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COPPER(II) AMMONIA COMPLEXES

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A. INTRODUCTION

More X-ray crystal structures have been determined for complexes of the copper(II) ion than for any other first row transition metal ion. Despite this, little attempt has been made to correlate this structural information with the electronic properties of the copper(II) ion. An attempt at such a correlation is made more difficult by the wide range of stereochemistries exhibited by the copper(II) ion and its tendency to give rise to a large number of structures which involve distortion from otherwise regular structures. In order to examine the effect of different stereochemistries on the electronic properties of the copper(II) ion, in the absence of steric and π-bonding effects, the most convenient ligand with which to work is ammonia. A wide range of complexes are formed with this ligand and more than twenty are of known crystal structure.

This article attempts to clarify the rather complex preparative chemistry of the copper(II) ammines, describes their structural and electronic properties and infrared spectra and attempts to relate these to the stereochemistries present.

B. SOLUTION STUDIES

Addition[1] of ammonia solution to an aqueous solution of the copper(II) ion results in the setting up of complex equilibria, involving the successive replacement of coordinated water by ammonia according to the equation:

$$\underset{\text{blue}}{\mathrm{Cu(H_2O)_6}^{2+}} + n\mathrm{NH_3} \rightleftharpoons \underset{\text{purple}}{\mathrm{Cu(NH_3)}_n\mathrm{(H_2O)}_{6-n}{}^{2+}} + n\mathrm{H_2O}$$

The successive formation constants[2] for these reactions are shown in Table 1 together with those for the $\mathrm{Ni(H_2O)_6}^{2+}$ cation. For nickel(II) these show a smooth decrease from K_1 to K_6, whereas for copper(II), K_6 is zero and K_5 is very small, indicating a negligible tendency to take up more than four ammonia groups. The enhanced stability of the species over the corresponding nickel(II) species is reflected in the combined formation constants β_4, namely 2.3×10^{12} and 5.6×10^7 respectively.

The changes in the electronic spectrum[3] of the aqueous copper(II) solution occuring on addition of aqueous ammonia, are shown in Fig.1. The absorption

TABLE 1

THE SUCCESSIVE FORMATION CONSTANTS[2] FOR THE NICKEL(II) AND COPPER(II) IONS WITH AMMONIA AS A LIGAND

	K_1	K_2	K_3	K_4	K_5	K_6
$\mathrm{Ni^{II}}$	500	150	50	15	5	1
$\mathrm{Cu^{II}}$	12,000	3,000	800	120	0.3	—

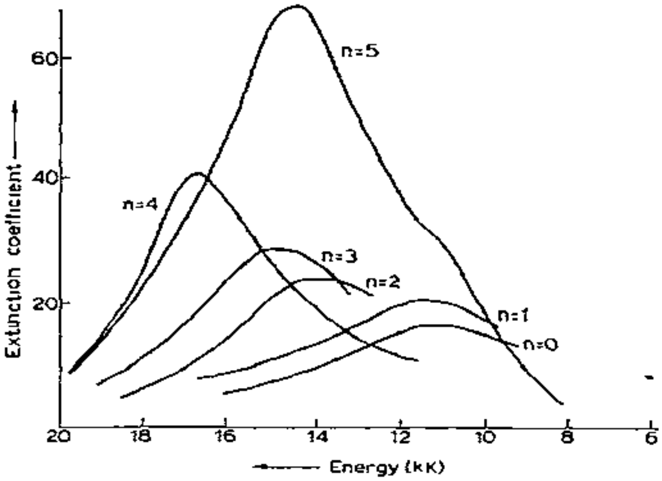


Fig. 1. Electronic spectra of $Cu(NH_3)_n(H_2O)_{6-n}{}^{2+}$ cations in aqueous solution.

maximum and the molecular intensity increases with increasing ammonia concentration up to $n = 4$, thereafter addition of further ammonia results in a substantial decrease in the energy of the absorption maximum and a substantial increase in the intensity. This has been termed[3,4] the "pentaammine effect" and is ascribed to the formation of a five coordinate $Cu(NH_3)_5{}^{2+}$ cation, probably associated with a molecule of water, $Cu(NH_3)_5(H_2O)_1{}^{2+}$. As the electronic spectrum of anhydrous copper nitrate in liquid ammonia closely resembles[5] the "pentaammine" spectrum in aqueous solution[3], the molecule of water may be only weakly associated with the copper(II) ion in the sixth coordinate position forming a tetragonal octahedral stereochemistry with non-equivalent ligands at unequal distances along the tetragonal axis.

C. PREPARATION AND THERMAL STABILITIES OF AMMINE COPPER(II) COMPLEXES

Reflecting this rather complex behaviour in solution is the existence of an extensive series of ammine copper(II) complexes in the solid state, involving copper to ammonia ratios from 1:1 to 1:6. Three routes may be used to prepare these complexes:

1. recrystallisation of the anhydrous or hydrated simple salt from aqueous ammonia solutions of various strengths;
2. recrystallisation of an anhydrous salt or lower ammine copper(II) complex from liquid ammonia;
3. controlled thermal decomposition of a higher ammine.

Method 1 is the most versatile and, depending upon the concentration of ammonia, the temperature, and the reaction time used, may yield complexes containing from one to five molecules of ammonia per copper(II) ion.

(i) $Cu(NH_3)_6X_2$

The hexaammines may be prepared[5-8], using method 2, either from the anhydrous halide ($X = Cl^-$ and Br^-), the pentaammine ($X = I^-$, BF_4^-, and ClO_4^-) or from the anhydrous tetraammine ($X = BF_4^-$ and ClO_4^-). They may also be prepared by passing dry ammonia gas over the anhydrous parent salt or lower ammine[7], but this procedure is believed to lead to phases containing more than six molecules of ammonia per copper(II) ion. Using these methods the hexaammines are prepared as pale blue powders (bubbling dry ammonia gas into a solution of anhydrous $CuBr_2$ in ethyl acetate is reported[9] to give $Cu(NH_3)_6Br_2$ in a crystalline form). All the hexaammines are extremely unstable and must be handled in an atmosphere of ammonia[8].

(ii) $Cu(NH_3)_5X_2$

The pentaammines may be prepared[10,11] using method 1, starting from the hydrated salts and concentrated ammonia solution (*d*, 0.88) at *ca.* 70° ($X = Br^-$, BF_4^-, ClO_4^-) and at 0° ($X = C_2O_4^{2-}$). $Cu(NH_3)_5I_2$ may be prepared from $CuCl_22H_2O$ plus two moles of KI in concentrated ammonia, $Cu(NH_3)_5Cl_2$ by careful decomposition of the hexaammine and $Cu(NH_3)_5SO_4$ from the anhydrous sulphate in liquid ammonia solution[11,12].

The double salts $NH_4[Cu(NH_3)_5]X_3$, where $X = ClO_4^-$ and PF_6^-, may be prepared by adding the required molar quantities of NH_4ClO_4 to a solution of $Cu(NO_3)_23H_2O$ in concentrated ammonia (*d*, 0.88) and NH_4PF_6 to a solution of $CuCl_22H_2O$ in concentrated ammonia (*d*, 0.88), respectively[11].

The pentaammines are more stable[13] than the hexaammines; Fig. 2 shows two examples of the thermogravimetric analyses of $Cu(NH_3)_5X_2$ complexes[11]. The chloride loses its fifth ammonia below 100°, while the tetrafluoroborate, double perchlorate and hexafluorophosphate require a temperature of *ca.* 150°. Thermal decomposition of the pentaammines yield the corresponding tetraammines in the case of the perchlorate, tetrafluoroborate and hexafluorophosphate. With the halides decomposition proceeds initially to the phase $Cu(NH_3)_{3.3}X_2$ and ultimately to the diammines.

(iii) $Cu(NH_3)_4X_2$

The tetraammines are best prepared by method 1 using hot dilute ammonia solution and the anhydrous or hydrated parent salt[14]. In the preparation of the tetraammines of complex anions (*e.g.* $[Cu(S_2O_3)_2]^{3-}$) it is convenient to start with

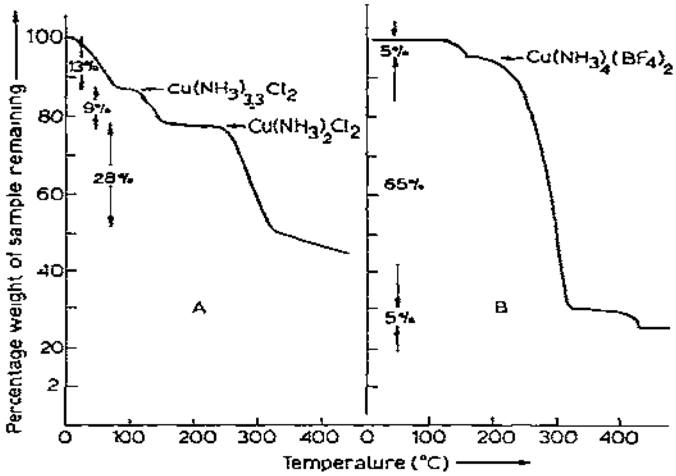


Fig. 2. Thermogravimetric analysis of A, $Cu(NH_3)_5Cl_2$; B, $Cu(NH_3)_5(BF_4)_2$.

an aqueous solution of the sodium salt of the anion and add it to an aqueous ammonia solution of copper acetate[14]. The latter does not form a tetraammine or pentaammine and the diammine is extremely soluble even in concentrated aqueous ammonia solution. With $X = \frac{1}{2}SO_4^{2-}$ and Cl^- the wet method gives the corresponding tetraammine monohydrate. Thermal decomposition of the corresponding pentaammines[11] (method 3) yields the tetraammines as amorphous powders, when $X = \frac{1}{2}SO_4^{2-}$, BF_4^- and ClO_4^-.

Despite the apparent stability of the $Cu(NH_3)_4(H_2O)_2^{2+}$ cation inaqueous solution (Table 1) the tetraammine copper(II) complexes are all rather unstable and need to be stored in a closed system. Loss of ammonia generally yields a diammine, but in a moist atmosphere hydrolysis may also occur.

(iv) $Cu_3(NH_3)_{10}X_6$

The decaammines are prepared by method 3, involving careful decomposition of the pentaammines; their formation is restricted to the halides. The bromide and iodide may also be prepared as black and brown crystals, respectively, by mixing the required molar amounts of copper acetate and KX or NH_4X in a very dilute aqueous ammonia solution[15]. The decaammines rapidly decompose to the diammines if left in the atmosphere.

(v) $Cu(NH_3)_2X_2$

The diammines[16] may be prepared using methods 1 and 3. Crystallisation from concentrated ammonia (*d*, 0.88) of the appropriate hydrated salt yields the diammine, ($X = \frac{1}{2}CO_3^{2-}$, $CH_3CO_2^-$, HCO_2^-). Thermal decomposition of the corresponding tetraammine gives the diammine ($X = NO_3^-$, $\frac{1}{2}SO_4^{2-}$, $\frac{1}{2}SeO_4^{2-}$, NO_2^-). $Cu(NH_3)_2(NO_2)_2$ exists in a high temperature green form and a room temperature purple form. $Cu(NH_3)_2Ag(SCN)_3$ may be prepared by boiling an aqueous ammonia solution of the corresponding tetraammine[17]; prolonged boiling yields $Cu(NH_3)_2(SCN)_2$. There are two forms of the diammine chloride and bromide[18]; the α-forms are prepared by bubbling dry ammonia gas into a solution of $Cu(NO_3)_2 \cdot 3H_2O$ and $LiX \cdot H_2O$ in acetone. The β-forms are obtained when the α-forms are recrystallised from a solution of the corresponding ammonium halide[19,20]. The isomers are sensitive to changes of temperature and pressure[21]:

$$\beta\text{-}Cu(NH_3)_2Br_2 \overset{80°}{\rightleftharpoons} \alpha\text{-}Cu(NH_3)_2Br_2$$

$Cu(NH_3)_2I_2$ is prepared by slow evaporation over P_2O_5 of the mother liquor obtained from the preparation of $Cu_3(NH_3)_{10}I_6$ (as above). Several diammine oxalates are obtained from the reaction of $CuC_2O_4 \cdot \frac{1}{2}H_2O$ and aqueous ammonia solution[16,22], and thermal decomposition of the products (Fig. 3).

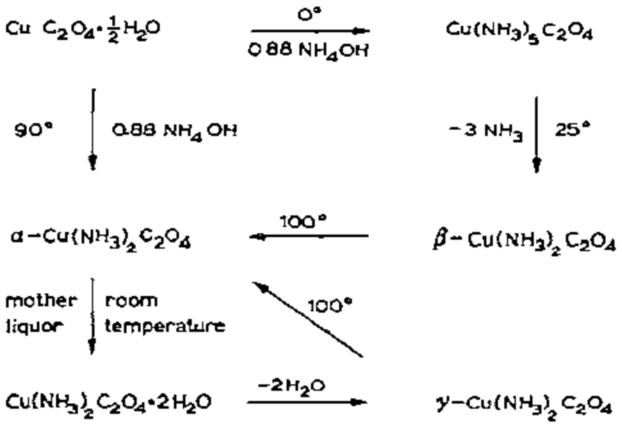


Fig. 3. The preparation of diammine copper(II) oxalate complexes.

(vi) $[Cu(N\text{-}N^*)_2NH_3]X_2$

A number of monoammine copper(II) complexes are known especially where chelate ligands are involved. Recrystallisation[23,24] of $Cuen_2X_2$ complexes from liquid ammonia yields the corresponding $[Cuen_2(NH_3)]X_2$ complexes as unstable bright blue crystals (when $X = Br^-$, I^-, NO_3^-, BF_4^-, and ClO_4^-); the chloride yields an amorphous powder. The perchlorate and tetrafluoroborate are more stable and may be prepared from concentrated aqueous ammonia solution. Recrystallisation of $Cubipy_2X_2$ ($X = ClO_4^-$, and BF_4^-) from concentrated aqueous ammonia (*d*, 0.88) yields only the monoammines [Cubipy$_2$(NH$_3$)]X$_2$ as pale blue stable crystals[25,26]. *N–N = chelate nitrogen ligand, *e.g.* ethylenediamine or α, α′-bipyridyl.

D. X-RAY CRYSTALLOGRAPHIC DATA

(i) *Single crystal data*

Crystal structures are reported for pentaammine, tetraammine, triammine and diammine complexes of the copper(II) ion (Table 2).

