-1} – 90cm^{-1})

	ν(M–X)	ν(M–N)	Other bands
$Co(2NH_2pyr)_2Cl_2$	325(s) 303(s)	242(ms) 225(m)	408(s) 210(m) 188(ms) 127(m,br)

Table 3.4 continued.

	ν(M–X)	ν(M–N)	Other bands
$Co(2NH_2pyr)_2Br_2$	263(s) 245(s)≡	220(ms)	176(ms) 154(m) 112(m)
$Co(2NH_2pyr)_2I_2$	238(s)	ca.245(sh) 228(s)	372(s) 170(m) 152(s)
$Zn(2NH_2pyr)_2Cl_2$	308(s,br)	224(m) 205(ms)	177(mw) 156(mw) 97(ms)
$Zn(2NH_2pyr)_2Br_2$	244(ms) 225(sh)	234(ms) 203(ms)	140(m) 132(m,br) ca.100(m)
$Zn(2NH_2pyr)_2I_2$	218(m)	233(mw) 200(s)	153(m) 95(m)

Planar

$Ni(2NH_2pyr)_2I_2$	388(s) 320(w) 305(w) 257(m) 223(m)		

≡ may be M–N or M–X.

CHAPTER 4.

Complexes of 4,6-dimethyl and 2,4,6-trimethylpyrimidine.

The compounds obtained with these ligands are listed in Table 4.1. 4,6-dimethylpyrimidine has substituents ortho to both nitrogen atoms. Steric interaction is such that no octahedral cobalt complexes can be obtained and, in the nickel system, only the chloride is octahedral. The di-substituted molecule appears to have a strong bridging tendency.

It is difficult to form complexes between 2,4,6-tri-methylpyrimidine and nickel or cobalt ions. An acceptable analysis was obtained for the 1:1 cobalt chloride complex but the nickel compounds could not be prepared as pure materials. Both ligands form copper complexes readily and these may be isolated in the crystalline state.

Electronic Spectra and Magnetic Properties (Tables 4.1 and 4.3)

On the basis of electronic spectra, a pseudo-tetrahedral structure can be assigned to $Co(dmp)X_2$ (X=Cl,Br) and to $Co(dmp)_{1.5}I_2$. As in the case of $Co(4Mepyr)Br_2$, there are two possibilities to be considered for $Co(dmp)X_2$ (X=Cl,Br). The compounds can either be polymers with bridging pyrimidine

molecules or halogen-bridged dimers.

The spectra bear a close resemblance to those of $Co(2NH_2pyr)_2X_2$ (X=Cl,Br) and the calculated Δ values are very similar (Tables 3.2 and 4.2). This suggests that there is a metal environment of two nitrogen and two halogen atoms and supports the existence of a polymeric structure. The total splitting between the three components of ν_2 is some $600cm^{-1}$ greater than that observed for $Co(2NH_2pyr)_2X_2$ and indicates a slightly increased distortion.

The postulated structure for $Co(dmp)_{1.5}I_2$ is shown in Figure 3. Presumably there is sufficient steric inter-

FIGURE 3.
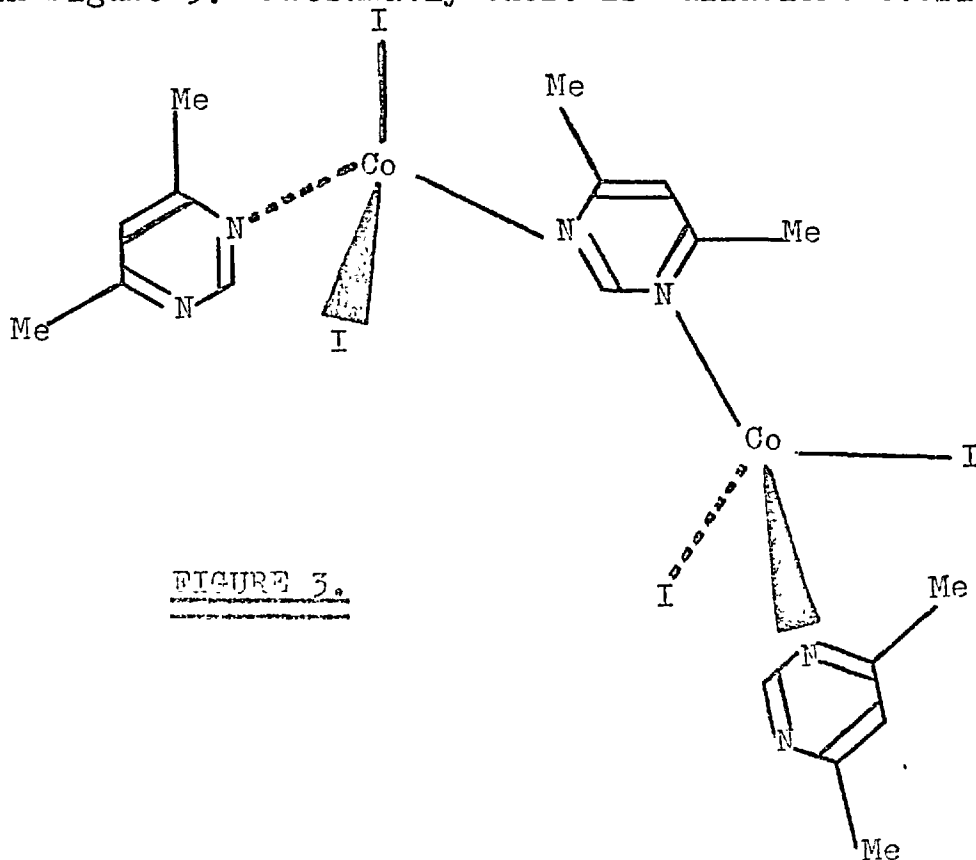
action between the methyl groups and iodine atoms to prevent the formation of a polymer: instead a single pyrimidine bridge links two pseudo-tetrahedral units. Although Δ is comparable to that of $Co(2NH_2pyr)_2I_2$, the extent of the ν_2 band splitting is somewhat smaller.

In each of the cobalt halide complexes, there is absorption in the region $4000-4400cm^{-1}$, that can be assigned to ν_1, or a component of ν_1. The exact position of the band is obscured by ligand overtone absorption.

The complex $Co(dmp)_2(NO_3)_2$ has an intense band system with quite similar energies to those of $Co(2Meimidazole)_2$ $(NO_3)_2$[41] and is best assigned an analogous structure with chelating nitrates.

The spectrum of $Co(tmp)Cl_2 \cdot 4H_2O$ is indicative of a pseudo-tetrahedral geometry. There is a strong multi-component band in the near infra-red region but centred at appreciably lower energy than the ν_2 band system of $Co(dmp)Cl_2$.

$Ni(dmp)Cl_2$ produces a spectrum like that of $Ni(4Mepyr)Cl_2$ with the bands slightly shifted to lower energy. The small distortion can again be explained by the presence of substituents which prevent a close approach of the ligand to the metal-halogen polymeric chain.

TABLE 4.1.

Electronic Spectra (cm^{-1}).

$Co(dmp)Cl_2$ 6190(s) 7320(s) 9200(s) <u>ca.</u>14290(sh) 16670(vs)

$Co(dmp)Br_2$ 5990(s) 6900(s) 8550(s) <u>ca.</u>15870(s) 16810(s,sh)

$Co(dmp)_{1.5}I_2$ <u>ca.</u>6100(sh) 6710(s) 8330(s) 15150(s)

$Co(dmp)_2(NO_3)_2$ <u>ca.</u>8000(s) 9430(s) 14710(ms) 17700(s) 21280(s)

$Ni(dmp)Cl_2$ <u>ca.</u>6580(m) 7630(m) <u>ca.</u>12050(m,sh) 12990(m) <u>ca.</u>16670(sh)
<u>ca.</u>21510(ms,sh) 22990(ms)

$Ni(dmp)Br_2$ 9620(s) 11360(sh) 15870(s,br)

$Ni(dmp)_2I_2$ 15630(s) 23260(vs)

$Cu(dmp)_2Cl_2$ 19050(s) <u>ca.</u>16130(s,sh)

$Cu(dmp)_2Br_2$ 16390(s)

$Co(tmp)Cl_2 \cdot 4H_2O$ 4670(vs) 4900(vs) 5500(vs) 6160(vs) 8620(sh,m) 14930(vs)
15870(sh,vs)

$Cu(tmp)_2Cl_2$ 15380(br,s) 19610(s)

$Cu(tmp)_2Br_2$ 14710(sh,s) 16000(s) 24040(vs)

$Cu(tmp)_{0.5}Cl_2$ 11630(s)

TABLE 4.2.

Parameters for Tetrahedral Cobalt Complexes.

	Observed (cm^{-1})			Calculated (cm^{-1})	
	ν_2	ν_3		Δ	B'
Co(dmp)Cl$_2$	7570	15,500		4400	740
Co(dmp)Br$_2$	7150	16,400		4200	730
Co(dmp)$_{1.5}$I$_2$	7045	15,150		4100	660

TABLE 4.3.

Magnetic Moments (B.M.).

Co(dmp)Cl$_2$	4.36	Cu(dmp)$_2$Cl$_2$	1.76
Co(dmp)Br$_2$	4.45	Cu(dmp)$_2$Br$_2$	1.73
Co(dmp)$_{1.5}$I$_2$	4.50		
Co(dmp)$_2$(NO$_3$)$_2$	4.54	Cu(tmp)$_2$Cl$_2$	1.81
Ni(dmp)Cl$_2$	3.10	Cu(tmp)$_2$Br$_2$	1.80
Ni(dmp)$_2$I$_2$	diamag.		

The ν_2 and ν_3 bands of Ni(dmp)Br$_2$ indicate an approximately tetrahedral geometry. The lowest energy spin-allowed band appears as a broad absorption, at about 4500cm^{-1}, with superimposed ligand vibrations. The intensity of the ν_2 band is sensitive to changes in symmetry being weak in strictly, or nearly strictly, tetrahedral symmetry but gaining in intensity in lower symmetries. The $\nu_2 : \nu_1$

intensity ratio for this compound is large compared with that of Ni(quinoline)$_2$Br$_2$[87] or Ni(N-Meim)$_2$Br$_2$[41] and could be evidence of an increased distortion.

Unlike the bromide, the magnetic and spectral properties of the iodide, Ni(dmp)$_2$I$_2$, are those of a planar compound.

Cu(dmp)$_2$Cl$_2$ exhibits a well-defined doublet in the visible region. It's spectrum resembles that of the square-planar complex Cu(acetylacetone)$_2$ and also those of Cu(2bromopyridine)$_2$Cl$_2$[62] and Cu(quinoline)$_2$Cl$_2$. In view of the very strong axial distortion and approximately square planar environment, the band at 19,230cm^{-1} is best assigned as the transition $^2B_1 \longrightarrow {}^2A_1$. It seems likely that this transition is obscured by the charge transfer band in Cu(dmp)$_2$Br$_2$ and that the observed band contains $^2B_1 \longrightarrow {}^2E$ and $^2B_1 \longrightarrow {}^2B_2$.

The spectra of Cu(tmp)$_2$X$_2$ (X=Cl,Br) may be similarly assigned. The presence of a third substituent in the pyrimidine ring leads to an increased distortion, which is reflected in the higher energy of the $^2B_1 \longrightarrow {}^2A_1$ transition observed for Cu(tmp)$_2$Cl$_2$.

It is unexpected that trimethylpyrimidine forms a compound of stoichiometry $Cu(tmp)_{0.5}Cl_2$ which must involve a bridging pyrimidine molecule, more especially as there is no tendency to form a compound of the type $Cu(CH_3COO)_2(L)_{0.5}$ which is readily produced by the other substituted pyrimidines. The position of the electronic band ($11,630cm^{-1}$) suggests the existence of a pseudo-tetrahedral chromophore. An analogous compound is obtained with dimethylpyrimidine and this gives a broad electronic band centred at $12,500cm^{-1}$.

Trimethylpyrimidine by-product.

The original preparative method for 2,4,6-trimethyl pyrimidine states that once the crystalline product has been obtained from the reaction, a further crop may be obtained from the mother liquor. However, it has been found, here, that the major component in this second extraction is not trimethylpyrimidine but a compound of formula C_5H_9NO. The spectral data is consistent with this structure.
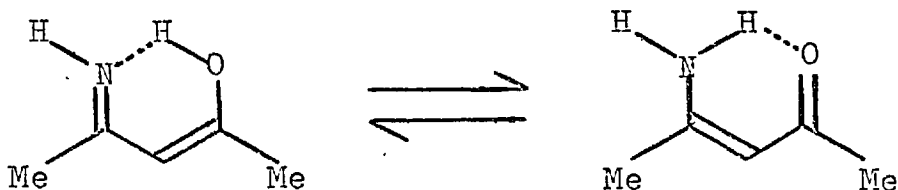
This compound readily acts as a ligand with divalent copper, nickel and cobalt. Copper complexes crystallise rapidly from ethanolic solutions, and crystalline compounds of the other metals are obtainable on careful evaporation.

Cobalt and nickel inner complexes of this ligand have been reported by Everett and Holm[93] during their studies on a series of bis(β-ketoamine) Co(II) complexes.
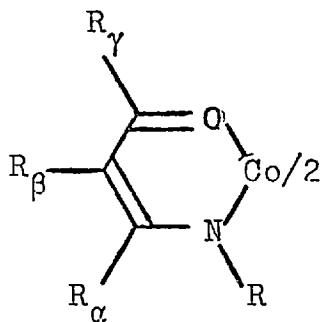
Vibrational Spectra

4,6-dimethylpyrimidine vibrations prevent an unambiguous assignment of the nitrate bands in $Co(dmp)_2(NO_3)_2$.

<u>Vibrational Spectra (400-90cm^{-1})</u> (Table 4.4)

Dimethylpyrimidine has bands at 430cm^{-1}(s), 410cm^{-1}(w,sh) and 283cm^{-1}(m) which move to higher frequencies on complexation. The lower band is seen clearly at about 298cm^{-1} in $Cu(dmp)_2Br_2$ and $Ni(dmp)Cl_2$ and it is probable that the absorption detected at about 320cm^{-1} in the tetrahedral compounds, $Co(dmp)X_2$ (X=Cl,Br) is of the same origin. Trimethylpyrimidine shows broad medium, intensity absorption around 285cm^{-1}, with maxima at 295cm^{-1} and 282cm^{-1}. In the compound, $Cu(tmp)_2Br_2$, the ligand absorption is present as three distinct bands of medium intensity at 321cm^{-1}, 310cm^{-1} and at 295cm^{-1}.

It can be seen from Table 4.4 that only one metal-nitrogen vibration is assigned for $Co(dmp)X_2$ (X=Cl,Br). In the case of the chloro compound, the broad absorption with maximum at 307cm^{-1} extends to 240cm^{-1} and could 'contain' the second M-N mode. This explanation is consistent with fortuitous degeneracy of the lower M-Br stretch and upper M-N stretch as seen in $Co(2NH_2pyr)_2Br_2$. The nature of the bands, in $Co(dmp)_{1.5}I_2$, around 200cm^{-1} allows no unique assignment.

It is surprising that $Cu(dmp)_2Cl_2$, unlike $Cu(5Mepyr)_2Cl_2$, produces two strong, resolved bands in the expected metal-chlorine region. One band is usually observed in compounds of the type CuL_2Cl_2 (L = α-substituted pyridine)[77] where the steric hindrance caused by the substituent produces an arrangement approaching planarity. The electronic spectrum of $Cu(dmp)_2Cl_2$ suggests that it is of this structural type. The spectrum of $Cu(tmp)_2Cl_2$ shows a single broad band centred at $315cm^{-1}$.

In the absence of any other bands between 200 and $260cm^{-1}$, the band at $248cm^{-1}$ in $Cu(dmp)_2Br_2$ and at $238cm^{-1}$ in $Cu(tmp)_2Br_2$ must result from metal-nitrogen and metal-bromine vibrations.

$Cu(tmp)_{0.5}Cl_2$ has absorption bands at $340cm^{-1}$ and at $294cm^{-1}$ that may be assigned as the metal-chlorine modes of a tetrahedral species.

TABLE 4.4.

Vibrational Spectra $(400-90\text{cm}^{-1})$.

Tetrahedral Species.

	$\nu(\text{M-X})$	$\nu(\text{M-N})$	Other bands
$Co(dmp)Cl_2$	342(s) 307(s,br)	223(m)	320(ms) 168(w) 140(s) 108(s)
$Co(dmp)Br_2$	270(s) 242(s)⊞	210(w)	320(w) 183(ms) 115(s) 85(s)
$Co(dmp)_{1.5}I_2$	ca. 270(w) ca.(w,sh)	225(m) ca.198(s) 138(m)	

Other Compounds.

$Cu(dmp)_2Cl_2$	329(s) 305(s) 248(s) 194(m) 157(ms) 93(ms,br)		
$Cu(dmp)_2Br_2$	298(w) 248(s) 193(w) 112(w,br)		
$Ni(dmp)Cl_2$	297(w) 270(m) 225(m)		
$Co(dmp)_2(NO_3)_2$	ca.300(m) ca.240(m,vbr)		
$Cu(tmp)_2Cl_2$	315(br,s) 238(s) 224(s) 196(m) 144(ms) 112(m)		
$Cu(tmp)_2Br_2$	321(m) 310(m) 295(m) 238(s) 196(w) 100(m)		
$Cu(tmp)_{0.5}Cl_2$	390(m) 340(m) 294(m) 255(w) 240(w)		

⊞ may be M-N or M-X.

Carboxylic Acid Complexes of Substituted Pyrimidines.

The compounds $Cu(CH_3COO)_2L_{0.5}$ (L = 5Mepyr, 4Mepyr, 2NH$_2$pyr, dmp) exhibit magnetic behaviour analogous to that of the pyridine adduct of copper acetate[94]. X-Ray crystal structure determinations[95,96] have established that $Cu(CH_3COO)_2$py has a dimeric structure similar to that of copper acetate monohydrate[97], but with pyridine molecules in the terminal positions. On the basis of similar properties, it can be assumed that the pyrimidine compounds contain the same type of dimeric unit, and, in view of the stoichiometry, the pyrimidine molecules must be acting as bridges between successive dimers.

The compounds $Cu(HCOO)_2L$ (L = 5Mepyr, 4Mepyr, 2NH$_2$pyr) also have behaviour typical of dimeric structures. It appears that the pyrimidine molecules act similarly to substituted pyridines[98] in inducing dimerisation of cupric formate.

The room temperature magnetic moments of the formates are smaller than those of the acetates but not markedly less as in the comparable pyridine system[98]; the paramagnetic resonance studies indicate the presence of significant amounts of monomeric impurities in these compounds.

FIG. 4

TEMPERATURE DEPENDENCE OF MAGNETIC SUSEPTIBILITY

$Cu(CH_3COO)_2(4Mepy+)_{0.5}$

$J = 310 \text{ cm}^{-1}$

$Cu(HCOO)_2(4Mepy+)$

$J = 440 \text{ cm}^{-1}$

DOTTED LINES REPRESENT
CALCULATED CURVES.
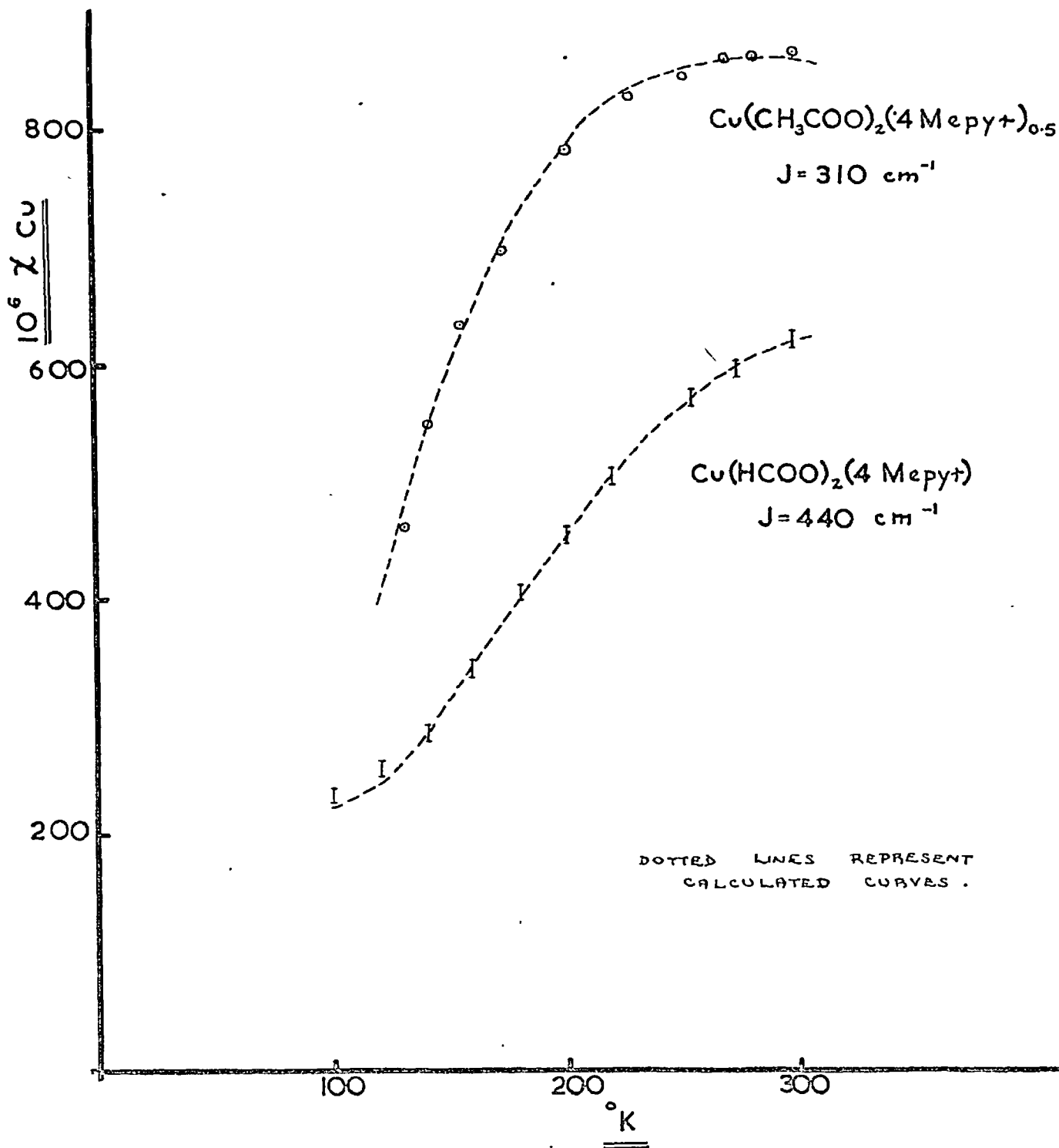
The main features of the reflectance spectra are similar to those of $Cu(CH_3COO)_2py$[99]. Band I occurs at lower energies relative to the pyridine adduct and, in the spectra of $Cu(HCOO)_2L$ (L = 5Mepyr, 4Mepyr), it contains a resolvable shoulder.

