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7. COPPER

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CONTENTS

INTRODUCTION

This annual report differs from that for 1979 [1] in the sense that it has been written in the context of that report, which highlighted the importance of the Jahn-Teller effect for copper(II) chemistry. Indeed, last year's review is frequently referred to in this article. This year's review is similar in that the same broad subdivisions have been used, but with one or two additional areas highlighted. A significantly shorter and less comprehensive review appeared in 1980, [2], covering the same period. A substantial review on biological copper [3] also appeared in 1980 and will be discussed in Section 7.5. A number of reviews have appeared containing a mention of some aspects of copper chemistry, but interestingly in one entitled "Some Trends in Inorganic Chemistry" [4] the only significant mention of copper chemistry was of lithium organocuprates, and a passing mention of the absence of any direct metal-metal bonding in dimeric copper(II) ethanoate type structures: it is hoped that this rather unbalanced view will be, in part, rectified by this current article.

It is perhaps apposite, at this point, to briefly consider the treatment of

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copper chemistry in undergraduate textbooks. 1980 was highlighted by the appearance of the 4th Edition of "Advanced Inorganic Chemistry" by F.A. Cotton and G. Wilkinson [5]. It includes an increase in coverage on copper from the 3rd edition (19 to 23 pages, plus 4 pages on biological copper), but the section suffers not only from a shift in emphasis to cluster chemistry, but also from an almost complete removal of any reference to the relationship between the electronic properties and the stereochemistry of the copper(II) ion. In this respect the 3rd Edition was more balanced. The 3rd Edition of Mackay and Mackay [6a] was due to appear as this article was written, as was a new text by Sharpe [6b], and these books will be discussed next year. However, in view of the tendency away from basic structural chemistry, it would seem appropriate to include in these Annual Reviews a section that involves an up-date of one or more areas of copper chemistry, in order to bring current text-books up-to-date for the reader. In the present review, the question of Copper(II) Stereochemistry has been selected.

7.1 THE STEREOCHEMISTRY OF COPPER(II) COMPLEXES

The stereochemistry of the copper(II) ion was reasonably described in 1970 [7], as in Fig. 1, with suitable examples to illustrate the structures. Alternative examples could readily be chosen, as in the various editions of Cotton and Wilkinson [5] at the start of the section on copper chemistry. But, with the possible exception of $K_2Pb[Cu(NO_2)_6]$ (which, incidentally, is incorrectly discussed on p. 912 of the 3rd edition of [5] - the application of the dynamic Jahn-Teller effect to cubic $K_2Pb[Cu(NO_2)_6]$ was partially understood even in 1966 [8], no doubt was ever expressed about considering these as static non-temperature variable structures, all established by room temperature X-ray crystallography. As a consequence of the application of the Jahn-Teller effect [9], particularly in the *three* potential well form which was discussed in some detail last year [1; p. 215-228; Fig. 1], the six-coordinate stereochemistries of the copper(II) ion are very susceptible to the effect of variable temperature, as are their EPR spectra [10]. Thus, the structures detailed in Fig. 1 may be listed in Table 1, according to their temperature variable and non-temperature variable types. Eight out of these fifteen structures are potentially temperature variable, and five of these {(i), (ii), (v), (vi) and (vii)} only arise [1,10] as artifacts of the fluxional model and are best described as *pseudo*-stereochemistries of the copper(II) ion (see Table 1). The elongated tetragonal and rhombic octahedral and compressed tetrahedral stereochemistries are genuine structures, which can occur with a static structure, but can also be modified by fluxional effects (*e.g.* Tutton salts [10,11]). Consequently, Fig. 1 in ref. [7] should now be redrawn and,

LINEAR - C_{2v}	TRIGONAL BIPYRAMIDAL		SQUARE PYRAMIDAL
$CuCl_2$(gaseous)	D_{3h}-$[Cu(NH_3)_2Ag(SCN)_3]$		C_{4v}-$[NH_4][Cu(NH_3)_5][PF_6]_3$
COMPRESSED TETRAGONAL	OCTAHEDRAL	ELONGATED TETRAGONAL	SQUARE OR RHOMBIC COPLANAR
OCTAHEDRAL	O_h-$K_2Pb[Cu(NO_2)_6]$	OCTAHEDRAL	D_{4h}-$CaCuSi_4O_{10}$
D_{4h}-$Rb_2Pb[Cu(NO_2)_6]$		D_{4h}-$[Cu(NH_3)_4(SCN)_2]$	D_{2h}-[Cu(3-Me-*acac*)$_2$]
COMPRESSED RHOMBIC	*cis*-DISTORTED	TRIGONAL OCTAHEDRAL	ELONGATED RHOMBIC
OCTAHEDRAL	OCTAHEDRAL	D_3-$[Cu(en)_3][SO_4]$	OCTAHEDRAL
D_2-$[Cu(dien)_2][NO_3]_2$	C_{2v}-$[Cu(bipy)_2(ONO)][NO_3]$		D_{2h}-$Ba_2[Cu(HCO_2)_6].4H_2O$
COMPRESSED TETRAHEDRAL	(TETRAHEDRAL)	ELONGATED TETRAHEDRAL	EIGHT COORDINATE
D_{2d}-$Cs_2[CuCl_4]$	T_d	$[Et_4N]_2[CuCl_4]$?	$Ca[Cu(CH_3CO_2)_4].6H_2O$

═══ STATIC STRUCTURES ONLY. ═ ═ ═ STATIC OR FLUXIONAL STRUCTURES. ‒ ‗ ‒ ‗ ‒ PSEUDO ONLY (arising through fluxional effects, and having no inherent existence as static structures).

Fig. 1: A summary of the known stereochemistries of the copper(II) ion, their idealised molecular symmetries, and the relationship between the regular and distorted geometries.

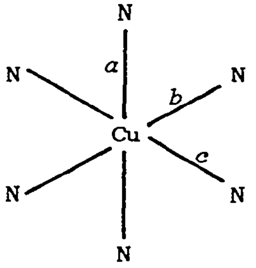
TABLE 1

Breakdown of copper(II) Stereochemistries into their temperature variable (A) and non-temperature variable (B) types.

(A) Temperature Variable:		
(i)	pseudo-octahedral	$K_2Pb[Cu(NO_2)_6]$
(ii)	pseudo-trigonal octahedral	$[Cu(en)_3][SO_4]$
(iii)	*Elongated tetragonal octahedral*	$[Cu(H_2O)_6][HCO_2]_2$
(iv)	Elongated rhombic octahedral	$Ba_2[Cu(HCO_2)_6].4H_2O$
(v)	pseudo compressed tetragonal octahedral	$Rb_2Pb[Cu(NO_2)_6]$
(vi)	pseudo compressed rhombic octahedral	$[Cu(dien)_2][NO_3]_2$
(vii)	pseudo-*cis*-distorted octahedral	$[Cu(bipy)_2(ONO)][NO_3]$
(viii)	pseudo-elongated tetrahedral	$[Et_4N]_2[CuCl_4]$
(B) Non-Temperature Variable:		
(ix)	Linear	$CuCl_2$(gaseous)
(x)	Trigonal bipyramidal	$[Cu(NH_3)_2Ag(SCN)_3]$
(xi)	Square pyramidal	$[NH_4][Cu(NH_3)_5][PF_6]_3$
(xii)	Square coplanar	$CaCuSi_4O_{10}$
(xiii)	Rhombic coplanar	$[Cu(3\text{-}Me\text{-}acac)_2]$
(xiv)	Eight coordinate	$Ca[Cu(CH_3CO_2)_4].6H_2O$
(xv)	Compressed tetrahedral	$Cs_2[CuCl_4]$

if up-dated in terms of complexes whose low temperature crystallography or EPR properties [10] have been recently established, give an entirely different summary of the stereochemistry of the copper(II) ion. Only five structures involve genuine static stereochemistries, three can be static or fluxional, and six arise through fluxional effects and have no inherent existence as static structures (see Fig. 1).

Probably, the best illustration of fluxional behaviour now involves $Cs_2Pb[Cu(NO_2)_6]$ (1), whose structure has been determined at room temperature



	a/Å	*b*/Å	*c*/Å	*T*
420 K	2.17	2.17	2.17	1.000
293 K	2.070	2.227	2.227	1.076
160 K	2.073	2.115	2.300	0.910

(1; $Cs_2Pb[Cu(NO_2)_6]$)

(293 K) [12], at 420 K [13], and at 160 K [14]. At 420 K, the structure is cubic [13] with a regular octahedral $\{CuN_6\}$ chromophore; at 293 K, it is compressed tetragonal octahedral; at 160 K, it is elongated rhombic octahedral with a tetragonality[†] of 0.91 [7], indicative of some residual fluxional behaviour [10]. Equally significant [10], the direction of the long axial Cu-N distance at 160 K corresponds with the equatorial Cu-N direction of the pseudo compressed octahedral structure at 293 K, a change in direction that is consistent with the three types of behaviour, (a), (b) and (c), of the fluxional model described in last year's review [1; Fig. 1].

This static/non-static sterochemical relationship is further complicated by the plasticity effect [1; (pp. 226-228), 11,15] which, due to the non-spherical symmetry of the copper(II) ion, enables it (for a given set of ligands) to give rise to distortion isomers [15], and to ranges of cation or anion distortion isomers, such as [Cu(dien)(bipyam)]X [16], $[Cu(bipy)_2Cl]X$ [17] or $M^I_2Pb[Cu(NO_2)_6]$ [8]. This means that not only does the precise structure of a copper(II) cation or anion vary depending upon the counter ion present for a series of *static* copper(II) distortion isomers but, in fluxional systems (such as the Tutton salts [11]) the basic static structure involved in the three potential Well systems is not necessarily the same from one complex to another. Consequently, the small differences in the E_{JT} and E_2 energies[¶] of the $M^I_2M^{II}[Cu(NO_2)_6]$ series of anion distortion isomers [1; (Table 2), 18] are due to inherent differences in the underlying static $\{CuN_6\}$ chromophore stereochemistry, which are measured by the electronic spectra due to their short lifetime (*ca.* 10^{-15} s) relative to that of the X-ray structural measurements (*ca.* 1.0 s). It is then an intriguing possibility that the use of EXAFS spectroscopy [19] in these fluxional copper(II) systems, due to the short time scale involved (*ca.* 10^{-16} s) may yield bond length data which relate to the basic static structure of the $\{CuN_6\}$ chromophore, and not to the time-averaged structure of the 90° misaligned chromophores, as revealed by X-ray crystallography due to its significantly longer time scale.

If the pseudo-structures illustrated in Fig. 1 are now excluded from the discussion, the genuine stereochemistries of copper(II) are reduced to the following five, if the uncommon linear (two-coordinate) and eight-coordinate geometries are neglected:

I Elongated tetragonal (or rhombic) octahedral
II Square (or rhombic) coplanar

[†] $\text{Tetragonality } (T) = \dfrac{\text{mean equatorial Cu-L distance}}{\text{mean axial Cu-L distance}}$

[¶] E_{JT} and E_2 are derived from optical spectroscopy, and discussed in [1].

III Compressed tetrahedral
IV Square pyramidal
V Trigonal bipyramidal

Of these, the occurrence of stereochemistries II to V are no different from any other first row transition metal ion and only a regular octahedral stereochemistry is absent. However, as the copper(II) ion in this structure is Jahn-Teller unstable [20], this static structure is replaced by the elongated tetragonal octahedral stereochemistry. Thus, although the consequences of the Jahn-Teller effect on the stereochemistry of the copper(II) ion is paramount in respect to the fluxional pseudo-structures, it only accounts for *one* new stereochemistry in the static structures, namely, elongated tetragonal octahedral. The absence of a regular tetrahedral structure with a $\dot{T}_2$ degenerate ground state [20] has been accounted for by the Jahn-Teller effect, but spin-orbit coupling is usually considered [21] to remove the degeneracy of the electronic ground state of the copper(II) ion in this stereochemistry, and the observed compressed tetrahedral structures of the copper(II) ion are considered to arise due to the non-spherical symmetry of the copper(II) ion [7] (see also Section 7.3.2).

If the static stereochemistries, I to V above, are drawn out as in Fig. 2, they can be arranged horizontally in terms of their basic coordination number, and vertically depending on whether the basic Cu-L_n chromophore is subject to a trigonal bipyramidal [17] or tetrahedral [22] sense of distortion. This generates four additional types of distorted stereochemistries namely, trigonal or tetrahedrally distorted elongated tetragonal octahedral or square pyramidal. It is then these four types of distorted structures that predominate in copper(II) complexes involving chelate ligands (especially macrocyclic ligands), where significant bond length and bond angle distortions occur, but for which the trigonal type distortions clearly outweigh the tetrahedral [1; Tables 4 and 5]. It is unfortunate that the origin of these distorted structures (that are clearly intermediate between the regular structures of Fig. 2, especially when *all* copper(II) stereochemistries are considered) are usually attributed to the *constraints* imposed by the chelate ligands in these complexes. The question has already been asked [15] "how far do the arrows of [15; Fig. 1] and Fig. 2 (above), represent continuous transitions from one type of coordination to another?", *i.e.* square coplanar to tetrahedral, with *structural pathways* [23] not only between the regular static stereochemistries of Fig. 2, but also between the intermediate distorted structures. Each structural pathway is then determined by a "dominant" normal mode of vibration [24] of the skeletal structure (Fig. 3), or by a linear combination of these to yield a sequence of crystallographically established structures, which represent individual points

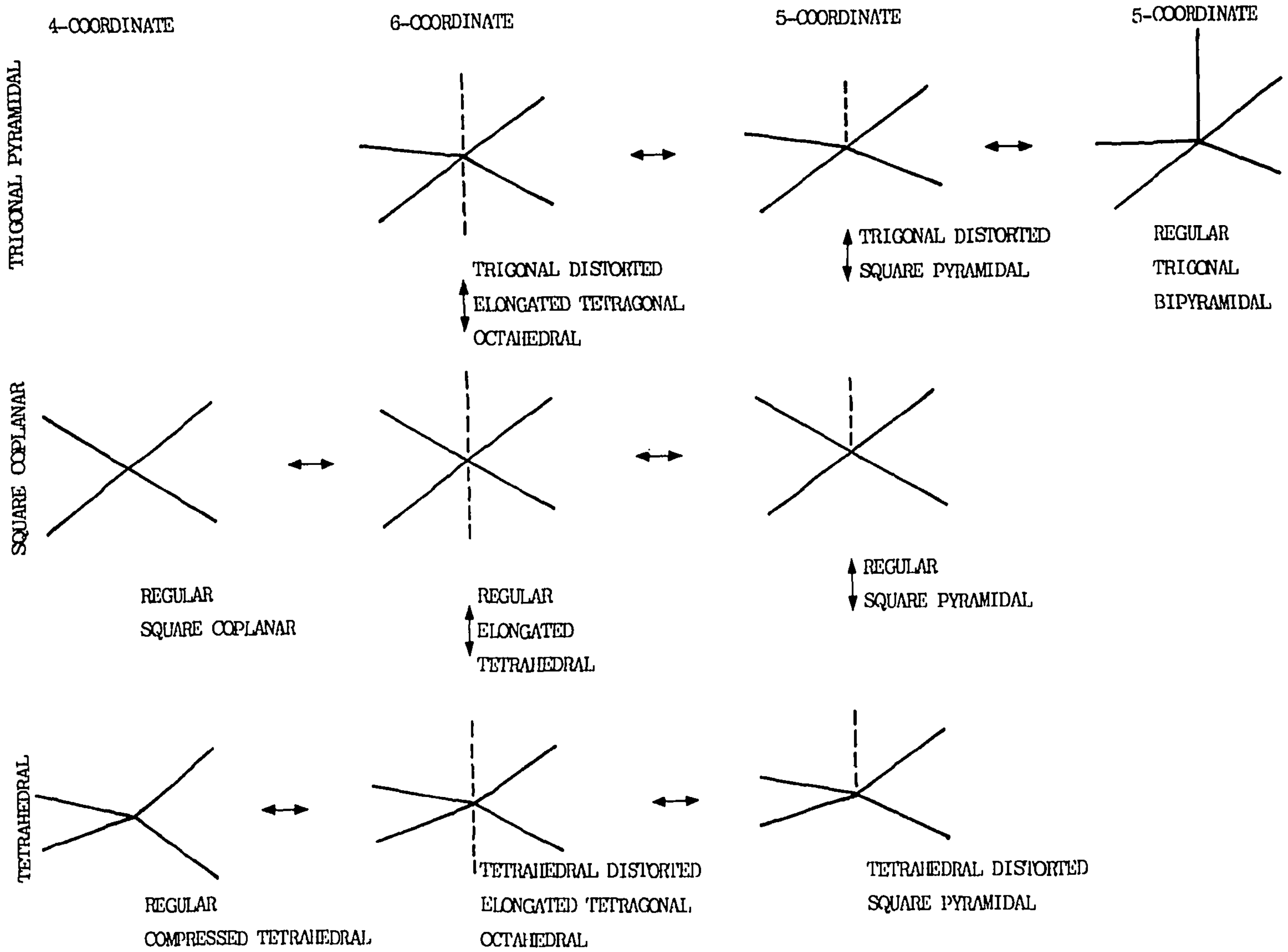


Fig. 2: The static stereochemistries of the copper(II) ion: Regular and Distorted structures.

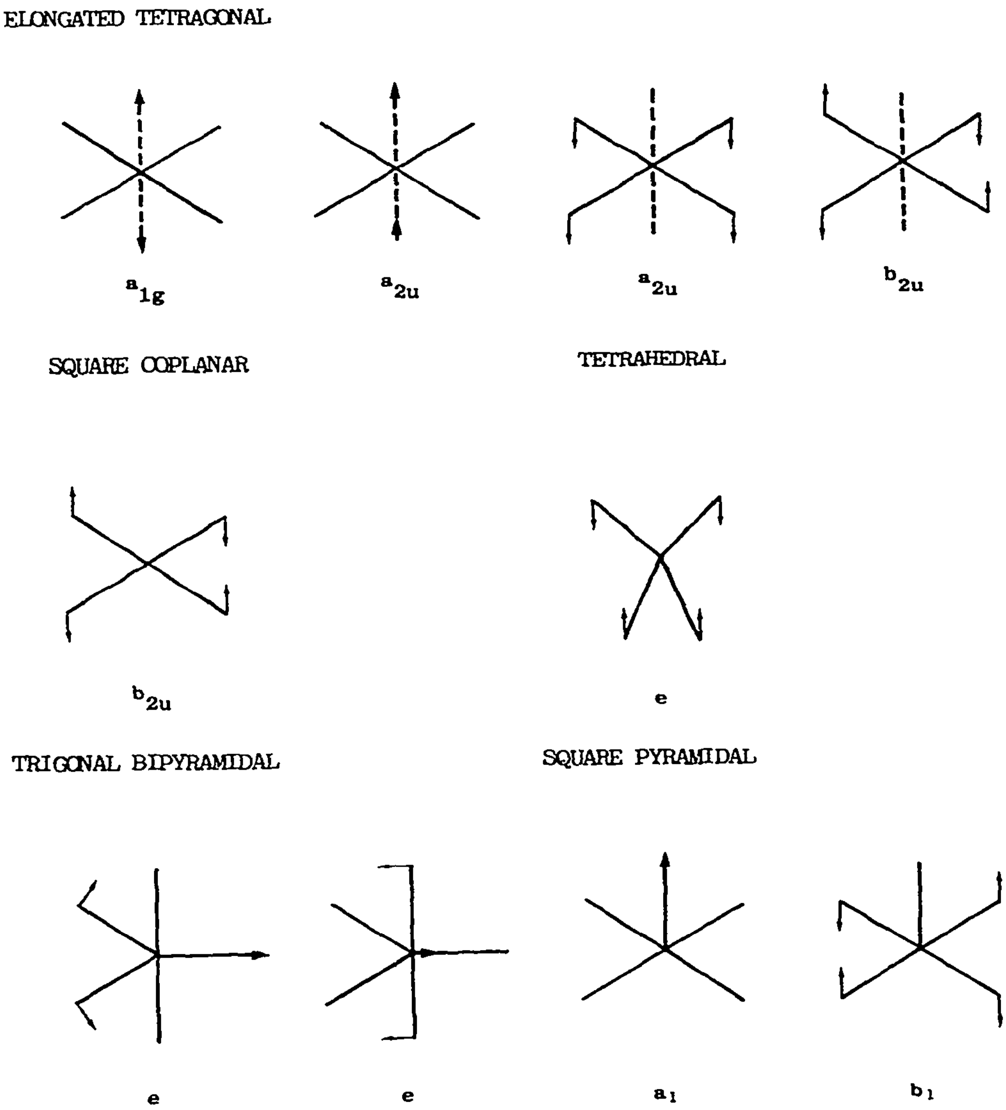
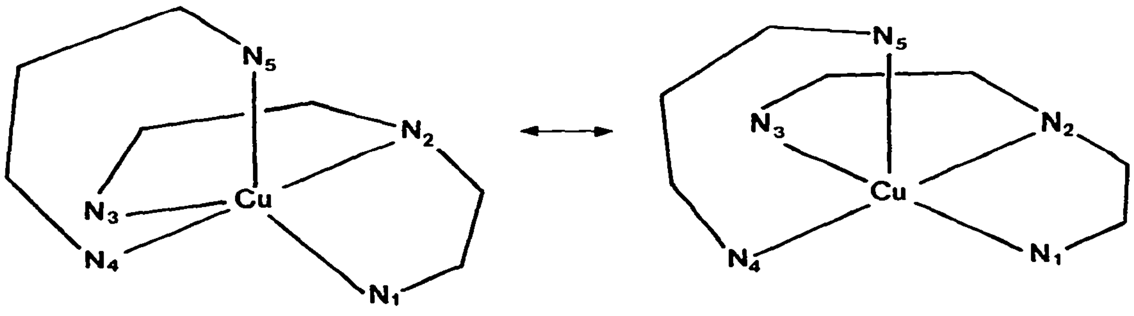