In the tetraammines the predominant symmetry is axial, but within this symmetry, coordination numbers of four, five and six occur (Fig. 4). The structures include the square-coplanar complex[27,30] (I), $Na_4Cu(NH_3)_4\{Cu(S_2O_3)_2\}_2$, the tetra gonal octahedral complexes[32] (II), $Cu(NH_3)_4(NO_2)_2$, with equivalent ligands in the long-bonded tetragonal positions, the complex[31] (III), $Cu(NH_3)_4PtCl_4$ with equivalent bridging ligands in the long-bonded tetragonal positions at equal distances and the complex[34] (IV), $Cu(NH_3)_4SeO_4H_2O$ with bridging groups in the long-bonded positions at unequal distances. The rhombic octahedral complex (V), $Cu(NH_3)_4(CuI_2)_2$, and the square-based pyramidal complex (VI), $Cu(NH_3)_4H_2O$-SO_4, have also been reported[33,34]. In complex (VI), the copper(II) ion lies 0.2 Å out of the plane of the four nitrogen ligands[34], in complexes (I)–(V) it lies in the plane. The least common structure is that of a strictly square-coplanar $Cu(NH_3)_4{}^{2+}$ cation; it is considered[27,30] to occur in $Na_4Cu(NH_3)_4\{Cu(S_2O_3)_2\}_2$ and $Cu(NH_3)_4(CuBr_2)_2$. Both complexes have the tetragonal axes of the CuN_4 chromophores aligned parallel and involve further copper(II) ions as the nearest neighbours at a distance of 5.76 and 5.71 Å respectively, along this tetragonal axis. This suggests the absence of bonding in this tetragonal direction and of a strictly square-coplanar CuN_4 chromophore. A reexamination[28,29] of the original X-ray crystallographic data[27] of $Na_4Cu(NH_3)_4\{Cu(S_2O_3)_2\}_2$ suggests that there is either an additional water or ammonia group present in the lattice, positioned midway between the copper(II) ions. A comparable structure has previously[30] been suggested for $Cu(NH_3)_4(CuCl_2)_2H_2O$ (Table 2) and also[44] for $(NH_4)Cu(NH_3)_5$-$(ClO_4)_3$. A reexamination of the preparative conditions for obtaining Na_4Cu-$(NH_3)_4\{Cu(S_2O_3)_2\}_2 \cdot L$ has established the existence of a blue monoammine ($L = NH_3$) and a violet monohydrate ($L = H_2O$); precession data showed that both are strictly isostructural. A reassessment[29] of the analytical data[14] on $Cu(NH_3)_4(CuBr_2)_2$ suggests that it is also a monohydrate; it has the same space group[30] as $Cu(NH_3)_4(CuCl_2)_2H_2O$, namely, *I4/mmm*, with a symmetrically placed water molecule bridging the copper(II) ions [Fig. 4 (III)]. These considerations indicate that there is no clear crystallographic evidence for the existence of a strictly square-coplanar $Cu(NH_3)_4{}^{2+}$ cation.

TABLE 2

CRYSTALLOGRAPHIC DATA, BOND LENGTHS AND DEGREE OF TETRAGONALITY

Complex	Space Group	Z	R%	Cu–N (R_S^N) Å	E.s.d.[a]	Cu–X (R_L^X) Å	Corrected (R_L^X) Å	$T = R_S^N/R_L^X$	Ref.
A. $Cu(NH_3)_4X_2$ complexes									
$Na_4Cu(NH_3)_4[Cu(S_2O_3)_2]_2$	*I4/m*	2	11.5	1.994	0.006	*Cu* 5.76	5.76	0.34	27
$Na_4Cu(NH_3)_4[Cu(S_2O_3)_2]_2 \cdot L^d$	*I4/m*	2	5.6	1.99	—	*N* 2.88	2.88	0.69	28, 29
$Cu(NH_3)_4(CuBr_2)_2$	*I4/mmm*	2	11.1	1.996	0.029	*Cu* 5.71	5.71	0.34	30
$Cu(NH_3)_4PtCl_4$	*P4/mnc*	2	16 (*hk*0)	2.04	—	*Pt* 3.21	—		31
$Cu(NH_3)_4(CuCl_2)_2 \cdot H_2O$	*I4/mmm*	2	9.7	2.025	0.020	*O* 2.73	2.81	0.72	30
$Cu(NH_3)_4(NO_2)_2$	*C2/m*	2		1.99		*N* 2.65	2.65	0.75	32
$Cu(NH_3)_4H_2O \cdot SO_4$	*P/mcn*	4	10	2.04	—	*O* 2.59	2.67	0.77	33
				2.05[c]					
				−2.06		*O* 3.37			
$Cu(NH_3)_4H_2O \cdot SO_4$[e]	*Pnam*	4	4.7	2.031	0.006	*O* 2.339	2.39	0.85	34
						O 3.475	3.54	0.57	
$Cu(NH_3)_4SeO_4$	*P*2₁/*n*		4.9	2.005	0.009	*O* 2.451	2.50	0.80	34
						O 2.607	2.66	0.75	
$Cu(NH_3)_4(SCN)_2$	*I2/m*	2	10.8	2.08	—	*S* 3.00	2.59[b]	0.80	35
$Cu(NH_3)_4(CuI_2)_2$	*P*$\bar{1}$	1	13.0	2.114	0.073	*I* 3.17	2.44[b]	0.88	30
				2.14[c]					
				2.163	0.063				
B. $Cu(NH_3)_3X_2$ complexes									
$Cu_2(NH_3)_3(NCS)_3$	*P*2₁/*c*	4	11.1	*N* 2.024	0.025	*S* 2.946	2.65	0.77[f]	36
				2.048		3.286			
				2.061					
				SCN 1.987					

TABLE 2 (*Continued*)

Complex	*Class*	*Space Group*	*Z*	*R%*	*Line-up of tetragonal axes*	*Environment of Cu(II) ion*	*Cu–N* (Å)	*Cu–X* (Å)	*Ref.*
C. $Cu(NH_3)_2X_2$ complexes									
α-$Cu(NH_3)_2Cl_2$	—	*Cmcm*	—	—	—	compressed tetragonal (chains)			37
β-$Cu(NH_3)_2Cl_2$[g]	cubic	—	—	10.0[a]	random	compressed tetragonal (random)			20
α-$Cu(NH_3)_2Br_2$[g]	monoclinic	*C2/m*	2	13.0[a]	parallel	rhombic	1.93	*Br* 2.54 *Br* 3.08	19, 38
β-$Cu(NH_3)_2Br_2$[g]	cubic	—	2	10.0[a]	random	compressed tetragonal	2.03	*Br* 2.88	20
$Cu(NH_3)_2(NCS)_2$	monoclinic	*Pnma*	4	—	nearly parallel	rhombic	2.03	*N* 1.99 *N* 1.97 *S* 3.05	18, 39
$Cu(NH_3)_2(CH_3CO_2)_2$	monoclinic	*$P2_1/c$*	2	—	nearly parallel	rhombic	1.97	*O* 2.07 2.77	40
$Cu(NH_3)_2CO_3$	monoclinic	—	4 (2 sets)	—	nearly parallel	square-based pyramidal	1.85 2.00	*O* 2.05 *O* 1.87 *O* 2.57	41, 42
α-$Cu(NH_3)_2C_2O_4$	ortho-rhombic	*$Pn2_1/a$*	4	10.9	not parallel	rhombic, but with unequal axial ligand bond lengths	1.93 1.99	*O* 2.02 *O* 2.05 *O* 2.48 *O* 2.33	22
$Cu(NH_3)_2C_2O_4 \cdot 2H_2O$[h]	—	—	—	—	—	compressed rhombic	1.98	*O* 2.10 *O* 2.15	22
$Cu(NH_3)_2Ag(SCN)_3$	hexagonal	*$P\bar{6}2c$*	2	13.0	parallel	trigonal bipyramidal	2.00	*N* 1.92	43
D. $Cu(NH_3)_5X_2$ complexes									
$(NH_4)[Cu(NH_3)_5](ClO_4)_3$	tetragonal	*$P\bar{4}2_1m$*	4	—	parallel	"square-coplanar"[i]	2.05	*N* 3.75	44

(a) E.s.d. = estimated standard deviation. (b) Estimated values. (c) Mean. (d) Monohydrate or monocenamine. (e) Copper(II) ion displaced 0.194 Å out-of-plane. (f) Calc. using mean of C-NH_3 bonds, 2.044 and Cu–S of 2.946. (g) Powder data only. (h) Preliminary data. (i) See text.

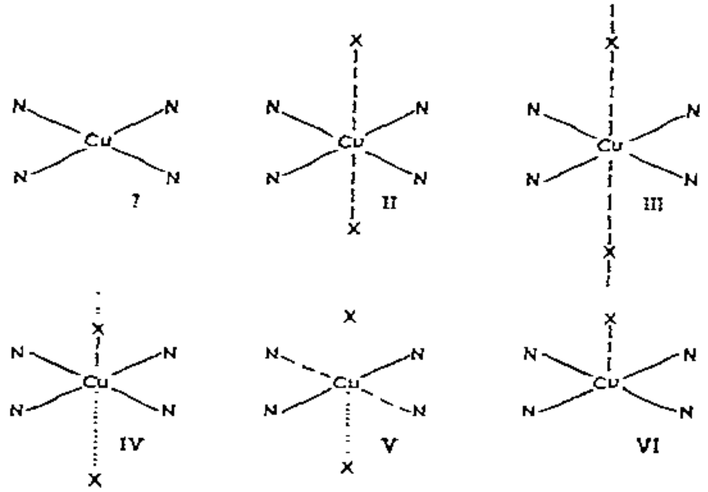


Fig. 4. The molecular structures of $Cu(NH_3)_4X_2$ complexes (see text for descriptions).

A square-based pyramidal stereochemistry is present[33] in $Cu(NH_3)_4H_2O\cdot SO_4$; the X-ray data for this complex have recently[34] been redetermined and appreciably reduced the Cu–N and Cu–O bond lengths, Table 2A. More significantly, the position of the copper(II) ion lies 0.2 Å above the plane of the four nitrogen atoms. The remaining tetraammine structures are tetragonal octahedral except[30] for $Cu(NH_3)_4(CuI_2)_2$, which has a significant rhombic distortion in the plane. Since the analysis has an R value of 13.0% the determination may not be very accurate especially as the Cu–N bond lengths 2.11 and 2.16 Å are significantly longer than that of 2.11 Å observed in the octahedral complex[45] $K_2PbCu(NO_2)_6$. A rhombic or tetragonal octahedral chromophore CuN_4X_2 would be expected to have a shorter Cu–N bond length than that[14] of a regular octahedral CuN_6 chromophore. By the same criterion, the Cu–N bond length of 2.08 Å in $Cu(NH_3)_4(SCN)_2$ is rather high. The structure of $Cu(NH_3)_4(NO_2)_2$, although determined using limited data agrees closely with that of the more accurately determined structure[34] of $Cu(NH_3)_4SeO_4$, notwithstanding the involvement of the nitrite group in nitro-coordination[32] rather than the anticipated nitrito coordination[14].

In tetragonal octahedral copper(II) complexes with six equivalent ligands, the tetragonal distortion[14] present (*T*) may be defined by R_S/R_L, where R_S is the in-plane copper-ligand bond length and R_L is the out-of-plane bond length. By considering the available crystallographic data on a large number of copper(II) complexes[14] the value of *T* was shown to be *ca.* 0.8 and to be independent of the type of ligand present. In $Cu(NH_3)_4X_2$ complexes the value of $R_L{}^X$ (obs.) is dependent upon the ligand atom X. If these are corrected to relate to the ligand atom in-the-plane, in this case nitrogen, by the relationship $R_L{}^X(\text{corr.}) = R_L{}^X(\text{obs.}) \times R_S{}^L/R_S{}^X$, the value of *T* is then a true measure of the tetragonal distortion present. The corrected values of $R_L{}^X$(corr.) are given in Table 2 along with the corresponding values of T. The values of $R_L{}^X$(corr.) are plotted against $R_S{}^N$ in Fig. 5. Using the original crystallographic data (points ● and ○), the points suggest that the shorter the axial bond length R_L the longer is the in-plane bond length R_S and that the latter are sensitive to the out-of-plane bond lengths. It emphasises that the groups present along the tetragonal direction are definitely coordinated to the copper(II) ion and not merely positioned by lattice packing factors. The term semi-coordination has been introduced[46] to describe this structural situation. The inclusion of the accurate data for $Cu(NH_3)_4SeO_4$ in Fig. 5 gives a point well off the best fit curve. The reassessment[28,29] of the crystal structure of the complex $Na_4Cu(NH_3)_4\{Cu(S_2O_3)_2\}_2H_2O$ [and along with it that of $Cu(NH_3)_4(CuBr_2)_2$-H_2O] indicating the presence of a semi-coordinated molecule of water or ammonia between the copper(II) ions, removes the two points for the two strictly square-coplanar complexes from Fig. 5. There is still a slight variation of $R_S{}^N$ with $R_L{}^X$(corr.), but the differences are now hardly significant. In the complexes $Na_4Cu(NH_3)_4\{Cu(S_2O_3)_2\}_2L$, (where L = H_2O or NH_3) and $Cu(NH_3)_4(CuBr_2)_2$-H_2O, the value of $R_L{}^X$(obs.) of 2.8–2.9 Å is longer than that predicted for semi-coordination[14] (ca. 2.5 Å) and the in-plane Cu–N bond lengths are still significantly shorter than those for the other tetraammines[14] of Fig. 5. This suggests that in these complexes the $Cu(NH_3)_4{}^{2+}$ cation is as near a strictly square-coplanar stereochemistry as it can attain. The observation of a high temperature factor parallel to the c-axis for the tetragonal groups suggests that the water or ammonia groups are either vibrating parallel to the tetragonal axis or that there is some disorder in their exact positions along the tetragonal axis. In the latter

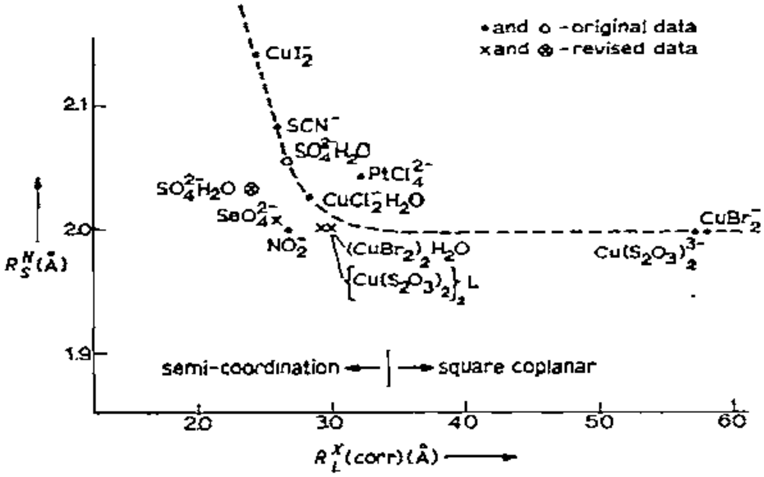


Fig. 5. A graph of the in-plane bond lengths ($R_S{}^N$) against the corrected axial bond lengths ($R_L{}^X$ corr.) for $Cu(NH_3)_4X_2$ complexes.

case the effective local stereochemistry may be considered as tetragonal octahedral with equivalent bridging ligands bonding at unequal distances (Fig. 4, IV).

