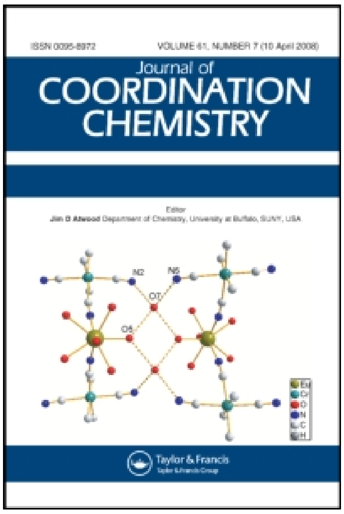

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COPPER(III) COORDINATION COMPOUNDS: CLASSIFICATION AND ANALYSIS OF CRYSTALLOGRAPHIC AND STRUCTURAL DATA

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Review

COPPER(III) COORDINATION COMPOUNDS: CLASSIFICATION AND ANALYSIS OF CRYSTALLOGRAPHIC AND STRUCTURAL DATA

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Copper is classed as a transition metal both from its physico-chemical properties and its biochemical behavior. This review includes thirty *formally* copper(III) compounds where crystal structure has been determined. Coordination number four dominates with mostly a square-planar arrangement about the copper(III) atom. Sulfur donor ligands by far prevail. In general the Cu–L bond distance elongated with a decreased oxidation state of copper in the sequence: Cu(III)–L < Cu(II)–L < Cu(I)–L. Examples of distortion isomerism exist.

Keywords: Copper(III); review; structures; coordination complexes

0 ABBREVIATIONS

bhmpb	1,2-bis(2-hydroxy-2-methylpropanamido)benzene
Bu_2dtc	N,N-di-*n*-butyldithiocarbamate
bz	benzoate
$C_2B_9H_{11}$	bis{(3)-1,2-dicarbollyl}
$C_6H_8S_4$	1,4-butanediyldithioethylene-1,2-dithiolate

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$C_8H_{12}N_8O_4$	1,2,4,5,8,9,11,12-octa-aza-3,10-dimethyltetradecane-6,7,13,14-tetrone
$C_9H_{15}N_6S_2$	dimethyl 2,2′-(1,3-dimethylpropane-1,3-diylidene) bis hydrazinecarboximido- thiolate(-3)
dddt	5,6-dihydro-1,4-dithiin-2,3-dithiolate
ded	1,1-dicarboethoxy-2,2-ethylenedithiolate
dmpm	bis(dimethylphosphine)methylene
dto	dithiooxalate
Et_2dtc	N,N-diethyldithiocarbamate
H_2aib_3	tri-α-aminoisobutyrate
im	imidazole
mnt	*cis*-1,2-dicyanoethylenedithiolate
per	perilenium
o-phen(bi)$_2$	o-phenylenebisbiuretate
pidtc	N-piperidyldithiocarbamate
pnp	Ph_3PNPh_3
Pr_2dtc	N,N-di-*n*-propyldithiocarbamate
py	pyridine
pydtc	N-pyrrolidyldithiocarbamate
qdt	quinoxaline-2,3-dithiolate
tpp	5,10,15,20-tetraphenylphosphinate
vfc	venus flytrap cluster; bis(dicarbollide) pyrazole

1 INTRODUCTION

Copper in the oxidation state +2, is the most common by far; other known oxidation states include +1, +3 and +4, and of these copper(I) is the most common. The chemistry of copper compounds has been extensively investigated, and the relationship between structure and reactivity, ranging from industrial catalysis to biomedical activity, is of major importance. The overwhelming majority of all X-ray studies of transition metal compounds are of copper compounds.

There are complete reviews of the crystallographic and structural data of copper(I) compounds,[1] mixed-valence Cu(I)–Cu(II),[2] and copper(II) compounds.[3–7] No complete review of the crystallographic and structural data of copper(III) compounds has yet appeared. This manuscript includes thirty published copper(III) structures which have been analyzed and classified in order to assist in understanding the stereochemical interactions in the coordination sphere of the copper(III) species.

2 MONOMERIC COPPER(III) COMPOUNDS

2.1 Coordination Number Four

There are twenty-two copper(III) derivatives in which the copper(III) atom is four-coordinate; the crystallographic and structural data are given in Table I. Air was passed through a solution of 5-methylisothiosemicarbazide and pentane-2,4-dione with monohydrate copper(II) acetate at ambient temperature giving green-black microcrystals of $Cu(C_9H_{15}N_6S_2)$. The geometry around the Cu(III) atom is intermediate between square-planar and tetrahedral with four N-donor atoms, which form CuN_4 core (Figure 1). There are two crystallographically independent molecules, which differ mostly by degree of distortion.

