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3. COPPER

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CONTENTS

INTRODUCTION

The 1981 Copper Review follows the same broad subdivisions as established for the Copper Reviews for 1979 [1] and 1980 [2] and covers the main journals through to the end of 1981. Figures, tables and structures from these earlier reviews have been frequently referred to within the year's review. The Review starts with a reappraisal of the use of the electronic and EPR spectra of mononuclear copper(II) complexes as a criterion of the copper(II) stereochemistry present.

1981 has been notable for the appearance of three reviews on aspects of copper(II) chemistry [3,4,5] and these will be dealt with under the relevant subdivisions. A useful compilation of complexes containing Cu-S bonds has also appeared [6] as part of a more extensive review of sulphur complexes. Two new textbooks on Inorganic Chemistry have appeared in 1981. A fourth edition of "Introduction to Modern Inorganic Chemistry" by K.M. Mackay and R.A. Mackay [7] is particularly welcomed by the author, who has recommended this text since its introduction in 1971, not only to General Degree students, but also to First and Second Year Honours students, as a less bulky alternative to "Advanced

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Inorganic Chemistry" by F.A. Cotton and G. Wilkinson [8]. The update of the Section on Valence Theory to include photoelectron spectra is particularly appropriate for the Honours students and the inclusion of a Section on X-ray powder photography in Experimental Methods (Chapter 7) would further enhance the value of this text. The introduction of a new Chapter on "Transition Metals: Selected Topics" (Chapter 16) follows the current fashion. The second book is a new text on "Inorganic Chemistry" by A.G. Sharpe [9]. A first reaction to this text was that its lay-out was rather old-fashioned, as all the familiar Chapters are present, but this impression is changed on further examination, as the text is a most readable introduction to Inorganic Chemistry, and attempts to connect the separate Sections by extensive cross-referencing. This readability reflects the extensive teaching experience of Alan Sharpe and reminded the author of the beautiful Quarterly Review [10] on "Some Aspects of the Inorganic Chemistry of Fluorine", which related Inorganic Chemistry and thermodynamics at a time when Quarterly Reviews were written to be read by undergraduate students. The coverage is again primarily for General Degree students, and Honours students up to second year. The new book on "Molecular Shapes" by Jeremy K. Burkett [11] discusses the theoretical models of inorganic stereochemistry, and places a dominant emphasis on the angular overlap description. This is very much a final honours and postgraduate students text, which admits that the AOM model is largely inadequate to describe the electronic properties and stereochemistry of copper(II) complexes [11, p. 177].

3.1 ELECTRONIC PROPERTIES AND STEREOCHEMISTRY OF COPPER(II) COMPLEXES

The 1980 Copper Review contained a summary, [2, Fig. 1] of the known stereochemistries of the copper(II) ion, including regular and distorted geometries subdivided in terms of static or pseudo structures, the latter arising due to the fluxional properties of the regular octahedral stereochemistry of the copper(II) ion [1,4]. This complicated behaviour is further compounded by the ability of a given copper(II) chromophore to occur with significantly different geometries, as in the $[Cu(dien)(bipyam)]X_2$, [12], and $[Cu(bipy)_2Cl]X$ [13] series of complexes, due to the plasticity effect of the copper(II) ion [14]. It would therefore be anticipated that this complicated stereochemical behaviour would rule out any possibility of using the electronic properties of the copper(II) ion, namely their EPR and electronic spectra, as a "criterion of stereochemistry". Attempts to do this for all types of complexes and presuming *only* regular stereochemistries is subject to uncertainty [15] and was rightly criticised [16]. Nevertheless, ten years later, in the light of a much more complex *overview* of copper(II) stereochemistry [2, Fig. 1], this use of

TABLE 1

The temperature variable "structures", EPR spectra and non-temperature variable electronic spectra of some fluxional copper(II) complexes

Complex	T/K	Chromophore	Stereochemistry	EPR Spectra (g)	$\tilde{\nu}/\mathrm{cm}^{-1}$
$Cs_2Pb[Cu(NO_2)_6]$	420	$\{CuN_6\}$	*pseudo*-octahedral	2.10	7000, 16000
	298	"	*pseudo*-compressed octahedral	2.06,2.16	7000, 16000
	160	"	static elongated octahedral	2.06,2.07,2.22	7000, 16000
$[Cu(en)_3][SO_4]$	298	$\{CuN_6\}$	*pseudo*-trigonal octahedral	2.13	8600, 16400
	158	"	*pseudo*-compressed octahedral	2.06,2.16	8600, 16400
$[NH_4]_2[Cu(OH_2)_6][SO_4]_2$	298	$\{CuO_6\}$	*pseudo*-compressed octahedral	2.071,2.218,2.360	12350, 11760, 10650, 6400
	145	"	static elongated rhombic octahedral	2.076,2.131,2.433	12720, 12200, 10900, 7350

electronic properties as a "criterion of stereochemistry" is worth re-examining [17].

The basic one-electron energy levels for the copper(II) ion in different stereochemistries are reasonably well established [18,19], and the guidelines set out in an earlier paper on an electronic criterion of stereochemistry are still valied [17]. Nevertheless, as the time scale [20] for electronic transitions is short, 10^{-15}, the electronic energies observed in the electronic spectra of fluxional complexes in the solid state are not time-averaged and relate to the underlying *static* extrema of the stereochemistry of the $\{CuL_n\}$ chromophore. Consequently, the electronic spectra cannot distinguish the fluxional pseudo stereochemistries [2, Fig. 1] from the underlying static structure, and there is a "sameness" about the electronic spectra of copper(II) complexes. As the time scale of the EPR spectra is longer, 10^{-9}-10^{-6}s, the EPR spectra do relate to the average pseudo stereochemistries arising from fluxional effects. Thus, $Cs_2Pb[Cu(NO_2)_6]$ (involving the $\{CuN_6\}$ chromophore) [2,(*1*)] is *pseudo* octahedral at 420 K, *psuedo* compressed octahedral at 298 K, and *static* elongated rhombic octahedral at 160 K, but its electronic spectrum is temperature independent, 7000 and 15000 cm^{-1} reflecting the underlying static elongated rhombic octahedral $\{CuN_6\}$ stereochemistry. On the other hand, its EPR spectra are temperature variable (see Table 1) and relate to the time average $\{CuN_6\}$ structures.

The *pseudo* trigonal octahedral stereochemistry of $[Cu(en)_3][So_4]$ at room temperature (Table 1) changes to a *pseudo* compressed stereochemistry at 158 K, and yields a temperature independent electronic spectrum, but exhibits a temperature variable EPR spectrum. Likewise, the fluxional elongated rhombic octahedra $\{CuO_6\}$ chromophore of $[NH_4]_2[Cu(OH_2)_6][SO_4]_2$ yields a temperature variable stereochemistry and EPR spectra, but again a temperature independent electronic spectrum.

In contrast to the above behaviour the occurrence of cation distortion isomers due to the plasticity effect [14] generate series of complexes in which the *same* chromophore has different geometries in the different crystal lattices, and will give rise to different *g*-values *and* different electronic spectra at *room temperature*. For the five-coordinate $\{CuN_5\}$ chromophore of the $[Cu(dien)(bipyam)]X_2$ complexes, [2, Fig. 4], the local molecular geometry varies from distorted trigonal bipyramidal to distorted square pyramidal, differences which *are* reflected in the different electronic spectra, Fig. 1(a) and which nicely reproduce the electronic spectra, Fig. 1(b), previously observed [21] for the more regular $\{CuN_5\}$ geometries of square pyramidal (in $K[Cu(NH_3)_5][PF_6]$) and trigonal bipyramidal (in $[Cu(tren)(NH_3)][ClO_4]_2$). The changes in the electronic spectra of the $[Cu(dien)(bipyam)]X_2$ complexes [13]

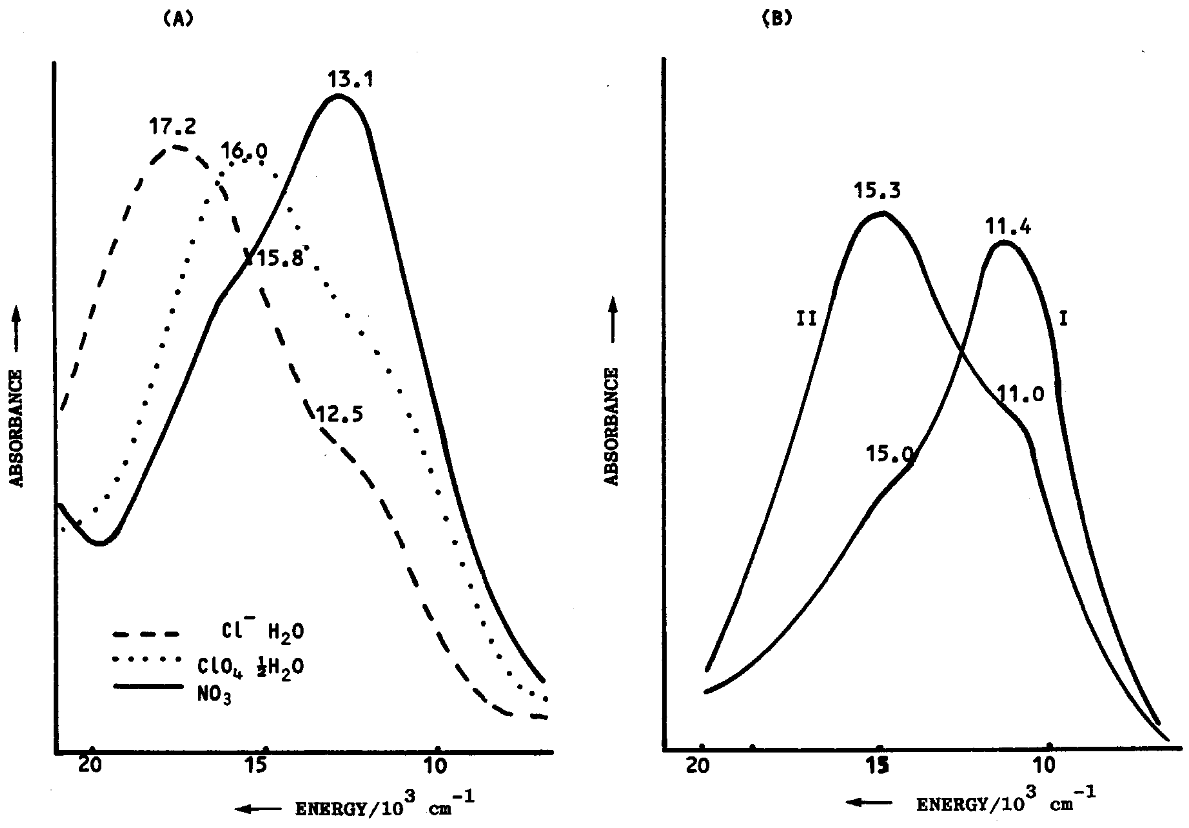


Fig. 1: The electronic reflectance spectra of (A) $[Cu(dien)(bipyam)]X_2$ and (B) $[Cu(tren)(NH_3)][ClO_4]_2$ (I) and $K[Cu(NH_3)_5][PF_6]_3$ (II).

represent one of the clearest examples of the use of electronic spectra of copper(II) complexes as a criterion of stereochemistry. An alternative series of cation distortion isomers exist in the $[Cu(bipy)_2Cl]X$ complexes [13] involving the five-coordinate $\{CuN_4Cl\}$ chromophore, whose stereochemistry varies [1, Fig. 6;2, Fig. 5] from near regular trigonal bipyramidal to square pyramidal distorted trigonal bipyramidal. Through this structural pathway [2, Figs. 5 and 7], there is a significant change in the electronic spectra, Fig. 2(a), from a single peak at 12500 to twin peaks at 10100 and 14160 cm^{-1}, clearly differentiating between the two extremes of stereochemistry in this series. There is a parallel change in their EPR spectra from axial for the trigonal bipyramidal complex ($g_{\perp}>g_{\parallel}\simeq 2.0$), to very rhombic for the square pyramidal distorted trigonal bipyramidal complex, $g_3>g_2>g_1\simeq 2.0$, Fig. 2(b).

It is then of interest to examine the corresponding electronic properties of the *cis*-distorted octahedral $[Cu(bipy)_2(OXO)]X$ series of complexes [22] which also form a structural profile, [2, Fig. 12]. Although the g-values display the appropriate variation with crystal structure (Table 2) consistent with the plasticity effect, the variation of the electronic spectra is only just significant and almost suggestive of fluxional behaviour. Nevertheless, the single-crystal g-values of $[Cu(bipy)_2(ONO)][NO_3]$ do suggest a small temperature variation [23] 77 K; 2.029, 2.175, 2.005; see section 3.3.1, which *is* consistent with a fluxional behaviour, and illustrates this novel use of the electronic properties to predict the fluxional behaviour of the *cis*-distorted octahedral stereochemistry, which must await final confirmation by the determination of a low-temperature crystal structure of $[Cu(bipy)_2(ONO)][NO_3]$. ¶

The structural pathway approach may then be used to link together a whole range of stereochemistries in the $[Cu(bipy)_2X]Y$ type complexes, (Fig. 3) of which twenty-five are of known crystal structure involving both five- and six-coordinate structures [1,2,11]. Relying on a *combination* of electronic spectra (one band or two) and EPR spectra (axial or rhombic g-values), Fig. 4 and Table 3, it is possible in this series of closely related complexes involving a constant $\{Cu(bipy)_2\}$ fragment to suggest that a spectroscopic criterion of stereochemistry does exist in copper(II) chemistry, in this case covering a very extensive range of copper(II) stereochemistries. In the literature, there is an increasing use of complementary electronic and EPR

¶ The low temperature crystal structure of $[Cu(bipy)_2(ONO)][NO_3]$ has now been determined [24a] and shown to be temperature variable (see Table 5) and confirms that the *cis*-distorted octahedral stereochemistry for the copper(II) is fluxional as predicted above from the electronic reflectance spectra.

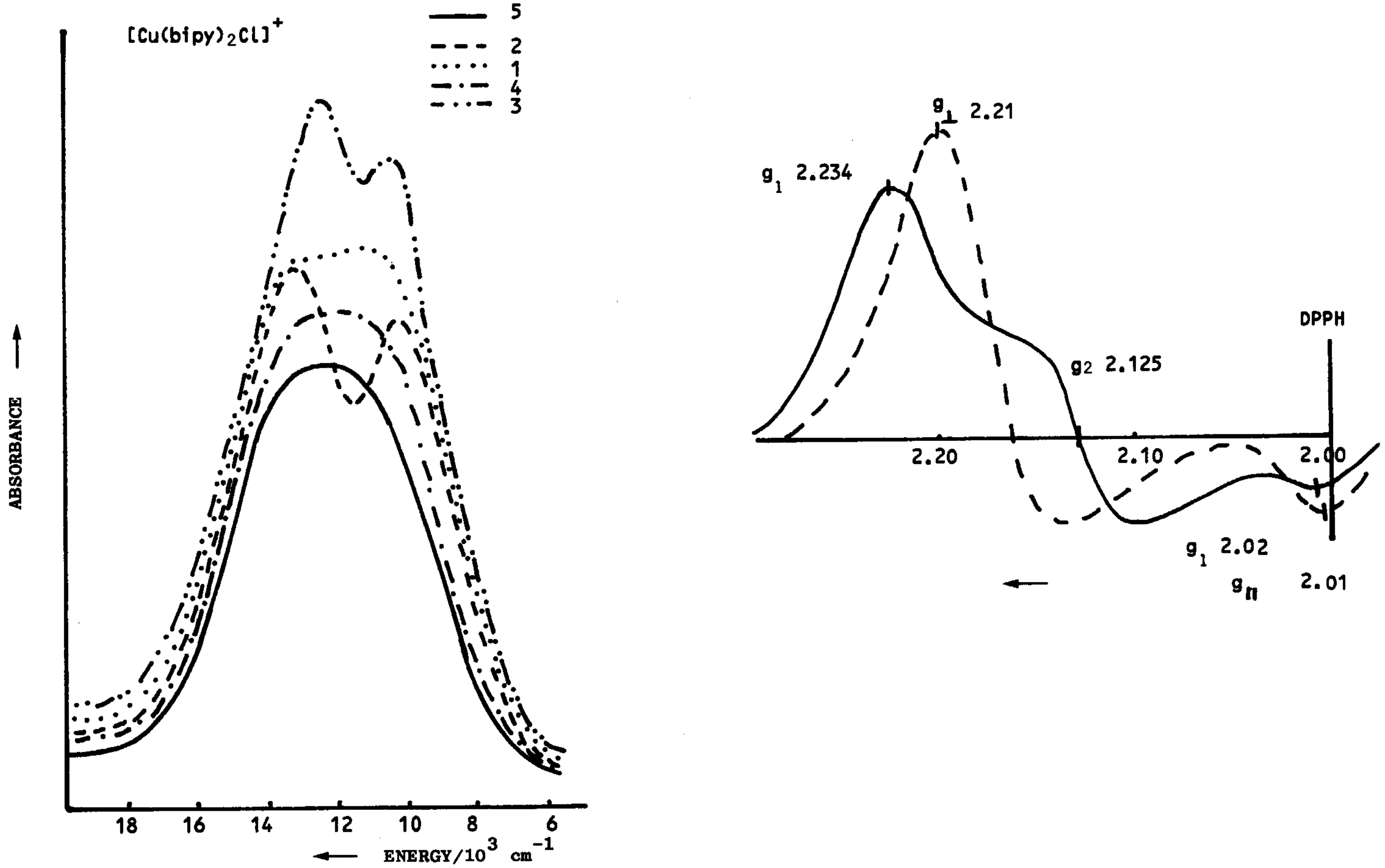


Fig. 2: The electronic properties of [Cu(bipy)$_2$Cl]X complexes: (A) reflectance spectra and (B) EPR spectra; (1) X = [ClO$_4$], (2) X = [NO$_3$].3H$_2$O, (3) X = [S$_5$O$_6$].3H$_2$O, (4) X = [CuCl$_2$], and (5) X = Cl.6H$_2$O

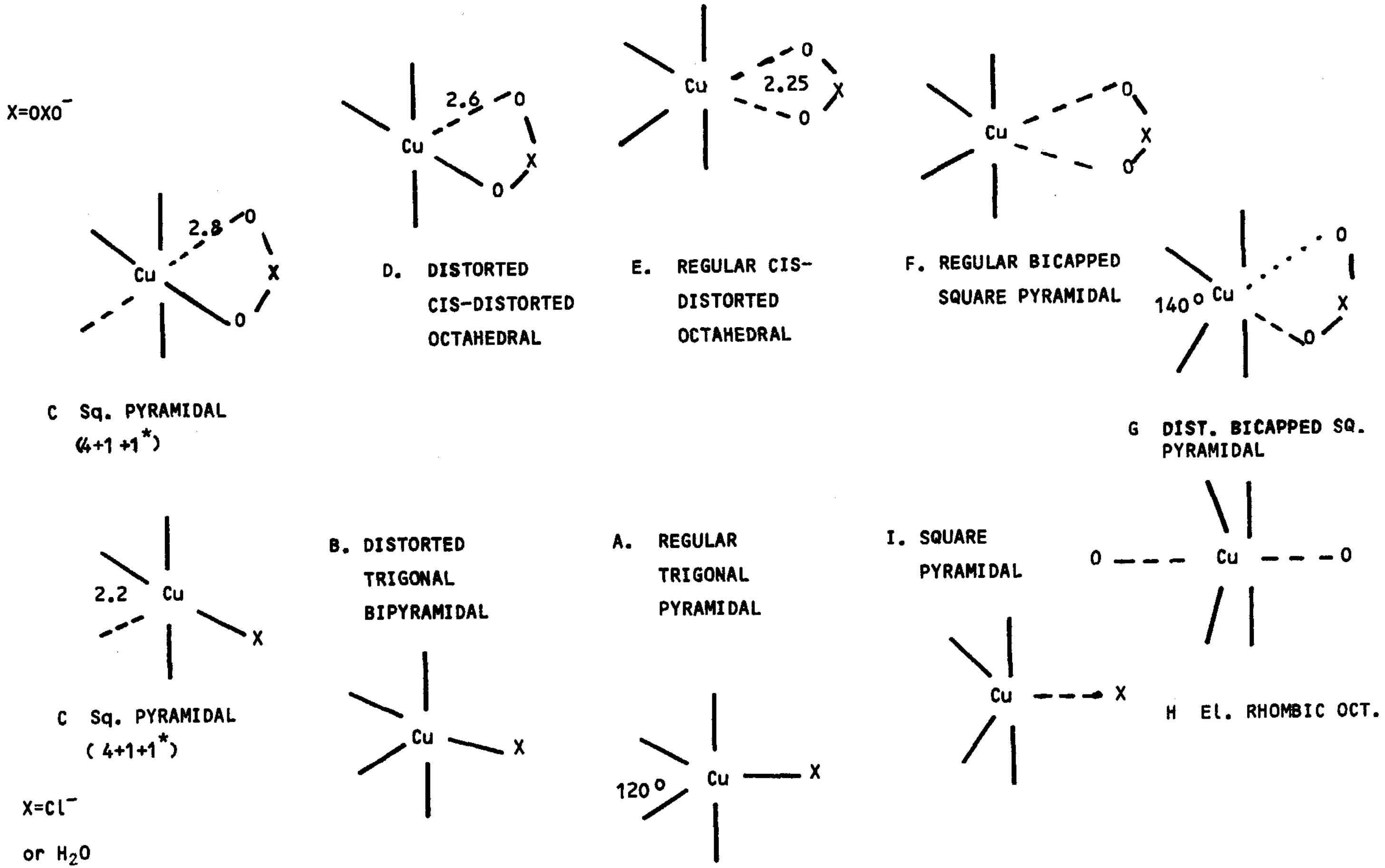


Fig. 3: Structural pathway for $[Cu(bipy)_2X]Y$ complexes

TABLE 2

The electronic and EPR spectra of some cation distortion isomers of the copper(II) ion

Complex	X	Chromophore	Stereochemistry	EPR Spectra (g)	$\tilde{\nu}/\mathrm{cm}^{-1}$
$[\mathrm{Cu(dien)(bipyam)}]\mathrm{X}_2$	$\mathrm{Cl}, \mathrm{H_2O}$	$\{\mathrm{Cu}N_5\}$	distorted square pyramid	-	12500sh,17200
	$\mathrm{ClO_4}, 0.5\mathrm{H_2O}$	"	intermediate	-	12000sh,16000
	$\mathrm{NO_3}$	"	distorted trigonal bipyramid	2.021,2.095,2.179	13100,15800sh
$[\mathrm{Cu(bipy)_2Cl}]\mathrm{X}$	$\mathrm{Cl}, 6\mathrm{H_2O}$	$\{\mathrm{Cu}N_4Cl\}$	near regular trigonal bipyramid	2.028,2.23	12500
	$\frac{1}{2}[\mathrm{S_5O_6}], 6\mathrm{H_2O}$	"		2.0,2.16,2.23	10470,13240
	$\mathrm{ClO_4}$	"	square pyramid distorted trigonal bipyramid	2.09,2.13,2.23	10100,14160
$[\mathrm{Cu(bipy)_2(ONO)}]\mathrm{X}$	$\mathrm{NO_3}$	$\{\mathrm{Cu}N_4O_2\}$	*cis*-distorted octahedron	2.019,2.174,2.205	9500,14600
	$\mathrm{BF_4}$	$\{\mathrm{Cu}N_4O_2\}$	square pyramid (4+1+1*)	2.020,2.136,2.203	9500,15000

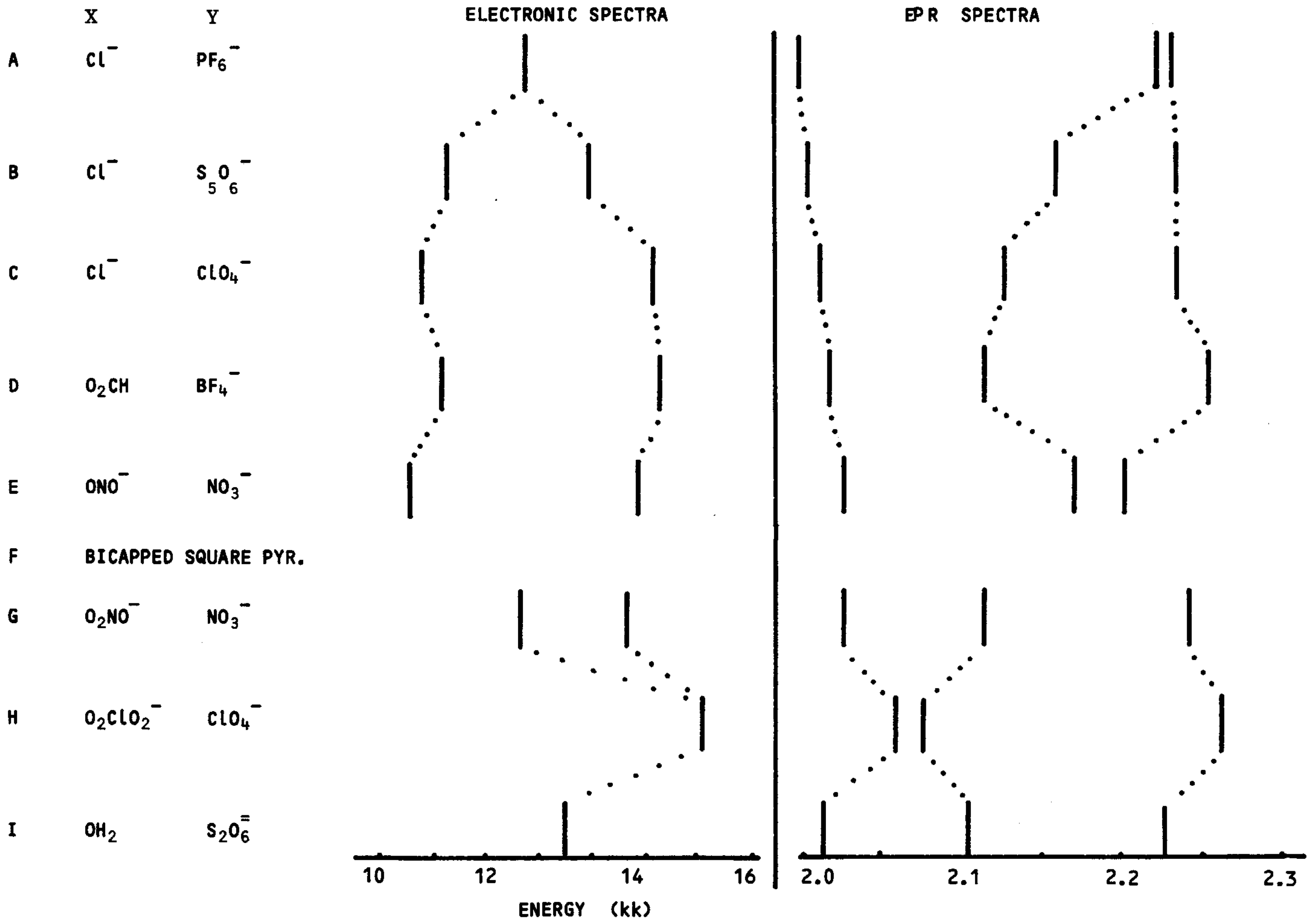


Fig. 4: $[Cu(bipy)_2X]Y$ complexes: (I) electronic energies and (II) single-crystal *g*-values

TABLE 3

Electronic Spectra and *g*-Values of some $[\mathrm{Cu(bipy)_2X}]\mathrm{Y}$ complexes

	Complex	$\tilde{\nu}/\mathrm{cm}^{-1}$	*g*-values
A	$[\mathrm{Cu(bipy)_2Cl}][\mathrm{PF_6}]$	11900	2.00, 2.23
B	$[\mathrm{Cu(bipy)_2Cl}]_2[\mathrm{S_5O_6}].6\mathrm{H_2O}$	10470, 13240	2.002, 2.160, 2.233
C	$[\mathrm{Cu(bipy)_2Cl}][\mathrm{ClO_4}]$	9900, 14150	2.007, 2.125, 2.234
D	$[\mathrm{Cu(bipy)_2(O_2CH)}][\mathrm{BF_4}].0.5\mathrm{H_2O}$	10200, 14360	2.015, 2.115, 2.255
E	$[\mathrm{Cu(bipy)_2(ONO)}][\mathrm{NO_3}]$	9500, 15200	2.026, 2.165, 2.196
F	$[\mathrm{Cu(dbpt)}]$	(10300), 14500	2.03, 2.12, 2.28
G	$[\mathrm{Cu(bipy)_2(ONO_2)}][\mathrm{NO_3}]$	11600, 13600sh	2.023, 2.110, 2.240
H	$[\mathrm{Cu(bipy)_2(O_2ClO_2)}][\mathrm{ClO_4}]$	15100	2.054, 2.065, 2.255
I	$[\mathrm{Cu(bipy)_2(OH_2)}][\mathrm{S_2O_6}]$	12450	2.011, 2.158, 2.225

spectra to predict structures. They have been used to study the complexes of the tripod ligand tris(2-benzimidazolylmethyl)amine and distinguish 5- and 6-coordinate structures [24b], and to distinguish mononuclear and dinuclear copper(II) complexes in a series of structural isomers of $[\mathrm{Cu}(N\text{-acetyl-}\beta\text{-alaninato})_2(\mathrm{OH_2})]_2.2\mathrm{H_2O}$ [25]. Nevertheless, in a series of binuclear copper(II) complexes [26] of 1,5,9-triazacyclotridecane with bridging μ-oxamido, μ-oxamato and μ-oxalato ligands, the electronic spectra from 5000-35000 cm^{-1} were reported both in the solid state and in solution, but the authors failed to report the EPR spectra, which may have been useful for distinguishing the trigonal bipyramidal and square pyramidal $\{\mathrm{Cu}N_3O_2\}$ chromophore stereochemistries that they suggested.

