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CONTENTS

6.1 1970—1979: Review articles 211
6.2 Copper(III) chemistry 214
6.3 Copper(II) chemistry 215
  6.3.1 The Jahn—Teller effect 215
  6.3.2 EPR spectroscopy 228
  6.3.3 Magnetism 231
  6.3.4 Copper(II) calculations 233
  6.3.5 Crystallography 235
  6.3.6 Macrocyclic chemistry 238
6.4 Copper(I) chemistry 241
6.5 Biological copper 243
6.6 The next decade: 1980—1989 245
References 246

6.1 1970—1979: REVIEW ARTICLES

A useful indication of the research interest in a particular area is the number of reviews appearing devoted solely to that area. In the period 1970—1979, fifteen significant reviews on copper chemistry have appeared [1—15] and a further seven contain significant sections on copper chemistry [16—22]. Interestingly, two reviews of copper(II) chemistry [15,22] have appeared in 1979. At the beginning of the decade, the reviews emphasized the preparative aspects of the coordination chemistry of copper(II) in particular, but increasingly the emphasis has changed to the relationship between the electronic properties [1—4] and stereochemistry, and the ability to use the various theoretical models [3] to calculate the electronic energies of a copper(II) ion in a given environment. Equally important has been the application of the consequences of the Jahn—Teller Theorem [23] to the understanding of the electronic properties of the copper(II) ion in certain situations, of the dynamic Jahn—Teller effect in high symmetry crystal systems [15—22], and of the pseudo-dynamic or fluxional effects [24] in low symmetry systems of the Plasticity effect [9] in accounting for the variable stereochemistry of the copper(II) ion in its complexes with the formation of distortion isomers (including cation and anion distortion isomers) [25] and of the cooperative Jahn—Teller effect [22] in both concentrated copper(II) complexes and when these are diluted in a diamagnetic host lattice.

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As the decade has developed, there has been an increasing move away from the preparation and properties of copper(II) complexes involving simple mono- and bidentate ligands to the area of macrocyclic ligands [26], where increasing geometrical constraints yield a wide range of distorted geometries.

The use of macrocyclic ligands to prepare dimeric [26] and trimeric copper(II) species has led to an increasing interest in the magnetism of these systems, primarily antiferromagnetic systems [27] but also ferromagnetic, especially as magnetic measurements down to near helium temperatures are now available. The increasing move away from simple ligands to binary and tertiary ligand systems is also noteworthy, if only in emphasising the complexity of these systems, especially in solution. While X-ray crystallography can characterise the species that crystallise from solution, the structure of the species present in solution is much less clear: although computer simulation of the solution equilibria [28] are helping, there has been an increase in the direct determination of species in solution by X-ray scattering experiments [29] that holds promise for the future.

A major impact of the decade has been the increasing availability of routine X-ray crystallographic facilities which has produced a plethora of papers describing the structures of isolated complexes of the copper(II) ion. Increasingly, the crystal structures of series of closely related copper(II) complexes have been determined [25] which, although crystallographically appearing to represent "potboiling" at its worst, yields the *most* information if the electronic properties can then be studied in detail and correlations obtained for a series of related structures. Noticeable in the decade has been the use of low temperature X-ray crystallography in characterising the low temperature structures of systems subject to the dynamic Jahn—Teller effect (including the $K_2Pb[Cu(NO_2)_6]$ [30] and $[Cu(en)_3][SO_4]$ [31] systems), and equally of pseudo-dynamic or fluxional systems (such as the $[NH_4]_2[Cu(OH_2)_6][SO_4]_2$ complex [32]). The recent availability of programmes for the computer-indexing of X-ray powder photographs [33] heralds the possibility of structure determination of copper(II) complexes for which single crystals are unobtainable and while the data [34] is much more limited and less accurate than single-crystal data, any data is much more attractive than no data, and this approach should be encouraged.

Of the various spectroscopic techniques relevant to copper(II) complexes, the infrared spectrum is still the most frequently reported [35], especially in the finger-print region, but yields little information that is not better determined from X-ray crystallographic studies. It yields tentative information on the mode of coordination or semi-coordination of a number of inorganic polyanions such as $[NO_3]^-$ and $[ClO_4]^-$ [36], but the best infrared data are only available from complexes of known crystal structure using single-crystal techniques [37,38] and normal coordinate analysis [39]. The electronic reflectance spectra of copper(II) complexes is probably the most easily determined electronic property to measure, but equally the most difficult from which to extract useful structural information [1,2], due to the flexible stereochemistry of the copper(II) ion (plasticity effect) [9]. The decade opened with a spate of polarised single crystal electronic spectra of selected copper(II) complexes [1,2]: this reduced to a dribble by the end of the decade [40,41] in view of the uncertainties associated with the assignment of these type of spectra, especially in low symmetry environments [42]. Nevertheless, the bulk of the assignments of the one-electron-orbital sequences [3] are "probably correct" and formed the basis of a review of the "Ligand Field Splittings in Copper(II) Compounds" in 1972, which was updated in 1979 [43].

Without any doubt, the most prolific spectroscopic technique of the decade for copper(II) complexes [1,2,4,17] is that of EPR, as this is now fairly easily measured both at room temperature and down to liquid helium temperatures, in solution, as a polycrystalline [1] sample and as single crystals [2]. In addition, the spectra may be measured on concentrated copper(II) complexes [1,2], which only yield crystal *g*-factors and for a copper(II) complex diluted in a diamagnetic host lattice, such as the corresponding zinc(II) complex, which yields the additional copper hyperfine and ligand super hyperfine data [17,44], where relevant. Probably the most important contribution that EPR spectra have made in the present decade is in the area of variable temperature EPR spectroscopy [15,22] associated with the dynamic and pseudo-dynamic [24] (fluxional) Jahn—Teller effect, and the incentive that these results have provided for the move into low temperature X-ray crystallography [30—32]. Only slightly less important has been the use of the EPR spectra to follow the consequences of the cooperative Jahn—Teller effect [22] in copper(II) doped systems with increasing concentrations of copper(II), such as $Ba_2Zn_{1-x}Cu_xWO_6$, and although the EPR spectra are complicated by the effect of exchange coupling with increasing copper concentration, this may in part be overcome by the complimentary use of electronic reflectance spectra (as these spectra are not complicated by this effect). In these copper(II) doped systems, the equating of the local CuL_x chromophore stereochemistry with the local ZnL_x chromophore stereochemistry is most *unlikely* [44], as it is more probable that the CuL_x chromophore stereochemistry of the pure copper(II) complex will occur: although the consequences of the cooperative Jahn—Teller effect may result in a compromise, in general this is nearer to that of the pure CuL_x stereochemistry. During the decade, EPR spectroscopy has played a significant rôle in identifying the existence or otherwise of the compressed tetragonal or rhombic octahedral stereochemistry for the copper(II) ion in its six coordinate complexes [1,2,15]. If the CuL_6 chromophore has an elongated rhombic octahedral stereochemistry, it is characterised by a set of *g*-factors $g_3 >> g_2 > g_1 > 2.0$ where $g_3 > g_2 > g_1$; if a compressed rhombic octahedral stereochemistry is involved, the *g*'s have $g_3 \approx g_2 >> g_1 \approx 2.0$. In all of the complexes of copper(II) known to have a compressed rhombic octahedral stereochemistry, $K_2Pb[Cu(NO_2)_6]$ [30] and $[Cu(en)_3][SO_4]$ [31] (at low temperature), Rb_2Pb-

$[Cu(NO_2)_6]$ [45], $Cs_2Pb[Cu(NO_2)_6]$ [46], $K_2[CuF_4]$ [47], $Ba_2[CuF_6]$ [48] and $[Cu(diethylenetriamine)_2][NO_3]_2$ [49] all have a set of g-factors $g_3 \approx g_2 >> g_1 > 2.0$, consistent with a compressed rhombic octahedral stereochemistry, but with the lowest g-factor significantly above 2.0. These pseudo compressed [30] sets of g-factors are now considered to arise from the presence of two elongated rhombic octahedral chromophores, with their elongation axes misaligned by 90°, but thermally coupled [15,22]. For this reason, the observed stereochemistry of the CuL_6 chromophore is best described as pseudo compressed octahedral [30], and is not considered to be a genuine static octahedral stereochemistry of the copper(II) ion, although this may exist [15,22] in certain copper(II) doped systems (such as $Ba_2[Zn_{1-x}Cu_xF_6]$). Increasing use has been made of the EPR technique to probe the stereochemistry of the copper(II) ion on porous silica gel [50] and on ion exchange zeolites [51].

However, the most important contribution to copper chemistry must be the rôle that biological copper [6,8,12,13] has played in stimulating research in the inorganic chemistry of copper; not only in the chemistry of the copper proteins, for which copper(I), copper(II) and copper(III) species are relevant, but also in systems where more than one type of copper is considered present [8] (type I, II and III), some characterised by a unique electronic spectra, the blue proteins, but equally by characteristic EPR spectra in some sites and by the absence of an EPR signal in other sites. The structural chemistry of the copper proteins culminated in 1978 in the elucidation of the structures of plastocyanin [52] and azurin [53] (to a resolution of 2.7 Å), which showed that both contained a tetrahedral copper stereochemistry involving two nitrogen atoms from two separate histidine groups and two sulphur atoms from a cysteine thiol and a methionine thioether; results that are consistent with the resonance Raman [54] and EXAFS [55] spectra. However, the importance of the biological copper story, great as this is in its own right, lies also in the impetus that it has given to the synthesis of potential model compounds in an attempt to simulate the unique electronic properties of the copper blue proteins and which, although never completely successful, came intriguingly close by the last year of the decade [56,57] (see later).

6.2 COPPER(III) CHEMISTRY

In view of its potential involvement in the redox properties of biological copper, surprisingly little has been published on the chemistry of copper(III). The glycylglycylalanine copper(III) system [58] has been characterised in solution by electrolytic oxidation, but is so unstable that a half-life of ca. 3 min has been estimated. Even more short-lived species have been recognised in the copper(III) peptide complexes [59], which react rapidly with base prior to redox decomposition.

6.3 COPPER(II) CHEMISTRY

Approximately 90% of the 1979 literature on copper is devoted to copper(II) chemistry.

6.3.1 The Jahn—Teller effect

The renewed interest in the Jahn—Teller effect [23] in the current year arises from the publication of two review articles [15,22] and one lengthy paper [60], and stems not so much from the original Jahn—Teller theorem which was published over 50 years ago, but from the fact that during the last 20 years "the theory has been brought into a form [60] appropriate for direct use in interpreting experimental data". In this respect, the first three pages of ref. 60 are the most readable summary to date. Previously, the effect had been described in terms of the potential energy diagram referred to as the warped "Mexican Hat" which can either be illustrated in three dimensions {see Fig. 1 of ref. 60}, or in two dimensions [61] {see Fig. 1}.

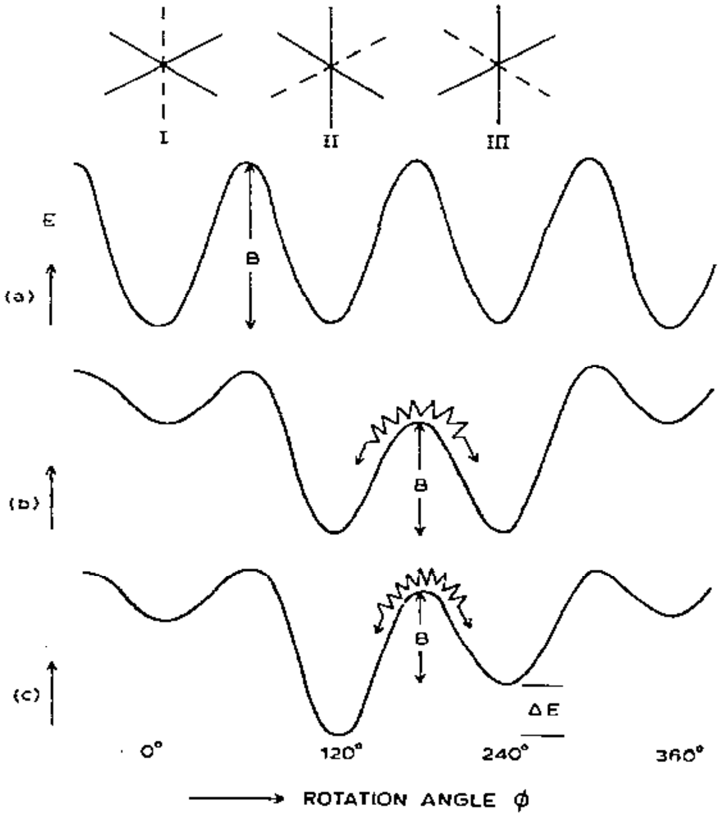

Fig. 1. The circular cross-section of the warped potential energy surface for (a) three Wells of equal energy, (b) two Wells of equal energy and (c) one low energy Well.