X-ray analysis of blue $(EtNH_3)[Cu(C_8H_{12}N_8O_4)]\cdot 5H_2O$ arising from the reaction of acetaldehyde with oxalohydrazide in the presence of Cu(III) atoms and molecular oxygen shows[9] that the complex anion, $[Cu(C_8H_{12}N_8O_4)]^-$ contains a Cu(III) atom which is surrounded by four N-donor atoms of the macrocycle ligand with an average Cu–N bond distance of 1.886 Å.

X-ray analysis of green $(NBu_4)[Cu\{o\text{-phen(bi)}_2\}]\cdot CHCl_3$ shows[10] the Cu(III) in the deprotonated amide nitrogen atoms of the macrocycle ligand, with an average Cu–N bond distance 1.85(1) Å.

In the series of tetra-coordinated copper compounds, the mean Cu–N (tetradentate) bond distance elongated with decreasing oxidation state of

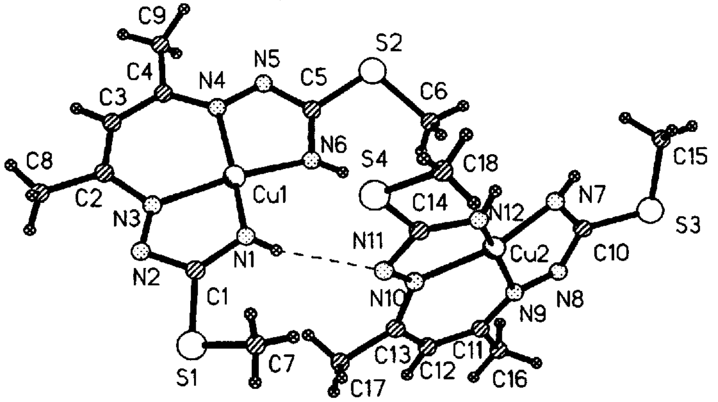

FIGURE 1 Structure of two crystallographically independent molecules, $Cu(C_9H_{15}N_6S_2)$.[8]

TABLE I Crystallographic and structural data for copper(III) compounds[a]

Compound *(color)*	*Crystallographic* *classification* *space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore*	*Cu–L* [Å]		*L–Cu–L* [°]		*Ref.*
$Cu(C_9H_{15}N_6S_2)^c$ (green black)	tr P-1 4	9.668(2) 10.769(2) 14.918(2)	70.87(1) 71.38(1) 73.01(2)	CuN_4	N^b	1.892(3,7) 1.904(2,3)	N,N^b	$82.4(1,2)^d$ $95.9(1)^e$ 103.9(1) 163.2(1,1.7)	8
$(EtNH_3)[Cu(C_8H_{12}N_8O_4] \cdot$ $5H_2O$ (blue)	m $P2_1/c$ 4	12.825(1) 15.561(1) 11.289(1)	 111.18(1)	CuN_4	N	1.886(—,10)	N,N	Not given	9
$(NBu^n)[Cu\{o\text{-phen(bi)}_2\}]$- $CHCl_3$ (green)	tr P-1 2	9.68(1) 10.75(1) 16.64(4)	93.4(1) 105.2(1) 94.32(5)	CuN_4	N	1.85(1,4)	N,N	Not given	10
$(pnp)[Cu(CF_3)_4]$ (colorless)	tg $P4_1$ 4	9.50(3) 42.452(10)		CuC_4	F_3C	1.951(16,3) 1.981(17,2)	C,C	90.5(7,1.2) 168.6(7,3.6)	11
$(pnp)[Cu(CF_2H)_4]$ (colorless)	tg $P4_1$ 4	9.443(1) 41.803(5)		CuC_4	C	1.925(9,6) 1.954(9)	C,C	90.0(6,2.1) 176.3(6,6)	12
$[Cu(Et_2dtc)_2]I_3$ (not given)	m P2/m 2	7.218(2) 14.929(3) 9.990(3)	 91.212(2)	CuS_4	S	2.210(3) 2.214(3)	S,S	$78.47(13)^f$	13
$[Cu(Pr_2dtc)_2]I_5$ (dark brown)	m $P2_1/c$ 4	10.346(2) 23.700(6) 15.707(3)	 129.34(2)	CuS_4	S	2.20(1,1)	S,S	$78.5(4,1)^f$ 101.4(4,0)	14
$[Cu(Bu_2dtc)_2]I_3^c$ (black)	m $P2_1/c$ 4	14.026(6) 8.62(1) 25.015(9)	 95.35(5)	CuS_4 CuS_4	S S	2.22(2,1) 2.22(2,0)	S,S S,S	$79.2(5)^f$ $78.7(6)^f$	15

