Spectroscopic and Redox Studies of Some Copper(II) Complexes with Biomimetic Donor Atoms: Implications for Protein Copper Centres

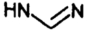
By **Ushio Sakaguchi** and **Anthony W. Addison**,*† Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1W5

The redox chemistry and e.s.r. spectra of a number of copper(II) complexes with nitrogen- and sulphur-donor ligands have been examined, including complexes with 2,2'-bi-imidazole, histamine, and cyclic and acyclic saturated amine and thioether ligands. The tetrahedral $Cu^{II}S_4$ centre generated by γ-irradiation of single crystals of a thioacetamide complex of Cu^I has a low value of $|A_{\parallel}|$. Tetrahedral distortion of otherwise tetragonal copper(II) centres increases $g_{\parallel}$ and decreases $|A_{\parallel}|$ for *N*-, *S*-, and *O*-donor ligands, and is a more effective source of reduction of $|A_{\parallel}|$ than charge effects. The quotient $g_{\parallel}/|A_{\parallel}|$ appears to be a convenient empirical index of distortion of the donor set from planar toward tetrahedral, indicating that most type I copper in proteins is tetrahedrally, rather than tetragonally, co-ordinated.

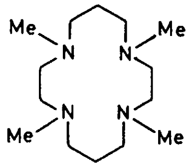
THE so-called 'blue' (type I) copper proteins have attracted much interest recently. The active sites of this group of proteins exhibit anomalous spectroscopic and redox properties that common copper(II) compounds of low molecular weight have seldom evinced.[1] Namely, (*i*) an intense blue colouration; the visible absorption spectra in the 600 nm region have ε values ranging from 1 000 to 5 000 dm^3 mol^{-1} cm^{-1}, which are *ca.* 50 times larger than those for ordinary low-molecular-weight copper(II) complexes; (*ii*) anomalously small copper nuclear hyperfine (h.f.) coupling constants in the e.s.r. spectra, $|A_{\parallel}|$ values being $<$ *ca.* 90×10^{-4} cm^{-1}; (*iii*) rather high reduction potentials.

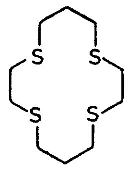
Chemical modification [2] and spectroscopic examinations [3-5] of blue copper proteins indicated the participation of nitrogen (histidine imidazole) and sulphur (cysteine and/or methionine) donors to Cu^{II}. In the case of oxidised *Populus nigra italica* plastocyanin these lines of reasoning have culminated in the *X*-ray crystallographic demonstration of a pseudo-tetrahedral CuN_2S_2 chromophore.[6] On the other hand, the recent results of Rorabacher and his co-workers [7] appeared to point to the irrelevance of the co-ordination geometry as a prime prerequisite in generating the spectroscopic and redox properties of these proteins. Indeed, for individual examples within this class of proteins, the geometrical structures (necessarily idealised) proposed recently for the copper(II) state of their active sites are rather diverse, including planar,[8] trigonal bipyramidal,[4] five-co-ordinate,[9] and distorted [10] as well as flattened or pseudo-tetrahedral.[11] The diversity of the above models results mainly from the paucity of e.s.r. data for copper(II)–sulphur complexes, especially for those with tetrahedral structures; in particular, the origin of the anomalously small h.f. coupling constants of this group of proteins is as yet uncertain. In view of this situation, it appeared most pertinent to investigate the e.s.r. properties of copper(II)–sulphur complexes having tetrahedral and square-planar structures.

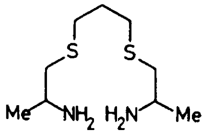
We have thus examined the e.s.r. spectra of a number of complexes, including those of the ligands below, containing Cu–S and Cu–N linkages, and compared them to copper proteins, particularly those of type I. Specifically, we obtained the single-crystal e.s.r. spectra of Cu^{II}–S_4 centres having a (flattened) tetrahedral structure, $[Cu(ta)_4]^{2+}$ (ta = thioacetamide), and the e.s.r. spectra of the other complexes above containing Cu^{II}–S bonds. We also report on the redox chemistry of several of these complexes.

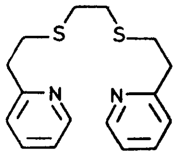

hist


H_2bim


Me_4cyclam


tctd


atu


pdto

EXPERIMENTAL

Materials.—*2,2'-Bi-imidazole* (*'glycosine,'* H_2bim). This was prepared by a modification of Debus's procedure.[12] 20% Aqueous glyoxal (0.6 l) was added, over 1 h, with stirring, to concentrated aqueous ammonia solution (2.1 l). After 12 h, the crystalline precipitate was filtered off, dried at 110 °C, recrystallised (charcoal) from 2-methoxyethanol, and dried *in vacuo* over P_4O_{10}, yield 3 g (3%) (Found: C, 53.9; H, 4.45; N, 41.5. Calc. for $C_6H_6N_4$: C, 53.7; H, 4.50; N, 41.8%).

1,4,8,11-*Tetrathiacyclotetradecane* (tctd). This was prepared by the method of Travis and Busch [13] from 3,7-dithianonane-1,9-diol, which was synthesised by the reaction of 1,3-dibromopropane with 2-mercaptoethanol.[14] The copper(II) complexes of tctd were obtained from the appropriate copper salts and tctd in nitromethane contain-

---

† *Present address:* Chemistry Department, Drexel University, Philadelphia, PA 19104, U.S.A.

ing acetic anhydride[15] {Found: C, 22.7; H, 3.75. Calc. for [Cu(tctd)][ClO$_4$]$_2$: C, 22.6; H, 3.80. Found: C, 23.1; H, 4.25. Calc. for [Cu(tctd)][BF$_4$]$_2$·H$_2$O: C, 22.9; H, 4.25%}. The blue hydrated tetrafluoroborate salt of [Cu(tctd)]$^{2+}$ was dried at 100 °C *in vacuo* for 6 h to yield the brown anhydrous salt {Found: C, 23.7; H, 3.90. Calc. for [Cu(tctd)][BF$_4$]$_2$: C, 23.8, H, 4.00%}.

The nickel complex [Ni(tctd)][BF$_4$]$_2$ was also prepared by the literature method.[15]

The nitrogen-ligand complexes were prepared by allowing copper(II) nitrate trihydrate to react with the free base in appropriate proportions (5% excess) in hot aqueous solution. If necessary, the solution was filtered before the complex was crystallised by the addition of Na[ClO$_4$] or K[PF$_6$], filtered off, and dried *in vacuo* over P$_4$O$_{10}$. The complexes with 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (Me$_4$cyclam), histamine [4-(2-aminoethyl)-imidazole, hist], 1,2-diaminoethane(en), and H$_2$bim were prepared this way {Found: C, 27.0; H, 2.35; N, 21.0. Calc. for [Cu(H$_2$bim)$_2$][ClO$_4$]$_2$, $C_{12}H_{12}Cl_2CuN_8O_8$, green prisms: C, 27.2; H, 2.30; N, 21.1. Found: C, 28.1; H, 5.85; N, 10.2. Calc. for [Cu(Me$_4$cyclam)][PF$_6$]$_2$, $C_{14}H_{32}CuF_{12}N_4P_2$, indigo prisms: C, 27.6; H, 5.30; N, 9.20. Found: C, 24.5; H, 3.75; N, 17.4. Calc. for [Cu(hist)$_2$][ClO$_4$]$_2$, $C_{10}H_{18}Cl_2CuN_6O_8$, violet crystals: C, 24.8; H, 3.75; N, 17.3%}.

Tetrakis(N-*methylimidazole*)*copper*(II) *perchlorate*, [Cu(mim)$_4$][ClO$_4$]$_2$, was prepared as above, but in methanol, as violet crystals (Found: C, 32.1; H, 4.10; N, 19.2. Calc. for $C_{16}H_{24}Cl_2CuN_8O_8$: C, 32.5; H, 4.10; N, 19.0%).

Bis(2,5-dithiahexane)copper(II) tetrafluoroborate, [Cu(dth)$_2$][BF$_4$]$_2$, and dichloro(2,5-dithiahexane)copper(II) were gifts from Dr. E. W. Ainscough.[16] Dr. B. Bosnich provided samples[5] of [Cu(atu)][ClO$_4$]$_2$ and [Cu(pdto)][ClO$_4$]$_2$.

