

Structural aspects of red copper(I) compounds

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ABBREVIATIONS

biq	biquinoline
bdtf	2,2'-bi-dithiol-fulvalene
C ₂ H ₅ S	thioethane
C ₂ H ₆ O ₂	ethylene glycol
C ₅ H ₆ N ₂ S	1-methylpyrimidine-2-thione
C ₅ H ₈ N ₂	2,3-diazabicyclo[2,2,1]hept-2-ene
C ₅ H ₄ NCOOH	nicotinic acid
i-C ₅ H ₄ NCOOH	isonicotinic acid
C ₅ H ₅ N ₄ S	6-mercaptopurine
C ₆ H ₄ O ₂	<i>p</i> -benzoquinone
C ₆ H ₅ N ₂	benzenediazonium

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C_6H_6	benzene
$C_6H_4N_2OS$	2-thiopyrrole-1,2-dicarboximide
C_7H_{16}	<i>n</i> -heptane
$C_8H_6N_2$	quinoxaline
$C_8H_6N_4S_2$	bis(pyrimidyl)disulphide
$\alpha-C_{10}H_7CS_3$	α -dithionaphtonate
$C_{12}H_{10}N_2S_3$	pentamethylene-thiouram monosulphide
$C_{12}H_{18}O_4S_2$	1,1-dicarbo-tetrabutyloxyethylene-2,2-dithiolate
$C_{12}H_{19}O_4S_2$	2,2-dicarbo-tetrabutyloxythioacetate
$C_{14}H_{12}N_2$	2,9-dimethyl-1,10-phenanthroline
$C_{14}H_{12}NOS$	<i>N</i> -phenylimino(<i>p</i> -tolylloxy)methanethiolate
$C_{20}H_{24}N_4S_4$	6,19,27,28-tetrathia-3,9,16,22-tetraazatricyclo[22,2,1.1]octaco- sa-2,9,11,13,15,22,24,26-octaene
$C_{24}H_{22}N_4$	5,5',3'',5''-tetramethyl-2,2':6',2'':6'',2'''-quarter pyridine
$C_{41}H_{33}N_3O_2P_2$	2,3-bis(triphenylphosphoranylidenamino)-maleic acid- <i>N</i> - methylimide
dead	diethyl ester of acetylenedicarboxylic acid
dmad	dimethyl ester of acetylenedicarboxylic acid
dmbipy	6',6'-dimethyl-2,2'-bipyridine
dmf	dimethylformamide
dppm	bis(diphenylphosphino)methane
F_3CSO_3	trifluoromethanesulphonate
(imidH) ₂ dap	2,6-bis[1-((2-imidazol-4-ylethyl)imino)ethyl]pyridine
[(imidH)(imidH)dap]	4-methyl-4-[6-(1-((imidazol-4-ylethyl)imino)ethyl)pyrid-2-yl]- 4,5,6,7-tetrahydro-1H-imidazol[4,5- <i>c</i>]pyridine
m	monoclinic
mad	cinnamylidene- <i>p</i> -toluidine
MeCN	acetonitrile
4-Meq	4-methylquinoline
NEt ₄	tetraethylammonium
NS ₃	disulphidodithionitrate
<i>o</i> -MeC ₆ H ₄ CS ₂	<i>o</i> -methyltrithioperoxybenzoate
(Me ₄ N ₂) ₂ CH	1,1,5,5-tetramethylformazonium
or	orthorhombic
paz	pyridazine
phen	1,10-phenanthroline
PhC=CPh	diphenylacetylide
Ph ₃ PNPPh	phosphoranimine
Ph ₃ PS	triphenylphosphinesulphide
PPh ₃	triphenylphosphine
PPh ₄	tetraphenylphosphonium
PhS	thiophenolate

Pr ₂ NCOS	<i>N,N</i> -dipropylthiocarbamate
ptp	3,6-bis(2-pyridithio)pyridazine
py ₂ dap	bis[2,6-[1-((2-pyridine-2-ylethyl)imino)ethyl]]pyridine
rh	rhombohedral
<i>o</i> -(SCH ₂) ₂ C ₆ H ₄	<i>o</i> -xylene- α,α' -dithiolate
SC ₆ H ₄ Me- <i>o</i>	<i>o</i> -methylbenzenthioate
SC ₆ H ₄ - <i>o</i> -SiMe ₃	<i>o</i> -(trimethylsilyl)benzenthioate
S ₂ C ₄ O ₂	dithiosquarate
S ₂ ct	dithio- <i>o</i> -toluate
tc	tropocoronade
tet	2,2'-bis(6-(2,2'-bipyridyl)biphenyl
tg	tetragonal
tmbipy	4,4',6,6'-tetramethyl-2,2'-bipyridine
tr	triclinic
trg	trigonal

1. INTRODUCTION

The chemistry of copper complexes has been an active field of research for a long time, and the relationships between structure, reactivity and catalytic activity have been of major interest. It is well known that copper(I) compounds are diamagnetic and colourless, except where colour arises from the anion or charge-transfer bands.

Red copper compounds have attracted increasing interest in recent years because the most common colours for copper compounds are blue to green (Cu(II)) and colourless to white or yellow (Cu(I)). We have looked for those conditions which are required for the mostly monomeric red copper(I) compounds [1]. While structural studies of some of the red copper(I) complexes have been carried out, there has been no comprehensive review of the data. In this study we have collected, analyzed and classified crystal and structural data, and reveal the variability which occurs in the stereochemistry of these red copper(I) compounds. The aim has been to find those conditions that determine the occurrence of these red derivatives. However, there is evidently no structural rationale for the observed red colour.

2. MONONUCLEAR RED COPPER(I) COMPOUNDS

2.1 Preparation

Mononuclear red copper(I) compounds have diverse stoichiometries. In general they can be prepared either directly by mixing the reactants, or by using electrochemical techniques. In most cases, the syntheses have been carried out under an inert atmosphere by reaction between a cuprous halide and an appropriate ligand in a

non-aqueous solvent (usually acetonitrile). Some red copper(I) compounds [2,3] have been observed by electrochemical reduction of the copper(II) analogue in acetonitrile with NaBF_4 as the background electrolyte.