Fig. 3: Selected Normal Modes of Vibration of Regular Stereochemistries.

in the structural pathway [23]. The cation distortion isomers of $[Cu(dien)(bipyam)]X_2.nH_2O$ [16] and of the $[Cu(bipy)_2Cl]X.nH_2O$ series, [1; (Table 4), 17] then represent individual structures along the structural pathway of regular trigonal bipyramidal to regular square pyramidal. As the constraints imposed by these chelate ligands are so different (compare Fig. 4 and Fig. 5), it is difficult to imagine that these constraints determined the



trigonal bipyramidal **square pyramidal**

Fig. 4: The Structural Pathway for the $\{CuN_5\}$ Chromophore of the $[Cu(dien)(bipyam)]X_2.nH_2O$ Complexes from trigonal bipyramidal to square pyramidal.

same individual skeletal $\{CuN_5\}$ or $\{CuN_4Cl\}$ structures alone; rather it seems that these structures are determined by the e' modes of vibration, or a linear combination of these [17]. Where non-equivalent ligands are involved as in the $[Cu(bipy)_2Cl]X.nH_2O$ series, then the alternative route A or route B (or C) type distortions (see Fig. 5) [17] will be determined by the appropriate linear combination of modes of vibration (see Fig. 6 [25]): $\nu_3 + \nu_4$ for route A and $\nu_7 + \nu_8$ for route B or C. Finally, the individual structures which map out a structural pathway must involve slightly different energies and may be used to draw a structural profile [23], connecting the total energy E, and some structural parameter, such as the $N_2\text{-}\widehat{Cu}\text{-}N_4$ angle, α_3, in the $[Cu(bipy)_2Cl]X.nH_2O$ series. Extended Hückel calculations were used to estimate the relative total energies E (Fig. 7) for a $[Cu(NH_3)_4Cl]^+$ cation, using the molecular geometry of the individual $[Cu(bipy)_2Cl]^+$ and $[Cu(bipy)_2(OH_2)]^{2+}$ cations.

In this way the seemingly wide range of stereochemistries of the copper(II) ion may be understood if they are first separated in terms of fluxional behaviour and basic static stereochemistries, and then the static structures linked by the normal modes of vibration to yield structural pathways connecting the regular structures *via* the alternative tetrahedral and trigonal distorted structures. Consequentially, by using this approach, the full potential and consequence of the Jahn-Teller effect is realised in the fluxional properties [10] and plasticity effect [15] in copper(II) stereochemistry.

7.2 COPPER(III) CHEMISTRY

The chemistry of copper(III) complexes continues to be relatively sparse.

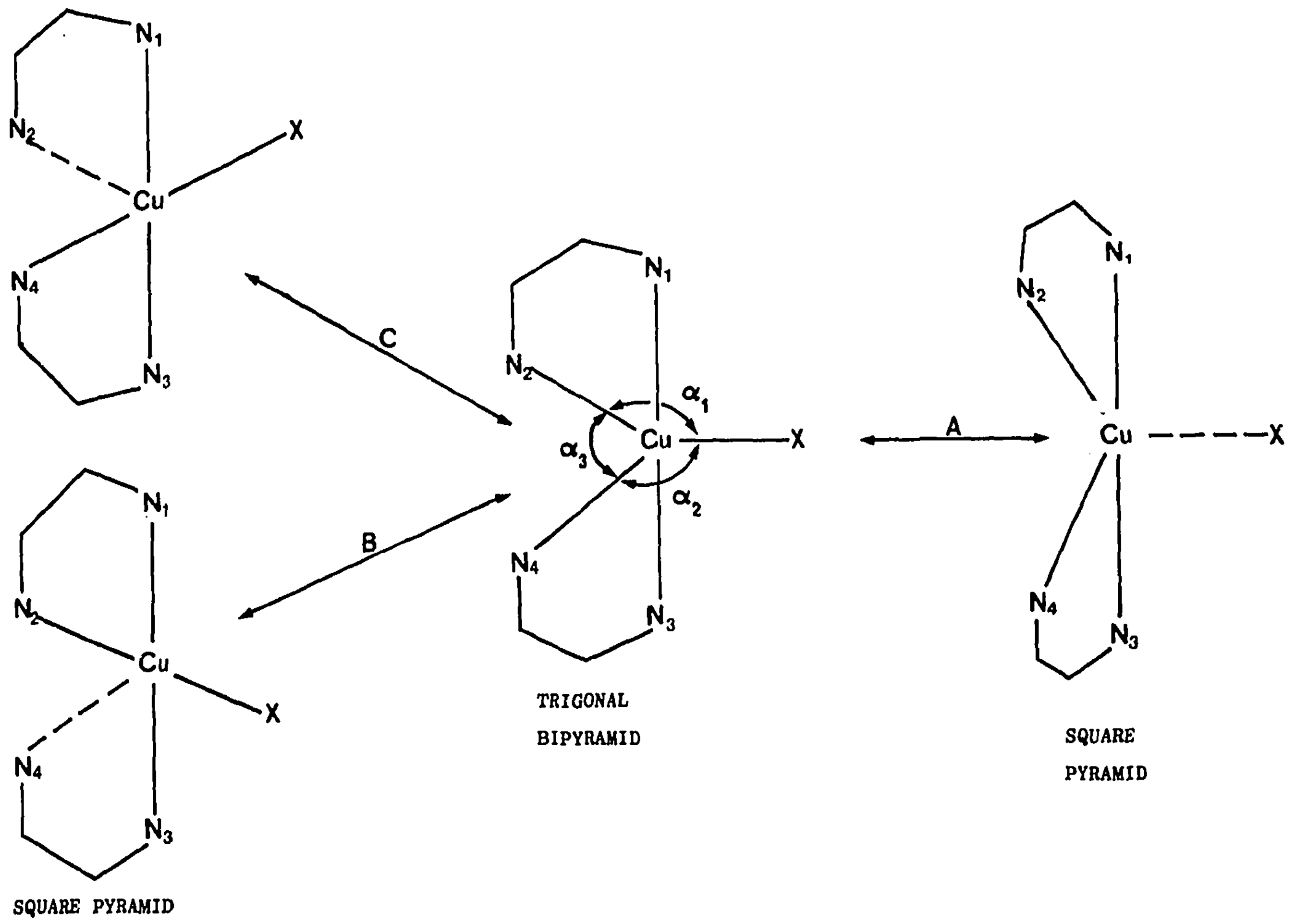


Fig. 5: The structural pathway for the {CuN_4X} chromophore of the [Cu(bipy)$_2$X]Y complexes for distortion from trigonal bipyramidal to square pyramidal, involving three alternative pathways. Routes B and C are symmetry related by the C_2 about the Cu-X bond. ———represents the axial bond of the square pyramid.

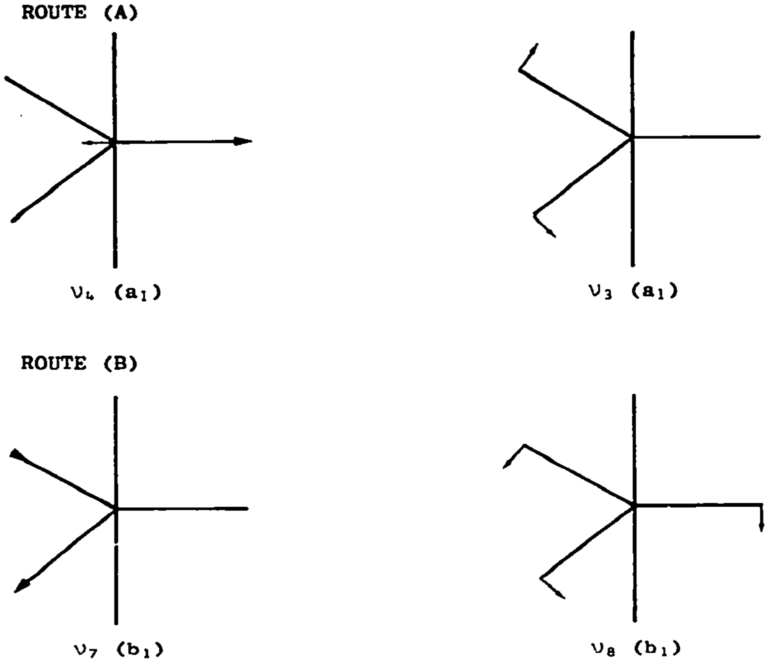


Fig. 6: Some of the normal modes of vibration of $\{CuN_2N'_2Cl\}$ which enable distortions *via* routes A or B (see Fig. 5).

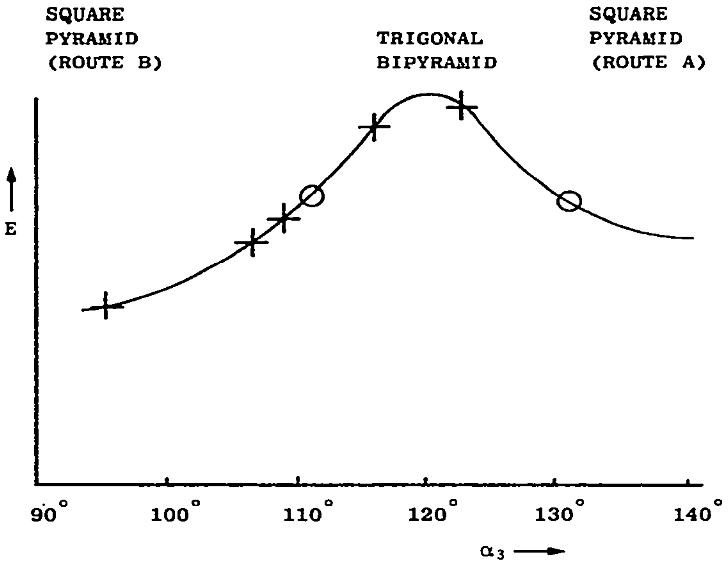


Fig. 7: Structural profile of the $[Cu(bipy)_2Cl]^+$ (+) and $[Cu(bipy)_2(OH_2)]^{2+}$ (O) cations.

The preparations of some iodate and persulphate salts of copper(III) have been reported using oxidising conditions and strongly alkaline solutions [26]. Copper(III) complexes of the tetra-aza-macrocyclic ligand, 1,4,8,11-tetra-azacyclotetradecane-5,7-dionate(2-) (which contains two deprotonated amido groups) have been generated in aqueous solution by chemical or anodic oxidation, and the copper(III) complex was characterised by its electrochemical properties [27]. Copper(III) complexes of dipeptide and tripeptide Schiff bases have been characterised by their electrode potentials [28], and copper(III) tetraglycine was studied by pulsed radiolytic techniques after reaction of the corresponding copper(II) complex with a variety of free radicals [29]. The entropy differences $S^{\circ}_{II}-S^{\circ}_{III}$ for several copper(III/II) peptide couples have been determined from cyclic voltammetric measurements as a function of temperature in a non-isothermal electrochemical cell. The data suggest that there is a change in the axial coordination of water on oxidation of copper(II) to copper(III) to give a square coplanar copper(III) complex, which in turn suggests that the copper(III) state might well be stabilised in a hydrophobic protein environment [30]. Some redox reaction of copper(III) tetraglycine [31] and oligopeptides [32] have also been reported.

7.3 COPPER(II) CHEMISTRY

7.3.1 Jahn-Teller Effect

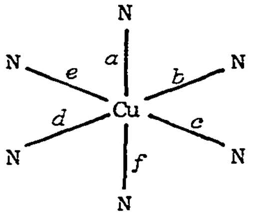
Problems associated with the key compounds in the saga of the application of the Jahn-Teller effect to copper(II) stereochemistry [1] still occupy the literature. A redetermination [33] of the crystal structure of K_2CuF_4 (probably the first compound with a compressed tetragonal octahedral structure to be determined by X-ray crystallography) has identified a multidomain structure associated with the alternative orientations of the elongation direction in the anti-ferrodistortive ordering present. Using a single domain crystal the space group has been redetermined as $D_{2h}{}^{18}$-*bcm*($D_{2d}{}^{10}$-$I\bar{4}c2$). The effect of uniaxial stress [34] on the EPR spectra of $Rb_2Pb[Cu(NO_2)_6]$ and $K_2Pb[Cu(NO_2)_6]$ has been shown to change the direction of the $g_{\parallel}$-factor, consistent with the change from a compressed to an elongated tetragonal octahedral $\{CuN_6\}$ chromophore. This change is consistent with the predicted behaviour of the three potential Well systems [1; Fig. 1], and consistent with a change in crystal phase as predicted by the Cooperative Jahn-Teller effect [35]. Probably the most interesting crystal structure to be determined in the current year (on a Jahn-Teller system) is that of $Cs_2Pb[Cu(NO_2)_6]$ (1) at 160 K [14]. Using neutron diffraction data, this γ-phase was demonstrated to have a monoclinic space group and involve an elongated rhombic octahedral $\{CuN_6\}$ chromophore with a tetragonality of 0.91 (indicating some residual fluxional behaviour). This structure completes the crystallographic evidence for the three types of behaviour, (a)-(c), predicted by the potential Well system [1; Fig. 1], in one and the same complex, namely $Cs_2Pb[Cu(NO_2)_6]$. This now becomes a classic example of the Cooperative Jahn-Teller effect [35], with an octahedral $\{\mathrm{Cu}N_6\}$ structure in the cubic α-phase at 460 K, a compressed $\{\mathrm{Cu}N_6\}$ structure in the orthorhombic β-phase at 293 K, and the elongated rhombic octahedral $\{\mathrm{Cu}N_6\}$ structure in the monoclinic phase at 160 K. Of equal interest is that the structure of the monoclinic phase was determined [14] by profile analysis of powder data, which nicely avoids many of the problems associated with single-crystal techniques (where a phase transition occurs at the low temperature it can generate a domain structure; see [10]). For fluxional complexes involving a relatively small molecular weight, this technique has a great deal to offer. This is particularly true where there is no phase transition, but only a change in the $\{\mathrm{Cu}L_6\}$ geometry to increasing elongated rhombic octahedral (as in the Tutton Salts [11]), an approach that has been demonstrated in the neutron profile refinement of $Rb_2[C_2O_4].D_2O_2$ at 5 K [36]. Such an approach has also been used in the neutron profile refinement of α-$Cu(O_2CH)_2$ at 4.2, 80 and 296 K [37], and these results are summarised in Table 2. Not only do the room temperature data compare very favourably with the low temperature data, but the tetragonality of 0.76 indicates a virtual absence of any fluxional behaviour in the $\{\mathrm{Cu}O_6\}$ chromophore, which has an essentially static structure at all three temperatures. Nevertheless, this paper demonstrates the potential of this technique to fluxional copper(II) systems of low molecular weight.

TABLE 2

Neutron Profile Refinement of the $\{\mathrm{Cu}O_6\}$ Chromophore of α-$Cu(O_2CH)_2$ at 4.2, 80 and 296 K [37].

	4.2 K	80 K	296 K	Single crystal
r\{Cu-O(1)\}/Å	1.947(5)	1.949(5)	1.950(5)	1.945(9)
r\{Cu-O(2)\}/Å	1.968(5)	1.968(5)	1.987(6)	1.942(9)
r\{Cu-O(3)\}/Å	1.987(5)	1.985(5)	1.993(5)	1.986(8)
r\{Cu-O(4)\}/Å	1.944(5)	1.941(5)	1.938(5)	1.928(10)
r\{Cu-O(3')\}/Å	2.371(5)	2.389(5)	2.410(5)	2.397(8)
r\{Cu-O(1')\}/Å	2.781(5)	2.786(5)	2.797(5)	2.790
Tetragonality	0.762	0.758	0.756	0.752

An attempt to determine the low temperature crystal structure of $[Cu(dien)_2][NO_3]_2$



(2; [Cu(dien)$_2$][NO$_3$]$_2$)

	293 K	150 K
a/Å	2.024	2.025
b/Å	2.222	2.219
c/Å	2.228	2.221
d/Å	2.175	2.140
e/Å	2.201	2.199
f/Å	2.030	2.020
T	1.098	1.085

(2) [38], which has a pseudo compressed octahedral {CuN_6} chromophore at room temperature, failed to show the predicted change to elongated tetragonal octahedral, and indicates that a temperature below 150 K will be required to produce this change. This result nicely illustrates the operation of the Cooperative Jahn-Teller effect [35], as the EPR spectra of the copper(II)-doped [Zn(dien)$_2$][NO$_3$]$_2$ (which is isomorphous and isostructural with the copper(II) complex), does demonstrate a change of spectra (see Fig. 8) consistent with

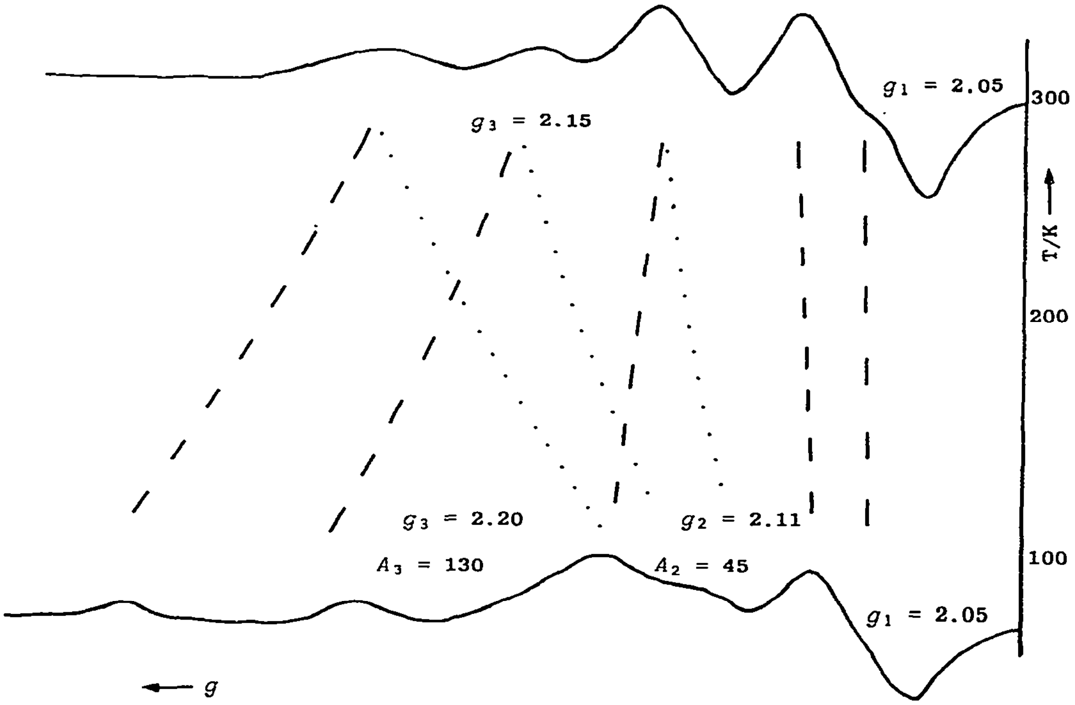


Fig. 8: Temperature Variation of g-factors for [(Cu/Zn)(dien)$_2$][NO$_3$]$_2$.

the change predicted [10] for a fluxional system. Despite the increasing understanding of the Cooperative Jahn-Teller effect [35], caution has been expressed concerning its operation in a range of molecular coordination complexes, where the electronic and EPR spectra are shown not to vary significantly with copper(II) concentration when doped (0.1-100%) in the isomorphous zinc(II) complex as a host lattice [39]. In *such* systems, the doped CuL_x chromophore structure should be equated with the known structure of the CuL_x chromophore of the concentrated (100%) copper(II) complex, and *not* with the structure of the ZnL_x chromophore of the pure zinc(II) complex. The term Non-Cooperative Jahn-Teller effect has been introduced to describe this type of behaviour.