$[Cu(pidtc)_2]PF_6$ [c] (black)	m $P2_1/c$ 4	7.816(2) 18.428(2) 13.883(2)	94.94(2)	CuS_4	S	2.206(2) 2.216(2)	S,S	78.5(1)[f]	16
				CuS_4	S	2.208(2) 2.222(2)	S,S	78.6(1)[f]	
$[Cu(pydtc)_2]ClO_4$ (not given)	m $P2_1/c$ 4	7.016(1) 13.082(1) 22.318(3)	122.04(1)	CuS_4	S	2.202(3) 2.215(4,2)	S,S	79.1(1,1)[f] 100.7(1,4) 175.0(2,2)	17
$(NEt_4)[Cu(C_6H_8S_4)_2]$ (dark green)	m C2/c 4	25.567(6) 8.011(3) 14.504(3)	106.17(2)	CuS_4	S	2.180(1) × 2 2.190(1) × 2	S,S	91.4(1)[d] 88.6(1) 180.0(1)	18
$(NBu_4)[Cu(dddt)_2]$ (blue black)	m $P2_1/c$ 4	17.937(2) 8.806(1) 21.962(3)	109.8(1)	CuS_4	S	2.177(3,2) 2.184(3,1)	S,S	92.5(1,2)[d] 90.6(1,3) 161.2(1,1.2)	19
$(HNMe_3)[Cu(dddt)_2]$ (blue black)	or Pnnm 2	9.211(2) 10.114(3) 10.956(4)		CuS_4	S	2.185(3,0)	S,S	91.8(2)[d]	19
$(PPh_4)[Cu(qdt)_2]$ [c] (not given)	m P2/n 4	23.709(2) 7.192(1) 24.188(2)	119.170(6)	CuS_4	S	2.184(1,4)	S,S	92.2(1)[d]	20
				CuS_4	S	2.189(1,6)	S,S	91.5(1)[d]	
$(per)_2[Cu(qdt)_2]$ (black)	tr P-1 2	11.1451(12) 12.5674(8) 15.5207(12)	95.374(8) 105.384(8) 92.095(9)	CuS_4	S	2.178(2,3)	S,S	87.10(7,1) 92.76(7,3)[d] 177.6(1,6)	21
$[N(P_2Ph_3)][Cu(dto)_2]$ (red)	m C2/m 4	13.528(2) 18.456(2) 15.354(2)	95.82(1)	CuS_4	S	2.164(1,0) 2.178(1,0)	S,S	87.48(5) 92.52(5)[d]	22
$K[Cu(ded)_2] \cdot Et_2O$ (not given)	m C2/c 4	13.781(3) 17.527(3) 12.903(2)	107.21(1)	CuS_4	S	2.190(5,0) 2.199(5,0)	S,S	78.14(24)[f] 101.87(2)	23

TABLE I (*Continued*)

