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MIXED-VALENCE COPPER(I)–COPPER(II) COMPOUNDS: ANALYSIS AND CLASSIFICATION OF CRYSTALLOGRAPHIC DATA

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CONTENTS

ABBREVIATIONS

ac	acetate
acacP	[*o*-(diphenylphosphino)benzoyl]pinacolate
apae	2-[(3-aminopropyl)amino]ethanolate
bipy	2,2′-bipyridine
bta	benzotriazolate

c	cubic
3-$CH_3OC_6H_4COO^-$	3-methoxybenzoate
t-C_6H_9NC	tert-butylisocyanide
dhbo	7,8,15,16,17,18,25,26,33,34,35,36-dodecahydrotetrabenzo[e,m,s,a][1,4,8,11,15,18,22,25]octaazacyclo-octacosine
dhm	1,3-diaminopropane-2-hydroxy-5-methylisophthalaldehyde
dmc	β,β-dimethylcysteaminate
2,5-dth	2,5-dithiahexane
en	ethylenediamine
Et	ethyl
m	monoclinic
mci	1-methyl-2-mercaptoimidazolate
Me	methyl
4-Metz	4-methylthiazole
miba	α-mercaptoisobutyrate
N-bh	*N*-benzoylhydrazine
$N_2H_5^+$	hydrazinium
$N_6P_6(NMe_2)_{12}$	dodeca(dimethylamino)cyclohexaphosphazene
or	orthorhombic
Pen	penicillaminate
$P(OEt)_3$	triethylphosphite
PPh_3	triphenylphosphine
tbec	1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane
tg	tetragonal
tht	tetrahydrothiophene
tr	triclinic

A. INTRODUCTION

Compounds containing a metal in two valence states are of special interest because of the possibility of easy electron transfer between these states [1]. Electron transfer between Cu(II) and Cu(I) is of central importance in a vast range of chemical and biochemical catalytic systems. Copper(II)–copper(I) electron transfer is also intrinsically interesting in comparison with the more well-studied iron, cobalt, and ruthenium electron-transfer couples. In these last couples, both oxidation states are six-coordinate and usually one or both oxidation states are inert, whereas copper(II) and copper(I) prefer different coordination numbers and stereochemistry and both oxidation states are highly labile and stereochemically flexible [2,3]. Thus a number of mixed copper(I)–copper(II) complex salts have been prepared and investigated [4]. Crystal structures of mixed Cu(I)–Cu(II) compounds have received considerable attention for what they may reveal about structural changes accompanying oxidation and reduction of copper in metalloenzymes [5]. They also prompted a wide range of theoretical treatments concerning their properties.

The chemistry of mixed Cu(I)–Cu(II) compounds, covering aspects of bonding has been an active field of study for some time; the number of crystal structure determinations in this time has increased. The material contained in this review has been obtained from published literature up until the end of 1985.

The aim of the review is to provide the first overall survey and classification of the structures for mixed copper(I)–copper(II) complex salts. The systems to be discussed here can largely be grouped into four classes: a series of copper compounds containing copper(I) anion and copper(II) cation species; a series of bi- and polynuclear ligand(s) bridged compounds; thiocyanate and selenocyanate Cu(I)–Cu(II) compounds; and a series of cluster Cu(I)–Cu(II) compounds.

B. COPPER COMPOUNDS CONTAINING COPPER(I) ANION AND COPPER(II) CATION SPECIES

(i) Preparation

The following synthetic methods have generally been used in the case of [6,7]

$$2CuCl_2 + L \rightarrow [CuClL][CuCl_2] + \tfrac{1}{2}Cl_2$$

Black $[Cu(bipy)_2][CuCl_2]_2$ was obtained by reaction between 2,2′-bipyridyl, $CuCl_2 \cdot 2H_2O$ and KCl in ethanol–water solution containing a few drops of conc. HCl at about 60 °C [8].

When *N*-benzoylhydrazine in hot water was added to $CuCl_2 \cdot 2H_2O$ in hot water, long green needles of $Cu(N\text{-bh})_2Cu_3Cl_5$ were obtained [9].

The compounds of the general formula $[Cu(NH_3)_4][CuX_2]_2$ were prepared [10,11] by mixing copper(I) and copper(II) salts (X = Cl) and also by partial reduction of copper(II) salts (X = Br or I).

Dark green $[Cu_2(apae)_2]_2[Cu(NCS)_4](NCS)$ [12] was obtained by two-step reactions. First aqueous solutions of KSCN and $Cu(NO_3)_2 \cdot 3H_2O$ in the molar ratio 2 : 1 were mixed and the black precipitate was separated. When a methanol suspension of the black precipitate was added to a stirred methanol solution of the amine, a dark green product was obtained.

By evaporation of a mixture containing sodium thiosulphate, copper(II) sulphate and tetraammine copper(II) sulphate to pale violet needles of composition $Na_4[Cu(NH_3)_4][Cu_n(S_2O_3)_2]_2$ [13] were obtained.

The courses of the redox reactions are highly dependent upon the specific conditions used: reagent and acid/base concentrations, medium, reaction temperatures, duration of reaction, and crystallization temperatures.

(ii) Structures

In Table 1 are collected structural data for mixed-valence compounds containing copper(I) anion and copper(II) cation species. Obviously, both coordination number and stereochemistry of copper(I) species differ from those of copper(II). While the copper(II) coordination number ranges from four to six, copper(I) coordination is just two and four. The structure of $[Cu^{II}Cl\{N_6P_6(NMe_2)_{12}\}][Cu^{I}Cl_2]$ [6] and $[Cu^{II}Cl(tbec)][Cu^{I}Cl_2](EtOH)_3$ [7] consists of Cu(II) complex cations and $[Cu^{I}Cl_2]^-$ anions. The $[Cu^{I}Cl_2]^-$ anion moiety is linear [6], or nearly linear [7]. The Cu(1)–Cl bond distances (Table 1) are slightly less than the sum of the covalent radii [14] of chlorine (0.99 Å) and copper(I) (1.18 Å) in a linear coordination (2.17 Å). The copper(II) complex cations [6,7] are surrounded by two ligands (one unidentate and one tetradentate) in the form of a distorted square pyramid, the equatorial plane of which consists of the four nitrogen atoms of the phosphazene ring (Cu(II)–N = 2.07(2,4) Å) in the former [6] and of the tbec ligand (Cu(II)–N = 2.09(2,4) Å) in the latter [7]. The apical position is occupied by a chlorine atom at a Cu(II)–Cl distance of 2.28(1) [6] and 2.371(6) Å [7], respectively. The first number in parentheses is the e.s.d., and the second is the maximum deviation from the mean value.

Figure 1 illustrates the schematic outline of $Cu^{II}(bipy)_2 \cdot (Cu^{I}Cl_2)_2$ [8]. The crystal structure reveals that the copper(I) atoms fall into two nonequivalent chromophores; two Cu(I) atoms (Cu(1) and Cu(2)) have a $CuCl_2$ chromophore and one Cu(I) atom (Cu(4)) a $CuCl_4$ chromophore (Table 1). The Cu(II) atom (Cu(3)) has a trigonal bipyramidal arrangement composed of the four nitrogen atoms of the two bipyridyl groups and the chlorine atom. The structure contains isolated $[Cu^{I}(1)Cl_2]^-$ ions, $Cu^{II}(3)(bipy)_2Cl$ groups, and infinite chains built from $Cu^{I}(2,4)$ and Cl atoms.

X-ray analysis of green needles of $Cu^{II}(N\text{-bh})_2Cu^{I}_3Cl_5$ [9] shows the two *N*-benzoylhydrazine bidentate chelates are arranged in an equatorial *cis* configuration around the Cu(II) atom, with chloride ions in the axial positions of a distorted octahedron. All five Cl^- ions per molecule are involved in bonding to the three Cu(I) atoms in an infinite cylinder of distorted tetrahedra.

In all the other examples in Table 1 the copper(I) atoms are tetrahedrally coordinated to four halide ions [10,11], four thiocyanate groups [12] or thiosulphate groups [13] and the copper(II) atoms have square-planar [10,11,13] and square-pyramidal [10,12] coordination.

The more common arrangement around the copper(I) atom is tetrahedral, while for copper(II), square-pyramidal five-coordinate species are most common. The most unusual structural feature of the mixed-valence compounds gathered in Table 1, is the alternating coordination number, two and four, in the copper(I) chlorine chain [8]. To our knowledge, this is the only example of this kind of diversity in the stereochemistry of copper(I) compounds.