The use of the electronic properties of a series of polymorphic forms [27], as in mono(oxalato)mono(2,2'-bipyridine)copper(II), is particularly informative, especially where some of the forms cannot be obtained as single crystals, and those that are can be examined by crystallography at a later stage. The use of spectroscopic techniques as an initial probe in complexes subject to thermochroism to quantify the colour changes [28] prior to detailed crystal structure determination is recommended, but it is then disappointing if the crystal structure is reported as for the elongated rhombic octahedral $\{\mathrm{Cu}N_4O_2\}$ chromophore of bis(2,2-dimethylpropane-1,3-diamine)diperchloratocopper(II), without any comment on the change in electronic spectrum that occurs from 20-120 K of 19100 to 18350 cm^{-1}. The correlation of the colour with crystallographic examination is welcomed, as in the three complexes of *cis*-1,3-cyclohexanediamine [29] in which

$[Cu(1,3\text{-}chxn)_2]Br_2$ and $[Cu(1,3\text{-}chxn)_2][NO_3]_2$ are wine red with a rhombic coplanar $\{CuN_4\}$ chromophore, while $[Cu(1,3\text{-}chxn)_2Cl][ClO_4]$ is blue-violet with a square pyramidal $\{CuN_4Cl\}$ chromophore, a difference that is sufficient to distinguish these two stereochemistries and use as a criterion of stereochemistry.

Nevertheless, several notes of *caution* must be added. This approach applies *only* to closely related series of complexes (see [17]), and the electronic spectra *must* be measured over the full range 5000-25000 cm^{-1}. Single-crystal g-values are more accurate than those measured from polycrystalline samples and, for *all* EPR spectra, crystal g-values only equate with local molecular g-values if serious misalignment is absent [18].

3.2 COPPER(III) CHEMISTRY

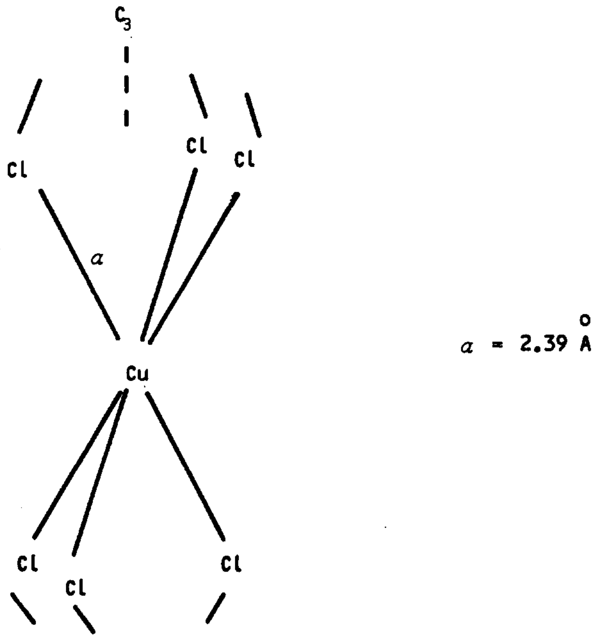
The review of the photochemistry of copper complexes included a brief section on charge-transfer of copper(III) complexes [3], and the self-exchange electron-transfer rate constant for copper(III/II) tripeptide complexes, has been determined by ^1H NMR line broadening experiments [30]. The kinetics and mechanism of the reduction of copper(III) peptide complexes by I^- has been reported [31] and the autooxidation of the sulphite anion by the copper(III) tetraglycine catalyst has been described [32]. The electropotential determination of the reactions of a copper(III) complex of the macrocyclic tetrapeptide suggests [33] that the complex is stable in neutral solution with a half-life of 5.7 weeks at 25 °C. The rates of oxidation of copper(II) peptide complexes by the hexachloroiridate(IV) anion have been measured using a pulsed-flow spectrometer [34]. An electro chemical study [35] of the trinuclear copper(II) system involving $[Cu_3O_p(OH)_{1-p}(\text{ligand})_3][ClO_4]_{2-p}$ (ligand = oximate bridges of Schiff bases), indicate that the unique *one*-electron oxidation $Cu_3^{II} \xrightarrow{-e} Cu_2^{II}.Cu^{III}$, is inhibited by protonation. The syntheses of some copper(III) dithiocarbamates have been reported [36] along with some copper(III)-containing perovskites, $(La_{3-x}, Ln_x)Ba_3[Cu^{II}_{5-2y}.Cu^{III}_{1+2y}]O_{14+y}$ [37].

3.3 COPPER(II) CHEMISTRY

3.3.1 Jahn-Teller Effect

The highlight of the year was the most enjoyable Jahn-Teller Conference [38b] held at the University of Nijmegen, Netherlands, from 22-25 September, 1981. The Conference involved all aspects of the Jahn-Teller Effect, but devoted two plenary lectures, Professor D. Reinen (Marburg, Germany) and Professor J.S. Wood (Amherst, U.S.A.), to the chemistry of Copper(II). The literature on the Jahn-Teller Effect has clearly separated into two groups - (a) those complexes containing copper(II) octahedra involving bridging ligands (such as K_2CuF_4 [39] and $CsCuCl_3$ [40]) and (b) those complexes containing isolated $\{CuL_6\}$ chromophores [23], which are well separated from each other by organic ligand atoms, and by lattice anions (as in $[Cu(bipy)_2(ONO)][NO_3]$). In the former class of complexes Cooperative Jahn-Teller ordering [41,42], *via* the common bridging atoms, results in anti-ferromagnetic coupling of the elongated rhombic octahedra, and generates pseudo octahedral or pseudo compressed octahedral structures [1, Table 1], while in the latter class the pseudo compressed octahedral and pseudo *cis*-distorted octahedral $\{CuL_6\}$ chromophore is associated with molecular crystal-packing factors, and the position of the copper ion on, or near, a crystallographic special position, and the pseudo structures arise from the non-Cooperative Jahn-Teller Effect [43].

In the Cooperative Jahn-Teller series for octahedral complexes, the crystal structure of $CsCuCl_3$ [40] has been redetermined over a range of temperatures, and the trigonal octahedral $\{CuCl_6\}$ chromophore in this linear chain structure (*1*) at high temperature (470 K) has been reinterpreted as a disordered structure



(*1*; $CsCuCl_3$)

involving three elongated tetragonal octahedral chromophores describing the three static stereochemistries of the dynamic Jahn-Teller Effect [1, Fig. 1(a)]. This structure represents a breakthrough in the crystallographic description of the Jahn-Teller Effect for octahedral copper(II) complexes as it suggests that all pseudo copper(II) structures can be represented crystallographically as the appropriate weighted mixture of the underlying static distorted structures. Whether this means that the potential barrier B [1, Fig. 1] is less than or greater than thermal energy is not clear to the writer, as the three static disordered structures could represent genuine *static* disorder ($B>kT$) or could be a better fudging of a dynamically distorted $\{CuCl_6\}$ chromophore, ($B<kT$), in the sense that the marked anisotropy of the temperature factors of the regular trigonal octahedral $\{CuCl_6\}$ chromophore model indicate that this is not a good model. The clear improvement in the R-values, Table 4, of the static disordered model and the "normal" anisotropic temperature factors observed, leave no doubt about the correctness of the crystallographic model, but is less clear on its physical interpretation. In the same year room temperature (298 K) neutron diffraction powder measurements [39] (analysed by profile analysis) has reaffirmed the space group of K_2CuF_4 as $I4c2$(Z=8), a distorted K_2NiF_4 structure, $I3/mmm$ (Z=2). A single-crystal X-ray determination of the structure of K_2CuF_4 [44] in the higher space group has interpreted the structure to involve a *two*-dimensional disorder of the bridging fluoride ions caused by a multi-domain structure, which could be refined assuming two 90° misaligned elongated rhombic octahedral $\{CuF_6\}$ chromophores, r(Cu-F) = 1.909(7), 1.939(2), 2.238(7) Å. This is consistent with the originally reported pseudo compressed tetragonal octahedral $\{CuF_6\}$ chromophore [1, Fig. 1(b)], but again does not distinguish between genuine static disorder, $B>kT$, and a two-dimensional dynamic disorder, $B<kT$, as the observation of an isotropic EPR spectrum in the *ab* plane cannot distinguish these two possibilities in the concentrated K_2CuF_4. In contrast, the crystal structure of $Rb_3Cu_2Cl_7$[45]

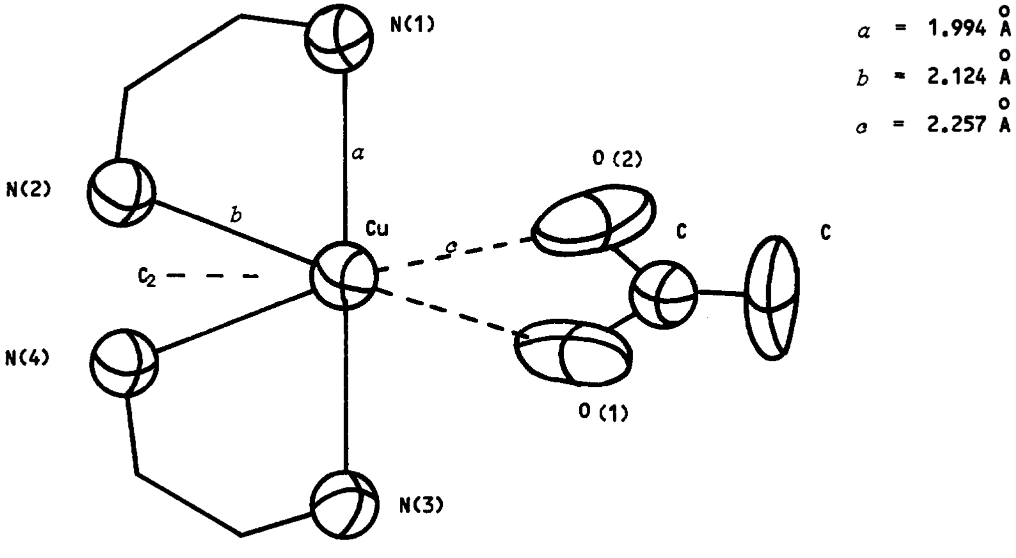
TABLE 4

R_W -values for $CsCuCl_3$ (430 K)

Model (Cl atom)	R_W	Number of Parameters
Isotropic thermal parameters	3.42	6
Cl-Disordered 3 sites	2.05	9
Cl-Disordered 4 sites	2.05	10

involves static elongated rhombic octahedral $\{CuCl_6\}^{4-}$ chromophores, ordered antiferrodistortively.

The crystallographic basis for a series of cation distortion isomers of the *cis*-distorted octahedral $\{CuN_4O_2\}$ chromophore was used [2, Fig. 12] to establish a structural pathway connecting the near regular *cis*-distorted stereochemistry to the very distorted square pyramidal (4+1+1*). The series has now been extended [22,23], Table 5, and the electronic properties of both the concentrated and of the copper complexes doped in their isomorphous host lattices have now been reported [23,38b,46,47]. The occurrence of the $[Cu(phen)_2(O_2CCH_3)]X.2H_2O$ (X = $[BF_4]^-$ or $[ClO_4]^-$ complexes with a *regular cis*-distorted octahedral $\{CuN_2N_2O_2\}$ chromophore (C_2 symmetry) (*2*) represents a corner stone in the structural pathway, with the copper(II) ion on a two-fold axis of symmetry.



(*2*; $[Cu(phen)_2(O_2CCH_3)][ClO_4].2H_2O$)

The remaining complexes involve asymmetric coordination of the $[OXO]^-$ group. This symmetry is best reflected by the plot of ΔN *vs.* ΔO (Fig. 5) where $\Delta N = r\{Cu\text{-}N(4)\} - r\{Cu\text{-}N(2)\}$ and $\Delta O = r\{Cu\text{-}O(2)\} - r\{Cu\text{-}O(1)\}$. The anisotropic thermal parameters in the $[Cu(phen)_2]^{2+}$ cation of (*2*) are normal, but those of the ethanoate oxygen atoms exhibit marked anisotropy with the major axis of the ellipsoids orientated nearly parallel (13°) to the Cu-O directions. The polycrystalline EPR spectrum) (*2*) is markedly temperature variable, Fig. 6(a),

TABLE 5

The local molecular structures of $[Cu(chelate)_2(OXO)]Y$ type complexes (see [22,24a,38a] for references) at room temperature and at low temperature

	T/K	$r\{Cu\text{-}N(2)\}$/Å	$r\{Cu\text{-}N(4)\}$/Å	$r\{Cu\text{-}O(1)\}$/Å	$r\{Cu\text{-}O(2)\}$/Å	α_1	ΔN/Å	Δ*O*/Å
$[Cu(bipy)_2(ONO)][BF_4]$		2.053(5)	2.141(5)	2.117(6)	2.463(6)	164.5°	0.088	0.346
$[Cu(phen)_2(O_2CCH_3)][BF_4],2H_2O$		2.123(4)	2.123(4)	2.261(5)	2.261(5)	150.4°	0.0	0.0
$[Cu(phen)_2(O_2CCH_3)][ClO_4],2H_2O$		2.124(4)	2.124(4)	2.257(5)	2.257(5)	150.3°	0.0	0.0
$[Cu(phen)_2(O_2CCH_3)][BF_4]$		2.061(5)	2.215(4)	1.999(4)	2.670(5)	154.4°	0.154	0.671
$[Cu(phen)_2(ONO)][BF_4]$		2.048(4)	2.167(3)	2.072(3)	2.597(3)	154.5°	0.119	0.525
$[Cu(bipyam)_2(ONO)][NO_2]$		2.095(9)	2.095(5)	2.074(16)	2.074(6)	162.9°	0.0	0.0
$[Cu(bipyam)_2(O_2CCH_3)][NO_3]$		2.032(6)	2.158(6)	2.029(6)	2.673(6)	161.3°	0.126	0.644
$[Cu(bipyam)_2(ONO)][BF_4]$		2.025(5)	2.141(5)	2.109(6)	2.551( )	163.4°	0.116	0.439
$[Cu(bipy)_2(ONO)][NO_3]$	298	2.074(4)	2.085(4)	2.230(5)	2.320(5)	157.8°	0.011	0.090
	165	2.071(2)	2.089(4)	2.204(3)	2.320(3)	158.4°	0.027	0.147
$[Cu(phen)_2(O_2CCH_3)][ClO_4]$	298	2.098(4)	2.130(4)	2.220(4)	2.421(5)	154.7°	0.032	0.201
	198	2.097(3)	2.144(4)	2.167(6)	2.533(6)	155.1°	0.057	0.366

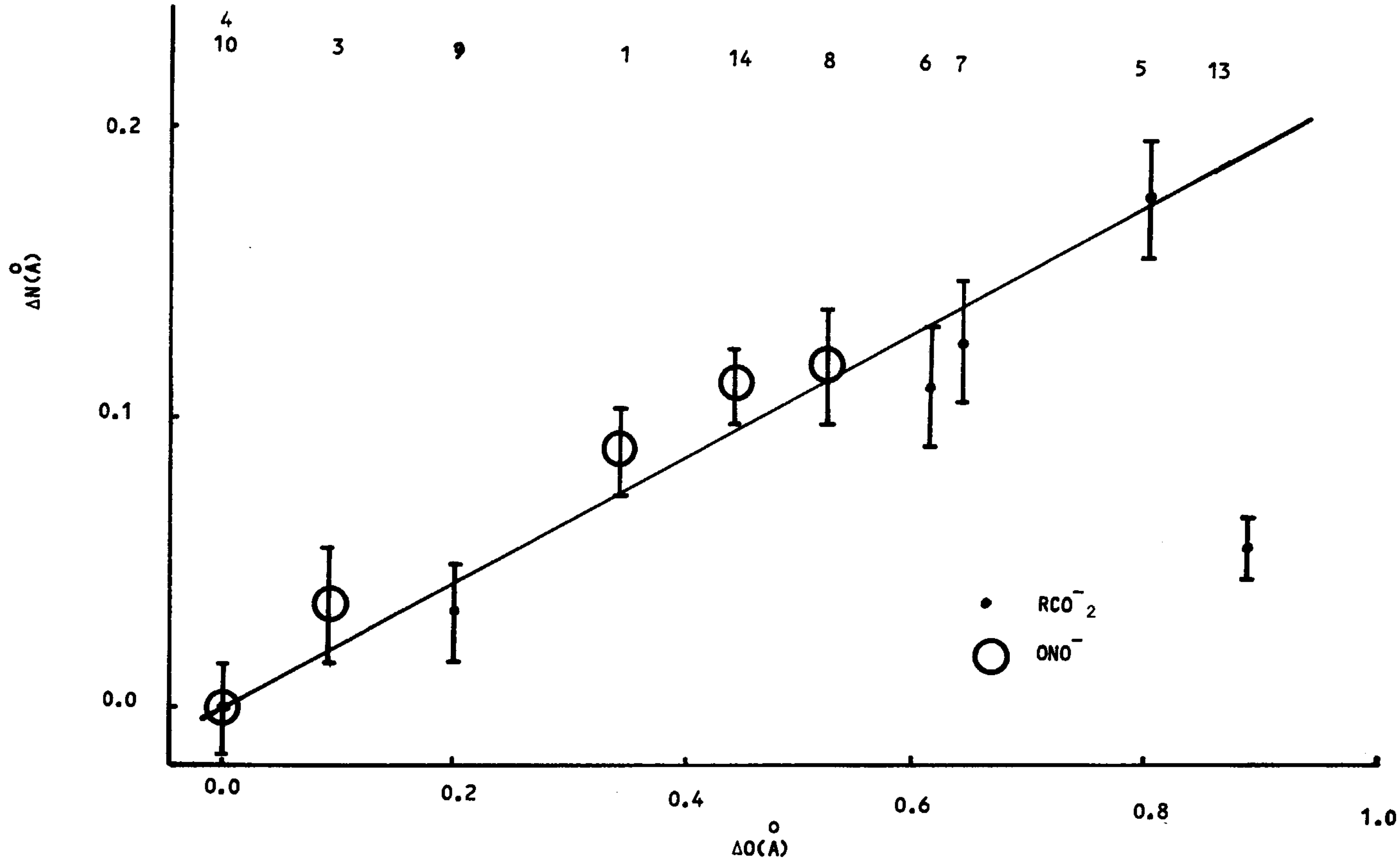


Fig. 5: Correlation of *ΔN*(*r*{Cu-N(4)}-*r*{Cu-N(2)}) and *ΔO*(*r*{Cu-O(2)}-*r*{Cu-O(1)}) distances (Å) (see [22] for numbering scheme).

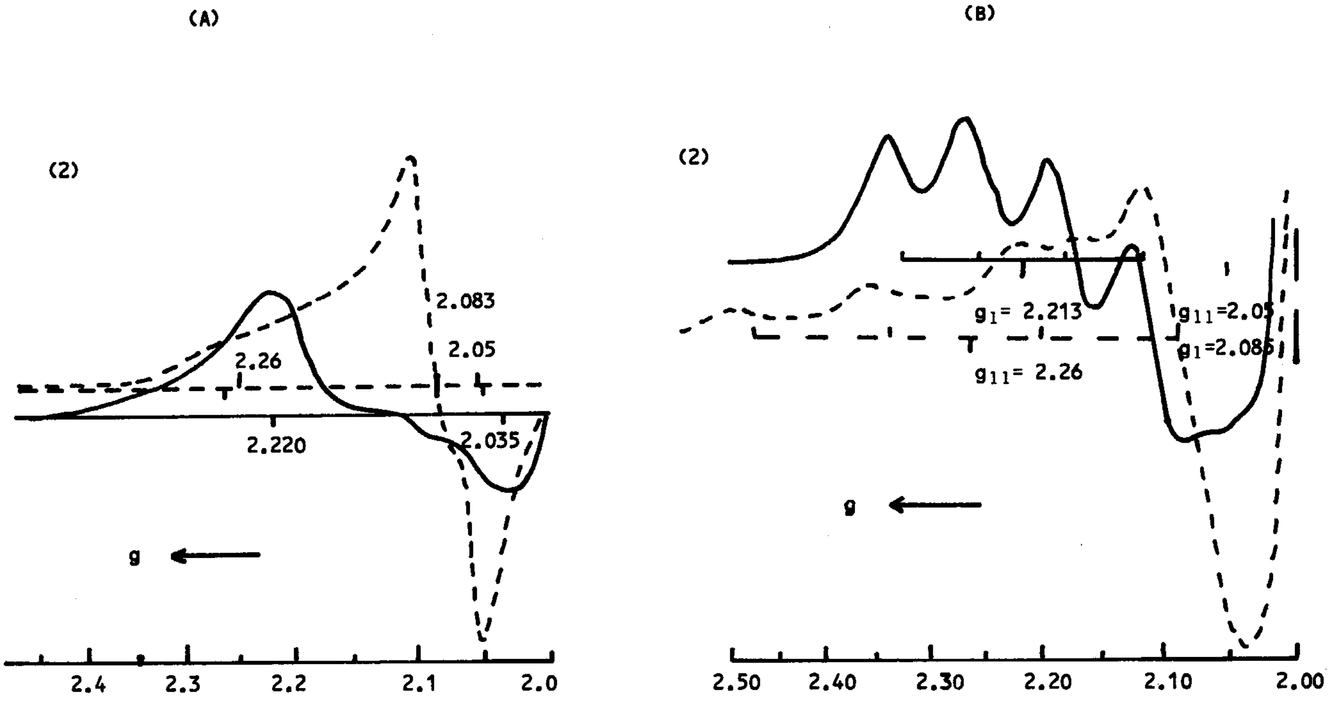


Fig. 6: The EPR spectra of (A) $[Cu(phen)_2(O_2CCH_3)][ClO_4].2H_2O$ and (B) 10% copper(II)-doped $[Zn(phen)_2(O_2CCH_3)][BF_4].2H_2O$, at room temperature (——) and at low temperature (- - - . -).

and when doped in the corresponding isomorphous $[Zn(phen)_2(O_2CCH_3)][ClO_4].2H_2O$ complex as a host lattice, Fig. 6(b), suggests a change in *g*-values, consistent with a change in stereochemistry from compressed octahedral ($g_\perp$=2.213 and $g_\parallel$=2.05) to elongated octahedral, $g_\parallel$=2.26 and $g_\perp$=2.085. The corresponding single-crystal rotation spectra, Fig. 7(a), have been measured in the CuN(2), N(4),O(1),O(2) plane;at room temperature the EPR spectrum is isotropic (including copper hyperfine structure) in all directions, but at liquid nitrogen temperature the angular variation is only consistent with two magnetic centres whose maximum *g*-value corresponds with the Cu-O(1) and Cu-O(2) directions. A comparable behaviour is observed in the single-crystal EPR spectrum of (*2*), Fig. 7(b), but the magnitude of the effect is not so marked. Similar temperature effects have also been reported [23] for the EPR spectra of the copper(II) ion doped in $[Zn(bipy)_2(ONO)][NO_3]$, but *not* for the pure copper(II) complex [23]. This behaviour is consistent with a two-dimensional fluxional behaviour of the $\{CuN_2N'_2O_2\}$ chromophore of (*2*), Fig. 8(a), rather than the static disorder of Fig 8(b), which can be rationalised in terms of a dynamic pseudo Jahn-Teller Effect, and implies that this stereochemistry of the pseudo *cis*-distorted octahedral $\{CuN_2N'_2O_2\}$ chromophore is *not* a static six-coordinate stereochemistry of the copper(II) ion. This behaviour is consistent with the invariance of the electronic reflectance spectra (see Section 3.1). Interestingly, the crystal structure of (*2*) failed to refine as a disordered structure (50% site occupation factor). Thus, whether the structure of the $[Cu(phen)_2(O_2CCH_3)][ClO_4]2H_2O$ complex is a genuine fluxional pseudo dynamic system, or just static disordered, is not clear and must await further data, hopefully, from low temperature X-ray data.[¶]

In a Plenary Lecture at the Sixth Jahn-Teller Conference at Nijmegen [38b], Professor D. Reinen reported an interesting EPR spectrum for $[Co(NH_3)_6][CuCl_5]$, the classic example of a trigonal bipyramidal $[CuCl_5]^{3-}$ anion, Fig. 9(a), which crystallises in a cubic space group, but with relatively large anisotropic thermal parameters associated with the three inplane ligands. At room temperature, its EPR spectrum is isotropic, Fig 9(b), but a 77 K the spectrum is axial with $g_\perp$ = 2.198 and $g_\parallel$ = 2.076, consistent with a *pseudo* compressed type stereochemistry ($g_\perp > g_\parallel$ >2.0). Professor Reinen then made the interesting suggestion that the trigonal bipyramidal stereochemistry of the copper(II) ion was not a genuine stereochemistry, but an artifact of the high symmetry cubic lattice, and arises

