Coordination Chemistry Reviews, *126* (1993) 71–92

Structural aspects of red copper(I) compounds

Milan Melnik and Luba Macaskova
Department of Inorganic Chemistry, Slovak Technical University, Radlinskeho 9, 812 37 Bratislava (Slovakia)
Clive E. Holloway
Department of Chemistry, York University, 4700 Keele Street, North York, Ont. M3J 1P3 (Canada)

(Received 5 May 1992)

CONTENTS

ABBREVIATIONS

biq	biquinoline
bdtf	2,2′-bi-dithiol-fulvalene
C_2H_5S	thioethane
$C_2H_6O_2$	ethylene glycol
$C_5H_6N_2S$	1-methylpyrimidine-2-thione
$C_5H_8N_2$	2,3-diazabicyclo[2,2,1]hept-2-ene
C_5H_4NCOOH	nicotinic acid
i-C_5H_4NCOOH	isonicotinic acid
$C_5H_5N_4S$	6-mercaptopurine
$C_6H_4O_2$	*p*-benzoquinone
$C_6H_5N_2$	benzenediazonium

Correspondence to: C.E. Holloway, Department of Chemistry, York University, North York, Ont. M3J 1P3, Canada.

0010-8545/93/$24.00

C_6H_6	benzene
$C_6H_4N_2OS$	2-thiopyrrole-1,2-dicarboximide
C_7H_{16}	*n*-heptane
$C_8H_6N_2$	quinoxaline
$C_8H_6N_4S_2$	bis(pyrimidyl)disulphide
α-$C_{10}H_7CS_3$	α-dithionaphtonate
$C_{12}H_{10}N_2S_3$	pentamethylene-thiouram monosulphide
$C_{12}H_{18}O_4S_2$	1,1-dicarbo-tetrabutyoxyethylene-2,2-dithiolate
$C_{12}H_{19}O_4S_2$	2,2-dicarbo-tetrabutyoxythioacetate
$C_{14}H_{12}N_2$	2,9-dimethyl-1,10-phenanthroline
$C_{14}H_{12}NOS$	*N*-phenylimino(*p*-tolyloxy)methanethiolate
$C_{20}H_{24}N_4S_4$	6,19,27,28-tetrathia-3,9,16,22-tetraazatricyclo[22,2.1.1]octacosa-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-*N*-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
$(imidH)_2dap$	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-c]pyridine
m	monoclinic
mad	cinnamylidine-*p*-toluidine
MeCN	acetonitrile
4-Meq	4-methylquinoline
NEt_4	tetraethylammonium
NS_3	disulphidothionitrate
o-$MeC_6H_4CS_2$	*o*-methyltrithioperoxybenzoate
$(Me_4N_2)_2CH$	1,1,5,5-tetramethylformazonium
or	orthorhombic
paz	pyridazine
phen	1,10-phenantroline
PhC=CPh	diphenylacetylide
Ph_3PNPh	phosphoranimine
Ph_3PS	triphenylphosphinesulphide
PPh_3	triphenylphosphine
PPh_4	tetraphenylphosphonium
PhS	thiophenolate

Pr_2NCOS	*N,N*-dipropylthiocarbamate
ptp	3,6-bis(2-pyridithio)pyridazine
py_2dap	bis[2,6-[1-((2-pyridine-2-ylethyl)imino)ethyl)]pyridine
rh	rhombohedral
o-$(SCH_2)_2C_6H_4$	*o*-xylene-α,α′-dithiolate
SC_6H_4Me-*o*	*o*-methylbenzenthiolate
SC_6H_4-*o*-$SiMe_3$	*o*-(trimethylsilyl)benzenthiolate
$S_2C_4O_2$	dithiosquarate
S_2ct	dithio-*o*-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(II) 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 $CuCl(Ph_3PNPh)$ [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 $[Cu(mad)_3](F_3CSO_3)\cdot 0.5C_6H_6$ [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, $[Cu\{(imidH)_2dap\}](BF_4)$ [2] and $[Cu\{(py)_2dap\}](BF_4)$ [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 $(imidH)_2dap$ ligand. In the latter example [3], the pentadentate $(py)_2dap$ 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, $(imidH)_2dap$ and $(py)_2dap$, 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 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

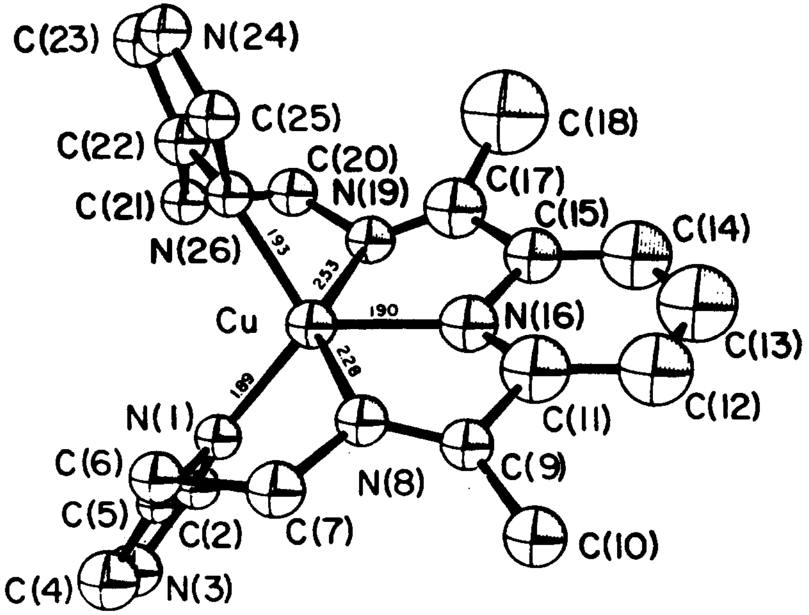

Fig. 1. View of the structure of [Cu{(imidH)$_2$dap}]$^+$ cation [2].