Inspection of the data in Table 1 reveals that the mean Cu–L bond distance increases with coordination number. For example, the mean Cu(I)–Cl distance of 2.083 Å found for the $CuCl_2$ chromophore is about 0.290 Å smaller than that found in $CuCl_4$ species (2.373 Å). The Cu–L (terminal) distances are somewhat shorter than those of the Cu–L (bridge)

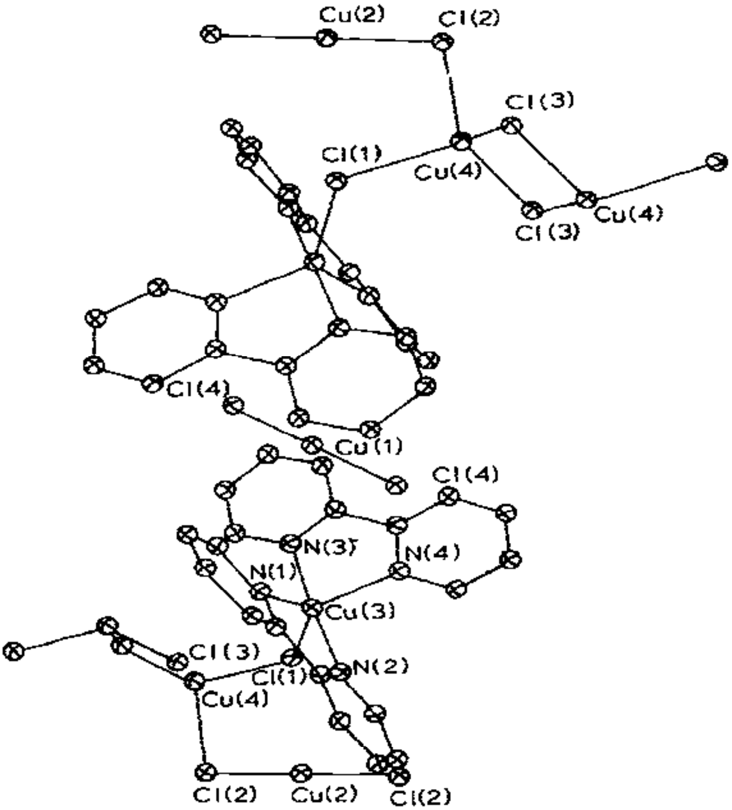

Fig. 1. Schematic outline of $Cu^{II}(bipy)_2(Cu^{I}Cl_2)_2$. Reproduced with permission from J. Chem. Soc., Dalton Trans. [8].

TABLE 1

Structural data for mixed-valence copper(II) "cation"–copper(I) "anion" compounds [a]

Compound	Crystal class	Space group	Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore [b]		Cu–L (Å)	L–Cu–L (°)	Ref.
[Cu^{II}Cl{N$_6$P$_6$(NMe$_2$)$_{12}$}]	m	$P2/n$	2	19.352 (8)		Cu^{I}Cl$_2$	Cl	2.06 (1)	179.5 (9)	6
[Cu^{I}Cl$_2$]				8.690 (6)	91.04 (4)			2.11 (1) [c]		
				14.069 (7)						
						Cu^{II}N$_4$Cl	N	2.07 (2, 4)	85.1 (8, 14.1) [d]	
							Cl	2.28(1)	109.7 (6, 10.1)	
[Cu^{II}Cl(tbec)]·[Cu^{I}Cl$_2$]	tr	$P\bar{1}$	2	14.912 (10)	110.5 (6)	Cu^{I}Cl$_2$	Cl	2.073 (10, 27)	169.5 (8)	7
·(EtOH)$_3$				15.054 (9)	103.7 (7)					
				13.809 (12)	67.68 (5)	Cu^{II}N$_4$Cl	N	2.09 (2, 4)	86.0 (4, 7) [d]	
							Cl	2.371 (6)	106.0 (4, 6.3)	
Cu^{II}(bipy)$_2$(Cu^{I}Cl$_2$)$_2$	tr	$P\bar{1}$	2	9.40 (2)	122.15 (13)	Cu^{I}Cl$_2$	Cl	2.115 (2, 25)	Not given	8
				10.68 (3)	103.67 (13)	Cu^{I}Cl$_4$	Cl	2.364 (2, 29)	Not given	
				15.34 (4)	105.93 (12)	Cu^{II}N$_4$Cl	N	2.032 (5, 43)	Not given	
							Cl	2.355 (2)		
Cu^{II}(N-bh)$_2$Cu$^I_3$Cl$_5$	or	$Pbca$	8	9.299 (2)		Cu^{I}Cl$_4$	Cl	2.397 (4, 599)	107.1 (1, 32.7)	9
				16.165 (3)						
				28.656 (6)		Cu^{II}O$_2$N$_2$Cl$_2$	O	1.938 (8, 8)	89.2 (3, 11.0)	
							N	2.009 (9, 0)	172.5 (4, 3.5)	
							Cl	2.946 (4, 184)		

$Cu^{II}(NH_3)_4(Cu^{I}Cl_2)_2 \cdot H_2O$	tg	*I*4/*mmm*	2	10.19 (2)		$Cu^{I}Cl_4$	Cl	2.359 (6)	109.4 (1, 2)	10
				10.19 (2)		$Cu^{II}N_4O$	N	2.025 (20)	90	
				5.468 (8)			O	2.734 (4)		
$Cu^{II}(NH_3)_4(Cu^{I}Br_2)_2$	tg	*I*4/*mmm*	2	10.37 (2)		$Cu^{I}Br_4$	Br	2.503 (4)	109.7 (2, 7)	10
				10.37 (2)		$Cu^{II}N_4$	N	1.996 (29)	90	
				5.713 (6)						
$Cu^{II}(NH_3)_4(Cu^{I}I_2)$	tr	$P\bar{1}$	1	7.386 (2)	102.58 (2)	$Cu^{I}I_4$	I	2.725 (15, 234)	109.4 (5, 10.9)	11
				9.985 (2)	81.85 (2)	$Cu^{II}N_4$	N	2.138 (68, 25)	91.1 (22, 10.6)	
				6.931 (2)	133.52 (2)					
$[Cu^{II}_2(apae)_2]_2[Cu(NCS)_4] \cdot (NCS)$	tg	*P*4/*n*	2	14.295 (10)		$Cu^{I}N_4$	N	1.999 (7)	Not given	12
				14.295 (10)		$Cu^{II}N_2O_2S$	N	1.995 (7, 13)	89.6 (2, 9.6)	
				10.359 (6)			O [e]	1.940 (6, 4)		
							S	2.732 (3)		
$Na_4[Cu^{II}(NH_3)_4] \cdot [Cu^{I}_n(S_2O_3)_2]_2$	tg	*I*4/*m*	2	13.814 (3)		$Cu^{I}S_4$	S	2.357 (12)	Not given	13
				13.814 (3)		$Cu^{II}N_4$	N	1.994 (6)	Not given	
				5.759 (2)						

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[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses following an average value is an e.s.d., the second number is the maximum deviation from the average value. [b] The chemical identity of the coordinated atom (ligand) is specified in this column. [c] The value corrected for libration. [d] The values of N–Cu–N and N–Cu–Cl angles.

[e] The bridge atom.

distances. In general, the mean Cu–L bond distance increases with increasing van der Waals radius of the ligating atom. For example, the mean Cu(I)–L distance (van der Waals radius) increases in the order: 1.999 Å (N, 1.55 Å) < 2.357 Å (S, 1.80 Å) < 2.373 Å (Cl, 1.75 Å) < 2.503 Å (Br, 1.85 Å) < 2.725 Å (I, 2.13 Å), for $Cu^{I}L_4$ species. In the given order, the mean Cu(I)–S distance of 2.357 Å is shorter than that of Cu(I)–Cl (2.373 Å) in spite of the fact that their van der Waals radii (1.80 Å(S) versus 1.75 Å(Cl)) are inverse. This disparity is presumably due to Cu(I)–Cl(bridge) versus Cu(I)–S(terminal)) bond distances, as noted above.

C. BI- AND POLYNUCLEAR-LIGAND(S) BRIDGED COPPER(I)–COPPER(II) COMPOUNDS

(i) Preparation

Bi- and polynuclear Cu(I)–Cu(II) compounds belong to very diverse stoichiometries. In general, they can be prepared two ways: either directly by a reaction between reactants [15,16,18–23] or by electrochemistry [17,24].

For example, the green crystals of $[Cu_2(dhbo)](ClO_4)_3$ [15] were obtained when a suspension of the octa-azamacrocycle (dhbo) in tetrahydrofuran was stirred with a methanol solution of copper(II) perchlorate.

The binuclear mixed-valence $[Cu_2(dhn)](ClO_4) \cdot 0.5CH_3OH$ [17] was prepared in a helium atmosphere from the binuclear copper(II) complex of the same composition in DMF by constant-potential electrolysis at −0.7 V. During the electrolysis the solution changed in color from green to blue-green. After reaction, diethyl ether was added to this solution and the dark brown solid which precipitated was recrystallized from boiling methanol, yielding dark brown needles of the mixed-valence complex.

Most of the compounds reported in Table 2 were obtained by reaction of a copper(II) salt with a ligand [15,19–23]. The ligand serves both as a ligand and as a reducing agent in the reaction. The green crystals of $Cu^{I}Cu^{II}(acacP)_2(O_2CC_6H_4P(O)Ph_2)$ [16] and $Cu^{I}Cu^{II}(acacP)_2(3\text{-}CH_3OC_6H_4CO_2)$ [18] were obtained by oxygenation of a yellow dichloromethane solution of the binuclear $[Cu^{I}(acacP)]_2$ in the presence of O_2 [16] and 3-methoxyperoxobenzoic acid [18].

(ii) Structures

From the bridge point of view, the mixed-valence copper compounds summarized in Table 2 can be divided into several groups. In the structure of $[Cu^{I}Cu^{II}(dhbo)](ClO_4)_3$ [15], both the Cu(I) and Cu(II) atoms have very similar coordination geometries (Fig. 2) and a short Cu(I)–Cu(II) bond distance of 2.445(4) Å: this distance is the shortest found in all related copper compounds. Interestingly, the sum of all the interatomic distances in Cu(I)N_4 and Cu(II)N_4 is constant at 8.22 Å.

The green crystalline compound $Cu^{I}Cu^{II}(acacP)_2(O_2CC_6H_4P(O)Ph_2)$ has been prepared as described above and its X-ray structural analysis reported [16]. Its molecular structure consists of trigonal planar copper(I) linked to square-pyramidal copper(II) (Table 2). An unusual structural feature is the manner in which the carboxylate bridges the two metals via one oxygen atom.