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[¶] **The low temperature crystal structure [38a] of $[Cu(phen)_2(O_2CCH_3)][ClO_4]$ has now been determined and is shown to be temperature variable (Table 5), in the sense of the structural profile (Fig. 3) predicted by the Fluxional Model.**

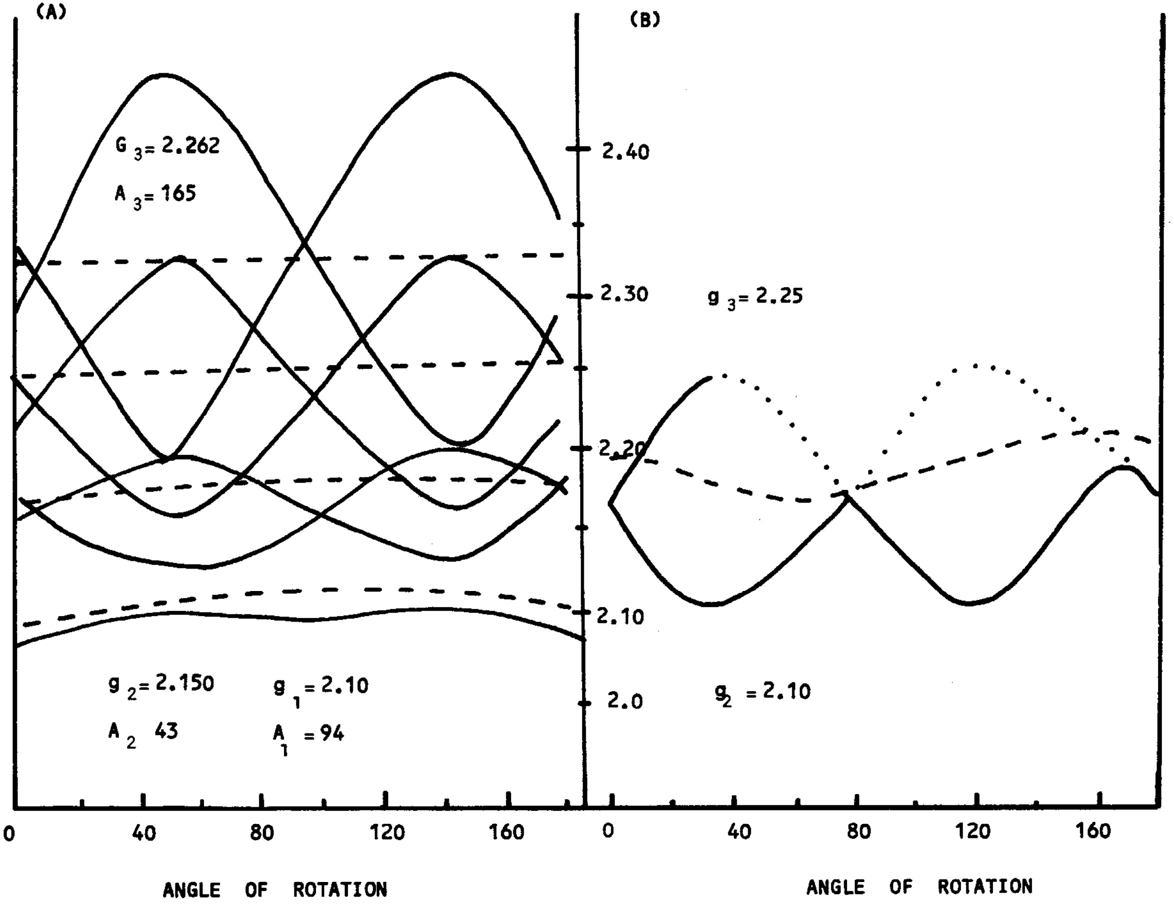


Fig. 7: The single-crystal EPR spectra of (A) 10% copper-doped [Zn(phen)$_2$(O$_2$CCH$_3$)][BF$_4$].2H$_2$O and (B) [Cu(phen)$_2$(O$_2$CCH$_3$)][ClO$_4$].2H$_2$O, both measured in the Cu,N(2),N(4),O(1),O(2) plane at room temperature (- - -) and at 77 K (——).

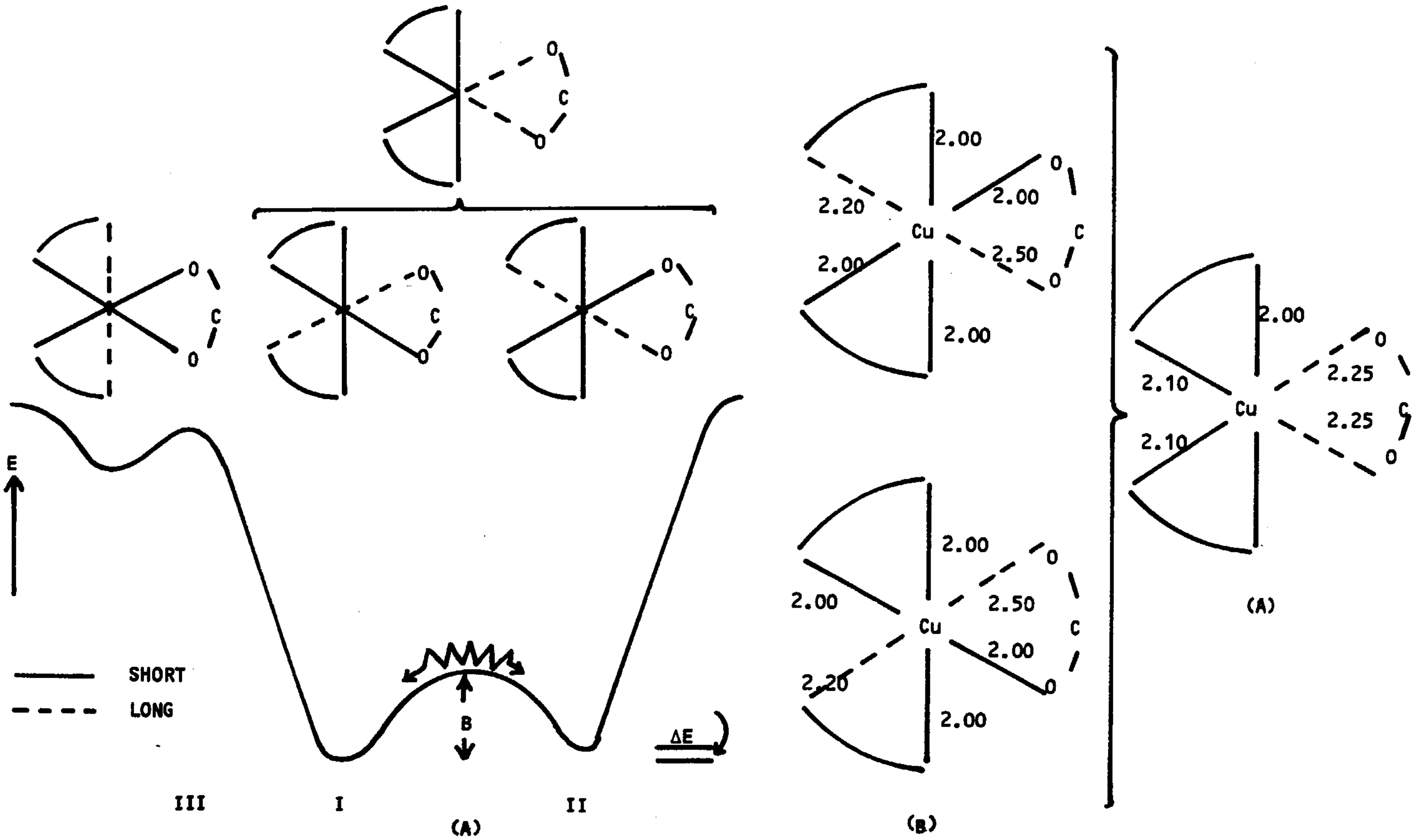


Fig. 8: [Cu(phen)$_2$(O$_2$CCH$_3$)]X: fluxional disorder (A) and static disorder (B) models.

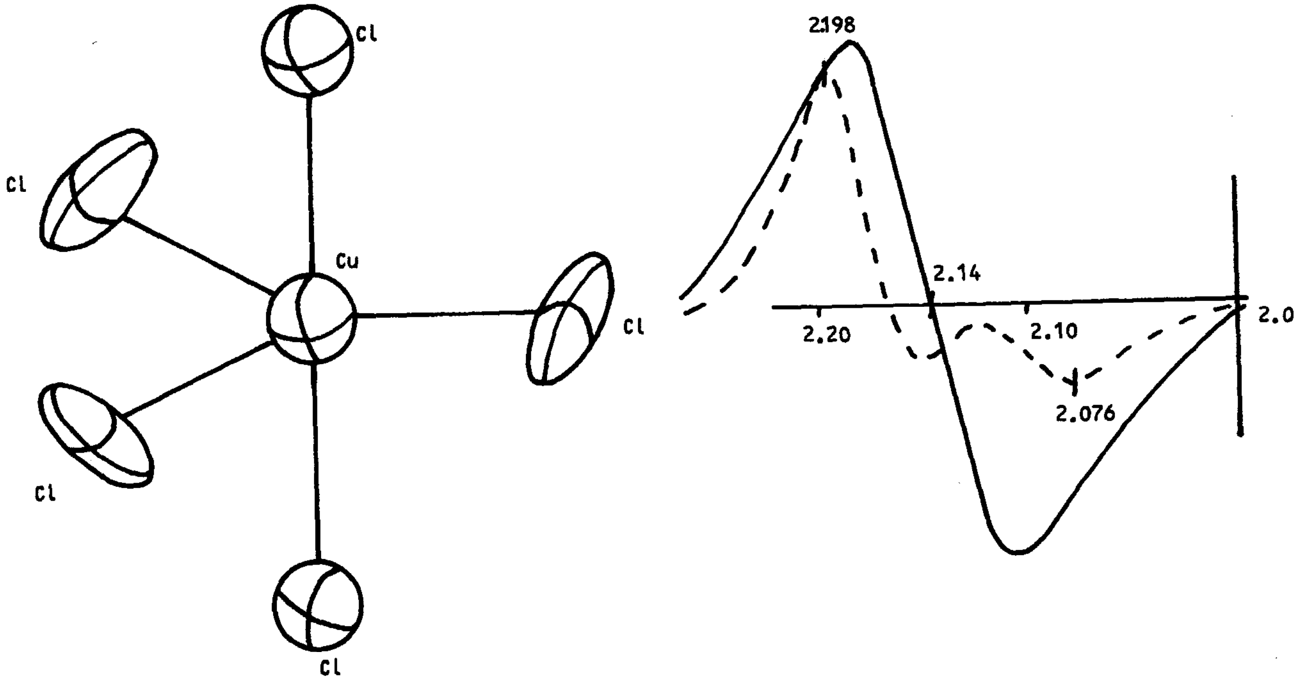


Fig. 9: [$Co(NH_3)_6$][$CuCl_5$]: (A) thermal ellipsoids of the {$CuCl_5$} chromophore and (B) the polycrystalline EPR spectra at room temperature (——) and at 77 K (- - - -).

due to the superposition of three square pyramidal $[CuCl_5]^{3-}$ anions aligned (see Fig. 10) with their three elongation axes parallel to the three C_2 axes of the D_{3h} point group. Consequently, the non-equivalent Cu-Cl distances of $[Co(NH_3)_6][CuCl_5]$ arise as an average of these misaligned square pyramidal $[CuCl_5]^{3-}$ anions such that $r\{CuCl_{ax}\}<r\{CuCl_{eq}\}$, and may be related by the symmetrical structural pathway of three-fold symmetry, Fig. 10. This model nicely accounts for the in-plane anisotropy of the thermal parameters, Fig 9(a), and with the pseudo compressed-type EPR spectrum observed at low temperature, which suggests that the three equal wells of the regular trigonal pyramidal system are replaced by a two equivalent well system at low temperature. It will then be of interest to see if this suggested dynamic pseudo Jahn-Teller system can be substantiated by low temperature X-ray structural data. In the light of this suggestion, the writer has re-examined the polycrystalline EPR spectra (down to 77 K) of $Cu(NH_3)_2Ag(NCS)_3$ and $[Cu(tren)(NH_3)][ClO_4]$ (both of which have regular trigonal bipyramidal structures [21,48]), those of $[Cu(bipy)_2Cl]Cl.6H_2O$, $[Cu(bipy)_2I]I$ and $[Cu(bipy)_2(NH_3)][BF_4]_2$ (all of which have near regular trigonal bipyramidal stereochemistries [49-51]) and copper(II) doped $[Zn(tren)(NH_3)]$-$[ClO_4]_2$[21]. Not one of these systems gave any indication of a change in their EPR spectra that paralleled the behaviour of $[Co(NH_3)_6][CuCl_5]$, and implies that if a change occurs, it must occur at temperatures nearer to liquid helium temperatures in these complexes. The structural pathway of Fig. 10 also suggests a dynamic pseudo trigonal pyramidal pathway for the $[Cu(bipy)_2Cl]X$ type complexes [1, Fig. 5] and implies that the range of structures observed [13] in this series may not originate in the Plasticity Effect alone [14], but may also be related by a dynamic pseudo Jahn-Teller Effect. If so, it also suggests that the even more extensive pathway of Fig. 3 is related by the pseudo Jahn-Teller Effect connecting not only non-regular stereochemistries (including non-equivalent ligands), but also different coordination numbers from five to six.

The magnetic susceptibility of $[Cu(en)_3][So_4]$ has been measured parallel and perpendicular to the room temperature c-axis [52]; antiferromagnetic ordering is found to occur at 109 mK and the compound orders as a three-dimensional Heisenberg antiferromagnetic with J/k_B 0.03 K. The far-infrared spectra [53] of the $K_2Pb[Cu(NO_2)_6]$ complex has been determined and shown to contain additional bands compared with the corresponding nickel(II) complex. These have been explained on the basis of the dynamically distorted copper complex where the life-time [20] of the infrared measurement (10^{-13}s) is short relative to the static $\{CuN_6\}$ chromophore of the dynamic Jahn-Teller Effect. A similar effect has been observed in the infrared normal coordinate analysis of the $[Cu(C_5H_5NO)_6][ClO_4]_2$ complex [54], which requires a reduction of the site symmetry from S_6 to C_i for the copper(II) complex. The ^{14}N nuclear quadrupole

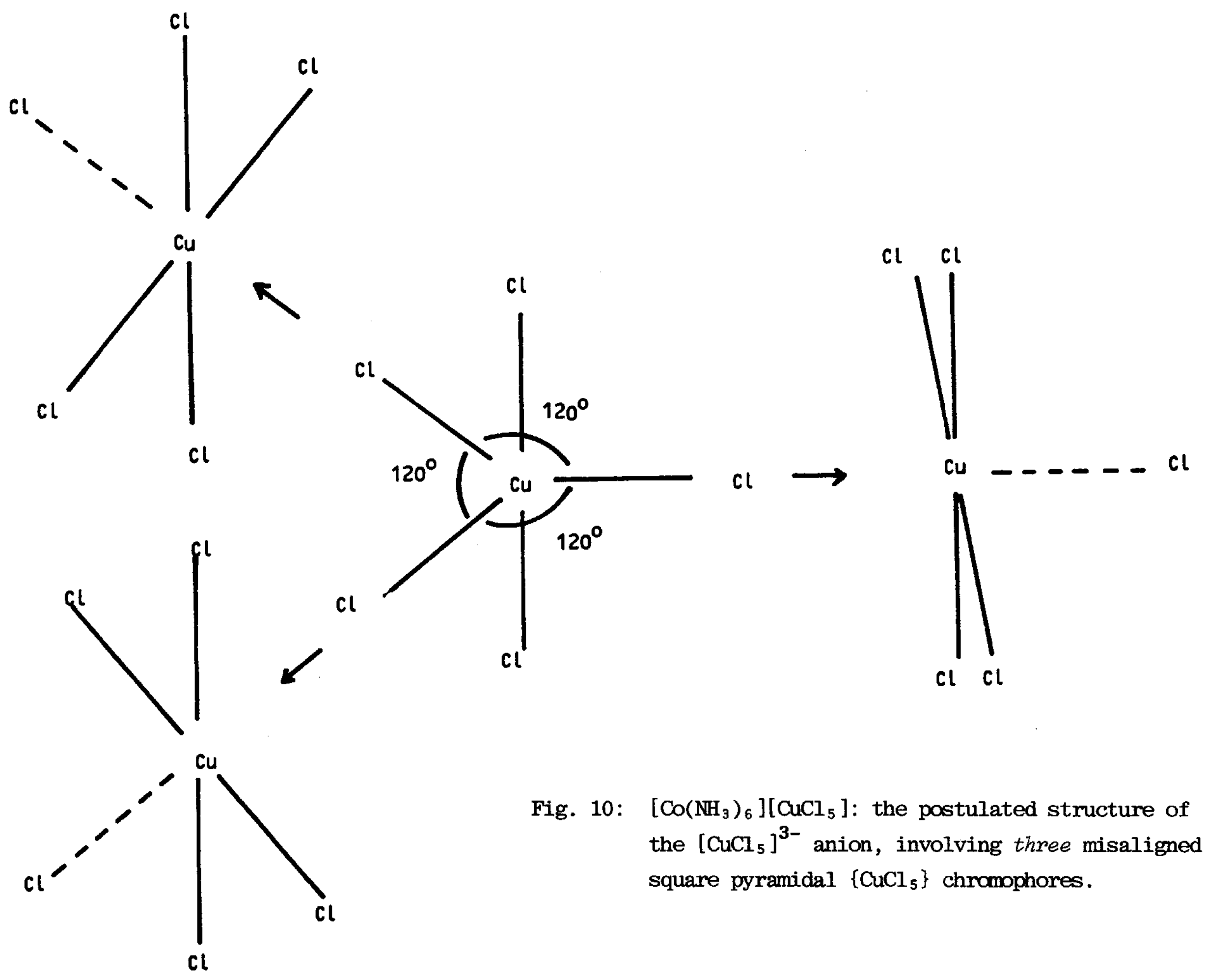
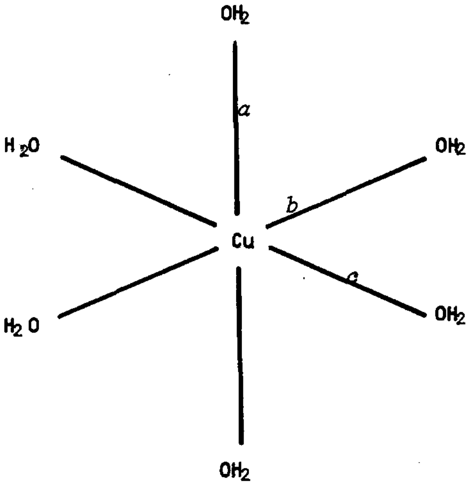


Fig. 10: $[Co(NH_3)_6][CuCl_5]$: the postulated structure of the $[CuCl_5]^{3-}$ anion, involving *three* misaligned square pyramidal $\{CuCl_5\}$ chromophores.

resonance spectra of $K_2Sr[Cu(NO_2)_6]$, $K_2Ba[Cu(NO_2)_6]$ and $Cs_2Pb[Cu(NO_2)_6]$ [55] have been reported over a temperature range, but could not be interpreted in terms of the change from a dynamic to static Jahn-Teller Effect in the caesium complex. The crystal structure of $[NH_4]_2[Cu(OH_2)_6][SeO_4]_2$ [56] (*3*) has been reported to be isomorphous with the corresponding $K_2[Cu(OH_2)_6][SeO_4]_2$ [57],



a = 2.237 Å
b = 2.031 Å
c = 1.990 Å
T = 0.895

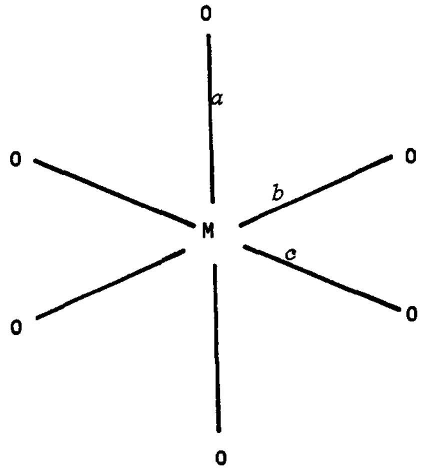
(*3*; $[NH_4]_2[Cu(OH_2)_6][SeO_4]_2$)

but not with the corresponding $[NH_4]_2[Cu(OH_2)_6][SO_4]$ [58].. The $\{CuO_6\}$ chromophore has a centrosymmetric elongated rhombic octahedral structure with a high tetragonality, 0.899, suggestive of a fluxional two-dimensional $\{CuO_6\}$ chromophore [1, Fig. 2]. The observed distortions from octahedral symmetry in copper(II) complexes $[Ml_6]$ and trans$[Ml_4L'_2]$ are well described in qualitative terms by s-d mixing, and the relative stabilisation energies of the square coplanar $[ML_4]$ and $(ML_2L'_2]$ units *via* the angular overlap model, with no recourse to the first and second order Jahn-Teller Effect [59].

7.3.2 EPR spectroscopy

The Sixth Jahn-Teller Conference at Nijmegen represented the highlight of the year in EPR spectroscopy [38b] in which the pure physics aspects received the most attention. The more chemical aspects of EPR spectroscopy continue to receive attention, both in pure copper(II) complexes, and when doped in diamagnetic host lattices. Increasingly, the importance has been recognised of measuring the EPR spectra over a temperature range in order to identify fluxional $\{CuL_6\}$ chromophores [4,41]. A substantial review of fluxional copper(II) complexes [4] summarised the limited variable temperature crystallographic evidence for temperature variable copper(II) structures and then devotes 70% of the review to the EPR evidence for fluxional behaviour. The most convincing evidence for fluxional behaviour involves both temperature variable structural and EPR data [1,2] of concentrated copper(II) complexes, which although they may have the advantage of known crystal structures, their EPR spectra may be less informative due to the unavoidable presence of exchange coupling effects due to misalignment of the $\{CuL_6\}$ chromophores. Historically, the first evidence for a fluxional copper environment came from the copper(II) doped $K_2[Zn(OH_2)_6][SO_4]_2$ system [60] and an extensive literature now exists [4] on the EPR of copper(II) doped systems. However, these systems also lack precise information on the structural data on the doped $\{CuL_6\}$ chromophore, and it is necessary to extrapolate to the structure of the concentrated copper(II) complex for this structural data. Unfortunately, in systems involving bridging ligand atoms, the structure of the concentrated and doped systems may involve a phase change, due to the Cooperative Jahn-Teller Effect [41], with a consequent structure change, which is best "detected" by a change in the electronic reflectance spectra. For this reason, the complementary use of electronic reflectance and EPR spectra of copper(II) doped systems over a concentration range is recommended as a help in identifying a change of structure with change in copper concentration. Even in more molecular type copper(II) lattices, where no change in structure of the $\{CuL_6\}$ chromophore occurs with dilution (the non-Cooperative Jahn-Teller Effect [43]), the lack of change of reflectance electronic spectra with concentration suggests the absence of a serious change in the $\{CuL_6\}$ structure and hence that the EPR parameters of the dilute system may be equated with the structural data obtained for the concentrated complex [4,41,43].