2.2 Structures

Structural data for mononuclear red copper(I) compounds are listed in Table 1. The coordination number around copper(I) ranges from two to five. There are two examples [4] in which the copper(I) atom has just two donor atoms, nitrogen and chlorine. The mean Cu–N bond length of 1.903 Å is shorter than that of Cu–Cl at 2.096 Å, with a mean N–Cu–Cl bond angle of 175.9°. The asymmetric unit $\text{CuCl}(\text{Ph}_3\text{PNPh})$ [4] contains two crystallographically independent molecules, differing mostly by degree of distortion.

Another four complexes [5–7] have the coordination number three with a trigonal planar environment for the copper(I) atoms. A central CuN_3 unit is found in $[\text{Cu}(\text{mad})_3](\text{F}_3\text{CSO}_3) \cdot 0.5\text{C}_6\text{H}_6$ [5] with the ideal geometry of a trigonal plane (N–Cu–N = 120.0°). In the remaining three examples, the trigonal plane is distorted. The mean Cu–L bond distance (van der Waals radius) increases in the order 2.01 Å (N, 1.55 Å) < 2.18 Å (Cl, 1.75 Å) < 2.275 Å (S, 1.80 Å).

The most common stereochemistry for the copper(I) complexes is tetrahedral. As expected, the mean Cu–L bond distances of 2.055 Å (N), 2.334 Å (Cl) and 2.386 Å (S) are longer than those found for the three- and two-coordinate Cu(I) compounds.

Finally, there are only two examples, $[\text{Cu}\{(\text{imidH})_2\text{dap}\}](\text{BF}_4)$ [2] and $[\text{Cu}(\text{py})_2\text{dap}](\text{BF}_4)$ [3], in which each copper(I) atom is five coordinated. The structure of the cation of the former derivative [2], shown in Fig. 1, has a trigonal bipyramidal geometry about the Cu(I) atom with the five N atoms of the $(\text{imidH})_2\text{dap}$ ligand. In the latter example [3], the pentadentate $(\text{py})_2\text{dap}$ ligands envelopes the copper atom in the same fashion.

The compounds summarized in Table 1 can be divided into two groups on the basis of their ligands. The most common group [2,4,5,8–16] contains an unsaturated ligand with empty π anti-bonding orbitals which can act as an electron acceptor, e.g. 1,10-phenanthroline, 2,2'-bipyridine, $(\text{imidH})_2\text{dap}$ and $(\text{py})_2\text{dap}$, all bonded through their N donor atoms to the soft copper(I) central atom, and all of which are quite bulky. The degree of coordination ranges from digonal through trigonal, tetrahedral to trigonal bipyramidal. The second group [6,7] have only trigonal bipyramidal arrangements about the copper(I) atom, and the ligands are saturated S atom donors.

The electronic spectra of these compounds, which are far from complete, generally exhibit a broad band in the visible region with a maximum around $21\,000\text{ cm}^{-1}$. For a fuller discussion, it is necessary to know the intensities of the reported bands, which have only been sporadically reported. However, it can be

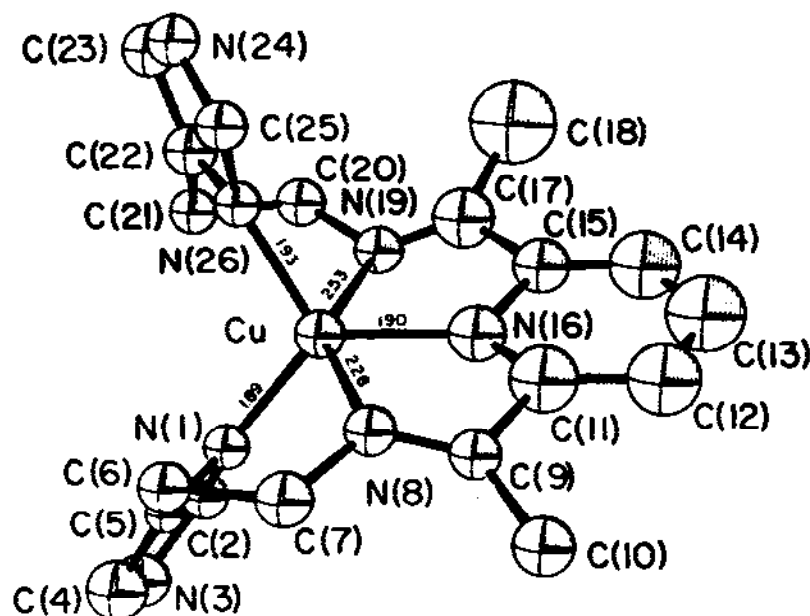


Fig. 1. View of the structure of $[\text{Cu}(\text{imidH})_2\text{dap}]^+$ cation [2].

surmised that this absorption, especially for the first group of compounds, can be assigned to an allowed metal–ligand charge transfer band (MLCT) from the copper(I) to the ligand, and is responsible for the red colour of these derivatives. In the second group, the transition can be assigned as a ligand-to-metal charge transfer band (LMCT).

3. BINUCLEAR RED COPPER(I) COMPOUNDS

3.1 Preparation

The binuclear red copper(I) compounds are usually obtained by direct reaction of ligands with copper(I) salts in non-aqueous solutions [17–20,21,22], or by electrochemical reduction of the corresponding copper(II) compounds [23], or by reduction of Cu(II) ion in the presence of (or by) the ligand [22].

3.2 Structures

Structural data for the binuclear red copper(I) compounds are listed in Table 2. The structures are tabulated in the order of increasing distance between the copper(I) atoms. There are seven distinct types of bridging, the distorted edge-shared bitetrahedral structure being the most common [17,18,23–25]. The two bridging S atoms of *o*-methylbenzenthiole ligands bring the copper(I) atoms to within 2.613(3) Å with