The elimination of these strictly square coplanar tetraammines from the data of Fig. 5 weakens the crystallographic evidence for the concept[14] of varying tetragonal distortion (see later) suggested by Fig. 5 (but see CuO_6 systems, ref. 68). It raises the question of whether a strictly square coplanar $Cu(NH_3)_4{}^{2+}$ cation can actually exist with purely σ-bonding ligands. The existence of the square coplanar $Cu(acac)_2$ complexes would suggest that this stereochemistry for the copper(II) ion is only stable if the in-plane ligands can also be involved in a π-bonding function. The only way in which a $Cu(NH_3)_4{}^{2+}$ cation can remain stable is for semi-coordination to occur above and below the plane, especially with potentially π-bonding ligands[14].

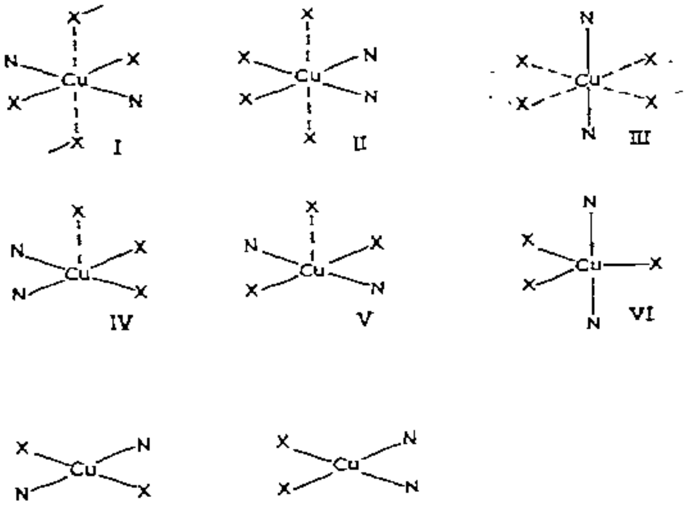


Fig. 6. The molecular structures of $Cu(NH_3)_2X_2$ complexes.

The stereochemistries present in the diammines are much more varied (Table 2C) and dependent upon the anion present. With only two ammonia groups available the anion must occupy two positions in a four coordinate, three in a five coordinate and four in a six coordinate complex (Fig. 6); consequently extensive bridging may occur. In practice no strictly square-coplanar diammines are known. Two five coordinate diammine complexes are known. The carbonate[41,42] has a square-based pyramidal stereochemistry (IV), with a bidentate carbonate group in the plane, the two ammonia groups assuming a *cis*-configuration. These involve the shortest observed copper–nitrogen bond length of 1.85 Å and 2.00 Å. $Cu(NH_3)_2Ag(SCN)_3$ has an almost regular[43] trigonal bipyramidal stereochemistry (VI) with all of the trigonal axes aligned. The ammonia groups coordinate out of the plane at 2.00 Å and the three thiocyanate nitrogens coordinate in the plane at 1.92 Å, at the trigonal angle of 120° imposed by the stacking of the planar $Ag(SCN)_3^{2-}$ anions. A compressed tetragonal octahedral stereochemistry, Fig. 6 (III), occurs in α-$Cu(NH_3)_2Cl_2$ [37], β-$Cu(NH_3)_2Br_2$ [20] and β-$Cu(NH_3)_2Cl_2$[20], but the structures of the first two complexes have been determined only from powder data. The rhombic octahedral stereochemistry normally occurs with an elongated tetragonal disortion (I) as in α-$Cu(NH_3)_2Br_2$ [19,38], $Cu(NH_3)_2(SCN)_2$, (Ref. 18, 39), $Cu(NH_3)_2(CH_3CO_2)_2$ [40] and α-$Cu(NH_3)_2C_2O_4$ [22]. A compressed rhombic distortion[22] has been suggested in a preliminary communication on $Cu(NH_3)_2C_2O_4 \cdot 2H_2O$.

The published X-ray crystallographic data[44] for $(NH_4)[Cu(NH_3)_5](ClO_4)_3$, Table 2, suggest that it should be formulated as a square-coplanar $Cu(NH_3)_4^{2+}$ cation with ammonia groups occupying the tetragonal positions at a distance of 3.75 Å, a non-honding distance. Although the electronic spectra[48] of this complex have been interpreted in terms of a square-coplanar $Cu(NH_3)_4^{2+}$ cation, a more recent examination[11] of both its electronic spectra and ESR spectra suggest that this complex should best be described as a pentaammine rather than a tetra-amine and that the crystal structure is in error.

The only triammine[36] of known crystal structure is $Cu_2(NH_3)_3(SCN)_3$, the molecular structure of the copper(II) ion is tetragonal octahedral, with one thiocyanate and three ammonia nitrogen atoms bonding in the plane. The tetragonal positions involve semi-coordinated thiocyanate sulphur atoms at slightly different distances, 3.29 and 2.94 Å (Fig. 4, IV).

(ii) X-ray powder data

Due to the difficulty of obtaining the higher ammines of copper(II) in other than a polycrystalline form, plus the low stability of many of these complexes to loss of ammonia, little attempt has been made to carry out single crystal X-ray work on either the hexaammines or pentaammines of the copper(II) ion (but see references 7, 9 and 11). Powder X-ray data, Table 3, have been obtained in both series[8,7,11] but are plagued by the uncertainty of the precise phase examined. In the original hexaammine report[6], the samples were preheated before taking the X-ray measurements and could well be contaminated by the presence of lower ammines. In more recent reports[7,8], although the samples were loaded in an ammonia atmosphere, no definite check on the samples examined was carried out and differing results were obtained. A further complication is that many of the pentaammine copper(II) complexes[11] are also cubic, with comparable unit cell parameters. As they can be isolated in crystalline form and are rather more stable than the corresponding hexaammines, the powder data are more reliable and suggest a face-centred cubic lattice. A Weissenberg photograph of a single crystal of $Cu(NH_3)_5(BF_4)_2$ confirms[11] this cubic structure and indicates a very low intensity for the reflections at high θ-value (compared with the values for the isomorphous

TABLE 3

X-RAY POWDER DATA

X	*Type of unit cell*	*a*[a]	*c*[a]	*c*[a]*/a*
A. $Cu(NH_3)_6X_2$ (ref. 8)				
Cl	Tetragonal	10.27	9.42	0.917
Br	Fcc	10.25		
I	Fcc	10.78		
BF_4	Fcc	11.16		
ClO_4	Fcc	11.34		
B. $Cu(NH_3)_5X_2$ (ref. 11)				
Cl	Tetragonal	10.29	9.37	0.918
Br	Fcc	10.34		
I	Fcc	10.76		
BF_4	Fcc	11.13		
ClO_4	Fcc	11.31		

C. $M^{II}(NH_3)_6X_2$ (ref. 11)					*$K_2PbM^{II}(NO_2)_6$ (ref. 49)*
M	*Br^-*	*I^-*	*BF_4^-*	*ClO_4^-*	
Ca	10.39	10.91	11.31	11.45	
Ni	10.34	10.88	11.27	11.41	10.60
Cu	10.25	10.78	11.16	11.34	10.70
Zn	10.46	10.96			

[a] ± 0.01 Å; Fcc = face centred cubic.

$Ni(NH_3)_6(BF_4)_2$ complex). The latter suggests some high thermal motion or disorder in the lattice which may well be accounted for in terms[11] of freely rotating $Cu(NH_3)_5{}^{2+}$ cations.

In the light of the existence of the pentaammines the structure of the hexaammines have been formulated[11] (see later for the electronic and infrared evidence) as $Cu(NH_3)_5X_2 \cdot NH_3$, in which the sixth ammonia molecule occupies a vacant lattice site in the pentaammine lattice. If this is the case, then many of the difficulties observed in the early literature, for example, the difficulty of obtaining phases with exactly six molecules of ammonia and the possible formation of solid solutions[7] between the pentaammines and the hexaammines, are understandable.

The powder data on $Cu(NH_3)_6X_2$ ($X = Cl^-$, Br^- and I^-) have been interpreted[7] assuming a tetragonally distorted octahedral CuN_6 chromophore giving Cu–N bond lengths of 2.1 and 2.6 Å, results which although reasonable ($T = 0.81$), conflict with the pentaammine structures suggested by the electronic spectra of these complexes. If a local tetragonal octahedral copper(II) ion stereochemistry were present, the unit cell parameter $\bar{a}$ should be intermediate[8] between those of the corresponding nickel(II) and zinc(II) hexaammines (as[49] in the cubic $K_2PbM^{II}(NO_2)_6$ complexes, Table 3). In all of the cases examined (Table 3) the copper(II) hexaammines have a lower $\bar{a}$-value than the nickel complex[8].

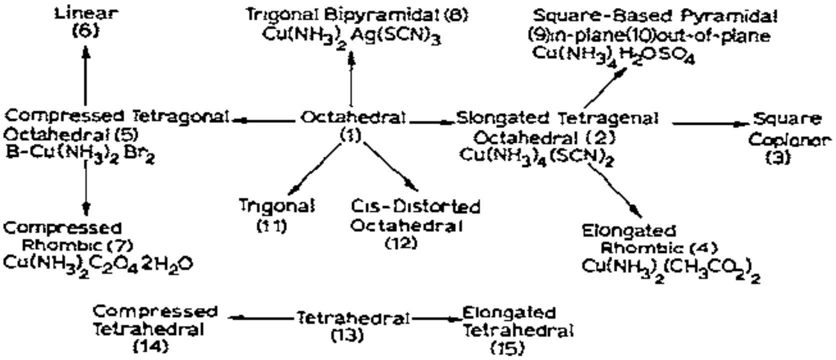


Fig. 7. The fifteen basic stereochemistries of the copper(II) ion, with examples from ammine complexes.

The structural data on α- and β-$Cu(NH_3)_2Cl_2$ were obtained from the interpretation of the X-ray powder data of these cubic complexes[37,38].

Fig. 7 summarises the fifteen known stereochemistries for the copper(II) ion and illustrates those which occur in the copper(II) ammines with definite examples.

E. MAGNETIC DATA

Table 4 shows some examples[50] of the room temperature magnetic moments of the various copper(II) ammine complexes; they all lie above the spin-only value of 1.73 B.M. and occur in the range 1.8–2.0 B.M. normally found for copper(II) complexes in the absence of any antiferromagnetic coupling. The values are consistent[51] with an orbitally non-degenerate ground state for the copper(II) ion, the slight increase above the spin-only value arising from the mixing in of an orbitally degenerate excited state into the ground state via spin–orbit coupling. The latter effect is clearly dependent upon the symmetry of the excited states present and upon their energies, both of which will depend upon the stereochemistry present. However, the total contribution to the magnetic moment by this mechanism is so

TABLE 4

SOME REPRESENTATIVE ROOM TEMPERATURE MAGNETIC MOMENTS (B.M.) FOR $Cu(NH_3)_xX_2$ COMPLEXES[50]

$Cu(NH_3)_5(BF_4)_2$	1.89	$Cu(NH_3)_4H_2O \cdot SO_4$	1.87
$(NH_4)[Cu(NH_4)_5](PF_6)_3$	1.85	$Cu(NH_3)_2Ag(SCN)_3$	1.83
$Na_4Cu(NH_3)_4[Cu(S_2O_3)_2]_2NH_3$	1.90	$[Cuen_2NH_3](BF_4)_2$	1.85
$Cu(NH_3)_4(NO_2)_2$	1.84	$[Cubipy_2NH_3](ClO_4)_2$	1.92[a]
$Cu(NH_3)_4(SCN)_2$	1.81		

[a] Ref. 25.

small, and the accuracy with which μ can be measured is such that no stereochemical information can be obtained from the measurement of the room-temperature magnetic moments. More information would be available from the measurement of single crystal magnetic anisotropies[52,53], but to date no such data are available on the ammines of copper(II).

Consequently although the observed magnetic moments are consistent with a single unpaired electron in these copper(II) ammines, they cannot distinguish between a $d_{x^2-y^2}$ ground state (for an elongated tetragonal environment) or a d_{z^2} ground state (for a compressed tetragonal environment).

F. ELECTRON SPIN RESONANCE

(i) General introduction

The copper(II) ion with a d^9 configuration, has an effective spin of $s = \frac{1}{2}$ and associated spin angular momentum of $m_s = \pm\frac{1}{2}$ leading to a doubly degenerate spin energy state in the absence of a magnetic field. On application of a magnetic field this degeneracy is removed and transitions occur between the two levels given by the condition $h\nu = g\beta H$. For a free electron, the Landé splitting factor g has the value 2.0023, whilst for an electron in a crystal field the value can differ from 2.0023; g is only isotropic in a cubic environment, in axial and rhombic crystal

TABLE 5

THEORETICAL EXPRESSIONS FOR THE g-VALUES FOR A COPPER(II) ION IN LIGAND FIELDS OF DIFFERENT SYMMETRIES[54,55]

1. *Octahedral*	$g_i = 2 - \dfrac{6k_i^2}{10D_q}$
2. *Tetragonal: a) elongated*	$g_\perp = 2 - \dfrac{2k_\perp^2\lambda}{E(^2E_g - {}^2B_{1g})}$
	$g_\parallel = 2 - \dfrac{8k_\parallel^2\lambda}{E(^2B_{2g} - {}^2B_{1g})}$
b) compressed	$g_\perp = 2 - \dfrac{6k_\perp^2\lambda}{E(^2E_g - {}^2A_{1g})}$
	$g_\parallel = 2.00$
3. *Rhombic, elongated*	$g_x = 2 - \dfrac{2k_x^2\lambda(\cos\alpha - \sqrt{3}\sin\alpha)^2}{E(^2B_{3g} - {}^2A_g)}$
	$g_y = 2 - \dfrac{2k_y^2\lambda(\cos\alpha + \sqrt{3}\sin\alpha)^2}{E(^2B_{2g} - {}^2A_g)}$
	$g_z = 2 - \dfrac{8k_z^2\lambda\cos^2\alpha}{E(^2B_{1g} - {}^2A_g)}$

fields two and three different g-values are obtained, respectively. The expressions for these are given in Table 5. In practice, the observed crystal g-values for copper(II) complexes will be determined by: a) the symmetry of the ligand field about the copper(II) ion; b) whether the tetragonal axes of the copper(II) ions present in the unit cell are aligned parallel. This must be the case if the number of molecules (Z) in the unit cell is one, but is not necessarily the case, if the number is greater than one. If all the tetragonal axes are aligned parallel then the crystal g-values accurately reflect the local copper(II) ion environment g-values, and these may be measured using either single crystal techniques or (slightly less accurately) by measurements upon polycrystalline samples. Table 6 lists some typical copper(II) ammine g-value data in which the observed g-values reflect the local copper(II) ion g-values. For the axial spectra[56] G, equal to $(g_{\parallel}-2)/(g_{\perp}-2)$, approximately equals 4.0 and is evidence that a $d_{x^2-y^2}$ ground state is present. The g-values for a regular trigonal bipyramidal-stereochemistry have been shown[17] to be equivalent to those for a compressed tetragonal distortion. The ESR spectrum[17] of

TABLE 6

TYPICAL g-VALUES FOR $Cu(NH_3)_xX_2$ COMPLEXES IN WHICH *A*, THE TETRAGONAL AXES ARE ALIGNED PARALLEL AND *B*, THE TETRAGONAL AXES ARE NOT ALIGNED OR THEIR ALIGNENT IS UNKNOWN

A.				
$Cu(NH_3)_6(BF_4)_2$	$g_t = 2.115$			
$Cu(NH_3)_5(BF_4)_2$	$g_t = 2.126$			
		$g_{\perp}$	$g_{\parallel}$	G
$NH_4Cu(NH_3)_5(PF_6)_3$		2.033	2.240	4.52
$Cu(NH_3)_5SO_4$		2.051	2.230	4.51
$Cu(NH_3)_4(SCN)_2$		2.056	2.237	4.23
$Cu(NH_3)_4(NO_2)_2$		2.052	2.234	4.50
$Na_4Cu(NH_3)_4\{Cu(S_2O_3)_2\}_2 \cdot NH_3$		2.058	2.230	3.96
$Na_4Cu(NH_3)_4\{Cu(S_2O_3)_2\}_2 \cdot H_2O$		2.052	2.200	3.85
	g_1	g_2	g_3	G
$Cu(NH_3)_2(CH_3CO_2)_2$	2.049	2.100	2.214	—
$Cu(NH_3)_2(NCS)_2$	2.058	2.278	—	4.79
$Cu(NH_3)_2Ag(SCN)_3$	2.207	2.004	—	—
B.				
$Cu(NH_3)_4(ClO_4)_2$	2.046	2.227	—	4.93
$Cu(NH_3)_4(NO_3)_2$	2.049	2.126	2.175	—
$Cu(NH_3)_2(NO_3)_2$	2.068	2.231	—	3.4
$Cu(NH_3)_2SO_4$		2.155		
$Cu(NH_3)_2SeO_4$		2.192		
$[Cubipy_2NH_3](ClO_4)_2$		2.009 2.207		—
$[Cubipy_2NH_3](BF_4)_2$		2.008 2.219		—
$[Cuen_2NH_3]I_2$		2.048 2.218		4.54
$[Cuen_2NH_3](NO_3)_2$		2.045 2.200		4.44

$Cu(NH_3)_2Ag(SCN)_3$ shows a low g-value only slightly greater than 2.00 consistent with a d_{z^2} ground state in this trigonal-bipyramidal stereochemistry.