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.
$[CuCl(Ph_3PNPh)]$[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)			
$[CuCl(C_{41}H_{33}N_3O_2P_2)]$	CuNCl	N	1.938(1)	(N,Cl)	174.9(1)	4
		Cl	2.118(1)			
$[Cu(mad)_3] \cdot F_3CSO_3 \cdot 0.5C_6H_6$	CuN_3	N	1.999(5)	(N,N)	120.0	5
$[Cu(NS_3)(Ph_3PS)]$	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)	
$Cu(mad)_2Cl$	CuN_2Cl	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
$[Cu(C_{14}H_{12}N_2)_2]Br \cdot H_2O$	CuN_4	N	2.044(5,17)	(N,N)	110.4(2,28.0)	9
$[Cu(C_{14}H_{16}N_2)_2]Cl \cdot 2H_2O$	CuN_4	N	2.041(5,4)	(N,N)	110.6(2,29.6)	9
$[Cu(C_{14}H_{12}N_2)_2]NO_3 \cdot 2H_2O$	CuN_4	N	2.040(4,13)	(N,N)	110.4(2,27.7)	9
$[Cu(C_{14}H_{12}N_2)_2]NO_3 \cdot 2H_2O$	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)	
$[Cu(tet)]ClO_4 \cdot 2MeCN$	CuN_4	N	2.034(4,33)	(N,N)	81.1(2,5)	12
					125.0(2,16.9)	
$[Cu\{(imidH)(imidH) \cdot dap\}] \cdot BF_4$	CuN_4	N	2.047(10,66)	(N,N)	78.3(4)	2
					90.6(4,4)	
					132.0(4,9.0)	

$[Cu(C_{14}H_{12}N_2)(CN)_2]\cdot(NBu_4)\cdot 3H_2O$	CuN_2C_2	N	2.14(−,2)	(N,N)	78.3	13
		NC	1.96(−,3)	(N,C)	111(−,8)	
$[Cu(NS_3)(PPh_3)_2]$	CuP_2S_2	S	2.304(2,−)	(S,S)	94.90(8)	14
		P	Not given			
β-Cu(phen)$(PPh_3)(BH_4)$	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)	
β-Cu(phen)$(PPh_3)(BD_4)$[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)	
$Cu(C_6H_4N_2OS)Cl(PPh_3)_2$	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)	
$[Cu\{(imidH)_2dap\}](BF_4)$	CuN_5	N_{eq}	1.905(31,28)	(N_{eq},N_{eq})	119.8(15,8.8)	2
		N_{ax}	2.282(31)	(N_{eq},N_{ax})	90.9(12,19.6)	
		N_{ax}	2.534(29)	(N_{ax},N_{ax})	146.7(12)	
$[Cu\{(py)_2dap\}]BF_4\cdot 0.5CH_2Cl_2\cdot 0.5H_2O$	CuN_5	N_{eq}	2.070(14,38)	(N_{eq},N_{eq})	120.0(5,8.1)	3
		N_{ax}	2.257(14,17)	(N_{eq},N_{ax})	90.8(6,23.2)	
				(N_{ax},N_{ax})	148.5(6)	

---

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

[b] The chemical identity of the coordinating atom or ligand.

[c] There are two crystallographically independent molecules.

[d] By neutron diffraction.

TABLE 2

Crystallographic data of binuclear red copper(I) compounds[a]

Compound	Chromophore	M–L (Å)		M–M (Å) M–L–M (degrees)	L–M–L (degrees)		Ref.
$[Cu(SC_6H_4Me\text{-}o)(phen)]_2 \cdot MeCN$	CuN_2S_2	N^b	2.10(1,4)	2.613(3)	$(N,N)^b$	79.3(4,2)	23
		μS	2.337(6,42)	68.0(1,2)	(N,S)	117.1(4,8.6)	
					(S,S)	106.4(2,1.0)	
$[Cu_2(dmad)(tc\text{-}6,6)]$	CuN_2C_2	N	1.912(6,11)	2.788(1)	(N,N)	84.3(2,2)	17
		μC	1.943(7,9)		(N,C)	118.2(3,2.1)	
					(C,C)	39.5(3,0)	
$[Cu_2(dead)(tc\text{-}6,6)]$	CuN_2C_2	N	1.909(3,3)	2.806(1)	(N,N)	83.9(2,2)	17
		μC	1.948(4,13)		(N,C)	118.3(2,2.3)	
					(C,C)	39.6(2,0)	
$[Cu(C_{12}H_{10}N_2S_3)I]_2$	CuS_3I	S	2.363(2)	2.964(2)	(S,S)	102.86(5,83)	18
		μS	2.398(2,61)		(S,I)	106.68(5)	
		I	2.535(2)			130.06(5)	
$[Cu_2(tc\text{-}5,5)Br] \cdot [Li(12\text{-}crown\text{-}4)_2]$	CuN_2Br	N	2.009(9,15)	2.975(3)	(N,N)	80.9(3,3)	19
		μBr	2.314(6,6)	80.01(1)	(N,Br)	139.1(3,1.2)	
$[Cu(ptp)]_2(ClO_4)_2$	CuN_4	N	2.016(3,8)	3.422(1)	(N,N)	109.8(1,16.4)	20

$[Cu(S_2ct)(dppm)]_2$	CuP_2S_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)	
$[Cu(C_5H_5N_4S)Cl_2]_2 \cdot 2H_2O$	$CuCl_2S_2$	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)	
$[Cu(C_{24}H_{22}N_4)]_2 \cdot (ClO_4)_2 \cdot H_2O$	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)	
$[Cu_2(C_{20}H_{24}N_4S_4)(NCS)] \cdot (ClO_4)$	CuN_2S_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_3S	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)	

---

[a] 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.