The magnetic properties of copper acetate monohydrate have been rationalised by postulating a strong interaction between the equivalent parts of copper ions through exchange forces[100]. This coupling produces a spin-singlet ground state with a spin-triplet as the first excited state. The molar susceptibility, per cupric ion, can be represent by

$$\chi_m = \frac{g^2N\beta^2}{3KT} \cdot \frac{1}{1+1/3 \exp (J/KT)} + N\alpha \qquad (1)$$

where g = Landé factor, N = Avogadro's Number, β = Bohr magneton. K = Boltzman constant, T = temperature, ° Absolute, and Nα is the temperature independent paramagnetic contribution per mole of Cu(II)[101,102]. J represents the singlet-triplet separation. It is known as the exchange coupling constant and is a measure of the interaction in the compound under consideration.

The temperature variation of the magnetic susceptibility of $Cu(CH_3COO)_2(4Mepyr)_{0.5}$ is shown in Figure 4. The theoretical curve was plotted using equation (1) and the $g_{av.}$ value obtained by paramagnetic resonance experiments;

$N\alpha$ was taken to be 60×10^{-6} c.g.s. units. A suitable fit with the experimental data was obtained for $J = 310 cm^{-1}$. Similar treatment of the other acetate complexes yields the parameters listed in Table 4.5.

As stated above, the formate complexes could not be obtained in a completely pure state. It is possible to adapt equation (1) to include the effect of the impurity if it is assumed to be a monomeric cupric species with a normal magnetic moment, i.e. 1.9 B.M., and that it obeys the Curie Law. This gives –

$$\chi_{exp} = \frac{Ng^2\beta^2}{3kT} \cdot \frac{(1-X)}{1 + 1/3 exp.(J/kT)} + \frac{X(0.448)}{T} + N\alpha \quad (2)$$

Where X is the mole fraction of monomeric impurity.

The powdered samples of the formates have susceptibilities of about 230×10^{-6} c.g.s. units at $90^{\circ}K$. If these are considered to be the result of the monomer and temperature independent paramagnetism, then substitution in equation (2) leads to a value of 0.03 for the mole fraction of impurity. The experimental results for $Cu(HCOO)_2(4Mepyr)$ are shown in Figure 4 together with the theoretical curve plotted using (2) and the parameters $J = 440 cm^{-1}$, $g_{av.} = 2.18$ (ch. 6) and $N\alpha = 60 \times 10^{-6}$ c.g.s. units.

The estimated J values for these formate systems (Table 4.5) are appreciably larger than those of the corresponding acetates, an observation concordant with all other previously studied systems of this type[98].

TABLE 4.5.

Magnetic Properties of Dimeric Carboxylate Compounds.

	Temp.(^{O}K)	(B.M.)	J(cm^{-1})
$Cu(CH_3COO)_2(5Mepyr)_{0.5}$	294	1.51	270
$Cu(CH_3COO)_2(4Mepyr)_{0.5}$	296	1.43	310
$Cu(CH_3COO)_2(2NH_2pyr)_{0.5}$	294	1.52	270
$Cu(CH_3COO)_2(dmp)_{0.5}$	294	1.44	310
$Cu(HCOO)_2(5Mepyr)$	295	1.26	410
$Cu(HCOO)_2(4Mepyr)$	294	1.19	440
$Cu(HCOO)_2(2NH_2pyr)$	296	1.21	430

TABLE 4.6.

Diffuse Reflectance Spectra (cm^{-1})

		Band I	
$Ch(CH_3COO)_2(5Mepyr)_{0.5}$		14490(s)	25640(s)
$Cu(CH_3COO)_2(4Mepyr)_{0.5}$		14490(s)	25450(s)
$Cu(CH_3COO)_2(2NH_2pyr)_{0.5}$		14930(s)	27030(s)
$Cu(CH_3COO)_2(dmp)_{0.5}$		14430(s)	
$Cu(HCOO)_2(5Mepyr)$	ca.8400(sh)	14490(s)	
$Cu(HCOO)_2(4Mepyr)$	ca.8500(sh)	14490(so	25320
$Cu(HCOO)_2(2NH_2pyr)$		14390(s)	23810(s)

FIG. 5.
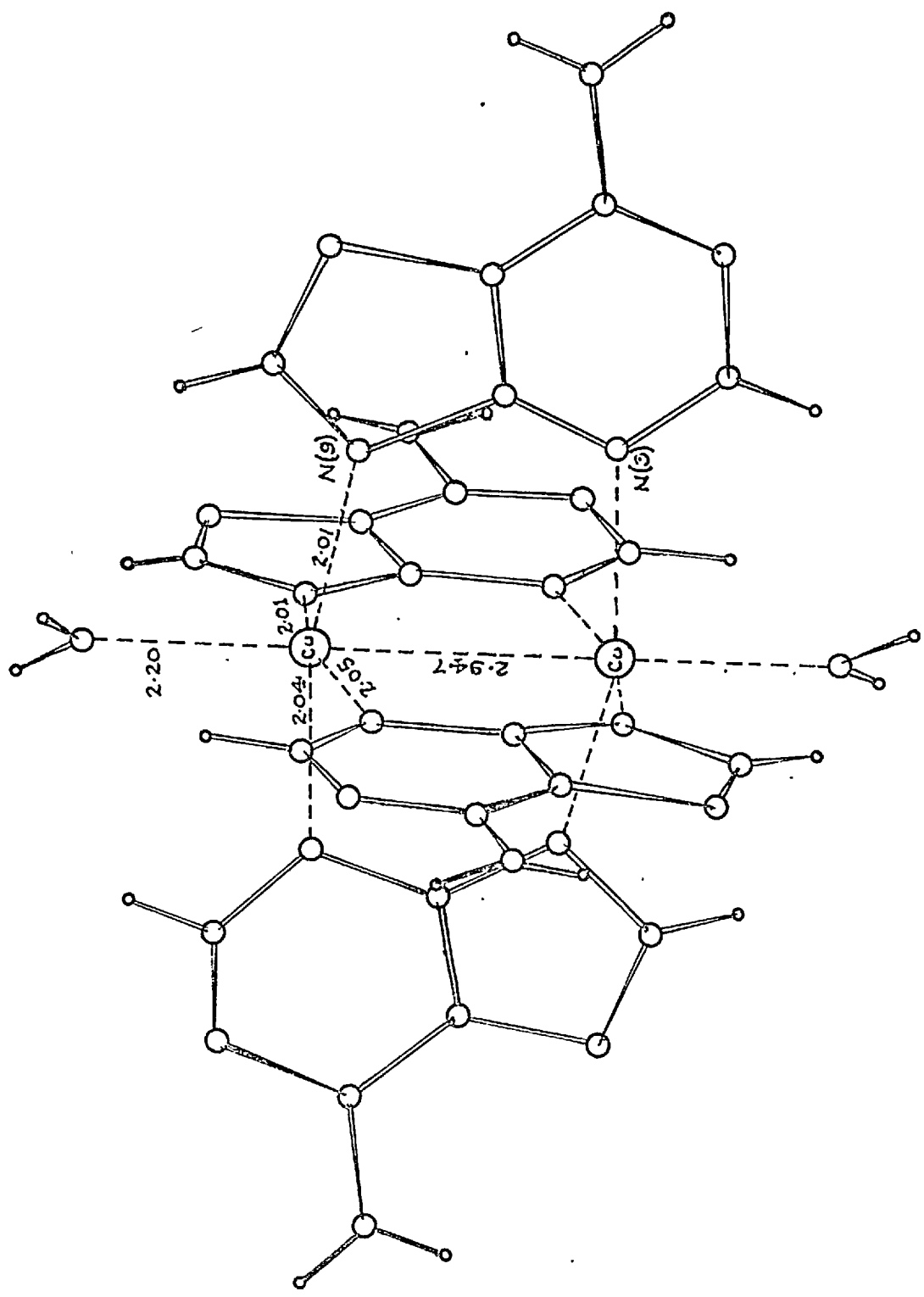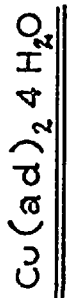
Cu(ad)$_2$ 4 H$_2$O

CHAPTER 5.

Adenine Complexes.

As well as an inner complex, $Cu(ad)_2 4H_2O$, adenine (adH) is known to form copper complexes of stoichiometry $Cu(adH)_2X_2 \cdot nH_2O$ and $Cu(adH)X_2$[31]. The 2:1 compounds are obtained as crystalline materials in moderately acidic media, and the 1:1 compounds as powders, using a large excess of metal ion and strongly acidic conditions. Before the isolation of these compounds, potentiometric titration studies[103] had demonstrated copper complexation by adenine and it had been suggested that a chelate structure was formed using N(7) and the primary amino group at C(6).

Sletten[104] has made a single crystal X-ray study of the inner complex (fig.5) isolated by Weiss and shown it to have an interesting dimeric structure in which pairs of copper ions are held 2.947 $\overset{o}{A}$ apart by four bridging adenine anions co-ordinated via N(3) and N(9). A water molecule completes the co-ordination environment of each metal ion. The fact that N(9) is a donor atom negates any relationship between this compound and the involvement of copper with DNA, since this is the point of attachment of the ribose. However, the structure, which is closely related to that of copper acetate monohydrate presents the possibility of magnetic

exchange and this is of intrinsic interest. The preparation
and study of this compound was the starting point for the
present investigation of adenine; the esr studies are
discussed in Chapter 6 and the bulk magnetic susceptibility
measurements will be presented at this point.

There is some discrepancy concerning the number of
water molecules associated with the copper adenine dimer.
Weiss' preparative method was used in this work and the
air-dried crystalline material analysed as a tetrahydrate.
This is in good agreement with Sletten's crystal density
measurements and contrary to Weiss' original formulation
with three water molecules. Sletten does note that the
compound loses its crystalline structure when dried over
silica gel and also states that Weiss' analysis referred
to the powdered material. (This is not apparent from Weiss'
paper.)

In the present work, the bulk susceptibility measure-
ments were made on powdered samples and were originally
taken to relate to the tetrahydrate[105]. A recent personal
communication to Dr. D.M.L. Goodgame indicates that there
is close agreement between these magnetic properties and
those of the compound, $Cu(ad)_2 \cdot 3H_2O$,[*] whereas preliminary
studies on the tetrahydrate[*] suggested a larger J value and
Neel temperature.   Since Brookes' studies also

[*] Compounds prepared by R. Brookes, Chemistry Department,
University of Melbourne.

FIG. 6.

TEMPERATURE DEPENDENCE OF SUSCEPTIBILITY FOR Cu(ad)₂3H₂O
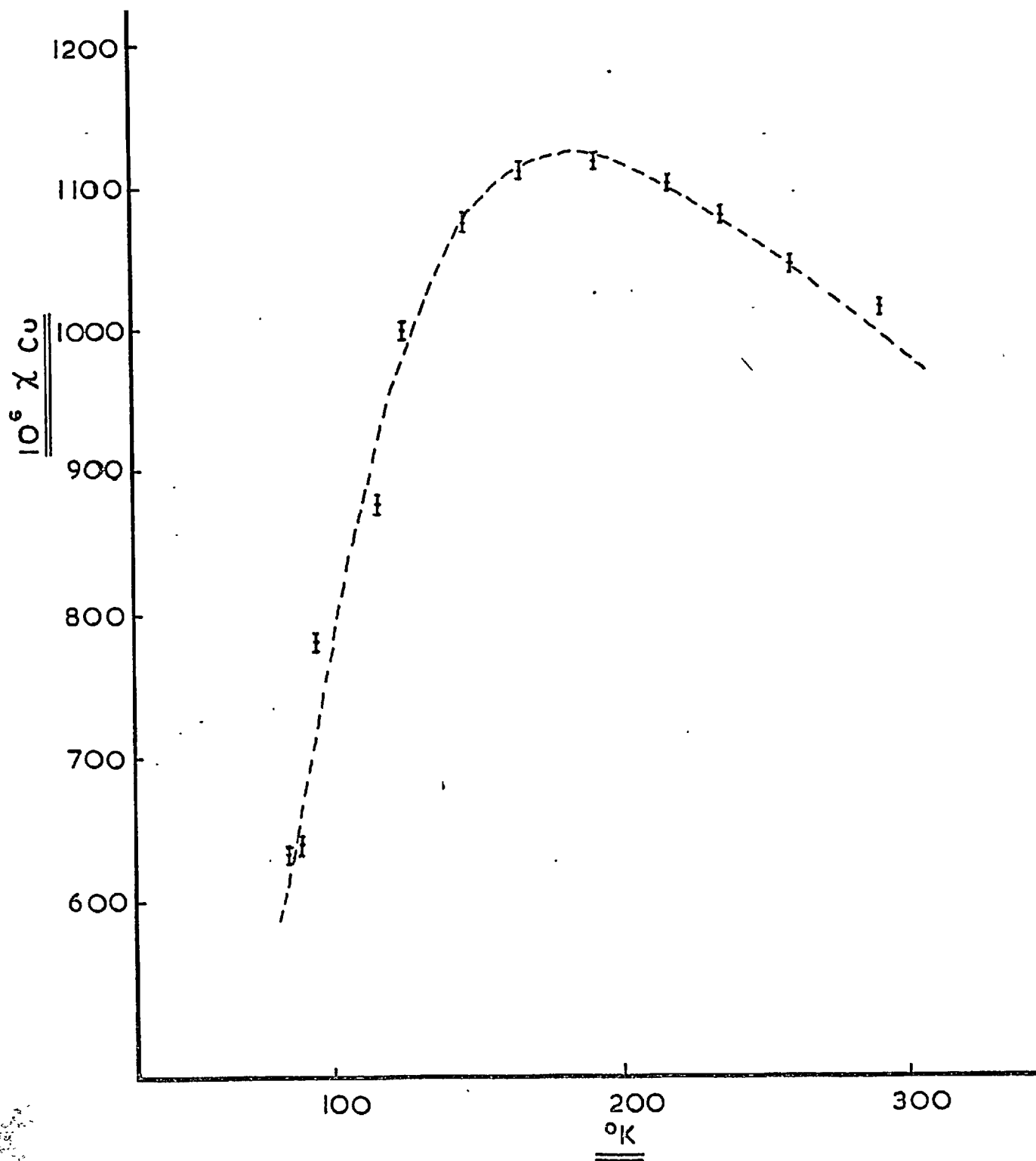
substantiate the magnetic properties of $Cu(adH)_2Cl_2.3H_2O$
to be presented here, it can be concluded that the
behaviour observed for the inner complex is, in fact, that
of the trihydrate, and that conversion of the tetra- to
the tri-hydrate occurred on powdering the sample for the
packing of the Gouy tube.

Measurements of the bulk magnetic susceptibility of
$Cu(ad)_2.3H_2O$ gave a value of 1.55 ± 0.02B.M. at 295°K for
the effective magnetic moment per copper ion, a value which
is well below that of magnetically dilute compounds. The
temperature dependence of the susceptibility in the range
$90^{\circ}-300^{\circ}$K (Figure 6) is typical of an antiferromagentically
coupled pair of cupric ions giving an S=0 ground state with
an S=1 level at Jcm^{-1} above this. The Neel temperature for
the compound is about 195°K. Using equation (1) and the
parameters, $N\alpha = 60x10^{-6}$ c.g.s.u, $J = 210cm^{-1}$ and $g = 2.05$
a theoretical curve may be plotted that gives a satisfactory
agreement with the experimental results.

The copper -copper distance in the trihydrate is not
known. However, for the tetrahydrate (Cu-Cu = 2.947 $\overset{o}{A}$)
Brookes has found a J value of $270cm^{-1}$. This is closely

FIG. 7.

SUPER EXCHANGE IN Cu(ad)$_2$ 4H$_2$O

(a)

(b)
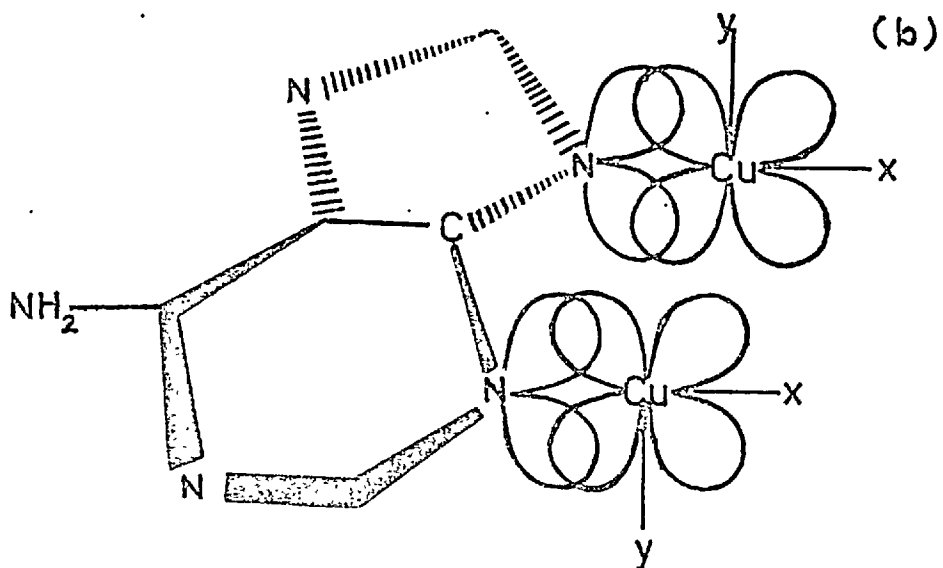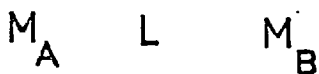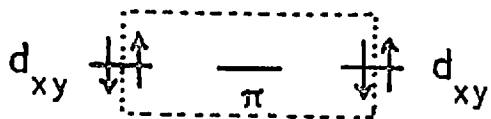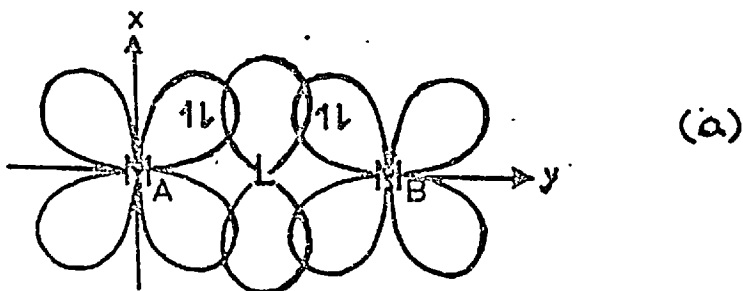
comparable to the value of the exchange integral for copper acetate monohydrate ($J = 286cm^{-1}$) in which there is a substantially smaller separation of the copper atoms ($Cu-Cu = 2.64 \overset{o}{A}$). This observation suggests that in $Cu(ad)_2.4H_2O$, exchange takes place through the bridging adenine molecules, a possibility that was recognised by Sletten.

This type of super-exchange mechanism, in which the intervening ligand transmits the interaction between the spins on neighbouring cations, has become increasingly favoured to account for spin coupling in dimeric copper acetate systems[106,107].

In the copper adenine dimer, if the x and y axes of the metal ion orbitals are taken to be directed along the Cu-N bonds (the copper atoms actually lie slightly out of the plane), then the d_{xy} orbitals are suitably disposed for π-bonding with the adenine molecules. The mechanism of the exchange can be appreciated by a consideration of the simplified model (Figure 7) in which M_A and M_B represent copper ions and L an intervening ligand. Non-orthogonality of the metal d_{xy} orbitals and a suitable, empty ligand pπ orbital will allow a net overlap and a pathway is

available for transfer of electrons from the metal atoms to the ligand. Since electron transfer from M_A and M_B to the ligand orbital must give a pair of electrons spinning in opposite senses, the remaining electrons in each d_{xy} orbital will have an anti-parallel alignment and there will be magnetic coupling of antiferromagnetic sign for the unpaired electrons on the copper ions.

Similar exchange takes place when the two copper ions are linked by the π delocalised systems of the adenine anions. Overlap of the filled d_{xy} orbitals on each copper ion with one empty, anti-bonding π molecular orbital, delocalised over N(3) and N(9), will give rise to super-exchange interaction which is antiferromagnetic.