If the tetragonal axes in the unit cell are not aligned parallel, then the observed *crystal* g-values are not simply related to the g-values of the local copper(II) ion environment[56]. If the complexes are of known crystal structure then the observed g-values may be related to the local g-values[57]. It is not possible to specify precisely the local g-values if the crystal structure is unknown, but three situations are observed in practice.

Isotropic Spectra

These are predicted for a copper(II) ion in a regular octahedral or tetrahedral stereochemistry, neither of which occur in practice (but see ref. 45). They can occur with a dynamically distorted octahedral stereochemistry, or one involving pseudo-rotation of a $CuL_6{}^{2+}$ chromophore, this situation is believed to[49,58] occur in $K_2PbCu(NO_2)_6$. An isotropic ESR spectrum would also occur if a CuL_6 chromophore of symmetry lower than octahedral was undergoing free rotation in the crystal lattice; the $Cu(NH_3)_5{}^{2+}$ cation, thought[11] to be present in the penta-ammines and hexaammines of the copper(II) ion, is considered to be freely rotating in these complexes and exhibits an isotropic ESR spectrum. The observation of some type of tetragonal ESR spectrum at temperatures lower than room temperature is consistent[11] with the termination of free rotation at this lower temperature. The most common reason for observing an isotropic ESR spectrum is through extensive exchange coupling between grossly misaligned local copper(II) ions, as in α-$Cu(NH_3)_2Br_2$. In these cases the line width is so broad[16] that it is sometimes difficult even to observe an ESR spectrum (*e.g.* β-$Cu(NH_3)_2Br_2$).

Axial spectra

This type of spectrum is most commonly observed with tetragonal local copper(II) ion environments in which the tetragonal axes are aligned parallel. For[14] $Cu(NH_3)_4(SCN)_2$ $g_\perp = 2.056$, $g_\parallel = 2.237$ and $G = 4.23$. This type of spectrum may also be observed, with systems of symmetry lower than tetragonal, where the misalignment is small. The effect of exchange coupling is then to decrease the spread of the observed g-values which is reflected in the observation of a G-value lower than 4.0; thus $Cu(NH_3)_2(NO_3)_2$ has an ESR spectrum with $g_\perp = 2.068$, $g_\parallel = 2.231$ and $G = 3.4$. Consequently the value of G is a useful indication of the extent of exchange coupling in tetragonal systems. The lower accuracy of the powder technique[59] for measuring the ESR of rhombic systems can result in the observation of an axial spectrum even when no misalignment is present. For example, $Cu(NH_3)_4(CuI_2)_2$ has an ESR spectrum with $g_\perp = 2.054$, $g_\parallel = 2.219$ and $G = 4.21$ measured as a powder but gives three g-values as a single crystal, $g_1 = 2.054$, $g_2 = 2.058$, $g_3 = 2.223$, the two lowest g-values not being resolved in the powder method.

Rhombic spectra

This type of spectrum can arise from the slight misalignment of rhombic or axial local copper(II) ion environments. The axial environments[33,34] of $Cu(NH_3)_4H_2O \cdot SO_4$ are misaligned by 61° and give rise to three g-values, $g_1 = 2.047$, $g_2 = 2.126$ and $g_3 = 2.172$. The effect of exchange coupling is to reduce the spread of the local g-values.

(ii) Experimental data

In the chemistry of the ammines of the copper(II) ion the most important items of information that the measurement of the ESR spectrum can give are:
a) a distinction[55] between a $d_{x^2-y^2}$ and a d_{z^2} ground state, Table 6. The latter is indicated by a low g-value (<2.04), the former by an axial (or approximately axial, $g_1 \approx g_2 = g_\perp$) spectrum with $G > 4.0$;
b) the angular directions[55] of the three crystal g-values with respect to the prominent face of a crystal. These directions can then be related to the directions of maximum polarisation or the single crystal polarised electronic spectra and enable the latter to be assigned in relation to the local molecular x-, y- and z-coordinate axes. In axial systems, where the tetragonal axes are simply related to the crystallographic axes[43,27], as in $Cu(NH_3)_2Ag(SCN)_3$ and $Na_4Cu(NH_3)_4\{Cu(S_2O_3)\}_2 \cdot NH_3$, this is a simple process[14]. In rhombic systems, where in general there is not a simple relationship between the local molecular axes and the crystallographic axes, such as $Cu(NH_3)_2(CH_3CO_2)_2$, it is much more complicated and the angular ESR data are invaluable in assigning the electronic spectra[15].

The ESR spectra of the hexaammines are most frequently isotropic at room temperature, but become anisotropic below room temperature[8]. That of $Cu(NH_3)_6Cl_2$ is exceptional in being anisotropic at room temperature but isotropic above 70°. The anisotropic spectra (at all temperatures) suggest the presence of exchange coupling ($G < 4.0$). None of the spectra show any evidence of a low g-value <2.04 and indicate a $d_{x^2-y^2}$ ground state, consistent with (but not diagnostic of) the square-based pyramidal structure[11] suggested for the $Cu(NH_3)_5^{2+}$ cation.

Similar comments apply to the ESR spectra observed[11] for the pentaammines except that the anisotropic spectra for the sulphate and hexafluorophosphate (Table 6) at room temperature and the perchlorate and iodide at low temperature, all show $G > 4.0$. They indicate much less evidence for the presence of exchange coupling and more certain evidence for a $d_{x^2-y^2}$ ground state and hence the proposed square-base pyramidal stereochemistry. The isotropic spectrum observed for the $Cu(NH_3)_5^{2+}$ cation in aqueous solution with $g = 2.118$ fits the equation $3g_i = 2g_\perp + g_\parallel$, and has been interpreted as due to a tumbling motion of the cation in solution[60].

All the tetraammines of known crystal structure, except the sulphate, have their tetragonal axes aligned parallel and consequently give rise to two g-values (but see $Cu(NH_3)_4(CuI_2)_2$). The $Cu(NH_3)_4X_2$ complexes (where $X = ClO_4^-$ and NO_3^-), give three g-values indicative of the presence of misaligned tetragonal axes and hence of exchange coupling in these complexes, the other properties of which indicate a tetragonal octahedral $Cu(NH_3)_4^{2+}$ cation[15].

The necessity of involving anion bridging in the diammines in order to make up the coordination number to six, increases the possibility of exchange coupling complicating the observed ESR spectra. This has already been noticed in the diammine halides[16]. Some evidence for the reversed tetragonal octahedral environment of some of these has been obtained from the dilution of these complexes in the appropriate isomorphous ammonium halide[61], Fig. 8. All three spectra indicate a low g-value of <2.05. In the diammine complexes, other than the halides, three g-values are observed, as in $Cu(NH_3)_2(CH_3CO_2)_2$, but only two g-values are obtained if the two lowest g-values are numerically close together [see $Cu(NH_3)_2(SCN)_2$]. The observed ESR spectrum[17] of $Cu(NH_3)_2Ag(SCN)_3$, Table 6, with $g_\parallel = 2.00$ and $g_\perp = 2.207$ has been used to establish an ESR criterion for trigonal bipyramidal structures. Exchange coupling through misaligned trigonal axes can still modify the observed crystal g-values[17]; this mechanism has been suggested to explain the isotropic ESR spectra observed[16] for $Cu(NH_3)_2SO_4$ and $Cu(NH_3)_2SeO_4$, which both have electronic spectra (see later) consistent with a trigonal-bipyramidal stereochemistry.

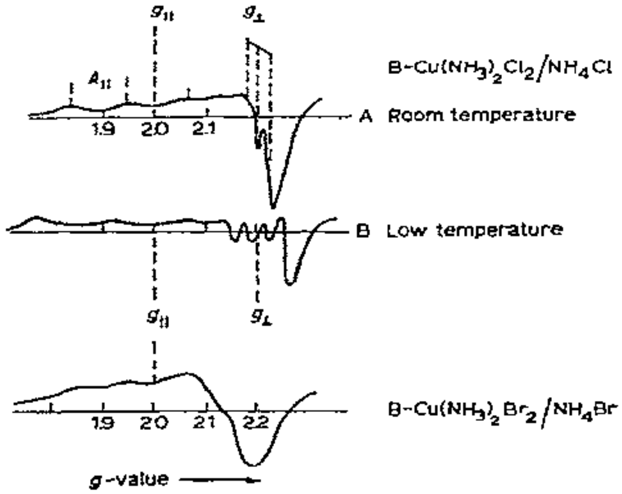


Fig. 8. The ESR spectra of $Cu(NH_3)_2X_2$ complexes diluted in NH_4X.

Both $Cu(NH_3)_2CO_3$ and $Cu(NH_3)_2C_2O_4$ have axial spectra with $G > 4.0$ consistent[16] with the rather distorted square-based pyramidal stereochemistries indicated by the X-ray data.

Of the monoammine complexes the spectra of the $[Cu(bipy)_2NH_3]X_2$ complexes[26], where $X = BF_4^-$ and ClO_4^- show (Fig. 9) a low g-value less than 2.04. This suggests a d_{z^2} ground state and is consistent with a distorted trigonal bipyramidal stereochemistry for these complexes (see electronic spectra). The ESR spectra of the $[Cuen_2NH_3]X_2$ type complexes[24] are complicated by exchange coupling but a number (such as the iodide, Fig. 9) shows two g-values with $G > 4.0$ consistent with a $d_{x^2-y^2}$ ground state and with a square-based pyramidal stereochemistry. The ESR spectra of the decaammines[15] are isotropic in agreement with the presence of strong exchange coupling suggested by the electronic spectra between the two non-equivalent stereochemistries (see later).

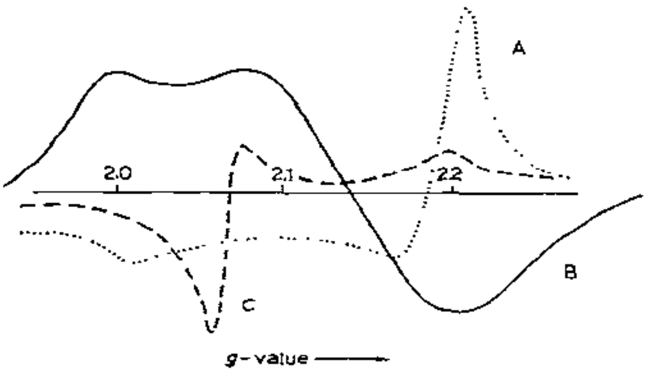


Fig. 9. The powder ESR spectra (first derivative) of A, $Cu(NH_3)_2Ag(SCN)_3$; B, $[Cubipy_2NH_3](ClO_4)_2$; C, $[Cuen_2NH_3]I_2$.

G. ELECTRONIC SPECTRA

The ammines of the copper(II) ion are characterised by colours ranging from the pale blue of the hexaammines[8] and pentaammines[11] to the royal blue to purple of the tetraammines[14]. A number of the ammines[16] are green, *i.e.* $Cu(NH_3)_2Ag(SCN)_3$, or red-brown, *i.e.* $Cu(NH_3)_4(CuBr_2)_2$[14], but these colours probably arise from the presence of low energy copper-anion charge transfer bands. In general, the colour of a copper(II) ammine gives little indication of the environment of the copper(II) ion present.

A better criterion of the stereochemistry of the copper(II) ion in a complex, is its electronic spectrum as this is determined by the relative ordering and the energies of the one-electron energy levels, Fig. 10. For the copper(II) ion these are simply related to the sequence of the symmetry representations derived from the single ^2D Russell–Saunders term. This relationship is illustrated for the copper(II) ion in an elongated tetragonal octahedral stereochemistry in Fig. 10. For simplicity the transitions between these levels will be labelled using the one-electron orbital levels rather than their symmetry representations as the latter change with symmetry. The relative energies of the *d–d* transitions of the copper(II) ion are such that the electronic transitions involved generally occur within 5.0 *kK* of each other. As the half-widths of these transitions can be as large as 3.0 *kK* the transitions tend to appear within the same band envelope with little or no resolution of the separate components. Attempts have been made to resolve such spectra[62] (measured in solution and in the solid state by reflectance[56,11]) into their gaussian components, but even when satisfactory the assignment of the individual bands can only be effected by intelligent guessing. More satisfactory, if not necessarily absolute, data may be obtained from the measurement[62] of the polarised single crystal electronic spectra of complexes but this requires that if there is more than one molecule in the unit cell, their local molecular axes should be approximately aligned. Under favourable circumstances the ordering of some of the one-electron energy levels present may be determined[64–69,14,53]. A very desirable prerequisite to such measurement is a knowledge of the one-electron orbital ground state of the copper(II) ion and the value of the ESR spectrum in distinguishing between the $d_{x^2-y^2}$ and d_{z^2} ground states (the only two which occur in practice in the ammine complexes), Fig. 7, has already been referred to. Given the ground state, the sequence of the one-electron orbitals may then be determined from the polarised spectra. The amount of data available on the polarised spectra of copper(II) ammines is rather restricted[14,15] (a recent review[70] of polarised electronic spectra listed seventeen examples of copper(II) complexes, not one of which involved ammonia as a ligand). The polarisation data now available will first be discussed and used to substantiate, where possible, the one-electron orbital sequences which have been tentatively suggested in the past, Fig. 11. Against this background, the much more extensive data available from the resolution of the reflectance spectra of copper(II) ammines of known crystal structure will be reviewed.