7.3.2 EPR Spectroscopy

EPR spectroscopy continues to attract a great deal of interest with single-crystal studies making the most impact. A beautiful paper [40] on the $[Cu(pyNO)_6]X_2$ (X = $[BF_4]$, $[ClO_4]$ or $[NO_3]$) system confirms the preliminary note on this system as a dynamic Jahn-Teller system, with the cooperative effects being ferrodistortive for the $[BF_4]^-$ salt, and with two different types of antiferrodistortive ordering for the $[ClO_4]^-$ and $[NO_3]^-$ salts. Estimates are made of the Jahn-Teller energy and radius of 2350 cm^{-1} and 0.28 Å, respectively, and Extended Hückel calculations predict the stability of the elongated distortion to be marginally higher than the compressed type distortion, and give a reasonable prediction of the g- and A-factors. The EPR spectra of fluxional systems have been used to establish that the copper(II)-doped $[Zn(dien)_2]X_2$ systems [41] are fluxional, and by extrapolation suggest that the $\{CuN_6\}$ chromophores of the pure copper(II) complexes have a fluxional elongated rhombic octahedral stereochemistry. The single crystal EPR spectra of copper(II)-doped $[Zn(py\text{-}3\text{-}SO_3)_2].4H_2O$ were amongst the first EPR spectra of copper(II)-doped systems to be reported which were taken to indicate a compressed rhombic octahedral $\{CuN_2O_4\}$ chromophore. A determination of the crystal structure of $[Cu(py\text{-}3\text{-}SO_3)_2].2H_2O$ and $[Zn(py\text{-}3\text{-}SO_3)_2].4H_2O$ has shown these to be isomorphous, but not isostructural, and the temperature variation of the EPR spectra of the copper(II)-doped $[Zn(py\text{-}3\text{-}SO_3)_2].4H_2O$, has now shown that this is a fluxional copper(II) system with an *elongated* rhombic octahedral $\{CuN_2O_4\}$ structure [42].

The rotational single-crystal EPR spectrum of copper(II)-doped $[Zn(dien)(bipyam)][NO_3]_2$ [43] is shown to be consistent with the monoclinic space group $P2_1/c$, and equates with the static distorted $\{CuN_5\}$ chromophore structure of the $[Cu(dien)(bipyam)][NO_3]_2$ complex. A detailed examination of the variation of the EPR and electronic reflectance spectra with copper(II) concentration in the doped system shows *no* variation and justifies considering this system as a Non-Cooperative Jahn-Teller system [39]. A systematic analysis of the g and A factors of a series of substituted bis(R-*N*-salicylaldiminato)-copper(II) complexes [44] doped into the corresponding palladium(II) complexes (planar) and zinc(II) complexes (tetrahedral) suggest a systematic decrease in the $g_{\parallel}$ and $A_{\parallel}$ values, which is justified by Angular Overlap calculations upon a rhombic coplanar to tetrahedral model system. This represents a very useful correlation, which would have been enhanced if the variation of the corresponding electronic energies had also been included, especially as the change in structures involved, lie along one of the structural pathways illustrated in Fig. 2. In the past year, one of the most interesting papers on tetrahedral copper(II) has been produced [45], involving the variable temperature single crystal EPR spectra of $[(C_2H_5)_4N]_2[CuCl_4]$ (see Fig. 9). At 4.2 K, the g values are axial with $g_{\parallel} > g_{\perp} > 2.0$, and are typical of values for the compressed $[CuCl_4]^{2-}$ anion. At room temperature, isotropic signals are obtained (which are very broad) at 2.29 and 2.16, but at intermediate temperatures (130-205 K) *two* magnetic sites are observed, both of which have $g_{\perp} > g_{\parallel} > 2.0$ and correspond to an "elongated" type $[CuCl_4]^{2-}$ geometry {Fig. 10(a)}. That the latter then changes to a normal type of EPR spectrum at 4.2 K ($g_{\parallel} > g_{\perp} > 2.0$) suggests that, at the intermediate temperature, a two-dimensional fluxional behaviour occurs, involving two compressed tetrahedral $[CuCl_4]^{2-}$ structures {Fig. 10(b)} (see [1; Fig. 1]), which has all the features of a pseudo dynamic Jahn-Teller effect. Thus, for the first time the tetrahedral copper(II) stereochemistry can be considered to have either a static or fluxional stereochemistry (see Fig. 1), and implies that the regular tetrahedral copper(II) stereochemistry is Jahn-Teller unstable (a possibility that had been previously ruled out by the assumption that spin-orbit coupling removed the triple degeneracy of the T_2 ground state [21]). For this reason, a pseudo dynamic Jahn-Teller description seems to be the more appropriate, but presumably can only apply to the elongated tetrahedral copper(II) complexes with equivalent ligands (*i.e.* $[CuCl_4]^{2-}$ or $[CuBr_4]^{2-}$), and not to the tetrahedral structures involving chelate ligands (*i.e.* $[Cu(bipyam)_2][ClO_4]_2$ or the [Cu(R-*N*-salicyladiminato)$_2$] complexes [44]). In this respect, it is of some interest that large thermal motion or disorder in the tetrahedral $\{CuS_4\}$ chromophores of $Cu_2^{I}Cu^{II}$(2,5-dithiohexane)$_6[ClO_4]_2$ [46] has been interpreted as due to a dynamic disorder, rather than the more usual static disorder.

The EPR spectra of $[Cu(OPPh_3)_2Cl_2]$, and of this complex doped in the isomorphous zinc(II) complex, have been recorded at 4.2 K with normal g values (2.46, 2.09 and 2.08), but with relatively low A values (40, 25 and 20 x 10^{-4} cm^{-1}) which are associated with the covalency of the Cu-Cl bonds [47]. Single-crystal EPR spectra have been reported of copper doped in anhydrous sodium oxalate, and the principal axes of the hyperfine and g-tensors shown to be coincident [48]. The EPR spectra of complexes of the type $K[Cu(en)_2][Fe(CN)_6]$

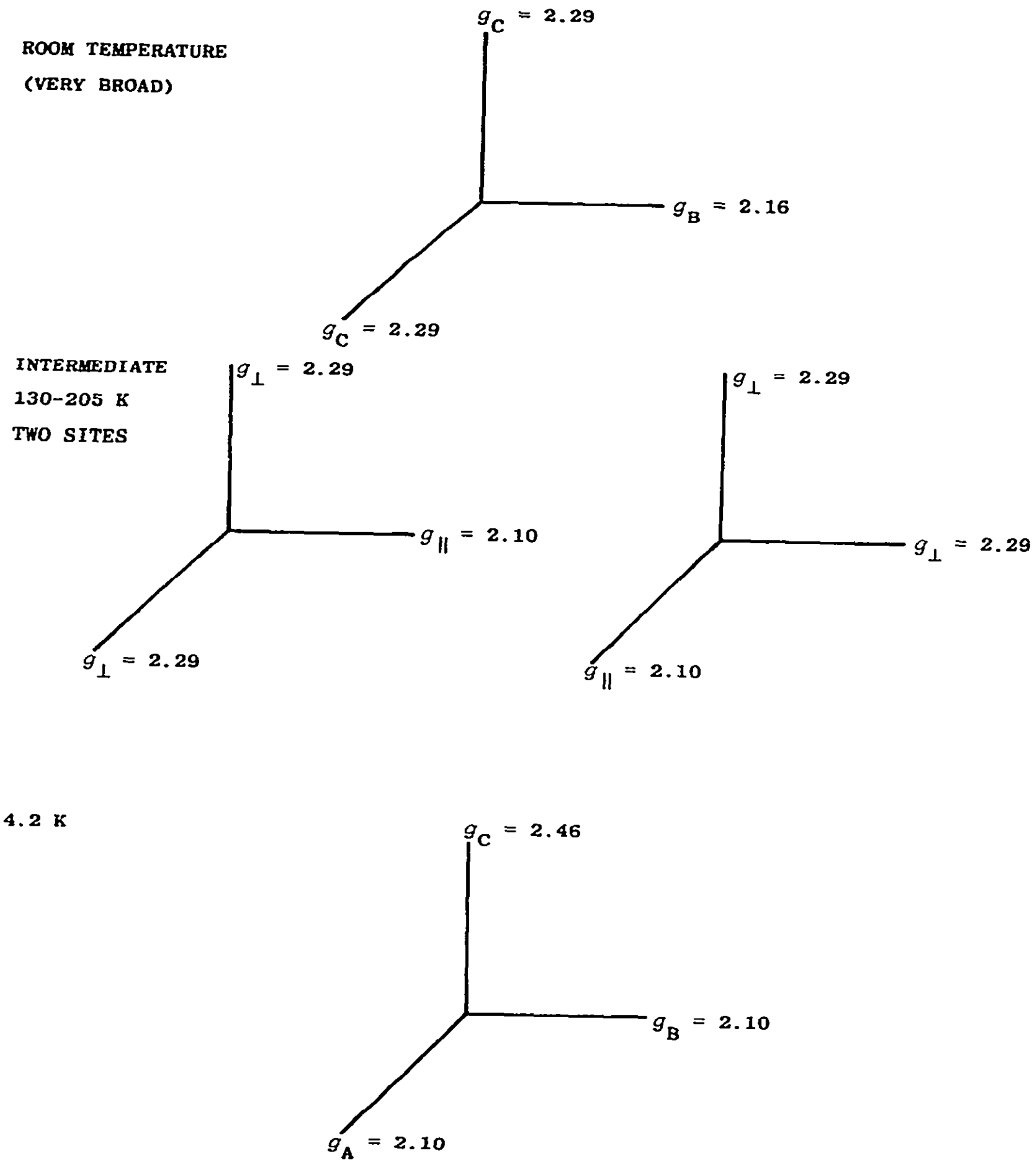
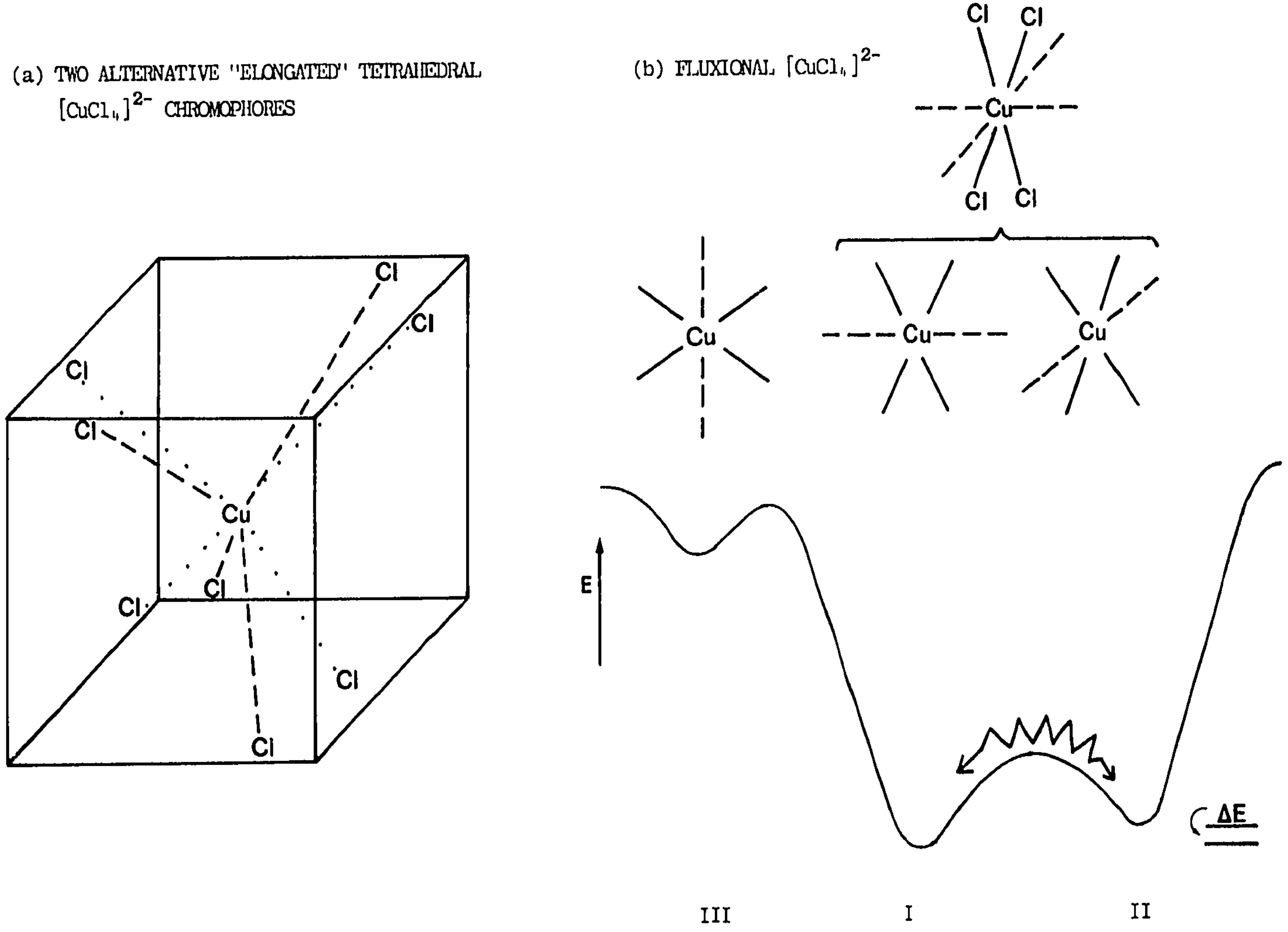


Fig. 9: The two magnetic sites of $[(C_2H_5)_4N]_2[CuCl_4]$.



(a) TWO ALTERNATIVE "ELONGATED" TETRAHEDRAL $[CuCl_4]^{2-}$ CHROMOPHORES

(b) FLUXIONAL $[CuCl_4]^{2-}$

Fig. 10: Fluxional tetrahedral $[CuCl_4]^{2-}$ anion.

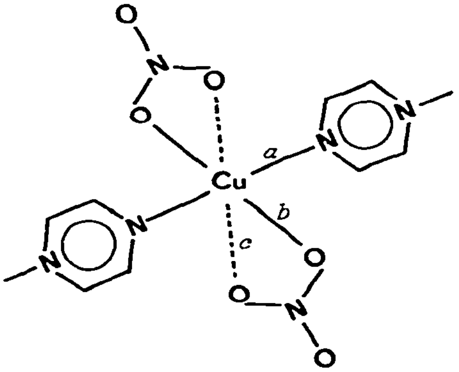
are of interest in that the solution spectra disappear with increasing concentration of the $[Fe(CN)_6]^{3-}$ anion, due to increasing magnetic interaction between the copper(II) cation and iron(III) anion [49]. The solution EPR spectrum of $[Cu(py)_4][ClO_4]_2$ [50] shows evidence for nitrogen hyperfine on g_1 and g_2 suggesting that only one species is present in solution. (*N*-acetyl-DL-valinate)copper(II) complexes with a range of nitrogen bases have EPR spectra that indicate [51] the structure is of the dimeric copper(II) ethanoate type, while the EPR spectrum with cyclohexylamine as a ligand suggests a means for distinguishing between equatorial and axial nitrogen coordination [52]. Attempts to use the measured $g_{\parallel}$ values for a series of square coplanar copper(II) complexes with various macrocyclic ligands to estimate covalency in the $\{CuN_4\}$ chromophore have demonstrated that the approach is not very reliable [53]. A number of EPR spectra of other copper(II) complexes in solution have been reported [54–56], and the EPR spectrum of a seven-coordinate copper(II) complex $[Cu(dapa)(H_2O)_2]$ [57] {dapa = 2,6-diacetylpyridinebis(semicarbazone)} has also been measured, but without any evidence that the EPR spectrum may be used to characterise the seven-coordinate geometry.

The first direct evidence for exchange in copper(II) tetraphenylporphyrin, with a Cu-Cu separation of 8.8 Å, has been reported in the observation of a low field, $\Delta M_s = 2$ transition EPR signal at 77 K [58]. Beautifully resolved EPR spectra [59,60] of the Mn^{2+}-Cu^{2+} couple (obtained by doping the dimeric $[Cu(pyNO)Cl_2].H_2O$ complex with manganese(II)) have been interpreted in terms of antiferromagnetic coupling of the Mn^{2+} spin ($\frac{5}{2}$) with the Cu^{2+} spin ($\frac{1}{2}$). By doping tetrakis(μ-benzoato-*O*,*O'*)bis(quinoline)dicopper(II) [61] with low concentrations of nickel(II), EPR spectra of the Ni^{II}-Cu^{II} pairs were obtained and interpreted with an effective spin Hamiltonian of $S = \frac{1}{2}$, yielding $g_1 = 4.51$; $g_2 = 3.44$ and $g_3 = 2.24$ (with the g_3 factor making an angle of 114° with the Ni-Cu direction). The coupling is ferromagnetic, consistent with the predominance of a $J_{x^2-y^2,z^2}$ coupling term.

The EPR spectrum of the copper(II) ion involved in a dimeric distorted trigonal bipyramidal/square pyramidal copper chromophore, bis(*N*,*N*-bis{2-(diethylamino)ethyl}-2-hydroxyethylamino-*O*)dicopper(II) diperchlorate, has been recorded, by doping the concentrated copper(II) complex (which is diamagnetic) with a small amount of zinc(II) to break open the Cu-Cu couples (3.044 A) [62]. The ^{63}Cu NQR spectra of CuF_2, $KCuF_3$ and $RbCuF_3$ have been recorded [63], along with the pulsed EPR spectra of some pseudo five-coordinate copper(II) complexes [64]. Multicentre contributions to the anisotropic hyperfine interactions have been recorded for $Cu(dithiocarbamate)_2$, including proton hyperfine couplings [65]. Ligand ENDOR spectra have been obtained for copper complexes doped in an appropriate diamagnetic host lattice, but their increasing complexity probably take them outside the field of interest of most coordination chemists [66–69].

7.3.3 Magnetism

A most interesting review of magnetism appeared in 1980 [70], which should be compulsory reading for all magnetochemists, and indeed coordination chemists. It emphasises the importance of single crystal magnetic anisotropy measurements, and the approximate nature and limitation of *k*-values, and puts into some perspective all the difficulties of calculating exchange interactions in magnetochemistry. A number of examples in copper chemistry are quoted and the difficulties of calculating the exchange interactions in the classical $[Cu_2(CH_3CO_2)_4(H_2O)_2]$ dimer is emphasised. Although this review [70] was described as a local view of magnetism, there is a place for these personal views of various aspects of coordination chemistry in the literature and this review clearly fills this requirement. The second review on Field-Dependent-Magnetic Phenomena [71] was much more specialised, and a most timely survey of this developing area of basic physics. Magnetic susceptibility measurements down to liquid helium temperature are now routine, and the emphasis has moved towards the comparison of series of complexes containing near equivalent bridging groups such as chloride ions [72–73], the oxalate anion [74], the carbonate anion [75], the $[Se_2O_5]^{2-}$ anion [76], and neutral bridging ligands such as the pyrazine molecule [77]. In general the interaction may be anti-ferromagnetic or ferromagnetic, with a predominance of the former, but more than one-directional and one-type of exchange interaction may be present [72–77]. In particular, in the seemingly simple complex $[Cu(NH_3)_2(CO_3)]$ [75], a novel cluster approach to analysing the two types of exchange interaction has been suggested. Clusters of six copper atoms give the best account, which yield intrachain coupling of $-5.2\ cm^{-1}$, and interchain coupling of $-2.6\ cm^{-1}$. In the bridging pyrazine complex [77] of $\{Cu(pz)(NO_3)_2\}_n$ (3), the susceptibility



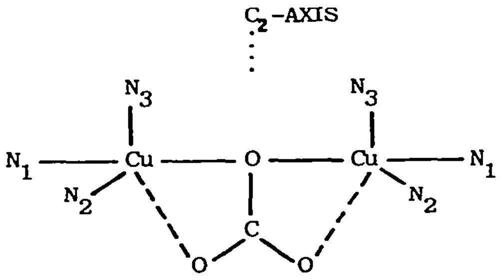
a = 1.98 Å
b = 2.01 Å
c = 2.49 Å

(3; $\{Cu(pz)(NO_3)_2\}_n$)

data was fitted to the linear chain Heisenberg expression, using the experimentally determined single-crystal *g*-factors; this use of physical data determined by one technique in another is to be encouraged. The magnetic susceptibility of a series of bis(5-X-uracil)copper(II) complexes [78], unsaturated carboxylate complexes [79], and basic copper(II) methanoates [80] have also been reported. The magnetic properties of sulphur containing ligands continues to be of interest; those for 5,5'-thiodisalicyclic acid [81], dimethylthiocarbamate [82] and diethylthiocarbamate [83] complexes have been reported.