TABLE 1

Crystallographic data of monomeric red copper(I) compounds^a

Compound	Chromophore	M–L (Å)	L–M–L (degrees)	Ref.
[CuCl(Ph ₃ PNPh)] ^c	CuNCl ^b	N 1.885(4)	(N,Cl) ^b 177.1(1)	4
		Cl 2.078(2)		
	CuNCl	N 1.885(4)	(N,Cl) 175.8(1)	
		Cl 2.091(1)		
[CuCl(C ₄ H ₃₃ N ₃ O ₂ P ₂)]	CuNCl	N 1.938(1)	(N,Cl) 174.9(1)	4
		Cl 2.118(1)		
[Cu(mad) ₃] · F ₃ CSO ₃ · 0.5C ₆ H ₆	CuN ₃	N 1.999(5)	(N,N) 120.0	5
[Cu(NS ₃)(Ph ₃ PS)]	CuS ₃	(NS ₃)S 2.214(2)	(S,S) 98.4(1)	6
		S 2.196(3,5)	(S,S) 130.8(1,2,9)	
[Cu(PhS) ₃](PPh ₄)	CuS ₃	S 2.275(4,1)	(S,S) 112.30(19,65)	7
		S 2.335(4)	135.37(20)	
Cu(mad) ₂ Cl	CuN ₂ Cl	N 2.020(2)	(N,N) 105.0(1)	5
		Cl 2.177(1)	(N,Cl) 127.5(1)	
[Cu(C ₁₄ H ₁₂ N ₂) ₂]ClO ₄	CuN ₄	N 2.069(–,71)		8
[Cu(C ₁₄ H ₁₂ N ₂) ₂]Br · H ₂ O	CuN ₄	N 2.044(5,17)	(N,N) 110.4(2,28.0)	9
[Cu(C ₁₄ H ₁₆ N ₂) ₂]Cl · 2H ₂ O	CuN ₄	N 2.041(5,4)	(N,N) 110.6(2,29.6)	9
[Cu(C ₁₄ H ₁₂ N ₂) ₂]NO ₃ · 2H ₂ O	CuN ₄	N 2.040(4,13)	(N,N) 110.4(2,27.7)	9
[Cu(C ₁₄ H ₁₂ N ₂) ₂]NO ₃ · 2H ₂ O	CuN ₄	N 2.06(1,2)	(N,N) 83.4(6,6)	10
			123.8(6,6,9)	
[Cu(dmbipy) ₂]BF ₄	CuN ₄	N 2.034(1,18)	(N,N) 81.94(6,28)	11
			124.79(4,5,54)	
[Cu(tet)]ClO ₄ · 2MeCN	CuN ₄	N 2.034(4,33)	(N,N) 81.1(2,5)	12
			125.0(2,16.9)	
[Cu{(imidH)(imidH) · dap}] · BF ₄	CuN ₄	N 2.047(10,66)	(N,N) 78.3(4)	2
			90.6(4,4)	
			132.0(4,9,0)	

$[\text{Cu}(\text{C}_{14}\text{H}_{12}\text{N}_2)(\text{CN})_2] \cdot (\text{NBu}_4) \cdot 3\text{H}_2\text{O}$	CuN_2C_2	N	2.14(-,2)	(N,N)	78.3	13
		NC	1.96(-,3)	(N,C)	111(-,8)	
$[\text{Cu}(\text{NS}_3)(\text{PPh}_3)_2]$	CuP_2S_2	S	2.304(2,-)	(S,S)	94.90(8)	14
		P	Not given			
$\beta\text{-Cu}(\text{phen})(\text{PPh}_3)(\text{BH}_4)$	CuN_2BP	N	2.14(1,1)	(N,N)	77.6	15
		B	2.32(1)	(N,P)	109.1(1,7)	
		P	2.227(2)	(N,B)	117.7(3,7.5)	
				(B,P)	118.0(2)	
$\beta\text{-Cu}(\text{phen})(\text{PPh}_3)(\text{BD}_4)^{\text{d}}$	CuN_2BP	N	2.13(2,2)	(N,N)	77.999(5)	15
		B	2.29(2)	(N,P)	109.3(7,3)	
		P	2.26(2)	(N,B)	118.1(8,8.1)	
				(B,P)	116.7(9)	
$\text{Cu}(\text{C}_6\text{H}_4\text{N}_2\text{OS})\text{Cl}(\text{PPh}_3)_2$	CuP_2ClS	P	2.294(5,3)	(P,P)	124.3(1)	16
		Cl	2.330(3)	(P,Cl)	107.2(1,4.9)	
		S	2.386(5)	(P,S)	104.4(2,1.8)	
				(Cl,S)	108.6(1)	
$[\text{Cu}(\{\text{imidH}\}_2\text{dap})](\text{BF}_4)$	CuN_5	N_{eq}	1.905(31,28)	$(\text{N}_{\text{eq}}, \text{N}_{\text{eq}})$	119.8(15,8.8)	2
		N_{ax}	2.282(31)	$(\text{N}_{\text{eq}}, \text{N}_{\text{ax}})$	90.9(12,19.6)	
		N_{ax}	2.534(29)	$(\text{N}_{\text{ax}}, \text{N}_{\text{ax}})$	146.7(12)	
$[\text{Cu}(\{\text{py}\}_2\text{dap})]\text{BF}_4 \cdot 0.5\text{CH}_2\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$	CuN_5	N_{eq}	2.070(14,38)	$(\text{N}_{\text{eq}}, \text{N}_{\text{eq}})$	120.0(5,8.1)	3
		N_{ax}	2.257(14,17)	$(\text{N}_{\text{eq}}, \text{N}_{\text{ax}})$	90.8(6,23.2)	
				$(\text{N}_{\text{ax}}, \text{N}_{\text{ax}})$	148.5(6)	

^aWhere more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is the e.s.d., and the second is the maximum deviation from the mean value.

^bThe chemical identity of the coordinating atom or ligand.

^cThere are two crystallographically independent molecules.

^dBy neutron diffraction.

TABLE 2
Crystallographic data of binuclear red copper(I) compounds*

Compound	Chromophore	M–L (Å)	M–M (Å) M–L–M (degrees)	L–M–L (degrees)	Ref.
[Cu(SC ₆ H ₄ Me-o)(phen)] ₂ · MeCN	CuN ₂ S ₂	N ^b 2.10(1,4) μS 2.337(6,42)	2.613(3) 68.0(1,2)	(N,N) ^b 79.3(4,2) (N,S) 117.1(4,8,6) (S,S) 106.4(2,1,0)	23
[Cu ₂ (dmda)(tc-6,6)]	CuN ₂ C ₂	N 1.912(6,11) μC 1.943(7,9)	2.788(1)	(N,N) 84.3(2,2) (N,C) 118.2(3,2,1) (C,C) 39.5(3,0)	17
[Cu ₂ (dead)(tc-6,6)]	CuN ₂ C ₂	N 1.909(3,3) μC 1.948(4,13)	2.806(1)	(N,N) 83.9(2,2) (N,C) 118.3(2,2,3) (C,C) 39.6(2,0)	17
[Cu(C ₁₂ H ₁₀ N ₂ S ₃)I] ₂	CuS ₃ I	S 2.363(2) μS 2.398(2,61) I 2.535(2)	2.964(2)	(S,S) 102.86(5,83) (S,I) 106.68(5) 130.06(5)	18
[Cu ₂ (tc-5,5)Br] · [Li(12-crown-4)] ₂	CuN ₂ Br	N 2.009(9,15) μBr 2.314(6,6)	2.975(3) 80.01(1)	(N,N) 80.9(3,3) (N,Br) 139.1(3,1,2)	19
[Cu(ptp)] ₂ (ClO ₄) ₂	CuN ₄	N 2.016(3,8)	3.422(1)	(N,N) 109.8(1,16,4)	20