In Fig. 1, the three potential energy minima (Wells I, II and III) correspond to three elongated tetragonal octahedral chromophores with their elongation axes (— — —) misaligned by 90° with respect to each other. In this form [60], the diagram is most informative to chemists, as it can now be readily extended from three equal potential energy Wells {Fig. 1(a)} to two equal low energy Wells {(II and III) in Fig. 1(b)} and to one low energy Well {(II) in Fig. 1(c)}. If all three Wells are of equal energy {Fig. 1(a)} and if {condition a(i)} $B <$ thermal energy ($kT \simeq 200$ cm^{-1}), then all three Wells will be equally occupied and the complex will exhibit apparent octahedral symmetry due to a dynamic distortion between the three elongated tetragonal distortions of the nuclear framework, and the complex will display a cubic or trigonal crystal structure. If {condition a(ii)} $B >$ thermal energy (kT), then this involves an equal mixture of the three elongated tetragonal octahedral chromophores of Fig. 1(a) with their elongation axes misaligned in three mutually perpendicular directions, and each Well thermally isolated, and the crystal system would still be cubic (or trigonal) in concentrated copper(II) complexes. For strong Jahn—Teller coupling [50], further warping occurs, and the situation illustrated in Fig. 1(b) involves the situation that Well(I) is of considerably higher energy than Wells (II) and (III), which are of approximately equal energy (and hence are approximately equally occupied). If {condition b(i)} $B <$ thermal energy (kT), then the two 90° misaligned CuL_6 chromophores are thermally accessible, and at any *one* copper site * a two-dimensional dynamic interconversion occurs of the elongation axes. If the thermal population of Wells (II) and (III) are approximately equal, the crystallographically determined CuL_6 stereochemistry will appear compressed octahedral, but is better described as pseudo compressed [30] in view of the two dimensional *dynamic* behaviour involved. If {condition b(ii)} $B >$ thermal energy (kT), then at any *one* crystallographic site there will be two disordered elongated tetragonal octahedral CuL_6 chromophores which only differ in the relative orientation of their elongation axes by 90°. With approximately 50% occupancy, the average chromophore stereochemistry will again appear to be compressed octahedral, but as this is not a genuine static copper(II) stereochemistry, this structural situation is better referred to as pseudo compressed rhombic octahedral [30].

Unfortunately, the measurement of the Cu—L bond distances, in both situations b(i) and b(ii) above, will only indicate a time averaged {for condition (i)} or a statistically averaged {for condition (ii)} pseudo compressed octahedral geometry for the CuL_6 chromophore and cannot directly distinguish between these two alternatives.

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* This structural situation should not be confused with the crystallographic situation [15,22] in which the 90° misaligned elongated octahedrons are present at adjacent copper positions, as in the lattice of $\{CAT\}_2CuCl_4$, which involves a slightly distorted two dimensional layering of elongated rhombic octahedral $CuCl_6$ chromophores, but the different orientations are related by the elements of symmetry of the space group *Pmma* and are *not* crystallographically distinguishable; a structural situation that is referred to as antiferrodistortive ordering.

If the potential energies of Wells (II) and (III) are significantly different {see Fig. 1(c)}, and if {condition c(i)} $B <$ thermal energy (kT), then the observed structure will be elongated rhombic octahedral, but the observed tetragonality (represented by T) [2] will be high (≈ 0.90) and temperature variable (where T is defined as the mean in-plane Cu—L bond distance divided by the mean out-of-plane Cu—L bond distance). If {condition c(ii)} $B >$ thermal energy (kT), and the potential energies of Wells(II) and (III) are well separated (by ΔE), then the elongated rhombic octahedral structure of Well(II) {see Fig. 1(c)} will predominate and the static non-temperature variable elongated rhombic octahedral stereochemistry will occur, as found for the majority of elongated rhombic octahedral complexes of the copper-(II) ion, with tetragonalities in the region of $T = 0.80—0.85$ [1,2].

Thus, the three diagrams of Fig. 1(a)—(c) contain all the structural situations required to account for the stereochemistries of the copper(II) ion (see Table 1). Condition a(i) not only describes the genuine dynamic Jahn—Teller systems such as $K_2Pb[Cu(NO_2)_6]$ [30], $[Cu(ompha)_3][ClO_4]$ [63] and $[Cu(en)_3][SO_4]$ [31], which all involve high symmetry chromophores (O_h or D_3) and involve six equivalent ligands, but also equally describes the lower symmetry CuN_6 chromophore [60] of $[Cu(tach)_2][NO_3]_2$ (C_{2h}), as well as the EPR behaviour of some copper-doped systems (see Table 1). Condition a(ii) could account for the occurrence of a high symmetry static Jahn—Teller effect, but no evidence for this situation in concentrated copper(II) complexes exists to date [62]. However, it may be linked to the observation of three independent magnetic sites (or domains) in the low temperature forms of $K_2Pb[Cu(NO_2)_6]$ [30], $[Cu(en)_3][SO_4]$ [31,65], $[Cu(ompha)_3][ClO_4]_2$ [63] and $[Cu(PyNO)_6][BF_4]_2$ [64]. Condition b accounts for the existence of the pseudo compressed octahedral stereochemistry of the copper(II) ion, involving in condition b(i) a two dimensional dynamic (or planar dynamic) Jahn—Teller effect, and in condition b(ii) two static elongated CuL_6 chromophores misaligned by 90°. These two situations cannot be distinguished crystallographically, but the former is usually considered to apply to the known copper(II) complexes which involve a compressed rhombic octahedral stereochemistry, although the latter cannot be ruled out {see Table 1b(i)}. The b(ii) situation is considered to apply in $[(Zn/Cu)(phen)_3][NO_3]_2 \cdot 2\,H_2O$ [66].

Condition c then accounts for the existence {c(i)} of fluxional rhombic octahedral copper(II) complexes and {c(ii)} of static rhombic octahedral complexes {Table 1, c(i) and c(ii), respectively}.

The above model for the effect of the Jahn—Teller theorem on the six coordinate copper(II) stereochemistry also predicts the order of magnitude of some of the parameters [60] involved, and the type of physical techniques that might be used to measure these quantitatively (see Table 2). The Jahn—Teller energy, $E_{JT} \approx 1500—2500\ cm^{-1}$, can be examined by optical

TABLE 1

Jahn—Teller systems; a summary of the behaviour of (A) concentrated copper(II) complexes and (B) copper(II)-doped zinc(II) complexes, classified by their behaviour according to the six cases of Fig. 1(a)—(c), (i) and (ii). (L.T.) represents a low temperature structure

(A)	(B)
a(i) $B < kT$	
$K_2Pb[Cu(NO_2)_6]$ [30]	$[(Cu/Zn)(en)_3][NO_3]_2$ [65]
$[Cu(ompha)_3][ClO_4]_2$ [63]	$[(Cu/Zn)(phen)_3][NO_3]_2 \cdot 2\ H_2O$ [66]
$[Cu(tach)_2][NO_3]_2$ [60]	$[(Cu/Zn)(hfacac)_2(py)_2]$ [24]
$[Cu(PyNO)_6]X_2$ [64]	$Sr_2[(Cu/Cd)(NO_2)_6]$ [74]
a(ii) $B > kT$	
—	$(Cu/Zn)(pyrazine)SO_4H_2O$ [62]
b(i) $B < kT$	
$Rb_2Pb[Cu(NO_2)_6]$ [45]	
$K_2Pb[Cu(NO_2)_6]$ [30] (L.T.)	
$[Cu(en)_3][SO_4]$ [31] (L.T.)	
$Cs_2Pb[Cu(NO_2)_6]$ [46]	
$[Cu(dien)_2][NO_3]_2$ [49]	$[(Cu/Zn)(dien)_2][NO_3]_2$ [67]
$K_2[CuF_4]$ [47]	
$Ba_2[CuF_6]$ [48]	
b(ii) $B > kT$	
—	$[(Cu/Zn)(phen)_3][NO_3]_2 \cdot 2\ H_2O$ [66] (L.T.)
c(i) $B < kT$	
$[NH_4]_2[Cu(OH_2)_6][SO_4]_2$ [68]	$[(Cu/Zn)(H_2O)_6]K_2[SO_4]_2$ [61]
$Rb_2[Cu(OH_2)_6][SO_4]_2$ [69]	
$[Cu(dien)_2]Cl[ClO_4]$ [67]	$Ba_2[(Cu/Zn)(HCO_2)_6]4\ H_2O$ [73]
$[Cu(dien)_2]Cl_2 \cdot H_2O$ [67]	$[(Cu/Zn)(dien)_2]Cl_2 \cdot H_2O$ [67]
$[Cu(dien)_2]Br_2 \cdot H_2O$ [67]	$[(Cu/Zn)(dien)_2]Br_2 \cdot H_2O$ [67]
$[Cu(phen)_3][NO_3]_2 \cdot 2\ H_2O$ [66]	$(Cu/Zn)(py3\text{-}SO_3)_2 \cdot 4\ H_2O$ [70]
$[Mg(OH_2)_6]H_2edta$ [72]	
c(ii) $B > kT$	
$K_2Ba[Cu(NO_2)_6]$ [71]	
$Cs_2[Cu(OH_2)_6][SO_4]_2$ [69]	$(Cu/Zn)(MeSat)_1$ [44]
$[Cu(tach)_2][ClO_4]_2$ [60]	$(Cu/Zn)(MeSaldpt)_1$ [44]

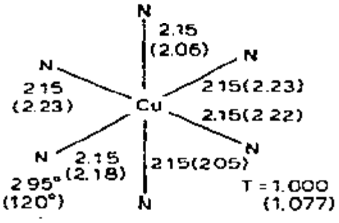
spectroscopy, the Jahn—Teller radius, $R_{JT} \approx 0.3—0.4$ Å, is available from X-ray diffraction data, and the angular barrier height, $B \approx 50—400\ cm^{-1}$, is available from EPR measurements.

1979 had yielded two most convincing pieces of X-ray crystallographic evidence [31,32] for the Jahn—Teller effect. Firstly, the low temperature structure of $[Cu(en)_3][SO_4]$ (1), which has shown that the regular trigonal octahedral $\{CuN_6\}$ chromophore of the room temperature structure

Table 2

Structural and spectroscopic data for some copper(II) complexes involving equivalent ligands [60]. (R.T. °K)

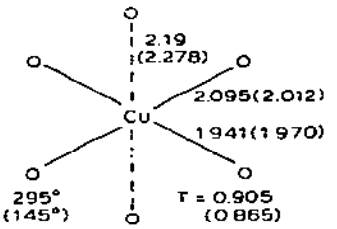
	d_0 (Å)	R_{JT} (Å)	E_{JT} (cm^{-1})	E_2 (cm^{-1})	$f = 2E_{JT}/R_{JT}^2$ mdyn Å^{-1}
(a) Dynamic					
$[Cu(en)_3][SO_4]$	2.150	0.358	2180	15 700	0.68
$K_2Pb[Cu(NO_2)_6]$	2.111	0.333	1750	16 500	0.63
$Tl_2Pb[Cu(NO_2)_6]$	2.118	0.308	1860	16 500	(0.78)
$[Cu(tach)_2][NO_3]_2$	2.164	0.329	—	—	0.80
(b) Pseudo dynamic					
$Rb_2Pb[Cu(NO_2)_6]$	2.136	0.252	1920	15 700	1.20
$Cs_2Pb[Cu(NO_2)_6]$	2.171	0.343	1920	16300	(0.75)
(c) Static					
$K_2Ca[Cu(NO_2)_6]$	2.138	0.303	1980	16 500	0.85
$K_2Sr[Cu(NO_2)_6]$	2.127	0.318	1900	16 500	0.75
$K_2Ba[Cu(NO_2)_6]$	2.132	0.308	1920	16 550	0.81
$[Cu(bipy)_3][ClO_4]_2$	2.134	0.355	2170	15 400	0.69
$[Cu(phen)_3][ClO_4]_2$	2.134	0.336	1900	15 200	0.67



(1) $[Cu(en)_3][SO_4]$; bond lengths in Å (throughout).

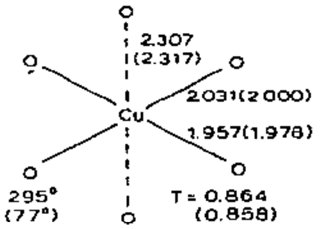
becomes compressed rhombic octahedral (120 K) as predicted [65] from the EPR spectra (pseudo reversed) measured at low temperature. The authors also argue from the anisotropic temperature factors [31] that the low temperature structure involves a pseudo compressed stereochemistry rather than a genuine compressed stereochemistry, and attempt to analyse the low temperature structure as a disordered structure involving three $\{CuN_6\}$ chromophores misaligned by 90°, in order to force the model of Fig. 1a(ii) on the system. Why the authors chose three disordered chromophores {Fig. 1a(ii)} rather than two disordered chromophores {Fig. 1b(ii)} is not clear, but a comparable attempt to re-analyse the room temperature structure (compressed rhombic octahedral) of $[Cu(dien)_2][NO_3]_2$ [49] in terms of *two* misaligned $\{CuN_6\}$ chromophores also failed to converge [67]. Equally interesting, the low temperature structure (ca. 150 K) of $[Cu(dien)_2][NO_3]_2$ [67] failed to show any significant difference from the compressed rhombic octahedral $\{CuN_6\}$ chromophore of the room temperature structure [49], a lack of change that parallels the lack of change in the low temperature structure of $K_2Pb[Cu(NO_2)_6]$ [30] from 296 to 193 K, which suggests that temperatures significantly lower than that of liquid nitrogen will be required to demonstrate crystallographically that the pseudo compressed rhombic octahedral stereochemistry does involve a two dimensional dynamic Jahn—Teller effect {Fig. 1b(i)}. Alternatively, could it be that these systems do involve two static misaligned chromophores *not* thermally connected {Fig. 1b(ii)}, as this would then account for the lack of temperature effect on the pseudo compressed stereochemistry?