The electronic spectrum of the solid compound showed a d-d band at $17,860 \text{cm}^{-1}$ and at ca.80°K a shoulder was observed (ca. $14,500 \text{cm}^{-1}$). It is probable that the absorption envelope contains all the d-d transitions as is thought to be the case for the $14,000 \text{cm}^{-1}$ band of cupric acetate. (A low frequency shoulder has also been observed for cupric acetate at low temperature.)[108]. The higher band energy of the adenine complex reflects the stronger ligand field compared with that due to the oxygen atoms in the acetate.

The magnetic properties of the compounds, $Cu(adH)_2X_2 \cdot nH_2O$ (X = Cl,Br,NO_3,1/2 SO_4) have been examined during the course of the present studies and they are all found to exhibit spin-coupling behaviour analogous to that in the inner complex. The room temperature moments lie in the range 1.43 B.M. (X=Br) to 1.61 B.M. (X=1/2SO_4) and the Neel temperatures range from ca.190°K (X=NO_3) to ca.240°K (X=Cl). All the compounds produce an esr signal like that of the inner complex. This similarity of behaviour is strong evidence that the dimeric unit is retained, even though the presence of anions would, in most cases, permit the formation of alternative, more common co-ordination geometries.

One of the compounds, $Cu(adH)_2Cl_2 \cdot 3H_2O$ has been examined by single crystal X-ray methods in the crystallography department[109]. As well as confirming the existence of a dimeric species, the structural data permit a meaningful comparison of magnetic parameters with other dimeric copper systems.

The compound crystallises from water as blue-green platelets which are orthorhombic. The unit-cell dimensions are $\underline{a}$ = 23.92, $\underline{b}$ = 13.844, $\underline{c}$ = 11.262 Å, $\underline{U}$ = 3729 Å^3 $\underline{D}_m$ = 1.66, $\underline{z}$ = 8, $\underline{D}_c$ = 1.63, space group $\underline{Cmca}$. The structure contains the complex cation $[Cu(adH)_2Cl]_2^{2+}$,

THE $[Cu(adH)_2Cl]_2^{2+}$ ION
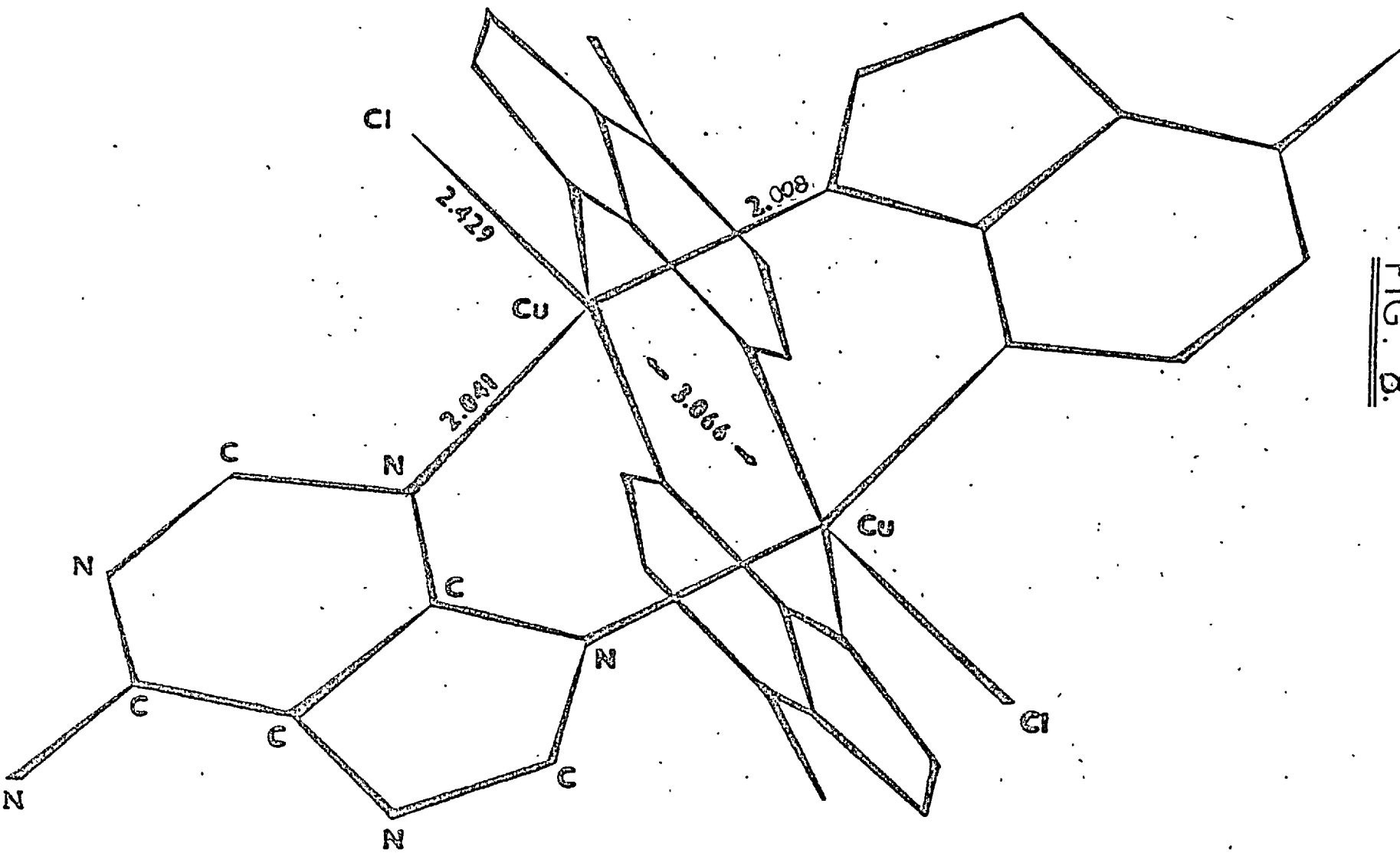
FIG. 8.

chloride ions, and molecules of water of solvation. The dimeric cation which has $2/\underline{m}$ crystallographic symmetry is shown in Figure 8. The copper-copper separation (3.066 Å) is appreciably larger than that found in the dimer $[Cu(ad)_2 \cdot H_2O]_2$. As a result, the tetragonal pyramidal co-ordination about the copper is more distorted with the metal atom 0.33 Å above the plane of the four nitrogen atoms. The copper-nitrogen bond lengths are very similar in both complexes.

The chloride ions together with the water molecules and all non-donor nitrogen atoms of the adenine form an intricate network of hydrogen bonds, in which bonds of the type O-H····N, N-H····O and O-H····Cl are involved.

In the earlier chapters, compounds of stoichiometry CuL_2X_2 (X= Cl, Br) were described where L = 5Mepyr, 4Mepyr, dmp and tmp. On the available evidence, all the compounds conform to the structural types found for similar hetero-cyclic amine complexes, namely polymeric, halide-bridged, tetragonal and planar. Therefore, it is significant that the dimeric unit found in the adenine inner complex persists in the compound $Cu(adH)_2Cl_2 \cdot 3H_2O$. On the basis of similar properties, this is almost certainly true for the other 2:1 compounds, though, in the case of the sulphate, water

molecules and not anions, will occupy the terminal positions.
During the course of this work, Kokoszka has reported magnetic
coupling for $Cu(adH)_2(ClO_4)_2 \cdot 3H_2O$[110]. The esr and magnetic
results on this compound indicate that it is structurally
similar to the compounds presently under discussion.

For each of the 2:1 compounds, a theoretical curve
of the temperature variation of susceptibility has been
plotted. The J values quoted in Table 5.2 are those giving
a best fit to the experimental data using g_{av} values
obtained from esr measurements and a value of 60×10^{-6} c.g.s.u.
for $N\alpha$. In the case of $Cu(adH)_2SO_4 \cdot 4H_2O$ a satisfactory
agreement could only be obtained by using equation (2)
which includes the effect of monomeric impurity. A J value
of $230cm^{-1}$ was obtained, if the level of impurity was taken
to be a 0.025 mole fraction. Since the esr spectra of all
these compounds contain a signal due to monomeric impurity,
calculations have been made to determine the effect of
impurity on the J values of the remaining compounds. If
allowance is made for a 0.015 mole fraction of monomer, the
J values increase by ca.5cm^{-1}. The presence of a 0.025mole
fraction would increase the J values by ca.10cm^{-1}.

Although the copper-copper distance in $Cu(adH)_2Cl_2 \cdot 3H_2O$
is significantly larger than that in $Cu(ad)_2 \cdot 4H_2O$, the extent
of the spin coupling is still quite comparable to that in

cupric acetate monohydrate. This observation reinforces the conclusion, drawn by Kokoszka, that in copper dimers of this kind, the spin-coupling proceeds predominantly via a superexchange mechanism involving the bridging groups and not by any significant direct metal-metal bonding.

The electronic spectra of $Cu(adH)_2X_2.nH_2O$ (Table 5.1) show a single, visible band at lower energy than that observed for the inner complex. Within the group X=Cl,Br,NO$_3$ there is a decrease in band energy with increasing donor capacity of X. When X =1/2 SO$_4$, there is a shift to a higher energy more comparable to that in the inner complex.

The possibility that the 1:1 compounds may involve a co-ordination site other than N(9) and therefore have biochemical relevance, has led to the preparation and examination of $Cu(adH)X_2$ (X=Cl,Br).

Variable temperature magnetic studies indicate the presence of antiferromagnetic exchange. The chloro-compound obeys the Curie-Weiss law down to 90°K (θ = -60) and $Cu(adH)Br_2$ has a Neel temperature of about 140°K (Figure 9). In view of the bridging tendency of adenine, it is possible that the compounds could be formed by both halogen and adenine bridges.

FIG. 9

TEMPERATURE DEPENDENCE OF THE MAGNETIC

SUSCEPTIBILITY OF Cu(adH)Br₂

FIG. 10.

93.

$Cu_3(C_5H_6N_5)_2Cl_8 H_2O$
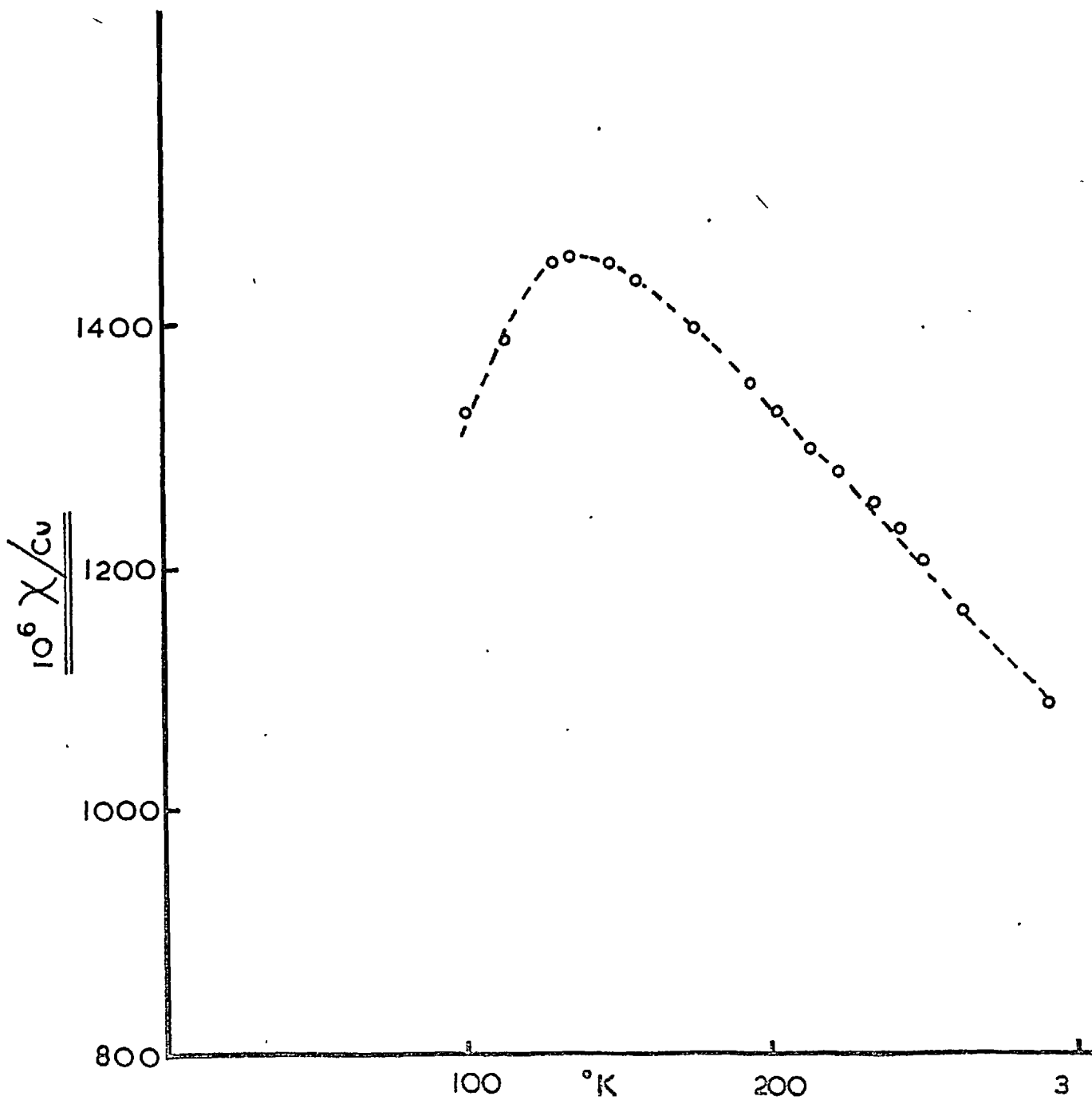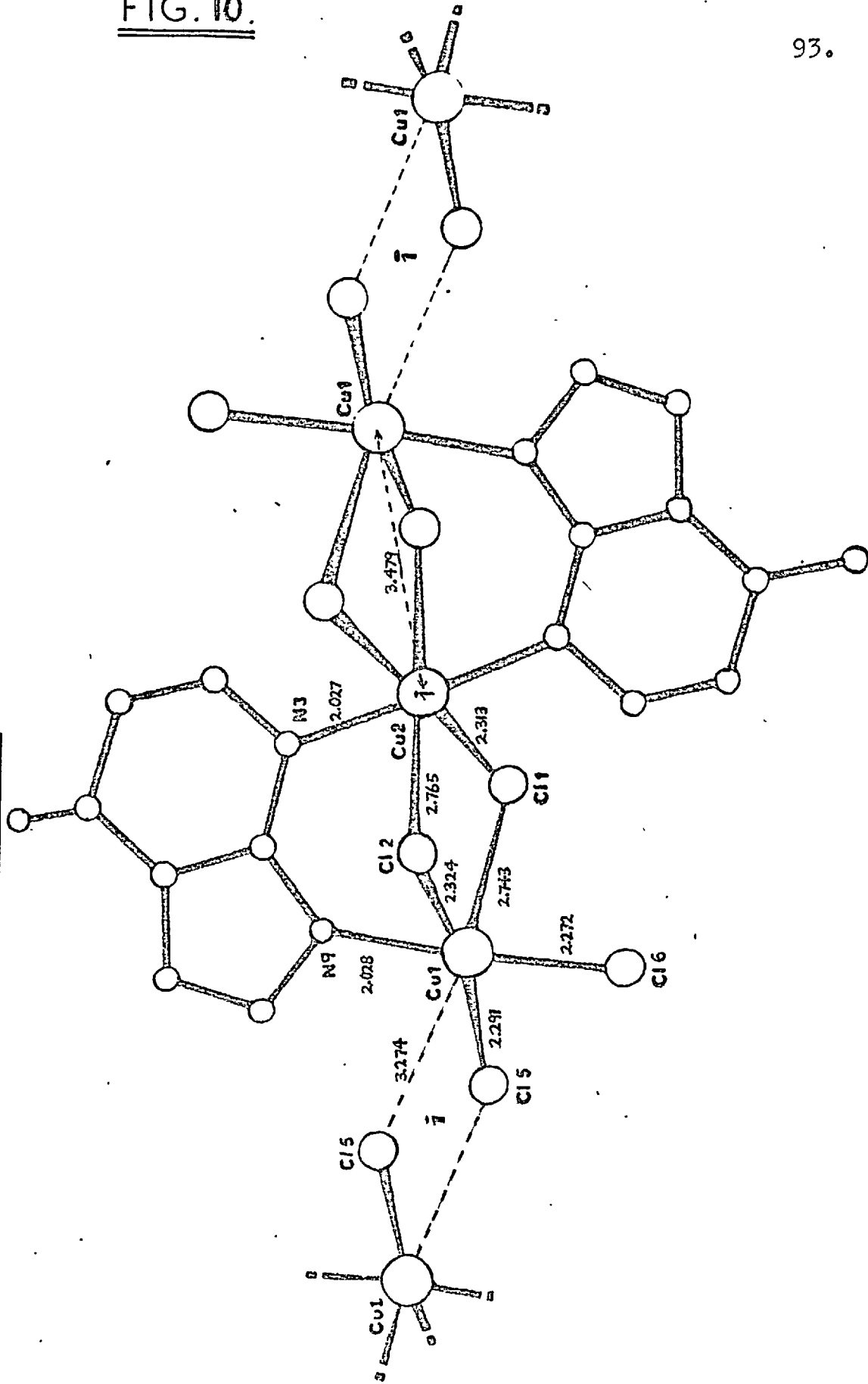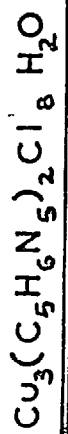
The electronic spectra do not present a clear
indication of the co-ordination geometry. The main band
(ca.11,500cm^{-1}) lies at lower energy than that of other
polymeric halogen-bridged species, involving copper, and
and it's position is more consistent with a pseudo-tetrahedral
arrangement.

In an attempt to produce crystalline samples of one
of these compounds, crystals of stoichiometry $Cu_3Cl_8(C_5H_6N_5)_2$.
$4H_2O$ have been isolated and a single crystal X-ray study
has been carried out in the crystallography department[111].
The structure, which is shown in Figure 10, contains
several features of interest. The complex is best thought
of as being trinuclear. The central copper atom, which lies
at a centre of symmetry, is six co-ordinate with four
bridging chlorine atoms and two N(3) atoms of the bridging
adenine molecules, completing a distorted octahedron. The
terminal copper atoms are effectively five-co-ordinate with
a geometry based on the square pyramid. Atoms Cl(5) of
adjacent trinuclear units occupy the sixth position, but at
a very long distance of 3.27 Å. There is the usual asymmetry
of copper-bridging chlorine bond distances with strong Cu-Cl
bonds of about 2.3 Å and weaker ones of about 2.75 Å. The
bridging adenine molecules co-ordinate via N(3) and N(9),
as in the dimeric units of $Cu(ad)_2.4H_2O$ and $Cu(adH)_2Cl_2.3H_2O$,
but here they span more widely separated copper atoms

(Cu–Cu = 3.5 Å). Despite the greater distortion, the Cu–N bonds are of similar length to those found in the other two compounds. This means that each copper atom has a plane of four strong bands, these planes are approximately parallel.

It has proved possible to show that the adenine molecules are protonated at N(1). This and other hydrogen atoms are part of a network of hydrogen bonds, in which bonds of the type N–H···O, N–H···Cl and O–H···Cl are involved.

This compound does not show the subnormal magnetic moment observed for $Cu(adH)_2Cl_2.3H_2O$; it's room temperature moment is 1.86 B.M. per copper ion[ж] and may be compared with that of $Cu(adH)Cl_2$ (1.84 B.M.) Both these compounds produce similar electronic and vibrational bands and neither shows the characteristic S=1 type of esr spectrum. It seems reasonable to conclude that $Cu(adH)Cl_2$, and also $Cu(adH)Br_2$, have an infinite chain structure with a bridging system like that in the trinuclear complex. This type of structure is known to exist for $Cu(1,2,4-triazole)Cl_2$[112]. It is interesting to note that this compound has an electronic band at about 13,800cm^{-1} with a very broad, low energy shoulder (ca. 9600cm^{-1})[62].

ж Measured on Faraday balance by Mr. D. Lowe.

All of the compounds studied here have demonstrated that adenine functions predominantly as a bridging ligand. One of the atoms involved in bridging, N(9), is the position at which the sugar is linked in DNA. This observation emphasises the difficulties involved in studying the simplified model system.

TABLE 5.1.

Diffuse Reflectance Spectra (cm^{-1}).

$Cu(ad)_2 \cdot 3H_2O$	14,500(sh)	17,860(s)	
$Cu(adH)_2Cl_2 \cdot 3H_2O$	16,000(s)	26,300(s)	
$Cu(adH)_2Br_2 \cdot 2H_2O$	16,130(s)	25,600(s)	
$Cu(adH)_2(NO_3)_2$	15,870(s)	26,600(s)	
$Cu(adH)_2SO_4 \cdot 4H_2O$	17,390(s)	25,320	
$Cu(adH)Cl_2$	11,430(s)	ca.12,900(s,sh)	23,500(s) 27,000(s)
$Cu(adH)Br_2$	11,240(s)	ca.12,900(s,sh)	ca.22,470(s,v.br)
$Cu_3(C_5H_6N_5)_2Cl_8 \cdot 4H_2O$	12,900(s)		

TABLE 5.2.

Magnetic Properties.