In the $[Cu^{I}Cu^{II}(dhm)]^+$ cation [17] the two four-coordinate copper atoms, Cu(I) and Cu(II), are each bonded to two imine nitrogen atoms and share the two bridging phenolate oxygens of the hexadentate Schiff-base ligand (dhm). The coordination about Cu(II) is square planar, and the Cu(II) lies in the best plane of the four ligating atoms. The Cu(I) atom is distorted over two sites, with different bond lengths and angles (Table 2), although the four coordinated ligand atoms are not noticeably disordered. The sum of all interatomic distances about Cu(II) (7.864 Å) is smaller than those about Cu(I) (8.168 and 8.576 Å, respectively). The two Cu(I)–Cu(II) distances (3.223(1) and 3.348(3) Å) are too large to indicate any metal–metal bonding. There is a relationship between the Cu(I)–Cu(II) distance and the Cu(I)–O–Cu(II) bridge angle namely, as the angle opens, the distance increases.

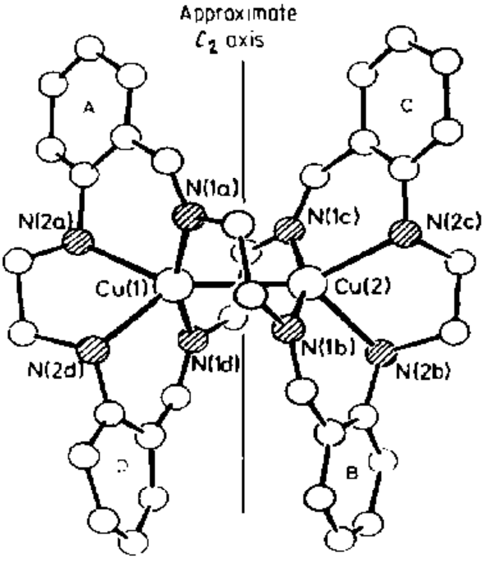

Fig. 2. Schematic outline of $[Cu^{I}Cu^{II}(dhbo)]^{3+}$. Reproduced with permission from J. Chem. Soc., Chem. Commun. [15].

TABLE 2

Structural data for bi- and polynuclear ligand(s) bridged Cu(I)–L_n–Cu(II) compounds [a]

Compound	Crystal class	Space group	Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore	[b]	Cu–L (Å)	Cu^I–Cu^{II} (Å)	L–Cu–L (°)	Cu^I–L–Cu^{II} (°)	Ref.
$[Cu^ICu^{II}(dhbo)](ClO_4)_3$	m	*Cc*	4	22.577 (7)		Cu^IN_4	N	1.92 (2, 4)	2.445 (4)	94.4 (8, 11.7)		15
				11.016 (4)	118.96 (2)			2.19 (2, 1)		159.8 (7)		
				20.909 (8)		$Cu^{II}N_4$	N	1.94 (2, 3)		95.3 (9, 9.7)		
								2.17 (2, 2)		158.0 (9)		
$Cu^ICu^{II}(acacP)_2$	tr	$P\bar{1}$	2	13.592 (4)	85.78 (3)	Cu^IOP_2	O [c]	2.102 (6)	3.269 (1)	115.0 (2, 9.1)	94.1 (2)	16
$\cdot(\mu\text{-}O_2CC_6H_4P(O)Ph_2)$				14.913 (5)	86.19 (2)		P	2.231 (6, 2)		129.8 (1)		
				18.501 (5)	72.61 (2)	$Cu^{II}O_5$	O	1.929 (7, 32)		91.1 (3, 10.2)		
							O [c]	2.358 (7)		174.8 (3, 1.0)		
$[Cu^ICu^{II}(dhm)](ClO_4)$	tr	$P\bar{1}$	2	11.861 (2)	104.27 (2)	$Cu^IN_2O_2$	N	1.962 (4, 12)	3.223 (1)	89.7 (1, 17.6)	104.2 (1, 2)	17
$\cdot 0.5\ CH_3OH$ [d]				8.265 (2)	104.68 (2)		O [c]	2.122 (3, 5)				
				14.076 (3)	100.88 (2)	$Cu^IN_2O_2$	N	2.029 (4, 30)	3.348 (3)	84.5 (2, 17.3)	104.8 (1, 1.0)	
							O [c]	2.259 (3, 19)				
						$Cu^{II}N_2O_2$	N	1.973 (3, 1)		90.0 (1, 10.7)		
							O [c]	1.959 (2, 8)				
$Cu^ICu^{II}(acacP)_2$-	tr	$P\bar{1}$	2	13.346 (3)	91.44 (2)	$Cu^IO_2P_2$	O	2.11 (1)	3.321 (2)	100.7 (3, 19.3) [e]	95.6 (3)	18
$(3\text{-}CH_3OC_6H_4CO_2)$				21.308 (5)	91.02 (2)		O [c]	2.524 (7)		119.8 (3)		
				9.312 (2)	81.44 (2)		P	2.237 (3, 13)		129.9 (1)		
						$Cu^{II}O_5$	O	1.940 (7, 25)		92.0 (3, 6.6)		
							O	2.249 (9)		171.2 (3, 2.1)		
							O [c]	1.926 (7)				
$Cu^ICu^{II}_2(ac)_5\{P(OEt)_3\}_2$	m	*Cc*	4	13.77 (4)		$Cu^IO_2P_2$	O [c]	1.95 (5)	3.28 (2)	104 (1, 3) [e]	102 (2, 4)	19
				19.10 (3)	125.6 (2)		O [c]	2.31 (6)		74 (2)		
				17.08 (4)			P	2.21 (3, 1)		127 (1)		
						$Cu^{II}O_5$	O	2.21 (6, 0)	2.56 (2) [f]			
							O [c]	2.15 (5)				
							O [c]	2.02 (5)				

$\mathrm{Cu^{I}_{2}Cu^{II}_{2}(ac)_6(PPh_3)_4}$	tr	$P\bar{1}$	1	10.898 (8)	121.03 (2)	$\mathrm{Cu^{I}O_2P_2}$	O	2.254 (5, 131)	3.772 (1)	112.1 (2, 15.8) [e]	125.1 (2)	20
				12.850 (4)	90.14 (5)		P	2.237 (2, 12)		57.3 (2)		
				19.877 (8)	117.98 (4)					127.4 (1)		
						$\mathrm{Cu^{II}O_5}$	O	1.981 (5, 8)	2.642 (1) [f]	92.7 (2, 10.0)		
							O	2.126 (4)		167.7 (2, 1)		
$\mathrm{Cu^{I}_{2}Cu^{II}_{2}(NH_3CH_2COO)_4Cl_6}$	tr	$P\bar{1}$	1	8.267 (2)	84.89 (1)	$\mathrm{Cu^{I}Cl_4}$	Cl	2.378 (2, 62)		Not given		21
				8.408 (2)	100.54 (1)							
				8.535 (2)	114.97 (1)	$\mathrm{Cu^{II}O_4Cl}$	O	1.978 (4)	2.708 (1) [f]	Not given		
							Cl	2.442 (2)				
$\mathrm{Cu^{I}Cu^{II}(4\text{-}Metz)_4Cl_3}$	m	$P2_1/n$	4	10.957 (2)		$\mathrm{Cu^{I}N_2Cl_2}$	N	1.978 (5, 3)	3.244 (1)	128.03 (19) [g]	81.08 (5, 53)	22
				15.457 (3)	108.61 (1)		Cl [c]	2.340 (2)		97.67 (5)		
				15.104 (2)			Cl [c]	2.662 (2)		105.74 (14, 8.61)		
						$\mathrm{Cu^{II}N_2Cl_3}$	N	2.000 (4, 2)		170.58 (18)		
							Cl	2.298 (2)		100.42 (5, 1.39)		
										159.15 (6)		
							Cl [c]	2.613 (1)		90.98 (13, 4.28)		
							Cl [c]	2.340 (1)				
$\mathrm{Cu^{I}_{3}Cu^{II}(tht)_3Cl_5}$	m	$P2_1/n$	4	12.2288 (6)		$\mathrm{Cu^{I}Cl_2S_2}$	Cl [c]	2.354 (1, 160)	3.158 (1)	102.98 (5, 12.66) [h]	92.86 (5, 15.93)	23
				13.0277 (7)	95.815 (4)		S [c]	2.299 (1, 53)		108.47 (5, 12.06)		
				14.0605 (7)						109.96 (5, 18.70)		
						$\mathrm{Cu^{II}Cl_4}$	Cl [c]	2.260 (1, 37)		95.92 (5, 70)		
										141.42 (6, 4.60)		

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[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses following an averaged value is a e.s.d., the second number is the maximum deviation from the average value. [b] The chemical identity of the coordinated atom (ligand) is specified in this column. [c] The bridge atom (ligand). [d] There is Cu(I) atom disordered over two sites. [e] The values of P–Cu(I)–O, O–Cu(I)–O and P–Cu(I)–P angles. [f] Distance between Cu(II)–Cu(II). [g] The values of N–Cu–N, Cl–Cu–Cl and N–Cu–Cl angles. [h] The values of Cl–Cu–Cl, S–Cu–S and Cl–Cu–S angles.

In Cu^{I}Cu^{II}(acacP)$_2$(3-CH$_3$OC$_6$H$_4$CO$_2$) [18], two non equivalent moieties —tetrahedral Cu^{I}O$_2$P$_2$ accommodated by the two phosphines and a bridging enolate oxygen, and the square-pyramidal Cu^{II}O$_5$ residues in the "hard" bis(β-diketonate) site—are linked by two acacP ligands. This was the first identified example of a one-electron oxidative addition to a bimetallic complex [18].