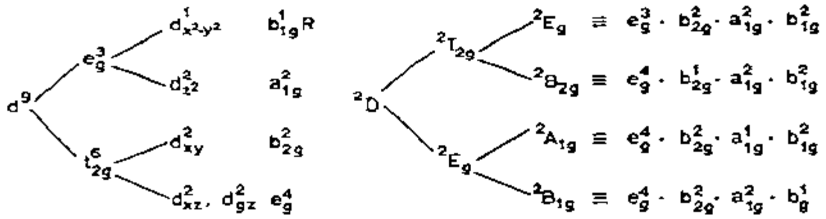


Fig. 10. The relationship between the spectroscopic terms and the one-electron energy configuration for a copper(II) ion in an elongated tetragonal octahedral ligand field of D_{4h} symmetry.

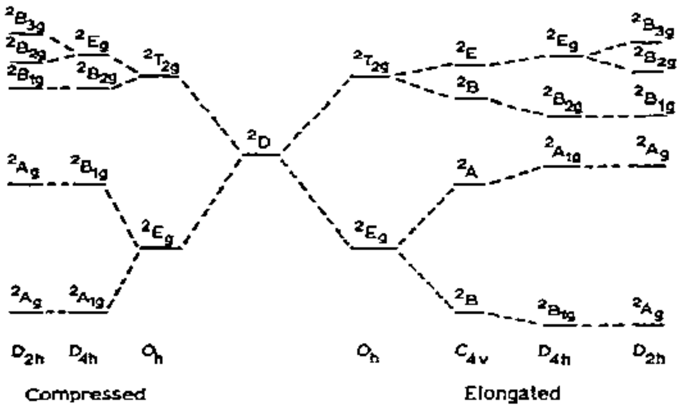


Fig. 11. The splitting of the ^2D term of the copper(II) ion in ligand fields of different symmetries.

(i) Polarised single crystal data

The best data available is on the tetraammine copper(II) complexes[14]; those for $Cu(NH_3)_4(NO_2)_2$ and $Cu(NH_3)_4(SCN)_2$ are very similar, the spectra of the latter being shown in Fig. 12 at room temperature and at liquid nitrogen temperature. Both complexes can be considered as tetragonal octahedral despite some uncertainties in the X-ray crystallographic data[32,35]. Both spectra involve the bulk of the intensity in xy-polarisation in a band at 17.5 *kK*. The z-polarised spectrum

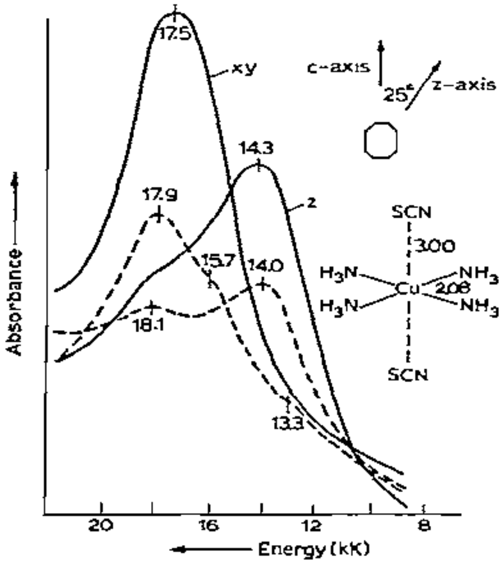


Fig. 12. The polarised electronic spectra and molecular structure of $Cu(NH_3)_4(SCN)_2$. (In this and following Figs., the solid line is the room-temperature spectrum, and the broken line the liquid nitrogen temperature spectrum.)

is much less intense with a maximum at 14.3 *kK*. The low temperature xypolarised spectrum of $Cu(NH_3)_4(SCN)_2$ shows some evidence of a weak shoulder at 15.7 *kK*. Both spectra have been assigned[14] in D_{4h} symmetry and the individual bands reasonably assigned as the $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$, $d_{z^2} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions respectively and establish a one-electron orbital sequence of $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz}, d_{yz}$ for the copper(II) ammines of tetragonal octahedral stereochemistry.

The original polarised electronic spectra of $Na_4Cu(NH_3)_4\{Cu(S_2O_3)_2\}_2$, Fig. 13, compares[14] very closely with that of $Cu(NH_3)_4(SCN)_2$, both in band positions and polarisation, substantiating the more recent X-ray crystallographic data[28] which considers the complex to be a tetragonal octahedral monoammine with the additional ammonia group positioned between the copper(II) ions along the c-axis. As the crystallographic data requires a centre of symmetry at the [0, 0, ½] position, the ammonia group cannot sit strictly on this position. It is considered to undergo an inversion vibration along the c-axis coupled with free rotation about this axis consistent with the high temperature anisotropy of the ammine group parallel to the c-axis. The establishment of an isostructural monohydrate[29] of the above tetraammine is of particular interest as the electronic spectra (for the ESR spectra and infrared spectra, see later) are clearly different from that of the monoammine, Fig. 13, and shows marked resemblance[14] to that of $Cu(NH_3)_4(CuBr_2)_2,H_2O$. The bands in both polarisations lie to significantly higher energy than those of the monoammine. In D_{4h} symmetry the $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transitions lie at 19.2 and 17.4 *kK* and the $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions at 18.4 and

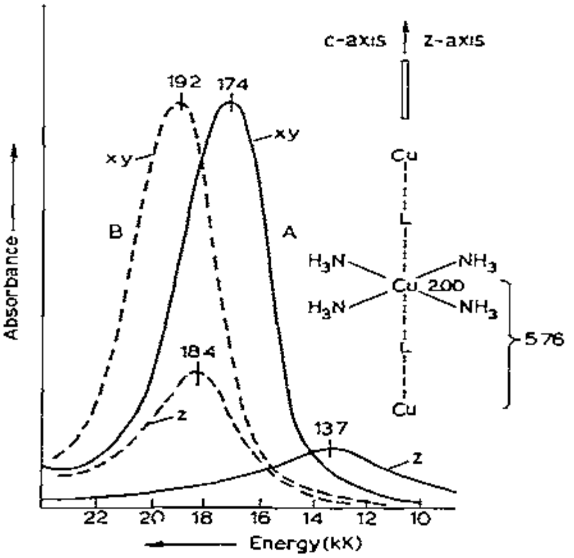
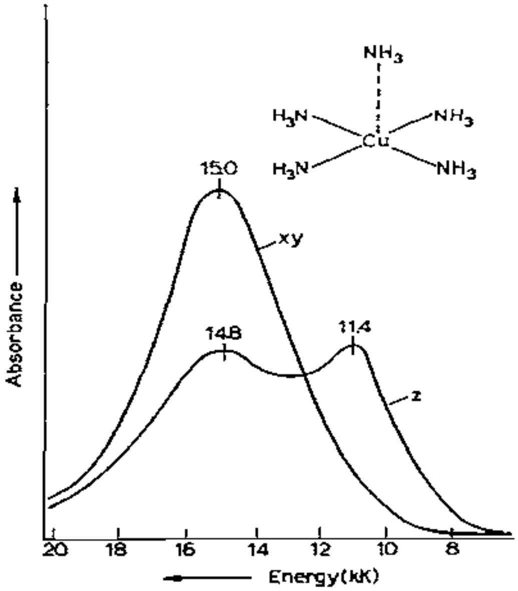


Fig. 13. The polarised electronic spectra and molecular structure of $Na_4Cu(NH_3)_4\{Cu(S_2O_3)_2\}_2,L$; A, NH_3 (—); B, H_2O (– – –).

13.7 *kK* for the monohydrate and monoammine, respectively. The greater energy of the monohydrate $d_{z^2} \rightarrow d_{x^2-y^2}$ transition suggests that the monohydrate involves a greater tetragonal distortion than the monoammine; *i.e.* the $Cu(NH_3)_4{}^{2+}$ ion is more nearly square-coplanar and the water molecule in the monohydrate is not coordinated to the copper(II) ion. In order to fulfil the centre of symmetry requirement of the [0, 0, ½] position, the water molecule is considered to lie in the plane at right angles to the c-axis and to be rotating about its centre of gravity.

The energy levels of a strictly square-coplanar $Cu(NH_3)_4{}^{2+}$ would be expected to occur (Fig. 11) at even higher energy[14] than those for a tetragonal-octahedral complex (an increase of 2.6 *kK* has been established for the CuO_4X_2 chromophore[68]). No tretraammine spectra[15] have been observed with energies appreciably higher than those observed above and suggest that a strictly square-coplanar $Cu(NH_3)_4{}^{2+}$ cation has not yet been prepared. The polarised single crystal spectra of $(NH_4)\,[Cu(NH_3)_5]\,(ClO_4)_3$ have been reported previously[48] and interpreted as a tetraammine, but in view of the uncertainty about the structure of the complex[44], this assignment should be treated with caution. Numerically, the transitions[48] are consistent with a tetragonal octahedral $Cu(NH_3)_4{}^{2+}$ cation (in conflict with the X-ray data), but the inability to reproduce this data and the resemblance of the electronic and infrared spectra to that of a pentaammine[11], leaves the structure of this complex uncertain.

The polarised single crystal spectra[15] of $(NH_4)Cu(NH_3)_5(PF_6)_3$ are shown in Fig. 14. Only two bands are observed at 11.4 and 15.0 *kK*, both appreciably



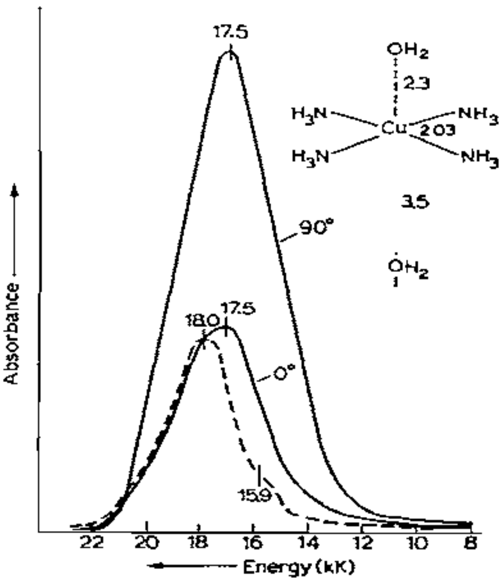
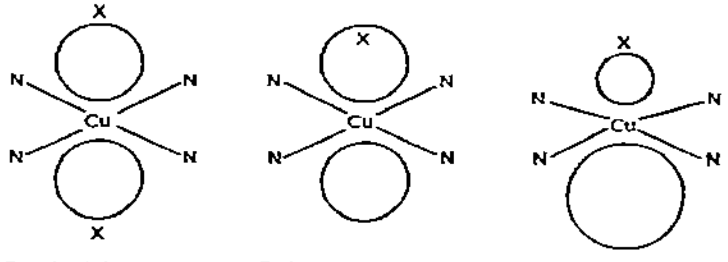


Fig. 14. The polarised electronic spectra and molecular structure of $NH_4[Cu(NH_3)_5](PF_6)_3$.

Fig. 15. The polarised electronic spectra and molecular structure of $Cu(NH_3)_4H_2O$, SO_4.

lower in energy than the bands of the tetragonal octahedral tetraammines and consistent with the reduced tetragonal distortion (Fig. 11) expected for the square-based pyramidal stereochemistry predicted for this complex. The polarised spectra have been interpreted[15], using the directions given by the single crystal ESR spectra in C_{4v} symmetry. The maximum at 15.0 kK has been assigned as the $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transition and the 11.4 kK band as the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition. A square-based pyramidal $Cu(NH_3)_4OH_2{}^{2+}$ stereochemistry has been confirmed recently[34] for the $Cu(NH_3)_4H_2O \cdot SO_4$ complex. The crystal structure is not ideal for polarisation measurements as the local molecular tetragonal axes of the four molecules per unit cell are misaligned by 61°. The polarised spectra[15] are shown in Fig. 15. It consists of a single intense maximum at 17.5 kK in xy-polarisation which simply loses intensity in z-polarisation. There is some evidence of a weak shoulder at low temperature. Of particular interest is that in going from a tetragonal octahedral to a square-based pyramidal tetraammine, $Cu(NH_3)_4(SCN)_2$ to $Cu(NH_3)_4H_2O, SO_4$ with a single Cu–OH_2 bond of 2.3Å, the position of the absorption maximum, 17.5 kK, does not change and the position of the low energy band, if anything, has increased in energy not decreased, as found in the pentaammines. Why the presence of a fifth ammonia group should have such a marked effect on the spectrum of the $Cu(NH_3)_4{}^{2+}$ cation while that of a single water molecule has much less effect, is not clear. The only obvious difference between these two ligands is the π-bonding potential of the water molecule. It may be significant that in the $Cu(NH_3)_4H_2O^{2+}$ unit of the sulphate complex the copper(II) ion is lifted 0.2 Å out of the plane of the four nitrogen atoms[34] towards the water molecule, leaving an "empty space" below the copper(II) ion; the second molecule of water lies at a distance of 3.7 Å. It is suggested, in order to account for these results, that the two electrons normally distributed equally in a d_{z^2} orbital above and below the copper(II) ion remain equally distributed in the $Cu(NH_3)_5{}^{2+}$ cation, Fig. 16B. The copper(II) ion then remains situated in the plane of the four nitrogen atoms and the degree of tetragonal distortion (as measured by the energy of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition) is reduced. In the $Cu(NH_3)_4OH_2{}^{2+}$ cation



A. Regular tetragonal octahedral

B. In-plane square-based pyramidol

C. Out-of-plane square-based pyramidal

Fig. 16. The distribution of the electron density in the d_{z^2}-orbital in square-based pyramidal stereochemistries.

the charge distribution is not equal, Fig. 16C, but is mainly distributed below the copper(II) ion which is then displaced out of the plane of the four nitrogen atoms. In this situation, the degree of tetragonal distortion as measured by the energy of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition is no longer strictly comparable to that obtained in the tetragonal octahedral complexes. The data in Fig. 15 suggest that the energy of the $d_{z^2} \rightarrow d_{y^2-y^2}$ transition has actually increased in energy relative to that of the tetragonal octahedral case as the copper(II) ion moves out of the plane of the four nitrogen atoms. The possibility that the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition lies at very much lower energy, namely below 5.0 *kK*, is ruled out as this would decrease the energy of the $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transition as well, this being equal to $10D_q + \frac{1}{2}E_{d_{z^2} \rightarrow d_{x^2-y^2}}$. The complex $Cu(NH_3)_2Ag(SCN)_3$ contains probably the best example[43] of a "regular" trigonal bipyramidal CuN_5 chromophore, with all of its trigonal axes aligned parallel. Fig. 17 shows the polarised spectra[15]. Two clear bands are observed, one at 10.5 *kK* in xy-polarisation and one at 14.6 *kK* in x-, y- and z-polarisation. There is also one or possibly two bands in xy-polarisation at approximately 13.3 *kK*. The single crystal ESR spectrum establishes that the g-value is isotropic within the xy plane. The appearance of three (or possibly four) electronic transitions is surprising as a crystal field model[71] would predict only the two transitions $d_{xy}, d_{xz} \rightarrow d_{z^2}$ and $d_{x^2-y^2}, d_{xy} \rightarrow d_{z^2}$ with the latter at lower energy. Either a symmetry lower than D_{3h} (C_2, D_2, or C_{2v}) is present or spin–orbit coupling is responsible. The possible energy level diagram including spin–orbit coupling[72] is shown in Fig. 18 along with the polarisations predicted for a D_{3h} double group.