[b] The chemical identity of the coordinating atom or ligand.

Cu—S—Cu angles of 68.0(1,2)°. This is the shortest Cu—Cu distance found in this series of compounds.

In another example [21] containing the $[Cu(C_{24}H_{22}N_4)]_2^{2+}$ cation, the copper(I) atoms are linked by both ligands in a bis-bidentate fashion $(2_{py} + 2_{py})$, via the nitrogen atoms of the ligand $C_{24}H_{22}N_4$. The distance between the copper(I) atoms is 3.90 Å, each of them being tetrahedrally coordinated.

The structure of the $[Cu_2(C_{20}H_{24}N_4S_4)(NCS)]^+$ 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 $[Cu_2(tc\text{-}5,5)Br]^-$ 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 $[Cu(ptp)]_2(ClO_4)_2$ [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,

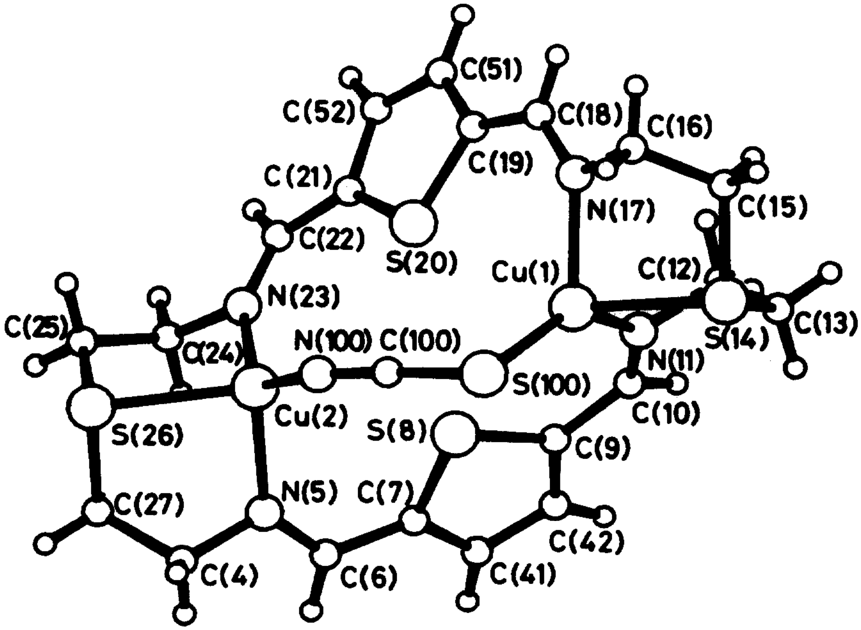

Fig. 2. View of the structure of $[Cu_2(C_{20}H_{24}N_4S_4)(NCS)]^{2+}$ cation [22].

especially the position of the charge transfer band, corresponds closely with those of the monuclear 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 $[CuS_6]_3^{3-}$ 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 $[CuC_3B_9H_{10}(4\text{-}(C_5H_4N)CO_2Me]$ 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 $(PPh_4)_2[Cu_4(C_2H_5S)_6]$ [28] is built up from $[Cu_4S_6]^{2-}$ 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 $[Cu_2Cl_2(4\text{-}Meq)_3]_2$ 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 $[Cu(PPh_3)H]_6$ 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.
$(Et_4N)_3[Cu(S_6)]_3$	CuS_3	S[b]	2.21	Not given	(S,μS)[b]	134.3	26
		μS	2.20	107.7	(μS,μS)	106.0	
$[Cu(\mu\text{-}H)(C_2B_9(4\text{-}C_5H_4N)\cdot CO_2Me)]_3\cdot 0.5C_7H_{16}$	CuB_3C_2H	B	2.229(8,119)	2.519(2)	(B,B)	47.2–162.0(3)	27
		C	2.635(9,1)		(B,H)	117.8(–,6.0)	
		μH	1.608			156.6	
$(PPh_4)_2[Cu_4(C_2H_5S)_6]\cdot 0.5C_2H_6O_2$	CuS_3	μS	2.281(3,33)	2.725(1,55)	(S,S)	119.9(1,9.5)	28
				73.4(1,1.7)			
$(PPh_4)_2[Cu_4(o\text{-}(SCH_2)_2\cdot C_6H_4)_3]\cdot MeCN$	CuS_3	μS	2.272(4,28)	2.726(2,27)	(S,S)	119.9(1,5.6)	29
$[Cu_4(C_5H_6N_2S)_6]\cdot(BF_4)_4$	CuS_3	S	2.241(1)	2.792(1,79)	(S,μS)	112.0(1)	30
	(2×)	μS	2.264(–)			127.8(1)	
			2.356(1)		(μS,μS)	120.2(1)	
	CuS_2N	N	2.035(3)		(N,S)	103.6(1)	
		μS	2.264(–)			142.6(1)	
			2.356(1)		(S,S)	113.7(1)	
$[Cu_2(4\text{-}Meq)_3Cl_2]_2$	$CuCl_3N$	N	2.019(4)	2.777(1)	(Cl,Cl)	103.3(1,8.2)	31
	(2×)	μCl	2.295(2)	71.4(1,7.4)	(N,Cl)	102.3(1,5.0)	
		μ_3Cl	2.355(2)			135.1(2)	
		μ_3Cl	2.772(2)				
	CuN_2Cl_2	N	2.057(5,12)	3.205(2)	(N,N)	103.9(2)	
	(2×)	μCl	2.355(1)	130.9(1)	(N,Cl)	112.6(1,9.5)	
		μ_3Cl	2.440(2)		(Cl,Cl)	103.0(1)	
$[Cu(o\text{-}MeC_6H_4CS_3)]_4$	CuS_3	S	2.229(1,8)	2.861(1,154)	(S,μS)	99.20(6,44)	32
		μS	2.251(2,41)	76.56(5,1.66)		131.82(6,4.82)	
					(μS,μS)	126.30(6,5.07)	
$[Cu(\alpha\text{-}C_{10}H_7CS_3)]_4\cdot 0.5CS_2$	CuS_4	S	2.223(2,3)	3.028(2,37)	(S,μS)	99.1(8,6)	33
		μS	2.253(2,34)	100.5(8,1.0)			