1,1′-Dimethyl-4,4′-bipyridylium bis(hexafluorophosphate) for use as an electrochemical standard in non-aqueous solution was prepared by simple metathesis of the dichloride salt in aqueous solution. The white prisms were dried *in vacuo* over P$_4$O$_{10}$ (Found: C, 30.6; H, 2.90; N, 5.85. Calc. for $C_{12}H_{14}F_{12}N_2P_2$: C, 30.3; H, 2.95; N, 5.90%).

2-Mercaptoethanol, di-*p*-tolyl disulphide, methyl phenyl sulphide (thioanisole), and 1,3-dibromopropane were obtained from Aldrich Chemical Co. Glyoxal, copper(II) nitrate, and 1,2-diaminoethane were purchased from Mallinckrodt, histamine and 1,1′-dimethyl-4,4′-bipyridylium dichloride from Sigma Corp., copper(II) perchlorate from Fluka A.G., and Me$_4$cyclam from Strem Chemicals. Solvent nitromethane and acetonitrile were distilled under N$_2$ before use for e.s.r. spectroscopy or electrochemistry, the latter compound from P$_4$O$_{10}$. Single crystals of tetrakis-(thioacetamide)copper(I) chloride, prepared according to Cox *et al.*,[17] were grown by slow evaporation from an ethanol solution.

γ-Irradiation.—Single crystals of [Cu(ta)$_4$]Cl were γ-irradiated at liquid-nitrogen temperature with a dosage of 3×10^6 R* using a ^{60}Co source of 1.4×10^5 R h^{-1} and transferred immediately to a liquid-nitrogen Dewar for e.s.r. measurements. Crystallographic axes and planes were identified by an *X*-ray technique. The angular variation of the *g* and *A* values was analysed by the method of least squares to obtain the principal axes and values of the *g* and *A* tensors.

Physical Measurements.—Absorption spectra were recorded on a Cary-14 spectrophotometer at ambient temperatures, e.s.r. spectra (usually with the complex at $\leqslant 5 \times 10^{-3}$ mol dm^{-3} in nitromethane) with a Varian E-3 *X*-band spectrometer calibrated with diphenylpicrylhydrazyl and an n.m.r. probe. Cyclic voltammetry and polarography at a platinum-disc (0.300 cm^2) electrode were performed (at 25 ± 0.2 °C in solutions deoxygenated by bubbling nitrogen or argon) using a PAR-173 potentiostat and PAR-176 *i*/*E* converter. Voltammetric data were recorded on a storage oscilloscope or *X*–*Y* recorder. The three-electrode cell included as the reference an Ag(s)|Ag[ClO$_4$] (0.01 mol dm^{-3}), [NEt$_4$][ClO$_4$] (0.1 mol dm^{-3}), MeCN electrode. We have measured this to be 0.30 V positive of the saturated calomel electrode (s.c.e.) in acetonitrile at 25 °C, and all potentials are thus referred to the s.c.e. Tetraethylammonium perchlorate was G. F. Smith polarographic grade, recrystallised from water and dried *in vacuo* over P$_4$O$_{10}$ before being used as the supporting electrolyte.

RESULTS

E.S.R. Spectra.—In contrast to γ-irradiated [Cu(NCMe)$_4$][BF$_4$],[18] the γ-irradiated single crystals of [Cu(ta)$_4$]Cl did not show any recognisable colour change. An example of the spectra is shown in Figure 1, in which the magnetic field is applied parallel to the crystallographic *c* axis. The lowest-field h.f. lines are characteristically split, due to the two copper isotopes (^{63}Cu and ^{65}Cu), and the high-field part of the spectra is dominated by large absorptions, which are most likely to be due to organic radical species, so that we could not observe the angular variation of high-field copper h.f. lines over the whole angular range of crystal rotation. The angular variation of each absorption line is given in Figure 2, where we note that two kinds of copper(II) species having different magnetic parameters and absorption intensities are produced. The magnetic parameters for both species, obtained by a least-squares method, are listed in Table 1. For both species the principal axes of the *g* and *A* tensors coincided and both tensors were axially symmetric. The dominant species have their g_z and A_z axes parallel to the *c* axis.

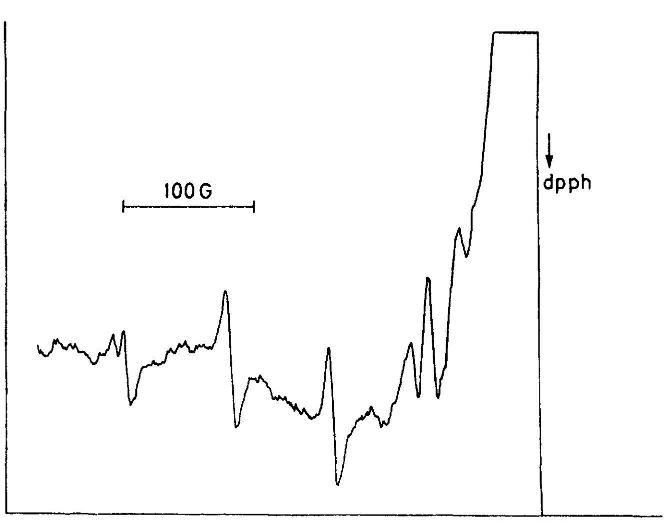


FIGURE 1 E.s.r. spectrum at 77 K of a γ-irradiated single crystal of [Cu(ta)$_4$]Cl with the static magnetic field along the *c* axis; dpph = diphenylpicrylhydrazyl

---

* Throughout this paper: 1 R = 2.58×10^{-4} Ci kg^{-1}; 1 G = 10^{-4} T; 1 Faraday ≈ 9.65×10^4 C; 1 atm = 101 325 Pa.

The frozen-glass e.s.r. spectrum of the macrocycle [Cu(tctd)][ClO$_4$]$_2$ is typical of most copper(II) complexes and was analysed without second-order corrections. The results are in Table 1.

TABLE 1

E.s.r. results for the complexes [a]

Species		g_1	$g_\perp$	g_2	$g_\parallel$ (g_3)	A_1	$A_\perp$ [b]	A_2	$A_\parallel$ (A_3)	A_0	g_0
[Cu(ta)$_4$]$^{2+}$	Major	2.027		2.027	2.152	24		24	87 [c]		
	Minor	2.034		2.034	2.080	35		35	69 [d]		
[Cu(tctd)][BF$_4$]$_2$	Solution [e]		2.032		2.099		37		161		
[Cu(tctd)][ClO$_4$]$_2$	Solution [e]		2.037		2.085		36		165	79	1.053
[Cu(dth)$_2$][BF$_4$]$_2$	Powder	2.029		2.041	2.099						
	Solution [e]		2.031		2.122		33		154	73	2.061
[Cu(atu)][ClO$_4$]$_2$	Solution [e]		2.042 [f]		2.155		35		183	84	2.078
[Cu(pdto)][ClO$_4$]$_2$	Solution [e]		2.052 [f]		2.164		24		174	74	2.087
[Cu$_2$(H$_2$bim)$_2$][ClO$_4$]$_2$	Solution [e,g]		2.060 [f]		2.262		13		176	67	2.129
[Cu(mim)$_4$][ClO$_4$]$_2$	Solution [e]		2.055		2.256		35		192	87	2.122
[Cu(hist)$_2$][ClO$_4$]$_2$	Solution [e]		2.048		2.227		23		195	78	2.114
[Cu(en)$_2$][ClO$_4$]$_2$ [h]	Solution [e]		2.047		2.206		30		205	88	2.100
[Cu(Me$_4$cyclam)][PF$_6$]$_2$	Solution [e]		2.049		2.215		25		175	75	2.104

[a] *Via* simple first-order spectral analysis. [b] h.f. coupling constants in 10^{-4} cm^{-1}, all as $|A|$. [c] The g_3 and A_3 axes coincide with crystal *c* axis. [d] Two sites: the crystal *c* axis coincides with g_1, and A_i and g_i coincide for both sites, while the *a* and *b* axes coincide with g_2 and g_3 or g_3 and g_2, respectively. [e] In MeNO$_2$ at 77 and *ca.* 300 K. $A_\perp$, $g_\perp$ estimated *via* $3A_0 = 2A_\parallel$ and $3g_0 = 2g_\perp + g_\parallel$, using $g_\parallel$, $A_\parallel$ at 77 K and g_0, A_0 at 300 K, except when otherwise noted. $A_\parallel \pm 0.001$ cm^{-1}, $g_\parallel \pm 0.002$. [f] $g_\perp$ estimated from central feature of superhyperfine structure at 77 K. [g] Containing 10% MeOH. [h] W. R. McWhinnie, *J. Inorg. Nuclear Chem.*, 1964, **26**, 21.