X-Ray analysis of the pale blue-green Cu^{I}Cu$_2^{II}$(ac)$_2${P(OCH$_3$}$_2$ [19] shows a unique structure (Fig. 3). The Cu$_2^{II}$(ac)$_4$ unit is associated with a Cu^{I}(ac){P(OEt)$_3$}$_2$ unit via axial Cu–O bonding to form a polynuclear chain, and as can be seen (Fig. 3) there are three distinct types of acetate ligand: three bridging the Cu(II) atom in the *syn-syn* configuration; one *syn-syn* bridging acetate [O(2)–C(17)–O(8)] with one oxygen atom [O(8)] also forming a monoatomic *syn-anti* bridge to the Cu(I) atom [Cu(3)]; and one *anti-anti* acetate [O(9)–C(18)–O(1)] connecting the two Cu(II) atoms [Cu(1) and Cu(2)] and also forming a monoatomic bridge to the Cu(I) atom [Cu(3)]. The data for the bond lengths and angles are given in Table 2. While the Cu(II)–Cu(I) [Cu(1)–Cu(3)] distance of 3.28(2) Å indicates the absence of a direct bond, the Cu(II)–Cu(II) [Cu(2)–Cu(1)] distance of 2.56(2) Å does infer a direct bond between the central atoms.

X-Ray analysis of Cu$_2^{I}$Cu$_2^{II}$(ac)$_6$(PPh$_3$)$_4$ [20] and Cu$_2^{I}$Cu$_2^{II}$(NH$_3$CH$_2$COO)$_4$Cl$_6$ [21] shows that while the former is composed of a centrosymmetric dimeric unit, [Cu$_2^{II}$(ac)$_4$] and two molecular Cu^{I}(ac)(PPh$_3$)$_2$ ligands, the latter involves two centrosymmetric dimeric subunits containing a couple of tetrahedral Cu(I) atoms, [Cu$_2^{I}$Cl$_6$]$^{4-}$, and couple of tetragonal Cu(II) atoms, [Cu$_2^{II}$(NH$_3$CH$_2$COO)$_4$]$^{4+}$. The Cu(II) dimeric unit contains four acetate [20]

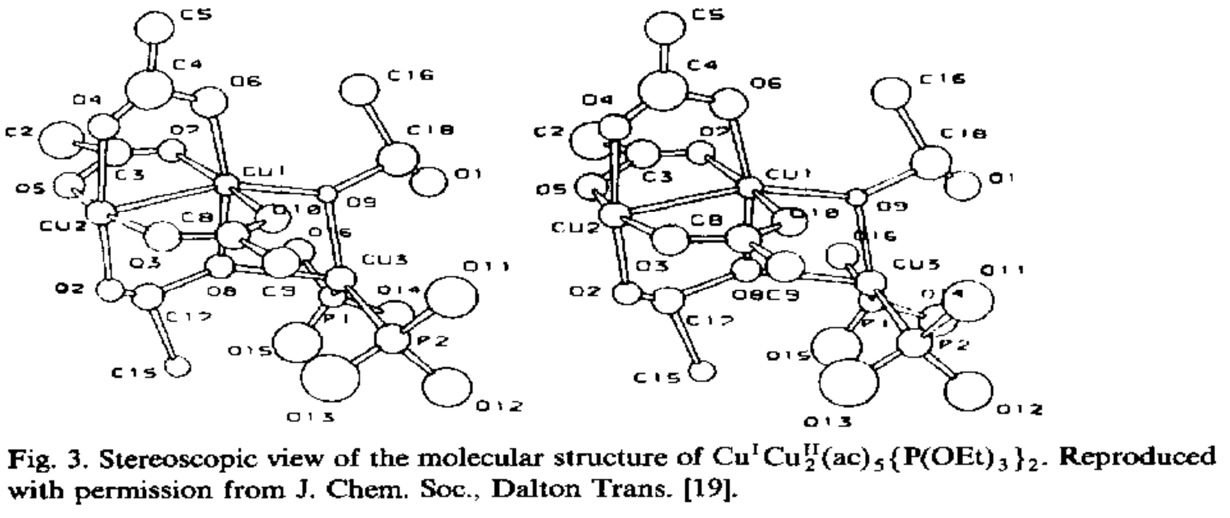

Fig. 3. Stereoscopic view of the molecular structure of Cu^{I}Cu$_2^{II}$(ac)$_5${P(OEt)$_3$}$_2$. Reproduced with permission from J. Chem. Soc., Dalton Trans. [19].

or four zwitterionic glycine [21] ligands bound with the Cu(II) atom via carbonyl groups in the same mode (*syn-syn*) as found in Cu(II) carboxylates [25]. The Cu(II)–Cu(II) and Cu(II)–O bond distances (Table 2) are comparable with those found in other Cu(II) carboxylates [25]. In $Cu^I_2Cu^{II}_2(ac)_6(PPh_3)_4$ two tetrahedral $Cu(ac)(PPh_3)_2$ fragments are bonded to the Cu(II) atoms through the oxygen atoms. In $Cu^I_2Cu^{II}_2(NH_3CH_2COO)_4Cl_6$ both subunits are bound to each other through the chloride bridge.

In another two examples, $Cu^ICu^{II}(4\text{-Metz})_4Cl_3$ [22] and $Cu^I_3Cu^{II}(tht)_3Cl_5$ [23], two unequal coordination spheres around Cu(I) and Cu(II) are doubly bridged by two chlorine atoms. In the former, the geometry at the Cu(II) atom is severely distorted square pyramidal, with the basal plane consisting of two N atoms from 4-methylthiazole ligands (Cu–N = 2.000(4,2) Å) and two *trans* chloride ions (Cu–Cl = 2.319(2,21) Å) while the apical site is occupied by the chloride ligand (Cu–Cl = 2.613(1) Å). The geometry about Cu(I) is a distorted tetrahedral arrangement (Table 2).

In the latter, the Cu(II), [Cu(1)], is bound to four chlorine atoms and the remaining three Cu(I) atoms are characterised by $Cu^IS_2Cl_2$ donor sets. The geometry around these Cu(I) atoms is a distorted tetrahedron (Fig. 4).

Examination of the composition of the compounds in Table 2 reveals that there is an example with octadentate [15], hexadentate [17], tri-, bi-, and unidentate ligands. Only in one example [16] does a Cu(I) atom have a trigonal planar geometry; in all other compounds Cu(I) atoms are tetrahedrally coordinated. (Square-pyramidal geometry about the Cu(II) atoms is very common.)

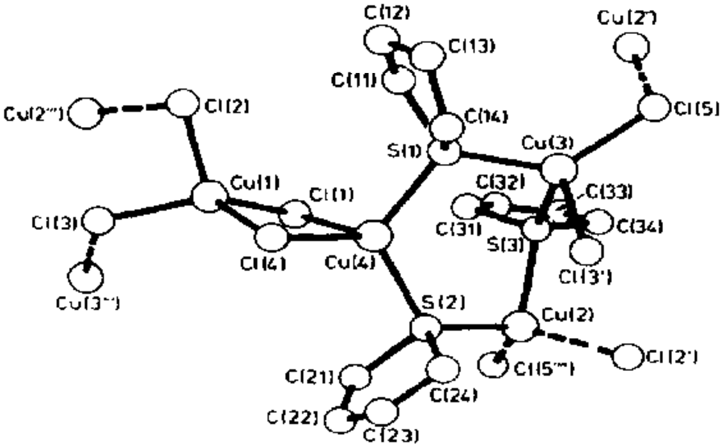

Fig. 4. Structure of $Cu^I_3Cu^{II}(tht)_3Cl_5$. Reproduced with permission from J. Chem. Soc., Dalton Trans. [23].

D. CYANO, THIOCYANATO AND SELENOCYANATO COPPER(I)–COPPER(II) COMPOUNDS

(i) Preparation

Two general methods have been used for the synthesis of cyano, thiocyanato and selenocyanato copper(I)–copper(II) compounds. The first includes partial reduction of copper(II) salts in the presence of a ligand (CN^-, SCN^- or $SeCN^-$) which is serving both as a ligand and as a reducing agent [26–28, 31–34].

The second includes partial oxidation of copper(I) salts by molecular oxygen [29,30].

(ii) Structures

Crystal and structural data for cyano, thiocyanato and selenocyanato copper(I)–copper(II) compounds are collected in Table 3. In general, chemical reduction of copper(II) salts with potassium cyanide (thio, or selenocyanide) in aqueous solution in the presence of ammonia or ethylenediamine, was used to prepare most of the mixed-valence compounds (Table 3). The dark red $Cu^I_4Cu^{II}(NH_3)_2(CN)_6$ [28,29] and dark green $Cu^I_3Cu^{II}(NH_3)_2 \cdot (H_2O)(CN)_5$ [29] compounds were prepared by slow air oxidation of cyano–copper(I) solutions in the presence of ammonia.

The structure of the green $Cu^I_2Cu^{II}(NH_3)_3(CN)_4$ [26,27] consists of infinite polymeric chains stretching in the *a* direction. Each Cu(II) atom is coordinated to three NH_3 molecules distributed over four positions, and to nitrogen atoms of the two cyano groups in a distorted octahedral geometry. The Cu(I) atoms have a distorted trigonal planar coordination with the carbon atom of the ordered cyano group and the ends of two disordered cyano groups. The Cu(II) and four Cu(I) atoms form the apices of a nearly planar pentagon, with cyano groups bridging the copper atoms.

Another two examples, $Cu^I_4Cu^{II}(NH_3)_2(CN)_6$ [28,29] and $Cu^I_3Cu^{II}(NH_3)_2(H_2O)(CN)_5$ [29], display polymeric networks with coordination numbers two and three for the Cu(I) atoms and four (in the former) or five (in the latter) for the Cu(II) atoms. The data for the bond distances and angles are given in Table 3.