$[Cu(2,4,6\text{-}Me_3C_6H_2CS_3)]_4Me_2CO$	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)		125.0(1,2.1)	
					(μS,μS)	133.1(1,1.9)	
$[Cu(PPh_3)H]_6 \cdot dmf$	CuH_3P	P	2.240(9,22)	2.542(6,53)			34
		μ_3H	Not given	2.655(6,23)			
$[Cu(C_{14}H_{12}NOS)]_6 \cdot 3CH_2Cl_2$	CuS_2N	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)	
$[Cu(Pr_2NCOS)]_6$	CuS_2O	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)	
$Cu_8(SC_5H_{11})_4(S_2CSC_5H_{11})_4$	CuS_3	S	2.273(6,10)	2.652–3.250	(S,S)	119.8(2,4.1)	37
	(4 ×)	μS	2.273(6,8)	74.3(2,3.5)			
		μ_3S	2.245(6,8)	87.7(2.20)			
				120.0(2,4)			
	CuS_3	μS	2.286(6,6)		(S,S)	119.5(2,10.5)	
	(4 ×)	μ_3S	2.275(6,30)				
$(PPh_4)_4[Cu_8(S_2C_4O_2)_6] \cdot CH_3CN$	CuS_3	μS	2.247(3,22)	2.844(2,58)	(S,S)	116.17(14,4.80)	38
				4.022(2,38)			
				78.52(8,2.31)			
$Cu_{10}(C_{12}H_{19}O_4S_2)_6 \cdot (C_{12}H_{18}O_4S_2)_2$	CuS_3	μ_3S	2.269(3,49)	2.820(2,236)	(S,S)	119.4(2,13.4)	39
	(8 ×)			74.40(9,7.74)			
	CuS_2O	μ_3S	2.198(3,11)		(S,S)	148.1(2)	
	(2 ×)	O	1.898(8)		(S,O)	105.2(3,5.6)	
$[Cu(SC_6H_4\text{-}o\text{-}SiMe_3)]_{12}$	CuS_2	μS	2.160(8,18)	Not given	(S,S)	174.7(3,5)	40
	(3 ×)			81.8(3,9.2)			
				132.2(3,8)			
	CuS_2	μ_3S	2.200(8,12)		(S,S)	163.6(3,7)	
	(3 ×)						
	CuS_3	μS	2.200(8,40)	Not given	(S,S)	84.7(3,10.9)	
	(6 ×)	μ_3S	2.285(8,38)	107.5(3,3.9)		134.0(3,1.5)	
				143.6(3,1.6)			