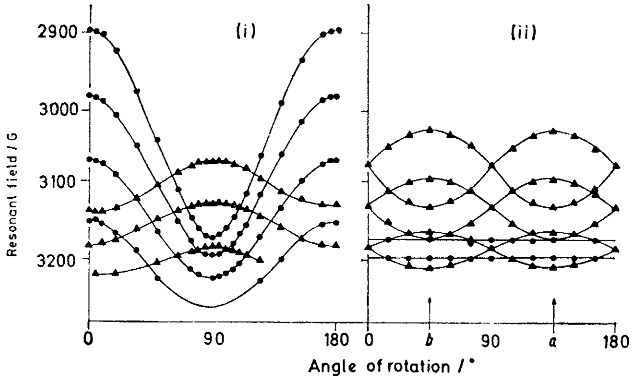


FIGURE 2 Angular variation of absorption lines of a γ-irradiated single crystal of [Cu(ta)$_4$]Cl. (*i*) Rotation about the (±110) axes; 0 and 180° correspond to the *c* axis. (*ii*) Rotation about the *c* axis. ● and ▲ represent the h.f. lines due to the dominant and the minor species, *a* and *b* are the crystallographic axes

The powder e.s.r. spectrum of [Cu(dth)$_2$][BF$_4$]$_2$ is presented in Figure 4. Clearly, the spectrum is lower than axially symmetric. More interestingly, while no splitting due to copper nuclear spins is apparent, the three peaks corresponding to g_x, g_y, and g_z are clearly resolved and the g_z linewidth is surprisingly small, approximating to 9 G (full width at half-height in the derivative spectra). The spectrum does not change appreciably with temperature over the range 4—300 K, and the g_z resonance maintains its appearance in both the *X*- and *Q*-band regions. This line narrowing appears to be the result of an electron-exchange process in the crystal. The frozen-glass e.s.r. spectra of [Cu(atu)][ClO$_4$]$_2$ and [Cu(pdto)][ClO$_4$]$_2$ (Figure 3), similar to that of [Cu(tctd)]$^{2+}$, are characterised by the parameters given in Table 1.

Amongst the *N*-donor complexes, one notes that the values of $A_\parallel$ and *g* are not greatly altered by the configuration of the donor imidazole rings. These must be almost coplanar with the copper in [Cu(H$_2$bim)$_2$]$^{2+}$, whereas they are canted 36 and 61° out of the CuN$_4$ plane in the analogous imidazole complex, [Cu(imH)$_4$][ClO$_4$]$_2$.[19] There is some difference in the appearance of the nitrogen superhyperfine structure on the $g_\perp$ region of the spectra. In the Me$_4$cyclam complex it is very poorly resolved, but $|A_\parallel(\text{N})|$ is *ca.* 15 × 10^{-4} cm^{-1} in all the compounds where it is resolved, namely those containing heteroaromatic nitrogen.

TABLE 2

Redox properties of the complexes

Species	Solvent [a]	E [b]/(V)	Process	$10^{10}D$/[c] m^2 s^{-1}
[Ni(tctd)]$^{2+}$	MeNO$_2$	−0.28	Ni^{II} → Ni^0	4.4
[Cu(tctd)]$^{2+}$	MeNO$_2$	0.55	Cu^{II} → Cu^I	5.6
	MeCN	0.61	Cu^{II} → Cu^I	9.2
		−0.69	Cu^I → Cu^I	
[Cu(dth)$_2$]$^{2+}$	MeCN [d]	0.75 [e]	Cu^{II} → Cu^I	
		−1.4	Cu^I → Cu^0	
		1.6	$n = 2$	
[Cu(dth)Cl$_2$]	MeNO$_2$	0.51 [e]	Cu^{II} → Cu^I	5.3
		−1.4	Cu^I → Cu^0	
[Cu(atu)]$^{2+}$	MeCN	−0.06	Cu^{II} → Cu^I	10
		−0.83	Cu^I → Cu^0	
		1.23	$n = 1$	
[Cu(pdto)]$^{2+}$	MeCN	0.38	Cu^{II} → Cu^I	9.9
		−0.78	Cu^I → Cu^0	
		1.5	$n > 2$	
[Cu(Me$_4$cyclam)]$^{2+}$	MeCN	−0.32 [f]	Cu^{II} → Cu^I	8.8
		−0.97	Cu^I → Cu^0	
		1.88	$n = 2$	
[Cu(mim)$_4$]$^{2+}$	MeNO$_2$	0.15	reduction	
[Cu(hist)$_2$]$^{2+}$	MeCN	poorly defined at > −2 V		10.3 [g]
[Cu(H$_2$bim)$_2$]$^{2+}$	MeCN [h]	0.00	Cu^{II} → Cu^I	8.1
C$_6$H$_5$SMe	MeCN	1.48	$n \geqslant 1$	} *i*
(p-MeC$_6$H$_5$)$_2$S$_2$	MeCN	1.5	$n \geqslant 1$	

[a] 0.1—0.2 mol dm^{-3} [NEt$_4$][ClO$_4$] supporting electrolyte. [b] Half-height potential *vs.* s.c.e. from r.p.e. polarogram. [c] ±10%, computed by application of the Levich equation [27] to the Cu^I → Cu^0 step. [d] Supporting electrolyte was [NEt$_4$][PF$_6$]. [e] Quasi-reversible in cyclic voltammetry. At 0.1 V s^{-1}, $|E_{p,c} - E_{p,a}|$ ~95 mV. [f] At r.p.e. In voltammetry, $E_{p,c}$ = −0.37 V and $E_{p,a}$ = 0.07 V at v = 0.1 V s^{-1}. [g] Computed from i_L at −2 V, where n = 2. [h] Containing 10% MeOH. [i] If n = 2, $D = 8.7 \times 10^{-10}$ and 7.8×10^{-10} m^2 s^{-1} respectively for diffusion-controlled i_L for these two entries. The solutions contained 1% trifluoroacetic anhydride.

Absorption Spectra.—The complex [Cu(tctd)][BF$_4$]$_2$ had absorption maxima at 555 (ε 2.8 × 10^3), 390 (6 × 10^3), and

350 nm (3.7×10^3 dm^3 mol^{-1} cm^{-1}) in dry nitromethane solution. Addition of methanol to the solution causes a gradual decrease in absorption coefficients and the shift of the 555 nm band to longer wavelength, while the remaining peaks are left undisplaced and eventually a constant spectrum is obtained (Figure 5). The resulting spectrum has absorptions at 674 (500), 390 (2×10^3), and 352 nm (2×10^3 dm^3 mol^{-1} cm^{-1}). In the presence of competitively co-ordinating solvents or ligands the complex is unstable. Even in nitromethane–methanol mixtures, the solution lost its blue colour after a couple of weeks. The assignment of the band at *ca.* 560—570 nm is still in dispute.[3,5] The two bands at *ca.* 350 and 390 nm may be explained by the splitting of thioether sulphur-to-copper charge-transfer transitions. Amundsen *et al.*[5] observed a similar splitting for copper(II) complexes with two or more (*cis* disposed) co-ordinated thioether units, and interpreted this as arising from the coupling of $R_2S(\sigma)$-to-copper charge-transfer transition moments.