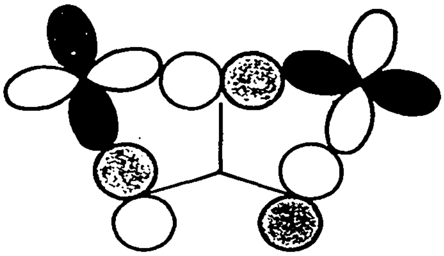
Magnetic susceptibility measurements on copper(II) oxydiethanoate hemihydrate, $[Cu\{O(CH_2CO_2)_2\}_2].0.5H_2O$, show a transition to a ferromagnetic system at 3.3 K, $J = +4.66\ cm^{-1}$, in this two-dimensional layer structure (using a two dimensional Heisenberg relationship) [84].

The magnetic properties of dimeric copper(II) systems continue to attract attention but the complete diamagnetism of μ-carbonato-bis(2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene)dicopper(II) perchlorate (4) must stand out as exceptional [85]. The two copper centres are approximately square pyramidal, with an almost linear $Cu\hat{O}Cu$ angle of 176.6° to provide an effective route for exchange coupling that must be antiferromagnetic in nature in view of the crystallographic two-fold axis through the bridging carbonate ion. With these guidelines, the orbitals of (5) are then suggested as suitable, with overlap, to provide an effective route for a strong exchange interaction.

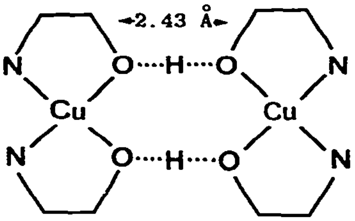


(4; $[Cu_2(2,4,4,9\text{-}Me_4\text{-}[12]\text{-}1\text{-}ene\text{-}1,5,9\text{-}N_3)_2(\mu\text{-}CO_3)][ClO_4]_2$)

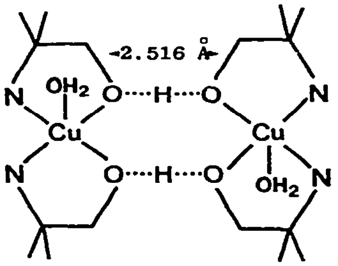
Less complete antiferromagnetic exchange coupling ($J = -56\ cm^{-1}$) occurs in the 2-aminoethanol copper(II) complex (6), which involves O...H...O bonded planar $\{CuN_2O_2\}$ monomers [86]. In the corresponding 2-amino-2-methylpropanol complexes, (7), the additional water molecules increase the $\{CuN_2O_2\}$ monomer units to square pyramidal $\{CuN_2O_3\}$, with O...H...O bridging links in the dimers to produce $J = -70\ cm^{-1}$, but there is no obvious relationship between the O...H...O distances and the exchange coupling, J. In the centrosymmetric phenoxy-bridged dimer, $[Cu_2(OPh)_2(en)_2(\mu\text{-}OPh)_2].2PhOH$ (8), the Cu...Cu distance is 3.215 Å and the magnetic properties are normal, with no evidence of exchange



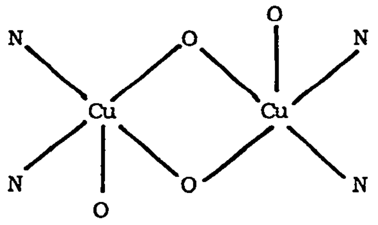
(5; Magnetic Interaction in (4))



(6; $[\{Cu(OCH_2CH_2NH_2)(HOCH_2CH_2NH_2)\}_2][NO_3]_2$)



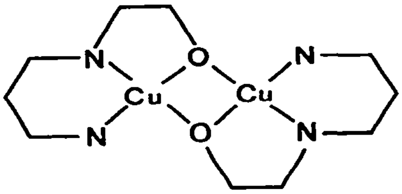
(7; $[\{Cu(OCH_2CMe_2NH_2)(HOCH_2CMe_2NH_2)\}_2][NO_3]_2$)



(8; $[Cu_2(OPh)_2(en)_2(\mu\text{-}OPh)_2].2PhOH$)

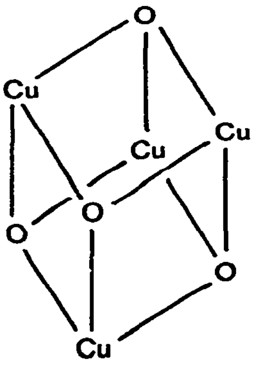
[87]. This paper also contains a useful list of references of the $Cu(\mu\text{-}O)_2Cu$ oxygen-bridged structures with the coordination numbers of the copper, their idealised geometry, the Cu-$\hat{O}$-Cu angles, the copper-copper separation, and μ_{eff} [87].

A model for exchange coupling in the roof-shaped hydroxy bridged dinuclear complexes, $[Cu_2(RNH_2)_4(\mu\text{-}OH)_2]^{2+}$, has been suggested [88], and the exchange coupling in copper(II) dimers involving purine type ligands has been reported [89]. Super exchange coupling in di-μ-bromo-bis{bromo(dimethylglyoxime)copper(II)} has been suggested [90]. The two crystallographically independent dimers of *catena*-μ-iodo-bis(μ-{2-{(3-aminopropyl)amino}ethanolato-*N*,*N*'-μ-*O*})dicopper(II) iodide dihydrate (9) show an intramolecular antiferromagnetic coupling from 93.2-303.2 K, with J = -65 cm^{-1} [91].

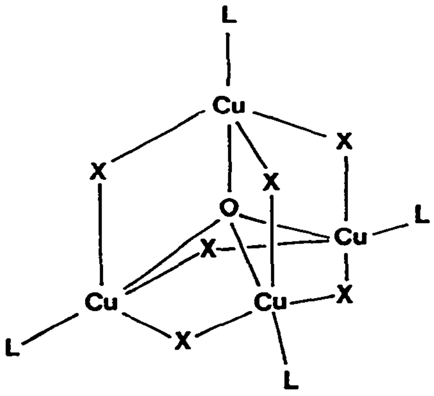


(9; $[Cu_2(C_5H_{13}N_2O)_2I]I.2H_2O$)

Increasing magnetic susceptibility data is being obtained on clusters containing four oxygen-bridged copper atoms with a cubane-type structure (10), as for $[\{CuX(OCH_2CH_2NR_2)\}_4]$ (R = Me, Pr or Bu; X = NCO or NCS) [92] and $[\{CuBr(OCH_2CH_2NEt_2)\}_4].4CCl_4$ [93] and also for the tetrameric $\{Cu_4OX_6L_4\}$ (11) (X = Br or Cl; L = Cl, Br, pyNO, dmso or $\{(CH_3)_2N\}_2CO$) complexes [94]. The cubane-type structures [95] have been analysed on the basis of the isotropic Heisenberg-Dirac-van Vleck model, and a linear relationship between the exchange interactions of *four* non-interacting intracluster "dimeric" pairs with antiferromagnetic interaction and the Cu-$\hat{O}$-Cu bridge angle established. The interaction between the "dimeric" pairs is, then, weak and ferromagnetic.

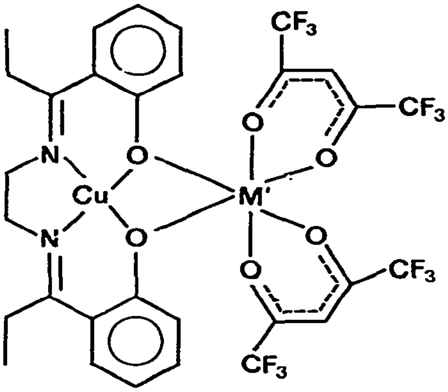


(10; Cubane{Cu$_4$*O*$_4$} unit)

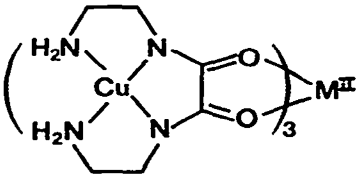


(11; {Cu$_4$OX$_6$L$_4$} unit)

The use of tetradentate Schiff bases as ligands to form binuclear complexes to study the relationship between structure and magnetic exchange continues in the complexes bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato){*N*,*N*'-ethylenebis[2-hydroxypropiophenoneiminato-*N*,*O*(2-)]copper(II)}M'(II) (M'(II) = Cu, Ni or Co) (12).



(12)



(13; M^{II}(Cu^{II}L)$_3$)

The magnetic interactions are antiferromagnetic and relatively weak, compared with halide-bridged complexes [96]. The synthesis and exchange interaction of the [M^{II}(Cu^{II}L)$_3$] type of tetranuclear complexes, (13; M^{II} = Co or Ni), with *N*,*N*'-bis(aminoalkyloxamidatocopper(II) have been reported [97], and involve strong antiferromagnetic interactions.

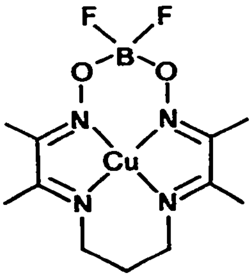
A series of trinuclear copper(II) complexes, with a suggested tetrahedral

$\{Cu_3O\}$ chromophore, of the type $[Cu_3(OH)L_3][ClO_4]_2$ [98] {L = RC(=NOH)C(=NAr)R'} have been synthesised, and their magnetic properties interpreted in terms of antiferromagnetic interaction.

In elastic neutron scattering has been used to determine the spin wave of $KCuF_3$ [99], and the crystallographic and magnetic structures of materials with three-fold orbital degeneracy such as $CaCu_3Ti_4O_{12}$ have been reported [100].

7.3.4 *Electronic Properties*

A reasonable activity has occurred in the area of copper(II) calculations, and the INDO Molecular Orbital method, as applied to all transition metal chlorides, has been reviewed [101], and includes a treatment of the $[CuCl_4]^{2-}$ anion. A more complete INDO calculation for the $[M(NO_2)_6]^{4-}$ anion has been carried out and although broadly in agreement with the experimental results, the quantitative agreement is only approximate [102]. The electronic structures of the copper halides CuF_2(linear), $CuCl_2$(linear), $[CuCl_4]^{2-}$(T_d,D_{2d} or D_{4h}) $[CuF_6]^{2-}$(D_{4h}) and $[CuCl_6]^{2-}$(D_{4h} or O_h) have been studied by INDO, MS-Xα and *ab initio*-SCF (RHF and UHF) methods [103]. Noticeable differences are observed between the different calculations and the final comment is that such calculations are "particularly difficult" for copper compounds and that correlation effects will have to be included in a systematic way. Xα calculations have also been carried out on the $Cu(C_2H_4)$ species which have been isolated by matrix isolation techniques [104]. More success has been observed in calculating the π-electron energy levels of the tetrakis(perfluorophenyl)porphyrincopper(II) complexes [105], and of the charge-transfer spectra of copper(II) imidazolate chromophores [106]. Molecular orbital levels of the difluoro-3,3'-(trimethylenedinitrilo)bis(2-butanone oximato)boratecopper(II), (14) have been



(14)

determined and the results are consistent with the slight tetrahedral distortion of the $\{CuN_4\}$ chromophore [107]. Consistent use of the angular overlap approach in reproducing the electronic energies, *g*-factors and magnetic properties of various copper(II) complexes [44,45,47] is noteworthy.

7.3.5 Spectroscopic Techniques

An extensive review of the vibrational fine structure of the electronic spectra of transition metal compounds has appeared, but the only copper data is that on [*N*-methylphenethylammonium]$_2$[CuCl$_4$] [108]. No polarised single-crystal electronic spectra of a pure copper(II) complex were reported in 1980, but the polarised single-crystal electronic spectrum of the copper(II)-doped [Zn(dien)(bipyam)][NO$_3$]$_2$ was reported [43], but (due to the misalignment in the monoclinic unit cell) only a tentative one-electron orbital sequence was prepared, namely, $d_{x^2-y^2}>d_{yz}>d_{z^2}>d_{xy}$. The infrared spectra [109] of the $Ba_2Zn_{1-x}Cu_xUO_6$ system has been used to show splitting of the Cu-O vibration as evidence for the Jahn-Teller effect in the high symmetry system. Raman scattering from layer type magnetic materials [110] of formula [RNH$_3$]$_2$[CuCl$_4$] have been measured around the magnetic ordering temperature, and resonance enhanced peaks have been observed at 180, 250 and 280 cm^{-1}. X-ray photoelectron spectroscopy has been applied to copper complexes, and the spectrum of the bis(biureto)copper(III) anion has been reported and compared with the analogous copper(II) complex [111]. The photoelectron spectra of a series of copper(I), (II) and (III) complexes with macrocyclic ligands has been used to suggest that there is about a 2 eV difference between the Cu 2p bonding energies of these three oxidation states, and that this can be used to identify their oxidation states in complexes where the oxidation state may be unknown [112]. An XPES study of [Cu(acac)$_2$] in the gaseous state has been reported [113]: the satellite structure in the copper 3s level spectra were considered to arise from a shake-up mechanism rather than from multiplet splitting. A UVPES study of gaseous copper(II) nitrate has been reported and assigned with the help of *ab initio* molecular orbital calculations; the ionisation energies of the nitrate groups are consistent with those of Ti(NO$_3$)$_4$, but with a higher negative charge [114]. The X-ray photoelectron spectra of copper complexes as models for metalloproteins have also been reported [115].

7.3.6 EXAFS studies

Two reviews have now appeared on the EXAFS spectroscopic technique (both written by physicists) which illustrate the application of this technique to the determination of the environment of transition metal ions in biological systems [116,117]. While recognising the importance of the EXAFS technique in the determination of the environment of transition metal ions in biological systems (where other means of obtaining this information are not available), it is also important from a coordination chemist's point of view that the distances obtained are confirmed by recording the EXAFS spectra of model compounds of *known* crystal structure. It is for this reason that it is rather disconcerting to find that, although the EXAFS spectrum of $CuSO_4.5H_2O$ yields a mean Cu-O distance of 1.95 Å for the four inplane Cu-O distance (compared with a distance of 1.97 Å from the X-ray crystal structure), the EXAFS spectra failed to yield any evidence for the second nearest neighbour's oxygen ligands at 2.4 Å [118]. The suggestion that these more distant oxygen atoms are involved in higher thermal motion than those at 1.95 Å suggests that the EXAFS spectra may be more fruitful if run at the temperature of liquid nitrogen. Whatever the reason, it is clearly desirable that the use of EXAFS spectra in biological systems be backed up by an appropriate choice of model compounds that reflect, as near as possible, the types of ligands thought to be present and the geometry about the copper(II) atom. A nice application of the EXAFS spectra has been to the structure of copperchloroanilato and bromoanilato complexes [119]. The bromide complex is particularly appropriate, as the EXAFS spectra at both the copper and bromine K absorption edge can be used. The spectra strongly support the planar ribbon structure (rather than the two-dimensional layer structure) for these complexes. The best reported use of EXAFS spectra in a copper biological system is in a study of the copper sites in native, cyanide- and azide- bound bovine superoxide dismutase, and a comparison of these spectra with those of $[Cu(imidH)_4(NO_3)_2]$ as a model compound [120]. The data from each form of the enzymes were different, and although containing two short Cu-N distances of *ca.* 2.00 Å, also contained Cu-N distances of *ca.* 2.2 Å, a distance that is unusual in ordinary copper(II) complexes (but see Section 7.5). In the model compound, the four Cu-N distances and one Cu-O distance were reproduced to 0.01 Å, but the second Cu-O distance was not reproduced at all. EXAFS spectra have been recorded [121] for $Cu/ZnO/Al_2O_3$ CO shift catalysts, prior to reduction; CuO is present, and after reduction Cu metal is detected with no evidence for Cu_2O being formed. The EXAFS spectra of iodine on clean copper metal surfaces have been reported [122]: on the (111) face the three-fold site (15a) is occupied, while on the (100) face the four-fold site (15b) is occupied. The EXAFS spectra of ruthenium and copper metals on silica supported catalysts have been determined, and show that RuCu clusters are present with the copper on the surface of the clusters [123]. A study has

(15a) (15b)

(15; Iodine on (a) the (111) face and (b) the (100) face of copper) been made of the chemical shifts of the K-absorption discontinuity of copper complexes in different oxidation states from 0 to III, and offers the possibility of distinguishing these different oxidation states [124].