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	CN	1.823(4)				41
	$CuN_2(C/N)_2$	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				
$Cu_2Br_3 \cdot (C_6H_5N_2)$	$CuBr_4$	μBr	2.45	2.86			43
		$\mu_4 Br$	2.57	3.09			
$\{(Me_4N_2)_2CH\}[Cu_2Br_3]$	$CuBr_4$	μBr	2.432(2,10)	2.948(2,44)	(Br,Br)	109.28(7,10.12)	44
		$\mu_4 Br$	2.600(2,20)	3.213(2,12)			
				73.35(6,5.68)			
				113.98(6,6)			
$[Cu_2(C_8H_6N_2)_3(ClO_4)] \cdot ClO_4$	CuN_3O	N	2.026(7,78)		(N,N)	104.9(3,3.8)	45
		O	2.536(8)			139.1(3)	
					(N,O)	100.0(3,15.1)	
	CuN_3O_2	N	2.023(6,43)		(N,N)	110.4(2,6.0)	
		$\mu_2 O$	2.385(8,0)			136.3(3)	
					(N,O)	95.4(3,2.8)	
$Cu(CN)(C_{14}H_{12}N_2)$	CuN_3C	N	2.126(9,5)		(N,N)	79.1(3)	46
		CN	2.008(11)		(N,N)	110.1(4,2.6)	
		NC	1.897(12)		(N,C)	117.9(4,8.0)	
$Cu(NCS)(C_{14}H_{12}N_2)$	CuN_3S	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_3C	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_3C	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_5H_5NCOOH)Cl	$CuCl_3N$	N	1.995(7)		(N,Cl)	107.2(3,2.7)	48
		μCl	2.354(3,38)			123.0(3)	
			2.488(3)		(Cl,Cl)	105.3(1,3)	
CuCl($C_5H_8N_2$)	CuN_2Cl_2	N	1.90(2,2)	3.36(1,4)	(N,N)	128.3(9)	49
		μCl	2.38(1,1)	89.8(4,1.0)	(N,Cl)	103.1(8,2.8)	
					(Cl,Cl)	117.3(4)	
Cu($C_8H_6N_4S_2$)Cl·H_2O	CuN_2Cl_2	N	1.966(3)		(N,N)	142.2(1)	50
		μCl	2.464(1)	84.26(4)	(N,Cl)	100.00(9)	
					(Cl,Cl)	95.74(4)	
CuCl(C_5H_5NCOOH)$_2$	CuN_2Cl_2	N	2.032(9,12)		(N,N)	118.8(4)	51
		μCl	2.377(4,14)	105.2(4)	(N,Cl)	108.1(3,4.4)	
					(Cl,Cl)	105.2(2)	
$(NH_4)[Cu_3Cl_4(C_6H_4O_2)_{1.5}]\cdot H_2O$	$CuCl_3C_2$	C	2.072(5,25)		(C,C)	38.3(2,1)	52
		μCl	2.280(2,15)	80.40(5,1.44)	(C,Cl)	117.8(2,7.2)	
		μCl	2.346(2,21)	88.64(5,1.54)	(Cl,Cl)	98.73(6,11.25)	
		μ_3Cl	2.504(1,16)				

---

[a] 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.

[b] The chemical identity of the coordinating atom.

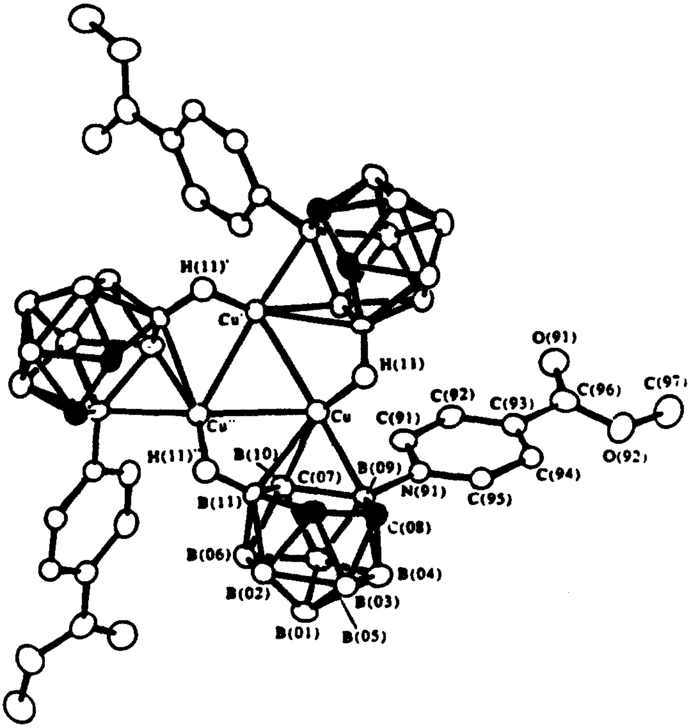

Fig. 3. Molecular structure of $[Cu_3(r\text{-}H)_3\{C_2B_9H_9(4\text{-}(C_5H_4N)CO_2Me\}]$ [27].

their Cu–Cu distances, ranging from 2.632(6) to 2.674(5) Å. The remaining Cu–Cu distances range from 2.494(6) to 2.595(5) Å, with each Cu(I) atom apically bonded to a PPh_3 ligand [34].

In another hexanuclear copper(I) compound [35], the copper(I) atoms define a distorted octahedron as shown in Fig. 5. This has been described in terms of two triangular faces consisting of Cu(I), Cu(2′) and Cu(3) together with their centrosymmetric equivalents. The six ligand moieties link Cu(I) atom triangles through donor S and N atoms, resulting in a "paddle-wheel"-shaped core, with CuNCS fragments as the "blades".

In the octanuclear compounds [37,38] the molecular structure is based on a Cu_8S_{12} cage with each copper(I) atom coordinated by three sulphur atoms. The overall description of the Cu_8S_{12} cores is of a cube of copper atoms inserted into a distorted icosahedron of sulphur atoms.