[Cu(S ₂ ct)(dppm)] ₂	CuP ₂ S ₂	P	2.245(6,5)	3.426(3)	(P,P)	114.4(2)	24
		S	2.390(6)		(P,S)	113.8(2,11.0)	
		S	2.507(6)		(S,S)	72.5(2)	
[Cu(C ₅ H ₅ N ₄ S)Cl ₂] ₂ · 2H ₂ O	CuCl ₂ S ₂	Cl	2.303(7,76)	3.543(9,87)	(Cl,Cl)	106.1(2,0)	25
		μS	2.253(6,9)	87.2(2,4)	(Cl,S)	112.7(2,17.5)	
		μS	2.736(6,6)		(S,S)	92.9(2,1)	
[Cu(C ₂₄ H ₂₂ N ₄)] ₂ · (ClO ₄) ₂ · H ₂ O	CuN ₄	N	2.02(1,1)	3.90	(N,N)	81.0(5,0)	21
		N	2.07(1,2)			122.0(5,6.0)	
						138.0(5,2.0)	
[Cu ₂ (C ₂₀ H ₂₄ N ₄ S ₄)(NCS)] · (ClO ₄)	CuN ₂ S ₂	N	2.048(14,12)	5.07	(N,N)	107.6(5)	22
		S	2.485(5)		(N,S)	93.38(46,17.44)	
		NCS	2.243(5)			140.66(37)	
	CuN ₃ S	N	2.033(15,32)		(S,S)	106.52(19)	
		SCN	1.952(11)		(N,N)	117.1(5,13.8)	
		S	2.451(5)		(N,S)	86.69(45,33)	
						121.92(45)	

^aWhere more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is the e.s.d., and the second is the maximum deviation from the mean value.

^bThe chemical identity of the coordinating atom or ligand.

Cu–S–Cu angles of $68.0(1,2)^\circ$. This is the shortest Cu–Cu distance found in this series of compounds.

In another example [21] containing the $[\text{Cu}(\text{C}_{24}\text{H}_{22}\text{N}_4)]_2^{2+}$ cation, the copper(I) atoms are linked by both ligands in a bis-bidentate fashion ($2_{\text{py}} + 2_{\text{py}}$), via the nitrogen atoms of the ligand $\text{C}_{24}\text{H}_{22}\text{N}_4$. The distance between the copper(I) atoms is 3.90 Å, each of them being tetrahedrally coordinated.

The structure of the $[\text{Cu}_2(\text{C}_{20}\text{H}_{24}\text{N}_4\text{S}_4)(\text{NCS})]^+$ cation is shown in Fig. 2 [22] where it can be seen that the two copper(I) atoms are bridged by a thiocyanate group in an end-to-end, 1,3-bridging mode. In addition, each copper atom is bonded to two imine nitrogens and one thioether sulphur of the macrocycle, and have very distorted tetrahedral environments.

The data in Table 2 show only one example [19] of copper(I) in a trigonal planar environment, all the others having distorted tetrahedral environments. There is an example of bridging via the bromine atom in $[\text{Cu}_2(\text{tc-5,5})\text{Br}]^-$ anion [19] with a Cu–Cu distance of 2.975(3) Å. Each copper atom has a trigonal-planar geometry with the CuN_2Br chromophore. In $[\text{Cu}(\text{ptp})_2(\text{ClO}_4)_2]$ [20], the cation consists of two pseudo-tetrahedral copper(I) centres separated by 3.422(1) Å, and bridged by two pyridazine groups with terminal pyridine donors to complete the four-coordination.

Overall, the coordinated ligands are similar to those found in the mononuclear red copper(I) compounds. Likewise, the electronic spectra of the binuclear derivatives,

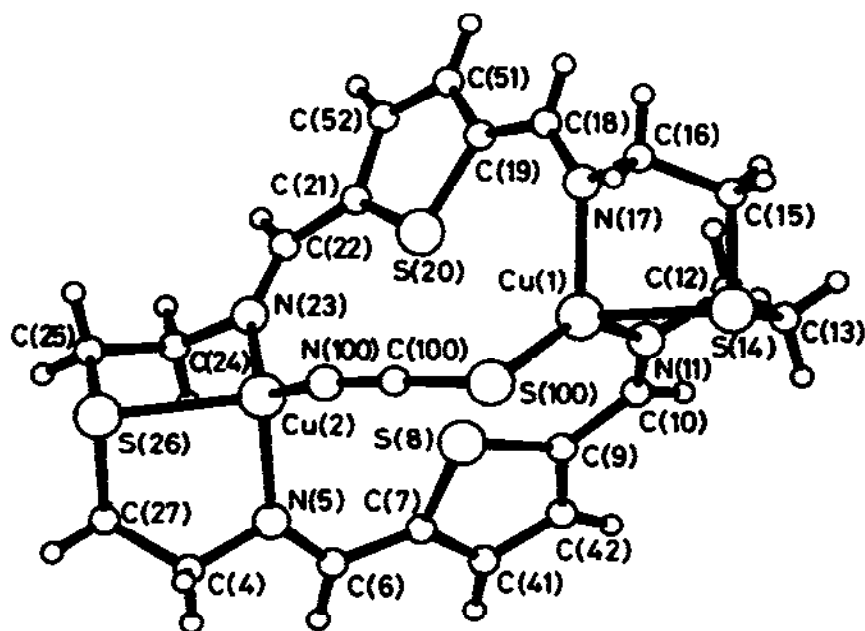


Fig. 2. View of the structure of $[\text{Cu}_2(\text{C}_{20}\text{H}_{24}\text{N}_4\text{S}_4)(\text{NCS})]^{2+}$ cation [22].

especially the position of the charge transfer band, corresponds closely with those of the mononuclear derivatives. In these derivatives, it can be seen (Table 2) that the Cu–Cu interatomic distance is directly related to the magnitude of the Cu–L–Cu bridging angle.