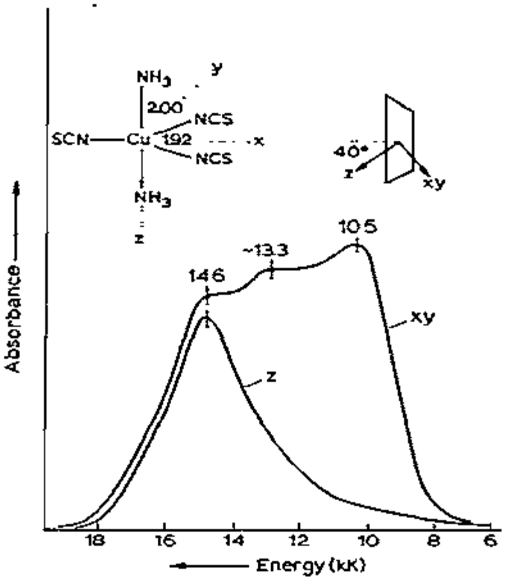
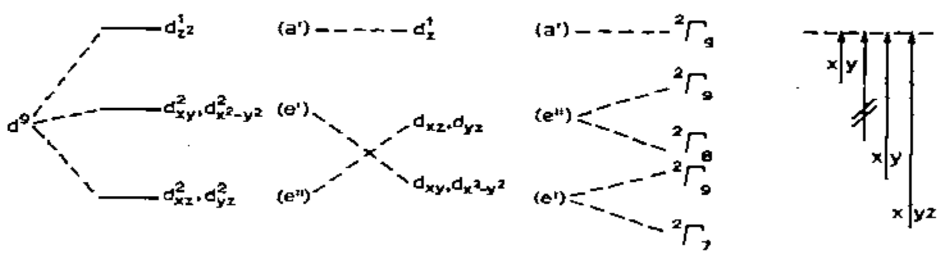


Fig. 17. The polarised electronic spectra and molecular structure of $Cu(NH_3)_2Ag(SCN)_3$.



a) Crystal field splitting D_{3h} symmetry
b) including out-of-plane π-bonding
c) including spin-orbit coupling
d) selection rules in D_{3h}^{1}

Fig. 18. The one-electron energy levels of the copper(II) ion in a crystal field of a) D_{3h} symmetry; b) including out-of-plane π-bonding; c) including spin–orbit coupling; d) the electronic selection rules in the D_{3h} double group.

As the splitting of the e' and e'' levels by spin–orbit coupling is less than 1.66 and 0.83 *kK* respectively, the polarised spectra allows the assignment of the band at 14.7 *kK* as the $^2\Gamma_7 \leftarrow {}^2\Gamma_8$ transition and those at 13.3 and 10.5 *kK* as the $^2\Gamma_9 \leftarrow {}^2\Gamma_8$ transitions. This assignment places the e' level at higher energy than the e'' level contradicting the order suggested by crystal-field calculations[71]. Some support for this reversal in order has been obtained from the interpretation (in C_{2v} symmetry) of the polarised electronic spectrum of the distorted trigonal bipyramidal complex [Cubipy$_2$I]I which also places the parent e' level above that of the e'' level[15]. These results suggest that a substantial amount of π-bonding is affecting the relative positions of the e' and e'' levels. As the ammonia molecule can only function as a

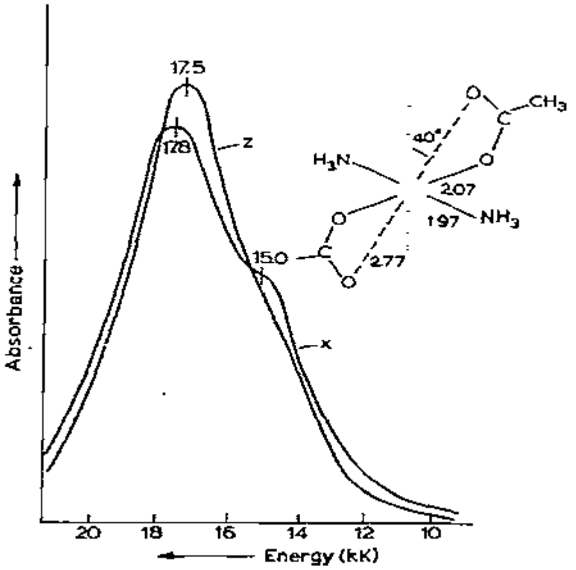


Fig. 19. The polarised electronic spectrum and molecular structure of Cu(NH$_3$)$_2$(CH$_3$CO$_2$)$_2$.

σ-bonding ligand, the π-bonding can only occur through the in-plane thiocyanate ligands, which can π-bond out of the plane through the d_{xz} and d_{yz} orbitals. It may be significant that the in-plane copper–nitrogen bonds are the shortest (1.92 Å) being appreciably shorter than those observed in other nitrogen-bonded copper thiocyanate complexes, 1.99[36] and 1.97 Å[40].

The polarised single crystal spectra[15] of $Cu(NH_3)_2(CH_3CO_2)_2$ are shown in Fig. 19; the local molecular structure is rhombic, but the two molecules in the unit cell[40] are misaligned by 60°. The polarisation data show a main band at 17.5–18.0 *kK* and a significant shoulder at 15.0 *kK*. The polarisation data have been tentatively interpreted in D_{2h} symmetry with the bands at 17.8, 17.5 and 15.0 *kK* assigned as the d_{xz}, d_{yz} and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions, respectively. The position of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition is less certain but probably lies at 17.5 ± 0.5 *kK*. The high energy of the latter transition reflects the relatively high tetragonal distortion of this complex towards square-coplanarity due to the displacement of the chelate oxygen groups 40° away from the z-axis. The separation of the d_{xz} and d_{yz} levels by 0.5 *kK* reflects a comparable rhombic distortion[66] to that present in $Ba_2Cu(HCO_2)_6 4H_2O$.

No polarised single crystal spectra have been obtained for a compressed tetragonal stereochemistry, but preliminary X-ray crystallographic data[22] have suggested that $Cu(NH_3)_2C_2O_4 \cdot 2H_2O$ has a compressed rhombic stereochemistry. The single crystal ESR spectrum was not able to confirm that this complex has a d_{z^2} ground state. The polarised single crystal spectra are shown in Fig. 20; they closely resemble those of an elongated rhombic CuO_6 chromophore with a $d_{x^2-y^2}$

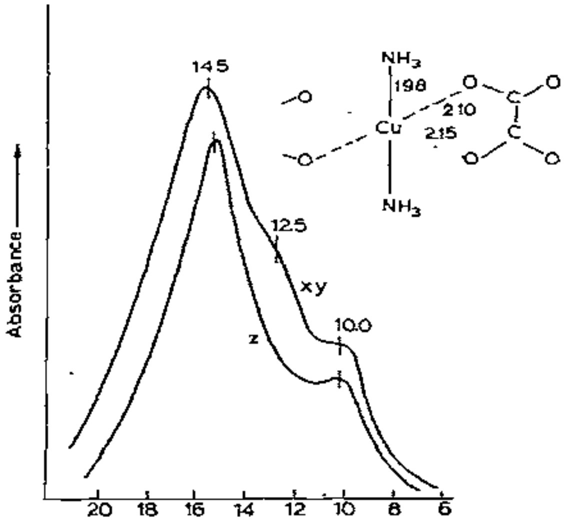


Fig. 20. The polarised electronic spectra and molecular structure of $Cu(NH_3)_2C_2O_4 2H_2O$.

ground state. A comparison of the energies of all three bands with those[66] of $Ba_2Cu(HCO_2)_6 \cdot 4H_2O$ is consistent with the tentative assignment of the lowest energy band at 10.0 *kK* as the $d_{x^2-y^2} \rightarrow d_{z^2}$ transition. The bands at 14.5 and 12.5 *kK* are then assigned as the $d_{xz}, d_{yz} \rightarrow d_{z^2}$ and $d_{xy} \rightarrow d_{z^2}$ transitions, respectively. However the close similarity of these spectra to those of $Ba_2Cu(HCO_2)_6 4H_2O$ and the failure to confirm the d_{z^2} ground state by the ESR studies places serious doubt upon this assignment.

The results of the assignments based upon polarised single crystal measurements are collected in Table 7.

TABLE 7

ASSIGNMENT OF THE POLARISED SINGLE CRYSTAL ELECTRONIC SPECTRA OF $Cu(NH_3)_xX_2$ COMPLEXES

Complex	*kK*	*Assignment*
$(NH_4)[Cu(NH_3)_5](PF_6)_3$	15.5	$d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$
	11.4	$d_{z^2} \rightarrow d_{x^2-y^2}$
$Na_4Cu(NH_3)_4\{Cu(S_2O_3)_2\}_2, NH_3$	17.4	$d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$
	13.6	$d_{z^2} \rightarrow d_{x^2-y^2}$
$Na_4Cu(NH_3)_4\{Cu(S_2O)_3)_2\}_2, H_2O$	19.2	$d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$
	18.4	$d_{z^2} \rightarrow d_{x^2-y^2}$
$Cu(NH_3)_4(NO_2)_2$	17.1	$d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$
	13.4	$d_{z^2} \rightarrow d_{x^2-y^2}$
$Cu(NH_3)_4(SCN)_2$	17.5	$d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$
	14.3	$d_{z^2} \rightarrow d_{x^2-y^2}$
$Cu(NH_3)_4H_2O,SO_4$	17	$d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$
$Cu(NH_3)_2(CH_3CO_2)_2$	17.8	$d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$
	15.0	$d_{xy} \rightarrow d_{x^2-y^2}$
	17.5 ± 0.5	$d_{z^2} \rightarrow d_{x^2-y^2}$
$Cu(NH_3)_2Ag(SCN)_3$	14.6	$\Gamma_7 \leftarrow \Gamma_8$
	13.3	$\Gamma_9 \leftarrow \Gamma_8$
	10.5	$\Gamma_9 \leftarrow \Gamma_8$
	[11.1	$\Gamma_8 \leftarrow \Gamma_8$]

(ii) Reflectance spectra

The reflectance spectra of a wide range of ammine complexes[8,11,14,16,24,26] of the copper(II) ion along with their approximate analysis into gaussian components are listed in Table 8. The relative intensities of the bands are given in brackets on the Beckman scale of 0–2. Representative spectra are shown in Figs. 21, 23, 24.

The hexaammines[8] and pentaammines[11] are characterised by virtually identical electronic spectra consisting of a relatively intense band at *ca.* 16.0 *kK* and a lower energy, lower intensity shoulder at *ca.* 11.0 *kK* with the centre of gravity of the band envelope clearly at lower energy than that of the corresponding tetraammines, Fig. 21. The latter emphasises the electronic effect of adding a fifth ammonia group to a $Cu(NH_3)_4^{2+}$ cation and is consistent with the reduction in the tetragonal distortion (as suggested in Fig. 11) from D_{4h} to C_{4v} symmetry. The

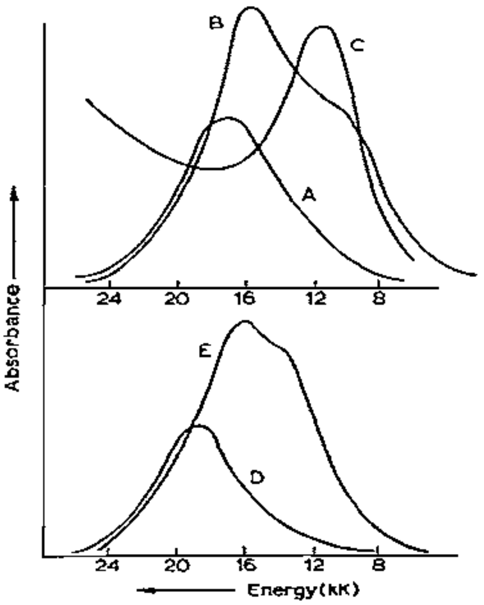
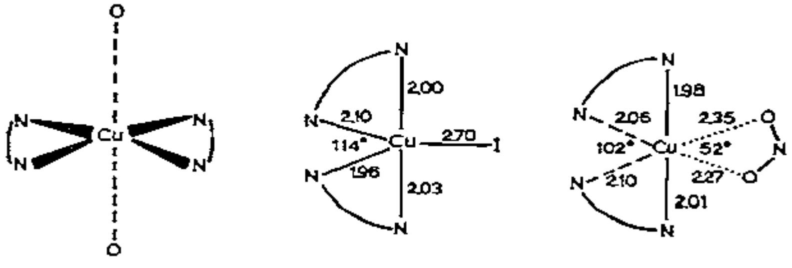


Fig. 21. The electronic reflectance spectra of A, $Cu(NH_3)_4(BF_4)_2$; B, $Cu(NH_3)_5(BF_4)_2$; C, $Cu(NH_3)_2Ag(SCN)_3$; D, $Cuen_2(ClO_4)_2$; E, $[Cuen_2NH_3](ClO_4)_2$.