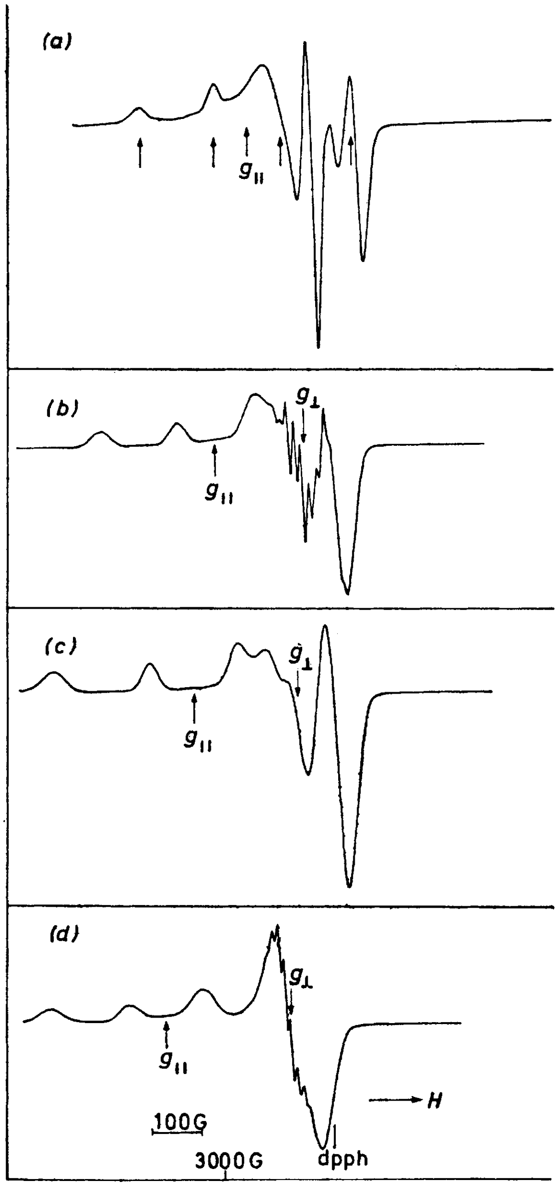


FIGURE 3 E.s.r. spectra in nitromethane at 77 K of (*a*) [Cu(dth)$_2$][BF$_4$]$_2$, (*b*) [Cu(pdto)][ClO$_4$]$_2$, (*c*) [Cu(en)$_2$][ClO$_4$]$_2$, and (*d*) [Cu(H$_2$bim)$_2$][ClO$_4$]$_2$. The arrows indicate the $g_\parallel$ features of the ions. The last two spectra demonstrate the effect of aromatic nitrogen on the appearance of the superhyperfine splitting in the $g_\perp$ region, while the sequence (*a*)—(*d*) illustrates the effect of the donor-atom sequence *S*,*N*(aliphatic),*N*(aromatic) on *g* and $A_\parallel$

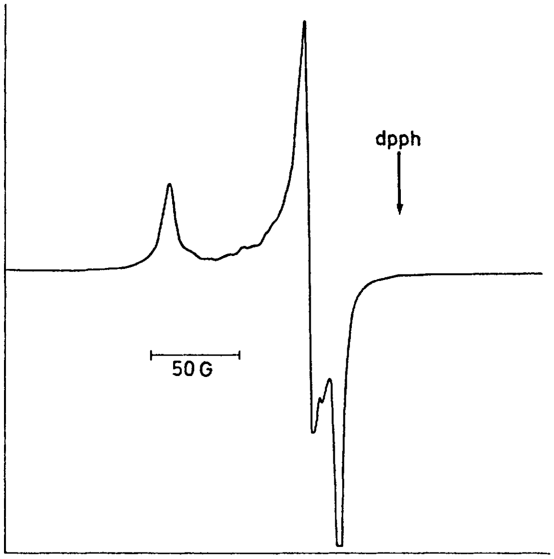


FIGURE 4 *X*-Band e.s.r. spectrum of [Cu(dth)$_2$][BF$_4$]$_2$ powder at 77 K

Redox Chemistry.—Of the 22 redox steps in Table 2, none is Nernstian, and only three could be considered quasi-reversible at platinum ($i_{p,a}/i_{p,c} > 0.90$, $|E_{p,c} - E_{p,a}| > 60$ mV) at the scan rates ($v \leqslant 1$ V s^{-1}), used here for cyclic voltammetry.

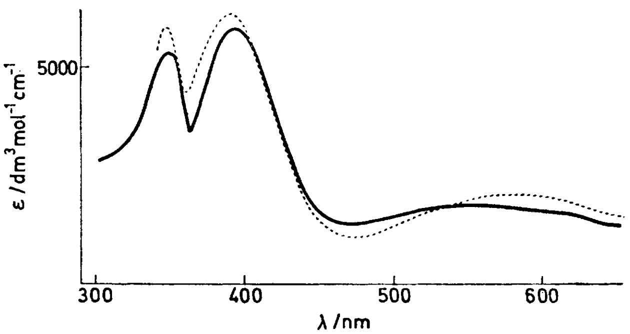


FIGURE 5 Absorption spectra of anhydrous [Cu(tctd)][BF$_4$]$_2$ in dry nitromethane (—) and methanol–nitromethane (· · ·)

The redox properties of [Cu(tctd)]$^{2+}$ are fairly representative of the type of behaviour observed for the quadridentate chelates. R.p.e. (rotating platinum electrode) polarography of a 0.61×10^{-3} mol dm^{-3} solution of [Cu(tctd)][ClO$_4$]$_2$ in MeCN–[NEt$_4$][ClO$_4$] (0.2 mol dm^{-3}) revealed two equivalent reduction waves, separated by 1.3 V. For the one at lower potential (−0.69 V), maintenance of the limiting current well below the $E_{\frac{1}{2}}$ value yielded an anodic stripping maximum on reversal of the scan direction, showing the formation of an insoluble conducting product. Similar anodic maxima were observed for all the other copper chelates in Table 2. Cyclic voltammetry showed that the wave at 0.61 V was quasi-reversible

($E_{p,a} - E_{p,c}$ 95 mV). Electroreduction of the purple solution at a platinum-mesh electrode at -0.2 V caused it to become colourless, and 0.97 ± 0.04 Faraday mol^{-1} were consumed. The redox behaviour of $[Cu(tctd)]^{2+}$ was similar in nitromethane solution. When an acetonitrile solution of the cation was saturated with carbon monoxide at 1 atm pressure the voltammogram for the first reduction step shifted anodically by 16 mV.

The ion $[Ni(tctd)]^{2+}$ is unstable in acetonitrile, yielding a precipitate of free ligand, but in $MeNO_2$–$[NEt_4][ClO_4]$, irreversible reduction of the intact macrocycle was observed. The limiting current ($i_L/c\omega^{\frac{1}{2}}$) associated with the process was almost twice that associated with the first reduction of $[Cu(tctd)]^{2+}$ in the same solvent, suggesting that $n = 2$ for $[Ni(tctd)]^{2+}$. The assumption of diffusion control of i_L at the r.p.e., demonstrated for $[Cu(tctd)]^{2+}$ by the linearity of a plot of i_L against $\omega^{\frac{1}{2}}$,[20] enables reasonable values to be calculated for the diffusion coefficients, on the above bases, and the values in Table 2 give $D\eta$ products within the limits $(3.0 \pm 0.4) \times 10^{-13}$ kg m s^{-2} for all the species studied.