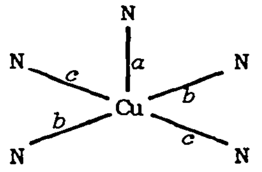
7.3.7 Crystallography

The predicted increase in emphasis on crystallography has continued. Using the breakdown of Figure 2, the five-coordinate geometry is most in evidence, with the square pyramidal geometry clearly out-weighing the trigonal pyramidal geometry. Rather surprisingly, the regular square pyramidal geometry yielded nine structures (see Table 3) characterised by near equal basal angles ($L_1\hat{Cu}L_3$ or $L_2\hat{Cu}L_4$; Table 3), which in the different structures vary from 158° to 173°, with the lower angles correlating with the shortest Cu-L_5 distance [125–133]. The crystal structure of $[NH_4][Cu(NH_3)_5][PF_6]_3$ (16) [125], represents the most regular

TABLE 3
Regular Square Pyramidal Copper(II) Structures[a]

	Chromophore	ρ	$r(Cu\text{-}L_5)/\text{Å}$	θ	ϕ	Ref.
$[NH_4][Cu(NH_3)_5][PF_6]_3$	$\mathrm{Cu}N_5$	0.27	2.193	164.0°	165.3°	[125]
$[\{Cu(dien)\}_2\{Fe(CN)_6\}].6H_2O$	$\mathrm{Cu}N_5$	0.28	2.21	163.8°	164.7°	[127]
$[Cu(acac)(hfacac)(phen)].2H_2O$	$\mathrm{Cu}N_2O_2O$	0.17	2.341	166.6°	168.9°	[128]
$[Cu(bipy)(O_2NCHCO_2)(H_2O)]$	$\mathrm{Cu}N_2O_2O$	0.18	2.227	167.4°	168.3°	[129]
$[N(2amet)pipzH_3][CuCl_5].2H_2O$	$\mathrm{Cu}Cl_5$	0.20	2.570	164.9°	165.1°	[126]
$[Cu(N,N'\text{-}Me_2enN\text{-}O)(C_2O_4)].2H_2O$	$\mathrm{Cu}N_2O_2O$	0.06	2.495	170.4°	173.0°	[130]
$[Cu(bpb)(H_2O)]$[b]	$\mathrm{Cu}N_4O$	0.19	2.286	161.1°	163.3°	[131]
$[Cu(hfacac)_2(ted)]$	$\mathrm{Cu}O_4N$	0.25	2.262	163.2°	166.9°	[132]
$[Cu(dmg)_2(imidH)]$	$\mathrm{Cu}N_5$	0.35	2.141	158.2°	159.9°	[133]

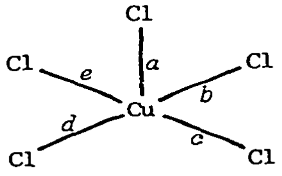
[a] Atom labelling and angles are defined in Fig. 11. [b] bpb = *N*,*N*'-bis(2-pyridinecarboxamide)-1,2-benzene.



a = 2.193 Å
b = 2.048 Å
c = 2.010 Å

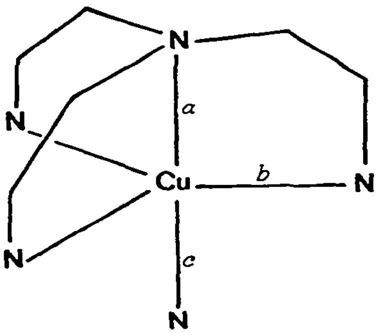
(16; $[NH_4][Cu(NH_3)_5][PF_6]_3$)

square pyramidal structure, with five σ-bonding ligands, and answers the twenty-year-old question of what structure the copper pentammines have, and also identifies the origin of the pentammine effect as ammonia is added to an aqueous solution of copper(II). Likewise, the structure of [*N*-(2-ammoniumethyl)piperaziniumH$_3$][CuCl$_5$] (17) contains the regular square pyramidal pentachlorocopper(II) anion [126], with basal angles that are not significantly different, and are almost identical to those of the pentamminecopper(II) ion. An apparently regular square pyramidal structure also occurs in (thiamine-pyrophosphate)(1,10-phenanthroline)aquacopper(II)dinitrate monohydrate [134] and in the copper(II) complex of the Schiff base of [Cu($C_{12}H_{15}N_2O_8P$)(H_2O)].H_2O [135]. By contrast, the near regular trigonal bipyramidal stereochemistry is most infrequent. The most regular is in [Cu(tren)(NH_3)][ClO_4]$_2$ (18), which again involves the σ-bonding {CuN_5} chromophore [125]. (16) and (18) then represent the two extreme geometries of the five coordinate {CuN_5} chromophore, and offer an interesting opportunity to compare the electronic properties of these two extremes.



a = 2.570 Å
b = 2.289 Å
c = 2.323 Å
d = 2.297 Å
e = 2.340 Å

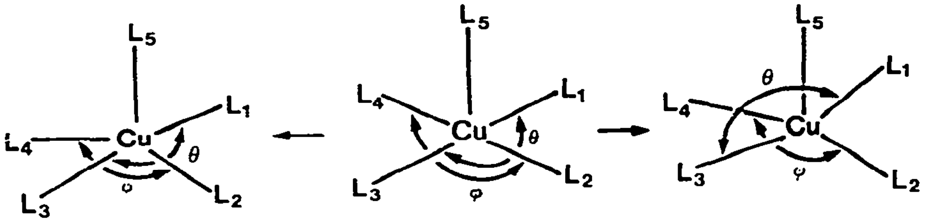
(17; [*N*(2amet)pipzH$_3$][CuCl$_5$])



a = 2.041 Å
b = 2.81 Å
c = 2.023 Å

(18; [Cu(tren)(NH_3)][ClO_4]$_2$)

In view of the structural pathways of the Fig. 2, it is of interest that only one crystal structure which involves a tetrahedral distortion of the square pyramidal stereochemistry (see Fig. 11), namely a violet glutathione copper(II)



trigonal distorted square pyramidal $\theta = 170^\circ$, $\phi = 140^\circ$

regular square pyramidal $\theta = \phi = 165 \pm 2^\circ$

tetrahedral distorted square pyramidal $\theta = 170^\circ$, $\phi = 140^\circ$

Fig. 11: Angular distortions of a square-based pyramidal CuL_5 chromophore, where $\theta = L_1\hat{Cu}L_3$ and $\phi = L_2\hat{Cu}L_4$.

complex [136] with the axial fifth ligand direction making an angle of 22° to the normal to the four equatorial ligands (due to the bridging disulphide unit within the anion), has been reported this year. Much more common (see Table 4(a)

TABLE 4

Some structural data on distorted five-coordinate copper(II) complexes.

(A) Square Pyramidal with Trigonal Distortions[a]

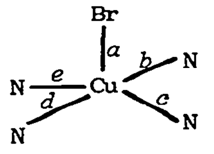
	Chromophore	$r(CuL_5)$/Å	θ	φ	Ref.
$KCuPO_4$	CuO_5	2.154	165.9°	147.6°	[137]
$[Cu(ebser)(H_2O)]$	CuN_2O_3	2.18	162.2°	152.4°	[138]
$[Cu(dpen)_2Br]Br$	CuN_4Br	2.547	164.8°	143.7°	[139]

(B) Trigonal bipyramidal with square pyramidal distortion[b]

	Chromophore	α_1	α_2	α_3	$r(Cu{-}N_4)$/Å	Ref.
$[Cu(ntbt)(ONO_2)][NO_3]$	CuN_4O	137°	104°	112.2°	2.120	[140]
$[Cu(bipy)_2I][ClO_4]$	CuN_4I	122.9°	122.8°	114.3°	2.100	[142]
$[Cu(bipy)_2Br][BF_4]$	CuN_4Br	134.5°	126.2°	99.4°	2.114	[142]

[a] Atom labelling and angles are defined in Fig. 11. [b] Atom labelling and angles are defined in Fig. 5.

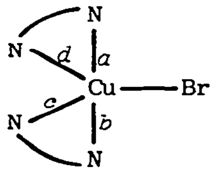
and [1; Table 5]) is a trigonal distortion of the square pyramidal structure (Fig. 2), as in $[Cu(dpen)_2Br]Br$ (19) [139], which follows the structural pathway



a = 2.547 Å
b = 2.073 Å
c = 2.111 Å
d = 2.078 Å
e = 2.073 Å

(19; [Cu(dpen)$_2$Br]Br)

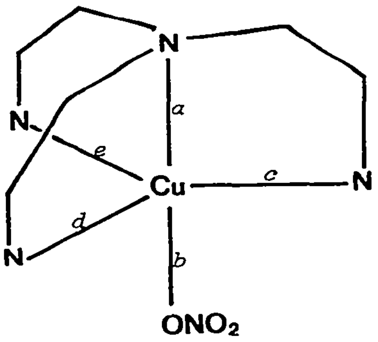
of the Berry Twist [1; Fig. 5]. In a similar manner, the trigonal bipyramidal structure with non-equivalent ligands can be reasonably regular {*cf.* [Cu(bipy)$_2$I]$^+$ [141,142], Table 4(b)}, with the angles α_1,α_2 and α_3 at *ca.* 120°, but it usually occurs with a structure distorted towards a square pyramidal structure with the Cu-N$_4$ bond representing the axial fifth ligand direction, as in [Cu(bipy)$_2$Br][BF$_4$] (20) [142]. In this complex, the Cu-N$_4$ direction is



a = 1.996 Å
b = 1.995 Å
c = 2.114 Å
d = 2.068 Å

(20; [Cu(bipy)$_2$Br][BF$_4$])

significantly longer than the remaining Cu-N distances, α_1 {see Table 4(b)} is significantly greater than 120°, and α_3 is significantly less than 120°. Even when the chelate ligand involved is a tripod type ligand, such as tris(2-benzothiazolylmethyl)amine, this square pyramidal distortion of the basic trigonal bipyramidal {CuN_4O} chromophore occurs, as in [Cu(ntbt)(ONO$_2$)][NO$_3$].½H$_2$O (21)

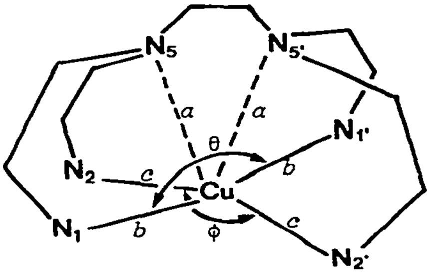


a = 2.059 Å
b = 1.938 Å
c = 2.058 Å
d = 2.120 Å
e = 2.048 Å

(21; [Cu(ntbt)(ONO$_2$)][NO$_3$].½H$_2$O)

[140]. As the chelate ligand constraints are so different in the complexes of Table 4, the directions of these distortions (Fig. 2) are best considered to originate in the modes of vibration of the nuclear framework.

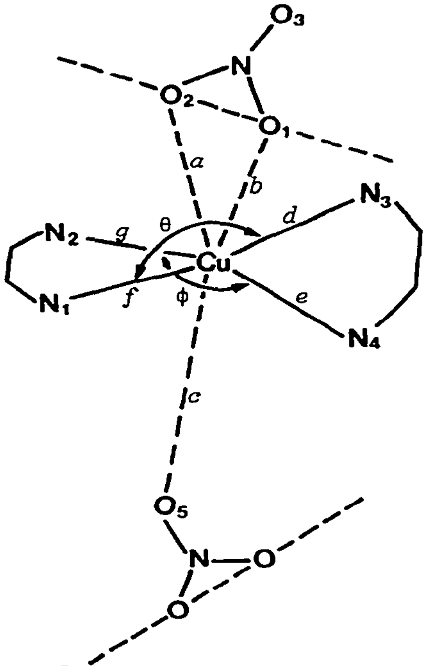
Related to the tetrahedrally distorted five coordinate square pyramidal geometry is the completely novel geometry of $[Cu(edtb)][BF_4]_2$ (22) (edtb = *N*,*N*,*N*'*N*'-tetrakis(2'-benzimidazolylmethyl)-1,2-diaminoethane) [143]. It involves a six



a = 2.5 Å
b = 1.99 Å
c = 2.03 Å
θ = 165.6°
ϕ = 142.9°

(22; $[Cu(edtb)][BF_4]_2$)

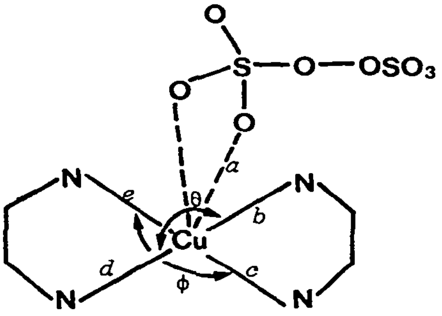
coordinate $\{CuN_6\}$ chromophore with four equatorial short bonds (*ca.* 2.00 Å) and two long bonds (*ca.* 2.5 Å), but with the latter both constrained by the ligand to lie above the equatorial plane, to yield a bicapped square pyramidal stereochemistry which, in (22), involves a crystallographic two-fold axis of symmetry. The four equatorial bond distances involve a pronounced tetrahedral distortion, with a very marked asymmetry in the bond angles of 165.6 and 142.9°: as the four equatorial bonds involve identical methyleneimidazole chelate links, there is no obvious reason why both the sense and magnitude of the equatorial distortion should be so different, unless the geometry is determined by a soft mode of vibration of the nuclear framework (Fig. 2). The structure of $[Cu(bipy)_2(ONO_2)][NO_3].H_2O$ has been redetermined to a higher accuracy [144], and while the structure (23) has not changed, its description has changed from distorted trigonal bipyramidal to distorted square pyramidal, and discussed in terms of the sense of the distortions illustrated in Fig. 11. An interesting feature of this structure is that it also has a tetrahedral distortion of the four equatorial ligands, which is closely comparable to that of (22). In addition, the presence of a long bonded $Cu–O_2$ bond of 2.832 Å in (23) suggests that the nitrate ion should be considered as an asymmetrical bidentate ligand, as the difference $\{r(Cu–O_2)-r(Cu–O_1)\}$ of 0.531 Å, is less than that of 0.7 Å previously set up as a criterion for the bidentate function of the coordinated nitrate group [145]. As the structure of (23) is then considered to be six coordinate, its stereochemistry should best be described as *distorted* bicapped



a = 2.832 Å
b = 2.301 Å
c = 3.062 Å
d = 1.896 Å
e = 2.023 Å
f = 1.973 Å
g = 2.051 Å
θ = 170.7°
ϕ = 140.7°

(23; $[Cu(bipy)_2(ONO_2)][NO_3].H_2O$)

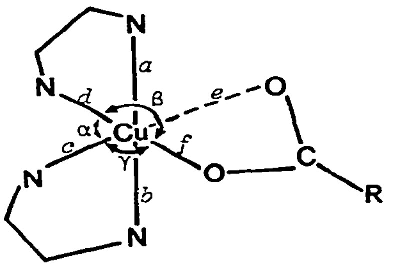
square pyramidal and is clearly related to (22). The structure of $[Cu(bipy)_2(OS_2O_7)].H_2O$ (24) [22] can also be described as distorted bicapped



a = 2.367 Å
b = 1.959 Å
c = 2.032 Å
d = 1.972 Å
e = 2.039 Å
θ = 172.6°
ϕ = 141.0°

(24; $[Cu(bipy)_2(OS_2O_7)].H_2O$)

square pyramidal (22). It is then of interest to examine the geometries of the $\{CuN_2N'_2O_2\}$ chromophores in the pair of cation distortion isomers $[Cu(bipy)_2(CH_3CO_2)]X$ (25) (X = $[ClO_4]$ or $[BF_4]$) [146] and $[Cu(bipy)_2\{py\text{-}2,6\text{-}(CO_2)_2\}].4H_2O$ (26) [147]. In all three structures there are five short bonds and a sixth long bonded carboxylate oxygen ligand, but



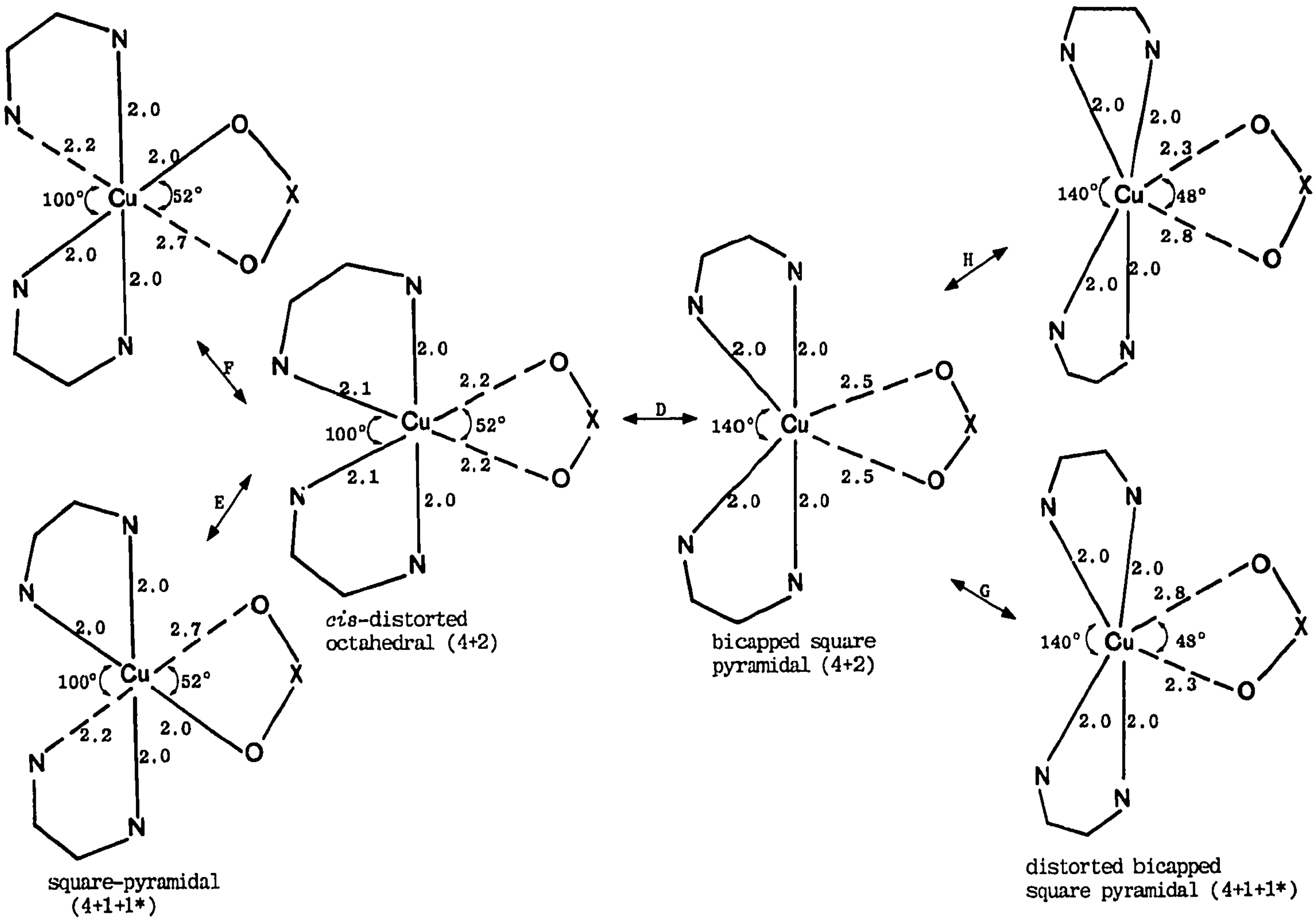
	(25)	(26)
a/Å	1.977	1.985
b/Å	1.994	1.985
c/Å	2.168	2.115
d/Å	2.056	2.062
e/Å	2.648	2.866
f/Å	2.036	2.029
α	111.6°	108.7°
β	147.7°	138.9°
γ	100.7°	112.4°

(25; $[Cu(bipy)_2(O_2CMe)][ClO_4]$)
(26; $[Cu(bipy)_2(O_2C\text{-}2\text{-}py\text{-}6\text{-}CO_2)].4H_2O$)

the geometry is best described as *cis*-distorted octahedral, with asymmetric distortion of the bidentate carboxylate group plus elongation towards square pyramidal (4+1+1*), with the Cu-N₄ bond representing the axial fifth ligand direction. The pattern of distortion of the complexes (22) to (26) are then correlated using the structural pathway of Fig. 12 and the normal modes of vibration of the parent tris(chelate)copper(II) complex represented in Fig. 13 [25]. If S_{1a} is the dominant mode then the regular *cis*-distorted and bicapped square pyramidal stereochemistry are involved, but if a linear combination of the S_{1a} and S_{2a} modes are involved, then the two distorted structures arise, namely, square pyramidal (4+1+1*) [148] or distorted bicapped square pyramidal.

The square coplanar stereochemistry continues to attract attention, for the $\{CuN_4\}$ chromophore in bis(5,5-diphenylhydantoinato)diamminecopper(II) [149] and the *trans*-$\{CuN_2Cl_2\}$ chromophore in $[Cu(diazepam)_2Cl_2]$ (diazepam = 7-chloro-1,3-dihydro-1-methyl-5-phenyl-3H-1,4-benzodiazepam-2-one) [150], in which atoms from the bulky ligands block the axial positions, have been investigated. The structures of the $\{CuN_2S_2\}$ chromophores in {*N*,*N*'-ethylenebis(monothioacetylacetiminato)}copper(II) [151,152], and the $\{CuS_4\}$ chromophore in bis(*N*,*N*-diisopropyldithiocarbamato)copper(II) [153] have also been reported. The crystal structure of the $\{CuO_4\}$ chromophore has been established in $Na_2[Cu(C_2O_4)_2].2H_2O$ [154], and in the ferromagnetic polymeric structure structure of $K_2Cu(CO_3)_2$ [155]. The strictly planar $\{CuO_4\}$ chromophore in $[\{cis\text{-}(CO)_4Re(MeCO)_2\}_2Cu]$ (27) has been maintained, but overall the molecule involves a "chaise-longue chair" structure [156]. A planar *trans*-$\{CuO_2N_2\}$ chromophore exists in the pair of distortion isomers of bis(*N*-cyclohexylsalicylideneiminato)copper(II); the brown form is monomeric, and the green form dimeric, with a long Cu-O distance of 2.6 Å to give a square pyramidal $\{CuO_2N_2O'\}$ chromophore [157].

The only monomeric copper(II) complex reported with a tetrahedral $\{CuN_4\}$



square-pyramidal
(4+1+1*)

cis-distorted
octahedral (4+2)

bicapped square
pyramidal (4+2)

distorted bicapped
square pyramidal (4+1+1*)

Fig. 12: The structural pathways for the $\{CuN_2N'_2OO'\}$ chromophore of the $[Cu(bipy)_2(OXO)]^+$ cation for distortion from regular *cis*-distorted octahedral to distorted square pyramid (route E and F) and to bicapped square pyramid (route D and routes G or H). Typical bond lengths and angles are marked.