4. TRI- AND OLIGONUCLEAR RED COPPER(I) COMPOUNDS

4.1 Preparation

These red copper(I) compounds are prepared by both chemical and electrochemical methods. A copper(II) salt can be reduced by ascorbic acid in the presence of the appropriate ligands, or in some cases excess of a ligand will act as the reducing agent. Some derivatives can be prepared by direct interaction of a copper(I) salt with ligands. Electrochemical procedures can also be used to reduce Cu(II) ion or to oxidize Cu(0) in the presence of appropriate ligands.

4.2 Structures

The crystallographic and structural data of the tri- and oligonuclear red copper(I) compounds are given in Table 3. Only two trinuclear examples have been found [26,27]. One of these [26] contains the $[\text{CuS}_6]_3^{3-}$ anion with a type of S_6^{2-} ligand forming a condensed ring system of a central Cu_3S_3 system and three seven-membered CuS_6 heterocycles. Each copper(I) atom has a distorted trigonal planar coordination sphere.

The other trinuclear example [27] contains three $[\text{CuC}_3\text{B}_9\text{H}_{10}(4-(\text{C}_5\text{H}_4\text{N})\text{CO}_2\text{Me})]$ units which are linked by both Cu–H–B and Cu–Cu interactions about a crystallographic three-fold axis. The resulting “pinwheel” ligand array around an equilateral triangle of copper(I) atoms is illustrated in Fig. 3.

There are seven examples of tetranuclear derivatives [28–33]. The structure of $(\text{PPh}_4)_2[\text{Cu}_4(\text{C}_2\text{H}_5\text{S})_6]$ [28] is built up from $[\text{Cu}_4\text{S}_6]^{2-}$ adamantane-type cluster units, separated by the bulky tetraphenylphosphine cations. The anion consists of a tetrahedron of copper(I) atoms inserted in a distorted octahedron formed by six *m*-sulphur atoms. Each copper atom is coordinated to a trigonal-planar array of sulphur atoms, which is a very common arrangement for copper(I) thiolates [29,30,32].

The structure of another tetranuclear complex is shown in Fig. 4. A discrete $[\text{Cu}_2\text{Cl}_2(4\text{-Meq})_3]_2$ molecule is centrosymmetric with the Cu–Cu distance of 2.777(1) Å, and has the “step” structure. Copper(I) atoms at the periphery of the “step” are coordinated by a pair of nitrogen ligands [31].

There are three examples [34–36] of hexanuclear copper(I) compounds. The $[\text{Cu}(\text{PPh}_3)\text{H}]_6$ molecule [34] contains a slightly distorted octahedral cluster of copper(I) atoms. The two mutually trans faces of this octahedron are enlarged with

TABLE 3

Crystallographic data of tri- and oligonuclear red copper(I) compounds^a

Compound	Chromophore	M-L (Å)	M-M (Å) M-L-M (degrees)	L-M-L (degrees)	Ref.
(Et ₄ N) ₃ [Cu(S ₆) ₃]	CuS ₃	S ^b 2.21 μS 2.20	Not given 107.7	(S,μS) ^b 134.3 (μS,μS) 106.0	26
[Cu(μ-H)(C ₂ B ₉ (4-C ₅ H ₄ N)·CO ₂ Me)] ₃ ·0.5C ₇ H ₁₆	CuB ₃ C ₂ H	B 2.229(8,119) C 2.635(9,1) μH 1.608 μS 2.281(3,33)	2.519(2)	(B,B) 47.2-162.0(3) (B,H) 117.8(-,6.0) 156.6 119.9(1,9.5)	27
(PPh ₄) ₂ [Cu ₄ (C ₂ H ₅ S) ₆]·0.5C ₂ H ₆ O ₂	CuS ₃	μS 2.272(4,28)	2.725(1,55) 73.4(1,1.7)	(S,S) 119.9(1,5.6)	28
(PPh ₄) ₂ [Cu ₄ (o-(SCH ₂) ₂ ·C ₆ H ₄) ₃]·MeCN	CuS ₃	μS 2.272(4,28)	2.726(2,27)	(S,S) 119.9(1,5.6)	29
[Cu ₄ (C ₅ H ₆ N ₂ S) ₆]·(BF ₄) ₄	CuS ₃ (2 ×)	S 2.241(1) μS 2.264(-) 2.356(1) 2.035(3) μS 2.264(-) 2.356(1)	2.792(1,79)	(S,μS) 112.0(1) 127.8(1) (μS,μS) 120.2(1) (N,S) 103.6(1) 142.6(1) (S,S) 113.7(1)	30
[Cu ₂ (4-Meq) ₃ Cl ₂] ₂	CuCl ₃ N (2 ×)	N 2.019(4) μCl 2.295(2) μ ₃ Cl 2.355(2) μ ₃ Cl 2.772(2)	2.777(1) 71.4(1,7.4)	(Cl,Cl) 103.3(1,8.2) (N,Cl) 102.3(1,5.0) 135.1(2)	31
	CuN ₂ Cl ₂ (2 ×)	N 2.057(5,12) μCl 2.355(1) μ ₃ Cl 2.440(2)	3.205(2) 130.9(1)	(N,N) 103.9(2) (N,Cl) 112.6(1,9.5) (Cl,Cl) 103.0(1)	
[Cu(o-MeC ₆ H ₄ CS ₃) ₄]	CuS ₃	S 2.229(1,8) μS 2.251(2,41)	2.861(1,154) 76.56(5,1.66)	(S,μS) 99.20(6,44) 131.82(6,4.82) (μS,μS) 126.30(6,5.07)	32
[Cu(α-C ₁₀ H ₇ CS ₃) ₄]·0.5CS ₂	CuS ₄	S 2.223(2,3) μS 2.253(2,34)	3.028(2,37) 100.5(8,1.0)	(S,μS) 99.1(8,6)	33