As expected, the behaviour of the two CuN_2S_2 chelates was similar. As well as the irreversible reduction processes, irreversible oxidations were observed at highly positive (>1 V) potentials for these and for $[Cu(Me_4cyclam)]^{2+}$ and $[Cu(dth)_2]^{2+}$. The apparent n values given in Table 2 for these oxidations were obtained from the currents observed for them in voltammetry or r.p.e. polarography relative to the highest-potential, $n = 1$, reduction process. For example, the voltammograms of $[Cu(Me_4cyclam)]^{2+}$ showed the oxidative peak current to be $2.02^{\frac{3}{2}}$ times the peak current for the $n = 1$ reduction.[21] The oxidations of the aromatic model thioether and disulphide are probably coupled to chemical processes, even in acetonitrile rendered 'super-dry' by addition of trifluoroacetic anhydride,[22] since the voltammetric peaks are dependent on scan rate. The $E_{\frac{1}{2}}$ values are indicative of the dependence of the oxidation on the presence of the sulphur atom rather than of the aromatic moieties.[23]

DISCUSSION

Redox Properties.—The electrochemical properties of the complexes establish the presence of an $n = 1$, $Cu^{II} \longrightarrow Cu^{I}$, reduction process in each case. The results obtained are concordant with the observations of previous workers,[24-26] to the effect that the Cu^{II}–Cu^{I} reduction potential is raised by the replacement of nitrogen-donor atoms by sulphur, the latter stabilising Cu^{I} with respect to Cu^{II} by virtue of its greater π-acceptor ability.[24] The Cu^{II}–Cu^{I} reduction potential for the aliphatic N_2S_2 donor system falls close to half-way between the $E_{\frac{1}{2}}$ values for the aliphatic S_4- and N_4-co-ordinated centres, and it seems reasonable to speculate that the $E_{\frac{1}{2}}$ of a similarly ligated $CuNS_3$ system should be the mean of the $E_{\frac{1}{2}}$ values of the first two types of centres. However, there is no evidence to dispute the proposal of Dockal *et al.*[26] that replacement of one nitrogen in a CuN_4 centre by a sulphur-donor atom markedly increases the $E_{\frac{1}{2}}$ value to that of the CuN_2S_2 system. The effectiveness of aromatisation of the nitrogen in raising the Cu^{II}–Cu^{I} potential is unaltered in these quadridentate ligand systems, in comparison with the unidentate square-planar systems examined by James and Williams.[24]

There appear to be some significant differences in redox behaviour which may be associated with changes in the flexibility of certain of the co-ordination spheres of these complexes. If the planar quadridentate ligand is inflexible, then the copper(I) product is expected to be relatively unstable with respect to decomposition products with co-ordination geometries (*i.e.* linear or tetrahedral) more commonly associated with copper(I) stereochemistry, such as $[Cu(NCMe)_4]^+$. For example, the complete irreversibility of the $[Cu(Me_4cyclam)]^{2+}$ reduction to the copper(I) state is presumably associated with ligand substitution in the reduced form, since the appearance of the reoxidation current peak at 440mV to anodic potentials of the $Cu^{II} \longrightarrow Cu^{I}$ current maximum in the cyclic voltammogram betokens the formation of a differently ligated ion in the reduced state. Similarly, under our experimental conditions, the reductions of $[Cu(atu)]^{2+}$ and $[Cu(pdto)]^{2+}$ are also irreversible. Irreversibility has also been observed for the reduction of square-planar copper(II) chelates with N_4 quadridentate ligands derived from pyrrole-2-carbaldiminate.[11]

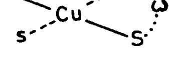
By contrast, no hindrance is expected to the adoption of a tetrahedral stereochemistry by the $[Cu(dth)_2]^+$ formed on reduction of $[Cu(dth)_2]^{2+}$, and accordingly this redox process is quasi-reversible (as opposed to irreversible), since the $[Cu(dth)_2]^{2+}$ can be regenerated without the intervention of ligand-removal processes which may be slow on the voltammetry time scale. Non-Nernstian behaviour of a system may be a property of the electrode as well as of the electroactive species itself.[27]

The complex $[Cu(tctd)][ClO_4]_2$ has been shown to have a coplanar CuS_4 unit,[7] while the copper(I) complex contains a chain polymer $[Cu(tctd)]^+$ cation in the solid state, in which the Cu^{I} is tetrahedrally co-ordinated as CuS_3S' (S' representing a sulphur atom from a second tctd ligand).[28] The fourth S donor may be replaced by a solvent molecule in solution,[28] and this would be consistent with our observation that $E_{\frac{1}{2}}$ is more positive in MeCN than in $MeNO_2$ (the former being the better donor). However, recent work has produced convincing evidence for five-co-ordinate Cu^{I},[29,30] including a copper(I) carbonyl adduct.[30] The anodic shift of the reduction potential of $[Cu(tctd)]^{2+}$ effected by treatment of the solution with carbon monoxide is interpretable only in terms of formation of a copper(I) carbonyl. Hence at least both $CuS_3(CO)$ and $CuS_4(CO)$ moieties must be considered as possible products, and a similar equivocalness must pertain with respect to the non-carbonylated $[Cu(tctd)]^+$ in a given solvent. For monocarbonyl formation in acetonitrile, the potential shift corresponds to a value of 10^5 m^2 N at 298 K for the equilibrium constant [29] of the reaction:

$$[Cu(tctd)]^+ + CO \rightleftharpoons [Cu(tctd)(CO)]^+$$

From the complete irreversibility and $n > 1$ nature of the oxidation processes observed at high (> 1 V) potentials for the complexes, we infer that these are ligand oxidations, although some cyclic tetramine complexes of Cu^{II} are known to be oxidisable to Cu^{III}.[31] The oxidations of the thioether systems are irreversible under these conditions, as is the oxidation of methyl phenyl sulphide, which occurs at a similarly high potential. Therefore no known copper proteins have reduction potentials that are so high that significant equilibrium electron transfer would be expected to occur, from an endogenous thioether or a disulphide unit, to the Cu^{2+}, in the ground state.

Copper(II) *Species produced by γ-Irradiation*.—Our assignment of the paramagnetic species produced by γ-irradiation of copper(II) ions is based on the following observations. (*i*) The lowest-field h.f. lines showed splitting characteristic of the isotopes ^{63}Cu and ^{65}Cu (see Figure 1). (*ii*) At some crystal rotations all the four h.f. lines (due to copper nuclear spins) could be observed (Figures 1 and 2). (*iii*) The γ-irradiation technique to produce Cu^{II} from Cu^{I} has been applied successfully to $[Cu(NCMe)_4][ClO_4]_2$[18] and $K_3[Cu(CN)_4]$.[32] When warmed to room temperature, such copper(II) species are reported [18,32,33] to decay rapidly and the e.s.r. signals attributable to copper(II) ions disappear, which is what we observed for irradiated crystals of $[Cu(ta)_4]Cl$. (*iv*) As is seen from Figures 2 and 3, three sets of e.s.r signals assignable to Cu^{II} appeared upon γ-irradiation at 77 K. Of these three, two had the same g and A values so that irradiation produced two kinds of copper(II) species. The major species had axial symmetry of the g and A tensors, the symmetry axis for both tensors being the crystal c axis. This last result can be expected from the crystal structure of the host crystal. The host crystal, which is tetragonal, contains two formula units in the unit cell, but by crystal symmetry they are expected to be magnetically equivalent. The copper(I) ion is surrounded almost tetrahedrally by four sulphur atoms in S_4 symmetry, and ω, the dihedral angle between the CuS_2 planes, is 84.2°.[34] The crystal c axis is the direction of compression (flattening) of the CuS_4 tetrahedra. Thus we assign this major species to tetrahedral $Cu^{II}S_4$ chromophores compressed along the crystallographic c axis. (*v*) Further support to the above assignment is provided by the absence of ligand superhyperfine structure in the e.s.r. spectra and by the fact that the principal g and A values are both small, which is expected for sulphur co-ordination,[35] and the $g_{\parallel}$, $|A_{\parallel}|$ data lie in the region defined by other CuS_4 centres (see below).