	Temp.($^\circ$K)	(B.M.)	J(cm^{-1})
$Cu(ad)_2 \cdot 3H_2O$	295	1.55 ± 0.02	210
$Cu(adH)_2Cl_2 \cdot 3H_2O$	295	1.45 ± 0.01	270
$Cu(adH)_2Br_2 \cdot 2H_2O$	296	1.43 ± 0.02	260
$Cu(adH)_2(NO_3)_2$	295	1.60 ± 0.03	210
$Cu(adH)_2SO_4 \cdot 4H_2O$	296	1.64 ± 0.03	230
$Cu(adH)Cl_2$	297	1.84	
$Cu(adH)Br_2$	295	1.60	
$Cu_3(C_5H_6N_5)_2Cl_8 \cdot 4H_2O$	295	1.86	

TABLE 5.3.

Temperature dependence of bulk susceptibilities for

A. $Cu(ad)_2 \cdot 3H_2O$

Temp($^\circ$K)	295	264	240	221	206	170	150	129	119	91	88
$10^6\chi$/Cu	953	984	1016	1040	1054	1046	1008	938	810	576	570

Diamagnetic correction = 115 x 10^{-6} c.g.s.u.

B. $Cu(adH)_2Cl_2 \cdot 3H_2O$

Temp($^\circ$K)	299	290	264	244	222	198	178	156	150	134	111	97
$10^6\chi$/Cu	838	840	860	870	858	835	785	710	665	590	395	295

Diamagnetic correction = 174 x 10^{-6} c.g.s.u.

TABLE 5.3 continued.

C. $Cu(adH)_2Br_2.2H_2O$

Temp(^{O}K) 300 265 246 217 197 183 176 162 156 136 116 102

$10^6\chi$/Cu 870 880 890 882 860 854 810 785 765 655 505 395

Diamgnetic correction = 183 x 10^{-6} c.g.s.u.

D. $Cu(adH)_2(NO_3)_2$

Temp(^{O}K) 298 270 250 210 179 149 130 111 110 100 97 90

$10^6\chi$/Cu 1015 1045 1065 1115 1115 1080 988 838 810 720 708 598

Diamagnetic correction = 125 x 10^{-6} c.g.s.u.

E. $Cu(adH)_2SO_4.4H_2O$

Temp(^{O}K) 296 279 259 236 201 180 146 120 104 91

$10^6\chi$/Cu 1012 1028 1062 1080 1095 1082 1005 785 709 480

Diamagnetic correction = 180 x 10^{-6} c.g.s.u.

In all cases $10^6\chi$/Cu is corrected for Nα = 60x10^{-6} c.g.s.u.

FIG. II.

VIBRATIONAL SPECTRA OF COPPER ADENINE COMPLEXES.

$Cu(ad)_2.3H_2O$

$Cu(adH)_2Cl_2.3H_2O$

$Cu(adH)_2Br_2.2H_2O$

$Cu(adH)Cl_2$

$Cu(adH)Br_2$

$cm.^{-1}$
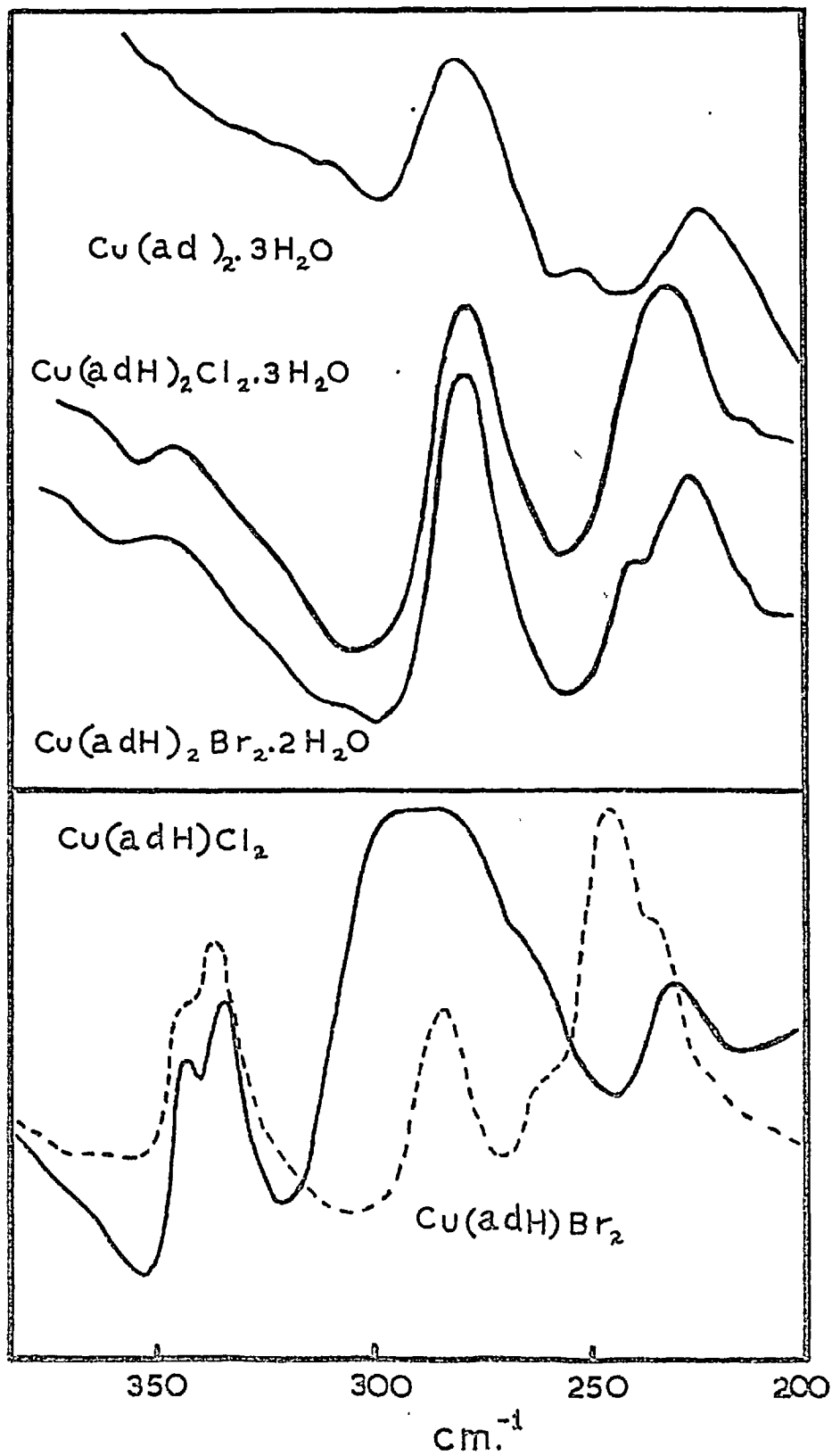
Vibrational Spectra (400-90cm^{-1}). Table 5.4

Above 200cm^{-1}, adenine produces two bands, one at
335cm^{-1} (m) and one at 245cm^{-1} (w). The higher energy
absorption is seen around 345cm^{-1} in the compounds
$Cu(adH)_2X_2.nH_2O$ and $Cu(adH)X_2$ (X=Cl,Br), while that at
lower energy appears at ca.253cm^{-1} in $Cu(ad)_2.3H_2O$ and
ca.263cm^{-1} in $Cu(adH)Br_2$. Below 200cm^{-1}, the spectrum
of adenine consists of broad, featureless absorption.

A comparison of the spectra of $Cu(adH)_2X_2.nH_2O$ with
that of $Cu(ad)_2.3H_2O$ (Figure 11) suggests that the bands
at ca,280cm^{-1} and ca. 225cm^{-1}, in each of them, can be
assigned as metal-nitrogen vibrations. In the chloro
complex, the lower energy band is of increased intensity
relative to that at higher energy. From this it can be
concluded that the expected copper-chlorine stretching mode
occurs at about 230cm^{-1}. The corresponding copper-bromine
absorption of $Cu(adH)_2Br_2.2H_2O$ is found at 145cm^{-1} (m,br).

The breadth of the higher energy band in $Cu(adH)Cl_2$
suggests that it is an envelope of a metal-nitrogen and a
metal-halogen vibration. This is substantiated by the
presence of a band at 285cm^{-1} (m) in $Cu(adH)Br_2$ that can
be attributed to a metal-nitrogen vibration. The copper-
bromine stretching mode occurs at 247cm^{-1}.

Below 200cm^{-1}, there is a halogen-sensitive band at 175cm^{-1} (Cl) and at 134cm^{-1} (Br). These may be compared with the bands in $Cupy_2X_2$ (Cl, 175cm^{-1} and Br, 130cm^{-1}) which have been assigned as the metal-halogen in-plane bending modes of the polymeric chain.

The spectrum of $Cu_3(C_5H_6N_5)_2Cl_8 \cdot 4H_2O$ has been run between 400 and 200cm^{-1} and is found to resemble that of $Cu(adH)Cl_2$ but with the bands moved to lower energies.

TABLE 5.4.

Vibrational Spectra ($400-90 cm^{-1}$)

Adenine	335(m) 245(w)
$Cu(C_5H_4N_5)_2 \cdot 3H_2O$	280(ms) <u>ca</u>.253(w) 225(m)
$Cu(C_5H_5N_5)_2 Cl_2 \cdot 3H_2O$	345(w) 278(ms) 233(ms) <u>ca</u>.125(w,br)
$Cu(C_5H_5N_5)_2Br_2 \cdot 2H_2O$	347(w) 280(ms) 238(m,sh) 225(m) 145(m,br)
$Cu(C_5H_5N_5)Cl_2$	343(m) 335(m) 288(s,br) 230(m) 175(s) 103(s,br)
$Cu(C_5H_5N_5)Br_2$	345(m) 339(m) 285(m) 263(w,sh) 247(ms) 235(m,sh) 134(ms)

Other Complexes of Adenine.

Preliminary investigations with adenine and cobalt (II) have shown that it is possible to obtain a deep-violet crystalline material which analyses as $Co(C_5H_5N_5)Cl_2$. The electronic spectrum resembles that of a tetrahedral species with very intense absorption at about $5000cm^{-1}$, $9000cm^{-1}$ and $18,000cm^{-1}$. When this material is prepared in air, the purple precipitate rapidly changes colour to dark brown and the electronic spectrum of this substance shows bands at $8900cm^{-1}$, $18,000cm^{-1}$ and $24,390cm^{-1}$.

Nickel (II) and manganese (II) interact with adenine and the compounds $Ni(adH)_2SO_4.4H_2O$ and $Mn(adH)Cl_2.2H_2O$ have been isolated. The pale green nickel complex has the spectrum of an octahedral complex with no detectable splitting of the v_1 band at room temperature. The dark pink manganese compound has an interesting spectrum with a strong band at $19420cm^{-1}$. The band is less intense than expected for a charge transfer band and it is possible that the compound does, in fact, involve manganese (III) and an adenine anion. Attempts to produce a bulk quantity of this complex have been unsuccessful.

CHAPTER 6.

Electron Spin Resonance (esr) studies on the copper systems.

The presence of pronounced magnetic exchange in the inner complex and the 2:1 copper adenine compounds is indicated by the X-band electron spin resonance spectra of polycrystalline samples. As in the spectra of cupric carboxylate dimers, absorptions are observed at resonance fields well above and well below the region (g_{eff} ca.2) where signals are normally found for Cu(II) with S=1/2 ground state. The spectra are those of a species with a resultant spin of S=1.

Although single crystal studies are necessary for the accurate determination of the magnetic parameters of these dimeric systems, it has recently been demonstrated that they may be obtained from the powder spectra[113]. An analysis of the spectra of randomly oriented organic triplets showed that it was possible to identify the resonance fields in which the external field was aligned with the principal magnetic axes, even though the observed spectrum was a sum over all possible orientations.

The spin Hamiltonian for the triplet state of dimeric copper compounds is given by[113]

$$\mathcal{H} = \beta HgS + DS_z^2 + E(S_x^2 - S_y^2) - 2/3D \qquad (3)$$

where D and E are the zero-field splitting parameters, β is the Bohr magneton. The magnetic axes are defined as the system of co-ordinates, x, y, z, fixed with reference to the copper-copper bond. When the external field is aligned with these co-ordinates, the resonance fields are given by

$$H_{x_1}^2 = (g_e/g_x)^2 [(Ho-D'+E)(Ho+2E')] \qquad (4)$$

$$H_{x_2}^2 = (g_e/g_x)^2 [(Ho+D'-E')(Ho-2E')]$$

$$H_{y_1}^2 = (g_e/g_y)^2 [(Ho-D'-E')(Ho-2E')]$$

$$H_{y_2}^2 = (g_e/g_y)^2 [(Ho+D'+E')(Ho+2E')]$$

$$H_{z_1}^2 = (g_e/g_z)^2 [(Ho-D')^2 - E'^2]$$

$$H_{z_2}^2 = (g_e/g_z)^2 [(Ho+D')^2 - E'^2]$$

where $Ho = h\nu/g_e\beta$, $D' = D/g_e\beta$, $E' = E/g_e\beta$ and g_e is the free electron g value.

In the case of the copper adenine inner complex, the E parameter appears to be zero, or, at least, very small for the xy bands are unsplit in all spectra (these were run at 295°, 125° (see Figure 12) and $50^\circ K)$[*]. When E is set equal to zero, the remaining parameters are given by

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X - BAND   SPECTRUM   OF   Cu(ad)$_2$ 3H$_2$O   AT 125°K

K-gauss

FIG. 12.

106.
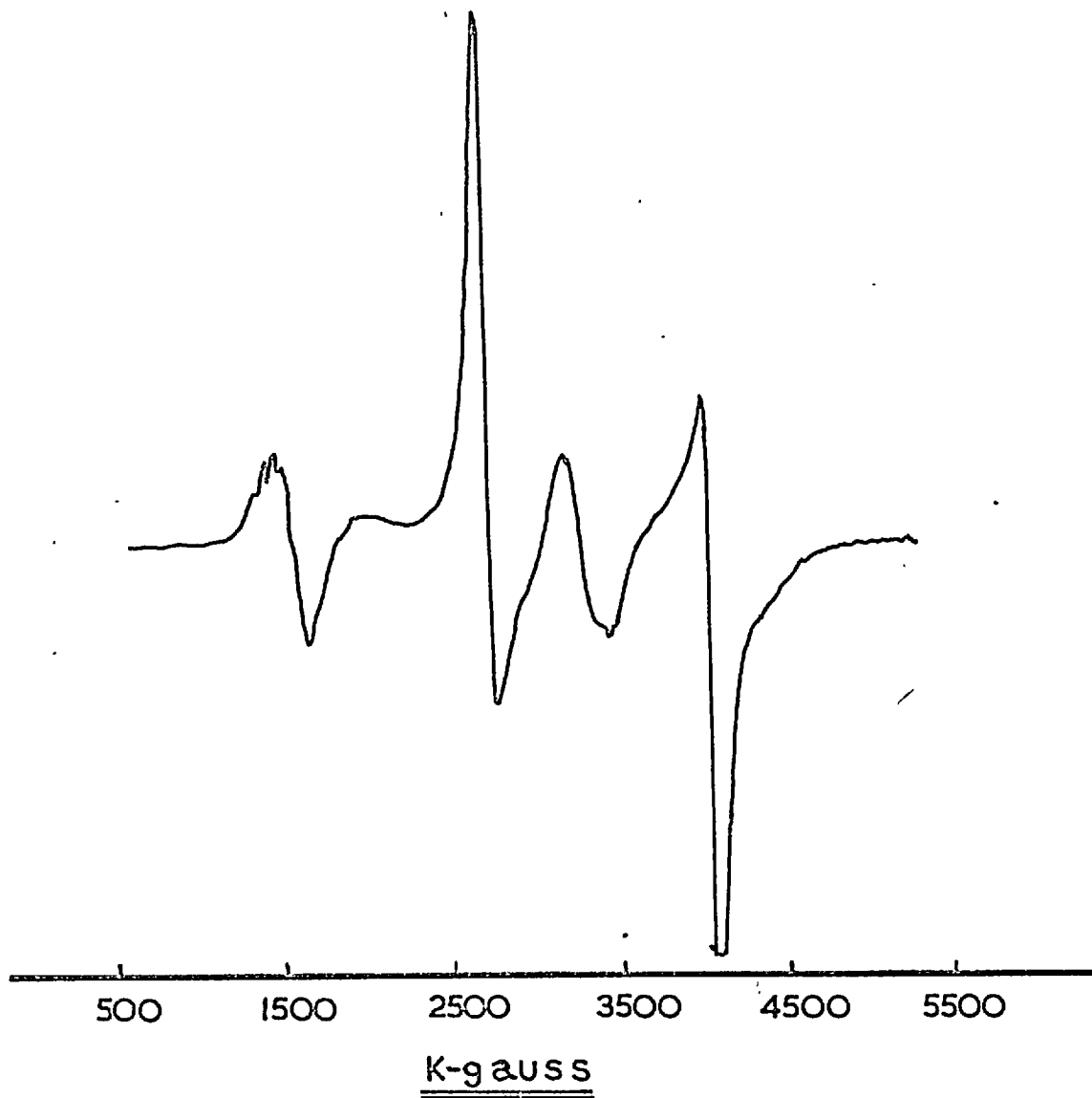
$$H_{xy_1}{}^2 = (g_e/g_{xy})^2 \; Ho \; (Ho-D') \qquad\qquad (5)$$

$$H_{xy_2}{}^2 = (g_e/g_{xy})^2 \; Ho \; (Ho+D')$$

$$H_{z_1} \;\; = (g_e/g_z) \; |\, Ho-D' \,| \;\cdot$$

$$H_{z_2} \;\; = (g_e/g_z) \; (Ho+D')$$

The axial fields are obtained by choosing a point on the side of the more intense peak closer to Ho; the distance of the point below the peak is equal to the magnitude of the less intense peak. This yields values for H_{xy_1} and H_{xy_2} of 2500 and of 3855 gauss, respectively, which when substituted in equations (5) give $g_{xy} = 2.03$ and $D = 0.125 cm^{-1}$.

Assignment of the almost symmetrical absorption centred at 1378 gauss to the $\Delta m=1$ transition H_{z_1} seems unlikely because this would require an unusually high value of g_z, ca.2.8. Also, there is no detectable high field line which would correspond to H_{z_2}. The absorption is probably due to the $\Delta m=2$ or 'half-field' transition. This type of transition is expected when $D < h\nu$, a situation which holds for the inner complex ($h\nu$ at X-band ca.0.3cm^{-1}). It has been observed as a strong line for organic molecules in triplet states [114].

At low temperatures, the band at 1378 gauss shows

copper hyperfine structure with splitting, A = 70 gauss.
It was only possible to resolve six of the expected seven
components, that at highest field being obscured by the
tail of the derivative curve which is not completely isotropic.
The observation of more than four hyperfine components does
confirm that this band arises from the dimeric unit and not
from an impurity.

The band at 3140 gauss increases in intensity with
decreasing temperature whereas the other bands become
weaker on cooling because of the depopulation of the $S=1$
level. It also becomes anisotropic being broader to low
field. These facts and its position at g_{eff} ca. 2.1, suggest
that if may be due to an impurity with a ground state of
$S=1/2$.

Bleaney and Bowers developed an expression for D in
terms of the g values and exchange constant J.[100]

$$D = -1/8 \ J \left[1/4 \ (g_z-2)^2 - (g_{xy}-2)^2 \right] \qquad (6)$$

The calculated parameters, D and g_{xy}, and the J
value, independently determined from susceptibility
measurements, may be substituted in this expression to
obtain a value for g_z. This, in turn, can be used to
predict the positions of H_{z_1} and H_{z_2} as 1800 gauss and

4300 gauss respectively. A weak absorption is in fact
seen near 1800 gauss, but at 4300 gauss the tail of the
absorption from H_{xy_2} is still quite strong and H_{z_2} is
unobserved. It has been reported that E_{z_2} is substantially
weaker than H_{z_1}.[113].

For all the compounds $Cu(adH)_2X_2 \cdot nH_2O$ (X=Cl,Br,NO$_3$,
1/2 SO$_4$) E is effectively zero and the magnetic parameters
are defined by the set of equations (5).

H_{z_1} can be seen most clearly when X=Br, or 1/2SO$_4$ (Fig.13)
and in the latter case, at low temperature (ca.125°K) it
shows copper hyperfine splitting (A=86gauss). It is
possible to resolve all seven components. In the same
spectrum there is evidence of H_{z_2}; five hyperfine components
of separation 86 gauss can be discerned in the tail of the
absorption from Hxy_2 where Hz_2 is predicted to occur.

The calculated parameters for the dimeric systems
are listed in Table 6.1 together with the average g values
used to calculated the theoretical cruves for the temperature
magnetic studies.

X-band spectra of polycrystalline samples of
$Cu(adH)X_2$ (X=Cl,Br) and of $Cu_3(C_5H_6N_5)_2Cl_8 \cdot 4H_2O$ show aniso-
tropic signals in the g=2 region as observed for S=1/2 copper
systems.

X-BAND SPECTRUM OF Cu(adH)$_2$SO$_4$.4H$_2$O (125°K)

FIG. 13.