Professor J.S. Wood has reviewed the EPR spectra of the $[Cu(PyNO)_6]X_2$ complexes [38b], and has extended the series [61] to the $[M(4\text{-}CH_3C_4H_4NO)_6][ClO_4]_2$ complexes (M=Cu or Zn). Despite the near octahedral stereochemistry of the zinc complex (*4*), the copper complex (*5*) involves an elongated rhombic octahedral $\{CuO_6\}$ chromophore which shows no evidence of temperature variability in the g-values. The g-values are of interest as they show no evidence of exchange narrowing in the pure copper complex, and individual g-values of the two misaligned copper(II) sites are observed in both the concentrated and copper doped complexes. The accurate measurement of the single-crystal EPR spectra of $Cu(SO_4)5H_2O$ has been used [62] to resolve the g-values into their two sets of local molecular g-values of the two independent $\{CuO_6\}$ chromophores in the unit cell, and the two $g_{\parallel}$ values are shown to correlate (±10°) with the long



	Zn	Cu	
a =	2.160	2.385	Å
b =	2.113	2.008	Å
c =	2.063	1.965	Å

(*4*; $[Zn(4\text{-}MepyNO)_6][ClO_4]_2$)
(*5*; $[Cu(4\text{-}MepyNO)_6][ClO_4]_2$)

Cu-O direction. The single-crystal EPR spectrum of $CuTiF_6.4H_2O$ [63], containing a misaligned $\{CuO_4F_2\}$ chromophore, has been shown to be essentially axial (g=2.41,2.086) over the temperatures 77, 295 and 463K. The single-crystal g-values of $[Cu(bipy)_2(NCS)][BF_4]$ (2.011, 2.139 and 2.245) have been shown [64] to involve a correlation of the highest g-value with the $Cu\text{-}N_4$ direction of the distorted square pyramidal $\{CuN_2N'_2N''\}$ chromophore present. This establishes that in the structural pathway of Fig. 3, the change from trigonal bipyramidal (A) to distorted square pyramidal (B) to (C), involves a rotation of the highest g-value by 30° in the xy-plane, consistent with the change in geometry. There is a corresponding rotation [24] of g-values from the near regular *cis*-distorted octahedral structure of $[Cu(bipy)_2(ONO)][NO_3]$, Fig. 11(a), to the square pyramidal distorted (4+1+1*) structure of $[Cu(bipy)_2(O_2CH)][BF_4]$, Fig. 11(b). While the change from *cis*-distorted octahedral (Fig. 11(a)) to distorted bicapped square pyramid [65] of $[Cu(bipy)_2(O_2NO)][NO_3]$ (Fig. 11(c)) involves no change in the directions of the inplane g-values, the magnitudes of the g-values are interchanged, Fig. 11(c). Consequently, in the structural pathways of Fig. 3, the directions and magnitudes of the local molecular g-values may also be used to support the use of the electronic reflectance spectra (see Section 3.1), as an electronic criterion of stereochemistry, [17]. Where copper hyperfine data is available, this may also be used to supplement the electronic and EPR spectral data to suggest the local copper(II) environment [66]. The single-crystal EPR spectra of [Cu(cyclops)I] [2; (*41*) and Table 6] have been reported doped in the

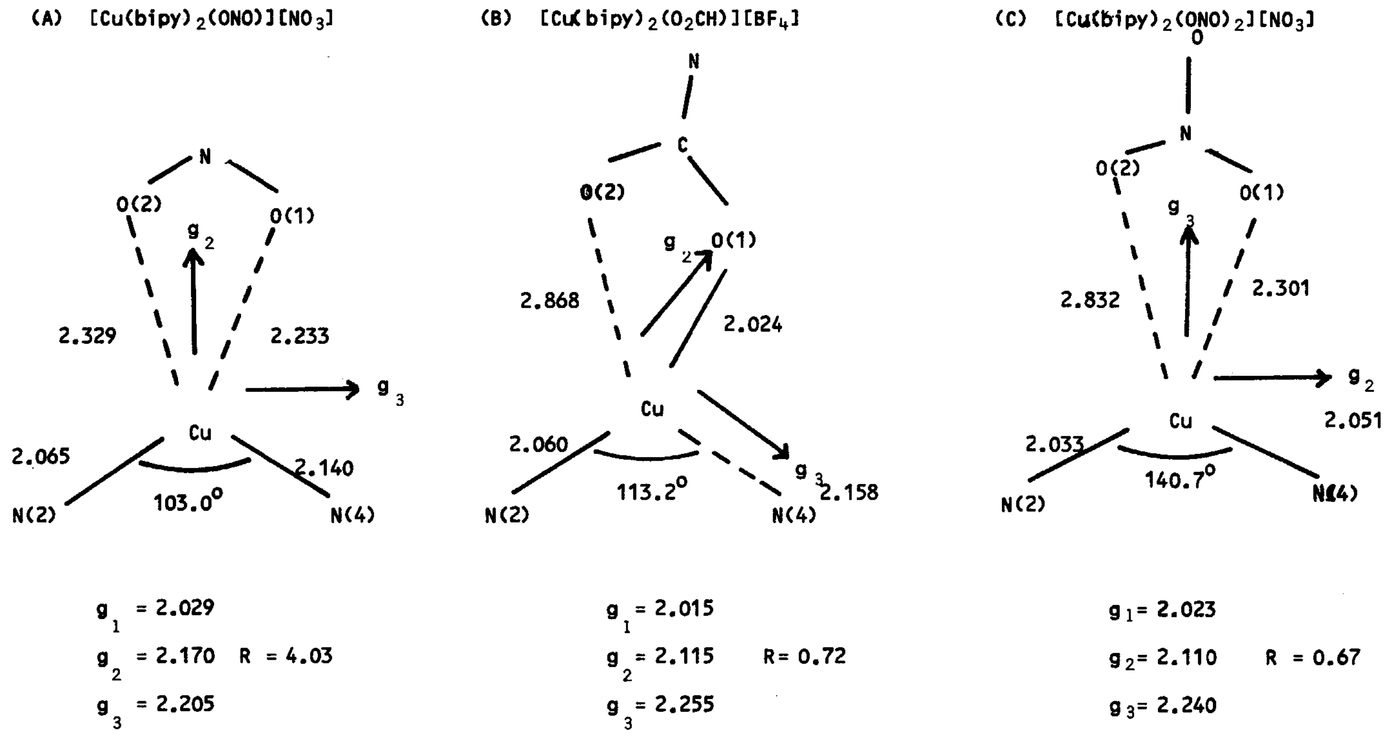


Fig. 11: [Cu(bipy)$_2$(OXO)]Y: the directions of the local molecular *g*-values

corresponding nickel(II) complex, and yield g-values of 2.05, 2.07 and 2.18 with $A_3 = 1.90\mathrm{x}10^{-4}\mathrm{cm}^{-1}$ [67]. The relatively low highest g-value is consistent with the relatively high ρ value [2, Table 6], but the A_3 value seems remarkably high, more consistent with that of a near square coplanar $\{CuN_4\}$ chromophore. In this paper the authors *assume* that the $\{CuN_4I\}$ geometry of the doped system equates with that of the more regular square pyramidal $\{NiN_4I\}$ chromophore (ρ = 0.23 A). If this were so, there would be a significant change in the electronic reflectance spectra of the pure copper complex and the doped system; unfortunately this was not reported probably due to the complication introduced by the spectra of the host lattice, but an electronic reflectance spectrum of the copper complex with the nickel complex as a reference would have been worth trying.

The EPR spectra of copper(II) complexes of crown ethers in solution have been used to establish a d_{z^2} ground state for a series of crown ethers involving 5-6 oxygen donors, but no electronic spectra were reported [68]. In [69], hyperfine coupling was used to establish the presence of two equivalent axial halide ions, while in [68] molecular orbital parameters were estimated assuming a compressed octahedral, a trigonal bipyramidal or pentagonal bipyramidal geometry for the copper environments. The local and cooperative Jahn-Teller interactions of the copper(II) ion in host lattices of tetragonally compressed octahedra have been examined [39] in the systems $K_2[(Cu_x,Zn_{1-x})F_4]$ and $Rb_2[(Cu_x,Zn_{1-x})F_4]$. For high values of x, the EPR spectra are exchanged, narrowed and correspond to a two-dimensional antiferrodistortive order of the elongated $\{CuF_6\}$ octahedra. At low x-values, the g-values are consistent with a time average compressed octahedra and a model is suggested balancing the strain effect of the compressed $\{ZnF_6\}$ octahedra against the non-spherical symmetry of the copper(II) ion, using a set of Jahn-Teller parameters (the linear and non-linear vibronic coupling constant were calculated for the Cu-F system).

The optical and EPR spectra of the copper(II) ion in single crystals of zinc, cadmium and mercury 1,2-diaminoethane fluoride complexes have been reported [70]: both the g-values and the electronic spectra are consistent with the presence of $\{CuN_4F_2\}$ chromophores. The principal axes of the g- and A-tensors of the copper(II) ion doped in the low symmetry lattice [71] may, (a), coincide with the direction for those of the host lattice, (b), distort the ligand positions of the host lattice, and (c) show no correlation with the host lattice. These three possibilities have been illustrated for the copper(II) ion doped in (i), a seven-coordinate complex, tetrakis(salicylate)tetraaquadicadmium(II), in (ii) a six-coordinate complex, bis(β-alanine)zinc(II)dinitrate tetrahydrate and (iii) an eight-coordinate complex, bis(salicylato)strontium(II) dihydrate.

The three examples are illustrated by single-crystal *g*-values, and bond direction/angular data, and the copper(II) ion in the eight-coordinate strontium complex is considered to occupy in interstitial site in the lattice. The effect of a phase transition on the copper(II) doped caesium chloride structure of $[NH_4]Br$ to a tetragonal phase below -38 °C is described [72]; while there is little change in the *g*-values (20 °C, 2.031 and 2.189; -85 °C, 2.033 and 2.187), there is a significant decrease in the observed hyperfine data, 178.4 to $153.8 \times 10^{-4} cm^{-1}$ with decreasing temperatures. The EPR and electronic spectra of a series of bis(*N*-substituted-2-picolinamine *N*-oxide)copper(II) tetraphenylborate complexes [73] have been reported, but little use was made of the electronic spectra to support the rhombic coplanar stereochemistry suggested. The EPR of the copper(II) ion in a $CuO\text{-}B_2O_3\text{-}Al_2O_3$ glass [74] and in $Cu^{-}H_2$ edta complexes [75] have been reported.

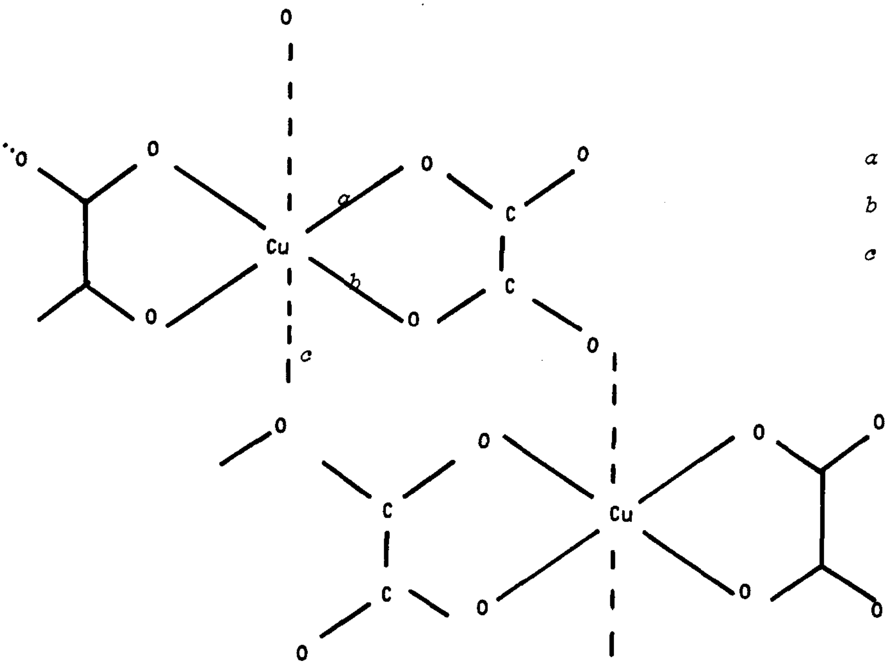
The EPR spectra of complexes with sulphur ligands have continued to attract attention. The crystal structure of bis(maleonitriledithiolato)copper(II)bis-(3,9-bis(dimethylamino)phenazothionine) [76] yields a structurally dilute lattice with rhombic coplanar $\{CuS_4\}$ units involved in weak antiferromagnetic coupling ($J = -2.6\ cm^{-1}$), and the EPR spectra is consistent with the weak triplet state of the coupled copper(II) ions. The EPR spectra of copper(II) dithiocarbamates and their mixed ligand complexes have been reported in solution [77]. In an analyses of copper(II) amino acid complexes, the high-field EPR spectra show evidence for nitrogen hyperfine coupling, and curve fitting of overlapping peaks of the second derivative spectrum was used to characterise the *cis* and *trans* isomers, $\{CuN_2O_2\}$ [78]. The EPR spectra of a series of 3-amino-5-methylisoxazole complexes [79,80] in the solid state and in solution have been used to characterise their electronic ground states. EPR measurements at X- and Q-band frequency of $Cu(N_1N\text{-}Et_2en)_2(NCS)_2$[81] at 273, 70 and 4.2 K have been used to determine whether the crystal *g*'s equate with the local molecular *g*'s. In the mixed ligand complexes [82] of Cu(3,3'-diaminodipropylamine)(1,3-diaminopropane)X_2, the EPR spectra have been used to distinguish a trigonal bipyramidal and a square pyramidal $\{CuN_5\}$ chromophore. The EPR spectra of mononuclear oxime complexes of copper(II) have been reported [83] in solution and in the solid state. The EPR spectra of copper(II) complexes of *N*,*N*'-bis(picolinoyl)-1,3-diaminepropane have been examined as a model for polypeptide ligands [84]. A further example of the EPR spectra of nickel(II)-copper(II) exchange-coupled pairs in dinuclear triketonal complexes [85] and of *ortho*-hydroxyketoximes [86] have been reported. Electron-electron spin-spin interactions have been observed in the EPR spectra of spin-labelled copper porphyrins; for piperidine nitroxyl, *J* is greater for the ester linkage rather than the amide linkage [87].

A combined EPR and proton ENDOR spectra determination at 10 K on copper(II) doped zinc ethanoate dihydrate has established the hyperfine coupling tensors of the four protons of the two coordinated waters [88], and establish the hydrogen bonding connections along the *b*-axis. Ligand ENDOR studies of copper(II) doped L-alanine single-crystals have been reported [89]. The single-crystal EPR spectra of the copper(II) ion doped in the novel seven-coordinate structure (trigonal capped square based pyramidal), $Cd(CH_3CO_2)_2 2H_2O$ structure [90] yield rhombic *g* and *A*-values, 2.4139, 2.1644, 2.0382 and 101.6, 25.3, 50.1 x 10^{-4} cm^{-1}, respectively. The extent of non-coincidence of the *g*- and *A*-tensors is 4^o in the *xy*-plane and yielded the quadrupole parameters *P* and *R* of 9.7 and 1.2 x 10^{-4} cm^{-1}, respectively, which were rotated 35^o from the *g*-directions in the *xy*-plane. There is an intriguing suggestion in this paper that the magnitude of the quadruple parameter *P* varies with the coordination number of the copper(II) ion, 5.6 - 11.0 x 10^{-4} cm^{-1} for six-coordination (and above), and 3.0 - 5.0 x 10^{-4} cm^{-1} for four coordination. If this could be established, it would be a most useful criterion in doped copper(II) systems, where the lack of X-ray structural information (*vide infra*) is a major problem, and could be tested using the non-cooperative Jahn-Teller systems [43].

Phonon modulation of the antisymmetric exchange has been established [91] from the temperature dependence of the line-widths of the EPR spectra of $[RNH_3]_2[CuX_4]$ salts. A study has been made of the angular anomalies in the X-band powder EPR spectra of copper(II) complexes with axial symmetry. [92].

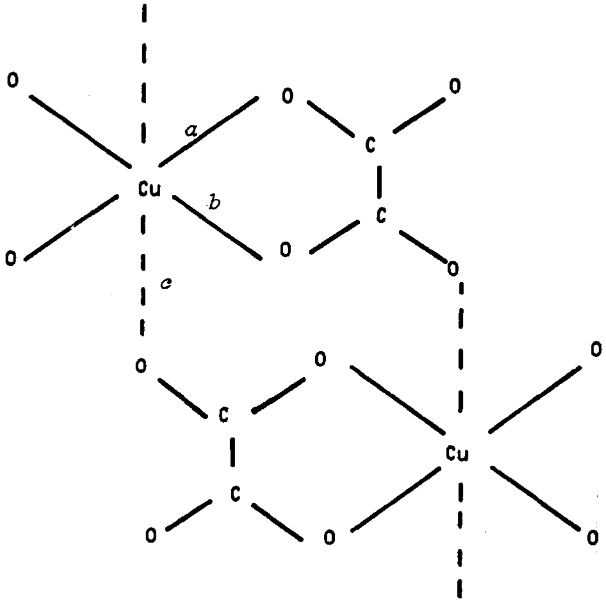
3.3.3 Magnetism

A most useful review of "Magnetism and the Metal Ligand Bond in Coordination Chemistry" [93] appeared early in 1981 and generally reviews the use of the angular overlap method to interpret magnetic data which the authors hope will "bring to an end the era of magneto-chemistry being simply a technique for counting unpaired electrons". The review also discusses the direct determination of molecular spin densities in paramagnetic transition metal complexes using the technique of polarised neutron diffraction and, although not involving copper complexes specifically, gives a useful introduction to the scope and limitations of this relatively new technique. Polarised neutron diffraction from single-crystals of aquabis(2,2'-bipyridine)-di-μ-hydroxo-dicopper(II) provides an experimental spin density synthesis, which reflects indirect rather than direct spin exchange between the ferromagnetically coupled copper atoms [94].



a = 1.933 Å
b = 1.939 Å
c = 2.586 Å

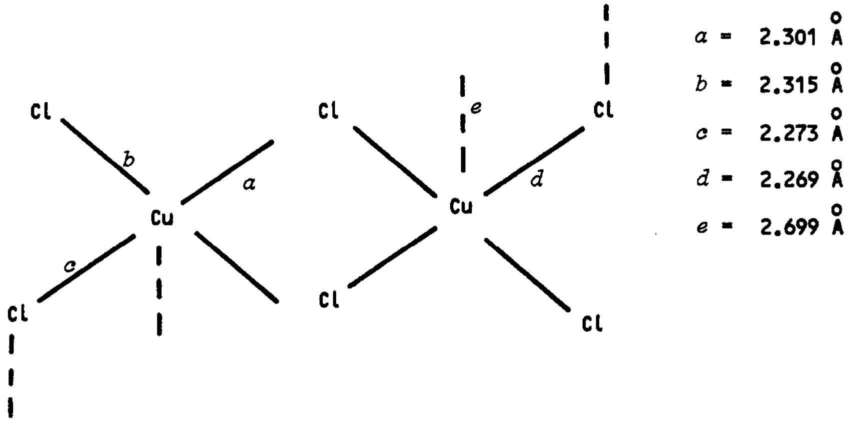
(6; $[C_6H_5CH_2NH_3]_2[Cu(C_2O_4)_2]$)



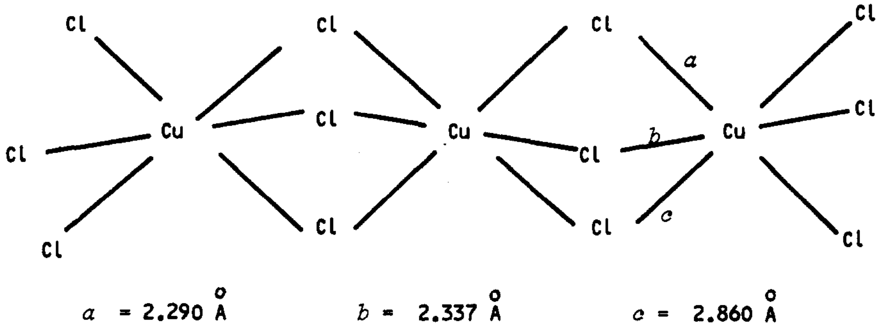
a = 1.931 Å
b = 1.937 Å
c = 2.883 Å

(7; $[1,3\text{-}pnH_2][Cu(C_2O_4)_2]$)

The search for a synthesis of one- and two-dimensional ferromagnetic copper(II) complexes continues, and a review of the structural features likely to involve the one-dimensional ferromagnetics has appeared [95]. Single crystal studies have been carried out on the "so-called" one-dimensional ferromagnetic crystal of $[Me_2NH_2][CuCl_3]$ [96] and the "quasi" one-dimensional ferromagnetic $CuCl_2$.dmso [97]. While the structure and magnetism of two two-dimensional copper(II) oxalates, $[BzNH_3]_2[Cu(C_2O_4)_2]$ and $[1,3\text{-pnH}_2][Cu(C_2O_4)_2]$, both involve essentially planar $[Cu(C_2O_4)_2]^{2-}$ anions, in the former complex dimerisation to give a centrosymmetric layer structure (*6*), has occurred, whereas in the latter complex a linear chain structure, (*7*), exists. (*6*) displays antiferromagnetic behaviour $J/k = -0.21$ K, while (*7*) can be fitted to a ferromagnetic, $S = \frac{1}{2}$, one-dimensional model $J/K = 19$ K with strong antiferromagnetic coupling between the chains [98]. Inter-layer exchange coupling in a quasi two-dimensional salt, $[C_nH_{2n+1}NH_3]_2[CuCl_4]$, has been studied by EPR spectroscopy [99] and, despite the presence of non-equivalent copper ions, the coupling is strong enough to give only a single EPR line in all directions. The crystal structures of $[NH_4](CuX_3)$ {X = Cl or Br} have been redetermined [100] and the structure of the planar dimer $[Cu_2Cl_6]^{2-}$ confirmed; the antiferromagnetic behaviour of the bromide was shown to be stronger than the chloride. The magnetic and EPR properties of some mixed metal $[Me_3NH]_3(Cd_{2-x}Cu_xCl_7)$ complexes have been reported [101]. Pressure dependence of the magnetic properties of the quasi two-dimensional antiferromagnetic $[EtNH_3]_2[CuCl_4]$ have been determined [102], the spin-flip field H_1 increases quadratically. In a series of papers [103-105] on the thermochromism of copper halide salts, the crystal structure of $[Me_2CHNH_3](CuCl_3)$ [103] has been



(*8*; $[Me_2CHNH_3][CuCl_3]$ - *Phase II*) determined (*8*) along with a phase transition, T_{th}, at -51 °C from brown phase I to σ-range phase II. The low temperature Phase II is triclinic, $P\bar{1}$, with bridged linear chains of $\{Cu_2Cl_6\}^{2-}$ dimers (*8*), while the high temperature Phase I involves tribridged chains of $\{CuCl_3\}_n^{n-}$ stoicheiometry, (*9*). The chain axes in the two phases are aligned and the $[Me_2CHNH_3]^+$ cations are ordered in phase II, but disordered in phase I. The ^1H NMR line width narrows at -51 °C for the *N*-deuterated salt, consistent with a dynamic two-fold disorder. The phase II linear chains are consistent with antiferromagnetically coupled dimers, with $S=0$ ground state, while the phase I linear chains are ferromagnetically coupled, and a sharp break in the susceptibility occurs at T_{th} indicating a first order phase transition. Deuteration of the $[RNH\ ]^+$ moiety raises T_{th} by 10 °C, indicating the presence of weaker N-H....Cl hydrogen bonds in phase I. In phase II, the local molecular structure involves a square pyramidal $\{CuCl_5\}$ chromophore, which changes to an elongated rhombic octahedral $\{CuCl_6\}$ chromophore in phase I. As this paper must represent one of the most complete examinations of a thermochromic phase change, it is unfortunate that the corresponding electronic spectra were not reported and examined with the same meticulous detail as the crystallographic and magnetic properties. The thermochromism of $[Me_2CHNH_3]_2[CuCl_4]$ (104] and $[Me_2CHNH_3](CuBr_3)$ [105] have also been characterised by structural and magnetic properties.



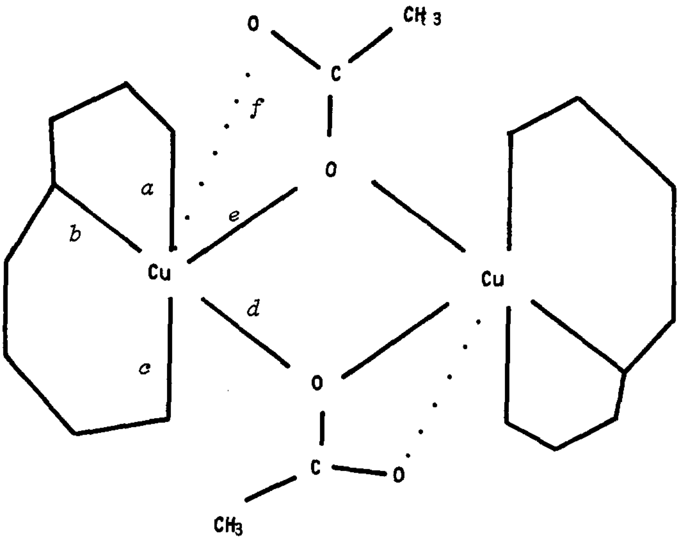
(*9*; $[Me_2CHNH_3][CuCl_3]$ - *Phase I*)

The magnetisation processes of the two-dimentional $Cu(HCOO)_2.4H_2O$ and $Cu(HCOO)_2.2(NH_2)_2CO.2H_2O$ have been reported [106], and their magnetic parameters estimated. Static spin correlations in the diluted two-dimensional ferromagnetic $K_2Cu_xZn_{1-x}F_4$ (see Section 3.3.1) have been discussed [107], along with the magnetic optical properties of the two-dimensional ferromagnetic K_2CuF_4 [108] which has been shown to exhibit linear magnetic birefringance. The magnetic properties of copper(II) complexes of phenylboronic acid have been described [109], and single-crystal data on the γ-form of bis(*N*-methyl-salicylaldimine)copper(II) have been examined [110]. Magnetic and structural studies of copper(II) dialkyldithiocarbamates continue to attract attention [111]. Structural studies have shown that there is an angle of 47.4° between the planes of the ligands in copper(II) maleonitrile dithiolate [76], with the anions stacked in pairs along the *c*-axis. Susceptibility measurements indicate an antiferromagnetic exchange coupling, J = 2.6 cm^{-1}, while the single crystal EPR spectra (*g*-values, *A*-values and zero field splitting parameters) have been compared with tensors calculated using semiempirical molecular orbital data. The magnetic susceptibility of the highly electrically conducting complexes, $\mathrm{CuL}_n(\mathrm{TCNQ}^-)_2$ (L = 2,2'-bipyridine, 1,10-phenanthroline or 1,2-diaminoethane) [112] suggest that the $\mathrm{Cu}^{2+}\mathrm{L}_n$ chelates are partially reduced to the $\mathrm{Cu}^{+}\mathrm{L}_n$ chelate. The equilibrium (1) produces conduction electrons in the TCNQ colums, which

$$\mathrm{Cu}^{2+}\mathrm{L}_n(\mathrm{TCNQ}^-) \rightleftharpoons \mathrm{Cu}^{+}\mathrm{L}_n(\mathrm{TLNQ}^-)(\mathrm{TCNQ}^0) \qquad (1)$$

stack in the unit cell. An extensive review has appeared of the mono-. bi-, tetra- and polynuclear copper(II) halogenocarboxylates, covering extensive magnetic and crystallographic data [3], with numerous correlations of the Cu-L distances, and the magnetic exchange *J*-values. Binuclear caffeine adducts of copper(II) ethanoate and copper(II) chloroethanoates yield unusually high antiferromagnetic interactions [113].