A square-pyramidal geometry about the Cu(II) atom in $Cu^I_2Cu^{II}(en)_2(CN)_4 \cdot H_2O$ [30] is built up with bidentate ethylenediamine ligands (Cu–N = 2.015(4,19) Å) in the basal plane, and with a water molecule at the apex (Cu–O = 2.441(4) Å). The Cu(I) atoms are tetrahedrally linked together by cyano ligands. The crystal structure of blue violet $Cu^I_2Cu^{II}(en)_2(CN)_2(SeCN)_2 \cdot H_2O$ [32] as well as $Cu^I_2Cu^{II}(en)_2(CN)_3(SeCN) \cdot H_2O$ [33] is similar to that of $Cu^I_2Cu^{II}(en)_2(CN)_4 \cdot H_2O$ [30].

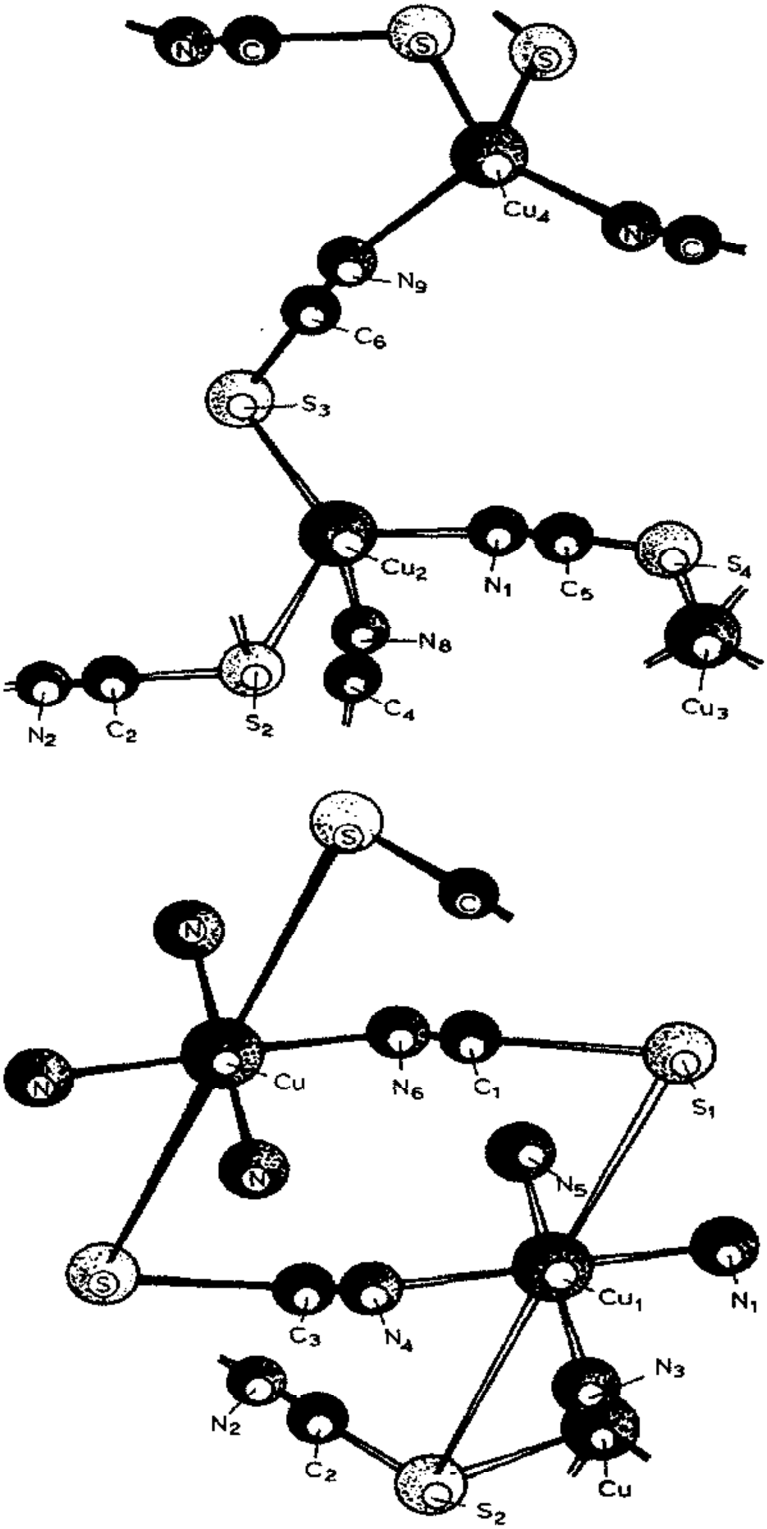

Fig. 5. Coordination of (a) Cu(I) and (b) Cu(II) in the crystal of $Cu^{I}Cu^{II}(NH_3)_3(NCS)_3$. Reproduced with permission from Inorg. Chem. [31].

TABLE 3

Structural data for cyano, thiocyanato and selenocyanato Cu(I)–Cu(II) compounds [a]

Compound	Crys-tal class	Space group	Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromo-phore	[b]	Cu–L (Å)	L–Cu–L (°)	Ref.
$\{Cu^I_2Cu^{II}(NH_3)_3(CN)_4\}_n$ [c]	or	*Ab*2*m*	8	12.674 (5)		Cu^IC_3	NC	1.98 (–, 11)	117 (–, 10)	26
		(*Abm*2)		12.242 (5)		$Cu^{II}N_6$	CN	1.93 (–, 3)	89 (–, 15)	
				14.577 (6)			H_3N	2.05 (–, 20)	173 (–, 4)	
$\{Cu^I_2Cu^{II}(NH_3)_3(CN)_4\}_n$ [d]	or	*Cmca*	8	12.273 (6)		Cu^IC_3	NC	1.936 (8, 36)	118.5 (3, 7.2)	27
				13.646 (8)		$Cu^{II}N_6$	CN	2.019 (8, 0)	89.7 (5, 7.6)	
				12.777 (7)			H_3N	2.092 (10, 118)	172.7 (6, 8)	
$\{Cu^I_4Cu^{II}(NH_3)_2(CN)_6\}_n$	m	*C*2/*c*	4	17.709 (9)		Cu^IC_2	NC	1.84 (–, 2)	163.2	28, 29
				6.762 (3)	126.40 (3)	Cu^IC_2N	NC	1.93 (–, 2)	117.3 (–, 10.7)	
				13.157 (6)			CN	1.97		
						$Cu^{II}N_4$	CN	2.01 (2×)	90 (–, 3)	
							H_3N	2.02 (2×)		
$\{Cu^I_3Cu^{II}(NH_3)_2(H_2O)$ $(CN)_5\}_n$	m	$P2_1/n$	4	6.733 (3)		Cu^IC_2	NC	1.81 (–, 2)	140	29
				21.60 (1)	109.09 (4)	Cu^IC_2N	NC	1.90 (–, 1)	Not given	
				9.330 (5)			CN	1.89		
						$Cu^{II}N_4O$	CN	1.99 (–, 3)	Not given	
							H_3N	1.99 (–, 1)		
							H_2O	2.34		
$Cu^I_2Cu^{II}(en)_2(CN)_4 \cdot H_2O$	m	*Cc*	4	14.774 (10)		$Cu^IN_2C_2$	NC	1.970 (4, 11)	109.3 (2, 8.7)	30
				7.749 (4)	112.39 (3)		CN	2.028 (5, 75)		
				14.272 (9)		$Cu^{II}N_4O$	(en)N	2.015 (4, 19)	91.7 (2, 7.8)	
							H_2O	2.441 (4)		
$\{Cu^ICu^{II}(NH_3)_3(NCS)_3\}_n$ [e]	m	$P2_1/c$	4	8.40 (1)		$Cu^IN_2S_2$	SCN	2.001 (25, 5)	108.8 (7, 6.3)	31
				7.17 (1)	97.3		NCS	2.423 (8, 47)		
				19.52 (2)		$Cu^{II}N_4S_2$	H_3N	2.044 (24, 20)	90.8 (8, 8.1)	
							SCN	1.987 (23)	173.0 (1.0, 2.5)	
							NCS	3.116 (8, 170)		

$\{Cu^{I}_2Cu^{II}(en)_2(CN)_2 \cdot (SeCN)_2 \cdot H_2O\}_n$	m	*Cc*	4	8.879 (2)		$Cu^{I}N_2CSe$	CN	1.987 (18, 10)	109.2 (6, 10.1)	32
				15.824 (1)	106.80 (1)		NC	1.908 (16, 4)		
				13.493 (2)			SeCN	2.029 (18, 4)		
							NCSe	2.631 (3, 18)		
						$Cu^{II}N_4O$	(en)N	2.043 (18, 40)	90.1 (6, 7.4)	
							H_2O	2.483 (14)	176.4 (7, 4)	
$\{Cu^{I}_2Cu^{II}(en)_2(CN)_3 \cdot (SeCN) \cdot H_2O\}_n$[f]	tr	*P*1	2	8.445 (3)	119.58 (2)	$Cu^{I}N_2CSe$	CN	1.962 (14, 2)	108.6 (6, 11.0)	33
				7.903 (3)	118.59 (2)		NC	1.929 (15)		
				8.444 (3)	93.63 (3)		NCSe	2.731 (3)		
	m	*C*2	2	13.331 (4)		$Cu^{I}NC_2Se$	CN	1.973 (14)	108.6 (6, 11.3)	
				8.670 (2)	122.60 (2)		NC	1.946 (15, 16)		
				8.267 (3)			NCSe	2.745 (3)		
						$Cu^{II}N_4O$	(en)N	2.010 (15, 31)	92.0 (7, 9.2)	
							H_2O	2.331 (19)	171.1 (7, 1.4)	
$\{Cu^{I}_6Cu^{II}_3(CN)_6(SeCN)_6 \cdot (en)_6\}_n$	m	$P2_1/c$	2	9.083 (3)		$Cu^{I}N_3C$ (2×)	CN	2.004 (6, 20)	109.15 (24, 11.20)	34
				31.918 (6)	93.10 (2)		NC	1.930 (6)		
				8.594 (2)			SeCN	2.057 (6)		
						$Cu^{I}Se_2NC$ (4×)	CN	1.959 (6, 45)	108.65 (17, 29.57)	
							NC	1.925 (6, 33)		
							NCSe	2.684 (1, 223)		
						$Cu^{II}N_4Se_2$ (1×)	(en)N	2.008 (5, 6)	90.57 (18, 5.86)	
							NCSe	3.168 (1, 0)		
						$Cu^{II}N_5$ (2×)	(en)N	2.007 (7, 20)	91.34 (25, 7.07)	
							SeCN	2.435 (6)	174.29 (26, 1.92)	