The copper(I) framework of a decanuclear cluster [39] consists of two Cu_4 subunits. Of the four ligands surrounding each of the subunits, three are $C_{12}H_{19}O_4S_2$ and the fourth is $C_{12}H_{18}O_4S_2$. The latter connects the Cu_4 fragment to the bridging copper atom by coordination via O and S atoms. A third coordination site on the

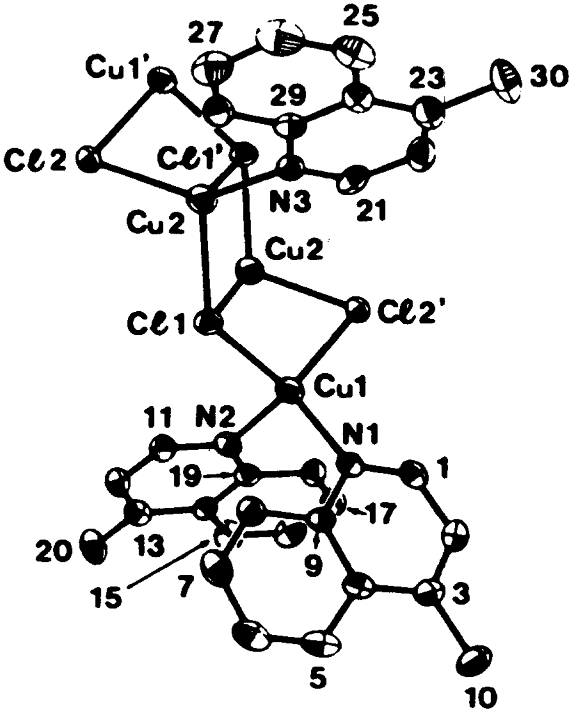

Fig. 4. Structure of $[Cu_2Cl_2(4\text{-Meq})_3]_2$ [31].

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

As shown in Fig. 6, the structure of $[Cu(SC_6H_4\text{-}o\text{-}SiMe_3)]_{12}$ consists of discrete dodecanuclear clusters of unique molecular geometry [40]. The structure was described as a molecular "paddle wheel" with the $Cu_{12}S_{12}$ as a core.

The remaining compounds given in Table 3 are polynuclear. The structure of $Cu(CN)(C_{14}H_{12}N_2)$ [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 cm^{-1}. Polarized single-crystal spectra [41,46] show two bands at 19 000 cm^{-1} and 22 000 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].

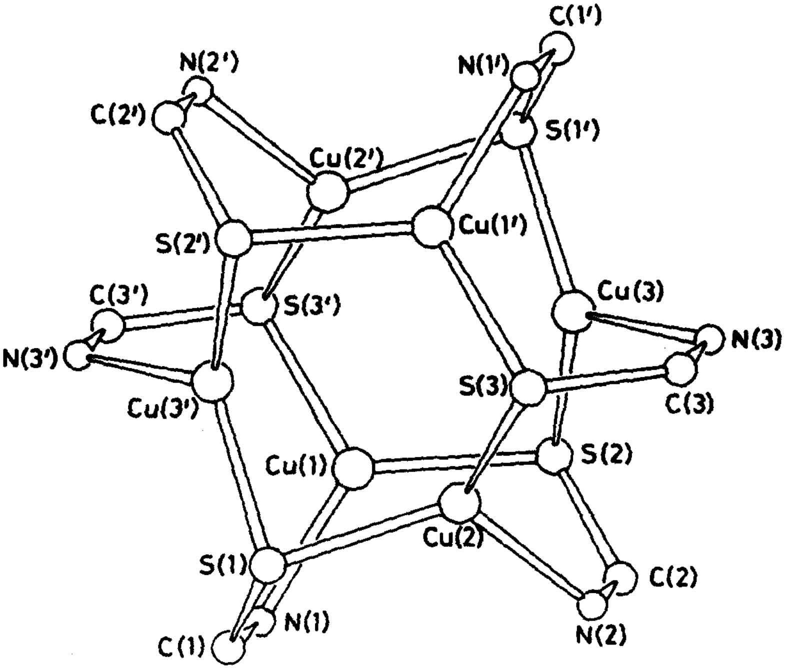

Fig. 5. View of the central core of $[Cu(C_{14}H_{12}NOS)]_6$ [35].

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).

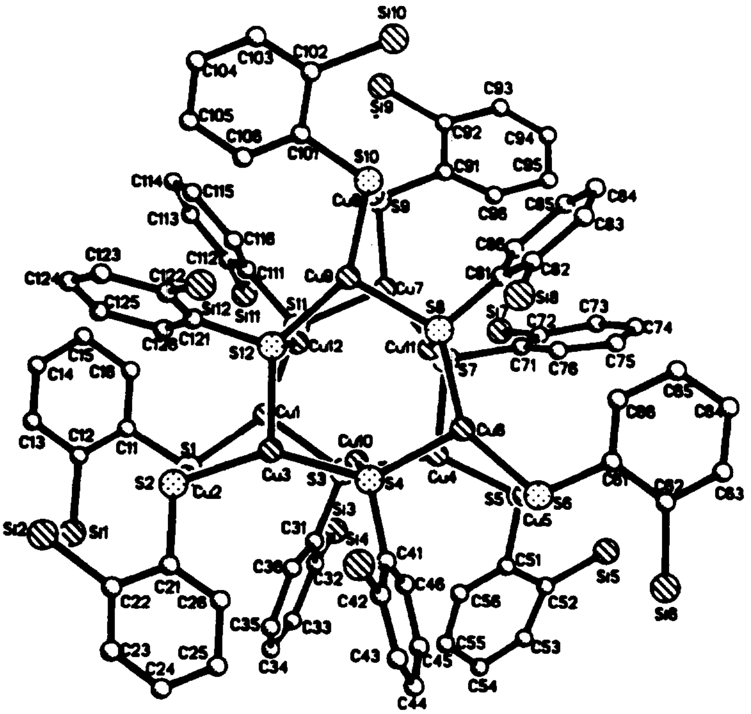

Fig. 6. View of the structure of $[Cu(SC_6H_4\text{-}o\text{-}SiMe_3)]_{12}$ [40].