[Cu(2,4,6-Me ₃ C ₆ H ₂ CS ₃)] ₄ Me ₂ CO	CuS ₃	S	2.230(3,8)	3.087(2,488) (S,μS)	100.8(1,1.8)	32
		μS	2.220(3,18)	82.15(8,4.82) (μS,μS)	125.0(1,2.1) 133.1(1,1.9)	
[Cu(PPh ₃)H] ₆ ·dmf	CuH ₃ P	P	2.240(9,22)	2.542(6,53)		34
		μ ₃ H	Not given	2.655(6,23)		
[Cu(C ₁₄ H ₁₂ NOS)] ₆ ·3CH ₂ Cl ₂	CuS ₂ N	N	2.027(4)	2.836(1,38) (N,S)	119.1(1)	35
		μS	2.245(1)	3.184(1,122) (S,S)	114.9(1)	
[Cu(Pr ₂ NCOS)] ₆	CuS ₂ O	O	2.08(2,2)	2.882(5,175) (O,S)	114.3(5,61)	36
		μS	2.23(1,3)	83.8(3,2.7) (S,S)	121.4(3,2.1)	
Cu ₈ (SC ₅ H ₁₁) ₄ (S ₂ CSC ₅ H ₁₁) ₄	CuS ₃ (4 ×)	S	2.273(6,10)	2.652–3.250 (S,S)	119.8(2,4.1)	37
		μS	2.273(6,8)	74.3(2,3.5)		
		μ ₃ S	2.245(6,8)	87.7(2,20) 120.0(2,4)		
	CuS ₃ (4 ×)	μS	2.286(6,6)		(S,S) 119.5(2,10.5)	
(PPh ₄) ₄ [Cu ₈ (S ₂ C ₄ O ₂) ₆]·CH ₃ CN	CuS ₃	μ ₃ S	2.275(6,30)			38
		μS	2.247(3,22)	2.844(2,58) (S,S)	116.17(14,4.80)	
				4.022(2,38) 78.52(8,2.31)		
Cu ₁₀ (C ₁₂ H ₁₉ O ₄ S ₂) ₆ ·(C ₁₂ H ₁₈ O ₄ S ₂) ₂	CuS ₃ (8 ×)	μ ₃ S	2.269(3,49)	2.820(2,236) (S,S)	119.4(2,13.4)	39
				74.40(9,7.74)		
	CuS ₂ O (2 ×)	μ ₃ S	2.198(3,11)		(S,S) 148.1(2)	
[Cu(SC ₆ H ₄ - <i>o</i> -SiMe ₃)] ₁₂	CuS ₂ (3 ×)	O	1.898(8)		(S,O) 105.2(3,5.6)	40
		μS	2.160(8,18)	Not given	(S,S) 174.7(3,5)	
				81.8(3,9.2) 132.2(3,8)		
	CuS ₂ (3 ×)	μ ₃ S	2.200(8,12)		(S,S) 163.6(3,7)	
	CuS ₃ (6 ×)	μS	2.200(8,40)	Not given	(S,S) 84.7(3,10.9)	
		μ ₃ S	2.285(8,38)	107.5(3,3.9) 143.6(3,1.6)	134.0(3,1.5)	

TABLE 3 (continued)

Compound	Chromophore	M—L (Å)	M—M (Å) M—L—M (degrees)	L—M—L (degrees)	Ref.
[Cu ₃ (CN) ₃ (bq) ₂] _n	CuN ₂ CuN ₂ (C/N) ₂	CN 1.823(4)			41
		N 2.096(4)		(N,N) 77.7(2)	
		NC 1.896(5)		(N,C/N) 103.6(2)	
		N/C 1.946(4)		(N,C) 115.3(3) (C,N/C) 129.2(2)	
[Cu(dbtf)Cl] _n	CuCl ₂	Cl 2.401	2.45		42
		Cl 2.489			
Cu ₂ Br ₃ · (C ₆ H ₅ N ₂)	CuBr ₄	μBr 2.45	2.86		43
		μ ₄ Br 2.57	3.09		
{(Me ₄ N ₂) ₂ CH}[Cu ₂ Br ₃]	CuBr ₄	μBr 2.432(2,10)	2.948(2,44)	(Br,Br) 109.28(7,10,12)	44
		μ ₄ Br 2.600(2,20)	3.213(2,12)		
			73.35(6,5.68) 113.98(6,6)		
[Cu ₂ (C ₈ H ₆ N ₂) ₃ (ClO ₄)] · ClO ₄	CuN ₃ O	N 2.026(7,78)		(N,N) 104.9(3,3,8)	45
		O 2.536(8)		139.1(3)	
	CuN ₃ O ₂	N 2.023(6,43)		(N,O) 100.0(3,15.1)	
		μ ₂ O 2.385(8,0)		(N,N) 110.4(2,6.0) 136.3(3)	
Cu(CN)(C ₁₄ H ₁₂ N ₂)	CuN ₃ C	N 2.126(9,5)		(N,O) 95.4(3,2,8)	46
		CN 2.008(11)		(N,N) 79.1(3)	
		NC 1.897(12)		(N,N) 110.1(4,2.6)	
				(N,C) 117.9(4,8.0)	
Cu(NCS)(C ₁₄ H ₁₂ N ₂)	CuN ₃ S	N 2.077(6,1)		(N,N) 80.8(2)	46
		SCN 1.943(6)		(N,N) 119.3(2,1.8)	
		NCS 2.323(2)		(N,S) 112.4(2,8.6)	

CuCN(paz)	CuN ₃ C	N	2.122(6)		(N,N)	101.0(3,8.4)	47
		CN	1.956(11)		(N,C)	117.2(5,6.8)	
		NC	1.915(8)				
	CuN ₃ C	N	2.115(6)		(N,N)	102.6(3,2.7)	
		CN	1.932(8)		(N,C)	115.7(5,10.4)	
		NC	1.909(12)				
Cu(i-C ₅ H ₅ NCOOH)Cl	CuCl ₃ N	N	1.995(7)		(N,Cl)	107.2(3,2.7)	48
		μ Cl	2.354(3,38)			123.0(3)	
			2.488(3)		(Cl,Cl)	105.3(1,3)	
CuCl(C ₅ H ₈ N ₂)	CuN ₂ Cl ₂	N	1.90(2,2)	3.36(1,4)	(N,N)	128.3(9)	49
		μ Cl	2.38(1,1)	89.8(4,1.0)	(N,Cl)	103.1(8,2.8)	
					(Cl,Cl)	117.3(4)	
Cu(C ₈ H ₆ N ₄ S ₂)Cl · H ₂ O	CuN ₂ Cl ₂	N	1.966(3)		(N,N)	142.2(1)	50
		μ Cl	2.464(1)	84.26(4)	(N,Cl)	100.00(9)	
					(Cl,Cl)	95.74(4)	
CuCl(C ₅ H ₅ NCOOH) ₂	CuN ₂ Cl ₂	N	2.032(9,12)		(N,N)	118.8(4)	51
		μ Cl	2.377(4,14)	105.2(4)	(N,Cl)	108.1(3,4.4)	
					(Cl,Cl)	105.2(2)	
(NH ₄)[Cu ₃ Cl ₄ (C ₆ H ₄ O ₂) _{1.5}] · H ₂ O	CuCl ₃ C ₂	C	2.072(5,25)		(C,C)	38.3(2,1)	52
		μ Cl	2.280(2,15)	80.40(5,1.44)	(C,Cl)	117.8(2,7.2)	
		μ Cl	2.346(2,21)	88.64(5,1.54)	(Cl,Cl)	98.73(6,11.25)	
		μ_3 Cl	2.504(1,16)				

*Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is the e.s.d., and the second is the maximum deviation from the mean value.