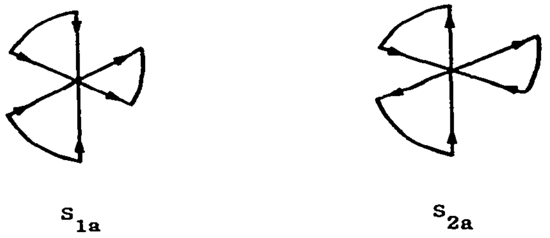
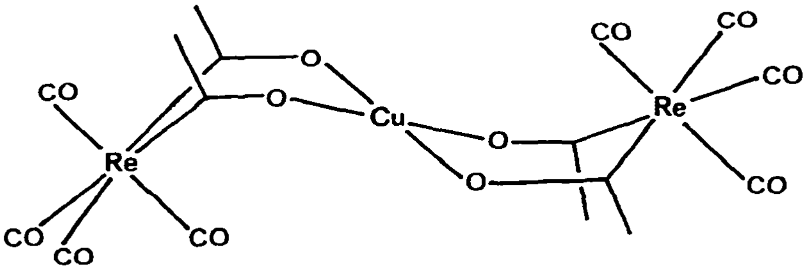


Fig. 13: Some normal modes of vibration of $[Cu(chelate)_3]^{2+}$

structure, this year, is bis(2-pyridyl-2-pyrimidylamine)copper(II) with a dihedral angle of 5.38°, and includes a very commendable attempt to correlate the $\{CuN_4\}$ structure with the electronic energies measured from the electronic reflectance spectra [158].



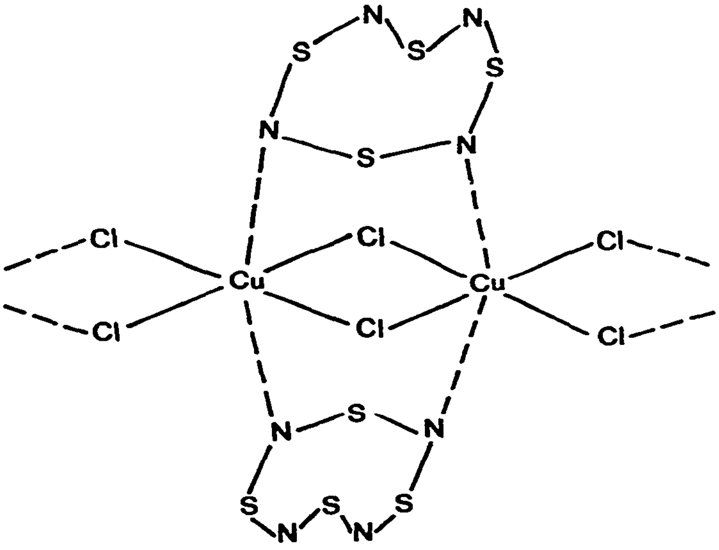
(27; $[\{cis\text{-}(CO)_4Re(MeCO)_2\}_2Cu]$)

The 1980 literature contains the crystal structures of eleven copper(II) complexes [159–168] involving an elongated rhombic octahedron (see Table 5), only one of which ($[Cu(py)_4(CF_3CO_2)_2]$) involves a tetragonality significantly greater than 0.85, suggesting a possible fluxional $\{CuL_6\}$ chromophore; in the remainder the stereochemistry is assumed to be static elongated rhombic octahedral. An almost tetragonal elongated octahedral $\{CuO_6\}$ chromophore (T = 0.78) (with a tetrahedral distortion) occurs in bis-μ-(benzoato-*O*,*O*')-μ-bis(benzoato)bis-μ-(2-dibutylaminoethanolato)bis(ethanol)tricopper(II) [169], and involves two further rhombic coplanar $\{CuNO_3\}$ chromophores. S_4N_4 forms a complex with copper(II) chloride, $CuCl_2S_4N_4$ (28) [170], involving chains of bridging $\{CuCl_4\}$ units bridged by the nitrogen atoms of the S_4N_4 units. The distorted elongated rhombic octahedral $\{CuN_2O_2O_2\}$ chromophore (29) occurs in (1,5-diazacyclooctane)dinitratocopper(II), with bidentate nitrate groups involved in off-the-*z*-axis coordination [171], and with the equatorial $\{CuN_2O_2\}$

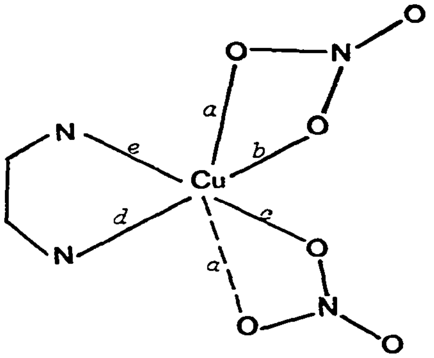
TABLE 5
Elongated Rhombic Octahedral Copper(II) Complexes.

	Chromophore	Tetragonality	Ref.
[Cu(2,2-dimethylpropane-1,3-diamine)$_2$(ClO$_4$)$_2$]	$CuN_2N_2O_2$	0.778	[159]
Bromo-(2-hydroxyethyl)ethylenediamine)CuBr	CuN_2OBrBr_2	–	[160]
Bis(3,3-thiopropanoatopropanoic acid)Cu.2H$_2$O	$CuO_2O_2O_2$	0.706	[161]
Bis(isopropylthio)ethanoatocopper(II).2H$_2$O	$CuO_2S_2O_2$	–	[162]
Cu(Hpyridoxamine)$_2$(NO$_3$)$_2$.H$_2$O	$CuN_2O_2O_2'$	0.804	[163]
Cu(pyridoxamine)$_2$.2H$_2$O	$CuN_2O_2O_2'$	0.716	[163]
CuK$_2$H$_2$(PCrO$_7$)$_2$	$CuO_2O_2O_2$	0.770	[164]
Bis(*N*-acetyl-DL-tryptophanato)Cu(py)$_2$.2H$_2$O	$CuN_2O_2O_2$	0.760	[165]
Cu(pyridine)$_4$(CF$_3$CO$_2$)$_2$	$CuN_2N_2O_2$	0.864	[166]
Cu(Cimetidine)$_2$(ClO$_4$)$_2$	$CuN_2N_2S_2$	–	[167]
Cu(Cr$_2$O$_7$).2H$_2$O	$CuO_2O_2O_2$	0.828	[168]

involved in a tetrahedral twist (as the molecule has nearly two-fold symmetry). A comparable geometry also occurs in (*N*,*N*,*N*'*N*'-tetraethyl-1,2-diaminoethane)bis(chloroethanoate)copper(II) [172] and [Cu(teen)(NO$_3$)$_2$] [173]. Off-the-*z*-axis coordination of carboxylate anions generate a seven-coordinate



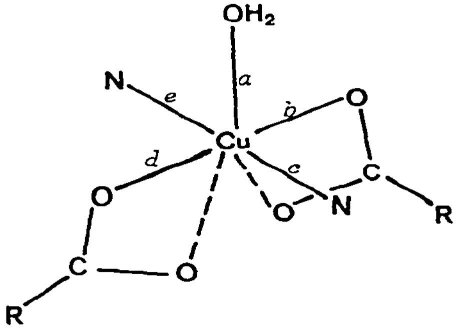
(28; $\{CuCl_2(S_4N_4)\}_n$)



a = 2.50 Å
b = 1.987 Å
c = 2.003 Å
d = 1.979 Å
e = 1.975 Å

(29; [Cu$(NO_3)_2$(1,5-diazacyclooctane)])

geometry in aquabis(3-methylpyridine)dibenzoatocopper(II) (30) [174] and bisaquabis(methylamine)dibenzoatocopper(II) [175]. $TlCu_3S_2$ has been shown to have the $CsAg_3S_2$ structure [176].

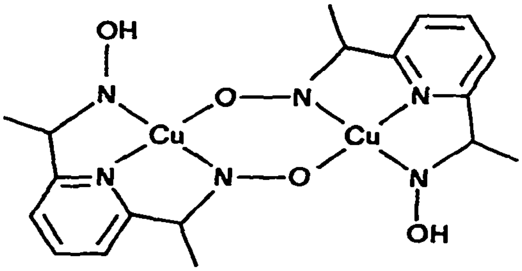


a = 2.302 Å
b = 1.964 Å
c = 2.023 Å
d = 1.924 Å
e = 1.991 Å

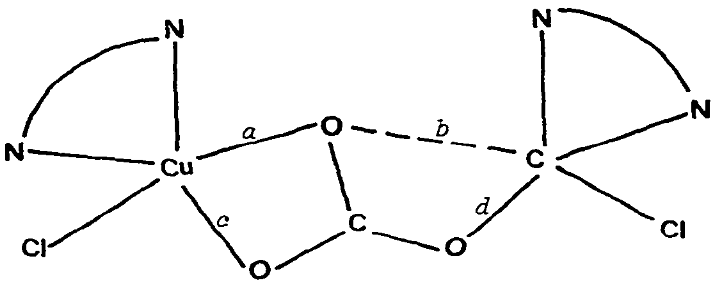
(30; [Cu(3-Mepy)$_2$$(OH_2)$$(O_2CPh)_2$])

Neutron diffraction studies have been used to establish disorder in the $[NH_4]^+$ cations of $[NH_4]_2[CuCl_4].2H_2O$ [177], and to determine the hydrogen bonding in copper dihydrogen diphthalate dihydrate [177].

Crystallographic studies on dimeric copper(II) species continue actively, the structure of [Cu(2,6-diacetylpyridinedioxime)]$_2$$[BF_4]_2.2H_2O$ (31) [178] contains a bridged dimer, involving rhombic coplanar {Cu*N*$_3$*O*} chromophores. The asymmetric bridging $[CO_3]^{2-}$ anion in $[Cu_2Cl_2(teen)_2($*asym*-μ-$CO_3)]$ (32) [179], establishes a dimeric structure involving different distorted five coordinate copper chromophores {*cf.* (4)}. Bis(*N*-isopropyl-2-methyl-1,2-diaminopropane)-μ-oxalato-oxalatodicopper(II) monohydrate [180] involves an asymmetric bridging oxalate between a rhombic coplanar {Cu*N*$_2$*O*$_2$} chromophore and a trigonally



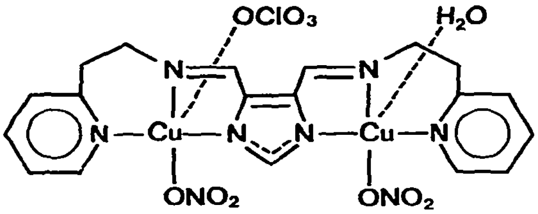
(31; $[\{Cu(2,6\text{-diacetylpyridinedioxime})\}_2][BF_4]_2.2H_2O$)



a = 2.09 Å
b = 2.40 Å
c = 1.97 Å
d = 1.94 Å

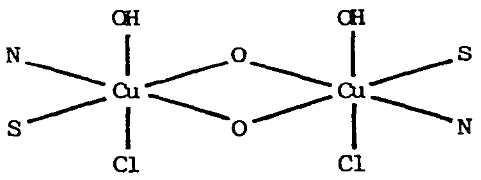
(32; $[Cu_2Cl_2(teen)_2(asym\text{-}\mu\text{-}CO_3)]$)

distorted square pyramidal $\{CuN_2N_2O\}$ chromophore with a near trigonal angle of 149.8° {*cf*. Table 4(a)}. $[Cu_2(1,1,1,7,7,7\text{-exafluoroheptane-}2,4,6\text{-trienato})_2(CH_3OH)_2]$ [181] contains a symmetrically bridging dimer with near regular square pyramidal chromophores, while $[Cu(2,6\text{-bis}\{N\text{-}[2\text{-}(4\text{-imidazolyl})ethyl]iminomethyl\}\text{-}4\text{-methylphenolate})_2(H_2O)(OH)][BF_4][SiF_6]_{\frac{1}{2}}.0.5H_2O$ [182] contains two less symmetrical square pyramidal $\{CuO_5\}$ chromophores. In bis(*N*,*N*-bis{2-(diethylamine)ethyl}-2-hydroxyethylamino-*O*)dicopper(II) diperchlorate [62], the alkoxide oxygens bridge two five coordinate $\{CuN_3O_2\}$ chromophores with trigonal distorted square pyramidal structure (basal angles of 160.6° and 138.7°). The structure of $[Cu_2(bpim)(NO_3)_2(ClO_4)(H_2O)].H_2O$ (bpim = 4,5-bis[{2-(2-pyridyl)ethylimino}methyl]-imidazolate) (33) [183] is of interest in that a bridging imidazolate ion is

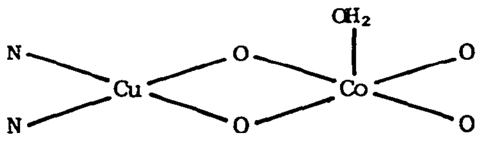


(33; $[Cu_2(bpim)(NO_3)_2(ClO_4)(OH_2)].H_2O$)

involved between two square pyramidal {Cu*N*$_3$*OO'*} chromophores. Bridging between two six-coordinate {Cu*SNO*$_2$*ClO'*} chromophores is involved in (34) [184].



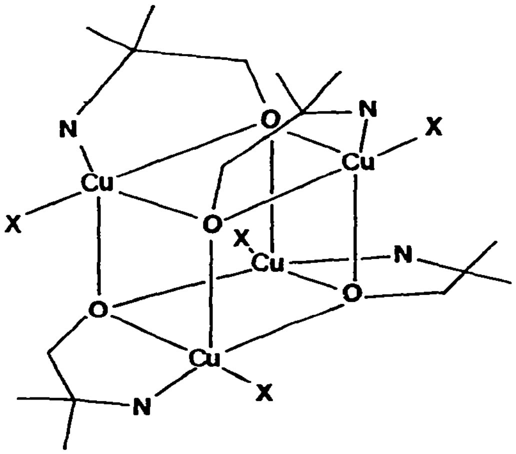
(34; [Cu$_2${*N*-(2-ethylthioethyl)-3-aminopropanol}$_2$(OH)$_2$Cl$_2$])



(35; [CuCo{(fsa)$_2$en}(OH$_2$)].6H$_2$O)

The dimeric [Cu$_2$(RCO$_2$)$_4$] unit still attracts attention, as in [Cu$_2^{II}$(NH$_3$CH$_2$CO$_2$)$_4$][Cu$_2^{I}$Cl$_6$] [185], and in the 1,4-diazabicyclo[2.2.2]octane and *N*,*N*-dimethylformamide adducts of copper(II) ethanoate [186], and these have been shown to have Cu-Cu separations of 2.633 and 2.616 Å, respectively: these data are in conflict with the reported magnetic moments of *ca*. 1.90 μ_B at room temperature. Heteronuclear complexes of copper(II) also continue to attract attention, as in [CuCo{(fsa)$_2$en}(H$_2$O)].6H$_2$O ({H$_4$(fsa)$_2$en} = *N*,*N'*-bis(2-hydroxy-3-carboxybenzylidene)-1,2-diaminoethane) (35) [187], which involves a rhombic coplanar {Cu*N*$_2$*O*$_2$} chromophore and a square pyramidal {Co*O*$_4$*O*} chromophore.

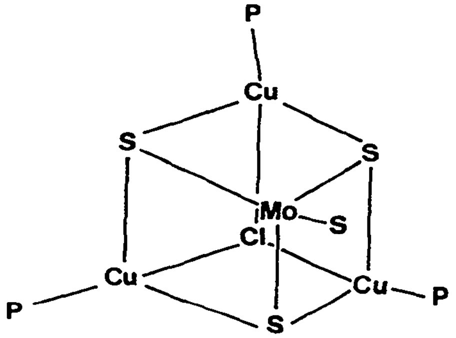
The cubane type structure (36) of (2-amino-2-methyl-1-propanolato)chloro-copper(II) and bromo-copper(II) tetramers have been reported [188], and involve



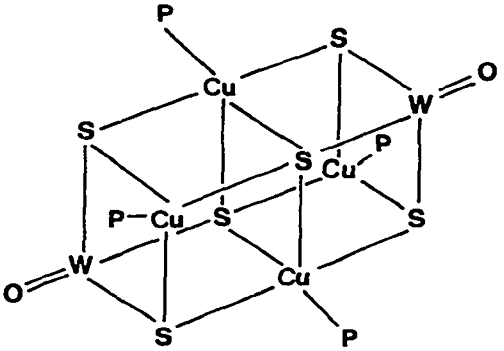
(36; [Cu$_4$X$_4$(NH$_2$CMe$_2$CH$_2$O)$_4$])

a distorted square pyramidal {Cu*O*$_3$*NX*} chromophores. This structure also occurs in [{CuCl(OC$_2$H$_4$SC$_2$H$_4$OH)}$_4$] [189], and in tetrakis{dichloroethanoato-μ-(2-

-dimethylaminoethanolato)copper(II)} [190]. The tetrameric structure of $[Cu_4(5'\text{-}IMP)_2(phen)_4(H_2O)_4][NO_3]_2$ (5-IMP = inosine monophosphate^{3-}) also involves a square pyramidal chromophore [191]. A mixed copper-molybdenum cubane-type structure occurs in (37) [192], and the structure of $[\{Cu_4W_2S_6\}(PPh_3)_4O_2]$ is related to two fused cubane-type cages (38) [193]. The structure of Cu_3SnP_{10} has



(37; $[\{Cu(PPh_3)\}_3(MoS)S_3Cl]$)

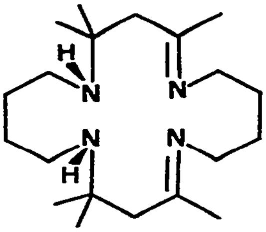


(38; $[\{Cu(PPh_3)\}_4(WO)_2S_6]$)

been described as containing a decaphosphaadamantane anion $[P_{10}]^{6-}$ and a four centre $SnCu_3$ cluster [194].

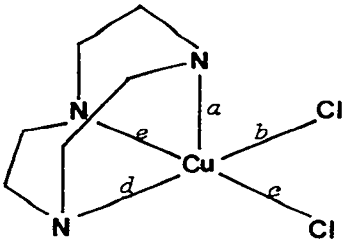
7.3.8 Macrocyclic Chemistry

Continuing effort has gone into the preparation and characterisation of macrocyclic complexes of the copper(II) ion, particularly of mononuclear complexes [195-202]. Square coplanar complexes have been structurally characterised, such as 5,10,15-triphenyl{2^2-oxobenzo[$2^3 2^4$]cyclohexa[a,b]-porphinato(2-)}copper(II) [203a] and {7-(2-pyridyl)-dibenzo[b,k][1,5,9,13]-tetrazacyclopentadeca[4,9]diene(2-)copper(II)} [203b], with the latter involving a tetrahedral twist (29°). The effects of coordinated anionic ligands have been examined on the blue-to-red conversion of the copper(II) complex of *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetrazacyclotetradecane using spectrophotometric techniques [204]. X-ray crystallography has been used to establish the Cu-Cu distance of 3.8 Å in the cofacial dicopper hexyldiporphyrin [205]. *Cis*- and *trans*-isomers of tetraazamacrocyclic copper(II) complex have been prepared [206], where the *cis* and *trans* refer to the relative positions of the two double bonds in the [18]dienN$_4$ macrocyclic ligand (39). In the two isomers the differing strain of the CuN_4 structure results in the *cis* form having a clear tetrahedral distortion (with a dihedral angle of 36.6°), while the angle is only 11.5° in the *trans* complex. As with monomeric coordination complexes, macrocyclic ligands can produce five-coordinate chromophores, whose stereochemistry can be regular



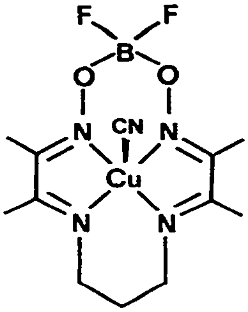
(39; *cis*-[18]dieneN$_4$)

square pyramidal as in [Cu(tbcyclen)Cl][NO$_3$], with basal angles of 148.5 and 148.3° [207]. Equally, trigonally distorted chromophores can also arise as in [Cu(O-en-N-tnH$_4$)Cl][ClO$_4$] [208], in which the {CuN_2O_2Cl} chromophore has basal angles of 171.7° and 150.8° characteristic of a trigonal distortion, and in {dibenzo[b,o][1,5,9,13,17]pentaazacyclocicosa-4,13-diene}copper(II) diperchlorate [203b] the basal angles of 164.5 and 151.5° with a {CuN_5} chromophore are also characteristic of a trigonal distortion. But even with irregular coordination by macrocyclic ligands as in dichloro(1,4,7-triazacyclononane)copper(II) (40)



a = 2.246 Å
b = 2.268 Å
c = 2.312 Å
d = 2.038 Å
e = 2.063 Å

(40; [Cu([9]aneN$_3$)Cl$_2$])



(41; [Cu(cyclops)(CN)].MeOH)

[209], almost equal basal angles are involved (167.0 and 168.2°), whereas in [Cu(spermidine)Br_2] [210], a trigonal distortion is present, with basal angles of 151.2 and 175.2°. The crystal structures of the fourth and fifth complexes in a series of five regular square pyramidal {CuN_4L} chromophores of type (41) (see Table 6) [211,212] involving the cyclic quadradentate ligand cyclops have been determined. The series is characterised by the formation of very regular square pyramidal structures (*i.e.* near equal basal angles), but with the copper(II) ion lifted out of the plane of the four nitrogen ligands by up to 0.58 Å. Moreover, the copper-axial ligand bond lengths are relatively short, when the different covalent radii of this fifth ligand are taken into account. There is a maximum difference of 0.2 Å in Cu--L_5 distance, which correlates inversely with the increase in the ρ-value, and also corresponds with a decrease in the mean basal angles from 162.5 to 146.2 (see Table 6) and an increase in the mean equatorial Cu-N distances from 1.94 to 2.042 Å (a difference of *ca.* 0.1 Å). What is equally surprising is that this series of complexes involves a considerable shift in the band maximum of the electronic spectra from 19230 cm^{-1} (in the hydrate) to 13698 cm^{-1} (in the cyanide complex), a difference of 5532 cm^{-1}. This substantial difference enabled the authors to suggest an alternative spectrochemical series for these strong axially interacting ligands, namely, $H_2O>I^->py>NCO^->CN^-$, a sequence that is more than justified by the structural data of Table 6, but which contrasts with the more usual spectrochemical series for these ligands of $I^-<H_2O<NCO^-<py<CN^-$: this suggests an almost complete reversal in the rôle of the cyanide ligand. Equally, unexpected is the very high energy 19230 cm^{-1} for the [Cu(cyclops)(H_2O)][ClO_4] complex, whose geometry is not too dissimilar to that of the pentaammine copper(II) cation

TABLE 6
Structural Data on $[Cu(cyclops)L]^+$ complexes [211, and references therein].