The low temperature crystal structure of $[NH_4]_2[Cu(OH_2)_6][SO_4]_2$ [32] (2) has been determined and shows a significant change in stereochemistry



(2)

$[NH_4]_2[Cu(OH_2)_6][SO_4]_2$



(3)

$Rb_2[Cu(OH_2)_6][SO_4]_2$

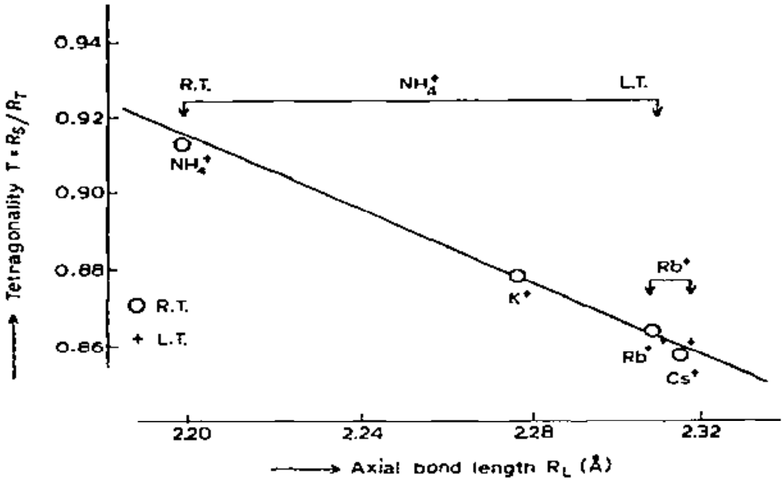


Fig. 2. Copper Tutton salts — tetragonality v. axial Cu—O bond length, R_L.

of the elongated rhombic octahedral $\{CuO_6\}$ chromophores with decreasing temperature such that the tetragonality decreases from 0.905 to 0.865 at ca. 145 K. This change contrasts with the almost insignificant change observed previously [75] for the $Rb_2[Cu(OH_2)_6][SO_4]_2$ complex (3) from 0.864 to 0.858 at 77 K, which suggests that while $[NH_4]_2[Cu(OH_2)_6][SO_4]_2$ is clearly fluxional {Fig. 1c(i)}, the rubidium salt is almost non-fluxional, and virtually static {Fig. 1c(ii)}. If the tetragonalities of the various copper Tutton salts are plotted against the mean out-of-plane bond-length R_L {Fig. 2}, including the low temperature data, there is a significant correlation such that the tetragonality is clearly a function of the atomic size of the cation present. The significant change in tetragonality of the ammonium Tutton salt with temperature nicely demonstrates that the tetragonality is clearly a function of temperature, and not just of the atomic size of the cation present.

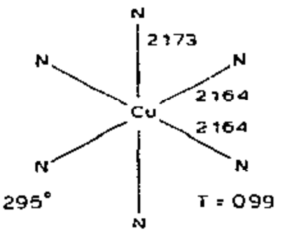
Further indications of the presence of a fluxional $\{CuL_6\}$ chromophore from the X-ray crystallographic data [60] can be obtained from the marked anisotropy of the thermal motions of the six ligand atoms, and is reflected in the root-mean-square displacements along and perpendicular to the Cu—L bond direction. This has been better expressed [60] in the form $\Delta U^{1/2}$(Cu—L), where the ligand displacements are corrected for the displacements of the copper atom and the ΔU's represent a bond displacement {Table 3}. For dynamic systems, the $\Delta U^{1/2}$(Cu—L) is >0.10 Å, and for static systems $\Delta U^{1/2}$(Cu—L) is <0.10 Å. Not only does this distinguish the dynamic and static $\{CuL_6\}$ chromophores, but also characterises the pseudo compressed rhombic octahedral stereochemistries as two-dimensional dynamic systems consistent with Fig. 1b(i).

TABLE 3

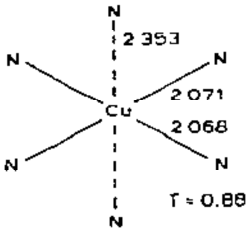
Some $\Delta U^{1/2}$ (Cu-ligand) Å values for some CuL_6 (and NiL_6) chromophores

	L(1)	L(2)	L(3)
$[Cu(en)_3][SO_4]$	0.176		
$[Ni(en)_3][SO_4]$	0.097	—	—
$[Cu(tach)_2][ClO_4]_2$	0.095	0.136	0.151
$[Cu(tach)_2][NO_3]_2$	0.147	0.143	0.143
$[Ni(tach)_2][NO_3]_2$	0.052	0.052	—
$[Cu(dien)_2][NO_3]_2$	0.248	0.063	0.186
[Cu(trispyrazolborate)]$_2$ modification 1	0.07	0.04	<0.00
modification 2	0.15	0.12	0.07
$[NH_4]_2[Cu(OH_2)_6][SO_4]_2$	0.125	0.115	0.036
[Cu(Methoxyacetate)$_2$]2 H_2O	0.102	0.097	0.118

The crystal structures [60] of two complexes of the $[Cu(tach)_2]^{2+}$ cation have been determined {(4) and (5)}; the perchlorate (5) shows an elongated rhombic octahedral chromophore stereochemistry {Fig. 1c(ii)} ($T = 0.88$), whilst the nitrate (4) is very nearly regular octahedral, with a tetragonality of 0.99 and a crystallographic symmetry of C_{2h}. A semi-rigid body analysis of the whole $[Cu(tach)_2]^{2+}$ cation and of the temperature factors of both $[Cu(tach)_2][NO_3]_2$ and $[Ni(tach)]_2[NO_3]_2$ yield $\Delta U^{1/2}$(Cu—N) values {Table 3} which indicate that the nitrate has a dynamic and the perchlorate a static $\{CuN_6\}$ chromophore stereochemistry.



(4)

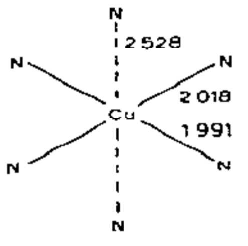


(5)

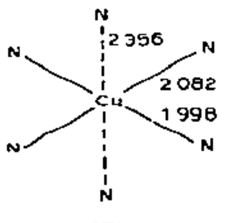
(4) $[Cu(tach)_2][NO_3]_2$

(5) $[Cu(tach)_2][ClO_4]_2$

The crystal structure [76] of $[Cu(HBPz_3)_2]$ has been determined (triclinic $P\bar{1}$, $Z = 2$) with two independent $\{CuN_6\}$ chromophores: both have centrosymmetric elongated rhombic octahedral stereochemistries {(6) and



(6) T = 0.792



(7) T = 0.866

(6) $[Cu(HBpz_3)_2]$ (modification 1); measured at room temperature

(7) $[Cu(HBPz_3)_2]$ (modification 2); measured at room temperature

(7)} but with a significant difference between the stereochemistries of the two {CuN_6} chromophores, with tetragonalities of 0.792 and 0.866, respectively. From the $\Delta U^{1/2}$(Cu—N) values {Table 3}, the former has a static {CuN_6} stereochemistry consistent with its lower tetragonality, while the latter has a two-dimensional fluxional behaviour, as in the $[NH_4]_2[Cu(OH_2)_6][SO_4]_2$ system.

Considerably more indirect information is available on these dynamic and fluxional Jahn—Teller systems from the temperature variation of the EPR spectra. The static elongated stereochemistry [60] of $[Cu(tach)_2][ClO_4]_2$ is reflected in a non-temperature-variable EPR spectrum, down to 4 K g_c = 2.061, g_b = 2.100 and g_a = 2.203, consistent with an elongated rhombic octahedral stereochemistry, not withstanding that these are crystal g-factors. The temperature variation of the EPR spectrum of $[Cu(tach)_2][NO_3]_2$ [60] is much more interesting, as it is isotropic at room temperature, {Fig. 1a(i)}, pseudo-reversed down to 120 K, {Fig. 1b(i)}, and statically distorted below 120 K, {Fig. 1b(ii)} (or possibly {Fig. 1b(i)}), as at 120 K the nitrate undergoes a phase change. The single crystal EPR spectrum is isotropic at room temperature, and clearly splits into two peaks consistent with two magnetic sites, which persist almost unchanged down to 4.2 K and yield the single crystal g-factors of 2.047, 2.081 and 2.250, which are closely comparable to those for the perchlorate at low temperature. Between room-temperature and 120 K there is little anisotropy in the g-factors, and the directions of the g's undergo a complicated rotation with respect to the Cu—N directions, with decreasing temperature, which is further complicated by the C_{2h} site symmetry. The results of a low temperature crystal structure of this most intriguing system, preferably measured above and below the phase transition of 120 K, is awaited with interest, especially as the EPR suggests a pseudo compressed {CuN_6} stereochemistry above 120 K and an elongated rhombic octahedral {CuN_6} stereochemistry below 120 K. If substantiated, this would represent the first crystallographic evidence for the transition of a pseudo-compressed octahedral stereochemistry to an elongated rhombic octahedral {CuN_6} chromophore.

A review [15] of the six coordinate complexes (of the copper(II) ion) with $g_{\parallel} < g_{\perp}$ in the solid state is most timely, and collects together a great deal of EPR data on complexes of the copper(II) ion published over the last ten years, with particular emphasis on the significance, from a stereochemical point of view, of the pseudo reversed type of EPR spectra for copper(II) complexes, and the physical significance of the pseudo compressed octahedral stereochemistry discussed above. The authors are at pains to emphasise the difference between ferrodistortive ordering of elongated rhombic octahedra and antiferrodistortive ordering, and the real difference between crystal g-factors and local molecular g-factors, but then unfortunately they confuse these when discussing the g-factors of the antiferrodistortive order of $\{CAT\}_2[CuCl_4]$ and in the crystal g's of the undiluted crystals in Table 4 of ref. 15. Likewise, they omit to mention that the occurrence in an EPR

TABLE 4

X-ray crystallographic data upon some five-coordinate complexes

(a) [Cu(dien)(bipyam)]$X_2 \cdot nH_2O$ [25]

	X = [NO_3], $n = 0$	X = [ClO_4], $n = \frac{1}{2}$	X = Cl, $n = 1$
Cu—N(1) (Å)	2.032 (19)	2.026 (5)	1.990 (12)
Cu—N(2) (Å)	2.039 (18)	2.023 (4)	2.013 (12)
Cu—N(3) (Å)	2.071 (18)	2.052 (5)	2.020 (12)
Cu—N(4) (Å)	1.991 (19)	1.993 (4)	1.998 (11)
Cu—N(5) (Å)	2.150 (19)	2.170 (3)	2.126 (11)
N(1)—Cu—N(3)	135.5 (7)°	151.9 (1)°	159.1 (5)°
N(2)—Cu—N(4)	172.0 (8)°	167.9 (1)°	162.7 (5)°

(b) [$Cu(bipy)_2Cl$]$X \cdot nH_2O$ [83]

	X = Cl, $n = 6$	X = [Cu^ICl_2], $n = 0$	X = $\frac{1}{2}$[S_5O_6], $n = 3$
Cu—N(1) (Å)	1.989	1.995	1.998
Cu—N(2) (Å)	2.077	2.063	2.089
Cu—N(3) (Å)	1.970	1.986	1.988
Cu—N(4) (Å)	2.087	2.086	2.105
Cu—Cl (Å)	2.361	2.355	2.293
N(2)—Cu—Cl	118.7°	111.1°	130°
N(4)—Cu—Cl	118.6°	133.4°	122.1°
N(2)—Cu—N(4)	122.8°	115.5°	107.3°

(c) [$Cu(bipy)_2(OH_2)$]X complexes [83,84]

	X = $[S_5O_6]^{2-}$	X = $[S_2O_6]^{2-}$
Cu—N(1) (Å)	1.973	1.977
Cu—N(2) (Å)	2.024	2.039
Cu—N(3) (Å)	1.983	1.977
Cu—N(4) (Å)	2.123	2.039
Cu—O (Å)	2.054	2.158
N(2)—Cu—O	143.6°	115.0°
N(4)—Cu—O	104.9°	115.6°
N(2)—Cu—N(4)	111.4°	129.8°

spectrum of $g_\perp > g_\parallel$ can also be associated with a five-coordinate trigonal bipyramidal stereochemistry for the copper(II); an unfortunate omission for those not familiar with copper(II) stereochemistry.