A survey of the data in Tables 1–3 shows that the mean Cu(I)—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 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-

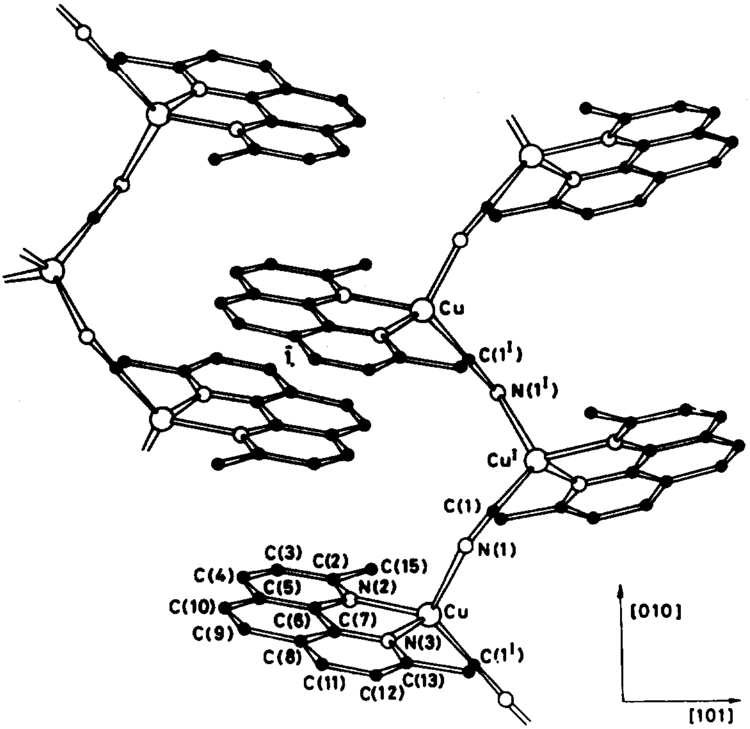

Fig. 7. Projection of the structure of $Cu(CN)(C_{14}H_{12}N_2)$ [46].

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.

ACKNOWLEDGEMENTS

The authors wish to thank those who gave permission for reproduction of figures, and the Ministry of Education, Slovak Republic, for financial support.

REFERENCES

1 M. Melnik, L. Macaskova, J. Mrozinski and D. Szymaszek, Acta Chim. Hung., 128 (1991) 945.
2 J.A. Goodwin, G.A. Bodager, L.J. Wilson, D.M. Stanbury and W.R. Scheidt, Inorg. Chem., 28 (1989) 35.
3 J.A. Goodwin, D.M. Stanbury, L.J. Wilson, C.W. Eigenbrot and W.R. Scheidt, J. Am. Chem. Soc., 109 (1987) 2979.
4 A. Maurer, D. Fenske, J. Beck, W. Hiller, J. Strähle, E. Böhm and K. Dehnicke, Z. Naturforsch. Teil B, 43 (1988) 5.
5 L. Stamp and H. Von Dieck, Inorg. Chim. Acta, 147 (1988) 199.
6 H.W. Roesky, K.K. Pandey, M. Noltemeyer and G.M. Sheldrick, Acta Crystallogr. Sect. C, 40 (1984) 1555.
7 D. Coucouvanis, C.N. Murphy and S.K. Kanodia, Inorg. Chem., 19 (1980) 2993.
8 A.Y. Kon, I.F. Burshtejn, N.N. Proskina and B.T. Ibragimov, Koord. Chim., 13 (1987) 260.
9 J.F. Dobson, B.E. Green, P.C. Healy, C.H.L. Kennard, Ch. Pakawatchai and A.H. White, Aust. J. Chem., 37 (1984) 649.
10 R. Hamalainen, U. Turpeinen, M. Ahlgren and T. Raikas, Finn. Chem. Lett., (1978) 199.
11 Ph. J. Burke, D.R. McMillin and W.R. Robinson, Inorg. Chem., 19 (1980) 1211.
12 E. Müller, C. Piguet, G. Bernardinelli and A.F. Williams, Inorg. Chem., 27 (1988) 849.
13 T. Ogura, E. Shemesh, N. Scott, G.J. Pyrka and Q. Fernando, Inorg. Chim. Acta, 149 (1988) 57.
14 J. Bojes, T. Chivers and P.W. Codding, J. Chem. Soc. Chem. Commun., (1981) 1171.
15 B.E. Green, C.H.L. Kennard, G. Smith, M.N. Elcombre, F.H. Moore, B.D. James and A.H. White, Inorg. Chim. Acta, 83 (1984) 177.
16 K.K. Pandey, M. Noltemeyer, G.M. Sheldrick and R. Saheb, Z. Naturforsch. Teil B, 39 (1984) 586.
17 G.M. Villacorta, D. Gibson, I.D. Williams, E. Whang and St. J. Lippard, Organometallics, 6 (1987) 2426.
G.M. Villacorta, D. Gibson, I.D. Williams and St. J. Lippard, J. Am. Chem. Soc., 107 (1985) 6732.
18 P.J.H.A.M. van de Leemput, J. Willemse, J.A. Cras and L. Groen, Recl. Trav. Chim. Pays Bas, 98 (1979) 413.
19 G.M. Villacorta, Ch. P. Rao and St. J. Lippard, J. Am. Chem. Soc., 110 (1988) 3175.
20 S.K. Mandal, L.K. Trompson, E.J. Gabe, F.L. Lee and J.P. Charland, Inorg. Chem., 26 (1987) 2384.
21 J.M. Lehn, J.P Sauvage, J. Simon, R. Ziessel, C. Piccinni-Leopardi, G. Germain, J.P. Declercq and M. Van Meerssche, Nouv. J. Chim., 7 (1983) 413.
22 A. Lavery, S.M. Nelson and M.G.B. Drew, J. Chem. Soc., Dalton Trans., (1987) 2975.
23 R.K. Chadha, R. Kumar and D.G. Tuck, Can. J. Chem., 65 (1987) 1336.
24 A.M. Monotti Lanfredi, F. Ugozzoli, A.M. Camus and N. Marsich, Inorg. Chim. Acta, 99 (1985) 111.
25 M.R. Caira and L.R. Nassimbeni, Acta Crystallogr. Sect. B, 31 (1975) 1339.
L. Pope, M. Laing, M.R. Caira and L.R. Nassimbeni, Acta Crystallogr. Sect. B, 32 (1976) 612.
A.L. Shoemaker, P. Singh and D.J. Hodgson, Acta Crystallogr. Sect. B, 32 (1976) 979.
26 A. Müller and U. Schimanski, Inorg. Chim. Acta, 77 (1983) L187.
27 H. Chyul Kang, Y. Do, C.B. Knobler and M.F. Hawthorne, Inorg. Chem., 27 (1988) 1716.
28 M. Baumgartner, H. Schmalle and E. Dubler, Polyhedron, 9 (1990) 1155.