^bThe chemical identity of the coordinating atom.

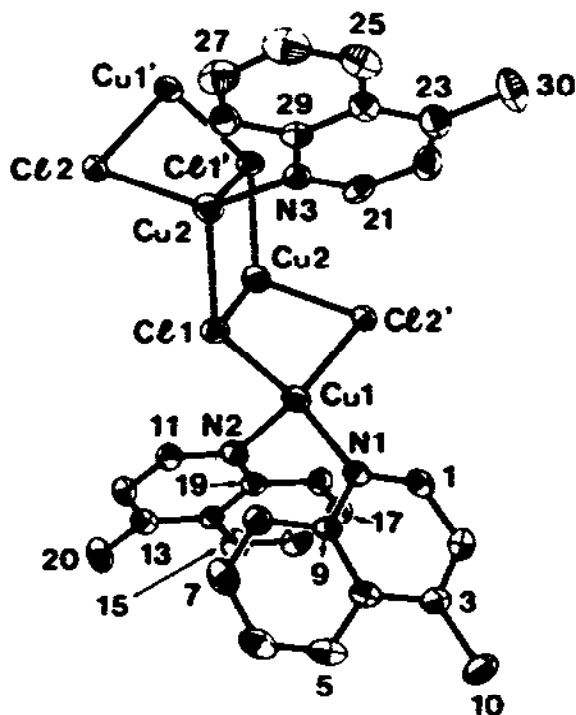


Fig. 4. Structure of $[\text{Cu}_2\text{Cl}_2(4\text{-Meq})_3]_2$ [31].

bridging copper is occupied by a dithio acid sulphur atom on the adjacent Cu_4 fragment.

As shown in Fig. 6, the structure of $[\text{Cu}(\text{SC}_6\text{H}_4\text{-}o\text{-SiMe}_3)]_{12}$ consists of discrete dodecanuclear clusters of unique molecular geometry [40]. The structure was described as a molecular “paddle wheel” with the $\text{Cu}_{12}\text{S}_{12}$ as a core.

The remaining compounds given in Table 3 are polynuclear. The structure of $\text{Cu}(\text{CN})(\text{C}_{14}\text{H}_{12}\text{N}_2)$ [46] is shown in Fig. 7 as an example of these. It consists of one-dimensional zig-zag chains of tetrahedral copper(I) atoms linked by cyanide groups. Stacks of 2,9-dimethyl-1,10-phenanthroline molecules are formed by the fitting of centrosymmetric polynuclear sequences.

In the polynuclear derivatives, the copper(I) atom can be found in two, three, four, five and even six coordination. The latter two coordination states have only two and one examples, respectively, three and four coordination being by far the most common, as might be expected. The electronic spectra which are available for some of these derivatives show the familiar broad band around $21\,000\text{ cm}^{-1}$. Polarized single-crystal spectra [41,46] show two bands at $19\,000\text{ cm}^{-1}$ and $22\,000\text{ cm}^{-1}$. These are responsible for the reddish appearance of the compounds and are assigned, at least for the unsaturated ligand cases, as MLCT [53].

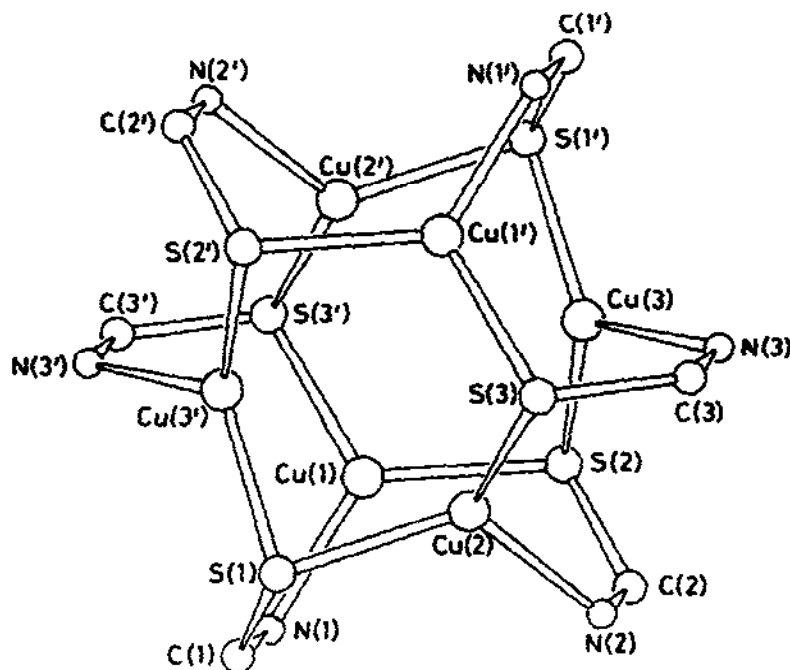


Fig. 5. View of the central core of $[\text{Cu}(\text{C}_{14}\text{H}_{12}\text{NOS})]_6$ [35].

5. SUMMARY

From a preparative point of view, the red copper(I) compounds fall into four main categories. These are (a) direct interaction of ligands with copper(I) salts; (b) electrochemical oxidation of Cu(0) or reduction of Cu(II) salts; (c) reduction of copper(II) salts in the presence of excess of a reducing ligand; (d) reduction of copper(II) salts in the presence of the appropriate ligands plus ascorbic acid as the reducing agent. In general, the course of the redox reactions are highly dependent upon the specific conditions used, such as concentration of reactants and temperature, and especially on the medium employed.