An important review [22] to appear in 1979 was that on the "Local and Cooperative Jahn—Teller Interaction in Model Structures", which is related primarily to copper(II) chemistry. The local Jahn—Teller theorem was developed, but extended in terms of tunnelling effects and strain theories, to cover the Cooperative Jahn—Teller effect. Importance was placed on the different effects of the structure of the basic host lattice involving isolated octahedral cations, as in elpasolite structures (i.e. $Ba_2Zn_{1-x}CuW_xO_6$), or bridging anion structures, as in the structure of $KCuF_3$. Great emphasis was placed on the occurrence of multi-stage phase transitions from:

(a) static to two dimensional dynamic;

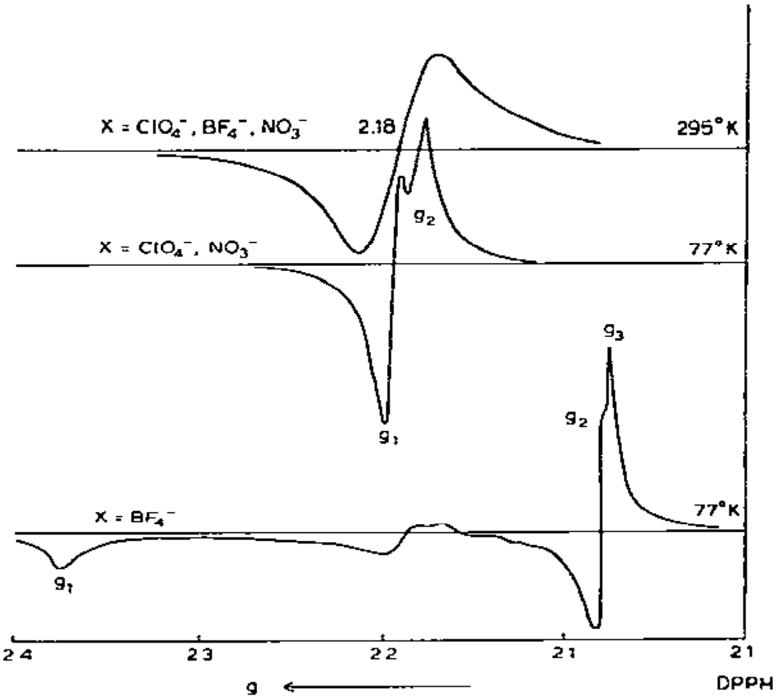


Fig. 3. The powder EPR spectra of some $[Cu(PyNO)_6]X_2$ complexes (where X = $[BF_4]$, $[NO_3]$ or $[ClO_4]$) at 295 and 77°K.

(b) two dimensional to fully dynamic systems.
An informative interpretation of these phase transitions was given in terms of ferro- and antiferrodistortive ordering (which nicely compliments that given in ref. 15), which can be used to suggest, from low temperature magnetic data [77], that the low temperature structures of $[Cu(PyNO)_6][BF_4]_2$ and $[Cu(PyNO)_6][ClO_4]_2$ involve ferrodistortive and antiferrodistortive ordering [77] in their structures, consistent with their planar antiferromagnetism and one-dimensional ferromagnetism, respectively. These results are supported [64] by the powder and single crystal EPR spectra of the copper(II) doped system $[(Zn_{1-x}Cu_x)(PyNO)_6]X_2$ (see Fig. 3). The effect of temperature on the EPR spectrum [22] of 10% $Ba_2(Zn_{1-x}Cu_x)WO_6$ demonstrates the transition from a dynamic $\{CuO_6\}$ environment to a static elongated rhombic octahedral stereochemistry in the ferrodistortive structure at 4.2 K. The effect of copper(II) ion concentration is nicely illustrated (see Fig. 4) in the $Ba_2(Zn_{1-x}Cu_x)WO_6$ system, where there is a phase transition from a cubic (*Fm3M*) to a tetragonal (*I4/mmm*) space group as x increases, the precise temperature of the phase transition changing with increasing x and showing a corresponding increase in the energy of the band maxima of the electronic spectrum, especially for that of the lowest energy band {Fig. 4(c)}, which is

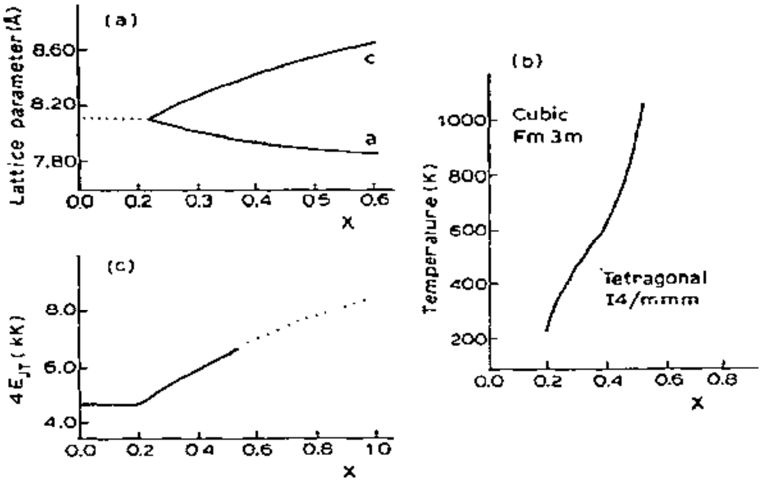
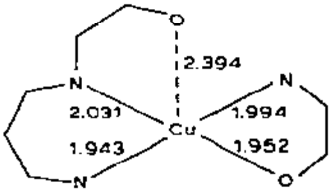


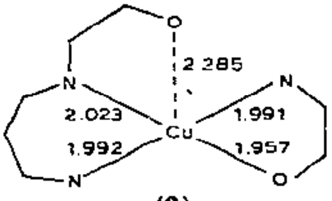
Fig. 4. Phase lines (a, b) and E_g ground state-splitting (= $4E_{JT}$) (c) for the mixed crystals $Ba_2(Zn_{1-x}Cu_x)WO_6$.

assigned as the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition (whose energy is equivalent to $4E_{JT}$). The article concluded that in the isomorphous substitution by copper(II) ions of a regular octahedral lattice site, the Jahn—Teller effect induces an elongated rhombic octahedral stereochemistry with either ferrodistortive or antiferrodistortive lattices, with a slight preference for the latter, especially in elpasolite type lattices.

The final consequence of the Jahn—Teller effect is the Plasticity Effect [9], which stems from the ability of the copper(II) to accommodate, within a given set of ligands, a range of different geometries and within a given geometry, a range of differing degrees of distortion of that geometry. These differences arise *partly* due to the cooperative Jahn—Teller effect in these concentrated copper(II) systems. Few additional examples of distortion isomers have been recognised in the current year but that of $[Cu(HBPz_3)_2]$ [76] (6) and (7) is an example where two distinct types of $\{CuN_6\}$ chromophore stereochemistry exist within the same unit cell. Both are elongated rhombic octahedral, but with differing tetragonalities (0.792 and 0.866) due to differing packing factors in the lattice, further complicated in this case by differing degrees of fluxional behaviour. A more straightforward case exists in the two independent molecules in the unit cell [78] of L-Asparaginato-L-histidinatocopper(II) {(8) and (9)}. The extension [25] of the concept of



(8)



(9)

(8) [Cu(L-Asp.)(L-Hist.)] (modification A)

(9) [Cu(L-Asp.)(L-Hist.)] (modification B)

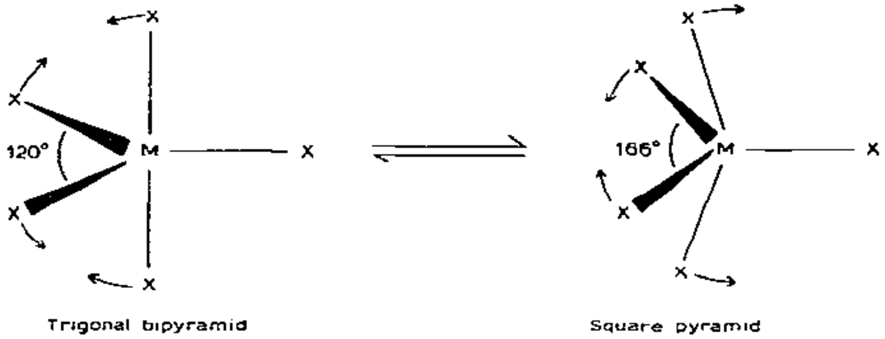
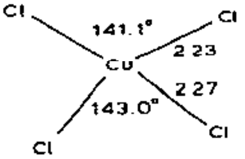


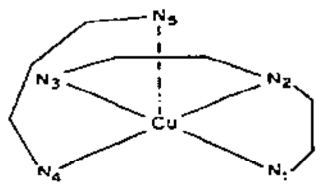
Fig. 5. The Berry Twist mechanism for interconversion of a regular trigonal bipyramid to a square pyramid via the e mode of vibration.

distortion isomers to include cation and anion distortion isomers has greatly increased the applicability of the plasticity effect and equally demonstrated how dramatic can be the changes both in the stereochemistry involved and in the corresponding electronic properties. The best example of anion distortion isomers is the series of $M'M''[Cu(NO_2)_6]$ complexes [15,20,60] where, depending on the nature of M′ and M″, the anion stereochemistry can be octahedral, elongated rhombic octahedral or pseudo compressed rhombic octahedral, complicated by the presence of dynamic Jahn—Teller effects as discussed above and generating clearly different EPR spectra (but only showing small differences in the $4E_{JT}$ energies of 7.0—8.8 kK) [60]. Likewise, the variation in stereochemistry [79] of the $[CuCl_4]^{2-}$ anion from compressed tetrahedral to square rhombic coplanar depending on the cations present results in significant shifts in the electronic energies of the *d*—*d* transitions present, which can be used to "predict" the $\{CuCl_4\}$ stereochemistry present {e.g. see (10)}. The cation distortion isomers of the series

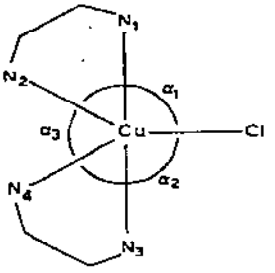


(10) $[C_{10}H_{16}N_2][CuCl_4]$

of copper Tutton salts [32] has been referred to above. In the series of $[Cu(dien)(bipyam)]X_2$ (11) complexes [25], the basic five-coordinate $\{CuN_5\}$ stereochemistry is clearly intermediate between square-base pyramidal and trigonal bipyramidal (Fig. 5), depending on the anion present {see Table 4(a)}. There are angular distortions present such that, as the N(1)—Cu—N(3) angle increases (in the series nitrate, perchlorate, chloride) towards 180°, there is a significant decrease in the value of the N(2)—Cu—N(4) angle from 180°. This suggests that the stereochemistry of the $\{CuN_5\}$ framework of the three cation isomers are connected by the mechanistic



(11) $[Cu(dien)(bipyam)]X_2$



(12) $[Cu(bipy)_2Cl]Cl$

pathway of the Berry Twist [80] (Fig. 5). The changes in geometry are also reflected in the electronic spectra of the three complexes, which show a shift in the band maximum from 13100 to 17200 cm^{-1} in the sequence of Table 4(a), consistent with the shift in the electronic energies calculated using the crystal field model and the local molecular geometry.

While the almost regular trigonal bipyramidal geometry of the $[Cu(bipy)_2Cl]^+$ cation of $[Cu(bipy)_2Cl]Cl \cdot 6\,H_2O$ [81] (12) has been known for 10 years, more distorted forms of this cation are now known [82,33] {see Table 4(b)} which show a decrease of the N(2)—Cu—N(4) bond angle from 122.8° for (12) to 115.5° for $[Cu(bipy)_2Cl][CuCl_2]$ to 107.3° for $[Cu(bipy)_2Cl]_2[S_5O_6] \cdot 3\,H_2O$, with a parallel decrease in the Cu—Cl bond distance from 2.361 to 2.293 Å in this sequence. These changes also parallel the changes associated with the route A of the Berry Twist mechanistic pathway specific to the $[Cu(bipy_2)X]Y$ system (see Fig. 6). The structures of the two cation distortion isomers $[Cu(bipy)_2(OH_2)][S_5O_6]$ [83] and $[Cu(bipy)_2(OH_2)][S_2O_6]$ [84] {see Table 4(c)} represent two alternative distortions {route B and route A, respectively, in Fig. 6} and are accompanied by a clear elongation of the Cu—O distance from 2.054 to 2.158 Å with a corresponding increase of the N(2)—Cu—O angle from 111.4° to 129.8°, significantly above the trigonal angle of 120°.

A visual illustration of the plasticity effect is the occurrence of thermochromism in copper(II) complexes. The crystal structures of the red and blue-violet form of $[Cu(N,N\text{-}Et_2en)_2][ClO_4]_2$ [85] show that both are rhombic coplanar but with no significant differences in the Cu—N bond distances, at 2.001, 2.068 and 2.016, 2.016 Å, respectively, and with no semi-coordination of the perchlorate anions. The observed differences in colour (20.6 and 19.7 kK, respectively) are associated not with differences in tetragonality, but to differences in the in-plane field strength of the nitrogen ligands caused by a difference in conformation of the methylene rings.