29 J.R. Nicholson, I.L. Abrahams, W. Clegg and C.D. Garner, Inorg. Chem., 24 (1985) 1092.

30 D.M.L. Goodgame, G.A. Leach, A.C. Skapski and K.A. Woode, Inorg. Chim. Acta, 31 (1978) L375.

31 Th.C.W. Mak, M.A.S. Goher and A.K. Hafez, Inorg. Chim. Acta, 146 (1988) 103.

32 J.A. Schuerman, F.R. Fronczek and J. Selbin, Inorg. Chim. Acta, 148 (1988) 177.

33 T. Kaluo, G. Hong, X. Xiaojie, Z. Gongdu and T. Youqi, Sci. Sin. Ser. B, 27 (1984) 456.

34 M.R. Churchill, S.A. Bezman, J.A. Osborn and J. Wormald, Inorg. Chem., 11 (1972) 1818.
S.A. Bezman, M.R. Churchill, J.A. Osborn and J. Wormald, J. Am. Chem. Soc., 93 (1971) 2063.

35 N. Narasimhamurthy, A.G. Samuelson and H. Manohar, J. Chem. Soc. Chem. Commun., (1989) 1803.

36 R. Hesse and U. Aava, Acta Chem. Scand., 24 (1970) 1355.

37 R.K. Chadha, R. Kumar and D.G. Tuck, Polyhedron, 7 (1988) 1121.

38 F.J. Hollander and D. Coucouvanis, J. Am. Chem. Soc., 99 (1977) 6268.

39 D. Coucouvanis, D. Swenson, N.C. Baenziger, R. Pedelty, M.L. Caffery and S. Kanodia, Inorg. Chem., 28 (1989) 2829.
D. Coucouvanis, D. Swenson, N.C. Baenziger, R. Pedelty and M.L. Caffery, J. Am. Chem. Soc., 99 (1977) 8097.

40 E. Block, M. Gernon, H. Kang, G. Ofori-Okai and J. Zubieta, Inorg. Chem., 28 (1989) 1263.
E. Block, M. Gernon, H. Kahg, Sh. Liu and J. Zubieta, J. Chem. Soc. Chem. Commun., (1988) 1031.

41 G. Dessy, V. Fares, P. Imperatori and G.O. Morpurgo, J. Chem. Soc. Dalton Trans., (1985) 1285.

42 F. Sanz, An. Fis., 72 (1976) 43.

43 Chr. Romming and K. Werstad, J. Chem. Soc. Chem. Commun., (1965) 299.

44 J.R. Boehm, A.L. Balch, K.F. Bizot and J.H. Enemark, J. Am. Chem. Soc., 97 (1975) 501.

45 P. Lumme, S. Lindroos and E. Lindell, Acta Crystallogr. Sect. C, 43 (1987) 2053.

46 G.O. Morpurgo, G. Dessy and V. Fares, J. Chem. Soc. Dalton Trans., (1984) 785.

47 D.T. Cromer and A.C. Larson, Acta Crystallogr. Sect. B, 28 (1972) 1052.

48 M.A.S. Goher and T.C.W. Mak, Inorg. Chim. Acta, 101 (1985) L27.

49 G.S. Chandler, C.L. Raston, G.W. Walker and A.H. White, J. Chem. Soc. Dalton Trans., (1974) 1797.

50 Ch.J. Simmons, M. Lundeen and K. Seff, Inorg. Chem., 18 (1979) 3444.

51 M.A.S. Goher and Th.C.W. Mak, Inorg. Chim. Acta, 127 (1987) L13.

52 T. Uechi, H. Yamaguchi, I. Ueda and K. Yasukouchi, Bull. Chem. Soc. Jpn., 53 (1980) 3483.

53 A.A. DelPaggio and D.R. McMillin, Inorg. Chem., 22 (1983) 691.

54 M. Melnik, Coord. Chem. Rev., 47 (1982) 239.

55 C. Kratky, E. Nachbaur and A. Popitsch, Monatsh. Chem. 112 (1981) 529.