Kgauss

110.
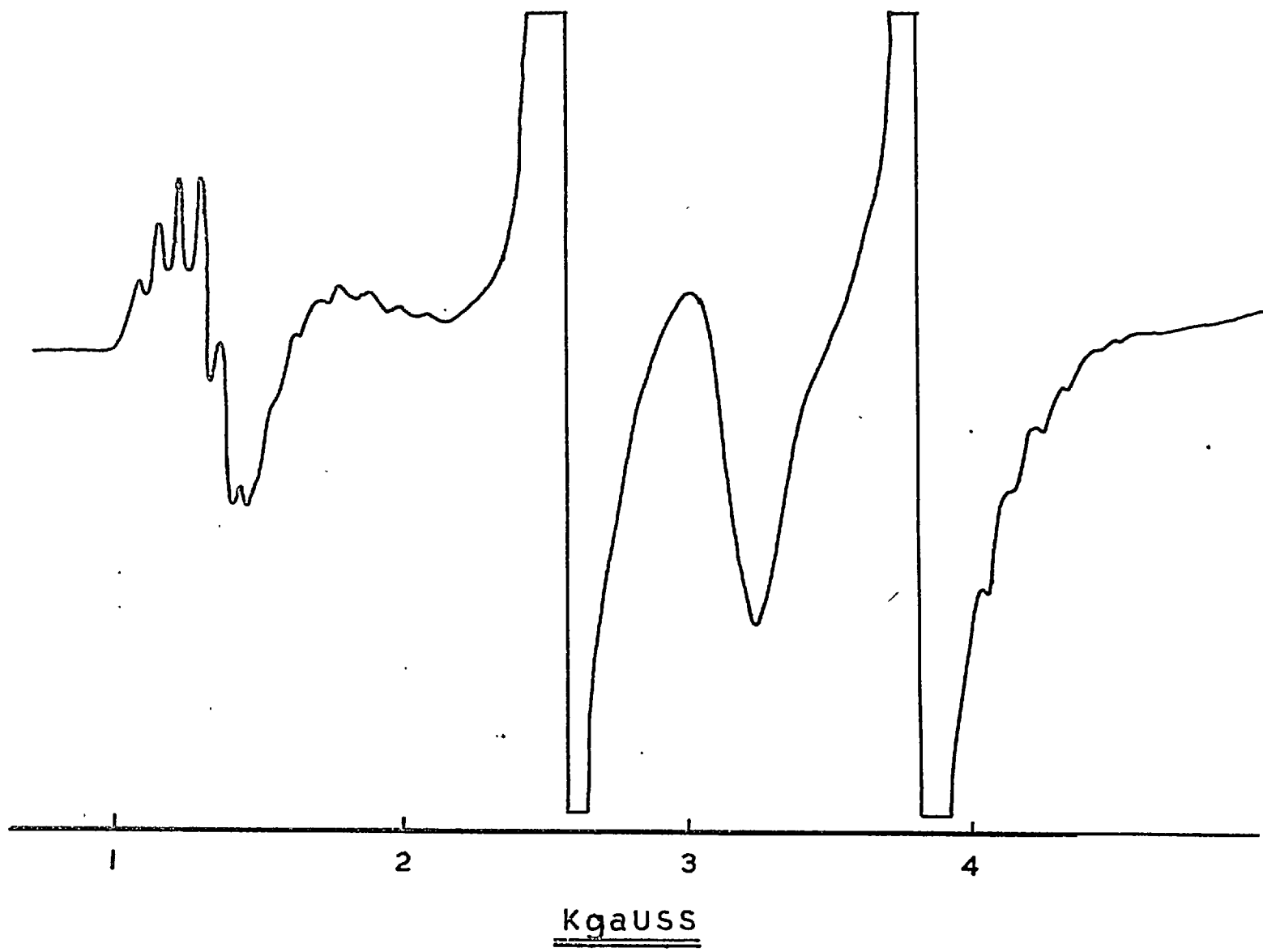
TABLE 6.1.

E.s.r. Parameters: Dimeric Adenine Compounds.

	$g_{xy}(\pm 0.01)$	$g_z(\pm 0.03)$	g_{av}	$D(\pm 0.005)cm^{-1}$
$Cu(C_5H_4N_5)_2 \cdot 3H_2O$	2.03			0.125
$Cu(C_5H_5N_5)_2Cl_2 \cdot 3H_2O$	2.06	2.20	2.11	0.117
$Cu(C_5H_5N_5)_2Br_2 \cdot 2H_2O$	2.07	2.21	2.12	0.118
$Cu(C_5H_5N_5)_2SO_4 \cdot 4H_2O$	2.07	2.23($\pm$0.02)	2.13	0.117
$Cu(C_5H_5N_5)_2(NO_3)_2$	2.06	2.20	2.11	0.116

Esr Spectra of Copper Carboxylate Compounds.

The spectra of the dimeric copper acetate and copper formate complexes may also be analysed using the method of Wasserman et al.[113] For these compounds D is greater than $h\nu$ and Hx_1, Hy_1 and $\Delta m = \pm 2$ are not observed. In $Cu(CH_3COO)_2L_{0.5}$ (L=5Mepyr, 4Mepyr, dmp) and in $Cu(HCOO)_2L$ (L-5Mepyr, 4Mepyr 2NH$_2$pyr) there is no detectable splitting of the mid-field peak, over a temperature range, and thus E is effectively zero. Under these conditions, the observed resonance occurs at fields given by

$$H_{xy}^2 = (g_e/g_{xy})^2 \left[Ho(Ho + D')\right] \qquad (7)$$

$$H_{z1} = -(g_e/g_z)(Ho - D')$$

$$H_{z2} = (g_e/g_z)(Ho + D')$$

X - BAND SPECTRUM OF Cu(CH₃COO)₂(2NH₂pyr)₀.₅ AT 140°K.

FIG. 14.

112.

K-gauss
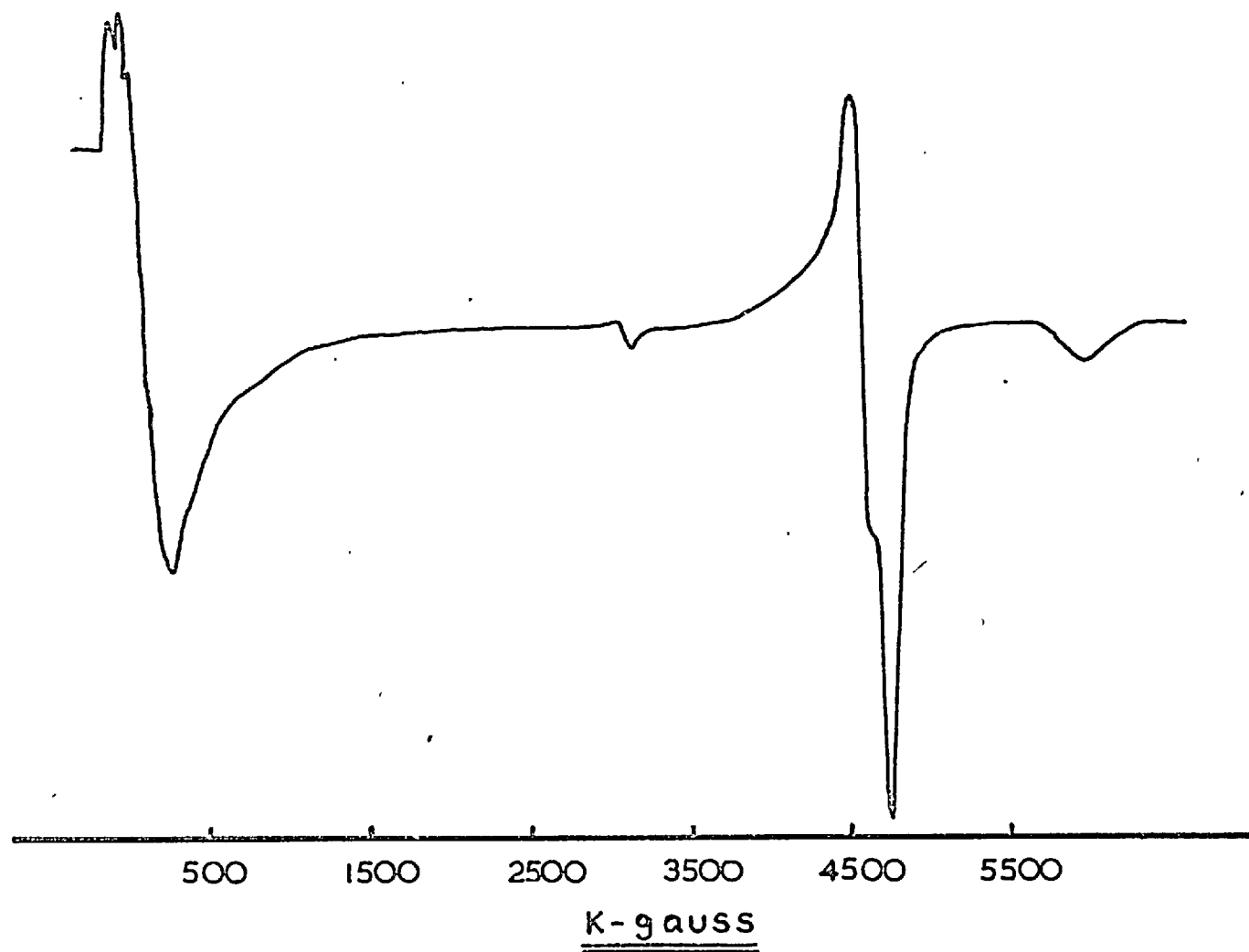
In the low temperature spectrum of $Cu(CH_3COO)_2(2NH_2pyr)_{0.5}$ the mid-field line is split indicating that E departs from zero and an estimate of the size of this parameter is $0.009cm^{-1}$ (Figure 14). The mid-point of the split line (E=0) was used in calculations on this compound.

For the purposes of comparison, esr powder spectra of copper acetate monohydrate have been obtained. At low temperature H_{xy} appears as a split line and E is estimated to be $0.018cm^{-1}$. The calculated parameters $g_z = 2.33 \pm 0.02$ $g_{xy} = 2.07 \pm 0.02$ $D = 0.34cm^{-1}$ are concordant with literature values of single crystal data: $g_z = 2.344 \pm 0.01$, $g_x = 2.053$ ± 0.005, $g_y = 2.093 \pm 0.005$, $D = 0.345cm^{-1}$ [115].

In all the acetate dimers, H_{z_1} shows hyperfine splitting (A=63 gauss) when measurements are made at reduced temperatures (ca.113°K) but only for $Cu(CH_3COO)_2(dmp)_{0.5}$ are the seven components resolvable. In the other acetates, H_{z_1} occurs at such low fields that the beginning of the derivative curve is not clearly seen.

Substitution in equations (7) gives the set of parameters presented in Table 6.2. The g and D values of $Cu(CH_3COO)_2L_{0.5}$ compare closely with those calculated from powder spectra of $Me_4N[Cu(CH_3COO)_2NCS]$: $g_z = 2.36$, $g_{xy} = 2.07$,

$D = 0.34 \text{cm}^{-1}$ [116] .The magnetic parameters $g_z = 2.40\pm0.02$, $g_{xy} = 2.08\pm0.02$ and $D = 0.39\pm0.01 \text{cm}^{-1}$ have been reported from similar studies on copper cyanoacetate [117].

In the spectra of $Cu(HCOO)_2L$, the resonances occur at higher fields and the calculated values of D are significantly larger than those of the acetate dimers. A similar value has been observed for $Me_4[Cu(HCOO)_2NCS]$: $D = 0.44 \text{cm}^{-1}$.

The room temperature spectra of the formates contain a small peak at about 3200 gauss. The fact that the intensity of this line in increased with decreasing temperature shows that it is caused by $S = 1/2$ impurity. An estimate of the level of impurity has been made during the bulk magnetic susceptibility studies. The low temperature spectrum of $Cu(CH_3COO)_2(2NH_2pyr)_{0.5}$ has a weak absorption, in this region, which can be taken to indicate the presence of trace quantities of $S = 1/2$ impurity.

Esr spectra of copper-pyrimidine complexes.

X-band spectra have been obtained on powdered samples of the substituted pyrimidine complexes and have been analysed according to the method of Kneubühl [118].

TABLE 6.2.

Esr parameters: Dimeric Carboxylate Compounds.

	g_z	g_{xy}	g_{av}	D
$Cu(CH_3COO)_2(5Mepyr)_{0.5}$	2.38	2.09	2.19	0.34
$Cu(CH_3COO)_2(4Mepyr)_{0.5}$	2.37	2.07	2.18	0.35
$Cu(CH_3COO)_2(2NH_2pyr)_{0.5}$	2.39	2.09	2.19	0.35
$Cu(CH_3COO)_2(dmp)_{0.5}$	2.38	2.08	2.18	0.35
$Cu(HCOO)_2(5Mepyr)$	2.38	2.08	2.18	0.43
$Cu(HCOO)_2(4Mepyr)$	2.37	2.07	2.18	0.43
$Cu(HCOO)_2(2NH_2pyr)$	2.42	2.08	2.20	0.43

The spectra of CuL_2Cl_2 (L = 5Mepyr, dmp, tmp) are consistent with a D_{2h} trans structure with weak axial interactions: similar spectra have been observed for substituted pyridine complexes[119,120]. As may be expected the spectra of the 1:1 complexes, $CuLCl_2$, (L = 5Mepyr, $2NH_2pyr$) are less well resolved because of the increased possibility of exchange coupling. The position of g_z has been estimated for these compounds (Figure 15). Resolution is also poor for the bromo complexes, CuL_2Br_2 (L = dmp, tmp). A single line spectrum is observed for $Cu(tmp)_2Br_2$ while $Cu(dmp)_2Br_2$ produces a signal like that of $Cu(5Mepyr)Cl_2$.

Pseudo-tetrahedral structures have been proposed for

$Cu(4Mepyr)Cl_2$ and $Cu(tmp)_{0.5}Cl_2$ and both these compounds produce signals with three g components. However, $Cu(dmp)_{0.5}Cl_2$, which on the basis of its electronic spectrum, is structurally analogous to $Cu(tmp)_{0.5}Cl_2$, shows only a single line centred at g = 2.14.

$CuL_2(NO_3)_2$ (L = 4Mepyr, 2NH_2pyr) and $Cu(5Mepyr)_2(NO_2)_2$ give spectra indicative of axial symmetry, while the nitrates of 5-methylpyrimidine give extremely broad signals centred at g = 2.1.

The complexes $Cu(5Mepyr)_4(ClO_4)_2.2H_2O$ and $Cu(4Mepyr)_3(ClO_4)_2.2H_2O$ give unresolved two g value spectra similar to that of $Cu(5Mepyr)Cl_2$, while $Cu(2NH_2pyr)_4(ClO_4)_2$ .4H_2O gives a substantially broadened isotropic signal centred at g = 2.06.

g_z

3000 gauss   3200
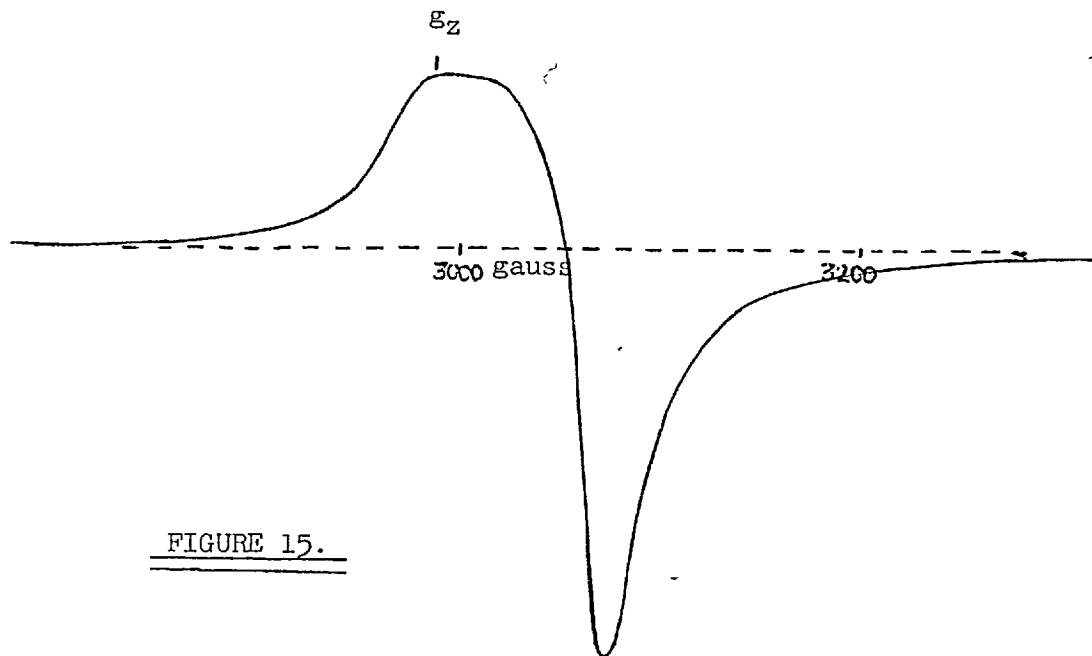
FIGURE 15.

TABLE 6.3.

X-band Spectra of some Copper-Pyrimidine Complexes.

	$g_{//}$ (g_z)	g_y	$g_\perp$	g_x
$Cu(5Mepyr)_2Cl_2$	2.21		2.05	
$Cu(5Mepyr)Cl_2$	2.20		2.05	
$Cu(5Mepyr)_2(NO_2)_2$	2.26		2.06	
$Cu(5Mepyr)(NO_2)_2$	2.20		2.01	
$Cu(5Mepyr)_4(ClO_4)_2.2H_2O$	2.16		2.06	
$Cu(4Mepyr)Cl_2$	2.22	2.06		2.02
$Cu(4Mepyr)_2(NO_3)_2$	2.32		2.07	
$Cu(4Mepyr)_3(ClO_4)_2.2H_2O$	2.11		2.04	
$Cu(2NH_2pyr)Cl_2$	2.21		2.05	
$Cu(2NH_2pyr)_2Br_2$	2.11		2.00	
$Cu(2NH_2pyr)_2(NO_3)_2$	2.22		2.07	
$Cu(2NH_2pyr)_4(ClO_4)_2.4H_2O$	—	2.06	—	
$Cu(dmp)_2Cl_2$	2.21	2.11		2.06
$Cu(dmp)_2Br_2$	2.19		2.04	
$Cu(dmp)_{0.5}Cl_2$		2.14		
$Cu(tmp)_{0.5}Cl_2$	2.26	2.17		2.08
$Cu(tmp)_2Cl_2$	2.16		2.08	
$Cu(tmp)_2Br_2$	—	2.09	—	

CHAPTER 7.

Copper Complexes of Other Purine Bases.

An initial study of copper complexation by xanthine(xa), guanine (gu) and purine (pu) has been made and the results are reported here for comparison with the adenine system and to provide a basis for future investigation.

Purine

Guanine

(a) Xanthine; R = H
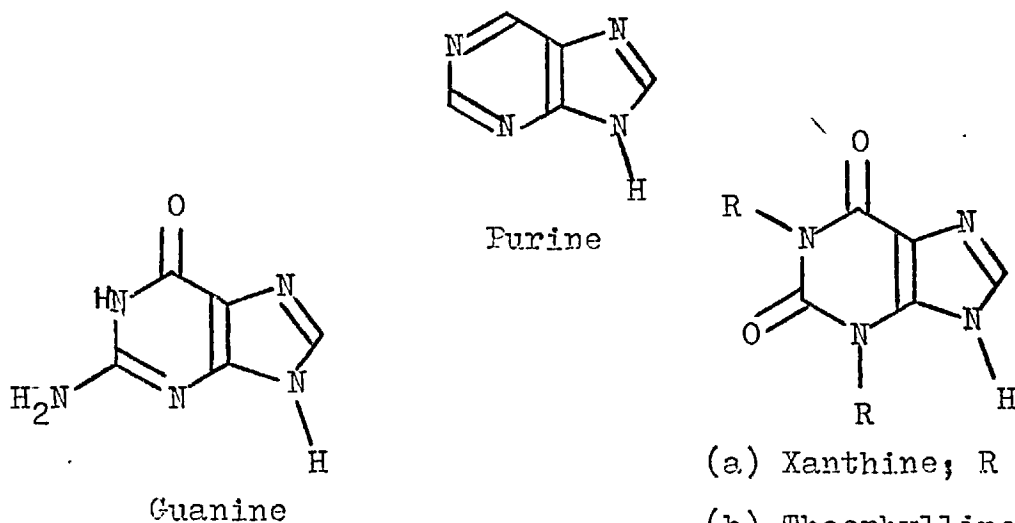
(b) Theophylline; R = Me

In agreement with Weiss' work[32] it has not proved possible to isolate copper inner complexes of these purine bases. An inner complex is formed by 1,3-dimethylxanthine (theophylline) but the donor sites are different from those employed by adenine since the molecule has a substituent at N(3).

Guanine forms compounds of the type $CuguX_2.nH_2O$ and $Cugu_2X_2.nH_2O$, whereas for xanthine, only 2:1 complexes appear to exist. (Weiss has previously established that complexes

of these stoichiometries are formed by these bases.)

Aqueous and ethanolic media have been used to prepare purine complexes: it was not possible to isolate 2:1 complexes from either. The compounds obtained from ethanol appear to be based on the stoichiometry $Cu_2pu_3X_2$ but do not give wholly acceptable analyses, while those obtained from water analyse as 1:1 compounds.

Xanthine and guanine are unsubstituted at $N(3)$ and $N(9)$ and there is the possibility that their 2:1 complexes bear a structural resemblance to $Cu(adH)_2X_2.nH_2O$. To examine this possibility the esr spectra of these compounds have been studied.

At room temperature, and at low instrument gain, $Cu(xa)_2Cl_2.3H_2O$ produces an intense two g value spectrum. At low temperature $(113^{\circ}K)$ $Cu(gu)_2SO_4.3H_2O$ gives the spectrum shown overleaf.