6.3.2 EPR spectroscopy

EPR spectroscopy still continues to flourish, and involved three conferences [86] in 1979, of which only the Nottingham conference [87] devoted

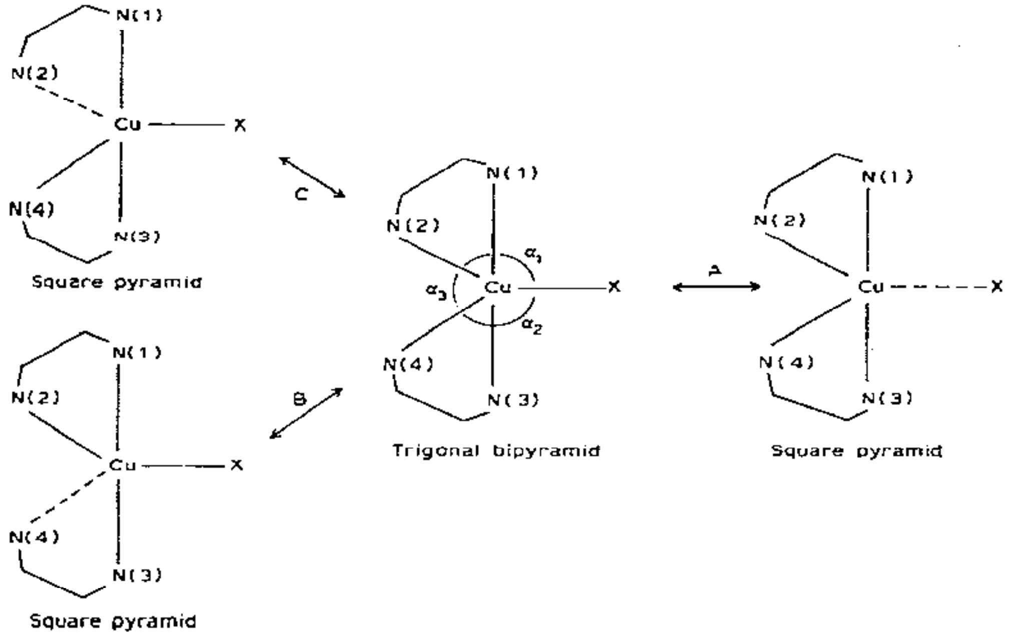
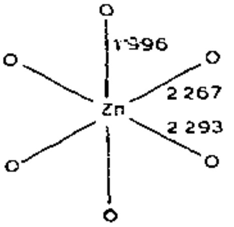


Fig. 6. The mechanistic reaction pathway for the $\{CuN_4X\}$ chromophore of the $[Cu(bpy)_2X]Y$ complexes for distortion from trigonal bipyramid to square pyramid involving three alternative pathways. Routes (B) and (C) are symmetry related by the C_2 about the Cu—X bond.

a significant proportion of its time to the EPR of copper (both to its coordination chemistry and to copper in a biological environment, see later). The EPR spectra of the copper phthalocyanine complexes continue to attract attention: the nitrogen-15 labelled complex [88], produced some beautifully resolved spectra and the award for the best poster display at the Nottingham conference. The EPR spectra of copper octaethylporphyrin [89] yielded evidence of dimer formation. The EPR spectra of copper thiocomplexes continue to be reported both as powder [90] and single-crystal [91] data. The advantages of the latter are increasingly demonstrated in the elegant data on copper(II)-doped calcium and strontium salicylate dihydrates [92], with a suggested "eight-fold" coordination of the copper(II) (based on the structure of the host lattice), which although tentative is more substantive than the (corrected) set of data on copper(II)-doped strontium ethanoate hemihydrate [93] which was carried out in the absence of structural details of the host lattice. Equally, the proton hyperfine coupling [94] of copper(II) doped in $[NH_4]_2[Mg(OH_2)_6][SO_4]_2$ was used to describe the position of the hydrogen atom in this potentially fluxional system. In the 4-nitrophenol adduct of *N,N'*-ethylenebis(salicylidimiminato)copper(II) doped in the corresponding metal(II) complex as a host lattice [95], it was suggested, as the EPR parameters of the adduct and the parent copper(II) complex show little difference, that the different values relate to hydrogen-bond effects in the adduct. The EPR data [96] of copper-doped $[\{Zn_{3.5}O(O_2CMe)_5(py)\}_2]$ $\{g = 2.2930, 2.2674, 1.996$ and $A = 164.55 \times 10^{-4}, 32.45 \times 10^{-4}, 18.5 \times 10^{-4}$ $cm^{-1}\}$ are of interest, in that the g-factors are not temperature-variable and this suggests a compressed rhombic octahedral stereochemistry consistent with the stereochemistry of the $\{ZnO_6\}$ chromophore (13). The authors

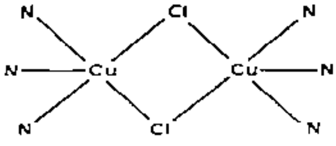


(13) $[\{Zn_{3.5}O(O_2CCMe)_5(py)\}_2]$

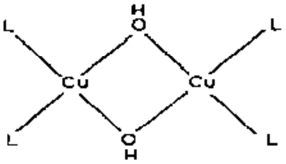
comment on the significance of the lowest g-factor of 1.996, being below the free electron value, which is difficult to understand in the absence of ligand atoms with high spin-orbit coupling constants (such as bromide or iodide). Equally interesting is the high A-value of 164.55×10^{-4} cm^{-1} associated with the lowest g-factor (not with the highest g-factor as reported in Table 3 of ref. 96, see Fig. 4 of ref. 96), and usually taken as evidence for clear 4s and $3d_{z^2}$ mixing in this ground state, which suggests that the $\{CuO_6\}$ chromophore in this system may well involve a genuine compressed rhombic octahedral stereochemistry comparable, if not exactly equal to, that of the $\{ZnO_6\}$ chromophore of the host lattice. In view of the current interest in this stereochemistry it would be of interest to examine the effect of increasing copper(II) ion concentration (Cooperative Jahn—Teller effect) on the electronic properties of this system, especially on the electronic reflectance spectra. In the same area, an equally interesting set of g-factors [97] have been obtained from the EPR spectra of copper(II) complexes in solution with methionine ($g_1 = 2.007$, $g_2 = 2.112$, $g_3 = 2.190$ and $A_1 = 50 \times 10^{-4}$, $A_2 = 85 \times 10^{-4}$ and $A_3 = 90 \times 10^{-4}$ cm^{-1}), which are consistent with a distorted trigonal bipyramidal stereochemistry. However, as the authors did not make it clear how these parameters were obtained from the published spectra (see Fig. 4(c), in ref. 97) and in the absence of variable temperature spectra, the possibility of a fluxional six-coordinate stereochemistry should not be ruled out. The use of polycrystalline and solution EPR spectra along with the electronic spectra in solution [98] continue to be used to characterise the stereochemistries of the species present in solution, not withstanding the possibility of more than one species in solution, but which can still be justified for closely related complexes, such as $[Cu(en)_2][ClO_4]_2$ and $[Cu(pn)_2][ClO_4]_2$. The use of powder EPR[99] to estimate the value of the zero field splitting parameter, D, in a series of copper(II) complexes with unsaturated carboxylic acids is also reported. The additional information obtainable from copper(II) doped into their corresponding host lattices, especially for single crystals, is well known, but the observation [100] of pronounced orientation effects of [Cu(acac)$_2$] and [Cu(salim)$_2$] complexes in a stretched polyvinyl alcohol film as a host lattice must represent a most novel experimental system. The linear electric field effect on the EPR spectrum [101] of single-crystals and powders of $Cs_2[(Cu/Zn)Cl_4]$ has suggested that the effect may be of value in determining the local site symmetry of the copper(II) ion in the dark blue copper(II) proteins azurin and stellacyanin. The use of copper—nitroxyl interactions [102] to determine the electron—electron coupling constants of 300—415 G has been reported for the spin labelled complex (3-(*N*-(2,2,5,5-tetramethylpyrrolin-3-yl-1-oxy)amido)-4,10-dimethyl-5,9-diazatrideca-4,9-diene-2,12-diene)copper(II).

6.3.3 *Magnetism*

There is a continuing interest in the magnetic properties of copper(II) complexes particularly in the presence of antiferro- and ferromagnetic coupling [27]; very few papers report magnetic data [103] (usually accompanied by EPR spectra) without novel crystallographic data. The rôle of bridging halide ions in producing an infinite layer structure is still evident (e.g. the chloride ion in $[N_2H_5]CuCl_3$ [104] or the bromide ion in *catena*-μ-dibromobis(3,5-dimethylpyridine)copper(II) [34], as is that of organic bridging ligands, such as pyrazine (e.g. bis(pyrazine)copper(II) perchlorate [105] or (2,5-dimethylpyrazine)copper(II) nitrate [106]). The magnetism of dimers involving homo-di-nuclear copper complexes [107] is extensive and has been well characterised in *N,N'*-ethylenebis(salicylideniminato)copper(II) bis(hexafluoroacetonato)copper(II) [108], which is antiferromagnetic with $J = -20.4$ cm^{-1}, but in view of the two distortion isomers present ($T = 0.866$ and 0.808 for modifications A and B, respectively), the J value can only be an average value over the two different Cu—Cu environments. A dimer containing two short chloro bridges $\{Cu_2Cl_2\}$ [109] is involved in chloro {hydrotris(1-pyrazolyl)borato copper(II)} (14), with a Cu—$\bar{\text{Cl}}$—Cu angle of 94.5°, which gives



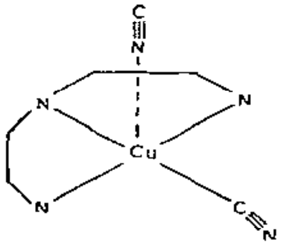
(14) $[\{CuCl(HBPz_3)\}_2]$



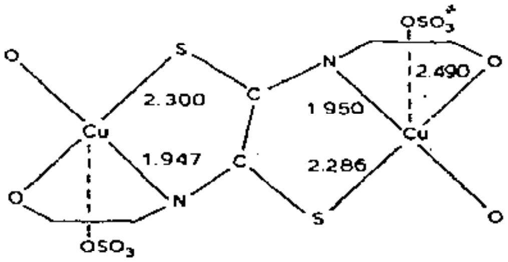
(15) $[\{Cu(C_6H_{11}NH_2)_2(OH)\}_2][ClO_4]_2$

rise to a ferromagnetically coupled ground state $2J/k = 48.6°$. The structure of di-μ-(benzyl-oxo)-bis(2,2,6,6-tetramethylheptane-3,5-dionato)copper(II) [110] indicates an oxygen bridged dimer which displays antiferromagnetic exchange ($2J = -647$ cm^{-1}), whereas in the roof shaped dimer (15) of tetrakis(cyclohexylamine)di-μ-hydroxo-dicopper(II) perchlorate [111] (which has a dihedral angle of 147.5°), the antiferromagnetic coupling is significantly reduced (to $2J = -256$ cm^{-1}). The use of polarised neutron scattering experiments to determine the position of the valence electrons in aquabis(2,2′-bipyridine)di-μ-hydroxo(sulphato) dicopper(II) [112], which is also ferromagnetically coupled ($2J = 48$ cm^{-1}), showed that there is no electron spin-density between the copper atoms, suggesting that the mechanism of magnetic coupling is essentially one of super-exchange. The determination [113] of the antiferromagnetic exchange ($J = 298$ cm^{-1}) by inelastic neutron scattering spectroscopy in the $[\{Cu(CD_3CO_2)_2(D_2O)\}_2]$ dimer as not temperature-variable has resolved one uncertainty about this system, but cannot be used to discriminate between the direct or super-exchange mechanisms for the coupling between the two copper(II) ions; hopefully the use of polarised neutron scattering will resolve this twenty-five-year-old problem. The structure of the dimer has been determined in [{Cu(*N*-acetylglycinate)-$(H_2O)\}_2]$ [114], and in the methanol and ethanoic acid adducts of $[\{Cu(CH_3CO_2)_2\}_2]$ [115]. In this latter work, an attempt has been made to correlate the Cu—Cu distance with the Cu—fifth ligand distance for a number of these dimeric ethanoate structures.

A single imidazole bridging structure is proposed for bis{bis(glycylglyanato)copper(II)}-μ-imidazole [116], and a linear cyanide ion bridging rôle has been proposed for {Cu(2,2′,2″-terpyridine)(CN)} nitrate monohydrate [117] (16), and determined for [Cu_2(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)$_2$(CN)] [ClO_4] [118]. There is antiferromagnetic coupling present in all of these systems [117]. In this last complex, the symmetrically bridging cyanide anion links two trigonal bipyramidal chromophores to yield weak antiferromagnetic coupling ($J = -4.8$ cm^{-1}), and was discussed in terms of the linear bridging rôle of the cyanide anion. The planar bridging rôle of the dithiooxamide ligand has been described [119] in di-μ-aqua-bis{μ-{*N*,*N*′-bis(2-hydroxyethyl)dithiooxamidato(2-)-*N*,*O*,*S*:*N*′,*O*′,*S*}-bis{aqua copper(II)sulphatocopper(II)} (17) which involves

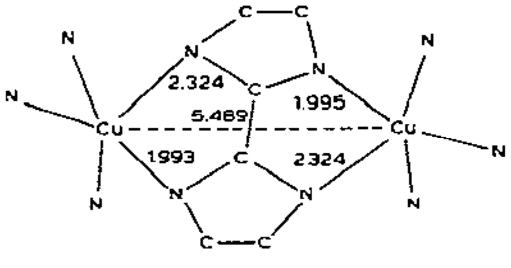


(16) $[Cu(terpy)(CN)][NO_3]\cdot H_2O$



(17) $[CuS_2C_2(N(CH_2)_2OH_2)(H_2O)_2]SO_4$

very strong antiferromagnetic coupling ($J = 523\ cm^{-1}$), despite the Cu—Cu distance of 5.65 Å. This is due to the presence of four short Cu—ligand distances (17). By contrast, the planar bridging rôle of the 2,2′-biimidazolate dianion in μ-2,2′-biimidazolate-bis(1,1,4,7,7-pentamethyldiethylenetriamine)-dicopper(II) tetraphenylborate [120] (18) results in zero exchange coupling



(18) $[Cu_2(Me_5dien)_2(biim)][BPh_4]_2$

($J \approx 0.5\ cm^{-1}$) between the copper(II) atoms separated by 5.49 Å due, presumably, to the presence of one short and one long bonding rôle for the Cu—N ligands (18).