L	$\bar{r}$(Cu-N)/Å	*r*(Cu-L)/Å	ρ	Basal Angles	$\tilde{\nu}^a/cm^{-1}$
H_2O	1.940	2.253	0.32	160.9 ,164.1	19230
I^-	1.956	2.742	0.38	155.4 ,158.4	15748
py	1.97	2.170	0.40	156.1 ,156.4	16860
NCO^-	2.001	2.038	0.58	145.2 ,146.7	13605
CN^-	2.042	2.042	0.56	146.1 ,146.3	13698
$[Cu(NH_3)_5]^{2+}$	2.029	2.193	0.27	164.0 ,165.6	15300,11000(sh)

[a] Bands in electronic spectrum.

$[NH_4][Cu(NH_3)_5][PF_6]_3$ (16) [125], and yet which has a band maximum at 15300 cm^{-1}, with a shoulder at 11000 cm^{-1}. In the copper ammine complexes [212], only the square coplanar $[Cu(NH_3)_4]^{2+}$ structure has a band maximum at 19000 cm^{-1}, and consequently, the value of 19230 cm^{-1} for [Cu(cyclops)(H_2O)][ClO_4] is most unexpected and appears to reduce to nonsense any possibility of a "spectroscopic criterion of stereochemistry", even in this series of closely related structures of known stereochemistry [213].

Elongated rhombic octahedral chromophores can be observed in the $\{CuS_3N_2Br\}$ chromophore involved in the complex of 1,11-diamino-3,6,9-trithiaundecane with $CuBr_2$ [214], whereas a $\{CuN_4O_2\}$ chromophore exists in [Cu(2,3,2-tet)]$[ClO_4]_2$ [215]. Equilibrium and kinetic measurements have been applied to macrocyclic copper(II) complexes. Edward's equation has been applied to the formation of adducts of copper(II) macrocyclic tetraamine complexes with anions [216]. Proton transfer and nucleophilic displacement reactions of the triply deprotonated tetraglycine complex of copper(III) have been reported [217], and the stability and kinetics [218] of tetradeprotonated {cyclo-(β-alanylglycyl-β-alanylglycyl)}-copper(II) have been measured. The photoinduced oxidation of axial and macrocyclic ligands in a copper(II) complex have been reported [219]. The preparation of asymmetric imidazole-bridging dicopper macrocyclic complexes {*e.g.* (33)} have been reported [220] and the enhanced stability of the imidazolate bridged dicopper(II) ion described; these complexes involve a binucleating macrocyclic ligand [221]. The preparation of imidazolate-bridged binuclear copper(II) complexes with tripodal ligands involving sulphur donor atoms have also been reported [222]. In a study of its redox behaviour, a dinuclear copper(II) cryptate is reported to behave as a two electron receptor site [223]. It has also been suggested that in dinuclear copper(II) cryptates [224], when there is elasticity between the two mononuclear chromophores, the magnetic exchange may vary with the elasticity and may consequently be temperature variable. A binuclear copper(II) complex with a macrocyclic ligand has been shown to undergo reduction to a binuclear copper(I) complex, and that binuclear copper(I) complex is found to activate the dioxygen molecule [225].

7.3.9 Preparative Chemistry

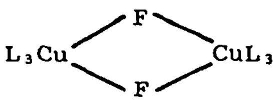
The 1980 literature contains a significant number of papers on the preparation of series of mononuclear copper(II) complexes, many straightforward (see Table 7) [226-241], but some involving novel preparative techniques. It is unusual to see an extensive series of fluoride complexes [242], as this anion tends to be ignored in a series of halide complexes, and yet this anion has yielded evidence for a postulated dimeric bridged fluoride complex (42) [243]. The reaction of copper(II) oxalate with 2,2'-bipyridine is very sensitive to the

TABLE 7

Preparation and characterisation of some monomeric copper(II) complexes

Complex or ligand	Characterisation	Ref.
isothiocyanato{1,1,1-tris(diphenylphosphinomethyl)ethane}copper(II)	*N*-bonded NCS	[226]
Hydrazine complexes	Redox reactions	[227]
Halo-xanthate complexes	Oxidation and addition reactions	[228]
β-imino amines-4-amino-4-methylpentane-2-one	Preparative	[229, 230]
Dibenzyl-aspartate and glutamate	Ester exchange reactions	[231]
Imidazole and dipeptides	Spectrophotometric	[232]
Copper(II)-hypophosphites	X-ray; IR	[233]
2-amino or 2,6-diaminopyridine	EPR	[234]
o-hydroxycrotonophenones	Preparative	[235]
N-benzyl or *N*-methyl-1,2-diaminopropane	Optical activity	[236]
Squarate complexes	Magnetic susceptibility; and EPR	[237]
2-dimethylaminopyridine *N*-oxide	IR; EPR; electronic spectra	[238]
2-hydroxy-3'-bromo-4-methoxy-5'-methylchalkone oxime	Thermalanalysis; spectrophotometry	[239]
N-methyl-2-picolinamine *N*-oxide	IR, EPR; electronic spectra	[240]
N,*N*'-dimethyl-2-picolinamine *N*-oxide	Preparative	[240]
Substituted-aminoguanidine	Magnetic susceptibility	[241]

conditions of preparation, but yields anhydrous and hydrated 1:1 complexes, which readily undergo polymorphic changes [244]. Three modifications of dichloro{2-(hydroxymethyl)pyridine *N*-oxide}copper(II) have been prepared and characterised by the temperature dependence of their magnetic susceptibility [245]; the yellow and deep green modifications suggest a dimer-type antiferromagnetism, while the greenish-yellow modification shows antiferromagnetic behaviour. A number of highly conducting Cu(chelate)(TCNQ)$_2$ complexes have been prepared [246]. The preparation of a copper(II) complex CuL$_2$Cl$_2$ with the



(42; $[Cu_2(dmpzlH)_6(\mu\text{-}F)_2][BF_4]_2$)

photochromic 2-(2',4'-dinitrobenzyl)pyridine ligand, L, has been reported [247], and its photochemical reaction in dioxan examined. The importance of ligand exchange chromatography in the ternary complexes copper(II)-*N*-substituted L-proline-D/L-α aminoacids have been examined [248].

TABLE 8
Preparation and characterisation of some dimeric copper(II) complexes

Complex or ligand	Characterisation	Ref.
[(Chelate)Cu(μ-OH) Cu(chelate)]	Air bubbled into a suspension of Cu° + chelate (bipy, phen, *etc.*)	[249]
biphenyltriazine	EPR; μ_{eff}; electronic spectra	[250]
μ-Oxalato, μ-Oxamido or μ-Oxamato	μ_{eff}; electronic spectra	[251]
Amido bridged	μ_{eff}; EPR	[252]
N,*N*-bis(2-diethylaminoethyl)-2-hydroxy ethylamine	EPR evidence of a d_{z^2} ground state	[253]
Bis(β-diketonato)Cu-diazole	Electronic spectra	[254]
$[Cu_2(cyclops)_2L][ClO_4]$	Magnetism; EPR, possibly a binuclear complex with single atom bridge	[255]
Succinate complexes	$[Cu_2(RCO_2)_4]$-type dimers; μ_{eff}	[256]

Table 8 reports the preparation and characterisation of some dimeric copper(II) complexes [249-256].

7.3.10 Kinetic and Redox Data

Metal ammine formation with copper(II) ions continue to be studied [257,258] and the effect of hydroxo complexes in the copper(II) methylamine system has been examined [259]. Complex formation in the copper(II) *meso*-tartate system [260] has been determined in both acid and neutral solution. Stability constants in non-aqueous solution [261] have been reported for the $CuCl_x$ system in dimethylformamide, and for the chloride ion with $[Cu_2(CH_3CO_2)_4]$ species in anhydrous ethanoic acid [262]. The metal-metal exchange reaction between bis(iminodiethanoato-*N*,*O*,*O'*)nickelate(II) and copper(II) suggest [263] the involvement of more than one dinuclear intermediate. The kinetics of ligand substitution have been observed [264] for bis(*N*-*tert*-butylsalicylaldiminato)-copper(II) in various alcoholic media using stopped-flow spectrophotometry. Ligand exchange reactions between copper(II) and nickel(II) chelates of different sulphur and selenium containing ligands [265] have been reported. Ligand substitution by cyanate, chloride and bromide ions at five-coordinate copper(II) centres have been followed spectrophotometrically in the UV region in aqueous [266] and dmso solution [267]. Nucleophilic substitution of bis(3-bromo-2,4-pentanedionato)copper(II) has shown that the bromide is replaced by succinimide, phthalimide, phenol or benzenethiol [268]. The electron transfer reaction between various copper(II) complexes and two electron donors such as ascorbic acid and 3,5-di-*t*-butylcatechol have been examined [269]. Mononuclear copper(II) complexes with distorted tetrahedral or trigonal bipyramidal chromophores (and some binuclear complexes) were readily reduced by the two electron donors, but not mononuclear planar copper(II) complexes. With one electron donors such as *N*,*N*,*N*',*N*'-tetramethyl-1,4-phenylenediamine or $[Cu^I(bipy)_2]^+$, no reduction occurs with mononuclear planar chromophores, but reduction does occur with dinuclear planar complexes [270]. Oxidations by the persulphate anion catalysed by the copper(II) ion have been reported [271,272]. The mutual influence of ligands, and redox reactions, have been discussed for $[Cu(pip)X_2]$ ($X = Cl^-$, Br^-, NO_3^- or ClO_4^-) in benzene solution [273]. The photooxidation of 2-hydroxyacids by copper(II) species in aqueous solution has been described [274], and the flash photolysis of copper(II) oxalate in aqueous solution suggests that a $CuCO_2$ species is responsible for the transient absorption band at 385 nm [275]. Polarographic studies of the oxidised glutathionecopper(II) system in basic solution show that the reaction 2GSH + 2Cu(II) = GSSG + 2CuI readily occurs [276]. A pulsed radiolysis study has shown that there is a very small kinetic salt effect on the reaction of $Cu(H_2edta)$ with the hydrated electron [277]. While it has already been shown that the $[Cu(NH_3)_n]^{2+}$ cation catalyses the oxidation of thiosulphate ions by molecular oxygen, it has now been shown that the 1:1 copper(II):bipy species is ten times faster than the copper(II):PVP system {PVP = poly(4-vinylpyridine)} [278]. The unusually slow redox properties of Cu^{II} cobalamines questions their use as models in biological systems [279]. The photoinduced electron transfer between $Ce^{3+}(aq)$ and $Cu^{2+}(aq)$ in sulphate solution has been examined by micro-flash excitation techniques [280]. The thermodynamic properties of copper(II) tertiary ligand systems have been examined [281-283]. The kinetics of solvent extraction of copper 8-hydroxy-quinoline complexes has been reported [284]. Standard thermodynamic data has been reported for the copper-sulphur bond [285] and for two macrocyclic complexes of the copper(II) ion using 1,5,9,13-tetraazacyclohexadecane [286] and 1,4,8,11-tetraazacyclotetradecane [287]. The heat capacity [288] measurements of bis(adiponitrile)copper(I) nitrate are a timely reminder that not all nitrate ions are ordered in the solid state. The use of EPR spectroscopy to establish the formation of transient $[Cu(CN)_4]^{2-}$ ions by anodic oxidation [289] is of interest, while the suggestion that a lipophilic copper complex $[LCu^{2-}S^-X^-]$ acts as an anion transport carrier [290] emphasises that electrochemistry can play a part in copper coordination chemistry. Likewise the visible region photochemistry of copper(II) complexes [291] adsorbed on optically transparent electrodes [292] emphasises that electrodes can play a part over and above those as the all important ion selective electrodes for the determination of copper.

7.3.11 Ion Exchanged Copper Systems

Despite all the new physical techniques available over the last ten years [293], little improvement in our understanding of the *coordination* chemistry of copper species on surfaces has occurred. The adsorption of the $[Cu(OH)_4]^{2-}$ anion on aluminas has been studied [294] by EPR spectroscopy, and suggests that only a small fraction was chemisorbed on the surface. The electronic properties of the $[Cu(en)_2]^{2+}$ ion on clay surfaces [295] have been examined and shown to be a function of the negative charge density of the minerals. The copper(II) ion on silica gel forms yellow surface compounds after heating at 900 °C in a dioxygen atmosphere [296]. On copper(II) exchanged Y-type Zeolite [297], a programmed desorption at 603 K was due to physically adsorbed oxygen, while that at 773 K was considered due to the desorption of lattice oxygen, induced by the adsorption of gaseous dioxygen. The mechanism of ion exchange in zirconium phosphates has been reported to involve the dehydration of the hydrated copper(II) ion [298]. The coordination of copper(II) ion by chelating cation exchange resins, involving 8-quinolinol groups in spheron oxime 1000, has been observed [299]. In the reduction of a copper(II) exchanged zeolite, the activity of the catalyst is considerably increased if ammonia is used as the reducing agent [300]. The structure of $CuCl_2$ and $CuBr_2$ complexes solubilised in cationic reversed micelles has been examined by the use of electronic and EPR spectroscopy [301].

7.4 BIOLOGICAL COPPER

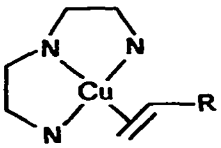
The appearance of a 30 page review [3] on this subject produces a very timely coverage of this area, but the overall impression gained suggested that there was little increase in the available knowledge of the coordination chemistry of copper in biological systems. It is to be hoped that the application of the EXAFS technique, by coordination chemists, to these systems will help to change this situation in the not too distant future. Probably the most publicity that copper gained in the current year was due to the suggestion that ascorbic acid in conjunction with copper(II) ions may be selectively toxic to malignant melanoma cells [302], and it has been tentatively reported to halt tumour growth in mice. Hopefully, copper may have yet another part to play in chemotherapy in the future. A study of the binding site of the thiocyanate anion on copper(II) in superoxide dismutase [303] has been reported using a wide range of physical techniques. Four different copper(II) species have been identified from the interaction of the copper(II) ion with the carnosine complex [304], primarily using EPR techniques. Chemical and spectroscopic studies have been reported on the binuclear copper-active sites of *neurospora tyrosinase* [305], using EPR and electronic spectroscopic techniques and optical dichroism. The interactions of copper(II) with L-histidine and glycylglycyl-L-histidine have been examined as a model for albumin [306].

7.5 COPPER(I) CHEMISTRY

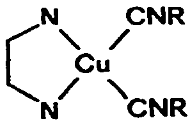
The use of lithium dialkylcuprates for the regio- and stereo-selective γ-substitution of allylic sulphoxides, and sulphones has been reported [307]. The use of copper(I) complexes (*e.g.* $[Cu(bipy)_2]Cl$) in the catalysed reduction of O_2 to water and the oxidation of alcohols, has been suggested as a model for the copper(I)-containing oxidase [308]. Copper(I) phosphine complexes containing Cu-N bonds are of use in reacting with alkyl halides to form *N*-substituted compounds [309]. A series of copper(I) complexes of 2-amino-5-methyl-1,3,4-thiadiazole and 2,5-dimethyl-1,3,4-thiadiazole have been prepared [310]. Complexes of copper(I) and (pyrazolyl)borate ligands of formulation $(CuL)_n$ {L = H_2BPz_2, Ph_2BPz_2, $HB(Me_2Pz)_3$ or BPz_4} have been reported [311]. The preparation of a water stable reversible CO_2 carrier involving a copper(I)-bicarbonato complex has been reported [312]:

$$Me_3COCu(PEt_3)_3 \underset{-CO_2}{\overset{+CO_2}{\rightleftharpoons}} Me_3COCO_2Cu(PEt_3)_3$$

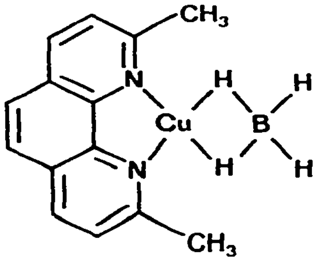
The crystal structure of bis(6,6'-dimethyl-2,2'-bipyridine)copper(I) tetrafluoroborate has been determined [313]; the $\{CuN_4\}$ chromophore has a tetrahedral structure, but with a significant distortion from a regular structure (the dihedral angle is 80.9°). A distorted tetrahedral structure also occurs in (diethylenetriamine)(hex-1-ene)copper(I) tetraphenylborate (43) [314], in



(43; $[Cu(dien)(hex\text{-}1\text{-}ene)][BPh_4]$)

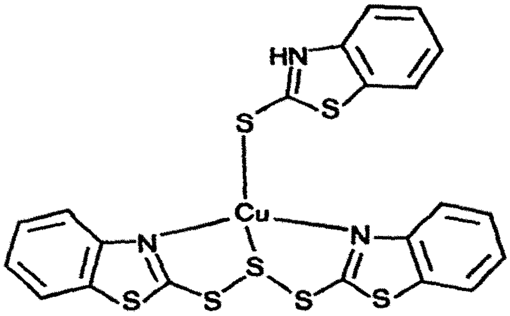


(44; $[Cu(tmen)(CNC_6H_{11})_2][BPh_4]$)

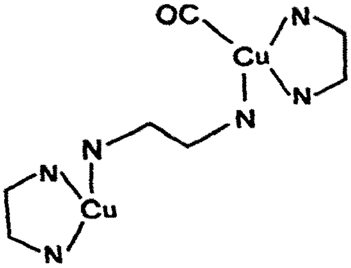


(45; $[Cu(2,9\text{-}Me_2phen)(BH_4)]$)