The signal is sufficiently broad to account for the total copper (II) content, but it is of relatively low intensity, and is obtained at much higher instrumental gain than that of $Cu(xa)_2Cl_2.3H_2O$. This may be construed as evidence for the existence of part of the copper (II) in a
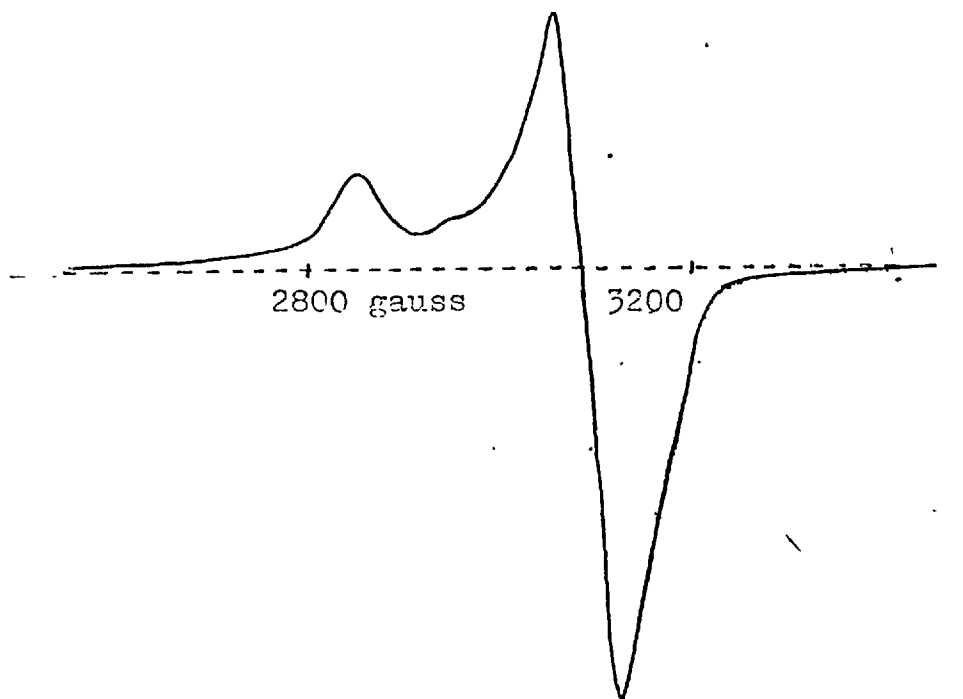
polynuclear form. Further increase of the signal level setting did not reveal high- or low-field components, which would arise from exchange interactions between cupric ions in a dimeric species.

The room temperature magnetic moments of the 2:1 compounds lie in the range usually observed for copper(II) complexes. This, together with the fact that they do not produce the characteristic dimer signal, suggests that neither xanthine nor guanine can couple copper atoms as does adenine in $Cu(adH)_2X_2 \cdot nH_2O$.

The presence of some purine bridges, in these compounds, cannot be discounted, since $Cu(adH)Cl_2$ and $Cu_3(C_5H_6N_5)_2Cl_8$. $4H_2O$, which involve halogen and adenine bridges, give anisotropic esr signals in the g=2 region, as observed for S=1/2 copper systems.

Recent esr studies have shown that 6-hydroxypurine (hypoxanthine) does form dimeric copper compounds[121]. It is unusual that the introduction of the 2-substituents (-OH and $-NH_2$) apparently leads to a breakdown of this unit. A study of molecular models indicates that there is unlikely to be a significant steric effect. In the case of xanthine, the increased acidity of the molecule is probably a determining factor, and, it is also possible that, for guanine, tautomerism disturbs the resonance system sufficiently to destabilise the dimer.

The inability of xanthine to form 1:1 complexes could be evidence of it's reluctance to use N(3) and N(9) as a bridging pair of atoms. Under conditions quite similar to those used in the preparation of $Cu(adH)Cl_2$, xanthine produces $Cu(xa)_2Cl_2.3H_2O$. The main electronic band of this compound is of comparable energy to those of polymeric halogen-bridged copper complexes. It is probable that the donor atom in this compound is N(9), or, N(3). The corresponding sulphate has a band system at lower energy. The position is compatible

with a tetrahedral geometry, but the intensity is not.

The compound, $Cu(theo)_2.4H_2O$, has a room temperature magnetic moment of 1.79 B.M. At low temperature ($113°K$), it produces an intense two g-value esr spectrum. A temperature range study of the bulk susceptibility shows that there is no magnetic exchange, an observation that lends support to chelate formation via $N(7)$ and $O(6)$. The co-ordination sphere may be completed by two of the available water molecules.

A similar compound is obtainable with nickel (II). This has the electronic spectrum of an octahedral compound with a small splitting of the v_1 band (Dt = +100).

There is a diversity of available donor sites in guanine and single crystal studies, on several representative compounds, are needed to identify which bonding atoms are usually employed. The only crystalline compound that has been isolated analyses as $Cu(guH)Cl_3.H_2O$. The main electronic band ($9510cm^{-1}$) is at substantially lower energy than that observed for the adenine trimer, or for the polymeric bridged compound $Cu(adH)Cl_2$.

When this compound was first studied, in 1968, it
appeared likely from the electronic spectrum that the
co-ordination geometry about the copper atom was either
tetrahedral or trigonal bypyramidal. However, the physical
evidence available could not distinguish between the two.
The room temperature esr spectrum showed only a broadened,
anisotropic signal in the g=2 region.

Quite recently, this problem has been resolved
by X-ray studies[±]. The compound is binuclear with chlorine
bridges and N(9) bonded guanine moities. Each copper atom
is penta-co-ordinate.
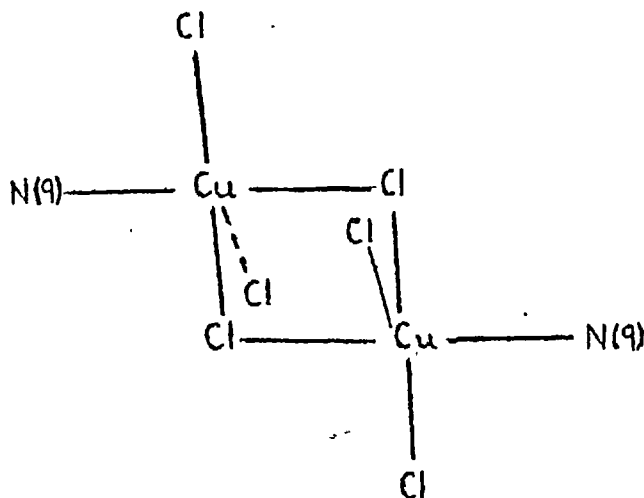
Vibrational Spectra (400-130cm^{-1}). Table 7.4.

The presence of strong ligand absorption across this region may obscure bands and certainly complicates interpretation. The inner complexes of theophylline produce closely similar absorption patterns; the band at ca.327cm^{-1} may be attributed to a metal-oxygen vibration and that at ca.250cm^{-1} to a metal-nitrogen mode.

There is a close agreement in band positions for the xanthine compounds $Cu(xa)_2Cl_2.3H_2O$ and $Cu(xa)_2SO_4.5H_2O$, although the relative intensity pattern is quite different. If the chloro complex has a halogen-bridged structure, then it is possible that the strong band at ca.295cm^{-1} is predominantly metal-halogen in origin while that at 255cm^{-1} is metal-nitrogen. (These energies are very like those observed for CuL_2Cl_2 (L = 4Mepyr, 5Mepyr)). The band at 188cm^{-1} could be the result of a metal-chlorine bending mode. No satisfactory explanation may be offered for the spectrum of $Cu(xa)_2SO_4.5H_2O$.

TABLE 7.1.

Electronic Spectra (cm^{-1}) and Magnetic Moments (B.M.).

$Cu(xa)_2Cl_2.3H_2O$	14080 26670	1.92
$Cu(xa)_2SO_4.5H_2O$	9760(sh) 12900	
$Cu_2(guH)_2Cl_6.2H_2O$	9510(vs) 27200(vs)	1.80
$Cu(gu)SO_4.6H_2O$	14710(s)	
$Cu(gu)_2SO_4.3H_2O$	14800(s) 25600(vs)	1.88
$Cu(gu)_2Cl_2.2H_2O$	ca.10530(sh) 13700	1.88
$Cu(theo)_2.4H_2O$	14930(s) 25640(vs)	1.73
$Ni(theo)_2.4H_2O$	ca.8770(sh) 9620 ca.14290(sh) 15380 ca.21740 25640	
$CupuSO_4.6H_2O$	ca.14810(vbr)	

TABLE 7.2.

ESR Parameters (X-band).

	$g_{//}$	$g_{\perp}$
Cu(theo)$_2$.4H$_2$O	2.31	2.08
Cu(xa)$_2$Cl$_2$.3H$_2$O	2.25	2.07
Cu(xa)$_2$SO$_4$.5H$_2$O	2.29	2.07

TABLE 7.3.

Temperature dependence of bulk susceptibility for Cu(theo)$_2$.
4H$_2$O.

Temp(^{O}K)	295	261	232	205	178	143	110
$10^6 \chi/Cu^{\text{\ae}}$	1276	1590	1683	1928	2220	2608	3228

Diamagnetic correction = 148 x 10^{-6} c.g.s.u.

æ Corrected for Nα = 60x10^{-6} c.g.s.u.

TABLE 7.4.

Vibrational Spectra $(400-130 cm^{-1})$.

xanthine	365(m) 350(s) ca.340(ms,sh)
guanine	ca.375(s) ca.358(s) 298(s) ca.215(m,br)
$Cu(xa)_2Cl_2.3H_2O$	360(m) 330(ms) 295(s) 255(mw) ca.248(w) 188(ms) 168(ms) 132(m)
$Cu(xa)_2SO_4.5H_2O$	367(m) 330(m) 292(m) 255(m) ca.250(m) ca.172(mw) 132(m)
$Cu(gu)SO_4.6H_2O$	395(ms) 350(m) 260(m) ca.240(m,sh)
$Cu(gu)_2SO_4.3H_2O$	382(s) 355(ms) 295(m) 255(m) 215(m,br)
$Cu(theo)_2.4H_2O$	327(ms) ca.300(m,br) ca.252(m,sh) 243(ms)
$Ni(theo)_2.4H_2O$	328(ms) 292(m,br) 255(m)
$Cu_2(guH)_2Cl_6.2H_2O$	345(m) 285(m)

CHAPTER 8.

EXPERIMENTAL.

Ligands. 5-methylpyrimidine was originally donated by Reilly Tar and Chemical Company., Inc. 4-methylpyrimidine (Newtown Maine), 2-aminopyrimidine, 4,6-dimethylpyrimidine (Emanuel), adenine, xanthine, guanine hydrochloride (KochLight) and theophylline hydrate (B.D.H.) were used without further purification.

Preparation of 2-methylpyrimidine.

The first stage of the three stage preparation was the condensation of acetamidine hydrochloride with ethyl malonate[122]. The amidine hydrochloride (94.5g.; 1mole) was added to a cooled solution of sodium ethoxide (69g.; 3gm atoms of sodium in 1 litre ethanol), and the precipitate of sodium chloride removed by filtration and ethanol washed. Ethyl malonate (160g.; 1mole) was added to the briskly stirred filtrate and the stoppered flask stored for 48 hours. During this time, a precipitate formed which was filtered off and dissolved in 1 litre of water. Addition of concentrated hydrochloric acid caused the formation of 2-methyl,4,6-dihydroxypyrimidine. Yield 82%. M.P.$>$ 360°C

The second stage was the conversion of the dihydroxy- to the dichloro- derivative. The conditions reported for this

preparation involve refluxing the dihydroxy compound with a
6:1 excess of phosphorus oxychloride until there is no
further evolution of hydrogen chloride (about 2 hours).
The excess oxychloride is then removed by distillation,
under reduced pressure, and a solid product obtained by
adding ice to the reaction flask. This procedure was
followed and a yellowish solid isolated and filtered from
solution.. Ether extraction, on the filtrate, and evaporation
of the ether layer gave a white, finely crystalline product.

A thin-layer chromatograph of these products and the
starting material was run using as solvent 25% acetone/
petroleum ether. (The dihydroxy compound was insoluble in
organic solvents and was boiled with water and applied to
the plate with an air blower to evaporate off the water).
This showed that the crystalline product consisted of two
components, the major, less polar one, being the dichloro-
derivative, and the minor, more polar one, the mono-chloro-
derivative. The yellowish material was a mixture of the
monochloropyrimidine and starting material.

The preparation was repeated using a refluxing time
of about 8 hours, and the reaction was carried to completion.
Yield 65%. M.P. 42-44°C.

The third stage was the dehalogenation of the 2-methyl-4,6-dihydroxypyrimidine[123]. The literature process involved reductive hydrogenation, in aqueous methanol, under reduced pressure. There was no hydrogen uptake and a thin layer chromatograph of the final reaction mixture showed the presence of more polar compounds than the original dichloro-compound. It would seem that the halo compound had been hydrolysed to hydroxy derivatives.

No suitable procedure could be found for this third stage.

Preparation of 2,4,6-trimethylpyrimidine [124].

11g. of acetylacetone was added to a solution of acetamidine hydrochloride (10g.) and potassium carbonate (28g.) in water (95cc). After a period of two weeks the compound separated out as long colourless, filiform needles (2.70g.). Yield 20%.

Isolation of 2,4,6-trimethylpyrimidine by-product.

The mother liquor was saturated with potassium carbonate and ether extracted to give a yellowish oil. 4g. were applied in ethereal solution to an alumina column

(grade V; 200gm.). Tri-methylpyrimidine was eluted by a 50% benzene/petroleum ether mixture and the by-product with di-ethyl ether. Evaporation yielded a white crystalline mass M.P. 31-6°C. The mass spectrum indicated a compound of molecular weight 99. Spectral data was consistent with the compound 2-amino-4-oxopent-2-ene. The nmr spectrum showed a broad, D_2O exchangeable NH group and the uv absorption at 300mμan-enone chromophore.

Analysis. C 57.4 (60.58) H 8.64 (9.15) N 13.89 (14.13).

Preparation of purine[125].

One of the preparative routes described by Bredereck was used. Aminoacetonitrile bisulphate (10.5g.) was neutralised and then refluxed with 120cc. formamide for about 3 hours. Fumes of ammonia were given off and there was some formation of a white crystalline material on the condenser walls. After refluxing, this was washed back into the flask with a small quantity of formamide. The mixture was allowed to cool until warm, and a small volume of water was added, together with 5.3g. of anhydrous sodium carbonate. The excess formamide was distilled off in vacuo using an oil pump and the dark coloured viscous residue boiled with two successive 100ml. portions of absolute alcohol. Any

insoluble material was removed by filtration, and washed
with small quantities of hot alcohol. The dark yellow
filtrate was distilled under reduced pressure (water pump)
and the residue heated in an open flask for about two hours
with 50cc. of 5N sodium hydroxide. During this procedure,
the volume of the solution was maintained by adding water.
The highest temperature reached was 120°C, although the
temperature quoted by Bredereck was 135°C. After cooling,
the solution was neutralised with 50cc. 4N sulphuric acid
and the precipitate filtered off and washed with successive
portions of hot water. The combined aqueous solutions were
extracted, continuously, from chloroform for three days.
There was some precipitation of a white crystalline material
around the inside of the vessel. At the end of this period,
the chloroform extract was distilled leaving a yellowish
solid. M.P. 204-8°C (literature for purine 216-7°C) Yield 40%.
A picrate was made by mixing saturated alcoholic solutions
of picric acid and the solid product. A dull-yellow precipitat
formed which was recrystallised from hot water as platelets.
M.P. 207-210°C (literature: purine picrate, yellow platelets
M.P. 208°C).

One of the critical stages in the preparation of
purine appeared to be the neutralisation of the amino-
acetonitrile bisulphate. The reaction was carried out
under nitrogen and dried methanol was used. The finely

powdered sulphate was covered with methanol, containing a
trace of phenolphthalein, and the stirred suspension was
treated with sodium methoxide over a period of one hour
until neutral to the indicator. A solution of 2.3g. of
sodium in 80cc. of methanol was added. The precipitated
sodium sulphate was filtered off and washed with methanol
(ca.20ml). The methanolic solution was then evaporated
down under reduced pressure (water pump) and the oily
liquid, aminoacetonitrile, used for the purine synthesis.
As a further precaution, the formamide used in the initial
condensation was dried over calcium oxide for 24 hours and
distilled under reduced pressure before use.

A mass spectrum of the product indicated that it was
about 90% purine with impurities of molecular weights 185 and
310. The nmr spectrum was run in deuterium oxide and showed
three aromatic protons: 2.00τ and 2.10τ (hydrogen doublet),
2.10τ (hydrogen singlet) and 2.20τ (hydrogen singlet).

Preparation of Complexes.

The calculated analysis figures are recorded in
brackets. All compounds were dried for a short period, in
vacuo, over phosphorus pentoxide unless otherwise stated.

Chapter 1: Complexes of 5-Methylpyrimidine.

$M(5Mepyr)Cl_2$ (M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II))

An ethanolic solution of the ligand (1mole) was added dropwise to a rapidly stirred solution of the appropriate metal chloride (1·1mole). In all cases there was rapid precipitation of the products. These were filtered off, washed with warm ethanol, and ether.

$Mn(5Mepyr)Cl_2$ white   C 27.34(27.25) H2.8(2.73) N12.98(12.70)

$Fe(5Mepyr)Cl_2$ yellow   C 27.24(27.18) H2.99(2.72)

$Co(5Mepyr)Cl_2$ violet   C 27.21(26.82) H2.90(2.70) N12.36(12.51)
Cl 31.3 (31.66)

$Ni(5Mepyr)Cl_2$ yellow-ish green C 26.88(26.80) H3.08(2.68) N12.60(12.50)

$Cu(5Mepyr)Cl_2$ light green   Cu 27.5(27.8) Cl30.9(31.1)

$M(5Mepyr)Br_2$ (M = Mn(II), Co(II), Cu(II))

Similar preparation to that of the chlorides. Slower precipitation using manganese salt.

$Mn(5Mepyr)Br_2$ yellowish white   Br 51.49(51.8)

$Co(5Mepyr)Br_2$ violet   Br 51.2(51.0)

$Cu(5Mepyr)Br_2$ greenish-yellow   C 19.32(18.91) H 2.13(1.89) Br50.0(50.4)

$Ni(5Mepyr)Br_2$.

A small quantity of 2,2'-dimethyoxypropane was added to an ethanolic solution containing a 1:1 mole ratio of ligand to hydrated metal bromide. On warming, a yellow precipitate began to form. This was filtered off and ethanol washed.

$Ni(5Mepyr)Br_2$ yellow Ni 18.5(18.75) Br 50.7(51.0)

$Ni(5Mepyr)(NO_3)_2.3H_2O$

Equimolar quantities of hydrated nickel nitrate and the ligand were dissolved in ethanol and ether added until a faint cloudiness developed. A pale blue solid formed on standing.

$Ni(5Mepyr)(NO_3)_2.3H_2O$ C 17.89(18.1) H 3.64(3.62) N 16.74(17.0) NO_3 37.35(37.5)

$Cu(5Mepyr)(NO_2)_2$.

1.25g. of hydrated copper sulphate were dissolved in a minimum quantity of water and 0.85g. of sodium nitrite were added. The mixture was diluted to twice the volume with methanol and was filtered into an ethanolic solution of 5-methylpyrimidine (0.30g.). The dark green filtrate was stored at $0^{\circ}C$ for 24 hours. A greenish black, crystalline

solid formed.

Cu(5Mepyr)(NO$_2$)$_2$ C 23.89(24.04) H 2.45(2.40) N 22.38(22.43)

Cu(5Mepyr)(NO$_3$)$_2$.

This compound formed as dark blue crystals from an ethanolic solution containing a 1:1 mole ratio of ligand to metal salt.

Cu(5Mepyr)(NO$_3$)$_2$ Cu 22.2(22.58) NO$_3$ 43.7(44.1).

Zn(5Mepyr)X$_2$ (X = Cl,Br,I).

White crystalline products were obtained on mixing warm ethanolic solutions of ligand (1mole) and the appropriate zinc salt (1mole).

Zn(5Mepyr)Cl$_2$ Cl 30.4(30.8)

Zn(5Mepyr)Br$_2$ Br 49.6(50.0)

Zn(5Mepyr)I$_2$ I 61.1(61.4)

Co(5Mepyr)$_2$(NCS)$_2$.

Concentrated ethanolic solutions of the ligand (2moles) and cobalt salt (1mole) were mixed. There was rapid precipitation of a violet-pink solid. This was filtered off and when dried was lilac in colour.

Co(5Mepyr)$_2$(NCS)$_2$ C 39.82(39.7) H 3.8(3.3) N 22.47(23.1)

$Co(5Mepyr)_2(NO_3)_2$.

This precipitated as a dark pink solid when warm concentrated ethanolic solutions of the cobalt salt (1mole) and ligand (2moles) were mixed. The compound was claret coloured when dried.

$Co(5Mepyr)_2(NO_3)_2$ C 32.0(32.4) H 3.3(3.24)

$Co(5Mepyr)_2I_2$.

Cobalt iodide was dissolved in warm ethanol and filtered into a concentrated solution of the ligand. 2,2'-dimethoxypropane was added to the dark green filtrate. After a few hours, addition of ether produced a dark green product.

$Co(5Mepyr)_2I_2$ I 50.4(50.66).

The same material was obtained when $Co(5Mepyr)_4I_2.4H_2O$ was left in vacuo over P_2O_5 for a period of days.

$Cu(5Mepyr)_2Cl_2$

Slow dropwise addition of a dilute solution of hydrated copper chloride (1mole), in ethanol, to a rapidly stirred solution of 5-methylpyrimidine (6moles) produced a light green, bulky precipitate. This was filtered off and washed with warm ethanol.

$Cu(5Mepyr)_2Cl_2$ Cu 19.0(19,5) Cl 22.1(22.0).

$\underline{Cu(5Mepyr)_2Br_2.}$

A similar preparative route to that of the chloride using a 3:1 mole ratio of pyrimidine to copper salt.