The minor species is also associated with copper(II) ions, owing to the splitting due to the two copper isotopes, but the symmetry of the g and A tensors is different from that of the host crystal. Further the $g_{\parallel}$,$|A_{\parallel}|$ data for this species appeared to fall well out of the region expected from $Cu^{II}S_4$ data (see below). Since γ-irradiation must yield ligand acetamide-derived radicals, in addition to the change of copper valence state, it seems possible that this trapped species may correspond to spin density trapped near a copper ion (*e.g.* on a co-ordinated sulphur). A similar situation has been noted previously for some γ-irradiated compounds.[32]

E.S.R. Properties of Copper(II)*–Sulphur Complexes*.—All the copper(II)–sulphur complexes investigated here exhibited a rather small g_1 value, often less than or close to 2.03. For complexes with nitrogen, oxygen, and/or halogen co-ordination, the presence of a lowest g value <2.03 has been suggested [36] to be indicative of a d_{z^2} rather than a $d_{x^2-y^2}$ (or less commonly a d_{xy}) ground state. Our results indicate that this criterion does not necessarily hold well for copper(II) complexes containing one or more Cu^{II}–S bonds, and a survey of the e.s.r. results for sulphur-containing copper(II) complexes also supports this opinion (see below). In $[Cu(dth)_2][BF_4]_2$, the co-ordination geometry around the copper ion is elongated tetragonal octahedral, with four equatorial Cu–S bonds and two axially semi-co-ordinate tetrafluoroborate anions.[37] The copper(II) ion in $[Cu(tctd)]$-$[ClO_4]_2$ has a similar tetragonal geometry with axially co-ordinated perchlorate groups.[7] Both complexes showed e.s.r. spectra characteristic of a (mainly) $d_{x^2-y^2}$ ground state. Therefore it is observed that sulphur co-ordination can give rise to a lowest g value close to 2.00, even in a ground state different from d_{z^2}.

Another salient feature of sulphur-co-ordinated copper(II) ions is that the $g_{\parallel}$ values for these complexes are rather small, compared with other planar or distorted octahedral complexes, covering a range from 2.08 to 2.15.*

Correlations between $g_{\parallel}$ and $A_{\parallel}$ arising from various factors have been noted for copper(II) complexes by previous workers.[11,35,38] Increasing the positive charge on a donor-atom set can reduce $|A_{\parallel}|$ and increase $g_{\parallel}$,[35] while it is now well established, particularly for CuN_4 systems, that tetrahedral distortion of a planar CuX_4 moiety markedly reduces $|A_{\parallel}|$ and increases $g_{\parallel}$ simultaneously.[11] Indeed, the $g_{\parallel}$ values for CuS_4 centres do tend to increase as the $|A_{\parallel}|$ values decrease (*e.g.* Table 1), and the situation is best illustrated by Figure 6, which reiterates the correlation between $A_{\parallel}$ and $g_{\parallel}$ for a given donor-atom set. The effect of tetrahedral distortion of the CuS_4 core on its $g_{\parallel}$ and $A_{\parallel}$ values is similar to that for the CuN_4 centres.[11] In fact, this type of relationship appears to pertain for all donor-atom types.[11,39] Figure 6 also shows most of the available data for CuN_2S_2, and representative species with various CuN_4, CuN_2O_2, and CuO_4 centres. Inspection of this Figure and the Tables reveals some noteworthy features.

(*i*) Tetrahedral distortion of a square-planar chromophore with any of the biomimetic (N, O, S) donors

---

* The available $g_{\parallel}$ and $A_{\parallel}$ data for CuS_4 centres are tabulated in Supplementary Publication No. SUP 22415 (8 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

reduces $|A_{\|}|$ and increases $g_{\|}$, shifting the ($g_{\|}$, $|A_{\|}|$) point for that CuX_4 core down and to the right in Figure 6.

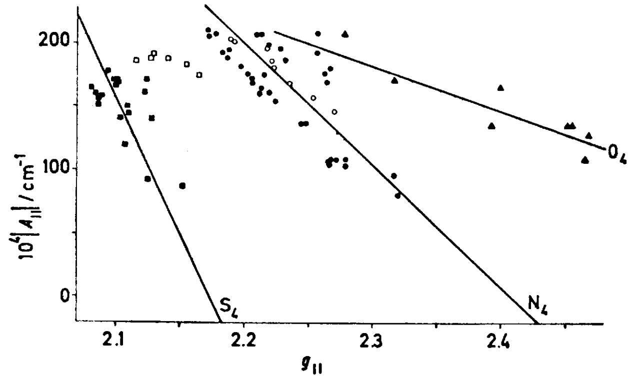


FIGURE 6 Scheme of $g_{\|}$, $A_{\|}$ data for inorganic Cu^{2+} centres with tetragonally or tetrahedrally disposed S_4 (■), N_4 (●), O_4 (▲), N_2O_2 (○), and N_2S_2 (□) donor-atom sets. For numerical data see SUP 22415. The N_4 delineator is based on data for both aromatic and anionic donors

(*ii*) Replacement of 'hard' or class (a) donor atoms by 'soft' or class (b) donor atoms tends to shift a CuX_4 centre of given geometry down and to the left in Figure 6. This shift to smaller *g* values indicates increased delocalisation of the unpaired spin density away from the copper nucleus, and has been often interpreted in terms of increased covalency in the metal–ligand bond.[40]

(*iii*) The above two factors appear to dominate over the effect of the net charge [35] of the CuX_4 moiety on its $g_{\|}$ and $A_{\|}$ values. This conclusion is illustrated by comparison of $[Cu(tctd)]^{2+}$ with $[Cu(C_2S_2O_2)]^{2-}$ ($g_{\|}$ 2.081, $|A_{\|}|$ 0.016 4 cm^{-1}) [41] and $[Cu(ta)_4]^{2+}$.

(*iv*) Thus in Figure 6, essentially diagonal regions are defined which contain copper centres of given donor-atom set, in which the $g_{\|}$ and $A_{\|}$ values vary in accord with the degree of distortion away from planarity of the co-ordination core (and with the core's charge, as recognised previously [35]). The diagonal lines in Figure 6 and 7 are intended to indicate the centres of these regions of $g_{\|}$, $A_{\|}$ as a function of donor-atom type.

(*v*) The diagonal shifting of $g_{\|}$ and $A_{\|}$ by tetrahedral distortion arising from the dependence of $g_{\|}$ on the dihedral angle, ω, suggests that the quotient $g_{\|}/|A_{\|}|$ may be a convenient empirical index of tetrahedral distortion. That indeed appears to be the case. This quotient ranges from *ca.* 105 to 135 cm for square-planar structures, the CuS_4 centres being at the high end of this range. These are exemplified by $[Cu(mnt)_2]^{2-}$ doped into the $[NMe_4]_2[Ni(mnt)_2]$ lattice (133),[41] the $[Cu(tctd)]^{2+}$ cation (126), $[Cu\{GaMe_2(pz)_2\}_2]$ (107),[42] bis(pentane-2,4-dionato)copper(II) (116),[43] and [Cu(salen)] (109 cm).[44,†] The quotient increases markedly on the introduction of tetrahedral distortion to the chromophore as in $[Cu(ta)_4]^{2+}$ (247), Cu^{2+} doped into the tetramethylthiouram disulphide lattice (231),[45] the sterically hindered $[Cu\{GaMe_2(Me_2pz)_2\}_2]$ (244),[42] bis(*N*′-t-butylpyrrole-2-carbaldiminato)copper(II) (210 cm),[11] and the diantipyrylmethane chelate complexes of Cu^{II}.[46] Examples of what are deduced to be rather more flattened tetrahedra are provided by the co-ordination spheres of Cu^{II} doped into the dipiperidylthiouram disulphide (152) [45] and zinc dialkyldithiophosphinate (154) [47] lattices, and bis(*N*-t-butylsalicylaldiminato)copper(II) (157 cm).[48] Halogeno-species will be discussed elsewhere.

(*vi*) On the $g_{\|}$, $|A_{\|}|$ scheme, points for complexes with uncharged aza-aromatic ligands (pyridine, imidazole) are shifted significantly to higher $g_{\|}$ value and slightly higher $|A_{\|}|$ value than those with saturated (amine) or anionic (aldiminate, amidate, dipyrromethanide) nitrogen donors. This introduces a limitation to the utility of the above simple criteria when applied to biological systems; electronic-absorption spectral data are also necessary if a distinction is to be made between oxygen donors and histidine imidazole.

Type I *Copper Proteins*.—Figure 7 contains most of the available $g_{\|}$,$A_{\|}$ data for copper proteins. In distinguishing between square planar and tetrahedral as two extreme geometries for describing the co-ordination of type I (blue) copper in proteins, Figure 6 and the discussion above offer the following points.