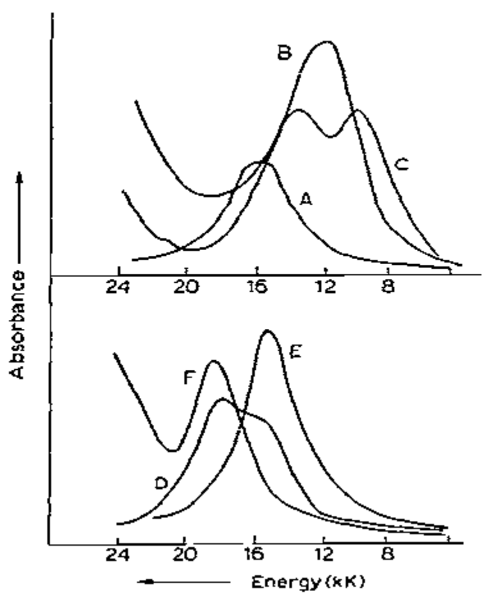
A. Cu bipy$_2$ $(ClO_4)_2$
Twisted tetragonal octahedral

B. [Cu bipy$_2$ I]I
Distorted trigonal bipyramidal

C. [Cu bipy$_2$ (ONO)]NO_3
Cis-distorted octahedral

Fig. 22. The molecular structure of some complexes of the $Cubipy_2^{2+}$ cation.

close similarity of the hexaammine and pentaammine spectra is striking and strongly suggests that the stereochemistry of the copper(II) ion is similar in both series of complexes. The difference between these spectra and those of a tetragonal octahedral stereochemistry for the $Cu(NH_3)_6^{2+}$ ion [as in the $Cu(NH_3)_4X_2$ complexes], Fig. 21A, argues against this environment for the hexaammines. The possibility of a $Cu(NH_3)_4^{2+}$ cation being present with a strictly square-coplanar stereochemistry is ruled out, by the earlier suggestion that this cation, due to an even higher tetragonal distortion than in the tetragonal octahedral tetraammines, would have an electronic spectrum at even higher energy than that of 17.5 *kK* shown by



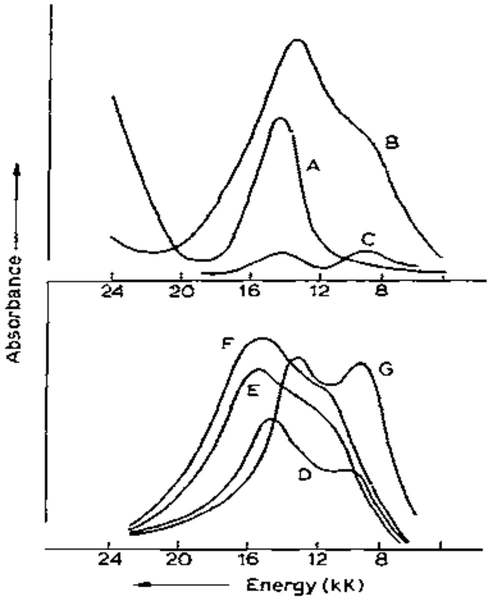


Fig. 23. The electronic reflectance spectra of A, Cubipy$_2$(ClO$_4$)$_2$; B, [Cubipy$_2$NH$_3$](ClO$_4$)$_2$; C, [Cubipy$_2$(ONO)]NO$_3$; D, Cu(NH$_3$)$_2$(CH$_3$CO$_2$)$_2$; E, Cu(NH$_3$)$_2$CO$_3$; F, Cu(NH$_3$)$_2$(NO$_2$)$_2$.

Fig. 24. The electronic reflectance spectra of A, α-Cu(NH$_3$)$_2$Cl$_2$; B, β-Cu(NH$_3$)$_2$Br$_2$; C, β-Cu(NH$_3$)$_2$Br$_2$ diluted in NH$_4$Br; D, Cu(NH$_3$)$_2$C$_2$O$_4$2H$_2$O; E, α-Cu(NH$_3$)$_2$C$_2$O$_4$; F, β-Cu(NH$_3$)$_2$C$_2$O$_4$; G, γ-Cu(NH$_3$)$_2$C$_2$O$_4$.

the latter[14]. The possibility of a trigonal bipyramidal stereochemistry for the common $Cu(NH_3)_5{}^{2+}$ cation of the hexaammines and pentaammines is not supported by the observation[17] of a single peak for the trigonal bipyramidal CuN_5 chromophore known to be present in $Cu(NH_3)_2Ag(SCN)_3$. The band maximum occurs at 12.8 *kK* at lower energy than the band maximum of the pentaammines, Fig. 21C.

The reflectance spectra of the tetraammines[14] are characterised by a single maximum at 17.5 *kK* of relatively low intensity with occasionally a weak shoulder on the low frequency side, the former is assigned as the $d_{yz}, d_{xz} \rightarrow d_{x^2-y^2}$ transition and the latter as the $d_{z^2} \rightarrow d_{x^2-y^2}$ by comparison with the single crystal spectra. As the bulk of the intensity resides in the former transition (see polarised spectra) reasonably accurate values for these two transitions may be obtained from these reflectance spectra.

Comparable changes in the electronic reflectance spectra are shown by the $Cuen_2{}^{2+}$ cation[56,67] upon addition of a molecule of ammonia[24], Fig. 21D and E. The tetragonal octahedral $Cuen_2X_2$ complexes have a single low intensity band at 19.0 *kK*. The adducts have a characteristic "pentaammine" type electronic spectrum, but at slightly higher energy than that of the pentaammines. The electronic spectra of the monoammine adducts[26] of the $Cubipy_2{}^{2+}$ cation are also significantly different from the parent cation; the latter cannot assume a strictly coplanar conformation due to steric hindrance by the hydrogen atoms[73] in the 3,3′ positions of the bipyridyl ligands. In $Cubipy_2(ClO_4)_2$ the conformation probably involves a tetragonal octahedral stereochemistry with the bipyridyls twisted out of the plane[26], Fig. 22; this twist is exaggerated to give a trigonal bipyramidal stereochemistry[74] in $[Cubipy_2I]I$ and a *cis*-distorted octahedral stereochemistry in $[Cubipy_2(ONO)]NO_3$. The close similarity of the reflectance spectra[76,26], Fig. 23B, of $[Cubipy_2I]I$ and $[Cubipy_2NH_3]ClO_4$ strongly suggest a trigonal bipyramidal stereochemistry (with the iodine atom of Fig. 22B replaced by a molecule of ammonia) for these adducts rather than a square-based pyramid, as suggested for the monoammine adducts of the $Cu(NH_3)_4{}^{2+}$ and $Cuen_2{}^{2+}$ cations, a difference presumably imposed by the steric requirements of the $Cubipy_2{}^{2+}$ cation.

The diammine complexes of the copper(II) ion exhibit the widest range of stereochemistries of any class of ammines due to the involvement of the anions present in coordination to the copper(II) ion. Consequently, they exhibit the widest range of reflectance spectra[16]. The spectrum of $Cu(NH_3)_2Ag(SCN)_3$ (Fig. 21C) has been already taken as characteristic[17] of a trigonal bipyramidal CuN_5 chromophore. The close similarity of the reflectance spectra, Table 8, of $Cu(NH_3)_2SO_4$ and $Cu(NH_3)_2SeO_4$ suggests a similar stereochemistry in these two complexes. The reflectance spectrum of the square-based pyramidal $Cu(NH_3)_2CO_3$, Fig. 23E, shows a relatively intense maximum at 15.75 *kK* typical of this stereochemistry, but shows no evidence of the low frequency shoulder characteristic of the pentaammine spectra. This complex has a fifth copper–oxygen bond of 2.57 Å comparable to that in $Cu(NH_3)_4H_2O,SO_4$ which also failed to produce a "pentaammine" type spectra. In the carbonate the relatively high intensity could be produced by the *cis*-arrangement of the two ammonia groups removing the strict in-plane centre of symmetry. The rhombic diammines, Fig. 23A, show relatively low intensity reflectance spectra, sometimes split into two bands, as in $Cu(NH_3)_2(CH_3CO_2)$ and $Cu(NH_3)_2I_2$ but occasionally only a single peak at approximately 17.0 *kK* as in $Cu(NH_3)_2(SCN)_2$ and $Cu(NH_3)_2(NO_3)_2$. $Cu(NH_3)_2(NO_2)_2$, Fig. 23F, and $Cu(NH_3)_2(ONO)_2$ have single bands at 18.2 and 16.7 *kK* respectively, consistent with the relative positions of the nitro and nitrito ligands in the spectrochemical series[4]; both spectra are rather more intense than that predicted for a rhombic stereochemistry, an intensity which may well arise from the close proximity of the ligand charge transfer bands of the nitrite ligands. The interpretation of the chloride and bromide spectra is less clear, Fig. 24. The β-chloride and the α- and β-bromides are characterised by a relatively intense maximum at 14.5 *kK* and a low frequency shoulder at 9.5 *kK*, whilst α-$Cu(NH_3)_2Cl_2$ has a single intense peak at 14.7 *kK*. All four spectra lie at rather lower energy than the remaining diammines, this fact and the relatively high intensity of the spectra may be associated with the reversed tetragonal stereochemistry present. The rather complicated number of phases isolated from the $Cu(NH_3)_2C_2O_4$ system has been summarised in Fig. 3.

TABLE 8

ELECTRONIC REFLECTANCE SPECTRA (*kK*) OF $Cu(NH_3)_xX_2$ COMPLEXES AND IN CERTAIN CASES THEIR GAUSSIAN COMPONENTS

Complex	*Electronic spectra*			*Gaussian components*		
1. *$Cu(NH_3)_6X_2$*						
Cl^-	16.4	11.2				
Br^-	16.2	11.0				
I^-	15.9	10.5				
ClO_4^-	15.9	11.0				
BF_4^-	15.6	10.9				
2. *$Cu(NH_3)_5X_2$*						
Cl^-	16.4 (1.3)	11.4 (0.8)		17.1	13.4	10.2
Br^-	16.3 (0.8)	11.8 (0.6)		17.0	13.2	10.4
I^-	16.1 (1.1)	11.6 (0.8)		16.9	13.2	10.3
ClO_4^-	15.9 (1.1)	11.2 (0.8)		16.8	13.0	10.0
BF_4^-	15.9 (1.2)	11.2 (0.8)		16.8	13.0	10.0
$\frac{1}{2}SO_4^{2-}$	17.0 (0.8)	11.6 (0.3)		17.6	16.2	12.3
$(NH_4)[Cu(NH_3)_5](ClO_4)_3$	15.9 (1.0)	11.2 (0.9)		15.8	13.0	10.4
$(NH_4)[Cu(NH_3)_5](PF_6)_3$	15.3 (1.0)	11.0 (0.7)		16.5	13.6	10.3
3. *$Cu(NH_3)_4X_2$*						
BF_4^-	17.3 (1.0)					
ClO_4^-	17.8 (0.9)					
$\frac{1}{2}SO_4^{2-}$	17.0 (0.75)					
$\frac{1}{2}SO_4^{2-} \cdot H_2O$	17.5 (0.8)					
4. *$Cu_3(NH_3)_{10}X_6$*						
Br^-	17.3 sh (1.5)	13.6 (2.0)				
I^-	masked	12.5 (1.1)				
5. *$Cu(NH_3)_2X_2$*						
α-Cl^-	14.7 (1.0)					
β-Cl^-	9.6 (0.8)	14.2 (1.3)	29.0 (1.6)			
α-Br^-	9.1 (0.7)	14.7 (1.1)	23.0 (1.7)			
β-Br^-	9.7 (0.9)	14.5 (1.2)	21.0			
I^-	16.0 (0.7)	18.5 (0.7)				
NO_2^-	18.2 (1.3)	30.0 (1.6)				
ONO^-	16.7 (1.2)	30.0 (1.6)				
NO_3^-	16.4 (0.8)					
SCN^-	17.0 (0.5)					
$CH_3CO_2^-$	15.7 (0.7)	17.7 (0.8)				
HCO_2^-	16.1 (1.1)					
$\frac{1}{2}CO_3^{2-}$	15.75 (1.4)					
$\frac{1}{2}SO_4^{2-}$	12.5 (1.4)					
$\frac{1}{2}SeO_4^{2-}$	12.5 (1.3)					
α-$Cu(NH_3)_2C_2O_4$	15.75 (1.1)	11.4 (0.7)				
β-$Cu(NH_3)_2C_2O_4$	15.75 (0.8)	11.4 (0.5)				
γ-$Cu(NH_3)_2C_2O_4$	13.5 (0.9)	9.3 (0.9)				
$\frac{1}{2}C_2O_4^{2-}$, $2H_2O$	14.7 (0.6)	13.5	10.0 (0.3)			
6. *$[Cuen_2NH_3]X_2$*						
Cl^-	17.3 (1.0)	12.2 (0.4)		17.7 (1.0)	14.7	10.8 (0.4)
Br^-	17.2 (0.9)	12.2 (0.5)		17.6 (0.9)	15.1	10.8 (0.45)
I^-	16.8 (1.4)	12.2 (0.8)		17.5 (1.4)	15.0	10.0 (0.75)
ClO_4^-	16.7 (1.5)	12.2 (1.4)		17.4 (1.4)	14.9	10.0 (1.2)
$\frac{1}{2}HgI_4^{2-}$	16.5 (1.1)	11.9 (0.6)		17.2 (1.1)	15.1	10.4 (0.6)
BF_4^-	16.5 (1.7)	12.2 (1.4)		17.2 (1.6)	14.7	10.0 (1.2)
NO_3^-	16.7 (1.2)	12.5 (1.0)		—	—	—
7. *$[Cubipy_2NH_3]X_2$*						
BF_4^-	12.3 (1.0)					
ClO_4^-	12.3 (1.2)					

The reflectance spectra[16] of $Cu(NH_3)_2C_2O_4$, $2H_2O$ resemble those of the diammine halides and support the compressed tetragonal stereochemistry[22] suggested for this complex. The specta of α- and β-$Cu(NH_3)_2C_2O_4$, Fig. 24, are of the pentaammine type and support the square-based pyramidal stereochemistry suggested for the α-form. The spectrum of γ-$Cu(NH_3)_2C_2O_4$ is unique in giving two almost equally intense peaks at the relatively low energies of 9.5 and 13.5 *kK*. This spectrum shows a clear resemblance[19,26] to that of the *cis*-distorted octahedral $[Cubipy_2(ONO)]NO_3$, (Fig. 23C) and suggests a similar stereochemistry for the oxalate. Unfortunately, this complex is only obtained as an amorphous powder which prevents single crystal work to confirm this suggestion.

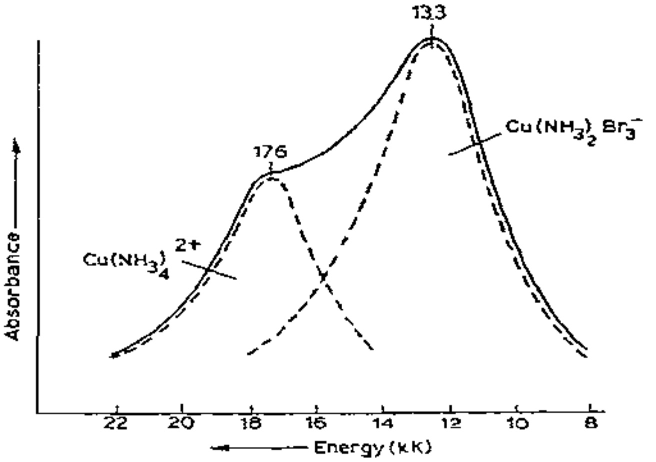


Fig. 25. The electronic reflectance spectrum of $[Cu(NH_3)_4]_2[Cu(NH_3)_2Br_3]Br_3$.

The reflectance spectrum[15] of the decaammine bromide is shown in Fig. 25. It shows a single relatively intense maximum at 13.3 *kK* and a substantial, high frequency shoulder, at 17.6 *kK*. This is interpreted in terms of a mixed stereochemistry in these complexes, namely, a tetragonal octahedral tetraammine plus a trigonal bipyramidal diammine and suggests the formulation: $[Cu(NH_3)_4]_2$-$[Cu(NH_3)_2Br_3]Br_3$.

The polarised single crystal and reflectance spectra establish a reasonably consistent sequence of energy levels for the copper(II) ammine complexes of different stereochemistries. The results substantiate the one-electron levels in Fig. 11 for the copper(II) ion in a nitrogen environment using the above experimental values. For the diammines, ligands other than ammonia such as oxygen and halide ions are present and the observed energies will be lower because of this.