6.3.4 Copper(II) calculations

While there has been very little activity in theoretical calculations upon copper(II), a general review [43] on the Angular Overlap method appeared which contains a section on copper(II). This updates the earlier review [3] on copper(II) ligand-field parameters. The former reports a rather depressing view of the application of the angular overlap model to the various copper(II) stereochemistries; there has always been a snag associated with the $[Cu(NH_3)_4X_2]$ systems (which need an e_π parameter) and for the square coplanar stereochemistry (which needs $d_{z^2} + s$ mixing) [43]. The regular and distorted trigonal bipyramidal stereochemistries are also poorly described by this model, as the polarised single crystal electronic spectra of neither $[Cu(NH_3)_2Ag(SCN)_3]$ nor $[Cu(phen)_2(OH_2)][BF_4]$ [121] can be fitted to the angular overlap parameters in a simple way to produce reasonable parameters.

The square coplanar stereochemistry of copper(II) has received the most attention this year. Two crystal structures of the rhombic coplanar $[CuCl_4]^{2-}$ anion have been reported [79]; bis(1-methyl-4-oxo-3,3-diphenylhexyldimethylammonium) tetrachlorocuprate(II) [122] and bis(creatinium) tetrachlorocuprate(II) [123], with Cu—Cl bond distances of 2.253/2.283 Å and 2.233/2.268 Å, respectively. A rhombic coplanar chromophore $\{CuO_2Cl_2\}$ has also been reported in diaquadichlorocopper(II) tetra(triphenylphosphine oxide) [124], with $\bar{r}(Cu—OH_2) = 1.90$ Å and $\bar{r}(Cu—Cl) = 2.23$ Å; the triphenylphosphine oxide is present only as lattice molecules, with the oxygen atoms involved in hydrogen bonding to the coordinated water molecules. Despite a dearth of polarised single crystal electronic spectra, a

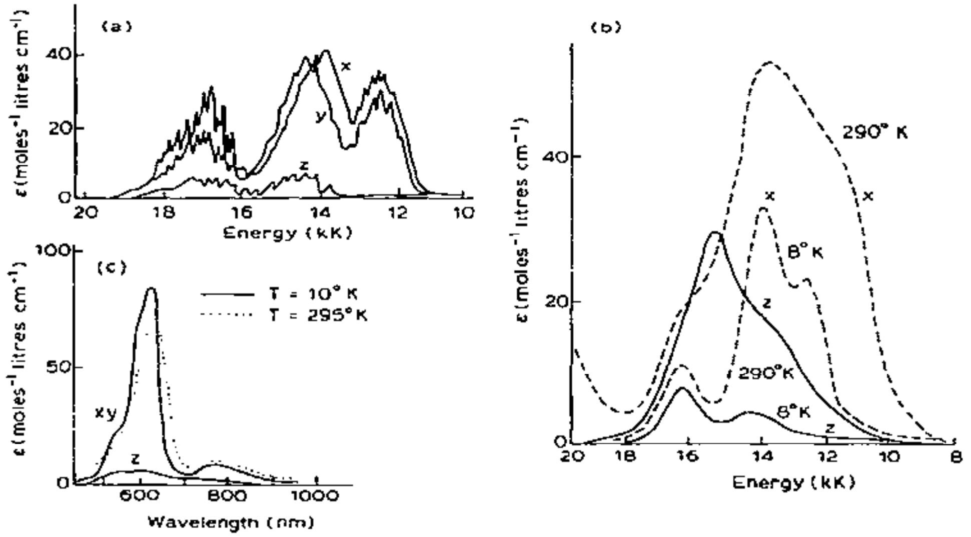


Fig. 7. The polarised single crystal electronic spectra of (a) $[(PhCH_2CH_2)MeNH_2]_2[CuCl_4]$, (b) $(creatinium)_2CuCl_4$ and (c) $CaCuSi_4O_{10}$.

beautiful paper [41] on bis(methylphenethylammonium) tetrachlorocuprate(II) has been published {see Fig. 7(a)}. Spectra down to liquid helium temperature are reported, with the best evidence for vibronic fine structure known for a copper(II) system to date. Unfortunately, the $[CuCl_4]^{2-}$ chromophores are misaligned in the unit cell, but a reasonable interpretation of the observed polarisations yield the one electron orbital sequence $d_{x^2-y^2} >> d_{xy} > d_{yz} > d_{yz} > d_{z^2}$, a sequence that agrees with the angular overlap treatment [3], except that the d_{z^2} orbital is $\approx$5000 cm^{-1} lower in energy than predicted, due to $4s$—$3d_{z^2}$ interaction. From an analysis of the vibronic fine structure, a distortion of the $[CuCl_4]^{2-}$ anion towards tetrahedral in the excited state is suggested. The polarised single crystal electronic spectra of the bis(creatinium) salt of $[CuCl_4]^{2-}$ [40] has also been reported, in which the $[CuCl_4]^{2-}$ anions are nearly aligned parallel and yield nicely polarised spectra, {see Fig. 7(b)} which, due to the crystal morphology, are restricted to the (100) face. The polarised spectra yield the same one-electron orbital sequence as above, with the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition assigned (rather by default) to the highest energy transition (16 530 cm^{-1}) and still requiring $4s$—$3d_{z^2}$ interaction to account for its relatively high energy. Despite the near alignment of the $[CuCl_4]^{2-}$ anion, the low temperature spectra of $(creatinium)_2[CuCl_4]$, disappointingly, shows no evidence for vibronic fine structure.

The polarised single-crystal electronic spectra [125] of $CaCuSi_4O_{10}$, "Egyptian Blue", has been reported down to 10 K {Fig. 7(c)} and yields in the effective symmetry of D_{4h} the one-electron orbital sequence $d_{x^2-y^2} >>$

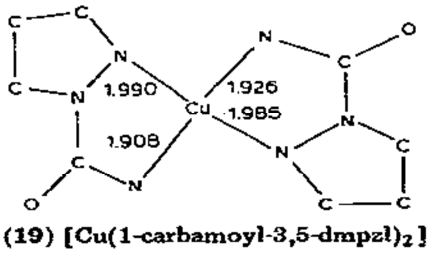
$d_{xy} > d_{xz}$, $d_{yz} > d_{z^2}$, which again requires $4s$—$3d_{z^2}$ interaction in order to yield reasonable angular overlap parameters.

A modified [126] INDO-MO study of the electronic spectra of open shell transition metal complexes, includes its application to the tetrahedral $[CuCl_4]^{2-}$ anion. A more complete [127] molecular orbital calculation of the square coplanar $\{CuN_4\}$ chromophores in $[Cu(NH_3)_4][PtCl_4]$, (β-phthalocyaninato)copper(II) and (tetraphenylporphinato)copper(II) complexes, including metal—ligand and ligand—ligand overlap integrals and charge-transfer states, has been reported. Using experimental g and A-values, reasonable bonding coefficients were obtained with σ bonding > out-of-plane π-bonding > in-plane π-bonding and requiring intuitively reasonable electronic energy levels (ca. 20 000 cm^{-1}) {rather than energies of up to 30 000 cm^{-1} normally quoted for these complexes} [128]. Increasing use is being made of Extended Hückel calculations to simulate the electronic properties, such as the electronic reflectance spectra [25] and exchange coupling in magnetic dimers [111,119], of the stereochemistry of copper(II) involving different angular distortions of the copper(II) environment.

An SCF—Xα—SW calculation [129] for the Cu_2 dimer in the gaseous state has been reported; complete potential energy curves were described and the bonding was considered to involve only a minor d-orbital contribution. A calculation [130] suggests that the elongated tetragonal octahedron for the copper(II) ion is more stable than the corresponding compressed tetragonal octahedron if excited state configurations involving the 4s orbital are included.

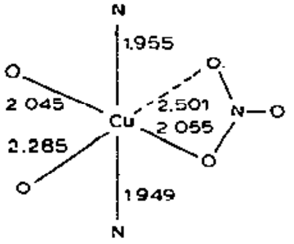
6.3.5 Crystallography

The reported crystal structures of copper(II) continue to be very extensive. Interest continues in "pyridine"-type complexes with the coplanar $\{CuN_2Cl_2\}$ chromophore, including *trans*-{dichlorobis(2,4-dimethylthiazole)copper(II)} [131], *trans*-{dichlorobis(*N*-methylimidazole)copper(II)} [132], *cis*-{dichloro(2,2'-*O*-phenylenebisbenzothiazole)copper(II)} [133], and *cis*-{dichlorobis(1,8-naphthyridine)copper(II)} [134]. By addition of 3,5-dimethylpyrazole to the cyanate ion ($[NCO]^-$), a rhombic near coplanar $\{CuN_4\}$ chromophore has been characterised in α-bis(1-carbamoyl-3,5-dimethylpyrazolate)copper(II) [135] (19). The compressed tetrahedral $[CuCl_4]^{2-}$ anion has been characterised in *N*-phenylpiperazinium tetrachloro-



(19) $[Cu(1\text{-carbamoyl-}3,5\text{-dmpzl})_2]$

cuprate(II) [79], and has a dihedral angle of 51.6°. The *d*–*d* spectra correlate with the dihedral angle in this and other complexes of known crystal structure {bis(4-phenylamino-2-phenyliminopent-3-enato-*NN'*)copper(II) [136] and bis(3,3'-dimethyl-2,2'-bipyridylamine) copper(II) [137], with dihedral angles of 67 and 57.4°, respectively}. Two complexes involving bis-{Cu(nitrogen chelate)X}Y systems have been reported with saturated nitrogen ligands: (3,6-diazo-1,8-diaminooctane)(isothiocyanato)copper(II) perchlorate [138] and bis(*N*-isopropyl-2-methyl-1,2-diaminopropane)(nitro)-copper(II) nitrite [139] both involve distorted trigonal bipyramidal stereochemistries, which is unusual, as a square-based pyramidal or elongated rhombic octahedral stereochemistry is normally found for these types of complexes. Equally interesting, the sense of the distortions (see Table 5) is square pyramidal, but the directions of the distortions are different; along the A route of the mechanistic pathway of the Berry Twist {Fig. 6} for *both* of the cation isomers of the former complex and along the B (or C) route for the latter complex. With a tetradentate ligand, as in *μ*-benzidine-bis(2,2'2''-triaminotriethylamine)dicopper(II) nitrate [140], the $\{CuN_4N\}$ chromophore stereochemistry is still trigonal bipyramidal, but with all four independent chromophores in the unit cell (see Table 5) distorted along the B (or C) route of Fig. 6. In bis(benzimidazol-2-ylmethanol-*N'*,*O*)(nitrato-*O*,*O*)copper-(II) nitrate monohydrate [141], (20) the distortion towards a square-base



(20) $[Cu(benzimidazol\text{-}2\text{-}ylmethanol)_2(NO_3)][NO_3]\cdot H_2O$

pyramid, route B (or C), is extreme (Table 5), such that the nitrate ion occupies an unsymmetrical coordination to yield a six coordinate, 4 + 1 + 1' type stereochemistry for the copper(II) ion. The square pyramidal stereochemistry is still well in evidence with monodentate ligands in *catena*-*μ*-methanoato-methanoatobis(pyridine)copper(II) monohydrate [142], with bidentate ligands in $[\{(cylidine)(2,2'\text{-}bipyridylamine)copper(II)\}_2]$ [143], with tridentate ligands in dichloro(*β*-thio-diglycol)copper(II) [144] and (L-methoxylglycinato)copper(II) [145] and with mixtures of bidentate and tridentate ligands in bis(2-aminoethyl)amine(2,2'-bipyridine)copper(II) nitrate dihydrate and bis(2-aminoethyl)amine(1,10-phenanthroline)copper(II) nitrate [146]. With tridentate ligands such as dien {bis(2-aminoethyl)amine}, the restricted bite of the linked five-membered rings distorts the copper(II) ion out of the plane of the three ligand nitrogens, towards a stereochemistry intermediate between that of square-based pyramidal and trigonal pyramidal

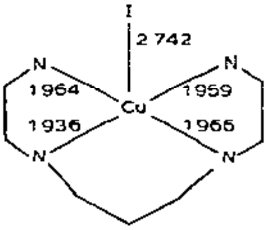
TABLE 5

The local molecular stereochemistries of some distorted five coordinate copper(II) complexes using the atom numbering of Fig. 6

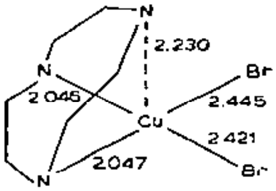
	$r(\mathrm{CuL}_1)$ (Å)	$r(\mathrm{CuL}_2)$ (Å)	$r(\mathrm{CuL}_3)$ (Å)	$r(\mathrm{CuL}_4)$ (Å)	$r(\mathrm{CuX}_5)$ (Å)	α_1	α_2	α_3	Struct. Route [a]	Ref.
[Cu(3,6-NH-od)(NCS)][ClO$_4$]	1.98	2.08	1.98	2.10	2.12	99°	116°	144°	A	[138]
[Cu(3,6-NH-od)(NCS)][ClO$_4$] 2nd chromophore	2.07	1.98	2.04	2.05	2.19	107°	105°	147°	A	[138]
[Cu(Ni2Mepn)$_2$(NO$_2$)][NO$_2$]	2.13	2.08	1.99	2.16	2.05	133.8°	127.1°	99°	B (or C)	[139]
[Cu$_2$(tren)$_2$(bzd)][NO$_3$]$_4$	2.04	2.04	2.06	2.11	2.03	135°	114°	108°	B (or C)	[140]
[Cu$_2$(tren)$_2$(bzd)][NO$_3$]$_4$ 2nd chromophore	2.03	2.06	2.06	2.14	2.02	136°	114°	106°	B (or C)	[140]
[Cu$_2$(tren)$_2$(bzd)][NO$_3$]$_4$ 3rd chromophore	2.04	2.04	2.06	2.13	2.04	132°	118°	107°	B (or C)	[140]
[Cu$_2$(tren)$_2$(bzd)][NO$_3$]$_4$ 4th chromophore	2.03	2.04	2.04	2.18	2.03	141°	111°	105°	B (or C)	[140]
[Cu(Hbim)$_2$(NO$_3$)][NO$_3$] · H$_2$O	1.96	2.05	1.95	2.28	2.06	158°	91°	111°	B (or C)	[141]