A comparison of the metal-metal bond energies in chromium(II) and copper(II) ethanoate dimers [114] indicates that the bond energy in the Cr-Cr bond is only 45 kJ mol^{-1} stronger than in the Cu-Cu bond. Crystal structure studies [115] have shown that in the complex $\{\mathrm{Cu(L)(CH_3CO_2)}\}_2.\mathrm{H_2O}.\ \mathrm{C_2H_5OH}$ (HL = *N*-(1,1-dimethyl-2-hydroxyethyl)salicylaldimine), the ethanoate ion functions as a single ethanoate bridge through the ethanoate oxygen atom (*10*). The dimers are non-centro symmetric with a distorted square pyramidal $\{\mathrm{Cu}NO_3O'\}$ chromophore, but with the sixth coordinate position occupied by the second ethanoate oxygen involving off-the-*z*-axis bonding at a distance of 2.724 Å. In this dimer, although a predominant antiferromagnetism is predicted, the magnetic susceptibility indicates a predominantly ferromagnetic behaviour. A ferromagnetic interaction [116] has also been observed for the copper(I)-copper(II) cluster $[\mathrm{Cu_6}^{\mathrm{II}}\mathrm{Cu}^{\mathrm{I}}{}_8\mathrm{L}_{12}\mathrm{Cl}]^{5-}$, where L is a deprotonated α-mercapto-isobutyric acid and D-penicillamine [116]. An antiferromagnetic exchange has been observed for a number of alternating chain compounds, such as *catena*-di-μ-dichloro-bis(4-methylpyridine)copper(II) and the magnetism has been fitted to the alternate chain Heisenberg-exchange model [117]. The effect of varying chelate ring size on the geometry and antiferromagnetic behaviour in di-μ-oxobridged dinuclear copper(II) complexes has been described [118], and the idea that trigonality about the bridging oxygen atom may be important is



a = 1.998 Å

b = 1.937 Å

c = 1.925 Å

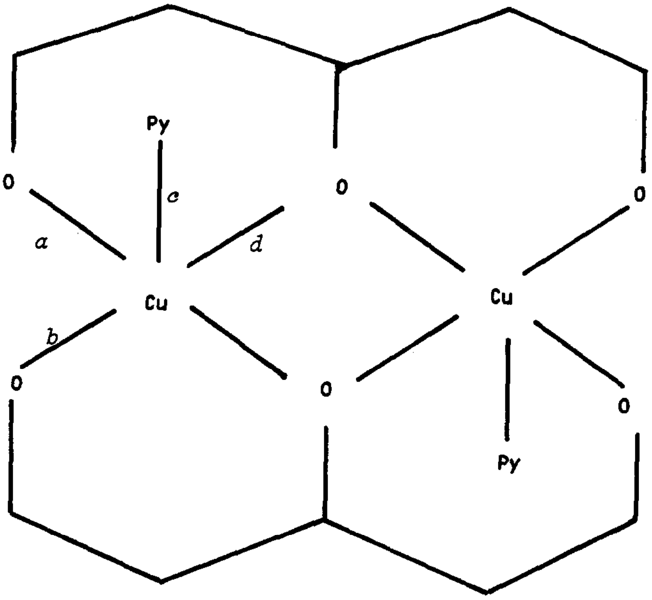
d = 1.952 Å

e = 1.446 Å

f = 2.621 Å

(10; $[\{Cu(L)(CH_3CO_2)\}_2].H_2O.EtOH$*)*

supported. The crystal structure of bis{1,5-bis(4-methoxyphenyl)-1,3,5-pentanetrionato}bis(pyridine)dicopper(II) [119] has been reported *(11)* and shown to exhibit strong antiferromagnetic behaviour, $2J = -825$ cm^{-1}, such



a = 1.890 Å

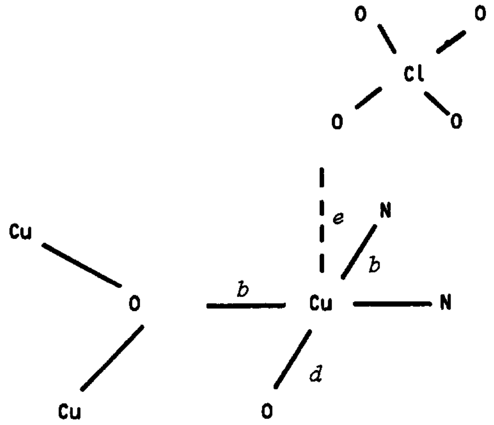
b = 1.908 Å

c = 2.298 Å

d = 1.962 Å

(11)

that the complex is virtually diamagnetic at room temperature. The synthesis, magnetic and spectral properties for some alkoxo-bridged copper(II) complexes have been reported [120], as well as for a trinuclear copper(II) hydroxo complex $[Cu_3(OH)L_3(ClO_4)][ClO_4]$ (LH = 3-(phenylimino) butanone 2-oxime), (*12*) [121]. The structure of (*12*) is of interest in that it involves a chelate bridging semi-coordinate perchlorate ion. The synthesis and magnetic properties of some chiral tetranuclear imino alkoxy complexes of copper(II) have been prepared by a template condensation procedure to yield tetranuclear $\{Cu_4O_4\}$ units [122], and a cluster approach to layer-type $Cu(NH_3)_2(CO_3)$ has been reported [123].



a = 1.969 Å
b = 1.962 Å
c = 1.981 Å
d = 1.911 Å
e = 2.428 Å

(*12*; $[Cu_3(OH)L_3(ClO_4)][ClO_4]$)

3.3.4 Electronic and other spectroscopic properties

Only one paper involving partial polarised electronic spectra [124], of the tetrahedral $\{CuN_4\}$ chromophore in $[NEt_4]_2[Cu(NCS)_4]$ along with single crystal EPR and INDO-MO calculations, has appeared in 1981, although the polarised single crystal electronic spectra of the copper(II) doped $[Zn(bipy)_2(ONO)][NO_3]$ has been reported over a concentration range 0.1-100% [23]. The solid state electronic spectra and circular dichroism spectra have been reported for $[Cu(tren)(NH_3)][ClO_4]$ [125], and the results compared with the theoretical transition probabilities based upon the dynamic ligand polarisation mechanism. It is found necessary to include the polarisability anisotropy of the chelate ring bonds to account for the optical activity and the overall negative d-d circular dichroism is found to characterise the S-conformation of the tren ligand in this five-coordinate complex. Circular dichroism studies of copper(II)-D-*o*-tyrosine complexes [126], copper(II)

Schiff base complexes, derived from camphor and histidine [127], and of mixed ligand complexes of copper(II) with chiral acids and amines [128] have been reported, but in no case do the studies lead to the assignment of the spectra. The use of ternary ligand complexes to probe the use of transient electric dichroism (enhanced circular dichroism in the presence of an applied electric field) of copper(II)-polystyrenesulphonate complexes [129] are reported. The electronic and circular dichoism spectra of copper(II) complexes with optically active ligands [130] have been used to suggest the formation if *cis-* and *trans-* isomers of the bis-ligand complexes. The electronic solution spectra of bis(*N*-substituted 1,2-diaminoethane)copper(II) complexes have been used to predict the Cu-N distances present, but the limitations of the crystal field model used places some reservations on the value of this approach [131]. The optical properties of Cu-doped ZnO have been interpreted as arising from a Cu^+ hole characterised by a near IR luminescent spectrum [132,133].

The metal oxidation state has been examined in tetraimine macrocyclic copper(II) complexes from an examination of the imine vibration bands between 1500-1700 cm^{-1}, which disappears on one-electron reduction of the complexes [134]. Circular polarisation measurements establish a large antisymmetric component of the Raman scattering from the breathing vibration of $[CuBr_4]^{2-}$ in ethanenitrile, when excited at 514 Å into the first Br→Cu charge-transfer (π) absorption band [135]. A pH dependence of the Raman scattering on the structure of 1:2 copper(II):L-histidine complexes in aqueous solution is reported [136]. Raman difference spectroscopy (RDS) [137] is suggested as a probe for the analysis of the molecular association of copper uroporphyrin with additional ligands [138]. Far-infrared and Raman spectroscopy have been used to probe the phase transition of $CsCuCl_3$ (see Section 3.3.1) [139]. Continuous and flash photolysis has been used to probe the photochemistry of copper(II) amino acid complexes [140], to induce the oxidation of the ligand and the reduction of the copper(II) to copper(I). An examination of the uv spectra of copper(II) complexes with imidazole and pyrazole ligands [141] indicates a red shift of 10,000-12,000 cm^{-1} for tetrahedral rather than square coplanar copper(II) complexes. Calorimetric, thermal expansion and optical measurements [142] confirm the phase transition of the perovskite layer compound $[EtNH_3]_2[CuCl_4]$. Phase transitions have been studied by ^{14}N quadrupole resonance [143] and by ^{13}C NMR studies [144]. Nuclear magnetic resonance isotropic shifts arising from equatorial coordination of the copper(II) aqua ion [145] have been reported, while bromine NMR studies have been made of tetrahedral copper(II) complexes of the type $[C_nH_{2n+1}NH_3]_2[CuBr_4]$ (n = 1 or 2) [146]. Nuclear relaxation times of a series of polycrystalline samples of copper(II) doped $[NH_4]_2[Zn(OH_2)_6][SO_4]_2$ have been measured [147] and used to obtain electron-spin relaxation times, which are found to vary exponentially with the metal-metal separation. X-ray photoelectron spectra have been used to examine the partitioning of Cu(II) and Cu(I) in copper ferrites [148] and the valence orbital binding energies and crystal structure in copper compounds [149]. The bonding between the copper metal atoms in $[Cu_2]$ have been examined [150] and the relative stability of *cis-trans* isomers of copper(II) compounds have been described using electron-vibration ideas [151]. The temperature dependence of the ^{63}Cu and ^{14}N nuclear quadrupole resonance frequencies in $KCu(CN)_2$ have been interpreted in terms of vibrational effects on the d_π-p_π bonding present between the copper and the carbon atoms [152].

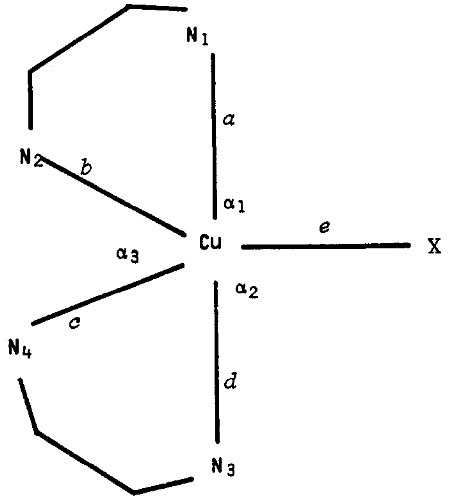
3.3.5 EXAFS Spectroscopy

The most important event of the 1981 EXAFS spectroscopy season was a Conference on "EXAFS for Inorganic Systems", held at the Daresbury SERC Laboratory on 28-29 March, 1981, preceding the initiation of the EXAFS facility at Daresbury by only a few months. Although copper received no special attention, it received frequent mention in complexes, glasses, surfaces and biological copper systems [153]. An extensive review of the EXAFS technique has been published [154].

In 1981, copper EXAFS spectroscopy received a surprisingly scant treatment in the literature - hopefully a pause while the Daresbury facility comes on-line. The application of EXAFS spectroscopy to the $[Cu(OH_2)_6]^{2+}$ in solution has yielded two poorly resolved lines which suggest that the axial ligands are only loosely bonded [155]. The use of rigid group analysis has been applied to the EXAFS spectra of the imidazole group in three tetrakis(imidazole)copper(II) complexes, and promises to be a useful technique for reducing the number of parameters in the curve fitting procedure [156]. A preliminary report of the EXAFS spectra of copper(II) oxalate hemihydrate suggests that four planar Cu-O distances of 1.98 Å are present [157]. The EXAFS spectrum of a Cu_xTi_{1-x} alloy has also been reported [158]. The EXAFS spectra of the copper site in Mollusean oxyhemocyanin [159] suggests that it involves copper(II) with a square coplanar structure of four nitrogen (or oxygen) ligands at 1.98 Å. The EXAFS spectrum of copper in cytochrome *c* oxidase gives direct evidence of 1-1.5 Cu-S distances at 2.27 A [160], while that of the copper site in deoxyhemocyanine suggested two Cu-N's at 1.95 Å and a long Cu-Cu interaction at *ca*. 5.6 Å (161). X-ray K-absorption spectra of some aminoacid and carbonato complexes of the copper(II) ion have been examined [162], and the X-ray spectra and electronic structure of copper halogenides are reported [163].

3.3.6 Crystallography

The pace of publication of crystal structure determination continues. More complete data is now available on the $[Cu(bipy)_2Cl]X$ series of complexes [13,164] which were used to establish the structural pathway of this cation, [2, Figs 5-7]. An additional example of the distorted geometry of this cation has appeared [165], namely $[Cu(bipy)_2Cl][C_3(CN)_5]$ (*13*), which fits the correlations established in [13]. The structure of $[Cu(bipy)_2(NCS)][BF_4]$ [64] (*14*) establishes that the thiocyanate anion is nitrogen coordinated with a distortion closely comparable to (*13*) in the corresponding structural pathway. The data of Table 6 establish that the distortions of [1, Fig. 5] also occurs



X = Cl		X = NCS	
a =	1.969 Å	*a* =	1.993 Å
b =	2.062 Å	*b* =	2.069 Å
c =	2.118 Å	*c* =	2.120 Å
d =	1.998 Å	*d* =	1.980 Å
e =	2.277 Å	*e* =	1.967 Å
α_1 =	138.5°	α_1 =	137.9°
α_2 =	114.2°	α_2 =	117.5°
α_3 =	107.3°	α_3 =	104.6°

(*13*; $[Cu(bipy)_2Cl][C_3(CN)_5]$)

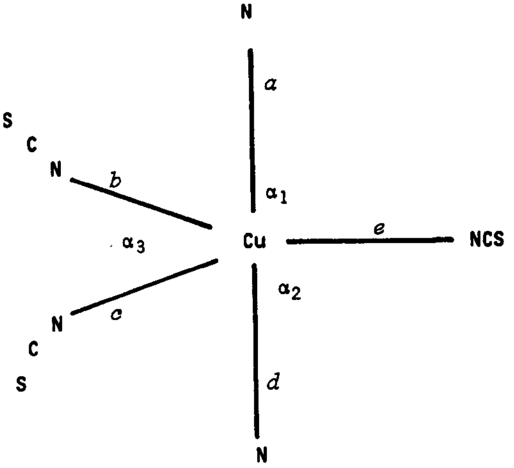
(*14*; $[Cu(bipy)_2(NCS)][BF_4]$)

TABLE 6

Square pyramidal distorted trigonal bipyramid $[Cu(chelate)_2X]Y$ complexes

	Chromophore	α_1	α_2	α_3	$r(Cu-N_4)$ Å	Ref.
$[Cu(bipy)_2Br]Br$	$\{CuN_4Br\}$	124.7°	128.6°	106.7°	2.075	166
$[Cu(bipy)_2I][I_3]$	$\{CuN_4I\}$	123.2°	123.2°	113.6°		167
$[Cu(phen)_2Cl][ClO_4]$	$\{CuN_4Cl\}$	127.6°	119.0°	113.4°	2.136	168
$[Cu(bipyam)_2Cl]Cl.4H_2O$	$\{CuN_4Cl\}$	158.0°	104.4°	97.5°	2.172	169

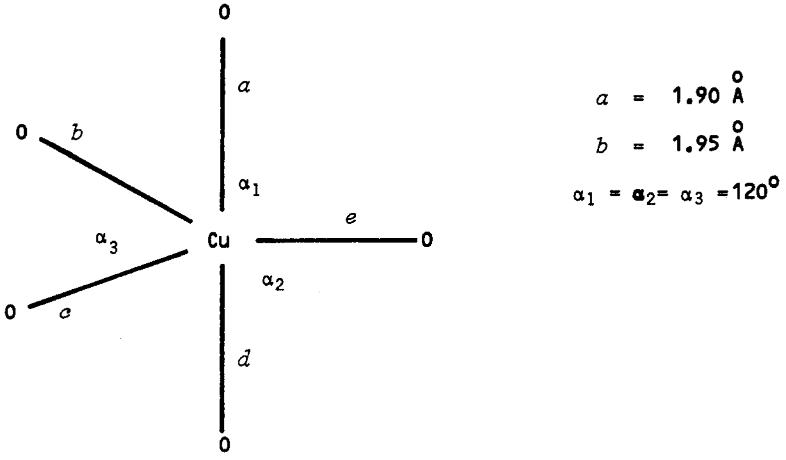
where X = Br or I, and for chelate ligands other than bipy, namely, 1,10-phenanthroline or di(2-pyridyl)amine [166-169], and suggest that the structural pathway is a general feature of [Cu(chelate)$_2$(halide)]X type complexes. Further data has been reported [12] on the structural pathway from trigonal bipyramidal to square pyramidal for the $\{CuN_5\}$ chromophore of the [Cu(dien)(bipyam)]X$_2$ series of complexes, [2, Fig. 4] and, in particular the use of the electronic reflectance spectra to establish a spectroscopic criterion of stereochemistry (Section 3.1). The crystal structure of K[Cu(hexamethylenetetramine)$_2$(NCS)$_3$].-2H$_2$O [170,171] is of interest, as a distorted trigonal bipyramidal chromophore $\{CuN_5\}$ (*15*) is involved, not only with the inplane bond lengths and bond angles



a = 2.092 Å
b = 2.102 Å
c = 1.983 Å
d = 2.086 Å
e = 1.980 Å
α_1 = 137°
α_2 = 108°
α_3 = 105°

(*15*; $K[Cu(C_6H_{12}N_4)_2(NCS)_3].2H_2O$)

distorted towards square pyramidal, but because the mean out-of-plane Cu-N distance, 2.097 Å, is significantly longer than the mean inplane Cu-N distance, 2.016 Å. This contrasts with the situation found in most trigonal bipyramidal copper(II) structures [1,2,13,18] but agrees with that earlier reported for Cu(NH$_3$)$_2$Ag(NCS)$_3$ [48]. A most unusual regular trigonal bipyramidal $\{CuO_5\}$ chromophore [172] exists in CuGaInO$_4$ (*16*), unusual as this geometry rarely exists with oxygen ligands bonded to the copper(II) ion. The three inplane oxygen ligands also display unusually high and anisotropic thermal parameters, with the maximum anisotropy lying in the trigonal plane, suggesting that the trigonal pyramidal geometry is an artifact of three misaligned square pyramidal chromophores, as for the [CuCl$_5$]$^{3-}$ anion (see Fig.10).



(*16; CuGaInO$_4$*)

The statistical analysis of the X-ray structural data for the $\{CuF_n\}$ chromophore has been used to plot an adiabatic potential surface for the $[CuF_6]^{4-}$ anion, from plots of R_{axial} and R_{eq}, and to develop a *two* minimum potential energy surface [173].

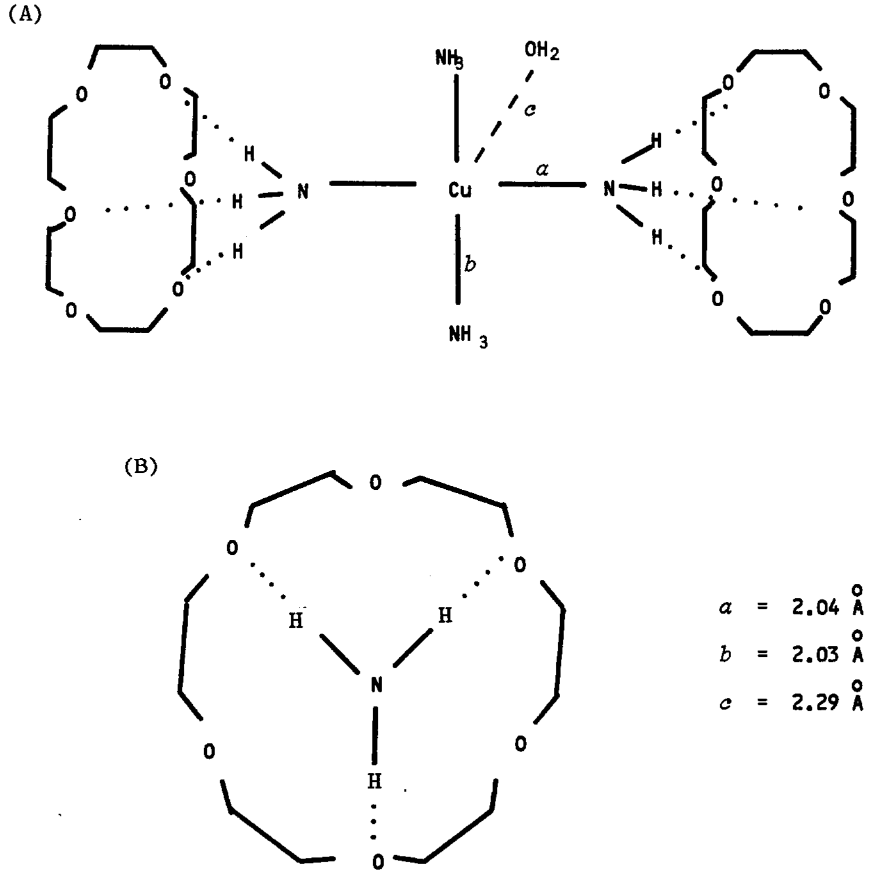
A number of square pyramidal structures have been reported, Table 7, involving approximately equal θ and ϕ values [2, Fig. 11], with only small distortions towards the trigonal bipyramidal stereochemistry. Among these [174] is a simple $[Cu(NH_3)_4(OH_2)]^{2+}$ cation complex with a crown ether, in which the NH_3 hydrogen bonds to form chains (*17*A) of H_3-Cu-NH_3-(crown ether oxygen) staggered links, (*17*B). A square pyramidal $\{CuN_4S\}$ chromophore has been reported for a complex of $[Cu(pre)]^+$ and 4-chlorothiophenolate anion preH = 3,9-dimethyl-4,8-diazamideca-3,4-diene-2-oxime-10-oximate) [179] and for (L-aspartate)(imidazole)copper(II) dihydrate [180].

The crystal structure of $K_2[Cu(CO_3)_2]$ [181] has been determined to high accuracy (R = 0.029) and used to evaluate the electronic structure of the copper(II) ion in a $\{CuO_4\}$ rhombic coplanar chromophore, r\{Cu-O\} = 1.919 and 1.933 Å. The final difference - Fourier synthesis showed non-centrosymmetric areas of positive and negative deformation charge density on opposite sides of the $\{CuO_4\}$ plane, and their populations refined to ±0.31 electrons at fixed axial positions, 0.55 Å from the copper(II) atom. This experiment represents the first clear evidence for the non-spherical symmetry for the copper(II) ion, as predicted previously [18]. What is equally interesting is that the carbonate ion bonds in two different ways, (*18*), such that *two* O(3) oxygen atoms are involved in long, 2.80 Å, off-the-z-axis coordination [182] to give, not a four-coordinate $\{CuO_4\}$ chromophore, but a six-coordinate $\{CuO_4O_2\}$ chromophore, which is better described

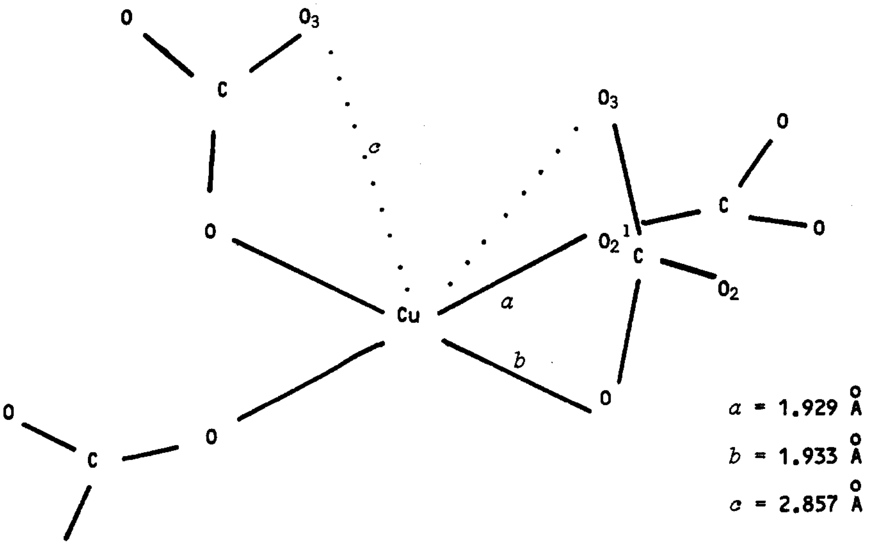
TABLE 7

Near regular square pyramidal copper(II) complexes

		ρ	$r(\mathrm{CuL_3})$/Å	θ/°	ϕ/°	Ref.
$[\mathrm{Cu(NH_3)_4(OH_2)(18\text{-}crown\text{-}6)}]$	$\mathrm{Cu}N_4O$	2.29	O-2.29	-	-	174
$[\mathrm{Cu(bipyam)(OH_2)_2F]F.3H_2O}$	$\mathrm{Cu}N_2O_2F$	0.0	O-2.218	164.0	173.1	175
$[\mathrm{Cu(1,1',4,7,7'\text{-}Me_5dien)Cl][ClO_4]}$	$\mathrm{Cu}N_3ClO$	0.168	O-2.68	179.4	159.5	176
$[\mathrm{Cu(dien)]_3[Fe(CN)_6]_2.6H_2O}$	$\mathrm{Cu}N_4N$	0.32	N-2.32	170.9	161.0	177
	$\mathrm{Cu}N_4O$	0.10	O-2.41	159.8	164.7	
$[\mathrm{Cu(ttda)(tren)][ClO_4]_2}$	$\mathrm{Cu}N_2O_2S$	0.153	O-2.180	163.9	173.6	178

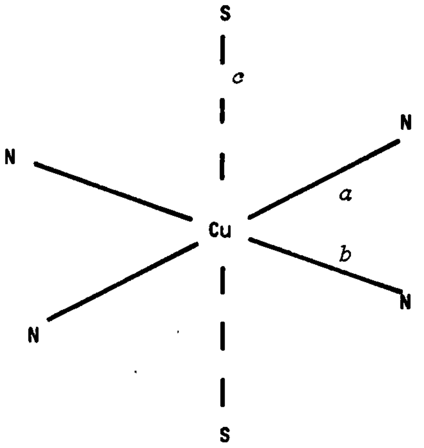


(17; $[\mathrm{Cu(NH_3)_4(OH_2)(18\text{-}crown\text{-}6)}]$)



(18; $K_2[Cu(CO_3)_2]$)

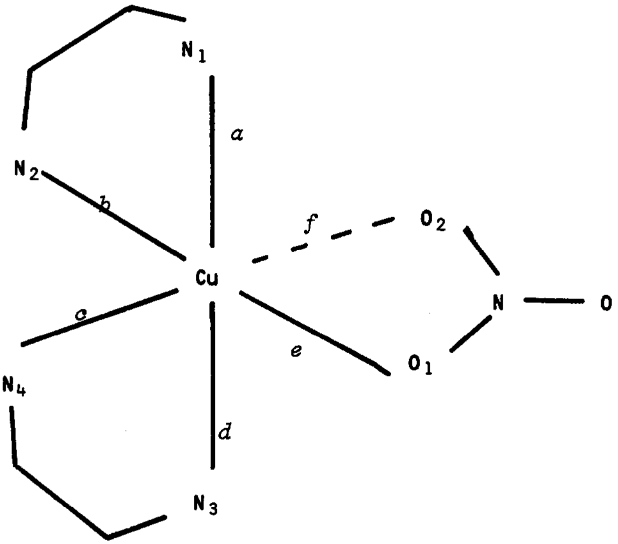
as a symmetrical bicapped square pyramidal stereochemistry. As this geometry involves weak interaction above the $\{CuO_4\}$ group, but not below it, it could well account for the non-centrosymmetric electron density above and below the $\{CuO_4\}$ plane with the +ve electron density below the $\{CuO_4\}$ plane away from the two 0(3) off-axis interactions. The $\{CuO_4\}$ chromophore of (*18*) also involves a significant tetrahedral distortion {0(1)1Cu10(1") = 175.31^{o} and 0(2')-Cu-0(2") = 166.46^{o}}, as first observed in the symmetrical bicapped structure of $Cu(edtb)(BF_4)_2$ [2, (*22*)], and in the unsymmetrical bicapped structures [65] of $[Cu(bipy)_2(O_2NO)][NO_3].H_2O$ (2, (*23*)] and $[Cu(bipy)_2(OS_2O_7)].H_2O$ [2, (*24*)]. A strictly rhombic coplanar $\{CuO_4\}$ chromophore exists in tetrakis(triphenylarsine oxide)copper(II) bis{(dichlorocuprate(I)} [183] and a similar $\{CuN_4\}$ chromophore exists in bis{2,2-bis(5-phenyl-2-imidazolyl)propane}-copper(II) diperchlorate [184], with the $[ClO_4]^-$ ion in the lattice. In bis 1,3-bis(5-phenyl-2-imidazoly)-2-thiopropane copper(II) diperchlorate [184], the perchlorate ions are still involved in the lattice, but the $\{CuN_4\}$ chromophore has two sulphur ligands at 2.824 Å to give a six-coordinate $\{CuN_4S_2\}$ chromophore. The synthesis of a series of copper(I) and copper(II) complexes of the ligands N,N'-bis{3-(2-thenylidenimino)propyl}piperazine (tipp) and *N,N'*bis{3-(2-thenylamino)-propyl}piperazine (tapp) have been reported [185] with extensive use of electronic and EPR spectra to establish the stereochemistry presented. This paper recognises the flexible stereochemistry of the copper(II) ion due to the plasticity effect [14] and reports the crystal structure at -150 °C for $[Cu(tapp)][ClO_4]_2$, a very tetrahedrally distorted $\{CuN_4\}$ chromophore (distortion 0.397 Å) with "incipient" interaction of the *S*-ligand at 3.469 Å (*19*), a distance too long for even semi-



a = 2.029 Å
b = 2.005 Å
c = 3.469 Å

(*19*; $[Cu(tapp)_2][ClO_4]_2$)

coordination [18]. The publication of the crystal structure of nitratobis-(2,9-dimethyl-1,10-phenanthroline)copper(II) trichloroethanoate trichloroethanoic acid [186] is of interest in that, on first sight (*20*) appears to involve an unsymmetrically coordinated nitrate group of a *cis*-distorted $\{CuN_4O_2\}$ chromophore,



a = 2.030 Å
b = 2.137 Å
c = 2.070 Å
d = 2.060 Å
e = 2.155 Å
f = 2.489 Å

(*20*; $[Cu(2,9\text{-}Me_2phen)_2(ONO_2)][Cl_3CO_2].Cl_3CCO_2H$)

but a closer examination reveals that the longest Cu-N distance in the plane involves the bond *trans* to the short Cu-O distance and not that *trans* to the long Cu-O distance. Notwithstanding this difference, the electronic reflectance spectrum involves two broad bands at 9260 and 12900 cm^{-1} typical of the distorted *cis*-octahedral $\{CuN_4O_2\}$ chromophore. Consequently, the structure of (*20*) represents a complex that does not fit the $\Delta N/\Delta O$ relationship of Fig. 5 or the structural pathway relationships of Fig. 3.