The data presented cover 60 red copper(I) compounds for which structural data are available to date. The number of examples of various geometries increases in the order four-coordinate (tetrahedral) < three-coordinate (trigonal planar) < two-coordinate < five-coordinate (trigonal bipyramidal) < six-coordinate. The ligands used range from mono-, through bi-, tri- and tetra- to pentadentate. The most common donor atoms are the softer nitrogen and sulphur atoms. The nuclearity of the derivatives ranges from mono-, through bi-, tri-, tetra-, hexa-, octa-, dodeca- to polynuclear. In one case [4], a distortion isomer [54] is found to occur, the two independent CuNCl chromophores differing mostly in their Cu–Cl bond lengths and N–Cu–Cl bond angles (Table 1).

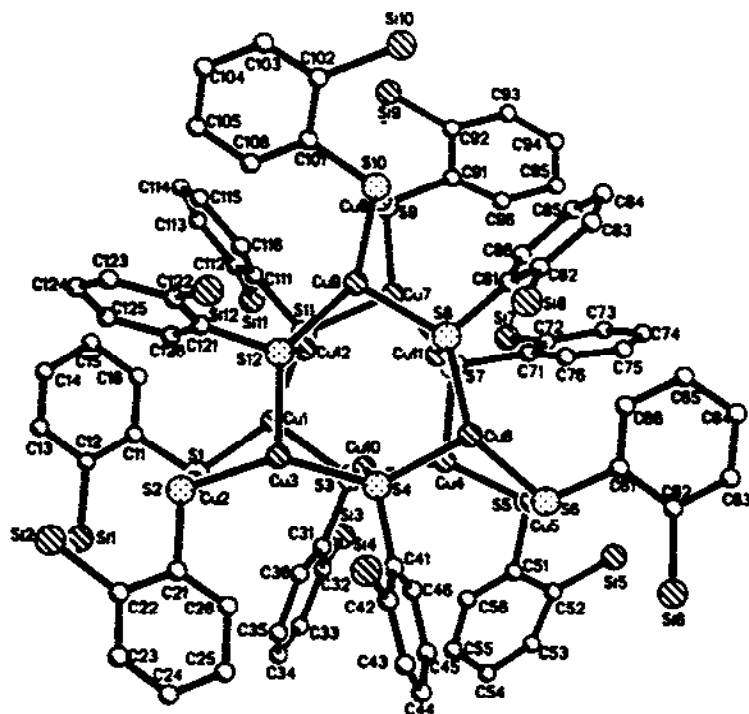


Fig. 6. View of the structure of $[\text{Cu}(\text{SC}_6\text{H}_4\text{-}o\text{-SiMe}_3)]_{12}$ [40].

A survey of the data in Tables 1–3 shows that the mean $\text{Cu(I)}\text{--L(atom)}$ bond length increases both with coordination number and with the van der Waals radius of the ligating atom.

The factors governing the choice of geometry in these compounds include the electronic configuration of the central atom, the crystal packing forces and the nature of the ligands. The presence of an electron-withdrawing ligand serves to stabilize the copper(I) oxidation state and gives rise to the broad band observed in the visible spectrum, with a maximum absorbance around $21\,000\text{ cm}^{-1}$. These are assigned as charge transfer bands and are responsible for the red colourations of these compounds. One would expect that thiol ligands would act only as electron donors, with little or no Lewis acidity. However, from Tables 1–3 it can be seen that many of the S donor ligands involved are unsaturated, with empty π -acceptor antibonding orbitals. Those that are not unsaturated mostly act as bidentate or bridging ligands, giving metal-containing ring structures where the possibility of some degree of delocalization exists.

However, the key spectroscopic data for these compounds is either completely absent from the literature, or, in many cases, given without intensity information. This severely limits comparison of these derivatives, although it is noted that there seems to be no direct structural explanation for the observed colour, such as coordina-

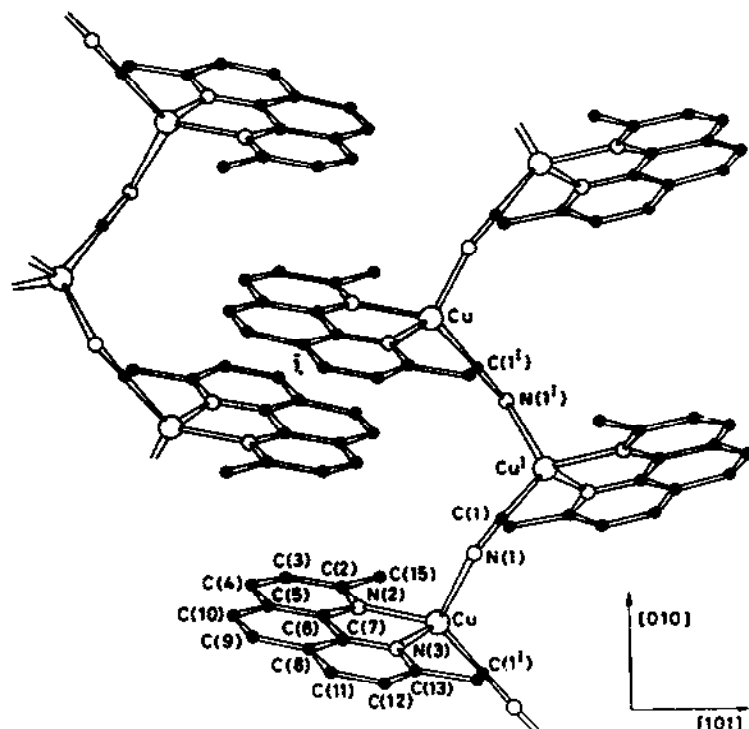


Fig. 7. Projection of the structure of $\text{Cu}(\text{CN})(\text{C}_{14}\text{H}_{12}\text{N}_2)$ [46].

tion number, stereochemistry or nuclearity. The underlying causes seem to be more complex than those found in the silver(I) analogues [55]. In this case, analysis of 22 crystal structures of Ag(I) compounds with "hard" bases demonstrated that the colour changes from colourless to red, depending on the number of Ag(I) atoms coordinated to the base donor atoms. The colourless compounds have coordination numbers of one and two, whereas the red compounds always show coordination numbers of three or four [55].

This study represents an overview of a chemical class of the redox-active metal copper(I) with redox-active ligands that give rise to stable complexes with a characteristic metal-to-ligand charge-transfer band in the visible region. The extent of the chemistry involved and the identification of some systematic trends have been illustrated and may serve to stimulate further interest and investigation in this area of chemistry.

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