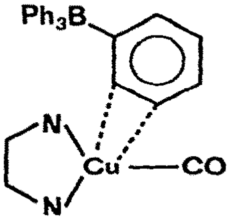
(*N*,*N*,*N*',*N*'-tetramethyl-1,2-diaminoethane)bis(cyclohexyl isocyanide)copper(I) **(44)** [314] and in (2,9-dimethyl-1,10-phenanthroline)(tetrahydroborato)copper(I) tetraphenylborate **(45)** [315]. The reaction of mercaptobenzothiazole in chloroform solution with solid $[Cu(H_2O)_6][ClO_4]_2$ yields $[Cu^I(C_7H_5NS_2)(C_{14}H_8N_2S_5)][ClO_4].2CHCl_3$ **(46)**, which involves an unusual sulphur insertion to form an -S-S-S-linkage [316]. A series of 2,4-dithiobiuret (dtbiH) complexes, [Cu(dtbiH)X]dmf (X = Cl, Br or I), $[Cu(dtbiH)_2A]$ (A = ClO_4, NO_3 or Cl) and $[Cu_2(Hdtbi)_3][SO_4]$ have been prepared [317], and the crystal structure of [Cu(dtbiH)Cl]dmf determined; the $\{CuClS_2.S'\}$ chromophore has a trigonal pyramidal structure. Addition compounds of Cu(I)/en/CO have been obtained and the crystal structure of $[Cu_2(en)_3(CO)_2][BPh_4]$ has been determined **(47)** [318]. It involves a centrosymmetric bridging dimer with a pseudotetrahedral $\{CuN_3C\}$ chromophore, while that of $[Cu(en)(CO)(BPh_4)]$ **(48)** [318] has a trigonal planar $\{CuN_2C\}$ chromophore, with two additional rather long Cu-C contacts at 2.919 Å. The structure of {(phenylazo)acetaldoximato-*N*,*N*'}{(phenylazo)acetaldoxime-*N*,*N*'}copper(I) **(49)** contains a hydrogen-bonded O...H...O (2.325 Å) dimeric structure involving local tetrahedral $\{CuN_4\}$ chromophores, with a dihedral angle of 94.4° [319]. The full structure of $[Cu_2(histamine)_3(CO)_2][BPh_4]_2$ [320]



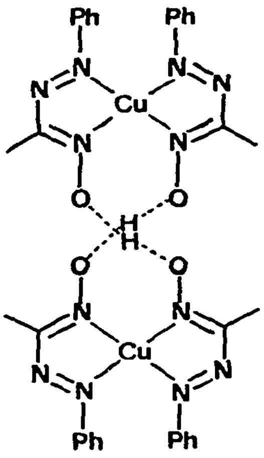
(46; $[Cu(C_7H_5NS_2)(C_{14}H_8N_2S_5)][ClO_4].2CHCl_3$)



(47; $[Cu_2(en)_3(CO)_2]^+$)

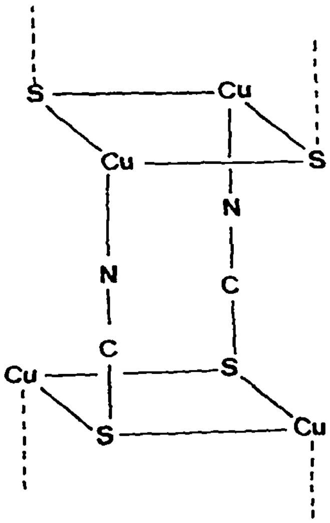


(48; $[Cu(en)(CO)(BPh_4)]$)

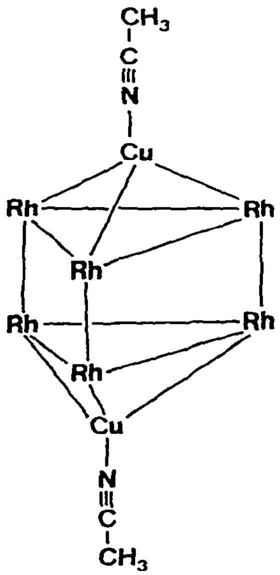


(49)

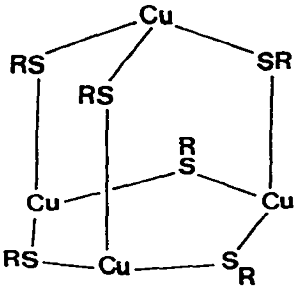
{*cf.* [1; (32)]} has been reported. The structure of the tris(thiocyanato)dicuperate(I) anion (50) involves a three-dimensional network of Cu(I) ions linked by bridging [NCS] groups, with pyridinium ions occupying cavities in the network [321]; each copper(I) ion involves a tetrahedral $\{CuS_3N\}$ chromophore. A novel



(50; [pyH][$Cu_2(SCN)_3$]-partial structure)



(51; $Cu_2Rh_6(CO)_{15}(NCMe)_2$; the carbonyl groups have been omitted for clarity) cluster compound, (51), involving copper(I) bonded to three rhodium atoms and an ethanenitrile ligand has been reported [322], while the tetrameric $[Cu_4(SC_6H_5)_6]^{2-}$ anion (52) involves a distorted trigonal planar $\{CuS_3\}$ chromophore

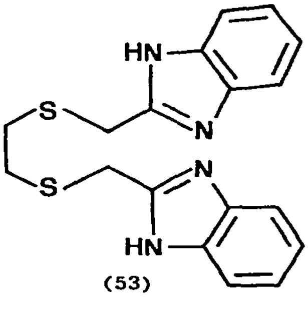


(52; $[PPh_4]_2[Cu_4(SPh)_6]$)

[323]: the Cu(I) atoms are arranged in a tetrahedron within an octahedron of sulphur atoms.

A pulsed radiolysis study has been carried out on the mechanism of the redox properties of copper(I) with 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene in aqueous solution; planar and tetrahedral $\{CuN_4\}$ chromophores are involved [324]. The photoluminescence from bis(2,9-dimethyl-1,10-phenanthroline)copper(I) has been observed at room temperature in CH_2Cl_2 [325]. In the thermionic emission sources, mass spectrographic evidence for $[Cu(NH_3)_3]^+$, $[Cu(NH_3)_4]^+$ and $[Cu(NH_3)_5]^+$ cations have been obtained, with the tetraamine cation predominant [326]. Infrared evidence has been obtained for the formation of copper(I)-ethene complexes in Y-type zeolites [327].

The equilibrium between Cu^{2+}, Cu^0 and Cu^+ has been examined by passing a solution of Cu^{2+} through a column of finely divided copper metal [328]. The ligand 1,6-bis(2'-benzimidazolyl)-2,5-dithiahexane (53) has been used to prepare a number of copper(I) and copper(II) complexes [329]. The infrared and

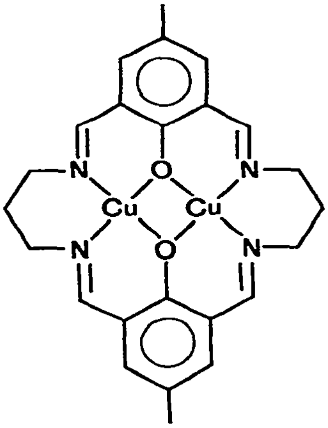


(53)

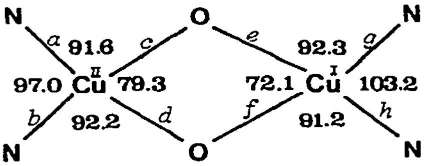
$N(CH_2CH_2SR)_3$

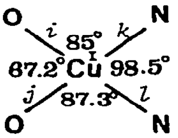
(54; R = Me, Et, Pr, $CHMe_2$ or CMe_3)

electronic spectra of a series of copper(I) and copper(II) complexes of 4,6-dimethylpyrimidine-2(1H)-one have been reported [330]. The tripod type ligands tris(2-alkylthioethyl)amine (54), have been used to prepare a series of potentially trigonal bipyramidal copper(I) and copper(II) complexes; the EPR and electronic spectra of the latter are consistent with this formulation [331]. The high temperature reaction of Cu, $K_2[CO_3]$ and sulphur yields the mixed-valence KCu_4S_3 [332], which crystallises with a unique double layered structure in which *all* the copper atoms involve {CuS_4} tetrahedra irrespective of the oxidation state of the copper. KCu_4S_3 shows a Robin and Day Class II behaviour, with an electrical conductivity characteristic of a metal; this is also consistent with its magnetic properties and its metallic reflectivity. The structures of $[Cu^I(pma)][BPh_4]$ or $[Cu^{II}(pma)(SO_4)]$ {pma = 2-pyridylmethylbis-(2-ethylthio)ethylamine} involve a trigonal pyramidal {CuN_2S_2} or square pyramidal {CuN_2S_2O} chromophore, respectively [333]. The condensation of 1,3-diaminopropane with 2-hydroxy-5-methylisophthalaldehyde in the presence of $[Cu(OH_2)_6][ClO_4]_2$ yields a binuclear copper(II) complex, which upon electrochemical reduction, yields a mixed Cu(I), Cu(II) complex (55), whose structure has been determined [334]. In



(55; $[Cu_2C_{24}H_{26}N_4O_6]Cl.\frac{1}{2}MeOH$)





	Cu(II)	Cu(I)
B-site	a = 1.974 Å	e = 2.118 Å
	b = 1.979 Å	f = 2.127 Å
	c = 1.967 Å	g = 1.950 Å
	d = 1.951 Å	h = 1.974 Å
A-site		i = 2.278 Å
		j = 2.240 Å
		k = 2.059 Å
		l = 1.999 Å

the mixed oxidation state complex, the copper(II) ion involves a rhombic coplanar $\{CuN_2O_2\}$ chromophore, but the copper(I) site is disordered, 65% being in the B site and 35% in the A site (55). In the B site the Cu is displaced 0.15 Å above the $\{N_2O_2\}$ plane towards an aromatic carbon atom (3.04 Å) while the Cu in the A site is displaced 0.65 Å towards the *same* aromatic carbon (2.55 Å): this A site is best described as square pyramidal copper(I). The crystal structure yielded no evidence for thermal electron transfer in the solid state, but does not rule out photoassisted electron transfer. If so, an interesting structural feature of (55) is the significantly different Cu–O distances, 2.00 Å to copper(II) but 2.12–2.28 Å to copper(I): such long copper-oxygen distances are comparable to the Cu–O distances (2.17 Å) from the EXAFS spectra, of native bovine superoxide dismutase, and raises the question of the precise oxidation state of the copper involved in the native enzyme [120].

The synthesis magnetism, spectroscopic properties and crystal structure of a novel Cu(I), Cu(II) cluster, $[Cu^{I}_{10}Cu^{II}_{2}(C_4H_5N_2S)_{12}(MeCN)_4]$ ($C_4H_5N_2S$ = 1-methyl-2-mercaptoimidazole) has been reported (Fig. 14) [335]. The centrosymmetric cluster involves four tetrahedral $\{Cu(I)S_4\}$ chromophores, four tetrahedral $\{Cu(I)NS_3\}$ chromophores, two linearly bonded $\{Cu(I)N_2\}$ chromophores and two square pyramidal $\{Cu(II)N_2S_2S'\}$ chromophores, with the basal angles of the latter showing a clear trigonal distortion at 150.9 and 175.4°. The electronic properties of the copper(II) site ($g_{\perp} = 2.04$ ($A_{\perp} = 0?$), $g_{\parallel} = 2.24$, $A_{\parallel} = 62G$), and the electronic spectra in MeCN (Fig. 15) which shows a very intense peak at 15748 cm^{-1} ($\varepsilon = 3800\ \ell\ mol^{-1}\ cm^{-1}$) are comparable to the known properties of the 'type 1' blue proteins, which exhibit low A values and an intense band at 15748 cm^{-1}, and only "fails" as a model compound in that the copper(II) environment is square pyramidal, rather than tetrahedral. Nevertheless, Fig. 14 must take first prize as the closest model of the 'blue proteins' of the 1980 season.

The crystal structure of the mixed Cu(I), Cu(II) complex pentathallium(I) μ_8-chloro-dodecakis(α-mercaptoisobutyrato)octacuprate(I)hexacuprate(II) hydrate has been reported [336]. The Cl atom is at the centre of a cube of eigh Cu(I) atoms with the six Cu(II) atoms above the six faces. The Cu^{I} atoms involve a trigonal $\{CuS_3\}$ chromophore and the Cu(II) atoms involve a tetrahedral $\{CuO_2N_2\}$ chromophore. The brown-black crystals have a band at 20619 cm^{-1}, which is interpreted as a S→Cu(I) charge-transfer band. The crystal structure of $Cu^{I}_{8}Cu^{II}_{6}\{SC\text{-}(CH_3)_2CH_2NH_2\}_{12}Cl.3.5SO_4]$ [337] is comparable, and involves a $\{ClCu_8Cu_6\}$ core; the Cu(I) atoms are trigonal planar $\{CuS_3\}$ chromophores and the Cu(II) are planar $\{CuN_2S_2\}$ chromophores. The complex has been shown to be weakly ferromagnetic ($J = 4.9\text{–}5.2\ cm^{-1}$), the coupling being transmitted *via* a –S–Cu(I)–S– pathway. The intense purple colour of this complex was ascribed to a S→Cu(II) charge-transfer band [337].

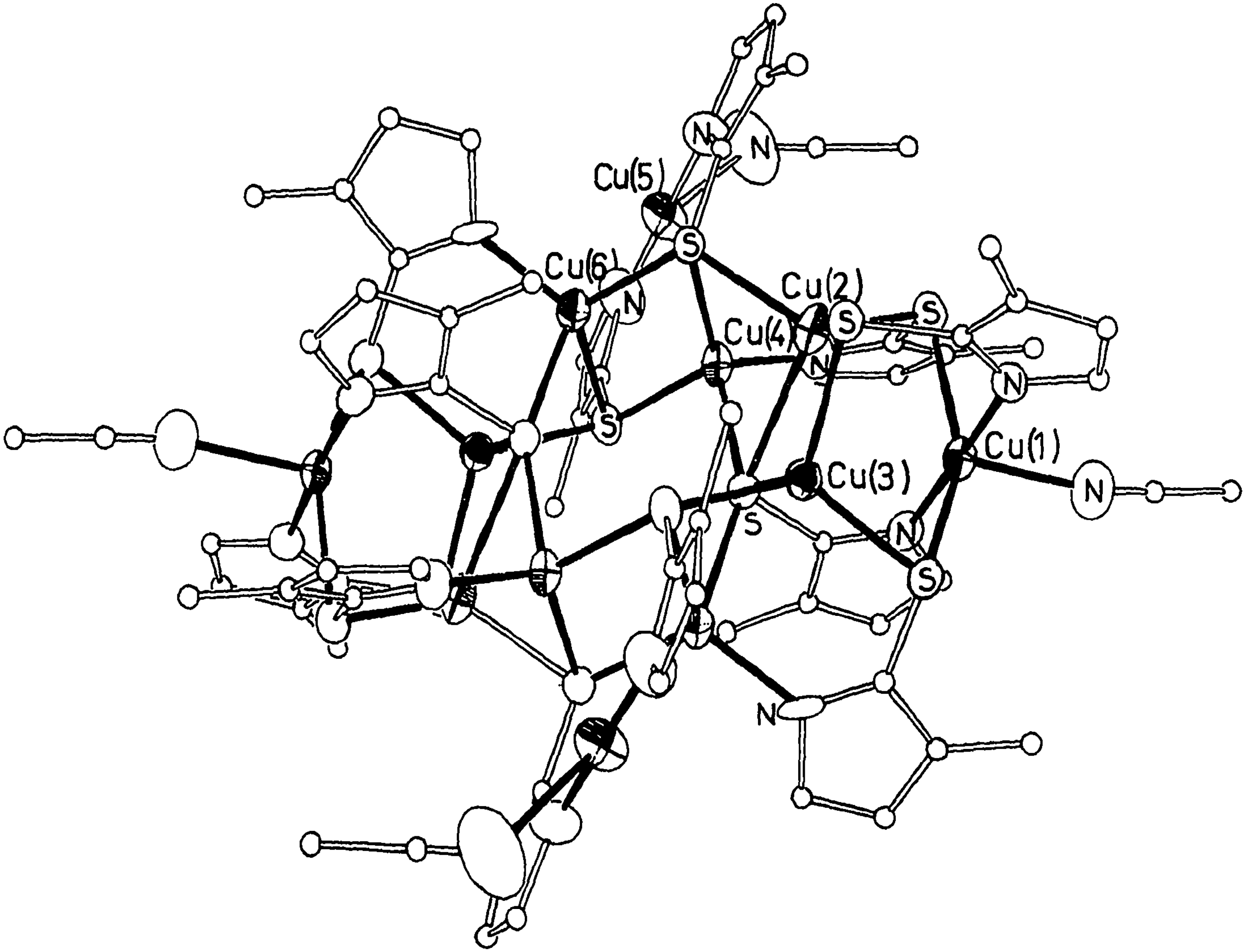


Fig. 14: Crystal Structure of $[Cu_{12}(C_4H_5N_2S)_{12}(MeCN)_4][BPh_4]4MeCN$ (reproduced with permission of the authors).

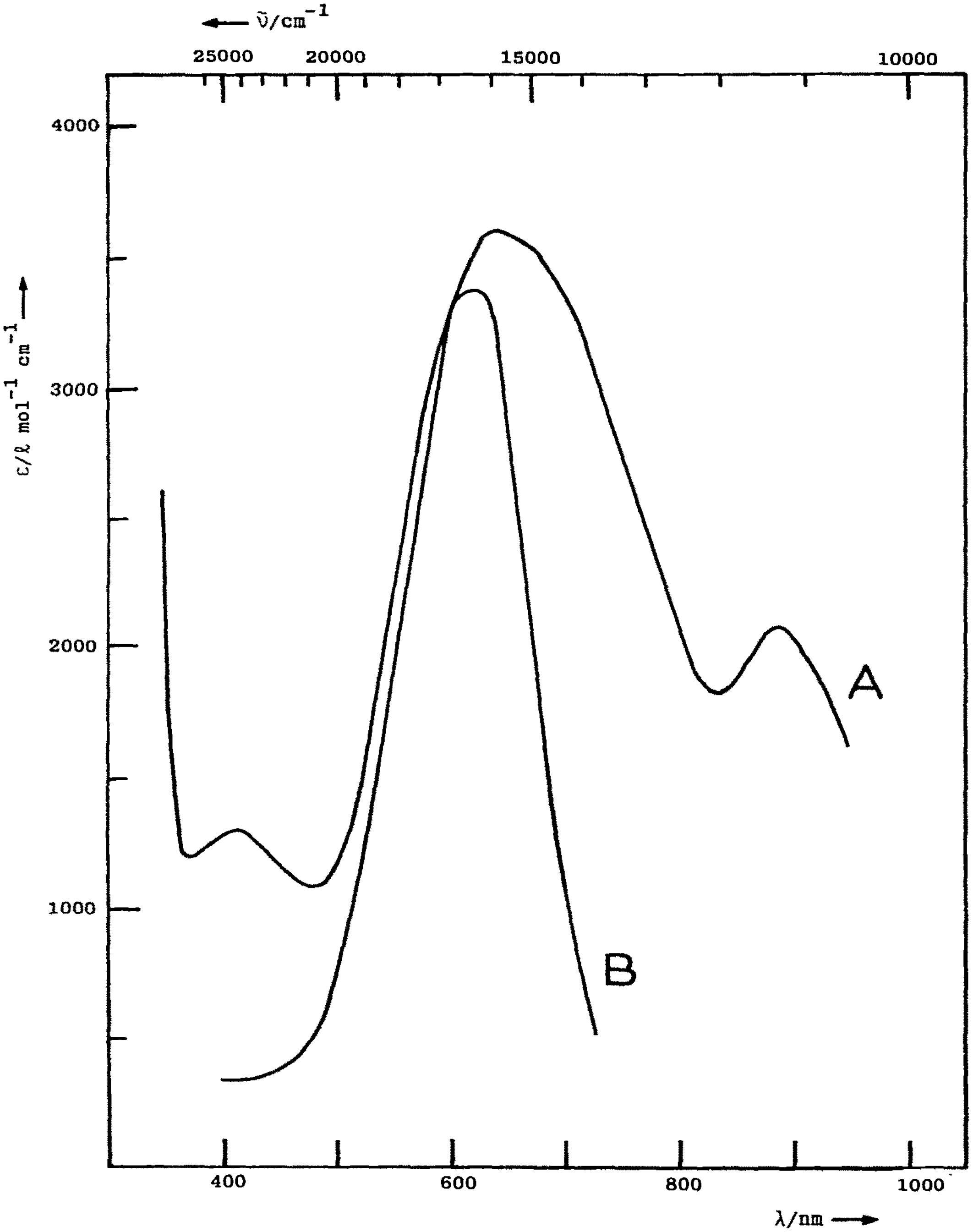


Fig. 15: The electronic spectra of (A) $[Cu_{12}(C_4H_5N_2S)_{12}(MeCN)_4][BPh_4]4MeCN$ in MeCN and (B) Pseudomonas Azuriu (reproduced with permission of the authors).

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