[a] See Fig. 6. 3,6-NH-od = 3.6-diazo-1,3-diaminooctane; Ni2Mepn = *N*-isopropyl-2-methyl-1,2-diaminopropane; Hbim = benzimidazol-2-ylmethanol.

and associated with the route A mechanistic pathway of the Berry Twist, {Fig. 6}. In the unit cell of μ-(*N*-salicylidene-L-valinato-*O*)-*N*-salicylidene-L-valinatodiaquadicopper(II) [147], there are two different copper(II) stereochemistries, a rhombic coplanar $\{CuNO_3\}$ and a square pyramidal $\{CuNO_3O'\}$, with the fifth ligand of the latter forming the bridging ligand (oxygen carboxylate). The elongated rhombic octahedral stereochemistry occurs in poly-bis(thiocyanato-*N*)bis-μ-(1,2,4-triazole-N^2,N^4)copper(II) [148] with the triazole ligand acting as a bridging ligand rather than the thiocyanate, and in (*N*-picolinylidene-*N'*-salicyloylhydrazinato)(*N*-picolinylidene-*N'*-salicyloylhydrazine)copper(II) perchlorate [149] rather than square pyramidal, as suggested. The two complexes *N*,*N*-methylethylenebis(*N*-methylcarbamylglycinato)copper(II) dihydrate and *N*,*N'*-ethylethylenebis-(*N*-methylcarbamylglycinato)copper(II) dihydrate [150], both $\{CuN_2O_4\}$ stereochemistries, are elongated rhombic with the ligand hexadentate and the two water molecules present as lattice waters; a situation that contrasts with the pentadentate function of H_2edta in $[Cu(H_2edta)(H_2O)]$ [151] with the water coordinated to the copper(II) ion. Probably the most regular square pyramidal stereochemistry occurs in iodo[difluoro{3,3'-(trimethylenedinitrilo) bis(2-butanone oximato)}borato]copper(II) [152] (21) with



(21) [CuI(cyclops)]



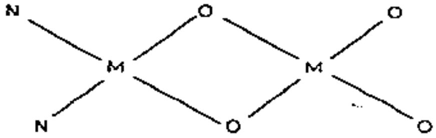
(22) $[Cu(\{9\}anN_3)Br_2]$

the copper(II) lifted 0.38 Å out of the plane of the four nitrogen ligands. In contrast, the structure of dibromo(1,4,7-triazacyclononane)copper(II) [153] (22) involves a very distorted square pyramidal stereochemistry due to the cyclic tridentate ligand. From the use [29] of X-ray scattering measurements on ammoniacal solutions of $CuCl_2 \cdot 2\ H_2O$, evidence for a $[Cu(NH_3)_4(OH_2)_2]^{2+}$ cation is obtained, with Cu—N and Cu—O bond distances of 2.03 and 2.33 Å, respectively. At higher ammonia concentrations, a higher ammine complex is formed with the inplane Cu—N distance of 1.93 Å and with apices of the octahedron occupied by either ammonia or water at a distance of 2.3 Å, in contrast to the pentaammine that is believed to occur in the solid state [1]. In this respect, the recent [154] characterisation of $[Cu(NH_3)_6][SO_4] \cdot NH_3$ is of interest, although no structural data were provided.

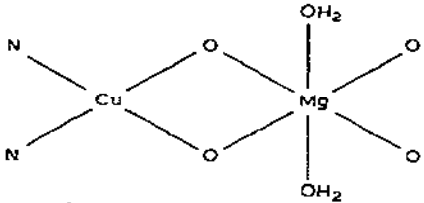
6.3.6 Macrocyclic chemistry

While the kinetic [155] and thermodynamic data of small molecules [156] have been reported, the use of macrocyclic ligands has produced a wealth of data [157], including crystallographic. Using potentially tetradentate macrocyclic ligands, not only pseudo-tetrahedral stereochemistries are obtained as from propanone and bis(1,4-diaminobutane)copper(II) perchlorate [158], but also square-based pyramidal, [Cu{(difluoro-3,3′-(trimethylenedinitrilo)bis(2-butanoneoximate)borate}(H_2O)}][ClO_4] [159] and nitrato(1,4,7,10-tetraazacyclododecane)copper(II) nitrate [160], in which a molecule of water and nitrate ion, respectively, fill the fifth coordination positions. This situation makes it rather difficult to predict the stereochemistry in these complexes if only stoicheiometry or even spectroscopic data are used, especially if potentially semi-coordinate anions are present that can increase the coordination number to six as in (C-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-aza-cyclotetradecane)copper(II) perchlorate [161] and (1,4,8, 12-tetra-azacyclopentadecane)copper(II) perchlorate [162]. The use of pentadentate [163,164] or hexadentate [165] ligands makes it easier to predict a five-coordinate stereochemistry, but even here the choice is between square pyramidal and trigonal bipyramidal, with square-based distorted trigonal bipyramidal stereochemistries also occurring (routes A and B, Fig. 6). The relatively weak complexing ability of crown ethers is nicely illustrated in 1 : 1 pentaoxa-1,4,7,10,13-cyclopentadecanedibromocopper-(II)dihydrate [166], where the ether is uncoordinated to the copper(II). The field of copper(II) macrocyclics has attracted studies of preparative [167], kinetic, thermodynamic [168] and redox properties as a function of chelate ring size and sequence. The plasticity effect has also been recognised in the blue and red forms of [CuL][ClO_4]$_2$ [161].

Routes to the synthesis of homo- and hetero-dinuclear macrocyclic copper(II) complexes have been reviewed [169] along with the known stereochemistry, magnetism and spectra. In general, using the notation discussed elsewhere [169], the homonuclear diatomic species {$CuN_2O_2CuO_4$} (23) are

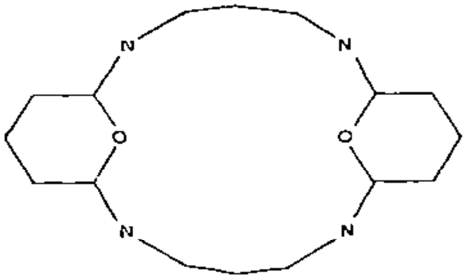


(23) {$CuN_2O_2CuO_4$}

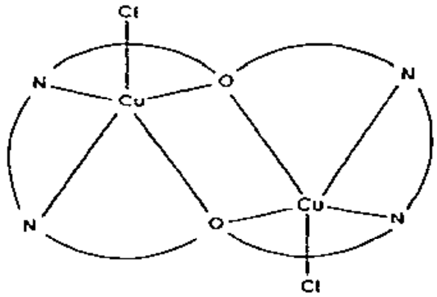


(24) {CuMg(fsaen)} 3 H_2O; fsaen = base from reaction of 1,2-diaminoethane with 3-formylsalicyclic acid

square pyramidal by dimerisation and the close approach of the copper(II) atoms results in an antiferromagnetic ordering, which reduces the magnetic moment to $\mu_{eff} \approx 1.0\ \mu_B$. Hetero-dinuclear species such as {$CuO_2N_2LiO_4$} involve both the {CuO_2N_2} and {LiO_4} in a rhombic coplanar stereochemistry, but if the Li is replaced by magnesium(II), two molecules of water are added and the magnesium assumes a rhombic octahedral stereochemistry (24). Both complexes are red, but the replacement of the magnesium(II) by barium(II) results in a shift in wavelength of the band maximum from 515 nm to 568 nm, presumably due to the distortion of the rhombic coplanar $\{CuO_2N_2\}$ chromophore by the different-sized magnesium and barium $\{MO_6\}$ octahedra. Heteronuclear complexes have been reported for the Schiff base of 1,2-diaminoethane and 3-formylsalicyclic acid, with a comparable chromophore $\{CuN_2O_2MgO_4(OH_2)_2\}$ [170], compared with the equivalent dimer in bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)magnesium-*N,N'*-ethylenebis(salicylidineaminato)copper(II) [171]. The geometry [172] of the ligand (25) is such that with $CuCl_2$ a symmetrical homonuclear diatomic species (26) is formed with a square-based pyramidal stereochemistry in which

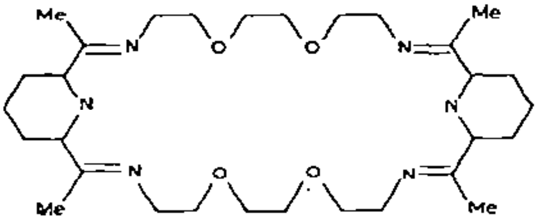


(25) 1,3-diaminopropane + 2-hydroxy-5-methyl-isophthaldehyde



(26) $[Cu_2Cl_2\{(25)\}]$

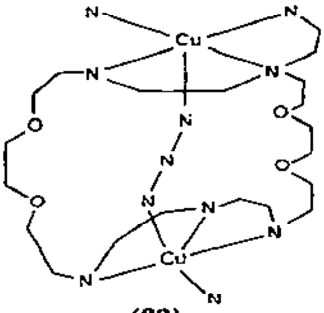
strong antiferromagnetic coupling reduces the magnetic moment to 0.6 μ_B, and which yet has a normal EPR spectrum with $g_\parallel = 2.24$ and $g_\perp = 2.06$. Using the larger ring system such as (27) [173], yields a complex $[CuL(N_3)]$-



30-membered macrocycle

(27)

$[ClO_4]$ in which the ligand folds to allow bridging by the $[N_3]^-$ anion (see also [174]), and the formation of two independent $\{CuN_5\}$ chromophores with a distorted square pyramidal stereochemistry (28) by Route A, (Fig.

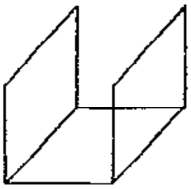


$[Cu_2\{(27)\}(N_3)_2][ClO_4]$

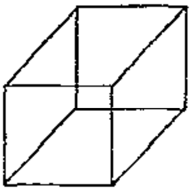
(28)

6) and no coordination by the ligand oxygen atoms.

Four tetranuclear copper(II) complexes have been reported having the cubane Cu_4O_4 nucleus; two, 2-diethylaminoethanolato(trichloroacetato)copper(II) tetramer [175] and tetrakis{chloroacetato-μ-(2-dienethylaminoethanolato) copper(II)} [176], have the open cubane structure (29) and one,

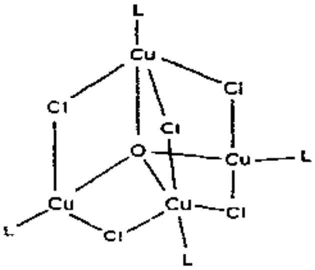


(29) Open cubane



(30) Closed cubane

{2-{(3-aminopropyl)amino}ethanolato} copper(II) tetramer sulphate octahydrate [177], has the closed cubane structure (30). Cu_4OCl_6(*N*-methyl-2-pyrrolidine)$_3$ (H_2O—*N*-methyl-2-pyrrolidine) [178] has a central μ_4-oxide ion (31) surrounded tetrahedrally by four copper atoms, the six Cl^- ions are



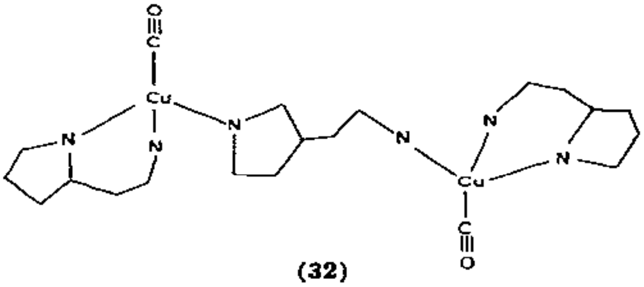
(31)

$Cu_4OCl_6(nmp)_3(OH...mmp)$

involved in μ_2 bridging of the Cu—Cu pairs and the four coordination of the Cu atoms is made up by *N*-methyl-2-pyrrolidine ligand.