A tetrahedral $\{CuN_4\}$ chromophore exists in bis(di-2-pyridamido)copper(II) [187] and the ligand field spectra are shown to correlate with those previously observed for this ligand by the authors. Distorted tetrahedral structures are observed [188] for the $\{CuN_2S_2\}$ chromophore of [*N,N'*-tetramethylenebis(methyl-2 amino-1-cyclopentane dithiocarboxylato)copper(II)] and for the $\{CuN_4O_2\}$ chromophore of some copper(II) salicylaldimine complexes [189,190].

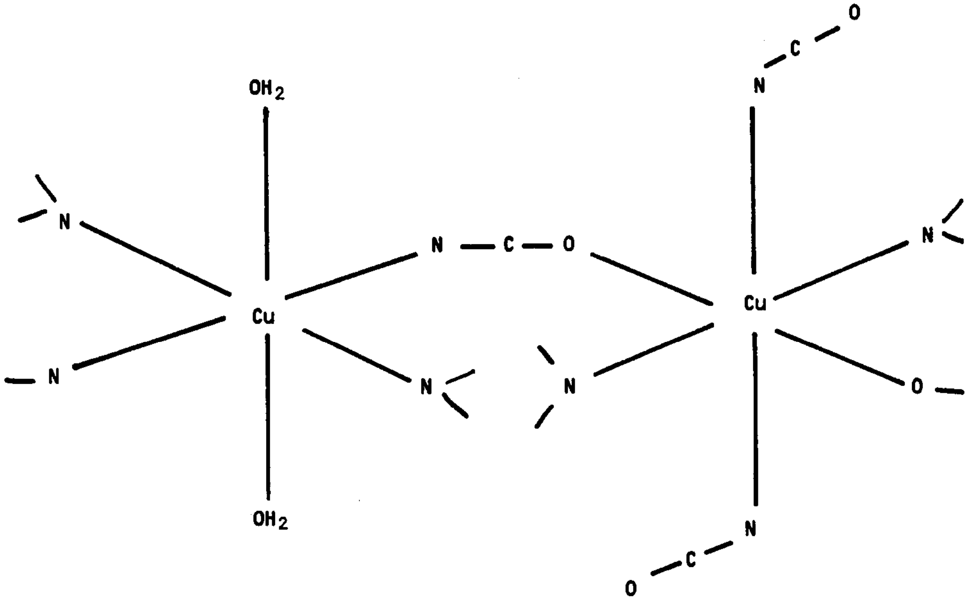
Table 8 lists a number of complexes whose crystal structures are shown to contain the elongated rhombic octahedral chromophore [191-200].

TABLE 8

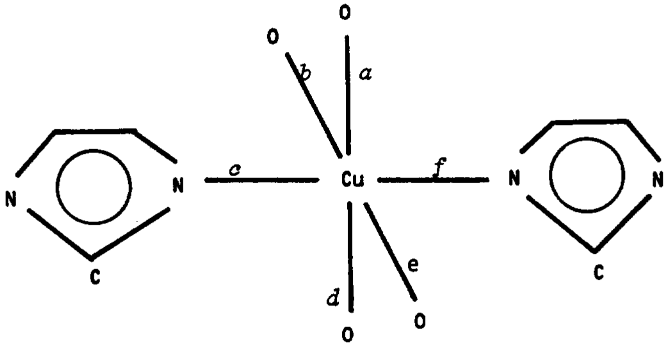
Elongated Rhombic Octahedral Copper(II) Complexes

	Chromophore	Ref.
Diaquatetrabis(3-methylpyridine)copper(II) diperchlorate	$\{CuO_2N_4\}$	191
Diaquabis(4-chlorophenoxyethanoato)copper(II)	$\{CuO_4O_2\}$	192
Bis(L-phenylephrinato)copper(II)	$\{CuN_2O_4\}$	193
(L-alaninato)(aqua)(L-histidinato)copper(II).3H_2O	$\{CuN_3O_3\}$	194
(3,4-dimethylpyridine)$_2$(ethanoato)$_2$copper(II).H_2O	$\{CuN_2O_2O_2'\}$	195
(3,4-dimethylpyridine)$_2$(propanoato)$_2$copper(II).H_2O	$\{CuN_2O_2O_2'\}$	195
Copper(II) (R,S)-1-amino-2-propanol chloride	$\{CuNOCl_4\}$	196
Bis(*O*-tricyanoethyleneoate)bis{di(2-pyridyl)amine}copper(II)	$\{CuN_4O_2\}$	197
Basic copper(II) methanoate	$\{CuO_4O_2\}$	198
Copper(II) dichlorophosphate	$\{CuO_4O_2\}$	199
Bis(4-methylpyridine)dichlorocopper(II)	$\{CuN_2Cl_2Cl'_2\}$	200a
Bis(aqua){di(2-pyridyl)amine}fluorocopper(II) cation	$\{CuN_2FO_2\}$	200b
(2,2'-bipyridine)chloro(tricyanoethenolate)copper(II)	$\{CuN_2ClCl'\}$	200c

An isocyanate bridged dimer occurs [201] in bis(3-aminopyridine)aquabis-(isocyanato)copper(II) (*21*), while a novel type of bidentate purine-metal bonding occurs [202] in *catena*-tetraaqua-μ-purine-copper(II) sulphate dihydrate (*22*). Dinuclear imidazolate bridged copper(II) complexes have been synthesised, and their spectroscopic and solution properties reported [203], and a novel structure has been reported [204] for [(pmdt)copper(II) imidazolate)cobalt(III)$(NH_3)_5$]$[ClO_4]_4$ {pmdt = 1,1,4,7,7-pentamethyldiethylenetriamine} (*23*). Square pyramidal chromophores have been reported [205] in the bridged dimers of di-μ-[2-{*N*-(2-hydroxylethyl)-2-aminoethyl}imino-3-butanone oximato]dicopper(II) perchlorate (*24*), in



(21; $[Cu(3\text{-aminopyridine})_2(OH_2)(NCO)_2]$)



a = 2.015 Å

b = 2.428 Å

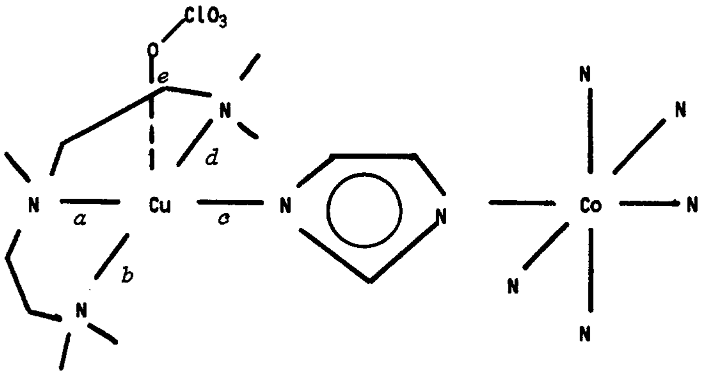
c = 1.903 Å

d = 2.015 Å

e = 2.469 Å

f = 2.036 Å

(22; $[Cu(purine)(OH_2)_4][SO_4].2H_2O$



a = 2.012 Å

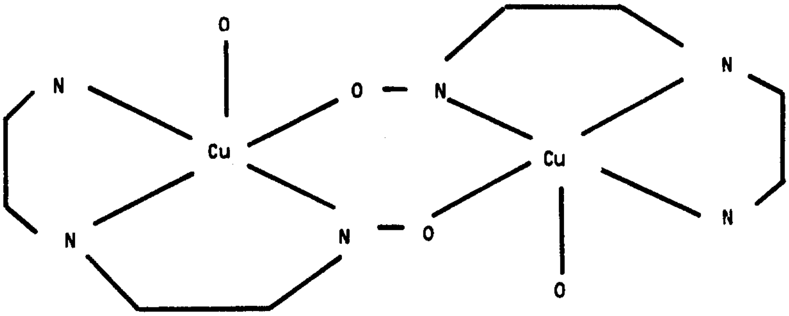
b = 2.046 Å

c = 1.954 Å

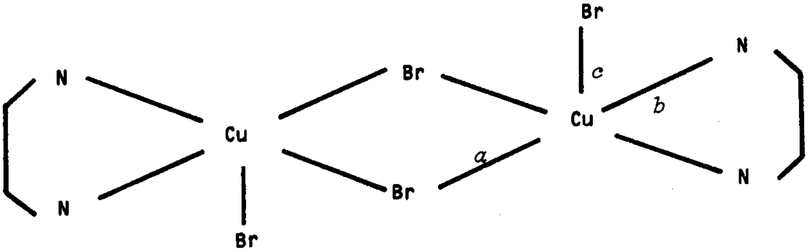
d = 2.054 Å

e = 2.886 Å

(23; $[(pmdt)Cu(imidazole)Co(NH_3)_5][ClO_4]_4$)

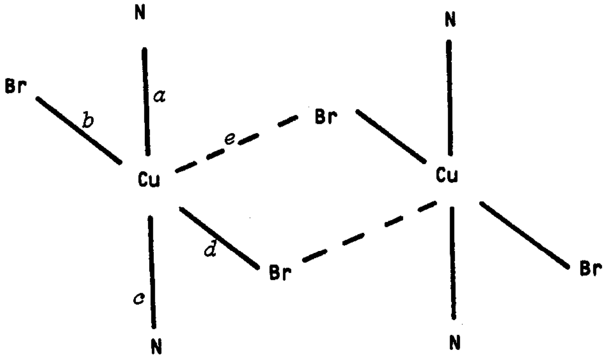


(24; $[Cu_2(C_8H_{16}N_3O_2)_2][ClO_4]_2$)



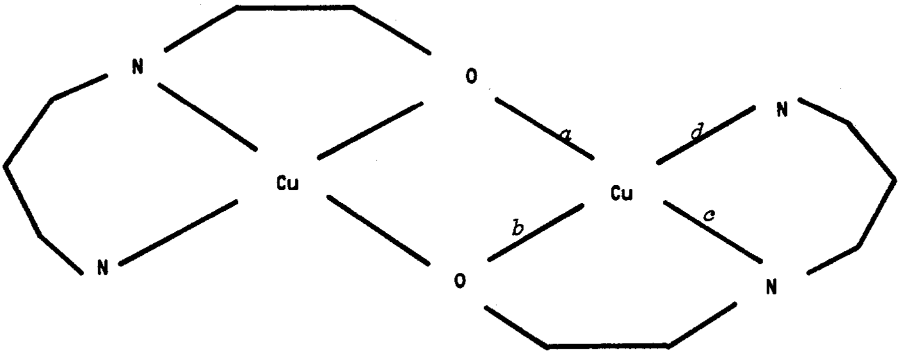
a = 2.36 Å
b = 1.99 Å
c = 3.43 Å

(25; $[Cu_2Br_4(C_{14}H_{12}N_2O_2)_2]$)



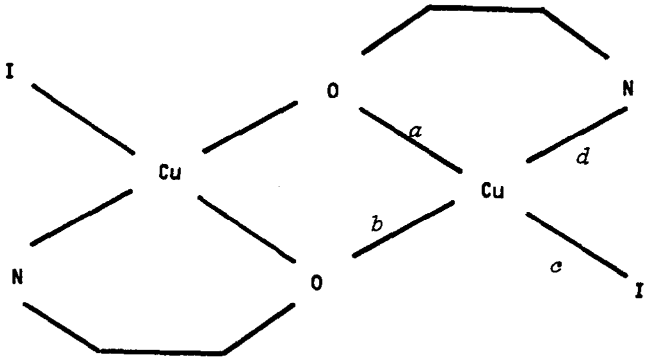
a = 1.99 Å
b = 2.42 Å
c = 1.98 Å
d = 2.49 Å
e = 3.03 Å

(26; $[Cu_2Br_4(C_4H_5NS)_4]$)



a = 1.94 Å
b = 1.94 Å
c = 2.01 Å
d = 1.98 Å

(27; $[Cu_2(C_5H_{13}N_2O)_2]_2[Cu(NCS)_4][NCS]$)



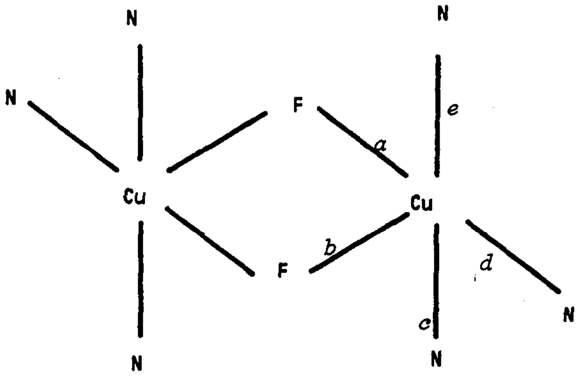
$a = 1.92$ Å

$b = 1.91$ Å

$c = 2.55$ Å

$d = 2.05$ Å

(28; $[Cu_2(C_6H_{14}NO)_2I_2]$)



$a = 2.258$ Å

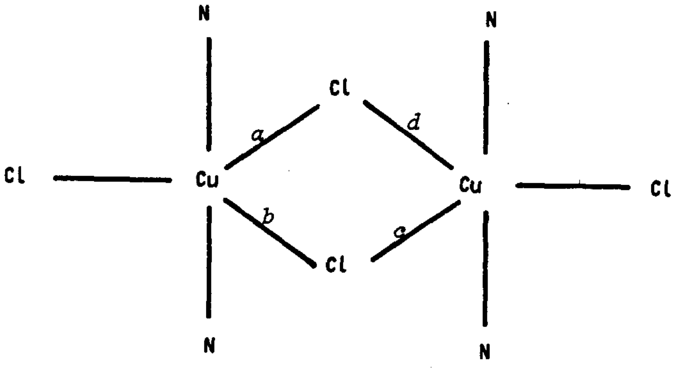
$b = 1.904$ Å

$c = 1.973$ Å

$d = 1.977$ Å

$e = 1.978$ Å

(29; $[Cu_2F_2(dmpzlH)_2(mpzlH)_4][BF_4]_2$)



$a = 2.29$ Å

$b = 2.69$ Å

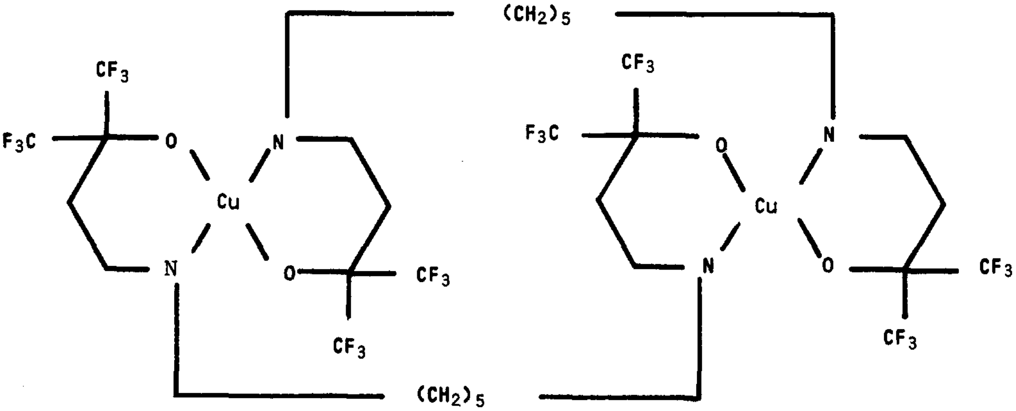
$c = 2.54$ Å

$d = 2.44$ Å

(30; $[Cu(C_6H_5N_3)Cl_2].H_2O$)

di-μ-bromobis bromo(diphenylethanedione dioxime)copper(II) (*25*) [206] and di-μ-bromo-bisbromobis(4-methylthiazole)dicopper(II) (*26*) [207]. Oxygen bridged dimers occur in tetraisothio-cyanatocuprate(I)-bis{μ-[2-{(3-aminopropyl)amino}-ethanolato]-*N*,*N'*,μ-*O*}dicopper(II) thiocyanate (*27*) [208] and bis{iodo - μ-(2-diethylaminoethanolato-*N*,μ-*O*)}copper(II) (*28*) [209]. A novel difluoro bridging dimer [210] occurs in di-μ_2-fluorobis(3,5-dimethylpyrazole)tetrakis(5-methyl-pyrazole)dicopper(II) bis(tetrafluoroborate) (*29*), and dichloro bridging [211] in di-μ-chloro-bis[bis(benzotriazole)chlorocopper(II) monohydrate (*30*) involving a trigonal bipyramidal $\{CuCl_3N_2\}$ chromophore.

The structure (*31*) of a dinuclear dimer, $C_{34}H_{40}Cu_2F_{24}N_4O_4$, involving fluorinated alkoxy groups has been reported [212] involving distorted *trans* coplanar $\{CuN_2O_2\}$ chromophores; large Cu-Cu separations [213] are also obtained in $[(CuCl_2C_{18}H_{20}N_3)_2].2H_2O$. Further dinuclear carboxylate structures [214] are reported as in *catena*-μ-(hexamethylenetetramine-*N*, *N'*)-[tetra-μ-ethanoato-dicopper(II)], tetra-μ-[(2,4-dichlorophenoxyethanoato)-bis(aqua)copper(II) dihydrate, [215], tetra-μ-[(2,4,5-trichlorophenoxyethanoato)bis(pyridine)]copper(II) [215] and bis(3,5-dimethylpyridine)tetra-μ-propanoato-dicopper(II) [216]. [215] is a particularly useful paper as it contains an up-to-date list, with references, of the thirty-four copper(II) complexes containing copper-copper carboxylate bridged dimers.

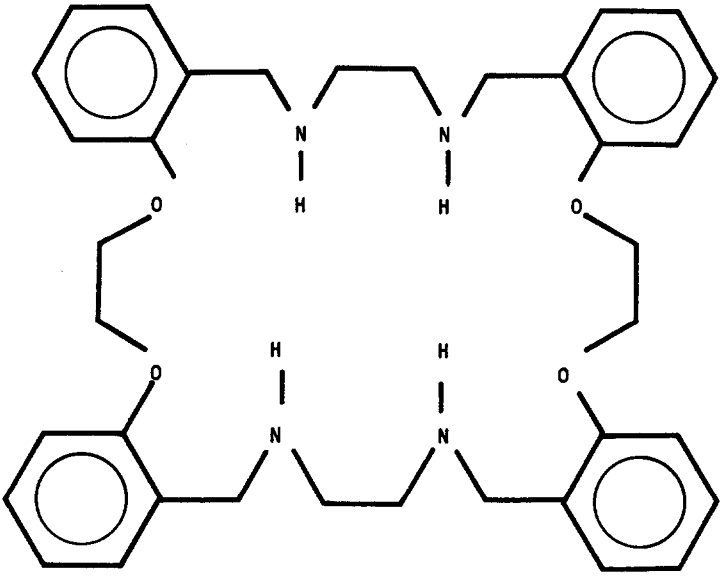


(*31*; $C_{34}H_{40}Cu_2F_{24}N_4O_4$)

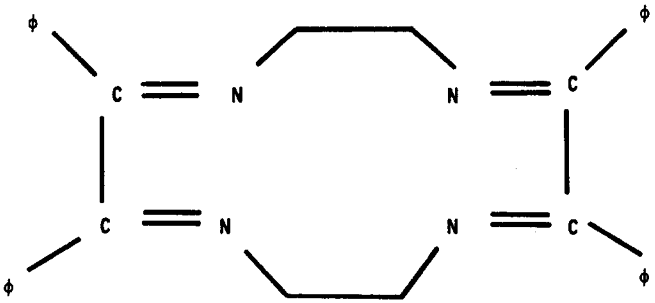
A tetranuclear alkoxy bridged structure occurs in the structures of four 2-{(2-μ(3-aminopropyl)amino}ethanolatocopper(II)-type complexes: $(CuLCl)_4.4H_2O$; $CuL(NO_3)_4.2H_2O$; $(CuLBr)_4.3H_2O$ and $(CuL_4)(SO_4)_2.8H_2O$ [217], and in bis{di-μ-ethoxolbis 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato}dicopper(II)] [218].

3.3.7 Macrocyclic Chemistry

An indication of the improved resolution of electron microscopy was a photograph of an image of the structure of chlorinated copper phthalocyanine, in which the structure of this classical macrocycle was clearly resolved [219]. The preparation of new macrocyclic ligands continues. Using the 28-membered O_4N_4 macrocycle L, (*32*; $C_{36}H_{44}N_4O_4$) the complexes $CuL(ClO_4)_2H_2O$ and $CuLBr_2H_2O$ have been prepared and characterised [220], and with 12-membered macrocyclic L' (*33*; $C_{32}H_{28}N_4$), a

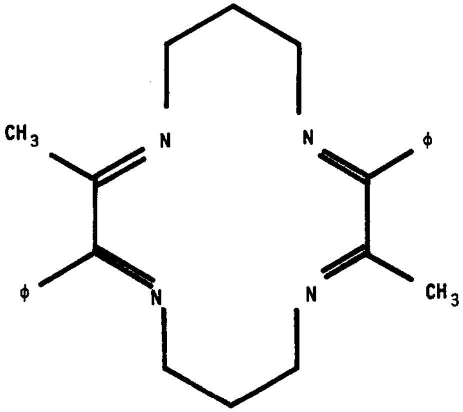


(*32*; $C_{36}H_{44}N_4O_4$)



(*33*; $C_{32}H_{28}N_4$)

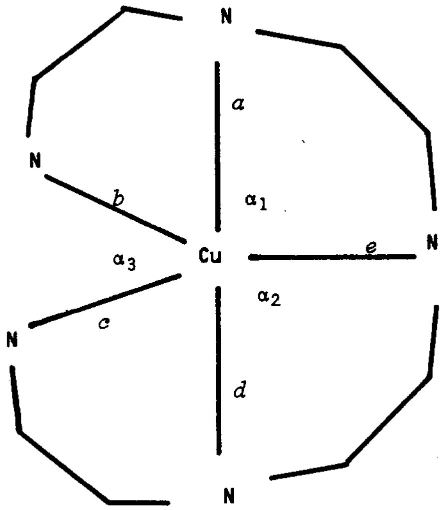
series of five copper(II) complexes, CuL'X$_2$, have been synthesised and characterised [221]. The coordination chemistry of a series of copper(II) tetraimine macrocycle yields four, five, and six-coordinate complexes, *viz.* [Cu(MePhTIM)X][PF$_6$] or [Cu(MePhTIM)L][PF$_6$]$_2$. {MePhtim = 2,9-dimethyl-3,10-diphenyl-1,4,8,11-tetrazacyclotetradeca-1,3,8,10-tetraene (*34*); X = NCS, Cl, Br or I; L = pyridine,



(34; MePhtim)

4-methylpyridine or *N*-methylimidazole} [222]. The electronic spectra in the solid state have established a reversal in the spectrochemical series as suggested for the [Cu(cyclops)L]$^{n+}$ cation [2; Table 6 and (*41*)], a result that is used to predict a square pyramidal structure for the five-coordinate MePhtim complexes. A qualitative MO calculation is used to explain the anomalous spectrochemical series observed, invoking significant π-acceptor and π-donor rôles for the fifth copper ligand. The incorporation of copper(II) into "picket fence" porphyrin isomers has been described [223].