$Cu(5Mepyr)_2Br_2$ C 29.09(29.2) H 3.07(2.9) N 13.33(13.6)

Br 38.5(38.9).

$\underline{Cu(5Mepyr)_2(NO_2)_2.}$

Copper nitrite is made 'in situ' as described for $Cu(5Mepyr)(NO_2)_2$ and is added to a solution of 5-methylpyrim-idine (0.94g.) in ethanol. Storage at 0^oC for 24 hours yielded translucent green platelets. This preparative method is adapted from that used by King to produce $Cupy_2(NO_2)_2$[126].

$Cu(5Mepyr)_2(NO_2)_2$ C 34.66(34.90) H 3.56(3.49) N 24.26(24.5).

$\underline{Cu(5Mepyr)_2(NO_3)_2.}$

This was prepared as for the 1:1 complex but using a 2:1 mole ratio of ligand to metal.

$Cu(5Mepyr)_2(NO_3)_2$ Cu 16.5(16.91) NO_3 32.4(32.95).

$\underline{Zn(5Mepyr)_2X_2.}$

Similar preparation to that of the 1:1 compounds using a 2:1 mole ratio of ligand to metal.

$Zn(5Mepyr)_2Cl_2$ Cl 21.4(21.85).

$Zn(5Mepyr)_2Br_2$ Br 38.2(38.61).

$Zn(5Mepyr)_2I_2$ I 49.5(50.1)

$M(5Mepyr)_2Br_2.2H_2O$ (M = Co(II), Ni(II)).
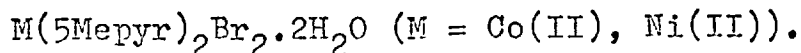
A dilute solution of the hydrated metal bromide (1 mole) in ethanol was added slowly to a briskly stirred ethanolic solution of the ligand (3.3moles). Precipitation was rapid giving bulky materials which were filtered off and washed with successive portions of warm ethanol.

$Co(5Mepyr)_2Br_2.2H_2O$ mauve C 27.22(27.1) H 3.41(3.61) N 12.61
(12.64)

$Ni(5Mepyr)_2Br_2.2H_2O$ pale C 27.67(27.10) H 3.55(3.61) N 12.67
green   (12.65)

$Co(5Mepyr)_3(ClO_4)_2.H_2O$.
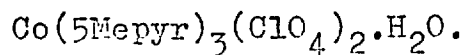
A solution containing a 2:1 mole ratio of ligand to metal was evaporated to small volume and allowed to. cool. An oil formed which was triturated with ether to give a pink solid. This was filtered off and ether washed. After drying, the compound was deep pink in colour..

$Co(5Mepyr)_3(ClO_4)_2.H_2O$ C 32.51(32.20) H 4.35(3.58) N 14.85
(15.05).
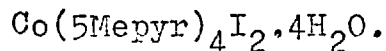
$Co(5Mepyr)_4I_2.4H_2O$.

Addition of ether to a concentrated solution of ligand (4mole) and cobalt iodide (1mole) in ethanol caused the precipitation of a pink solid.After filtering from solution, the product was washed with ether.

$Co(5Mepyr)_4I_2.4H_2O$ C 31.1(31.6) H 4.09(4.2) N 14.6(14.7)
I 34.0(33.4).

Cu(5Mepyr)$_4$(ClO$_4$)$_2$.2H$_2$O.
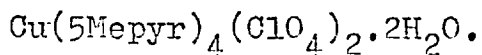
Obtained as royal-blue needles from a solution of alcohol containing a four-fold ligand excess.

Cu(5Mepyr)$_4$(ClO$_4$)$_2$.2H$_2$O   C 35.91(35.60)   H 4.26(4.16)   N 16.50
(16.65)

Cu(CH$_3$COO)$_2$(5Mepyr)$_{0.5}$.
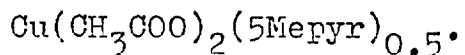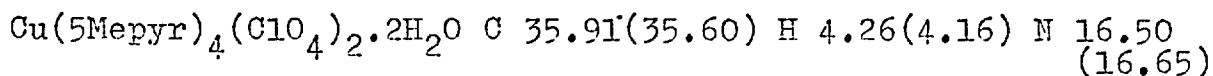
Cupric acetate (1mole) was dissolved in warm ethanol and filtered into a solution of 5-methylpyrimidine(1mole). An emerald green solid precipitated on cooling. This was filtered off and washed with successive portions of warm ethanol.

Cu(CH$_3$COO)$_2$(5Mepyr)$_{0.5}$ C 34.50(34.12)   H 4.21(3.94)   N 5.95(6.12).

Cu(HCOO)$_2$(5Mepyr).
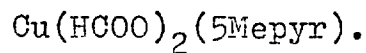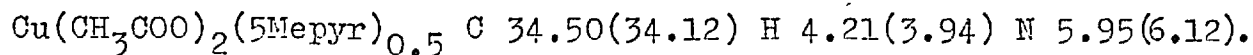
Prepared as for the acetate adduct using a 1:1 mole ratio and methanol as solvent.

Cu(HCOO)$_2$(5Mepyr)   C 34.47(33.92)   H 3.36(4.07)   N 11.45(11.31).
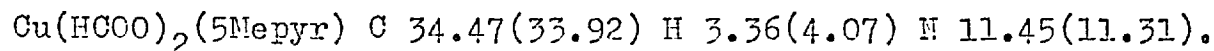
Chapter 2: Complexes of 4-Methylpyrimidine.

M(4Mepyr)X$_2$ (M = Mn(II), X = Cl,Br; M = Ni(II), X = Cl).
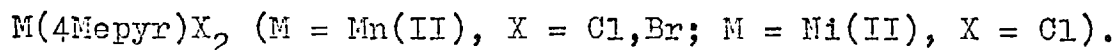
Prepared as described for M(5Mepyr)X$_2$.

Mn(4Mepyr)Cl$_2$ white   C 26.73(27.25)   H 3.66(2.73)   N 12.67(12.70)

Mn(4Mepyr)Br$_2$ pinkish   C 19.03(19.42)   H 2.01(1.94)   Br 51.4(51.72
white

Ni(4Mepyr)Cl$_2$ pale   Ni 25.9(26.24)   Cl 31.25(31.73).
green
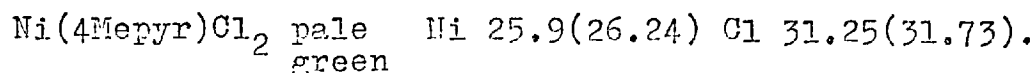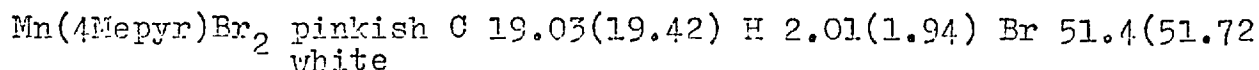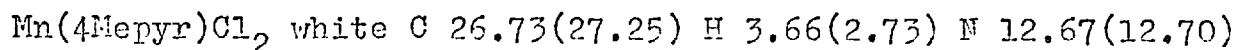
Co(4Mepyr)Br$_2$.

Evaporation of an ethanolic/2,2'-dimethoxypropane solution of ligand and hydrated cobalt bromide (in a mole ratio of 2:1) followed by the addition of ether until faint cloudiness developed gave a bluish product. After ether-washing and drying, the compound was bluish green in colour.

Co(4Mepyr)Br$_2$ C 18.5(19.18) H 2.44(1.92) N 8.13(8.63).

Cu(4Mepyr)X$_2$ (X = Cl,Br).

Slow addition of a dilute solution of ligand (1mole) to a rapidly stirred solution of metal salt (2mole) caused the precipitation of bulky, green powders. After filtration, the products were washed with successive portions of warm alcohol.

Cu(4Mepyr)Cl$_2$ Cu 28.4(27.8) Cl 30.6(31.06)

Cu(4Mepyr)Br$_2$ Cu 19.55(20.02) Br 49.8(50.32).

Zn(4Mepyr)X$_2$ (X = Cl,Br).

The compounds precipitate from ethanolic solutions containing a 1:1 mole ratio of ligand to metal.

Zn(4Mepyr)Cl$_2$ Cl 30.36(30.8)

Zn(4Mepyr)Br$_2$ Br 49.63(50.0).

$\underline{M(4\text{Mepyr})_2X_2}$. (M = Co(II), X = Cl; M = Ni(II), X = Cl,Br;

M = Cu(II), X = Cl,Br).

Prepared by adding an ethanolic solution of the appropriate metal salt (1mole) to a stirred solution of the ligand (2mole). The products precipitated rapidly and were filtered off and washed with ethanol. The same compounds were obtainable using an increased proportion of ligand, i.e. a 4:1 ligand to metal ratio.

$Co(4\text{Mepyr})_2Cl_2$ violet Cl 22.0(22.33)   H 4.21(3.77)
N 17.45(17.61)

$Ni(4\text{Mepyr})_2Cl_2$ green Ni 18.3(18.46) Cl 21.8(22.33)

$Ni(4\text{Mepyr})_2Br_2$ C 29.17(29.51) H 3.39(2.95) N 13.78(13.74)

$Cu(4\text{Mepyr})_2Cl_2$ pale blue Cu 20.2(19.69) Cl 21.55(22.0)

$Cu(4\text{Mepyr})_2Br_2$ yellowish-green Cu 15.2(15.45) Br 38.50(38.84).

$\underline{Co(4\text{Mepyr})_2Br_2 \cdot 2H_2O}$.

Ethanolic solutions of hydrated cobalt bromide (1mole) and ligand (2moles) were mixed. On evaporation to small volume, and cooling, violet crystals formed. These were filtered off and ether washed.

$Co(4\text{Mepyr})_2Br_2 \cdot 2H_2O$ C 27.13(27.1) H 3.64(3.61) N 12.37(12.64)
Br 36.0(36.08)

$\underline{Co(4\text{Mepyr})_2X_2}$ (X = NO_3, NCS).

Obtained as crystalline products from concentrated

alcoholic solutions containing a 2:1 mole ratio of ligand
to cobalt salt.

Co(4Mepyr)$_2$(NO$_3$)$_2$ C 32.01(32.27) H 3.23(3.91) N 21.97(22.57)

Co(4Mepyr)$_2$(NCS)$_2$.2H$_2$O C 36.53(36.08) H 3.73(4.01) N 21.54(21.05)

Co(4Mepyr)$_2$I$_2$.

An equimolar mixture of ether and 2,2^1-dimethoxypropane
was added to a concentrated ethanolic solution of ligand
and cobalt iodide (2:1 mole ratio). A dark green solid was
slowly precipitated. This was filtered off and ether-washed.

Co(4Mepyr)$_2$I$_2$ I 50.32(50.66) H 2.74(2.40) N 10.54(11.18).

Co(4Mepyr)$_2$(ClO$_4$)$_2$.4H$_2$O.

Ethanolic solutions of cobalt perchlorate (1mole) and
4-methylpyrimidine (2moles) were mixed. The solution was
evaporated to small volume and ether added until a cloudiness
developed. The orange crystals isolated were washed with
ether.

Co(4Mepyr)$_2$(ClO$_4$)$_2$.4H$_2$O C 22.72(23.17) H 3.87(3.85) N 10.43
(10.81).

Ni(4Mepyr)$_2$I$_2$.

Nickel iodide (1mole) was dissolved in ethanol and
filtered into a solution of the ligand (2mole). Careful

evaporation gave an oil which was triturated with 2,2'-dimethoxypropane and ether to give a yellow solid. This was filtered off and ether-washed.

Ni(4Mepyr)$_2$I$_2$ I 50.25(50.58) H 2.59(2.39) N 11.19(11.05).

Cu(4Mepyr)$_3$(ClO$_4$)$_2$.2H$_2$O.
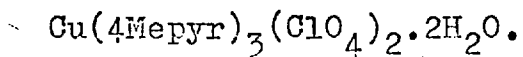
A solution containing a 4:1 mole ratio of pyrimidine to copper salt was evaporated to small volume. The oil obtained was triturated with 1,2 dimethoxyethane and ether giving a yellowish-green product. On filtering, this was washed with ether.

Cu(4Mepyr)$_3$(ClO$_4$)$_2$.2H$_2$O C 31.22(31.0) H 3.41(3.79) N 14.85
(14.46).

Cu(CH$_3$COO)$_2$(4Mepyr)$_{0.5}$.
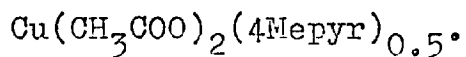
Prepared from a 1:1 mole ratio of pyrimidine to copper acetate as described for the corresponding 5-methyl derivative.

Cu(CH$_3$COO)$_2$(4Mepyr)$_{0.5}$ emerald   C 33.83(34.12) H 3.93(3.94)
green   N 6.16(6.12)
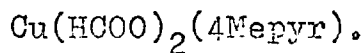
Cu(HCOO)$_2$(4Mepyr).

Similar preparation to that of the 5-methyl compound.

Cu(HCOO)$_2$(4Mepyr) C 33.97(33.92) H 3.23(4.07) N 11.15(11.31).

Impure Compounds.

Preparations involving Fe(II), nickel nitrate and cupric nitrate gave oils which were difficult to solidify, and materials thus prepared gave unacceptable analyses. No copper nitrite compound was isolable using the preparative method described for the 5-methyl complexes.

Chapter 3: 2-aminopyrimidine complexes.

$Co(2NH_2pyr)_2X_2$ (X = Cl,Br).

A warm ethanolic solution of hydrated cobalt halide (1mole) was added to a warm solution of ligand (2mole) in ethanol. The products formed rapidly as fine, dark-blue needles and were filtered off and washed with a small volume of ether.

$Co(2NH_2pyr)_2Cl_2$ Cl 21.75(22.2)
$Co(2NH_2pyr)_2Br_2$ C 23.74(23.48) H 2.27(2.45)

$Co(2NH_2pyr)_2I_2$.

Using concentrated ethanolic solutions and a 2:1 mole ratio of ligand to cobalt iodide, a fine, green, crystalline material was prepared. The product was filtered from solution and ether washed.

$Co(2NH_2pyr)_2I_2$ C 19.22(19.1) H 2.03(1.99) N 16.63(16.71).

$Co(2NH_2pyr)_2(NO_3)_2.$
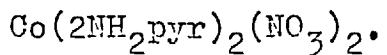
A solution containing a 2:1 mole ratio of ligand to cobalt nitrate was evaporated to small volume. Purplixh pink crystals formed after a few hours. These were filtered off and washed with ether.

$Co(2NH_2pyr)_2(NO_3)_2$ C 25.56(25.74) H 3.01(2.68) N 30.0(30.04).

$Co(2NH_2pyr)_2(NCS)_2.3H_2O.$
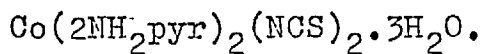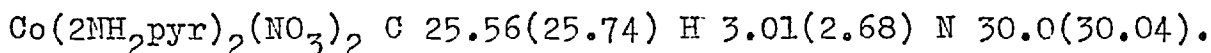
The product was obtained as a pink solid using the same method as that for the nitrate.

$Co(2NH_2pyr)_2(NCS)_2.3H_2O$ C 27.99(28.63) H 4.22(3.82) N 26.5 (26.73)
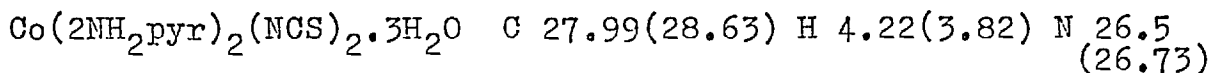
On drying, the dark blue compound $Co(2NH_2pyr)_2(NCS)_2$ was obtained.

$Co(2NH_2pyr)_2(NCS)_2$ C 32.5(32.85) H 2.99(2.79)

$Ni(2NH_2pyr)_2Br_2.3H_2O.$
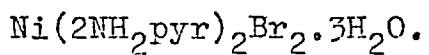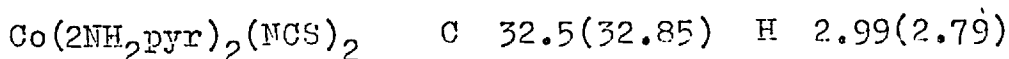
A concentrated solution of pyrimidine and hydrated nickel bromide, in 2:1 mole ratio, produced bright green crystals after about 24 hours.

$Ni(2NH_2pyr)_2Br_2.3H_2O$ C 20.47(20.77) H 3.78(3.46) N 17.88(18.18)
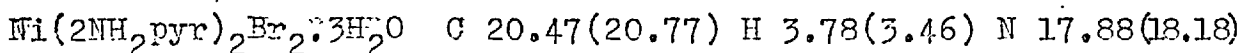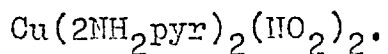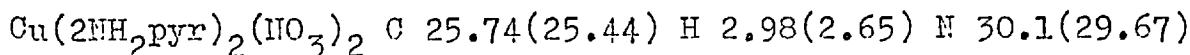
A lime-green chloro complex was similarly prepared.

$Ni(2NH_2pyr)_2Cl_2.2H_2O$ Ni 18.6(18.36) Cl 22.5(22.2)
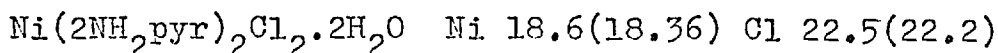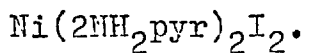
$Ni(2NH_2pyr)_2I_2$.

Preparation as for $Co(2NH_2pyr)_2I_2$. The compound was obtained as a dark green powder.

$Ni(2NH_2pyr)_2I_2$ Ni 11.4(11.68) I 50.2(50.52).

$Ni(2NH_2pyr)_2(NO_3)_2.H_2O$.
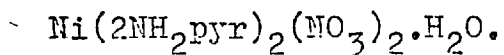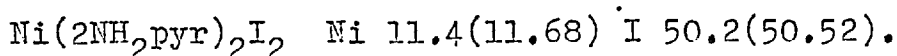
Similar preparation to that of the cobalt nitrate complex. The compound separated out as emerald-green crystals.

$Ni(2NH_2pyr)_2(NO_3)_2.H_2O$ C 24.84(24.57) H 3.27(3.07) N 29.12 (28.66)

$Cu(2NH_2pyr)_2X_2$ (X = Br,NO_3).
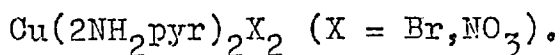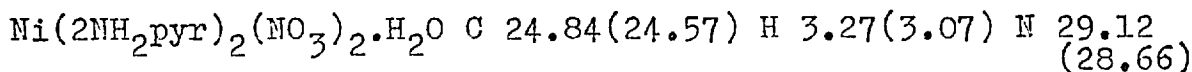
Addition of an ethanolic solution of the respective hydrated copper salt (1mole) to a solution of the ligand (2mole) causes rapid precipitation of the solid complex which was filtered off and washed with ether. The bromide is apple-green and the nitrate is dark bluish black.

$Cu(2NH_2pyr)_2Br_2$ C 23.6(23.23) H 2.64(2.42)

$Cu(2NH_2pyr)_2(NO_3)_2$ C 25.74(25.44) H 2.98(2.65) N 30.1(29.67)

$Cu(2NH_2pyr)_2(NO_2)_2$.
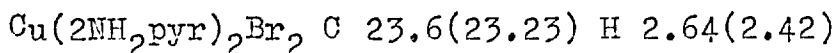
The compound was isolated as a dark-brown finely crystalline material using the preparative method of King[126].

$Cu(2NH_2pyr)_2(NO_2)_2$ C 27.76(27.8) H 3.00(2.90) N 32.82(32.42).
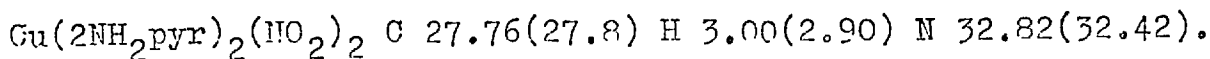
$M(2NH_2pyr)Cl_2$ (M = Co, Ni, Cu).

Dropwise addition of an ethanolic solution of the ligand (1mole) to a rapidly stirred solution of the hydrated metal salt (1.5mole) caused rapid precipitation of the products. These were filtered off, washed with warm ethanol and then ether.

$Co(2NH_2pyr)Cl_2$ violet Cl 31.2(31.58) C 21.4(21.4) H 2.92(2.22) N 18.37(18.65)

$Ni(2NH_2pyr)Cl_2$ pale yellow Ni25.8(26.13) Cl 31.2(31.6)

$Cu(2NH_2pyr)Cl_2$ green Cu 27.3(27.67) Cl 30.5(30.94).

$Zn(2NH_2pyr)_2X_2$ (X = Cl, Br, I, NO_3).

The compounds crystallised from a solution containing a 2:1 mole ratio of ligand to metal salt. The chloride and bromide gave white needle-like crystals and the iodide, white platelets. The crystals were separated by filtration and washed with ether.

$Zn(2NH_2pyr)_2Cl_2$ Cl 21.47(21.75)
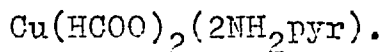
$Zn(2NH_2pyr)_2Br_2$ Br 38.2(38.5)

$Zn(2NH_2pyr)_2I_2$ I 49.47(49.83)

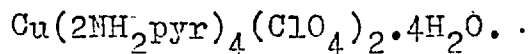$Zn(2NH_2pyr)_2(NO_3)_2.H_2O$ C 23.79(24.2) H 3.22(3.02) N 28.18(28.2)

$Cu(CH_3COO)_2(2NH_2pyr)_{0.5}$

Prepared as for the corresponding 5-methyl compounds.