6.4 COPPER(I) CHEMISTRY

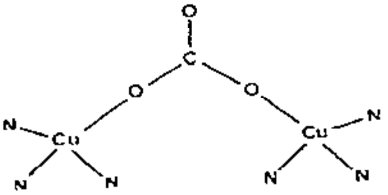
There is still a significant emphasis on preparation of copper(I) complexes. The reaction of copper(I) halides in pyridine with 4-benzoquinone gives the diamagnetic adduct [{CuX(py)}$_2$ · $C_6H_4O_2$] [179], and of the series of twenty-one poly(pyrazolyl)borate [180] complexes of copper(I), most involve four coordinate copper(I). However, the bis(pyrazolyl borate) complexes are formally three coordinate. Equilibrium binding constants have been reported [181] for [Cu^I (macrocyclic)] four-coordinate to [Cu^I(macrocyclic)L] five-coordinate complexes, where L is a monodentate ligand such as an isocyanide, phosphite, carbon monoxide or phosphine. The preparation [182] and infrared spectra of [Cu(CO)] [AsF_6] and [Cu(PF_3)] [AsF_6] have been reported and shown to have the highest CO stretch (2180 ± 5 cm^{-1}) yet reported. A composition [183] and equilibrium study of the $Cu^I(CO)Cl$ system has been reported. A spectrophotometric [184] investigation of the reduction of the $[Cu(bipy)_2(H_2O)_x]^{2+}$ cation in aqueous solution has suggested a rather complex rate law with the equilibrium concentration of the copper(I) and copper(II) species very dependent on the initial oxygen present. The crystal structure of the mononuclear bis(2,9-dimethyl-1,10-phenanthroline)copper(I) nitrate [185] has been reported to involve a tetrahedral $\{CuN_4\}$ chromophore with ionic nitrate ions, while the copper(I)-histamine system has been reported [186] as a reversible carbon monoxide carrier and the complex $[Cu^I_2(histamine)_3(CO)_2][BPh_4]_2$ (32) has been shown to involve a coordinated CO group to four-coordinate copper(I) atoms. Interest in the redox properties of the copper(I)/copper(II) system continues with the crystal structure of the aquabis(1,2-diaminoethane)copper(II) dicyanodi(selenocyanato)cuprate(I) [187], involving a square pyramidal copper(II) chromophore and a tetrahedral copper(I).



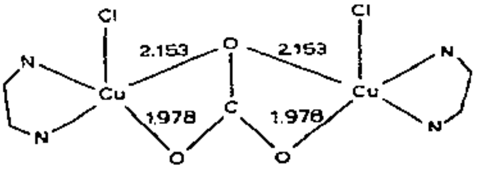
$[Cu_2(histamin)_3(CO)_2][BPh_4]_2$

(32)

The structure of chloro(2,4-dithiobiuret)copper(I)-*N*,*N*-dimethylformamide [188] involves a trigonal pyramidal CuS_2Cl with "long" Cu—S bond distances of 2.88 Å. Oxidation [189] of (1,3-bis{2-(4-methylpyridyl)imino}-isoindoline)(carbonyl)copper(I) yields two products, a carbonate-bridged species $[(CuL)_2(\mu\text{-}CO_3)]$ (33) which suggests direct oxygen addition to the coordinated CO groups, and a tetrameric species, $[(CuL)_3(CuLO)(\mu\text{-}OH)]$. The reaction [190] of *N*,*N*,*N'*,*N'*,-tetramethyl-1,3-diaminopropane with CuCl, CO and O_2 in anhydrous dichloromethane forms μ-carbonate-dichlorobis(*N*,*N*,*N'*,*N'*-tetramethyl-1,3-diaminopropane)dicopper(II) (34), a possible diamagnetic initiator for the oxidative coupling of phenols by oxygen. The

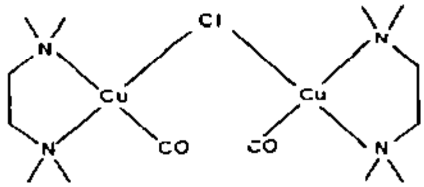


(33) $(CuL)_2(\mu\text{-}CO_3)$; L = 1,3-bis-{2-(4-methylpyridyl)imino}isoindoline

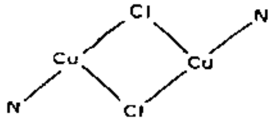


(34) $LCuCl(CO_3)ClCuL$; L = Me_4-1,3-pn

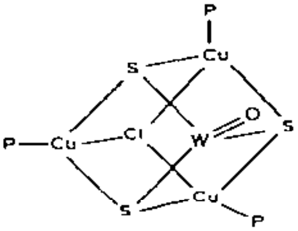
reaction [191] of copper(I) halides with CO in methanol with *N,N,N',N'*-tetramethyl-1,2-diaminoethane, but in the *absence* of air, produces a dinuclear copper(I) carbonyl (35) involving a single bridging Cl atom. In chloro(dipyramidin-2-yldisulphide)copper(I) monohydrate [192] (36) two short bonded chloride atoms occur as well as a centrosymmetric bridging dipyramidin-2-yldisulphide coordinating through nitrogen rather than sulphur. Using the macrocyclic ligand (25), homobinuclear species $Cu^{II}Cu^{II}$, $Cu^{II}Cu^{I}$ and $Cu^{I}Cu^{I}$ have been prepared [193] and their electrochemical and spectral properties reported. Both copper(I) species form stable carbon-monoxide addition compounds which are thought to involve five coordinate copper(I). The cubane-like geometry (30) has been confirmed for tetrameric (triphenylarsine)copper(I) iodide monobenzene [194], rather than the predicted step or chair structure. The crystal structure of $[\{Cu_3WS_3Cl\}(PPh_3)_3]$ [195] has been reported, and the structure is based upon a cubane $\{Cu_3WS_3Cl\}$ unit (37). Finally, using [196] the ligand 1,8-bis(pyridyl)-3,6-dithiaoctane (38; pdto), complexes of both copper(I) and copper(II) have been prepared. In $[Cu(pdto)][PF_6]$, a tetrahedral $\{CuN_2S_2\}$ chromophore is obtained, while in $[Cu(pdto)(ClO_4)][ClO_4]$, a square pyramidal $\{CuN_2S_2O\}$ chromophore is present, which suggests that the steric change accompanying electron transfer in copper(I) to copper(II) systems may account for some of the unique properties of the type I copper proteins. The dimeric structure [197] of (tricyclohexylphosphine)copper(I) chloride contrasts with the predicted tetrameric structure, while bis(tri-4-tolyphosphine)copper(I)oxotrithiotungsten [198] has a substituted cubane structure.



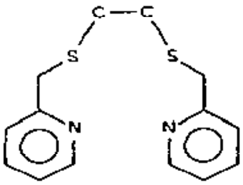
(35) $[Cu_2(tmen)_2(CO)_2Cl][BPh_4]$



(36) $[Cl(L)Cu]_n \cdot nH_2O$;
L = dipyrimidin-2-yl disulphide



(37) $[\{Cu_3WS_3Cl\}(PPh_3)_3O]$



(38) pdto

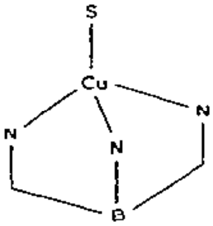
6.5 BIOLOGICAL COPPER

While the decade has been good for copper proteins, with the X-ray structure determination of plastocyanin [52] and azurin [53], 1979 has yielded no further refinement of these structures or data on new systems.

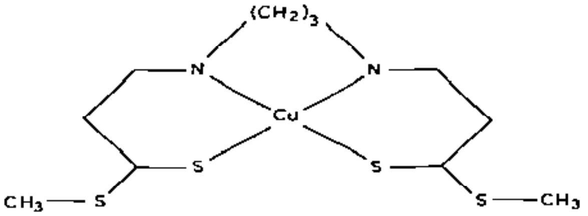
Spectroscopic studies of the blue copper proteins, such as *Rhus vernicifera* and *Polyporus versicolor* haccase [199a], show electronic bands in the near infrared region (electronic, CD and MCD spectroscopy) and EPR spectra that suggest a distorted tetrahedral $\{CuN_2SX\}$ environment, while spectra and chemical correlations [199b] of the dimer active sites of oxyhemocyanin suggest the presence of two tetragonal copper(II) atoms, bridged by a protein ligand and a linear peroxide. The rates and mechanism [200] of the copper(II) catalysed autooxidation of cytochrome *c*, myoglobin, and haemoglobin have been reported along with thermodynamic data on the electron transfer reactions of azurin, plastocyanin and stellacyanin [201]. An initial report [202] on the rate constants of the bonding sites in the redox reactions of the blue copper proteins with inorganic complexes and their variation with concentration has been published. In the use of copper(II) species as a spectroscopic probe in biological systems or simulated systems, thermodynamic studies of the copper(II) transport site of human serum albumin [203] are reported, along with the EPR and ^1H NMR spectra on the interaction [204] of copper(II) ions with ribonuclease A. Copper(II) interactions [205] with thermolysin (replacement of bound zinc(II) ions) have been followed by EPR and electronic spectral studies, while the interaction [206] with the guanosine-5-dihydrogen phosphate system suggests that there are two sets of magnetically coupled copper(II) ions. However, the EPR data only indicate that the coupling is antiferromagnetic, and yield no information on the structure. Catalysis of the system CO_2—HCO_3^- has been examined [207] in the presence of copper(II)-substituted bovine carbonic anhydrase B. The potentiometric and spectrophotometric studies [208] of the copper(II) complexes in aqueous solutions of methyldopa, methyllyrosine and catechol, as a quartenary system, has been optimistically studied, but not withstanding detailed computer simulation of the data, seems to be too complicated to produce convincing results. Absorption, CD and resonance Raman spectra of the copper(II)/poly(L-glutamic, L-tyrosine) [209] is more informative, yielding evidence for PhO^- anion coordination. The *cis*- and *trans*-isomers of bis(glycinato)copper(II) [210] have been examined by a novel thermal isomerisation in which the *cis*-monohydrate rehydrates to give the *trans*-monohydrate.

The single crystal polarised electronic spectra of bis(L-tyrosinato)copper(II) [211] have been reported and compared with the electronic and CD spectra in the powder and in solution. The EPR, ENDOR, CD and MCD spectra of ^{63}Cu doped cobalamin [212] has been interpreted in terms of a square coplanar $\{CuN_4\}$ chromophore with electronic energies of ca. 40 000 cm^{-1}, a value which seems totally at variance with any previous data on this stereochemistry [127]. A very nice study [213] of the spectroscopic and redox properties of the copper(II) ion in complexes using macrocyclic ligands involving sulphur atoms, including a single crystal study of Cu^I(thioacetamide)Cl subjected to γ-radiation at 77° K, suggests a possible correlation between the $g_{\parallel}$ and $A_{\parallel}$ values for tetrahedrally distorted square coplanar systems. The preparations of a series of copper(II) complexes containing penicillamine [214] and of histidine-containing binary amino acid—copper(II) complexes [215] have been reported.

Pride of place in the preparation of copper(II) complexes which attempt to simulate the electronic properties and structure of the copper sites of the blue proteins in the 1979 literature must go to the crystal structure of potassium 4-nitrobenzenethiolato(hydrotris(3,5-dimethyl-1-pyrazolyl)borato)-cuprate(I) diacetone [56], which has a trigonally distorted tetrahedral $\{CuN_3S\}$ stereochemistry (39). This paper contains a nice balance of preparative, crystallographic and spectroscopic (electronic, Raman and EPR spectra) techniques, which only in the final piece of data, the high numerical value of the $A_{\parallel}$-value (ca. 170×10^{-4} cm^{-1}) fails to simulate the properties of the type I copper sites of the blue proteins. The crystal structure and electronic properties [57] of the twisted *cis*-$\{CuN_2S_2\}$ chromophore (40) of {*N,N'*-trimethylenebis(methyl-2-amino-1-cyclopentenedithio)carboxylato} copper(II) also make interesting reading.



(39) K[Cu{HB(3,5-Me$_2$pz)$_3$}(SR)]



(40) Cu(mercaptobenzaldemine)

Finally, mention must be made of the technique EXAFS (extended X-ray absorption fine structure) [216], which yields information on the environment of the copper(II) ion in complexes, in biological systems and potentially, at least, in complexes absorbed on silica, alumina and in zeolites. It yields information on the type of ligand atoms present (i.e. nitrogen or sulphur) and their bond distances, but not, unfortunately, the bond angles. Nevertheless, this technique looks highly promising as a qualitative probe of the environment of the copper(II) ion in biological systems for comparison with model complexes, whose structures *can* be determined by X-ray crystallography, if their EXAFS spectra appear comparable to that of the biological system. EXAFS spectroscopy looks an attractive new technique in copper(II) chemistry comparable to Mössbauer spectroscopy in iron chemistry, and has already been used [217] to distinguish between two possible structures for $CuC_2O_4 \cdot 1/3\ H_2O$.

6.6 THE NEXT DECADE: 1980—1989

The next decade should yield more crystallographic structures of biological copper systems, to increasing accuracy, along with the characterisation of model complexes which simulate the structure and electronic properties of the copper proteins.

X-ray crystallography should proceed apace, with increasing use of low temperature structure determination of fluxional systems and neutron diffraction structure determination, to increase the definition of the hydrogen positions.

Improved computer facilities should provide the ability to carry out semiempirical calculations of the copper(II) ion in various stereochemistries, and even ab initio calculations involving an increasing number of ligand atoms.

The increasing availability of EXAFS facilities should provide structural information, not only on biological copper systems and synthetic model complexes, but also on copper(II) complexes diluted in diamagnetic host lattices or absorbed on silica gel or ion exchanged on zeolite structures. This will yield bond length data on the geometry of the doped copper(II) species for correlation with the accurate EPR data available from copper(II) doped systems. The use of EXAFS spectra measured over a temperature range could also yield structural information on potentially fluxional copper(II) systems comparable to low-temperature X-ray structure determination.

Improved techniques for measuring redox systems should yield more information on the kinetics of the copper(I)/copper(II) and copper(II)/copper(III) couples and further the understanding of the role of biological copper in vivo.

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