X-ray crystallography continues to be the main tool for determining the structure of macrocyclic complexes. The red crystals of [Cu(*trans*-[14]-diene]-[ClO$_4$]$_2$ have been shown [224] to involve a rhombic coplanar {CuN_4} chromophore. Five-coordinate geometry occurs in 2,6-bis[1-(2-imidazol-4-ylethylimine)ethyl]-pyridine copper(II), [Cu(imep)][ClO$_4$]$_2$ (*35*) [225], in which the {CuN_5} chromophore has a stereochemistry intermediate between trigonal bipyramidal and square pyramidal along the structural pathway of [2, Fig. 4]. In [Cu(cbpo)] cbpo = *N*,*N*'-bis[(5-chloro-2-hydroxyphenyl)phenylmethylene]-4-oxaheptane-1,7-diamine [226], the {CuN_2O_2O'} chromophore (*36*) is square pyramidal with a tetrahedral distortion of the inplane {CuN_2O_2} consistent with the route A distortion [2, Fig. 5]. The distorted square pyramidal geometry is more common, and occurs in [Cu(Me$_4$OHO[15]teteneN$_4$)][ClO$_4$] (*37*) [227], which dimerises to form a long Cu-O distance of 2.264 Å, with a slight trigonal twist to the basal plane with angles of 173.0 and 150.2 . The structure of cyano 3,3'-(1,3-propanediamino)-



a = 2.066 Å

b = 2.081 Å

c = 1.992 Å

d = 2.036 Å

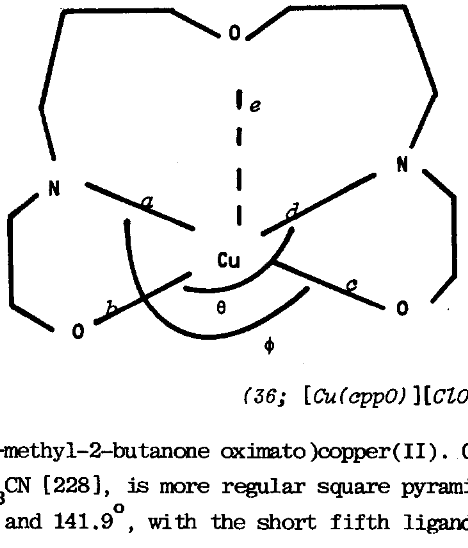
e = 1.923 Å

α_1 = 129.8°

α_2 = 116.8°

α_3 = 104.4°

(35; [Cu(imep)][ClO$_4$]$_2$)



a = 2.020 Å

b = 1.934 Å

c = 1.944 Å

d = 2.004 Å

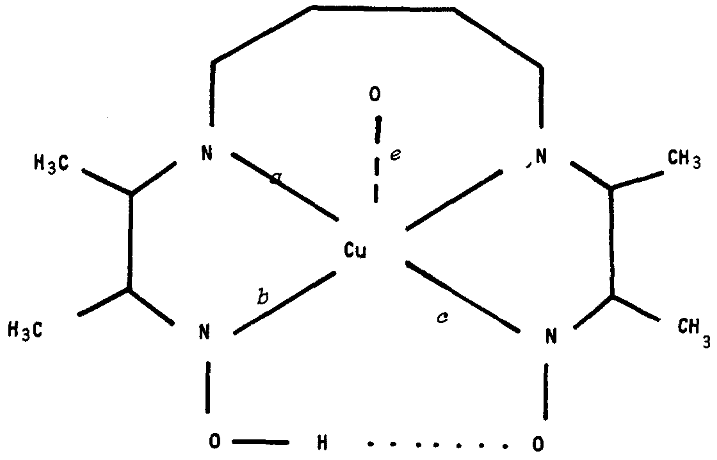
e = 2.575 Å

θ = 155°

ϕ = 163°

(36; [Cu(cppO)][ClO$_4$]$_2$)

bis(3-methyl-2-butanone oximato)copper(II). 0.5MeCN, [Cu(pnao-H)(CN)]. 0.5CH$_3$CN [228], is more regular square pyramidal, ρ = 0.5 Å and the inplane angles 140.8 and 141.9°, with the short fifth ligand contact at 2.154 Å, which gives a structure, (*38*), closely comparable to that observed in [Cu(cyclops)(CN)] [2;(*41*)]. A five-coordinate square pyramidal {CuN_3S_2} chromophore occurs [229] in two of a series of [CuL]X$_2$ and [CuLY]X {L = 17-membered Schiff-base obtained from cyclic condensation of 2,6-diacetylpyridine with 1,10-diamino-4,7-dithiadecane (*39*)} complexes, with one sulphur bonding out of the plane to yield near regular inplane angles, (157.9, 149,2°) and (165.2 and 158.9°) respectively. The condensation of one mole of 2,6-diacetylpyridine with two moles of diethylenetriamine yields a potentially seven *N*-donor ligand (L), which forms an



a = 1.957 Å

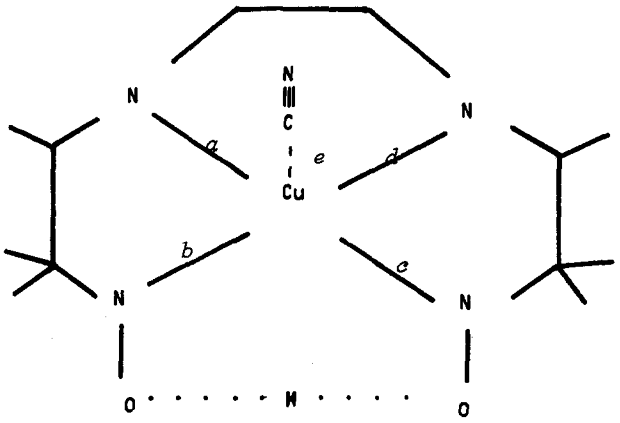
b = 1.978 Å

c = 1.985 Å

d = 1.990 Å

e = 2.264 Å

(37; [Cu(Me$_4$OHO[15]teteneN$_4$)][ClO$_4$])



a = 2.049 Å

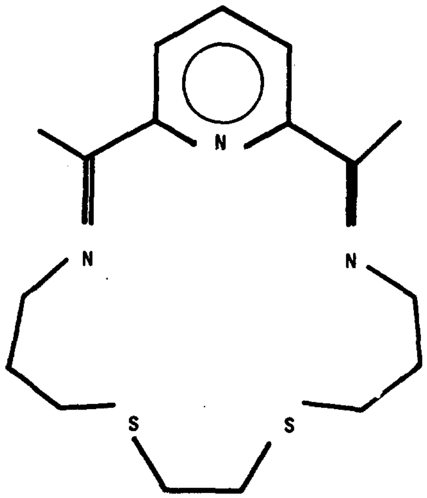
b = 1.979 Å

c = 1.977 Å

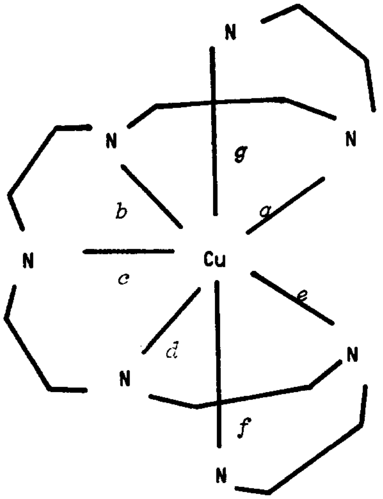
d = 2.037 Å

e = 2.154 Å

(38; [Cu(pnao-H)(CN)]0.5MeCN)



(39; L; 17-membered N_3S_2 macrocycle) unusual seven-coordinate complex $[Cu(L)][ClO_4]_2$ (*40*) with a distorted pentagonal

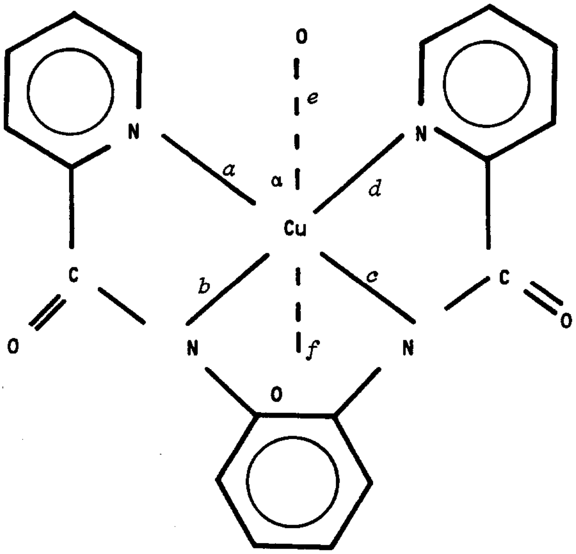


a = 2.217 Å
b = 2.565 Å
c = 2.335 Å
d = 2.263 Å
e = 1.398 Å
f = 1.997 Å
g = 1.994 Å

(*40*; $[Cu(L)][ClO_4]_2$)

bipyramidal $\{CuN_7\}$ chromophore. The electronic properties are consistent with a d_{z^2} ground state [230].

A number of sterically crowded macrocyclic complexes with a square coplanar structure have been reported, including {5,12-diphenyl-18,19-dioxo-17,18,19,20-tetrahydrotribenzo[e,i,m][1,4,8,11]tetra-azacyclo-tetradecinato}(dimethylformide)-



a = 2.072 Å
b = 1.922 Å
c = 1.941 Å
d = 2.085 Å
e = 2.798 Å
f = 2.693 Å
α = 163.5° Å

(*41*; [*Cu(6-mebpb)*])

TABLE 9

Preparation and characterisation of mononuclear copper(II) complexes

Ligand or complexes	Characterisation	Ref.
N-isopropyl-2-picolinamine *N*-oxide	IR, electronic and EPR spectra	245
2 diethylaminopyridine *N*-oxide	" " " " "	246
2-propylaminopyridine *N*-oxide	" " " " "	247
3-amino-5-methyl-isozalole	EPR spectra in solution	82
6,6'-dimethyl-2,2'-bipyridine		248
Schiff bases of 3-hydroxy-2-naphthoic acid hydrazide	Magnetism and spectra	249
N-*tertiary*-butyl-2-picolinamine-*N*-oxide	IR, EPR and conductivity	250
Copper sulphate and acetamide	Thermal gravimetric analysis	251
Dimethyl-2-aminopyridine *N*-oxide	Electronic and EPR spectra	252
Copper maleate	IR, μ_{eff}, X-ray, thermal	253
Schiff bases of μ-diketones and triamines	Visible and EPR spectra	254
N,*N*,*N'*,*N'*-tetramethyl-1,2-diaminoethane	Solution electronic spectra	255
Hexamethylenetetramine, thiocyanates	μ_{eff}, IR and electronic spectra	256
2-Picolylphenyl-2-lutidyl hydrazone derivative	Preparation	257
Phenothiazine	μ_{eff}, EPR, Thermal, conductivity	258
Heterocyclic thioamido ligands	Preparation	259
Tetradentate *N*-6 macrocyclic	Preparation	260
Acid hydrazides and acetylacetone	Preparation	261
4-substituted *N*,*N*-dimethylbenzamide	Preparation	262

Table 9 (Continued)

Ligand or complexes	Characterisation	Ref.
(D,L)-1,2-diaminopropaneic-*N*,*N*,*N'*,*N'*-tetracetic acid	Potentiometric and spectroscopic	263
8-hydroxyquinoline and pentane-2,4-dione		264
2-thioacetamido thiazole		265
Dimethyl- and trimethyl-benzoates		266
Copper uroporphyrin plus aromatic ligands		267
β-copper phthalocyanine	Improved purification	268
α-copper phthalocyanine	X-ray powder and magnetism	269
N-bromosuccinimide derivatives		
bis(benzoylacetone)(1.2-diaminoethane)Cu(II)	Methine carbon substitution	270
Di-β-(2-pyridyl)-α-alaninate + propanone	IR, NMR, visible and CD spectra	271
Isovaleric acid hydrazide	Preparation	272
Syn-thiophen-2-aldoxime	Preparation	273
$Cu(dithiocarbamate)_2$	Electronic spectra	274
Thiosalicylohydrazine	Polybasic ligand	275
Bis(diaryldithiophosphinato)copper(II) adducts	Visible and EPR spectra, $_{eff}$	276
Oxydiethanoate, thiodiethanoate and selenodiethanoate	Visible spectra and thermodynamic	277
Tetrathiafulvalene	Visible, IR, EPR, RRS, photoelectron	278
Vinylallenes from propargylic Tosylates	Preparation	279

copper(II) [231], and a series of complexes of ligands based on *(41)*, *viz.* *N,N'*-bis(6-pyridine-2-carboxamido)-*trans*-1,2-benzene [232,233], -1,2-cyclohexane [234,235,236], or -1,2-ethene [237] acting as tetradentate ligands [238]. The structure [239] of the complexes of a naturally occurring macrocycle, mugenic acid, with copper(II) has revealed a very distorted $\{CuN_2O_2O_2'\}$ elongated rhombic octahedral stereochemistry. The use of the thirty membered macrocyclic ligand [1,*(28)*] to form bridging dinuclear complexes, such as [1,*(27)*], has been extended to the bridging hydroxo complex $[Cu_2(L)(OH)][ClO_4]_3$ and the bridging imidazole complex $[Cu_2(L)(imid)][ClO_4]_3$ [240]. Dinuclear macrocyclic complexes of copper(II) have been reported [24] with *N,N',N'', N'''*-tetra(2-aminoethyl)-1,1,5,5-pentanetetraamide, which involve copper-copper separations of 4-8 Å. The crystal structures of three adducts of [CuYL] {HY = 2,9-bis(methoxymethyl)-2,9-dimethyl-4,7-dioxadecanedioic acid; L = water, pyridine or triphenylphosphine} show that all three complexes occur as *d*- or *l*- forms, and all contain $\{Cu(carboxylate)_2\}_2$ dimeric structural units [242].

The photochemistry of some copper(II) complexes with macrocyclic amine ligands [243] have been reported using flash photolysis, with evidence for copper(III) macrocyclic intermediates. The effects of macrocyclic ring size and anion on the equilibrium constants and thermodynamic parameters of copper(II)-cyclic polythio ether complexes have also been reported [244].

3.3.8 Preparative Chemistry

There is an extensive literature reporting the preparation and characterisation of copper(II) complexes, both monomeric and polynuclear species (Tables 9 and 10, respectively), using a wide range of physical techniques. In the hazardous world of non-aqueous solvent chemistry in perchloric acid, the preparation of $[NO_2][Cu(ClO_4)_3]$ and anhydrous $Cu(ClO_4)_2$ have been reported [289], and the volatility of the latter [290] has been confirmed. The solvent extraction of copper(II) complexes involving Schiff bases [291] or decanoic acid [292] or lauric acid in the presence of hexamine [293] have been reported. The influence of alkyl groups in alkylpyridine copper(II) cyanato complexes [294], and of distortion isomers of the copper(II)-NCO^--pyrazole system [295] have been reported.

3.3.9 Kinetic, Thermodynamic and Redox Data

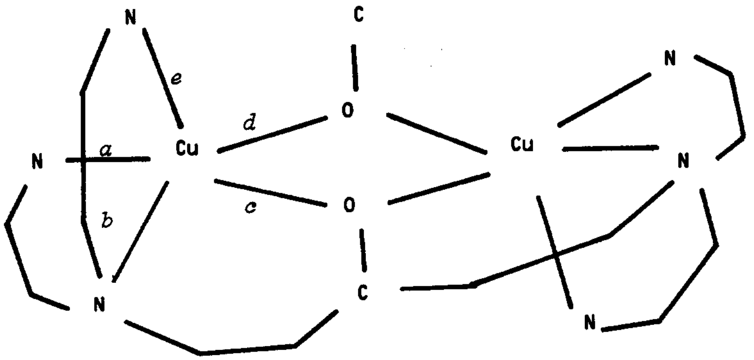
A major review [3] of the photochemical properties of copper complexes, has surveyed the charge-transfer spectra of copper(I), copper(II) and copper(III) complexes and the redox relationships between the different oxidation states. The types of complexes range from halide complexes to 1,2-diaminoethane-type

TABLE 10

Preparation and characterisation of polynuclear copper(II) complexes

Ligand	Characterisation	Ref.
Purine	Bridging purine ligand	280
2-Hydroxy pyridine N-oxide	X-ray powder, IR, VIS, μ_{eff}	281
$M(O_2CCH_3)_2.nH_2O$	Mixed salt formation	282
1,4-Bis[*N*,*N*-bis(3-salicylideneaminopropyl)aminomethyl]benzene	Catalytic role with O_2	283
Pyridine and quinoline adducts with $[Cu(O_2CCH_3)_2]_2$	Dioxane solution	284
3-[2-(dialkylamino)ethylthio]-1-propanol	Magnetism 80-300 K	285
α-Oximinoacetoacetarylamide thiosemicarbazones	IR, VIS, EPR, μ_{eff}	286
2-(4-isobutylphenyl)propanoic acid	Magnetism	287
Halopropanoic acid	UV, IR, and μ_{eff}	288

ligands and large macrocyclic ligands, and cover the extreme range of copper environments. A paper on the photochemistry of the copper(II) ion with macrocyclic amine ligands has also been published [296]. Characterisation of inner and outer-sphere chlorocomplexes of the copper(II) ion has been obtained by analysis of the absorption spectra and by thermodynamics [297]. The equilibria of copper(II) with sulphate ions in sulphuric acid solution [298], with pentone-2,4-dione in mixed aqueous solution [299], and with bipy in hexamethylphosphoric triamide solution [300] have been examined. The stabilities of the copper(II) ion with *N,N'*-dialkyl-1,2-diaminoethanes [301], with glycylglycyl-L histidine [302] and with *N,N'*-bis(β-carbamoylethyl)trimethylenediamine [303] have also been reported. The ΔG, ΔH, and ΔS thermodynamic data have been evaluated [304] for some 4-oximino-2-pyrazolin-5-ones with copper(II), and discussed in terms of ligand field effects. The proton transfer reactions of copper(II) tetraglycine complexes have been described [305] and the dissociation kinetics of copper macrocycles in acid solution reported [306]. Ligand substitution reactions in bis(*N*-alkylsalicylideneiminato)copper(II) complexes [307] have been determined by stop-flow spectrophotometry, and evaluated in terms of the $\{CuN_2O_2\}$ chromophore stereochemistry. The formation constants of ternary complexes of the copper(II) ion involving π-bonding ligands, such as 1,10-phenanthroline and acac derivatives have been determined by UV spectroscopy [308], and potentiometrically [309]. Potentiometric measurements have been used to characterise amine complexes of copper(II) with $[edda]^{2-}$ (which are used for treating rheumatoid arthritis) [310], and mixed-metal complexes with nickel(II), zinc(II) and cadmium(II) [311]. The kinetics of the incorporation of copper(II) in tetraphenylphorphine have been reported [312] in dimethyl sulphoxide solution. The mechanism of substitution of water in $[Cu(tren)(OH_2)]^{2+}$ by a series of pyridine derivatives have been studied using temperature-jump relaxation spectrophotometry, and the results support an associative mechanism [313]. Solvent exchange kinetics in ethanoic acid solution of the $[Cu_2(O_2CCH_3)_4]$ dimer have been examined by ^1H NMR line broadening techniques [314], and the same method has been used to examine self-exchange electron transfer in Cu(III)/Cu(II) tripeptide complexes [315]. In dimethylformamide, $[Cu^I(phen)_2][ClO_4]$ is oxidised to the copper(II) complex $Cu(phen)_2(HCO_3)(ClO_4).dmf$ [316], while copper(I) complexes containing 2,2'-bipyridine and tertiary phosphine ligands can activate dioxygen and catalytically oxidise ethanol to ethanal and hydrogen peroxide [317]. Activation of dioxygen by a binuclear copper(I) complex leads to hydroxylation of a new xylyl-binucleating ligand [318] to produce a phenoxybridged binuclear copper(IIO complex, $[Cu_2\{OC_6H_3[CH_2N(CH_2CH_2py)_2]_2\text{-}2,6\}(OMe)]$ (*42*). Aerial oxidations of 4-methylcatechol, catalysed by simple copper amine complexes, have been performed in aqueous solution (pH=6.5) [319], and followed by ^1H NMR line broadening and optical spectra. The mechanism of the copper ion catalysed



a = 2.005 Å
b = 2.095 Å
c = 1.964 Å
d = 1.946 Å
f = 2.218 Å

(42; $[Cu_2\{OC_6H_3[CH_2N(CH_2CH_2py)_2]_2\text{-}2,6\}(OMe)]$)

autooxidation of cysteine in alkaline solution has been followed by EPR measurements: the results cannot be explained by a simple Cu(II)/Cu(I) redox mechanism. but has been explained by invoking a thiyl- and superoxo-activated copper(II) complex [320]. Stop-flow spectrophotometry has been used to follow the homogeneous oxidative coupling catalysis with μ-carbonato dicopper(II) oxidative coupling initiators, of 2,4,6-trichlorophenol in methylene chloride [321]. A comment has been published on the kinetics and mechanism of copper(II) catalysed oxidation of malic acid by the peroxydisulphate anion [322].

A new differential method for determining the orders and rates of reactions in solid state reactions has been applied to copper(II) salicylate tetrahydrate [323], and the phase changes of $[C_nH_{2n+1}NH_3]_2[CuCl_4]$ {n = 11-16} complexes have been examined by differential scanning calorimetry, infrared spectroscopy and X-ray diffraction [324]. The formation constant of $[Cu(CN)_4]^{2-}$ has been reported along with its mode of decomposition [325]. Polarographic studies have been reported on the Cu(II)-oxalate-malonate system [326] and on the reduction of copper(II) polypeptide complexes [327]. *In situ* photoacoustic spectroscopy of thin oxide layers on metal oxides has been reported for copper in aqueous solution [328], and the dissociation kinetics of the (*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) cation (blue) have been reported in strongly acidic aqueous solution [329]. The rates of membrane transport of copper(II) ions through the use of urea or thiourea units have been reported [330]. The equilibria and species present in solutions used in the solvent extraction of copper in hydro-metallurgy have been reported and characterised using EPR spectroscopy [331].

3.3.10 Ion-Exchanged Copper(II) Systems

Due to their increasing importance as catalysts, the absorption of transition metal ions on silica gel and Lind molecular sieves have received increasing study (especially over the last ten years), particularly by EPR and electronic reflectance spectroscopy, but against a background of a total lack of crystallographic data concerning the metal environments. In the last few years, this situation has changed through the elegant work of Professor Karl Seff and his colleagues at the University of Hawaii, who have been able to characterise ion-exchanged zeolites to obtain crystallographic evidence for the transition ion environment in certain high symmetry zeolite structures, ion-exchanged with the $[M(OH_2)_6]^{2+}$ ions of manganese(II), cobalt(II), and zinc(II) followed by partial dehydration (both at room and low temperature). In the current year, the corresponding copper(II) story has been reported [332] and involves four crystal structures of vacuum desolvated copper(II) exchanged zeolite A - Cu_8A. The ion exchange was carried out at 100 °C in a flow system and desolvated at 350 °C to yield a composition $(Cu^{II})_5(Cu^{I})_3Si_{12}Al_{12}O_{48}.xH_2O$, referred to as Cu_8-A. The four structures examined involved dehydration at I, 350 °C in air, II, 350 °C in O_2, III, 450 °C, and IV, 500 °C, and the various structures involved are summarised in Fig. 12. The dominant copper(II) environment (Cu_5) is a trigonal planar $\{CuO_3\}$ chromophore with relatively long Cu-O distances of 2.11 - 2.15 Å, with a fourth OH group at 2.3 - 2.6 Å to give a trigonal pyramidal $\{CuO_3O'\}$ chromophore with $\rho = 0.0$ Å. The immediate fascination of this molecular geometry is that it is unknown in normal copper(II) complexes (*cf.* Section 3.3.1); the nearest approach could be the trigonal bipyramidal $\{CuO_5\}$ chromophore of $CuGaInO_4$ (*16*), which itself may not be a genuine static stereochemistry of the copper(II) ion. The trigonal planar $\{CuO_3\}$ geometry could then account for the observation of a d_{z^2}-type EPR spectrum of the dehydrated copper zeolite systems. The remaining three copper atoms in I involve copper(II) atoms in a tetrahedral monomer or a bridged dimer; in II, all the coppers are oxidised to copper(II), and the tetrahedral structure reverts to a distinct trigonal planar structure; in III, a trigonal pyramidal $\{CuO_3\}$, $\rho = 1.25$ Å exists, while in IV, six trigonal planar $\{CuO_3\}$ groups occur with the remaining two coppers occurring as copper metal on the surface of the zeolites. This superb piece of chemistry contains a number of important lessons for us all. Firstly, nature is more complex than molecular coordination chemists try to make it; secondly, unique geometries can still be characterised in less obvious copper situations; thirdly, only by pushing crystallography to the "limits of credibility" will such fascinating results be obtained. Nevertheless, even in such sophisticated systems as the zeolites the *art* of preparative chemistry is still required, as Professor Seff reported that he was unable to repeat the

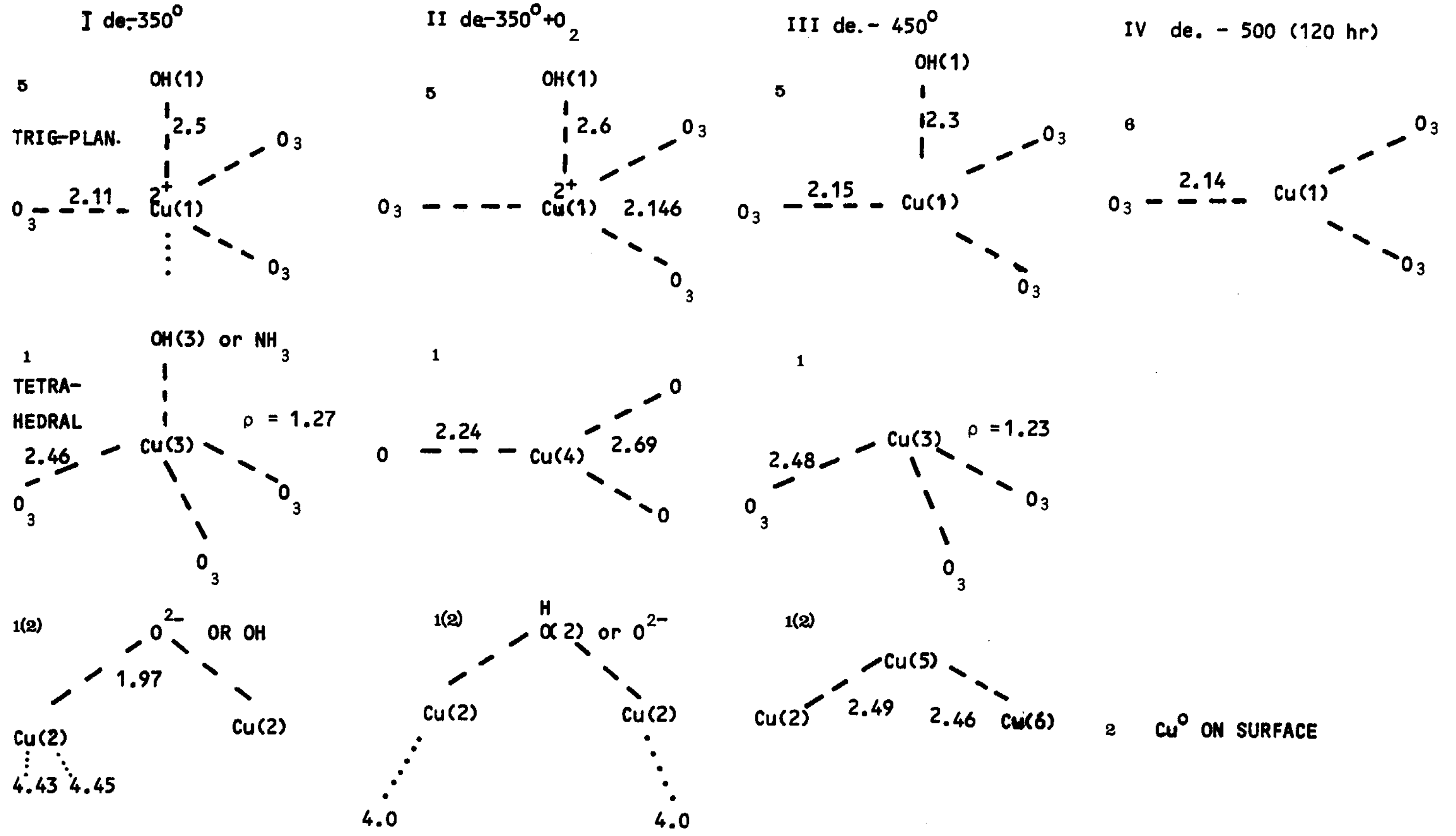
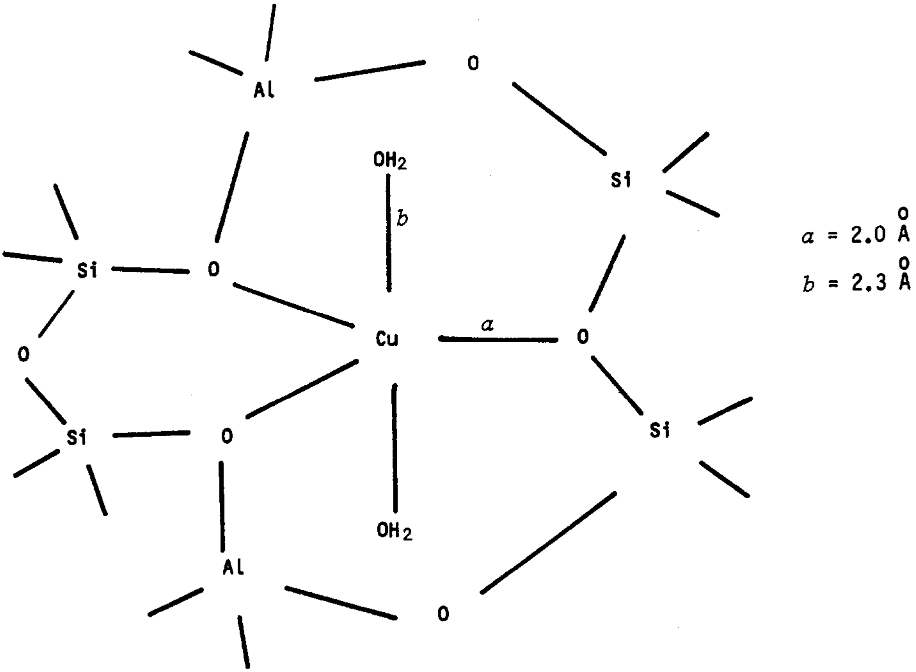


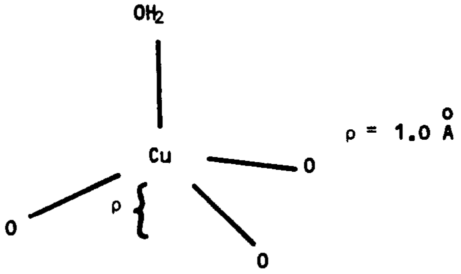
Fig. 12: Preparation by exchange at 100 °C of Cu₈-A

preparation of the single crystals on which this elegant piece of work was based.