(*a*) The low values (0.003—0.010 cm^{-1}) of $|A_{\|}|$ for these proteins cannot be accounted for by (anionic) charge effects alone. Sugiura and his co-workers [49] have isolated copper(II) complexes with copper(II)–thiolate linkages, and which exhibit low $|A_{\|}|$ values. By contrast, none of the CuS_4 moieties in Figure 6 has a simple thiolate ligand. However, we note that (*i*) the 600 nm region of the absorption spectra of these complexes is rather less intense than that of the proteins and (*ii*) the structures of these complexes are not known for certainty to be square planar. The inherently low symmetry of these complexes in any configuration presumably also contributes to the reduction of $|A_{\|}|$, while most of these models fall in a region in Figure 6 which is reasonable for the proposed donor atoms.

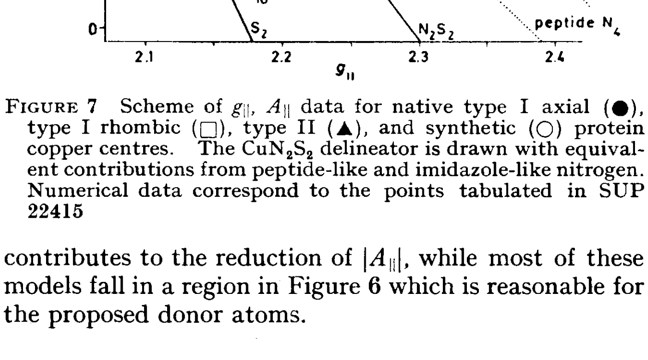


FIGURE 7 Scheme of $g_{\|}$, $A_{\|}$ data for native type I axial (●), type I rhombic (□), type II (▲), and synthetic (○) protein copper centres. The CuN_2S_2 delineator is drawn with equivalent contributions from peptide-like and imidazole-like nitrogen. Numerical data correspond to the points tabulated in SUP 22415

---

† H_2mnt = 1,1-Dicyano-2,2-dimercaptoethylene; pz = pyrazol-1-yl; H_2salen = ethylenebis(salicylideneimine); Me_2pz = 3,5-dimethylpyrazol-1-yl.

(*b*) Tetrahedral distortion would thus appear to be a prerequisite for any type I protein model which is to take the low $|A_{\parallel}|$ into account. The $g_{\parallel}/|A_{\parallel}|$ values range from 220 to 700 cm. There are no complexes of known square-planar structure for which $|A_{\parallel}|$ is <0.014 cm^{-1}, even with four sulphur ligands. Conversely, the 1 : 1 *p*-nitrobenzenethiolate and *O*-ethyl cysteinate adducts of [hydrotris(3,5-dimethylpyrazol-1-yl)borato]copper(II) have $|A_{\parallel}|$ values (0.017 cm^{-1}) [50] which are unexpectedly high since these complexes were presumed to be pseudo-tetrahedral. This is not readily accounted for, but the $g_{\parallel}$ values (2.286, 2.203 respectively) of the two complexes are markedly dissimilar, the former placing the *p*-nitrobenzenethiolate in the *N*,*O*-donor region of Figure 6.

(*c*) The rapid interconvertibility between Cu^{II} and Cu^{I} observed for type I copper [51] is not consistent with a square-planar structure. As exemplified by the [Cu(tctd)]$^{2+}$–[Cu(tctd)]$^{+}$ couple, reorganisation of the co-ordination sphere is expected even for a CuS$_4$ moiety. The need for a minimal reorganisation barrier in biological redox systems has often been discussed.[52]

The $g_{\parallel}$,$|A_{\parallel}|$ points for plastocyanins in Figure 7 fall very close to the delineator of the CuN$_2$S$_2$ region, at a point associated with considerable tetrahedral distortion. Indeed, as we have noted explicitly before,[53] all the type I copper centres fall within the CuN,S region, so that a CuN$_2$S$_2$ site would appear to be very frequent in these proteins, while we conclude on the above bases that these complexes are all quite tetrahedrally distorted rather than square planar. For umecyanin and *R. vernicifera* laccase type I Cu, an N$_3$S co-ordination sphere appears likely (points 8 and 9, Figure 7).

The azurins (points 6, 7, and 11) nearby in Figure 7 would also appear to fit this donor set, but are known to have both invariant cysteine *and* methionine residues in their sequences.[54] A CuN$_2$S$_2$ donor set for the azurins would therefore call for replacement of a plastocyanin-like imidazole nitrogen by lysine or peptide-anion nitrogen. The former has precedent as a donor in the myoglobin copper(II) complex.[55]

Finally, we note that there are a number of type I copper centres whose e.s.r. spectra have been interpreted as displaying considerable rhombicity ($\delta g = |g_x - g_y| =$ 0.01—0.08). This has been observed for even relatively narrow linewidths in only a few of the e.s.r. models in Figure 6. For example, $\delta g = 0.012$ for polycrystalline [Cu(dth)$_2$][BF$_4$]$_2$. Structural distortions which produce rhombicity may be expected to reduce $g_{\parallel}$ and $|A_{\parallel}|$ also, since the symmetry of the CuX$_4$ system is reduced. A potential source of symmetry reduction is the introduction of a fifth ligand. However, we note that a recently reported complex with a thioether donor at the apex of a square pyramid whose base is the donor set N$_2$O$_2$ has [56] $g_{\parallel} = 2.240$ and $|A_{\parallel}| = 0.017\,8$ cm^{-1}, which places this complex in the normal square-planar CuN$_2$O$_2$ region. Indeed, $g_{\parallel}$ and $A_{\parallel}$ seem relatively insensitive to even quite strong axial perturbations of a square-planar complex.[29] On the basis of the $g_{\parallel}$ and $A_{\parallel}$ values reported for blue copper centres, we deduce that the nitrogen and sulphur donors should be on the basal plane of the square pyramid, in order to dominate $g_{\parallel}$. Since it is clear that the $A_{\parallel}$ values relate to distorted structures, it appears that a purely square-pyramidal geometry is not likely. Distortion of the basal plane may carry the structure of the active site over into a trigonal-bipyramidal geometry. Indeed, such complexes have rather small hyperfine coupling constants (0.006 5—0.010 0 cm^{-1}), comparable to those in blue copper proteins. The few known trigonal-bipyramidal complexes of Cu^{II} are characterised by either a d_{z^2} ground state, with $g_{\parallel} < g_{\perp}$,[57] or by a large anisotropy in $g_{\perp}$.[58] The former situation has not been demonstrated for any type I copper protein, but it is apparent that trigonal-bipyramidal co-ordination cannot be discounted in modelling the highly anisotropic e.s.r. spectra associated with a small number of the blue copper proteins in Figure 7.

We thank the National Research Council of Canada, through a Negotiated Development Grant to the Bioinorganic Chemistry Group, for support, Drs. E. W. Ainscough and B. Bosnich for the gift of compounds, H. C. Freeman for communicating his results prior to publication, S. Rettig for determining the crystal axes, C. Schwertfeger for the *Q*-band e.s.r. spectra, and D. C. Walker for use of the ^{60}Co γ-source. A preliminary communication of this work has appeared.[53] The work was carried out while U.S. was on leave from the Department of Chemistry, Faculty of Science, Hiroshima University, Japan.

[8/585 *Received, 29th March*, 1978]

REFERENCES

[1] J. A. Fee, *Structure and Bonding*, 1975, **23**, 1; R. Österberg, *Co-ordination Chem. Rev.*, 1974, **12**, 309; H. Beinert, *ibid.*, 1977, **23**, 119.

[2] S. Katoh and A. Takamiya, *J. Biochem.* (*Japan*), 1964, **55**, 378.

[3] D. R. McMillin, R. A. Holwerda, and H. B. Gray, *Proc. Nat. Acad. Sci. U.S.A.*, 1974, **71**, 1339; D. R. McMillin, R. C. Rosenberg, and H. B. Gray, *ibid.*, p. 4760; E. I. Solomon, J. W. Hare, and H. B. Gray, *ibid.*, 1976, **73**, 1389.

[4] V. Miskowski, S.-P. W. Tang, T. G. Spiro, E. Shapiro, and T. H. Moss, *Biochemistry*, 1975, **14**, 1244.