H. ORBITAL REDUCTION FACTORS

When both the *g*-values and the assignment of the electronic spectra for an axial copper(II) complex are known accurately, it should be possible to determine the combined orbital and spin–orbit reduction parameters[66,77], *k*, from the expressions given in Table 5. The only ammine complexes for which sufficiently accurate data are available are the tetraammines[14]. The *k*-values obtained are listed in Table 9 along with the molecular orbital coefficients estimated from them. The more accurate values all lie between 0.73–0.78 and, where known, $k_\parallel \approx k_\perp$ (as found in the $Cuen_2X_2$ complexes[56,67]). As the energies of the $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transitions are most accurately known, the values of $k_\perp$ are generally more reliable than those of $k_\parallel$. Notwithstanding this, there appears to be no obvious relationship between the *k*-values and the lengths of the in-plane Cu–N bonds. In order to estimate the molecular orbital coefficients it is necessary to assume that β_1, (representing the in-plane π-bond coefficient) equals one. It is then possible to estimate α, the in-plane σ-bonding coefficient, and β the out-of-plane π-bonding coefficient. In the four complexes for which the *k* values are accurately known, the estimated coefficients indicate substantial in-plane σ-bonding and very little out-of-plane π-bonding. Comparable results have been found for the $Cuen_2X_2$ complexes[56,57]. In the trigonal bipyramidal complexes, only the value of $k_\perp$ is obtained, in the case of $Cu(NH_3)_2Ag(SCN)_3$ this equals 0.67 and is appreciably lower than the value of $k_\perp$ in the axial system above. Assuming that $k_\perp$ is still a measure of the α and β molecular orbital coefficients the value of 0.67 is consistent with the presence of appreciable out-of-plane π-bonding as was required above to explain the order of the *e*′ and *e*″ levels.

TABLE 9

COMBINED ORBITAL AND SPIN–ORBIT REDUCTION PARAMETERS $k_\perp$ AND $k_\parallel$ AND THE MOLECULAR ORBITAL COEFFICIENTS α, β, AND β_1

Compound	$k_\parallel$	$k_\perp$	α	β	β_1
$Na_4Cu(NH_3)_4\{Cu(S_2O_3)_2\}_2, H_2O$	0.76	0.78	0.78	1.0	1.0
$Na_4Cu(NH_3)_4\{Cu(S_2O_3)_2\}_2, NH_3$	0.78	0.77	0.78	1.0	1.0
$Cu(NH_3)_4(CuBr_2)_2, H_2O$	0.65–0.76	0.73	—	—	—
$Cu(NH_3)_4(NO_2)_2$	0.75	0.73	0.75	0.98	(1.0)
$Cu(NH_3)_4(SCN)_2$	0.74	0.76	0.74	1.0	(1.0)
$Cu(NH_3)_4H_2O,SO_4$	—	0.76	—	—	—
$Cu(NH_3)_2Ag(SCN)_3$	—	0.67	—	—	—

$k_\parallel \approx \alpha \cdot \beta_1$

$k_\perp \approx \alpha \cdot \beta$

I. INFRARED SPECTRA

(i) Ammonia vibrations

Table 10 summarises the ammonia and copper–nitrogen band frequencies of the ammines of copper(II). The ammonia vibrations change very little upon coordination[78], but there is a systematic variation[79] in the frequencies of the asymmetric deformation δ_d, ~ 1600 cm^{-1}, the symmetric deformation δ_s, 1180 cm^{-1} and the rocking mode ρ_r, 650 cm^{-1} in a series of $M^{II}(NH_3)_6Cl_2$ complexes [from iron(II) to zinc(II)], Table 11. The frequencies all increase to a maximum at copper and fall again to zinc. This sequence is said to reflect the Irving–Williams Series[79]: this may be true for the complexes excluding copper(II), but the previous data[8,11] have demonstrated that $Cu(NH_3)_6Cl_2$ should be formulated as a pentaammine rather than a hexaammine. The sequence probably reflects the increase in the metal nitrogen bond strength from manganese to nickel due to a decrease in ionic size of the divalent ions. The significantly larger jump in frequency from

TABLE 10

SOME INFRARED ASSIGNMENTS FOR $Cu(NH_3)_xX_2$ COMPLEXES (CM^{-1})

	NH_3 asymmetric deformation	*NH_3 symmetric deformation*	*NH_3 rocking*	*Cu–N stretching*	*N–Cu–N bending*
Hexaammines[78]	1609–1587	1229–1223 1105–1087 1058–1013	732–694	522–510 406–399	—
Pentaammines[11]	1645–1595	1302–1230 1272–1087	742–716	537–509 420–390	264–230
Tetraammines[14]	1635–1590	1300–1240	725–680	460–408	250–232
Diammines[16]	1673–1585	1310–1227	755–700 685–640	500–437	268–220

TABLE 11

SOME INFRARED DATA FOR THE SERIES [77,78] $M^{II}(NH_3)_6Cl_2$, $Mn^{II} \rightarrow Zn^{II}$

	Mn	*Fe*	*Co*	*Ni*	*Cu*	*Zn*
NH_3 degen. deform.	1592	1597	1602	1607	1609	1596
NH_3 sym. deform.	1134	1151	1163	1175	1229 1087 1013	1145
NH_3 rocking	617	641	654	650	732 519	645
M–N stretching	307	321	327	334	406	300

the nickel(II) to the copper(II) complex reflects the formation of an even shorter copper–nitrogen bond due to the formation of a tetragonally distorted (rather than regular octahedral) stereochemistry in which four significantly shorter in-plane bonds are formed.

This difference is also noticed in the sequence of metal–nitrogen frequencies in the series in Table 11, where there is an increase of only 27 cm^{-1} from manganese to nickel, but then one of 72 cm^{-1} from nickel to copper.

The close similarity of the infrared spectra of the hexaammines and pentaammines and their difference from the tetraammines, again emphasises the similarity in stereochemistry of the copper(II) ions present in both series of complexes (see copper–nitrogen vibrations).

The symmetric deformation mode is split into three components, 1229, 1087, 1013 cm^{-1} in the hexaammines[79], into two, 1225, 1087 cm^{-1} in the pentaammines[11], and appears as a single peak at 1230 cm^{-1} in the tetraammines[15] and diammines[16]. This splitting is consistent with a single type of short copper–nitrogen bond in the tetraammines, a short type and a long type of copper–nitrogen bond in the pentaammines and an additional even longer type of copper–nitrogen bond in the hexaammines, which may reasonably be considered to involve ammonia in the crystal lattice. What is surprising in view of this sensitivity of δ_s to stereochemistry is the small variation it shows within the tetraammine and diammine series. Bond length data are available in both series but there seems to be a complete absence of any correlation between these and the observed frequencies.

(ii) Copper-nitrogen vibrations

These would be expected to give rise to more specific stereochemical information. The metal–nitrogen bending modes all appear in the region 250–300 cm^{-1} irrespective of the stereochemistry present[78]. The copper–nitrogen stretching modes are more variable. In the tetraammines[15], a band at 408–440 cm^{-1} is assigned as the E_u, ν_{Cu-N} with the rather high frequency being due to the shorter bonds in copper complexes relative to those of other metals in Table 11. Thus the complex $Na_4Cu(NH_3)_4\{Cu(S_2O_3)_2\}_2NH_3$(Cu–N, 1.99 Å) absorbs at 436 cm^{-1} while $Cu(NH_3)_4H_2O, SO_4$ (Cu–N, 2.03 Å) absorbs at 423 cm^{-1} $Na_4Cu(NH_3)_4\{Cu(S_2O_3)_2\}_2, H_2O$ absorbs at 455 cm^{-1} suggesting a copper–nitrogen bond length of less than 1.99 Å consistent with the more nearly square-coplanar stereochemistry suggested to be present by the electronic properties. The rhombic tetraammine, $Cu(NH_3)_4(CuI_2)_2$ with two different in-the-plane copper–nitrogen bonds of 2.11 and 2.17 Å absorbs at 427 and 437 cm^{-1}. The pentaammines[11] are characterised by two bands in this region, a medium intensity one at 390–420 cm^{-1} and a broader band at 509–537 cm^{-1}. Both have been tentatively assigned as copper–nitrogen stretching modes. The band at 400 cm^{-1} is assigned as the asymmetric copper–nitrogen stretching vibration which has moved to slightly lower energy than the corresponding band in the tetraammines. This is consistent with the slight increase in copper–nitrogen bond length in this in-plane square-based pyramidal complex, in which the tetragonal distortion[14] is not too pronounced (see crystallography section). The band at 520 cm^{-1} is assigned as the symmetric copper–nitrogen stretch of the relatively long fifth (apical) copper–nitrogen bond. Some support for this assignment is the observation[24] of a band at a similar frequency in the $[Cuen_2NH_3]X_2$ complexes which has also been assigned a square-based pyramidal stereochemistry. The infrared spectra[79] of the hexaammines in this region are also seen to be closely comparable to that of the pentaammines, consistent with their formulation as $Cu(NH_3)_5X_2NH_3$.The infrared spectrum of $(NH_4)[Cu(NH_3)_5](ClO_4)_3$ with two bands at 536 and 417 cm^{-1}, is typical of a pentaammine rather than of a tetraammine. $(NH_4)[Cu(NH_3)_5](PF_6)_3$ is unique[11] in only having a single peak at 485 cm^{-1}, the reason for this is not understood.

The diamines[16] are characterised by single bands in the regions 437–500 cm^{-1} and 200–268 cm^{-1}. The former has been assigned as the assymmetric stretch of the linear $Cu(NH_3)_2{}^{2+}$ unit. In the diammines the copper–nitrogen bond lengths vary from 1.93–2.03 Å but there appears to be no correlation between the length of the copper–nitrogen bond lengths and the frequency of the ν_{Cu-N} band. Equally, the energy of the ν_{Cu-N} mode of the linear $Cu(NH_3)_2{}^{2+}$ does not appear to vary significantly with the overall stereochemistry of the copper(II) ion.

In the complex $Cu(NH_3)_2CO_3$ where the two ammonia groups have a *cis*-configuration, the infrared spectra[16] show two bands at 432 and 460 cm^{-1} which have tentatively been assigned as the symmetric and asymmetric stretching modes of the *cis*-$Cu(NH_3)_2$ group.

(iii) Polyatomic anion spectra

The infrared spectra of the polyatomic anions present in transition metal complexes may be used as criteria of their coordination. The tetrahedral symmetry (T_d) of the perchlorate[80], tetrafluoroborate[81] and sulphate[82] ions is lowered to C_{3v} symmetry when they act as monodentate ligands and to C_{2v} symmetry when they act as bidentate ligands. These different symmetries are reflected in the successive splitting of the triply degenerate ν_3 mode of the free ions and in the symmetric stretching ν_1 mode becoming infrared active. Thus the infrared spectra of $Cu(NH_3)_5(ClO_4)_2$[11] and $[Cuen_2NH_3](ClO_4)_2$[24] both indicate the presence of a free perchlorate ion and hence suggest that the cations are strictly five coordinate and do not involve coordination of the perchlorate ion in the sixth coordinate position. The infrared spectra[15], Fig. 26, of $Cu(NH_3)_4(ClO_4)_2$ and $Cu(NH_3)_4SO_4$ show clear evidence of splitting intermediate between that of the ionic and fully coor-

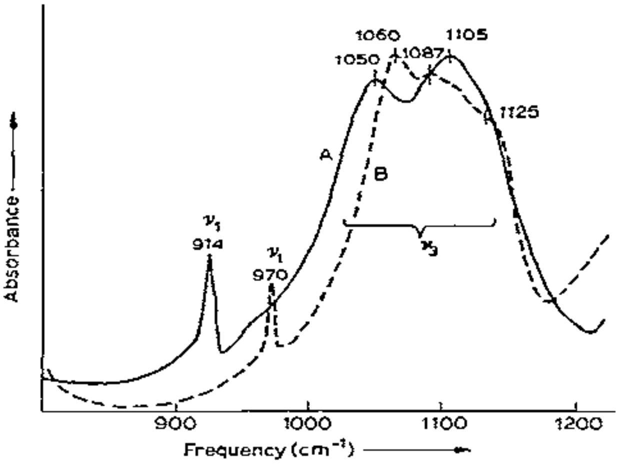


Fig. 26. The polyatomic anion infrared spectra of $Cu(NH_3)_4X_2$ complexes: A, $Cu(NH_3)_4(ClO_4)_2$; B, $Cu(NH_3)_4SO_4$.

dinated anions, indicative of weak or semi-coordination[46,56] and suggest the presence of a tetragonal octahedral stereochemistry, as indicated by the electronic properties of these complexes.

In the diammine[10] complexes of copper(II), the coordination number of the copper(II) ion is increased above two by the coordination of the anions present. If these anions are polyatomic then their infrared spectra can give evidence of their coordination to the copper(II) ion. In $Cu(NH_3)_2CO_3$, anion bands at 1560–1520, 1285–1260, 765 and 702 cm^{-1} are consistent with the presence of a bidentate carbonato group[78], rather than a monodentate or ionic carbonate group. $Cu(NH_3)_2(NO_2)_2$ occurs in two forms, the one involving nitro-coordination[78] having infrared bands at 1360 and 1325 cm^{-1}, assigned as the assymmetric and symmetric stretching modes of the coordinated nitro group. The second form has bands at 1368 and 1161 cm^{-1} consistent with nitrito coordination[78].

J. CONCLUSION

This article has reviewed, for the various ammines of the copper(II) ion, their rather complex preparative chemistry, X-ray crystallographic structures, ESR, electronic and infrared spectra. The above results have shown that useful stereochemical information may be obtained from a complementary examination of the electronic properties of the copper(II) ion in its complexes. The most immediately informative and easily measured electronic property is that of the electronic reflectance spectra. By comparing the spectra of a series of copper(II) complexes with the same ligand, in the present article ammonia, it is possible to distinguish at least six of the more common stereochemistries of the copper(II) tion, Fig. 7. The ESR spectra have proved invaluable for establishing the electronic ground state and in particular for distinguishing between a $d_{x^2-y^2}$ or a d_{z^2} ground state. The measurement of the polarised single crystal spectra of copper(II) complexes, has established at least a partial one-electron orbital sequence for the copper(II) ion in tetragonal octahedral, trigonal bipyramidal and rhombic stereochemistries.

This review has emphasised the limitations of much of the crystallographic data that exists in the literature. In the case of the copper(II) ammines, it has raised serious doubts oncerning the ability of the $Cu(NH_3)_4^{2+}$ cation to exist in a strictly square-coplanar stereochemistry. A great deal more work needs to be carried out on the measurement of the polarised single crystal spectra of copper(II) complexes with the emphasis placed on measuring a closely related series of complexes in each case. More spectra are required of square-based pyramidal complexes, with the copper ion both in- and out-of-the plane of the four coplanar ligands. Virtually no data exist on complexes with a compressed tetragonal or rhombic stereochemistry. An attempt to rectify some of these deficiencies is being carried out in the above laboratories.

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