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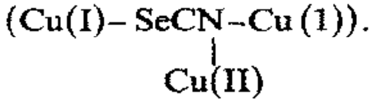
[a] Where more than one chemically equivalent distance or angle present the mean value is tabulated. The first number in parentheses is an e.s.d., the second number is a maximum deviation from the mean value. [b] The chemical identity of coordinated atom (ligand) is specified in this column. [c] Cu(I)–Cu(I) = 2.87 Å. [d] Cu(I)–Cu(I) = 2.868(3) Å. [e] Cu(I)–S–Cu(II) = 113.8 (2)°. [f] The crystal structure was solved in the two symmetry groups; Cu(I)–Se–Cu(I) = 172.9 (1)°.

The structure of the black needles of $Cu^{I}Cu^{II}(NH_3)_3(NCS)_3$ [31] is polymeric and consists of sheets of Cu(I) tetrahedra (Fig. 5(a)) cross-linked by pairs of Cu(II) octahedra (Fig. 5(b)). There are three types of thiocyanate groups in the structure, with bridging functions and bonding through the nitrogen and sulfur atoms. The first, which mutually bonds distorted octahedra, forms a strong Cu(II)–N bond (1.987(23) Å) and a very weak Cu(II)–S link (3.286(8) Å). The second type bonds only the Cu(I) tetrahedra and the third kind of thiocyanate group forms two Cu(I)–N and Cu(I)–S bonds and the sulfur atom is also bonded to the Cu(II).

The brown-violet compound $Cu^{I}_{6}Cu^{II}_{3}(CN)_6(SeCN)_6(en)_6$ [34] consists of a three dimensional skeleton formed by polymeric $[Cu^{I}_{6}(CN)_6(SeCN)_6]^{6-}_{n}$ anions. In the cavities are located $[Cu^{II}(en)_2]^{2+}$ cations (Fig. 6). While the Cu(I) atoms are tetrahedrally coordinated by cyano and selenocyanato ligands which are present as bridging groups, the stereochemistry about the Cu(II) atoms is different. $Cu^{II}(1)$ (Fig. 6) has an elongated tetragonal bipyramidal coordination with two ethylenediamine ligands in the plane and two SeCN groups bound through the Se atom at the apical positions. The remaining two Cu^{II} atoms [Cu(2)] are in a square pyramidal environment with two ethylenediamine molecules approximately in the plane and a SeCN group bound through the N atom at the apex. As can be seen (Fig. 6) there are two types of SeCN bridging ligands; as a bidentate, (Cu(I)–SeCN–Cu), and a tridentate,



$$(\mathrm{Cu(I)}\!-\!\underset{\substack{|\\ \mathrm{Cu(II)}}}{\mathrm{SeCN}}\!-\!\mathrm{Cu\,(1)}).$$

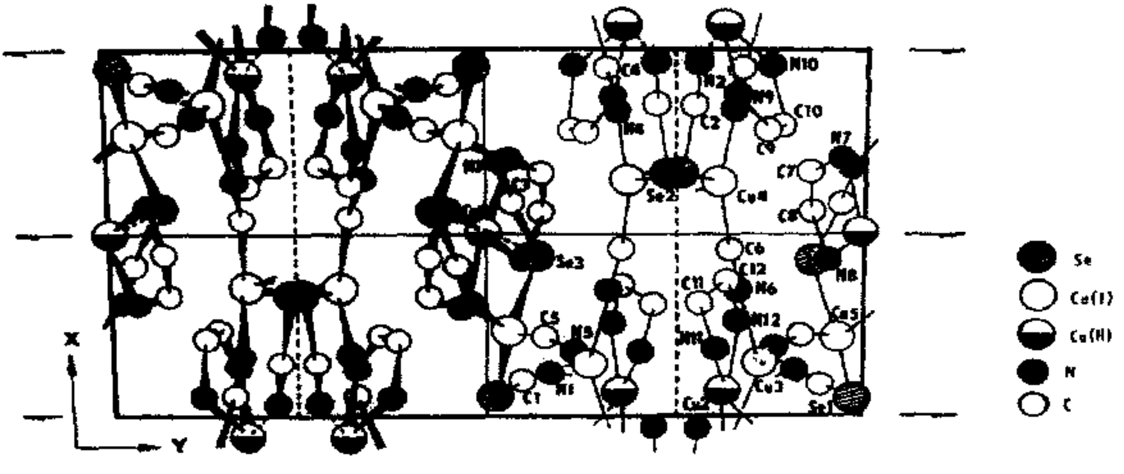


Fig. 6. Crystal structure of $Cu^{I}_{6}Cu^{II}_{3}(CN)_6(SeCN)_6(en)_6$ [34].

Inspection of the data in Table 3 reveals that there are marked stereochemical differences between the Cu(I) and Cu(II) atoms. The coordination numbers of the Cu(I) atoms range from two to four, and of Cu(II) atoms from four to six. There are two examples [28,29] in which the two types of Cu(I) are present with a classical trigonal geometry and with a very rare coordination number of two. Two kinds of Cu(II) atoms, square-pyramidal and distorted octahedral, have been found in $Cu^{I}_{6}Cu^{II}_{3}(CN)_6(SeCN)_6(en)_6$ [34]. Noticeably, all the neutral ligands (Table 3) are directly bonded only to the Cu(II) atoms. On the other hand the cyanide, thiocyanate and selenocyanate ions which do have the ability to stabilize metal ions in low formal oxidation states (presumably by accepting electron density into their π^* orbitals) are bonded preferentially to the Cu(I) atoms.

Comparison of the Cu(I)–C(CN) distances for the CuC_2 and CuC_3 chromophores reveals that the mean value (1.825(–, 20) Å) is noticeably shorter in the CuC_2 than in the CuC_3 unit (1.936(–, 154) Å). In addition, in the former the C–Cu–C angle increases with increasing Cu–C distance (Table 3). The Cu(I)–N(NC) distance also increases with increasing coordination number: 1.89–1.97 Å (1.93 Å) for trigonal geometry and 1.914–2.103 Å (1.967 Å) for tetrahedral geometry. On the other hand, no such tendency is seen for the Cu(I)–C(CN) distances for trigonal and tetragonal geometries; the mean value is similar for both (1.936 and 1.935 Å, respectively).

The mean Cu(I)–L bond distances (L = pseudohalogenide) are somewhat longer when L binds to the "soft" end, than when binding to the "hard" end. The difference between the two mean values, Cu(I)–C(CN) and Cu(I)–N(CN), increases from 0.023 Å for the CN group, to 0.422 Å (Cu(I)–N(NCS) and Cu(I)–S(SCN)) for the NCS group, and to 0.645 Å (Cu(I)–N(NCSe) and Cu(I)–Se(SeCN)) for the NCSe group. Also, the mean Cu(I)–N bond distance increases in the order 1.958 Å (NC) < 2.001 Å (NCS) < 2.043 Å (NCSe): the reasons for this include both steric and electronic factors. In general, the mean Cu(I)–L bond distance increases with increasing van der Waals radius of the ligating atom, as noted above.

Although Cu(I) is presumably a larger ion than Cu(II), the reduction in the number of coordinate bonds about Cu(I) relative to Cu(II) doubtless contributes to shortening the average Cu–L bond length of Cu(I). In fact, the mean Cu(II)–L bond length is noticeably longer than that of Cu(I)–L. For example, the mean Cu(II)–L versus Cu(I)–L distances are: 1.987 versus 1.958 Å (L = NC); 2.435 versus 2.043 Å (NCSe); 3.116 versus 2.423 Å (SCN); and 3.168 versus 2.698 Å (SeCN).

There are three types of neutral ligand: water, ammonia and ethylenediamine, and all are directly bonded to the Cu(II) atoms. The mean Cu(II)–L bond distance decreases in the order 2.399 Å ($L = H_2O$) > 2.039 Å (NH_3) > 2.017 Å (en), corresponding to increasing field strength in a spectrochemical series of the ligands in the order given [35].

E. CLUSTER COPPER(I)–COPPER(II) COMPOUNDS

(i) Preparation

Mixed valence copper(I)–copper(II) clusters shown in Table 4 was prepared by the following synthetic methods:

Dark blue $[Cu'_{10}Cu''_2(mci)_{12}(MeCN)_4](BPh_4)_2 \cdot (MeCN)_4$ [36] was prepared by mixing $[Cu'(MeCN)_4ClO_4]$ and $[Cu''(MeCO_2)_2 \cdot (H_2O)]_2$ with mciH in MeCN : MeOH (1 : 1) solution.

Five mixed-valence copper(I)–copper(II) clusters (Table 4) [37–39] were prepared by partial reduction of copper(II) salts in the presence of β,β-dimethylcysteamine [37], α-mercaptoisobutyric acid [38] or D-penicillamine [40], which serve both as ligands and as reducing agents.

Orange crystals of $Cu'_4Cu''(bta)_6(t\text{-}C_6H_9CN)_4$ were prepared via the reaction between copper(I) thiophenoxide and benzotriazole in dichloromethane. To this solution was added tert-butylisocyanide; after stirring for about 15 min an orange powder separated.