[5] A. R. Amundsen, J. Whelan, and B. Bosnich, *J. Amer. Chem. Soc.*, 1977, **99**, 6730.

[6] P. M. Colman, H. C. Freeman, J. M. Guss, M. Murata, V. A. Norris, J. A. M. Ramshaw, and M. P. Venkatappa, *Nature*, 1978, **272**, 319.

[7] M. D. Glick, D. P. Gavel, L. L. Diaddario, and D. B. Rorabacher, *Inorg. Chem.*, 1976, **15**, 1190.

[8] T. E. Jones, D. B. Rorabacher, and L. A. Ochrymowycz, *J. Amer. Chem. Soc.*, 1976, **97**, 7485.

[9] L. Morpurgo, A. Finazzi-Agro, G. Rotilio, and B. Mondovi, *European J. Biochem.*, 1976, **64**, 453.

[10] O. Siiman, N. M. Young, and P. R. Carey, *J. Amer. Chem. Soc.*, 1976, **98**, 744.

[11] H. Yokoi and A. W. Addison, *Inorg. Chem.*, 1977, **16**, 1341.

[12] H. Debus, *Annalen.*, 1859, **107**, 199.

[13] K. Travis and D. H. Busch, *Inorg. Chem.*, 1974, **13**, 2591.

[14] T. B. Rauchfuss, J. Shing Shu, and D. M. Roundhill, *Inorg. Chem.*, 1976, **15**, 2096.

[15] D. H. Busch and W. Rosen, *J. Amer. Chem. Soc.*, 1969, **91**, 4694.

[16] E. W. Ainscough, A. M. Brodie, and K. C. Palmer, *J.C.S. Dalton*, 1976, 2375.

[17] E. G. Cox, W. Wardlaw, and K. C. Webster, *J. Chem. Soc.*, 1936, 775.

[18] D. C. Gould and A. Ehrenberg, *European J. Biochem.*, 1968, **5**, 451.

[19] G. Ivarsson, *Acta Chem. Scand.*, 1973, **27**, 3523.

[20] J. Albery, 'Electrode Kinetics,' Clarendon Press, Oxford, 1975, p. 57.

[21] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **36**, 706.

[22] O. Hammerich and V. D. Parker, *Electrochim. Acta*, 1973, **18**, 537.

[23] V. D. Parker, *J. Amer. Chem. Soc.*, 1976, **98**, 98.

[24] B. R. James and R. J. P. Williams, *J. Chem. Soc.*, 1961, 2007.

[25] C. J. Hawkins and D. D. Perrin, *J. Chem. Soc.*, 1962, 1351; G. S. Patterson and R. H. Holm, *Bioinorg. Chem.*, 1975, **4**, 257.

[26] E. R. Dockal, T. E. Jones, W. F. Sokol, R. J. Engerer, D. B. Rorabacher, and L. A. Ochrymowycz, *J. Amer. Chem. Soc.*, 1976, **98**, 4322.

[27] A. W. Addison and J. H. Stenhouse, *Inorg. Chem.*, 1978, **17**, 2161.

[28] E. R. Dockal, L. L. Diaddario, M. D. Glick, and D. B. Rorabacher, *J. Amer. Chem. Soc.*, 1977, **99**, 4530.

[29] A. W. Addison, M. Carpenter, L. K.-M. Lau, and M. Wicholas, *Inorg. Chem.*, 1978, **17**, 1545.

[30] R. R. Gagné, *J. Amer. Chem. Soc.*, 1976, **98**, 6709; R. R. Gagné, J. L. Allison, R. L. Gall, and C. A. Koval, *ibid.*, 1977, **99**, 7170.

[31] R. L. Deming, A. L. Allred, A. R. Dahl, A. W. Herlinger, and M. O. Kestner, *J. Amer. Chem. Soc.*, 1976, **98**, 4132; D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, 1971, **10**, 463.

[32] S. Fujiwara in 'International Reviews of Science (Physical Chemistry),' ed. C. A. McDowell, Butterworths, London, 1975, Series 2, vol. 4, p. 55.

[33] R. D. Bereman, F. T. Wang, J. Najdzionek, and D. M. Braitsch, *J. Amer. Chem. Soc.*, 1976, **98**, 7266.

[34] M. R. Truter and K. W. Rutherford, *J. Chem. Soc.*, 1962, 1748.

[35] J. Peisach and W. E. Blumberg, *Arch. Biochem. Biophys.*, 1974, **165**, 691.

[36] B. J. Hathaway and D. E. Billing, *Co-ordination Chem. Rev.*, 1970, **5**, 143.

[37] E. N. Baker and G. E. Norris, *J.C.S. Dalton*, in the press.

[38] T. Vänngård, in 'Biological Applications of Electron Spin Resonance,' eds. H. M. Swartz, J. R. Bolton, and D. C. Borg, Wiley–Interscience, New York, 1972, p. 411; M. C. R. Symons, D. X. West, and J. G. Wilkinson, *J.C.S. Dalton*, 1975, 1696; H. Yokoi and T. Kishi, *Chem. Letters (Japan)*, 1973, 749.

[39] J. R. Wasson, H. W. Richardson, and W. E. Hatfield, *Z. Naturforsch.*, 1977, **B32**, 551,

[40] B. R. McGarvey, *J. Phys. Chem.*, 1967, **71**, 51; J. I. Zink and R. S. Drago, *J. Amer. Chem. Soc.*, 1972, **94**, 4550.

[41] L. K. White and R. L. Belford, *J. Amer. Chem. Soc.*, 1976, **98**, 4428.

[42] F. G. Herring, D. J. Patmore, and A. Storr, *J.C.S. Dalton*, 1975, 711.

[43] I. Adato and I. Eliezer, *J. Chem. Phys.*, 1971, **54**, 1472.

[44] M. F. Scullane and H. C. Allen, jun., *J. Co-ordination Chem.*, 1975, **4**, 255.

[45] R. A. Palmer, W. C. Tennant, M. F. Dix, and A. D. Rae, *J.C.S. Dalton*, 1976, 2345.

[46] D. K. Johnson, H. J. Stoklosa, J. R. Wasson, and G. L. Seebach, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1397.

[47] H. J. Stoklosa, G. L. Seebach, and J. R. Wasson, *J. Phys. Chem.*, 1974, **78**, 962.

[48] H. Yokoi, *Bull. Chem. Soc. Japan*, 1974, **47**, 3037.

[49] Y. Sugiura and Y. Hirayama, *J. Amer. Chem. Soc.*, 1977, **99**, 1581; Y. Sugiura, Y. Hirayama, H. Tanaka, and K. Ishizu, *ibid.*, 1976, **98**, 5577.

[50] J. S. Thompson, T. J. Marks, and J. A. Ibers, *Proc. Nat. Acad. Sci. U.S.A.*, 1977, **74**, 3114.

[51] J. V. McArdle, C. L. Coyle, H. B. Gray, G. S. Yoneda, and R. A. Holwerda, *J. Amer. Chem. Soc.*, 1977, **99**, 2483.

[52] R. J. P. Williams, G. R. Moore, and P. E. Wright, in 'Biological Aspects of Inorganic Chemistry,' eds. A. W. Addison, W. R. Cullen, D. H. Dolphin, and B. R. James, Wiley–Interscience, New York, 1977, p. 369.

[53] U. Sakaguchi and A. W. Addison, *J. Amer. Chem. Soc.*, 1977, **99**, 5189.

[54] L. Ryden and J.-O. Lundgren, *Nature*, 1976, **261**, 344.

[55] L. J. Banaszak, H. C. Watson, and J. C. Kendrew, *J. Mol. Biol.*, 1965, **12**, 130.

[56] D. P. Freyberg, G. M. Mockler, and E. Sinn, *Inorg. Chem.*, 1977, **16**, 1660.

[57] R. Barbucci, A. Bencini, and D. Gatteschi, *Inorg. Chem.*, 1977, **16**, 2117 and refs. therein.

[58] A. A. G. Tomlinson and B. J. Hathaway, *J. Chem. Soc. (A)*, 1968, 1685.