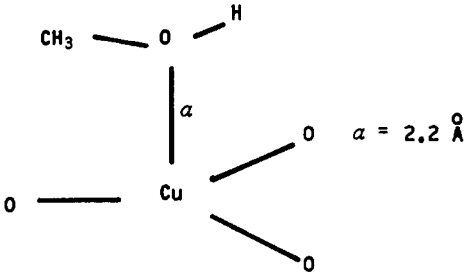
In the present year, four very interesting papers have appeared on the application of pulsed electron spin-echo modulation analysis [333-336]. This technique is an extension of EPR spectroscopy, involving analysis of the *decay* of a pulsed electron spin echo signal by the type of fourier transform analysis that is now familiar in EXAFS spectroscopy. Like this latter technique, it has the added advantage over EPR that it can yield, under favourable circumstances, copper-ligand distances. Thus, in *hydrated*-type zeolites, a trigonal bipyramidal $\{CuO_5\}$ chromophore (*43*) is suggested, a structure that is entirely creditable in the light of the crystallographic data for dehydrated zeolites described above. In the copper(II) exchanged Cs_7Na_5A-type zeolite, a $\{CuO_3(OH_2)\}$ chromophore with a trigonal pyramidal geometry (*44*) has been characterised by the spin echo technique [335], and located within the smaller sodalite units. By extending the spin echo technique to copper A-type zeolites with adsorbed methanol, or ethene, different geometries (*45*) or (*46*) were "suggested" for these adsorbed environments, respectively. While the Cu-O distance in (*45*) of 2.2 Å seems entirely reasonable, that of 3.5 Å in (*46*) seems exceptionally long even for weak coordination of an ethene molecule via its π-bond. Nevertheless, the modulation of the copper(II) unpaired electron signal offers a novel technique for studying copper(II) ions



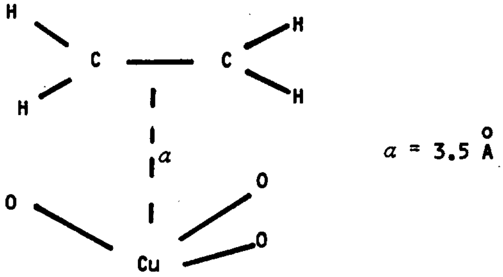
(43; $Cu(OH_2)_x$ in dehydrated A-type zeolite)



(44; $Cu(OH_2)_6$ on Cs_7Na_5A-type zeolite)



(45; $Cu.NaA$-type.CH_3OH)



(46; $Cu.NaA$-type.C_2H_4)

adsorbed on zeolites, and a promising future is predicted. Where the technique is extended to amorphous adsorbates, such as silica gel [336], no single-crystal X-ray data can be available and the spin echo technique offers a *unique* structural tool (comparable to EXAFS), which has demonstrated the existence of a $\{CuO_4(NH_3)_2\}$ species, but no Cu-O or Cu-N distances were reported.

The exchange of $H_2{}^{18}O$ water on partially exchanged copper(II)-Y zeolite indicates two types of water absorbates, only one of which can undergo exchange [337]. The exchange of $[Cu(NH_3)_4]^{2+}$, $[Cu(en)]^{2+}$, $[Cu(en)_2]^{2+}$, $[Cu(pn)]^{2+}$, and $[Cu(pn)_2]^{2+}$ on 4A and 5A-type zeolites have been described [338], and the heats of absorption of carbon monoxide on copper(II) exchanged Y-zeolites at a low surface coverage [339] have been reported. An EPR study of $Cu(acac)_2$ complexes adsorbed on silica gel from non-aqueous solutions [340] indicates that part of the $Cu(acac)_2$ retains the mobility of the initial solution, while the remainder is adsorbed. The possible use of clay supported copper(II) dimers containing oxygen bridges and nitrogen ligands to catalyse ring opening reactions of phenols [341], as a development of the geochemical aspects of waste disposal, is a timely reminder of the relevance of copper coordination chemistry to everyday life. The extension of exchange properties to synthetic inorganic compounds involving layer structures (such as zirconium phosphate) is continuing with the use of electronic reflectance spectroscopy to follow the changes in stereochemistry

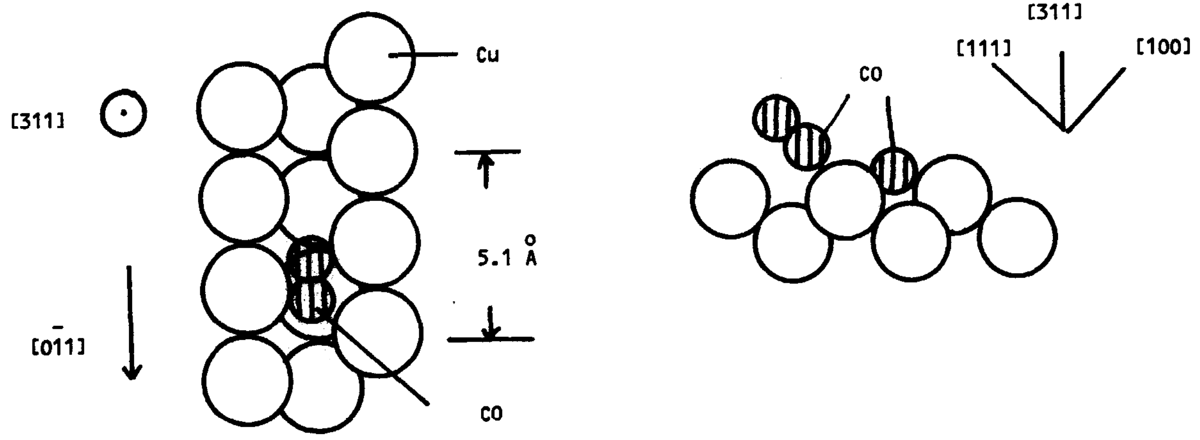


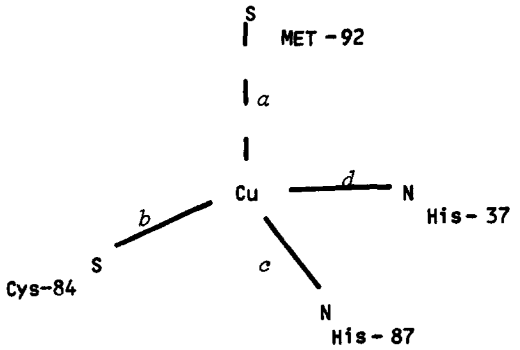
Fig. 13: Possible sites for coordination of carbon monoxide on the copper metal <311> face.

with the changes in phase produced by heat treatment [342].

The binding geometry of CO chemisorbed on the copper metal <311> plane has been studied by angle resolved photoemission spectroscopy; three distinct orientations are found (see Fig. 13), two with the C-O axis nearly perpendicular to the <100> and <111> faces, and one with the axis lying flat, with the C-O axis parallel to the <011> direction [343].

3.4 BIOLOGICAL COPPER

An impressive paper on the detailed electronic structure of the blue copper active site from a single-crystal electronic and EPR spectroscopic study of poplar plastocyanin single-crystals has been reported [344]. The $\{CuN_2S_2\}$ chromophore is reported to have a very distorted tetrahedral geometry (*47*), with the bond angles

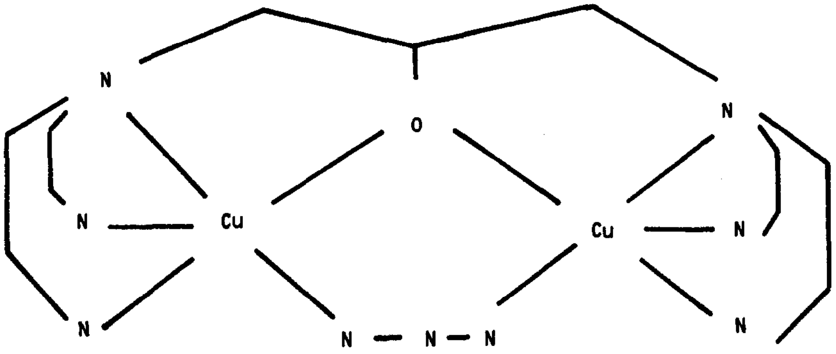


a = 2.90 Å
b = 2.13 Å
c = 2.10 Å
d = 2.04 Å

(47; poplar plastocyamine - CuN_2S_2)

varying from 85-132° (space group $P2_12_12_1$). The g-values (2.05, 2.23) suggest an approximately $d_{x^2-y^2}$ ground state, and the single-crystal g-values indicate that g_z lies approximately parallel to the long Cu-S_{Met-92} bond directions (2.90 A). The single-crystal spectra show virtually no polarisation, with a main bond at 17000 cm^{-1}, a less intense bond at 13500 cm^{-1}; Gaussian analysis resolved these bands into three dominant charge-transfer bands at 13350, 16490 and 17890 cm^{-1}, $S_{cyst} \rightarrow Cu(d_{x^2-y^2})$. An iterative ligand field calculation was used to determine the approximate energy level diagrams for the $\{CuN_2SS\}$ chromophore, with an elongated trigonal pyramidal stereochemistry of approximate C_{3v} symmetry. While the results reported may well be correct, the non-availability of atomic coordinates for the $\{CuN_2SS'\}$ chromophore make it impossible for the reader to check the use of single-crystal techniques as usually applied [18]. Nevertheless, the paper represents an important advance in our understanding of the electronic properties of biological copper systems.

A number of five-coordinate copper(II) complexes involving thio groups have been synthesised as possible models of type II copper systems, and their electronic and EPR spectra have been reported [345], whereas mercapto and disulphide copper(II) complexes are reported to simulate the sulphur to copper charge-transfer spectra of type I blue copper proteins [346]. Phenolato complexes of the copper(II) ion have been suggested as specific models for the metal bonding site in lacto-ferrin [347], and 1,3-bis-*N*,*N*-bis(2-benzoimidazolyl-methyl)amino-methylcyclohexanecopper(II) has been suggested as a model for the copper site in hemocyanine [348]. The chemical and spectroscopic properties (X-ray absorption edge, electronic and resonance Raman spectroscopy) have been used to characterise the binuclear copper active site of Rhus Laccase [349]. The crystal structure (*48*) of a binuclear unsymmetrically bridging model for the copper hemocyanin has been published

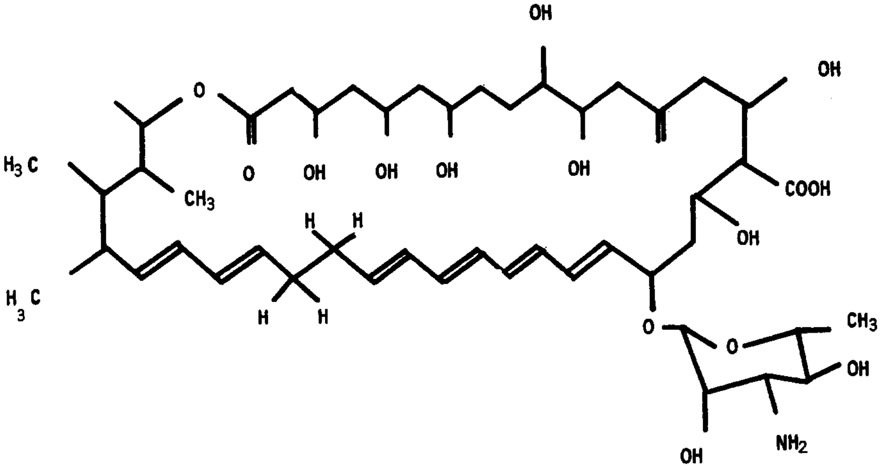


(*48*; $[Cu_2(L\text{-}Et)(N_3)][BF_4]_2$)

[350], involving benzimidazole ligands (L-Et), and an approximate square pyramidal $\{CuN_3ON\}$ geometry. Competitive inhibition binding of the binuclear copper active site in Tyrosinase has been examined [351] using electronic and EPR spectroscopy. Complexes of the polyene antibiotic nystatin (*49*) with copper have been examined in solutions [352], using their circular dichroism spectra. The characteristic of chelate antidotes for copper(II) poisoning have been reported [353].

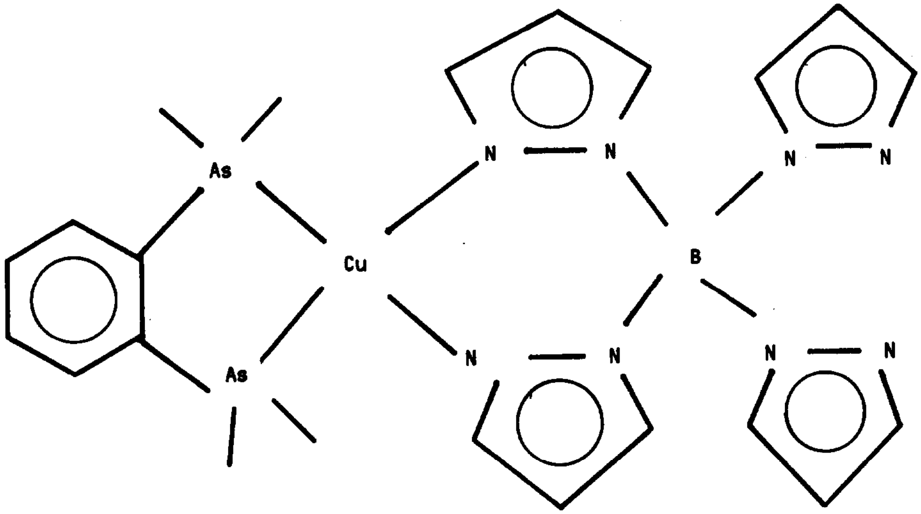
7.5 COPPER(I) CHEMISTRY

The review of the photochemistry of copper complexes [3] contains a substantial section on the charge-transfer spectra of copper(I) complexes. The synthesis of copper(I) complexes with 4-pyridine-carboxaldehyde with stoicheiometry 1:1, 1:2, 1:3, and 1:4 have been reported [354] and ternary complexes involving 2,9-dimethyl-1,10-phenanthroline, some oxygen donor chelates and copper(I) have also been described [355]. A tetrahedral $\{CuN_2As_2\}$ chromophore is reported in



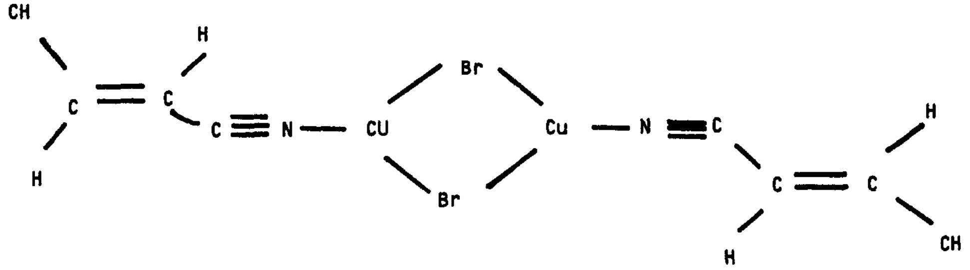
(49; nystatin)

[Cu(diars)(BPz$_4$-N^2,N^2)] (*50*) and a planar {CuAs_4} chromophore in [Cu(diars)$_2$][PF$_6$] [356]. Spectroscopic, structural and photochemical evidence has been reported

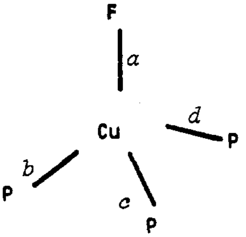


(50; [Cu(diars)(BPz$_4$-N^2,$N^{2'}$)])

for the dimeric bridging structure of CuX.crotonitrile (*51*) [357,358]. The crystal structure of fluorotris(triphenylphosphine)copper(I) ethanol (*52*) yields a tetrahedral {CuFP_3} chromophore [359]. Tetrahedral {CuI_5} chromophores with face to face coupling (*53*) are reported [360] in the strctures of [A]Cu$_2$I$_3$ and [B]Cu$_2$I$_3$ {A = tetramethylammonium, B = dimethyl(3-dimethyl(3-dimethylamino-2-aza-2-propenylidene)ammonium}. The structure of the dimeric Cu$_2$Br$_3$3(PPh$_3$).1.5 C$_6$H$_6$

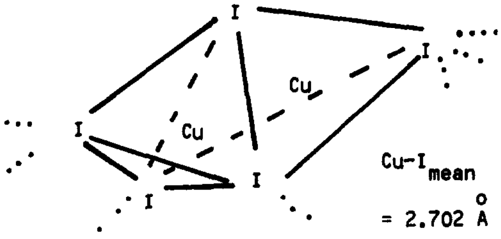


(51; $[Cu_2Br_2(crotonitrile)_2]$)

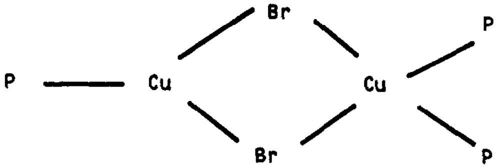


a = 2.062 Å
b = 2.316 Å
c = 2.310 Å
d = 2.325 Å

(52; $[CuF(PPh_3)_3]$)

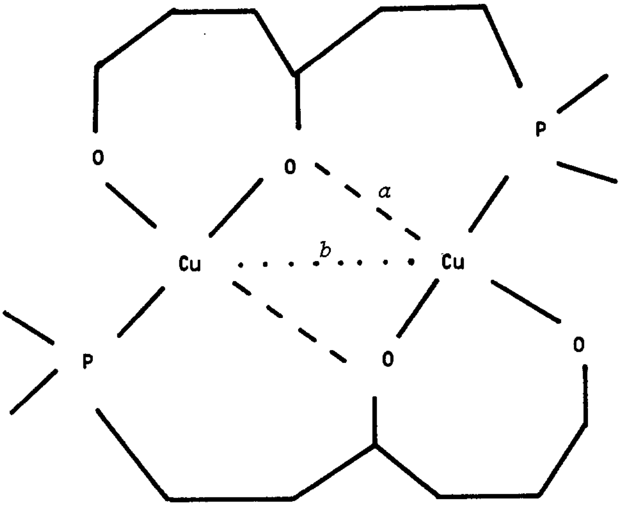


(53; $A\{Cu_2I_3\}$)



(54; $[Cu_2Br_2(PPh_3)_3].1.5C_6H_6$)

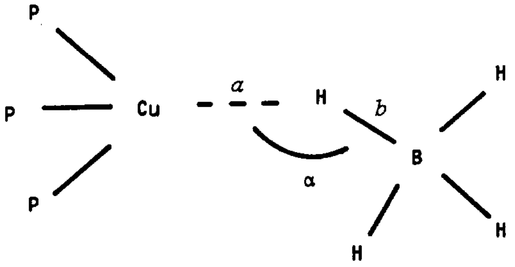
has been determined [361], and involves three and four coordinate chromophores (*54*), $\{CuBr_2P\}$ and $\{CuBr_2P_2\}$, respectively. The fluorescent properties of copper(I) triphenylphosphine complexes have been reported [362], and photostudies of $[Cu(bipy)(PPh_3)]^+$-type cations in solution and in low temperature glasses have been discussed in terms of inter-ligand and charge transfer states [363]. Photochromic alkali aluminoborosilicate glasses containing copper(I) halides can darken to 14% transmission (580 nm), with the formation of colloidal copper metal [364]. The use of macrocyclic ligands to generate dimeric structures [365] has been extended to copper(I) complexes, $[Cu_2L][ClO_4]_2.H_2O$, where L is the 30-membered macrocyclic ligand [1,(*27*)]. 2-(Diphenylphosphino)benzoyl pinacolone has been used to produce the "dicuprophene" (*55*) macrocycle, in which two trigonal pyramidal $\{CuO_2P\}$ chromophores "face" each other to form a weakly bonded dimer [366]. A combined neutron and X-ray diffraction single-crystal study of $[Cu^I(PPh_2Me)_3(HBH_3)]$ (*56*) at 15 K has been carried out [367], and shows the first



a = 3.159 Å

b = 3.768 Å

(55; dicuprophane)



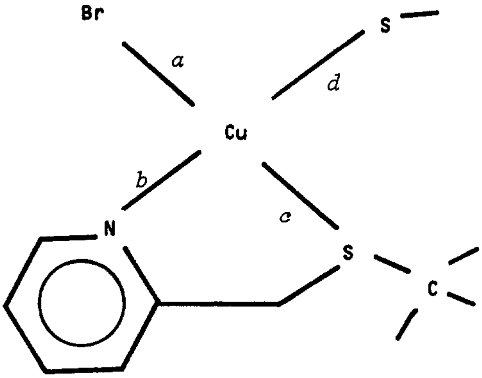
a = 1.697 Å

b = 1.170 Å

α = 121.7°

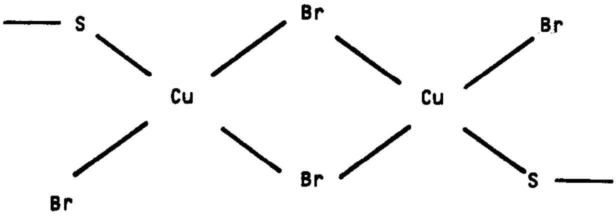
(56; $[Cu(PPh_2Me)_3(BH_4)]$)

accurate characterisation of a metal-hydrogen-boron bridge bond. The Cu-H-B bond is bent (121.7°) with a long Cu-H distance of 1.697 Å. Copper-sulphur bonds still dominate copper(I) chemistry [368], and analogous pseudo tetrahedral $\{CuS_4\}$ chromophores have been reported for copper(I) and copper(II). Some copper(I) complexes involving heterocyclic thioamide and thioformamide ligands have been prepared [369]. Using the ligand L, 2-(3,3-dimethyl(2-thiabutyl)pyridine, and its protonated cation $[LH]^+$, the complexes CuL_2Br (*57*) and $[Cu(LH)Br_2]$ (*58*) have been prepared [370]. The structures of some related copper complexes, one with mixed oxidation states, $[Cu^I(2,5\text{-dth})_2(ClO_4)]$, $[Cu^I{}_2Cu^{II}(2,5\text{-dth})_6][ClO_4]_4$ and $[Cu^{II}(2,5\text{-dth})_2][ClO_4]_2$ have been determined [371a], and contains $\{Cu^IS_4\}$ tetrahedron and $\{Cu^{II}S_4O_2\}$ elongated octahedra, with semi-coordinated perchlorate groups. A normal coordinate analysis of the adamantane-like cage of a $\{Cu^I{}_4S_6\}$ chromophore has been carried out [371b], and suggests that only weak Cu...Cu interactions are present. The first complexes of copper(I) with the $[S_3N]^-$ anion



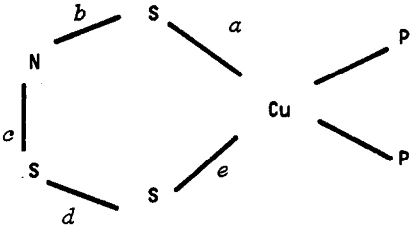
a = 2.424 Å
b = 2.109 Å
c = 2.357 Å
d = 2.310 Å

(57; [Cu(2-alkylthiopyridine)$_2$*Br])*



(58; [{Cu(2-alkylthiopyridineH)Br$_2$*}*$_2$*])*

have been prepared [372], and the X-ray structure shows both the shape of this anion and its mode of coordination in [Cu(PPh$_3$)$_2$(S$_3$N)] (*59*). The preparation of a new series of σ-alkylylide copper(I) complexes [373] and of copper(I) halide bis(trimethylsilyl)ethyne complexes [374] have been reported. The oxidation product of bis(2,2'-bipyridine)copper(I) perchlorate in nitroalkanes [375] has been identified as [Cu(bipy)$_2$(ONO)][ClO$_4$], one of the *cis*-distorted octahedral copper(II) complexes (see Section 3.3.2).



a = 2.304 Å
b = 1.541 Å
c = 1.593 Å
d = 2.058 Å
e = 2.304 Å

(59; [(Ph$_3$*P)*$_2$*Cu(S*$_3$*N)])*

Photoinduced electron transfer reactions involving $[Cu(2,9\text{-}Me_2phen)_2]^+$ with cobalt(III) complexes, chromium(III), and dioxygen have been described [376] and the rôle of the copper(I) complex in the oxygen atom transfer reactions from O_2 to PPh_3 has been suggested to involve a bridged oxygen copper(II) intermediate [377]. Binuclear copper(I) complexes which reversibly react with CO, such as Di-μ-halogeno-bis(2,2'-bipyridine)dicopper(I) have been described [378] and the structure of $[Cu_2(tren)_2(CO)_2X][BPh_4]$ determined [379; 1,(*35*)]. A theoretical investigation of the ground and core hole states of $[Cu(NH_3)_n(CO)]^+$ (n = 2 or 3) as models for the reversible bonding of CO to the copper(I) has been described [380]. The closed shell configuration of the electronic structure of Cu^+ in a NaCl lattice [381] and of the $[Cu(ethanediimine)_2]^+$ cation have been described [382] and compared with the experimental data. The phosphorescence of copper(I) complexes of aromatic mercaptans have been recorded [383] and specific heat anomalies in the thermochromic complex $Cu^I{}_2HgI_4$ have been described [384]. From the reaction of copper(I) with micella porphyrines and hemes, spectroscopic evidence for copper(I)-heme binuclear ion formation has been obtained [385].

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