Reaction between copper powder, potassium carbonate and sulphur at high-temperature yields the copper(I)–copper(II) compound of composition $KCu'_3Cu''S_3$ [41], the only example here where copper powder is used.

(ii) Structures

Crystal and structural data for copper(I)–copper(II) cluster compounds are summarised in Table 4. The stereochemistry of the cluster $[Cu^I_{10}Cu^{II}_2(mci)_{12}(MeCN)_4]^{2+}$ cation present in the dark blue $[Cu^I_{10}Cu^{II}_2(mci)_{12}(MeCN)_4](BPh_4)_2(MeCN)_4$ [36] is shown in Fig. 7 as a representative example. In this cluster, eight Cu(I) atoms are tetrahedrally coordinated by four S donor atoms [Cu(2) and Cu(3)], or three S and one N donor atom [Cu(4) and Cu(6)]; the remaining two Cu(I) atoms [Cu(5) and Cu(5′)] are linearly σ-bonded by two N atoms. The Cu(II) atoms [Cu(1) and Cu(1′)] are in a distorted square pyramid with the CuN_3S_2 chromophore. The data for bond lengths and angles are given in Table 4. As can be seen (Fig. 7) the eight Cu(I) atoms are each two-by-two doubly bridged by two S atoms with distances between them in the range from 2.547(1) to 2.724(1) Å.

The structure of the yellow hexagonal plates of $Cu^I_8Cu^{II}_6(dmc)_{12}Cl(SO_4)_{3.5} \cdot 20H_2O$ [37] consists of discrete $[Cu^I_8Cu^{II}_6(dmc)_{12}Cl]^{7+}$ clusters in which all four-coordinate copper atoms are linked by twelve three-coordinate mercaptide ions and an eight-coordinate chloride ion. Each cluster contains a $Cu_{14}S_{12}Cl$ core, which consists of a distorted icosahedral arrangement of 12 sulfur atoms with 8 of the 20 triangular icosahedral faces occupied by Cu(I) atoms which form an approximate cube. The chloride ion is located at

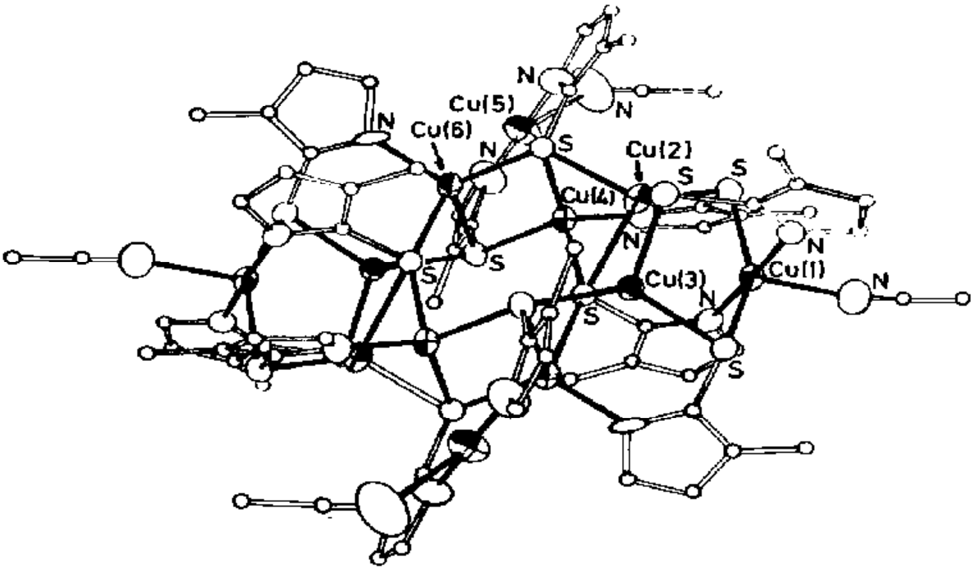


Fig. 7. View of the cluster cation $[Cu^{I}_{10}Cu^{II}_{2}(mci)_{12}(MeCN)_{4}]^{2+}$. Reproduced with permission from J. Chem. Soc., Chem. Commun. [36].

the common center of the cube and icosahedron. The remaining six Cu(II) atoms are located (approximately) along 6 of the 30 icosahedral edges.

Structural features of $[Cu^{I}_{8}Cu^{II}_{6}(miba)_{12}Cl]^{5-}$ [38] and $[Cu^{I}_{8}Cu^{II}_{6}(D\text{-}Pen)_{12}Cl]^{5-}$ [39] correspond closely to those reported for $[Cu^{I}_{8}Cu^{II}_{6}(dmc)_{12}Cl]^{7+}$ [37]. Data for the bond distances and angles are given in Table 4.

Red-orange crystals of neutral $Cu^{I}_{4}Cu^{II}(bta)_{6}(t\text{-}C_{6}H_{9}NC)_{4}$ [40] contain an octahedrally coordinated Cu(II) atom surrounded by four tetrahedrally coordinated Cu(I) atoms. Tridentate benzotriazole ions bridge each Cu(I) atom to three symmetry-related Cu(I) atoms and to the central Cu(II) atom. The stereochemistry about Cu(II) is a compressed octahedron with bond distances Cu–N (equatorial) 2.241(13) Å versus Cu–N (axial) of 2.085(16) Å. An approximately tetrahedral geometry about the Cu(I) atoms is built of three different bta ligands (Cu–N = 2.041(13,46) Å) and one tert-butyl isocyanide ligand (Cu–C = 1.882(17) Å).

In the structurally unique $KCu^{I}_{3}Cu^{II}S_{3}$ [41] all the copper atoms are crystallographically equivalent. Double layers of tetrahedrally coordinated (by S) copper atoms are separated by layers of potassium ions.

Inspection of the data in Table 4 reveals that tetrahedral coordination about Cu(I) and Cu(II) atoms is common. There is an example [36] in which three different environments occur about the Cu(I) atoms, namely with chromophores CuN_{2}, CuS_{4} and $CuS_{3}N$.

In general, the mean Cu–L distances increase with an increase in coordination number of both the central atom and the donor atom as well as with

TABLE 4

Structural data for cluster Cu(I)–Cu(II) compounds [a]

Compound	Crystal class	Space group	Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore	[b]	Cu–L (Å)	L–Cu–L (°)	Ref.
$[Cu^{I}_{10}Cu^{II}_{2}(mci)_{12}(MeCN)_{4}]\cdot(BPh_{4})_{2}\cdot(MeCN)_{4}$ [c]	tr	$P\bar{1}$	1	16.400	76.80	$Cu^{I}N_2$ (2×)	N	1.876 (8, 9)	179.2 (5)	36
				14.630	105.57	$Cu^{I}S_4$ (4×)	S	2.280–2.645 (2)	Not given	
				14.680	95.23	$Cu^{I}S_3N$ (4×)	S	2.280–2.645 (2)	Not given	
							N	1.980 (4, 4)		
						$Cu^{II}N_3S_2$	N	1.947 (5, 13)	175.4 (3) [d]	
							N	2.295 (8)	150.9 (1)	
							S	2.465 (3, 1)		
$Cu^{I}_{8}Cu^{II}_{6}(dmc)_{12}Cl(SO_4)_{3.5}\cdot 20H_2O$ [e]	m	$C2/c$	4	18.318 (3)		$Cu^{I}S_3Cl$	S	2.282 (6, 15)	120.0 (2, 2.1)	37
				21.826 (5)	110.17 (1)		Cl	2.866 (3, 14)	89.1 (2, 1.5)	
				28.829 (6)						
						$Cu^{II}N_2S_2$	N	2.02 (3, 3)	92.1 (11, 1.9) [g]	
							S	2.280 (6, 12)	94.4 (2, 2)	
									87.1 (8, 9)	
									174.1 (8, 4.9)	
$Tl_5[Cu^{I}_{8}Cu^{II}_{6}(miba)_{12}Cl]\cdot 12\,H_2O$ [h]	m	$C2/c$	4	18.339 (2)		$Cu^{I}S_3Cl$	S	2.27 (2, 3)	119.9 (6, 1.8)	38
				21.114 (2)	101.77 (2)		Cl	2.90 (7, 2)		
				24.858 (3)		$Cu^{II}O_2S_2$	O	1.93 (4, 6)	90 (2, 8)	
							S	2.24 (2, 2)		

$[Cu^{I}_{8}Cu^{II}_{6}(miba)_{12}Cl]\cdot[Co(NH_3)_6]$	tr	$P\bar{1}$		14.8	110.2					38
$\cdot xH_2O$		($P1$)		22.0	113.7					
				31.0	120.1					
$Tl_5[Cu^{I}_{8}Cu^{II}_{6}$(D-Pen)$_{12}Cl]\cdot n\ H_2O$ [i]	c	$F432$	32	50.847 (5)		$Cu^{I}S_3Cl$	S	2.27 (3, 7)	Not given	39
							Cl	2.85 (5.10)		
						$Cu^{II}N_2S_2$	N	2.08 (7, 7)	Not given	
							S	2.28 (3, 3)		
$[Cu^{I}_{8}Cu^{II}_{6}$(D-Pen)$_{12}Cl]\cdot[Co(NH_3)_6]$	m	$P2_1$		39.5						
$\cdot n\ H_2O$				22.8	117					39
				35.4						
$Cu^{I}_{4}Cu^{II}(bta)_6(t\text{-}C_6H_9CN)_4$ [j]	tg	$P42_1c$	2	13.836 (4)		$Cu^{I}N_3C$	N	2.041 (13, 46)	96.1 (5, 2.2) [k]	40
				13.836 (4)			C	1.882 (17)	120.7 (6, 3.7)	
				16.686 (4)						
						$Cu^{II}N_6$	N	2.085 (16) (2×)	90.0 (4, 1)	
							N	2.241 (13) (4×)	179.8 (5)	
$KCu^{I}_{3}Cu^{II}S_3$ [l]	tg	$P4/$	1	3.899 (4)		CuS_4	S	2.381 (2, 69)	109.80 (7, 5.19)	41
		mmm		3.899(4)						
				9.262(6)						