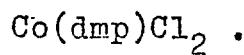$Cu(CH_3COO)_2(2NH_2pyr)_{0.5}$ C 32.29(31.4) H 4.08(3.72) N 9.94(9.2)

$Cu(HCOO)_2(2NH_2pyr)$.

Prepared as for the corresponding 5-methyl compound.
$Cu(HCOO)_2(2NH_2pyr)$ C 28.2(28.97) H 2.50(2.24).

$Cu(2NH_2pyr)_4(ClO_4)_2.4H_2O$.

Similar preparation to that of the analogous 5-methyl
compound. $Cu(2NH_2pyr)_4(ClO_4)_2.4H_2O$ C 27.46(26.9) H 3.37(3.92)
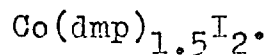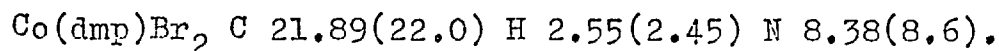N 22.06(23.5)

Chapter 4: 4,6-dimethylpyrimidine complexes.

$Co(dmp)Cl_2$.

An ethanolic solution containing a 2:1 mole ratio of
ligand to hydrated cobalt chloride was evaporated to small
volume. 2,2'-dimethoxypropane was added. Dark blue crystals
formed after standing ca.12hours and were filtered off and
washed with small quantity of ether. The same compound is
obtained using a 4:1 ligand to metal salt ratio.
$Co(dmp)Cl_2$ C 31.07(30.2) H 3.87(3.36) N 12.21(11.8).

$Co(dmp)Br_2$.
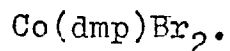
Using the same procedure as for the chloro compound,
a dark-blue oil was obtained which was triturated using a
1:1 mixture of 2,2'-dimethoxypropane and ether. The dark
blue powder was hygroscopic.
$Co(dmp)Br_2$ C 21.89(22.0) H 2.55(2.45) N 8.38(8.6).

$Co(dmp)_{1.5}I_2$.

A 2:1 mole ratio of pyrimidine to metal salt in

ethanolic solution was concentrated to half-volume. A 1:1 mixture of ether and 2,2'-dimethoxypropane was added. After a few hours, further addition of ether produced a dark green solid. This was filtered off and ether washed. The compound can be obtained in a crystalline form if left to precipitate over a period of days, 2,2'-dimethoxypropane being added at intervals. The crystalline material is less susceptible to moisture than is the powdered form.

$Co(dmp)_{1.5}I_2$ C 22.74(22.73) H 2.55(2.93) N 8,85(8,67).

$Co(dmp)_2(NO_3)_2$.
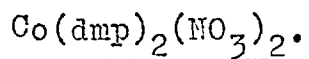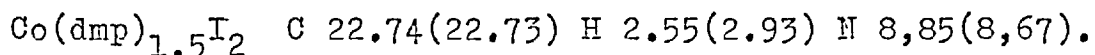
An ethanolic solution containing a 2:1 mole ratio of ligand to hydrated cobalt nitrate was evaporated to small bulk and allowed to stand. After a few days orange needles formed, which were filtered off and ether washed.

$Co(dmp)_2(NO_3)_2.6H_2O$ C 27.94(28.4) H 4.90(5.5) N 16.6(16.5)
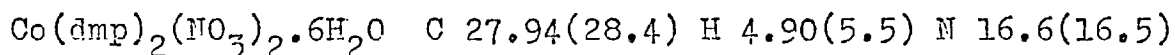
When this compound was stored over calcium oxide for several days, a homogeneous purple powder was produced.

$Co(dmp)_2(NO_3)_2$ NO_3 30.7(31.2).
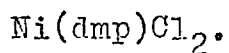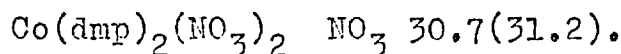
$Ni(dmp)Cl_2$.

Similar preparation to that of the 1:1 cobalt chloride complex. The same compound was obtained whether a 2:1 or a 4:1 mole ratio of ligand to metal salt is employed; it

precipitated as a greenish-yellow powder.

Ni(dmp)Cl$_2$ Ni 24.3(24.7)   Cl 30.2(29.87)

Ni(dmp)Br$_2$.

This was prepared as for Co(dmp)Br$_2$. The complex was obtained as a green powder, which lightened in colour as it was being filtered from the solution. When dried over calcium oxide, it assumed a dark blue colour. The compound is extremely hygroscopic, and rapidly turns green on exposure to the air.

Ni(dmp)Br$_2$ Ni 17.5(17.98) Br 48.3(48.94)

C 21.08(22.0) H 4.58(2.45) N 8.56(7.85).

Ni(dmp)$_2$I$_2$.

The complex was prepared as iridescent, green crystals by the procedure employed for Co(dmp)$_{1.5}$I$_2$.

Ni(dmp)$_2$I$_2$ Ni 10.5(11.1) I 47.2(48.04)

Cu(dmp)$_2$X$_2$ (X = Cl,Br).

A concentrated ethanolic solution of the hydrated metal salt (1mole) was added to an ethanolic solution of the ligand (2moles). There was rapid precipitation of purple, needle-like crystals in the case of the chloride and a dark brown powder in that of the bromide. The products were filtered and washed with ether.

$Cu(dmp)_2Cl_2$ Cu 17.9(18.13) Cl 20.0(20.26)

$Cu(dmp)_2Br_2$ Cu 14.1(14.43) Br 36.8(36.37).

$\underline{Cu(CH_3COO)_2(dmp)_{0.5}}.$

Similar preparation to that of the corresponding 5-methyl compound.

$Cu(CH_3COO)_2(dmp)_{0.5}$ C 35.73(35.8) H 4.21(4.25) N 5.68(5.95)

Complexes of 2,4,6-trimethylpyrimidine.

$\underline{Cu(tmp)_2Cl_2}.$

This compound crystallised as violet neeldes from a methanolic solution containing a 2:1 mole ratio of ligand to metal.

$Cu(tmp)_2Cl_2$ C 44.02(44.5) H 5.23(5.3) N 14.72(14.8)

$\underline{Cu(tmp)_2Br_2}.$

This compound was obtained as a dark green crystalline material from an ethanolic solution containing the ligand (2mole) and hydrated cupric bromide (1mole).

$Cu(tmp)_2Br_2$ C 36.12(35.9) H 4.46(4.28) N 12.10(11.95).

$\underline{Cu(tmp)_{0.5}Cl_2}.$

An ethanolic solution of ligand (1mole) and metal salt (1mole) was evaporated to small volume. Pale green needles

formed on standing.

$Cu(tmp)_{0.5}Cl_2$ C 21.95(21.6) H 3.10(2.57) N 7.13(7.18).

$\underline{Co(tmp)Cl_2.4H_2O.}$

The ligand (1mole) and metal salt (1mole) were
separately dissolved in ethanol and the two solutions mixed.
After evaporation to small volume, and cooling, ether was
added to precipitate the dark green product.

$Co(tmp)Cl_2.4H_2O$ C 25.3(26.0) H 4.23(5.5) N 8.31(8.66).

Chapter 5:   Adenine Complexes.

$\underline{Cu(ad)_2.4H_2O.}$[31]

0.676g.   (5mmol) of adenine were dissolved in 50ml.
0.1N sodium hydroxide. 22ml. of a 0.1M cupric sulphate solution
2.2mmol) were added slowly with shaking. On standing for
24 hours deep violet crystals separated out. These were
filtered off, washed with water and air-dried.

$Cu(ad)_2.4H_2O$ C 29.75(29.72) H 3.21(3.99) N 34.73(34.67)
            O 15.97(15.85) Cu 15.6(15.74).

$\underline{Cu(adH)_2Cl_2.3H_2O.}$

1.35g. (10mmol) of adenine were dissolved in 50ml. of
water acidified with 1ml. of concentrated hydrochloric acid.
0.85g. (5mmol) of hydrated cupric chloride in 10ml. of water
were added. The pH of the solution was raised by dropwise

addition of 2N sodium hydroxide until a colour change was apparent (pH ca.4). The dark blue/green solution was left to stand. After ca. 24 hours dark blue/green platelets had formed. These were filtered off and washed with water and methanol. The compound was air-dried.

$Cu(adH)_2Cl_2.3H_2O$ C 26.19(26.18) H 2.91(3.49) N 30.54(30.53)

Cl 14.74(15.48).

This compound was originally prepared by Weiss from adenine hydrochloride and was formulated with 1.5 water molecules.

$Cu(adH)_2Br_2.2H_2O.$

1.35g. (10mmol) of adenine were dissolved in 75ml. of hot water and 1.12g. (5mmol) of hydrated cupric bromide in 30ml. of water were added. On standing, the blue-green solution yielded platelets of the same colour. These were water washed and air-dried.

$Cu(adH)_2Br_2.2H_2O$ C 22.39(22.66) H 2.24(2.64) N 27.25(26.44).

$Cu(adH)_2SO_4.4H_2O.$

A solution of 1.25g. (5mmol) of cupric sulphate in 10ml. of water was added to a solution of 1.35g. (10mmol) of adenine in 50ml. of water acidified with 1ml. of concentrated sulphuric acid. N Sodium hydroxide was added dropwise with

shaking until the precipitate just redissolves on shaking.
On standing a dark blue compound separated out of the blue
green solution. This was washed (water, methanol) and dried
in air.

$Cu(adH)_2 SO_4.4H_2O$ C 24.21(23.93) H 2.88(3.59) N 27.66(27.92)

O 26.33(25.53).

This compound was originally formulated with one water
molecule.

$Cu(adH)_2(NO_3)_2$.

This was isolated as a blue-green microcrystalline
material using a ligand to metal mole ratio of 2:1.5 and a
preparative method similar to that described for the sulphate.

$Cu(adH)_2(NO_3)_2$ C 25.8(26.23) H 2.46(2.19) N 36.1(36.72).

$Cu(adH)Cl_2$. [31]

1.8g. (10mmol) of adenine hydrochloride were dissolved
in 25ml. of 0.1N hydrochloric acid. A solution containing
8g. (4.7mmol) of hydrated cupric chloride in 18ml. of water
were added. The mixture was boiled for about 10 minutes to
give a dull yellow precipitate. This was filtered off and
washed with water.

$Cu(adH)Cl_2$ C 22.56(22.26) H 1.95(1.86) N 26.24(25.97) Cu 24.2

(23.58)

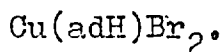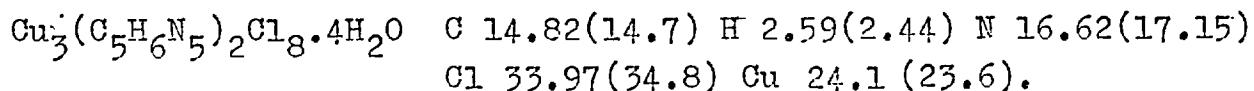$\underline{Cu_3(C_5H_6N_5)_2Cl_8.4H_2O.}$
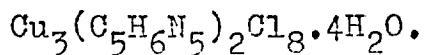
Obtained as lime green crystals from an acidic solution (ca.2M hydrochloric acid) containing a 5:1 mole ratio of adenine to hydrated cupric chloride.

$Cu_3(C_5H_6N_5)_2Cl_8.4H_2O$ C 14.82(14.7) H 2.59(2.44) N 16.62(17.15)
         Cl 33.97(34.8) Cu 24.1 (23.6).

$\underline{Cu(adH)Br_2.}$

1.35g. (10mmol) of adenine were dissolved in 25ml. of acidulated water and 4.5g. (40mmol) of hydrated cupric bromide in 20ml. of water were added. The mixture was boiled (ca.15 minutes) to give the red-brown product.

$Cu(adH)Br_2$ C 16.73(16.74) H 1.61(1.39) N 19.47(19.53).

$\underline{Ni(adH)_2SO_4 4H_2O.}$
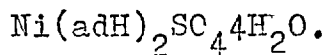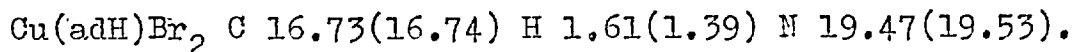
Adenine (2mole) was dissolved in the minimum quantity of hot water and an aqueous solution of the hydrated metal salt (1mole) was added. The pH was raised until the flocculent precipitate just dissolved on shaking. On standing (ca. 12 hours) a pale blue product precipitated out.

$Ni(adH)_2SO_4.4H_2O$ C 23.46(24.15) H 3.82(3.62) N 27.35(28.2)
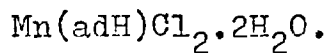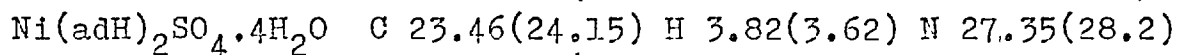
$\underline{Mn(adH)Cl_2.2H_2O.}$

An aqueous solution, containing a 2:1 mole ratio of ligand to metal, (pH ca.4) was evaporated to low volume.

Deep pink needles formed rapidly on cooling.

Mn(adH)Cl$_2$.2H$_2$O C 19.8(20.2) H 3.05(3.03) N 23.57(23.6).

Co(adH)Cl$_2$.

This preparation was carried out in an atmosphere of nitrogen. Adenine (2mole) was dissolved in M hydrochloric acid. An aqueous solution of cobalt chloride was added, and M sodium hydroxide was dripped into the mixture until a colour change was apparent (pH ca.6). On standing ca. 12 hours the deep violet solution yielded crystals of the same colour.

Co(adH)Cl$_2$ C 23.42(22.6) H 2.72(1.89) N 26.9(26.4)

Chapter 7:

$Cugu_2SO_4.3H_2O.$

0.208g. (1mmol) of guanine hydrochloride were dissolved in 10ml. of water acidified with concentrated sulphuric acid. A solution containing 0.5g. (2mmol) of cupric sulphate in 5ml. of water was added, and the pH of the resulting mixture was raised by dropwise addition of 2N sodium hydroxide. The solution was shaken after each addition. At about pH 3, an amorphous green product precipitated out. This was filtered off and washed with water.

$Cugu_2SO_4.3H_2O$ C 23.87(23.30) H 3.00(3.11) N 27.63(27.18).

$Cugu_2Cl_2.2H_2O.$

0.208g. (1mol) of ligand were dissolved in 10ml. of N hydrochloric acid and a solution of 0.68g. of hydrated cupric chloride (4mmol) in 5ml. of water was added. The pH of the mixture was raised to ca.6 by dropwise addition of sodium hydroxide. On standing for about 12 hours an amorphous light green material was precipitated.

$Cugu_2Cl_2.2H_2O$ Cu 12.92(13.44) Cl 14.50(15.02).

$CuguSO_4.6H_2O.$

The ligand (0.208g.: 1mmol) was dissolved in 10ml. of hot acidulated water and cupric sulphate (2.5g.: 10mmol) in 10ml. of water was added. The resulting solution was boiled for ca. ten minutes to produce a dark green compound. This

was filtered off and washed with warm water.

CuguSO$_4$.6H$_2$O.   C 13.86(14.35) H 2.76(4.05) N 17.38(16.7)

(guH)$_2$Cu$_2$Cl$_6$.2H$_2$O.

0.5g. (2mmol) of guanine hydrochloride were dissolved with heating in 10ml. of 2M hydrochloric acid. A solution of cupric chloride (2g. in 2ml. of water) was added. The mixture was cooled and ca. 5ml. of benzene were added. Orange crystals formed rapidly.

(guH)$_2$Cu$_2$Cl$_6$.2H$_2$O   C 17.47(17.6) H 1.98(2.58) N 20.83(20.55)

Cl 29.88(31.3) Cu 18.2(18.7).

Cuxa$_2$Cl$_2$.3H$_2$O.

0.15g. (1mmol) of xanthine were dissolved in ca. 15ml. of 4N hydrochloric acid and to this solution was added 0.51g. (3mmol) of hydrated cupric chloride. On standing for about 2 days a pale green compound separated out.

Cu(xa)$_2$Cl$_2$.3H$_2$O   C 23.97(24.4) H 2.15(2.84) N 22.30(22.8).

Cuxa$_2$SO$_4$.5H$_2$O.

0.15g. (1mmol) were dissolved, with heating, in ca. 25ml. of 2N sulphuric acid. 1.25g. (5mmol) of hydrated cupric sulphate were added and the pH was raised by dropwise addition of 2N sodium hydroxide until the flocculent local precipitate just dissolved on shaking. The solution was left to stand.

and after several days a light green compound precipitated out.

$Cu(xa)_2SO_4 \cdot 5H_2O$ C 21.32(21.7) H 2.05(3.25) N 19.51(20.25).

$Cu(theo)_2 \cdot 4H_2O$.

0.4g. of theophylline hydrate (2mmol) and 0.25g. of copper sulphate (1mmol) were dissolved in 20ml. of warm water. The solution was heated and the pH gradually raised. A colour change was apparent and, on boiling, a dark green compound formed. This was filtered off and washed with hot water.

$Cu(theo)_2 \cdot 4H_2O$ C 34.82(34.0) H 4.93(4.46) N 21.97(22.7).

$Ni(theo)_2 \cdot 4H_2O$.

Similar preparation to that of the copper complex.

$Ni(theo)_2 4H_2O$ Ni 11.49(11.96).

$CupuSO_4 \cdot 6H_2O$.

The ligand (1mole) was dissolved in water and the metal salt (1mole) was added. The solution was evaporated to small volume and allowed to stand. After standing some hours, a dark blue microcrystalline solid precipitated out.

$CupuSO_4 \cdot 6H_2O$ C 15.72(15.5) H 3.66(4.14).

Physical Techniques.

Electronic Spectra were obtained by diffuse reflectance using a Beckman DK2 spectrometer. The low temperature spectrum of $Cu(ad)_2.3H_2O$ was recorded using an attachment designed by Dr. D.M.L. Goodgame.

Magnetic measurements were made by the Gouy method using both permanent and electro-magnets; the variable temperature unit was constructed by Dr. D. Forster. Calibration was carried out using $Hg(Co(NCS)_4)$.

Infra-red spectra were recorded on Grubb Parsons Spectromaster ($4000-400cm^{-1}$), DM4 Mark II ($500-200cm^{-1}$) and 6M3 ($200-90cm^{-1}$) instruments. For the low energy region 1m.m. polythene discus were used as the window material and vaseline as the mulling agent.

X-band esr spectra were obtained on a Varian V 4500-15 spectrometer using Mn^{2+} in MgO as the calibrant.

Analyses. Carbon, hydrogen and nitrogen analyses were performed by the Microanalytical Department, Imperial College, Nickel was determined, gravimetrically, by precipitation with dimethylglyoxime, and copper by precipitation with α-benzoin oxime. Halogen content was determined by gravimetric analysis using silver nitrate and nitrate content using nitron.

CONCLUSION.

The pyrimidine bases, 5-methylpyrimidine and
4,6-dimethylpyrimidine, have a strong bridging character.
In the compounds $M(5Mepyr)_2Br_2 2H_2O$ (M=Co,Ni) and $Co(dmp)X_2$
(X=Cl,Br), the bridging tendency of the pyrimidine outweighs
that of the inorganic anions. It is possible that a
similar situation holds in $Cu(5Mepyr)(NO_2)_2$ and it is hoped
that a single crystal study of this complex may be made in
order to ascertain if this is so.

The variation in the type of complex formed by the
various substituted pyrimidine molecules seems to correlate
largely with steric effects. The methyl group, in 4-methyl-
pyrimidine, prevents the formation of the polymeric octahedral
MLX_2 compounds, which are readily produced by 5-methyl-
pyrimidine. The increased steric effect of two and three
methyl substituents is such, that there are no octahedral
cobalt complexes of 4,6-dimethyl and 2,4,6-trimethylpyrimidine.
These effects cannot explain the fact that $NiLCl_2$ (L = 4Mepyr,
dmp) adopts a polymeric structure which involves chlorine and
pyrimidine bridges.

The structural differences between $Ni(2NH_2pyr)_2X_2 \cdot nH_2O$
(X = Cl, n = 2; X = Br, n = 3) and the 2,1 nickel complexes

of the other pyrimidine molecules can be related to the
presence of the potentially hydrogen bonding amino group.
It is possible that this substituent is involved in other
2:1 complexes formed by 2-aminopyrimidine.

The behaviour of adenine is dominated by a bridging
tendency, and it has been shown that the copper-adenine
complexes cannot be related to any situation involving
nucleic acids. To determine whether copper-DNA interactions
involve adenine moieties, the N(9) substituted molecule
must be investigated and, particularly, the adenosine system
(this last is now under investigation in the Department).

Although xanthine and guanine do not appear to form
copper dimers involving N(9) and N(3) it is quite feasible
that N(9) atoms may act as binding sites in their copper
complexes. Until crystalline materials are obtained, and
studied, the identity of the binding sites of these molecules
with metal ions remains uncertain.

It would be of interest to develop the investigation of
purine bases with other metal ions. Adenine, guanine,
xanthine and theophylline interact with ferric ions in
alkaline media, and crystalline compounds can be isolated.
None of these, have, as yet been characterised. Guanine,

in the presence of cobalt (II) ions exhibits behaviour similar to that described for adenine.

It has been recognised[23] that most bivalent metals, other than cupric copper, stabilise the structure of DNA and it is thought that they interact with the phosphate groups. It has also been reported[14] that there are reproducible findings of Ni(II), Mn(II), Zn(II), Cu(II) in RNA's from widely differing sources and it has been suggested[16] that they maintain configuration by bonding to purine and pyrimidine bases. Therefore from a biochemical viewpoint, it would be valuable to extend any future study on purine and nucleotide bases to cover a wider range of first row transition metals than was permitted by the time available for the present study.

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