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[a] Where more than one chemically equivalent distance or angle is present the mean value is tabulated. The first number in parentheses is an e.s.d. and the second number is a maximum deviation from the mean value. [b] The chemical identity of coordinated atom (ligand) is specified in this column. [c] There are Cu(I)–Cu(I) distances from 2.547 (1) to 2.724 (1) Å. [d] The values of N–Cu–N and S–Cu–S angles. [e] Cu(I)···Cu(I) = 3.309 (4, 45) Å; Cu(I)–S–Cu(I) = 92.9 (2, 1.4)°; Cu(I)–Cl–Cu(I) = 70.53 (7, 1.22)°; Cu(I)–S–Cu(II) = 117.5 (2, 3.4)^{0}; Cu(I)–Cu(I)–Cu(I) = 90.00 (9, 77)°. [f] The values of S–Cu(I)–S and S–Cu(I)–Cl angles. [g] The values of N–Cu(II)–N; S–Cu(II)–S, *cis*-S–Cu(II)–N and *trans*-S–Cu(II)–N angles. [h] Cu(I)···Cu(I) = 3.35(1, 3) Å; Cu(I)–Cu(I)–Cu(I) = 90.0 (2, 1.3)°. [i] Cu(I)···Cu(I) = 3.30 (2, 7) Å, Cu(I)–Cu(I)–Cu(I) = 90.0 (6, 3.9)°. [j] Cu(I)···Cu(II) = 3.638 (2) Å; Cu(I)–Cu(I)–Cu(I) = 60.46 (4, 1.35)° and Cu(I)–Cu(II)–Cu(I) = 110.24 (5, 2.26)°. [k] The values of N–Cu(I)–N and N–Cu(I)–C angles. [l] From the structural results all Cu ions are equivalent; Cu–Cu = 2.757 and 2.970 (2) Å; Cu–S–Cu = 68.46 (2)–180.00 (7)°.

oxidation number of the central atom. For example, the mean Cu(I)–N bond distance for two coordinate Cu(I) is 1.876 Å but for four coordinate Cu(II) is 2.010 Å. The Cu(II)–N distance of 2.050 Å found for four coordinate Cu(II) is smaller than those found for five- or six-coordination which are 2.063 and 2.189 Å, respectively. The mean Cu(II)–S distance (four coordinate) of 2.295 Å is about 0.170 Å smaller than those of 2.465 Å (five coordinate).

F. MISCELLANEOUS COPPER(I)–COPPER(II) COMPOUNDS

When SO_2 was passed through an aqueous solution of copper(II) sulphate at about 70 °C red $Cu^I_2Cu^{II}(SO_3)_2 \cdot 2H_2O$ was obtained and its crystal structure determined [42]. This compound was the first structurally characterised copper(I)–copper(II) compound. The crystal structure consists of SO_3 trigonal pyramids, Cu^IO_3S tetrahedra and $Cu^{II}OH(H_2O)_2$ octahedra. The polyhedra are linked such that the SO_3 pyramids are joined with two $Cu^{II}O_6$ octahedra and with one Cu^IO_3S tetrahedron by corner-sharing through oxygen atoms and with one further Cu^IO_3S tetrahedron by having the S atom in common. The Cu(I)–S bond distances are 2.140(6) and 2.129(16,15) Å, respectively, and the L–Cu(I)–L angles are in the range 82.7 to 129.5°. The Cu(II)–O bond distances are 2.034(16) (2 ×), 2.467(15) (2 ×) and 1.924(18) Å (2 × , H_2O), and O_{eq}–Cu(II)–O_{eq} angles are in the range 76.5 to 91.4°.

The dark green crystalline compound $Cu^I_2Cu^{II}(2,5\text{-dth})_6(ClO_4)_4$ was prepared by mixing $Cu(ClO_4)_2 \cdot 6H_2O$ and 2,5-dithiahexane in methanol; its X-ray structural analysis has been reported [43]. The compound contains crystallographically equivalent Cu(I) and Cu(II) atoms. The copper atom is tetrahedrally surrounded by a thioether S_4 donor set (Cu–S = 2.27(2) Å, and S–Cu–S = 95(1) and 117(1)°).

G. CONCLUSIONS

From the preparation point of view, the mixed valence copper compounds fall mainly into four categories:

(1) partial reduction of copper(II) salts in the presence of a ligand which serves both as a ligand and as a reducing agent;

(2) addition of molecular oxygen to copper(I) salts;

(3) partial oxidation of copper(I) or reduction of copper(II) salts by electrochemistry;

(4) mixing a copper(I) salt with a copper(II) salt in a suitable medium.

In general, the course of the redox reactions are highly dependent upon the specific conditions used, mainly concentration of reagents, pH, medium, and temperature.

Quite generally, the stereochemical requirements for copper(I) and copper(II) are different [44]. The data for copper(I)–copper(II) compounds presented in this review may be summarised as follows. The number of examples representing the various geometries about copper(I) increases in the order: trigonal planar $\leqslant$ linear or nearly linear $\ll$ tetrahedral; and about copper(II): octahedral $<$ tetrahedral $\ll$ square-pyramidal. There are examples with two non-equivalent copper(I) moieties: $\mathrm{Cu^{I}C_2}$ and $\mathrm{Cu^{I}C_2N}$ [28,29]; $\mathrm{Cu^{I}Cl_2}$ and $\mathrm{Cu^{I}Cl_4}$ [8]; and $\mathrm{Cu^{I}N_2}$ with $\mathrm{Cu^{I}S_4}$ and $\mathrm{Cu^{I}S_3N}$ [36]. There is also such an example of copper(II) [34] where $\mathrm{Cu^{II}N_5}$ and $\mathrm{Cu^{II}N_4Se_2}$ chromophores are present.

There are two examples, $\mathrm{KCu^{I}_{3}Cu^{II}S_3}$ [41] and $\mathrm{Cu^{I}_{2}Cu^{II}(2,5\text{-}dth)_6(ClO_4)_3}$ [43] which contain crystallographically equivalent copper(I) and copper(II) atoms, with $\mathrm{CuS_4}$ chromophores and Cu–S bond lengths of 2.381(2,69) Å in the former, and 2.27(2) Å in the latter.

When the ligand type is considered several trends are noticeable. (a) There are examples with octa- [15] and hexadentate [17] ligands, but no examples with hepta- and pentadentate ligands. Uni-, bi-, tri-, and tetradentate ligands are more common. (b) In general, the neutral ligands are bonded to the Cu(II) atom.

A summary of the structural data for copper(I)–copper(II) compounds with different types of geometry is given in Table 5. Inspection of the data in Table 5 reveals that: (a) the mean Cu(I)–L bond distance increases with coordination number, which is not the case for Cu(II)–L distances; (b) the mean Cu(I)–L bond lengths, except $\mathrm{L = N}$, are found to be shorter than corresponding Cu(II)–L lengths; (c) in general, the mean Cu–L bond distance increases with increasing van der Waals radius of the ligating atom.

There are examples with a direct metal–metal bond between Cu(I)–Cu(II) [15,41], Cu(I)–Cu(I) [26,27,36], and Cu(II)–Cu(II) [19–21].

The factors governing the choice of geometry in these complexes include the electronic configuration of the central atom, crystal packing forces, and the nature of the ligands. For example, chelating ligands often play a substantial role in the nature of the overall structure, stereochemistry, and fluxional behaviour of the derivatives of the copper(I) and copper(II).

To our knowledge, this is the first overview of the almost forty mixed-valence copper structures which have been determined and illustrates the rich copper(I)–copper(II) chemistry as well as a few systematic trends which have been observed.

Multimetallic species occupy an important position in modern inorganic chemistry. They are ubiquitous in nature as active sites in a variety of

TABLE 5

Summary of copper–atom(ligand) bond distances (Å) [a]

Coord. atom (ligand)	Coord. number	Cu(I)	Coord. number	Cu(II)
N	2	1.867–1.885 (1.876)	4	1.910–2.190 (2.040)
	3	1.890–1.970 (1.930)	5	1.934–2.435 (2.038)
	4	1.880–2.200 (2.007)	6	1.900–2.241 (2.026)
O			4	1.870–2.210 (2.028)
	3	2.106	5	1.897–2.734 (2.210)
	4	1.950–2.524 (2.217)	6	1.931–1.946 (1.938)
C	2	1.800–1.860 (1.825)		
	3	1.900–2.090 (1.936)		
	4	1.892–1.977 (1.935)		
Cl	2	2.046–2.140 (2.083)	4	2.223–2.280 (2.260)
			5	2.280–2.613 (2.379)
	4	2.228–2.996 (2.552)	6	2.762–3.130 (2.946)
S			4	2.230–2.450 (2.295)
			5	2.946–3.286 (3.116)
	4	2.210–2.645 (2.358)	6	2.464–2.732 (2.554)
P	3	2.229–2.233 (2.231)		
	4	2.210–2.250 (2.230)		
Br	4	2.503		
Se	4	2.512–2.907 (2.698)		
I	4	2.575–2.959 (2.725)		

[a] The mean value is in parentheses.

metalloenzymes and play a significant and expanding role in industrial chemical catalysis.

It is hoped that this series of structural reviews will serve to stimulate further investigations in these interesting and useful areas of chemistry.

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