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore*	*Cu–L* [Å]		*L–Cu–L* [°]		*Ref.*
$[Cu^{III}(Et_2dtc)_2]$-	m	14.421(15)		$Cu^{III}S_4$	S	2.18(2,2)	S,S	78(1)[f]	24
$[Cu^{II}(Et_2dtc)Br_2]$	Cc	12.980(17)	106.82(8)			2.26(2)			
(black)	4	15.152(11)							
				$Cu^{II}S_2Br_2$	S	2.28(2,1)	S,S	71.4(8)[f]	
					Br	2.40(2,0)	Br,Br	96.8(2)	
$[Cu(H_2aib_3)]\cdot 2H_2O\cdot$	m	20.638(7)		CuN_3O	N	1.802(5,2)	N,N	87.1(2,5)[d]	25
$1.5NaClO_4$	$P2_1/c$	9.250(6)	92.80(3)			1.898(5)		172.5(2)	
(yellow brown)	4	11.362(5)			O	1.826(3)	N,O	87.6(2)[d]	
								98.1(2)	
								174.3(2)	
$(PPh_4)[Cu(bhmpb)]\cdot 2H_2O$	m	9.263(1)		CuO_2N_2	O	1.808(4,8)		Not given	26
(not given)	$P2_1/n$	14.446(3)	96.056(13)		N	1.808(4,5)			
	4	2.792(4)							
$Cu(CF_3(Et_2dtc)$	m	14.911(2)		CuC_2S_2	F_3C	1.863(5)	C,C	92.2(2)	27
(not given)	Cc	10.589(1)	114.2(1)			2.026(5)	S,S	79.33(5)[f]	
	4	8.765(1)			S	2.205(1,19)	C,S	94.4(1,7)	
								172.3(1,9)	
$Cu(Bu_2dtc)Br_2$	m	13.85(3)		CuS_2Br_2	S	2.193(6,0)	S,S	75.9[f]	28
(dark violet)	C2/c	14.94(3)	98.8(3)		Br	2.311(4,0)	Br,Br	103.2	
	4	7.28(2)							
$Cu(bz)_2(py)_2Cl$	m	15.979(1)		CuO_2N_2Cl	bzO	1.930(3,3)	O,O	89.8(2)	29
(blue)	$P2_1/n$	18.876(2)	92.94(1)		pyN	2.040(4,5)	N,N	168.6(3)	
	4	19.723(2)			Cl	2.274(3)	O,N	90.1(3,1.9)	
							O,Cl	89.0(2,8)	
							N,Cl	95.7(3,1.1)	
$\{P(Me)Ph_3\}[Cu(C_2B_9H_{11})_2]$	tr	11.74	97.9	CuB_6C_4	B	2.11(3,7)	B,B	50(—,3)	30
(dark red)	P-1	15.30	94.2		C	2.52(2,4)	C,C	35(—,1)	
	4	19.96	99.0				B,C	44(—,1)	

Cu(vfc)	or	7.1854(8)		CuB_6C_4	B	2.159(7,23)	B,B	90.7(2,6.0)	31
(deep purple)	$P2_12_12_1$	13.434(2)			C	2.240(5,17)		167.4(2)	
	4	19.980(2)				2.326(5,23)	C,C	113.23(21)	
$[Cu(mnt)_2][Fe(tpp)(imH)_2]\cdot$	tr	10.012(4)	71.42(4)	CuS4	S	2.172(2,5)	S,S	92.8(1,0)^d	32
4thf	P-1	11.604(6)	87.12(3)						
(dark) (at 143 K)	1	15.802(7)	78.45(4)						
				$Fe^{III}N_6$	tppN	1.994(3,12)	N,N	91.2(1,0)^e	
					imN	1.981(3,0)		91.1(1,2)	
$[Cu_3(Bu_3dtc)_6]\cdot$	tr	12.363(3)	95.76(2)	$Cu^{III}S_5$	S	2.221(7,2)	S,S	78.2(2,1)^f	33
$[Hg_2(\mu\text{-}Br)_2Br_4]$	P-1	13.789(4)	90.89(2)	(×2)	μS	2.226(6)		100.3(3,4)	
(at 233 K)	1	12.423(4)	86.00(2)			2.857(7)		166.7(3,1.3)	
(dark violet)				$Cu^{II}S_6$	S	2.297(6)	S,S	77.3(2)^f	
				(×1)	μS	2.337(6)		102.7(2)	
						3.141(6)		180.0	
				$HgBr_4$	Br	2.534(4,11)	Br,Br	123.0(1)	
					μBr	2.724(3,10)	μBr,μBr	91.0(1)	
							Br,μBr	110.1(1,4.1)	
$[Cu_3(Bu_2dtc)_6]\cdot$	tr	12.715(2)	95.29(2)	$Cu^{III}S_5$	S	2.216(4,3)	S,S	78.6(1,2)^f	34
$[Hg_2(\mu\text{-}Br)_2Br_4]$	P-1	13.194(3)	90.06(2)	(×2)	μS	2.225(4)		99.9(1,7)	
(dark violet)	1	12.363(4)	84.18(2)			Not given		167.1(1,1.0)	
(at 193 K)				$Cu^{II}S_6$	S	2.312(3)	S,S	77.0(1)^f	
					μS	2.325(3)		103.1(1)	
						Not given		180.0	
				$HgBr_4$	Br	2.532(2,3)	Br,Br	120.52(5)	
					μBr	2.728(2,14)	μBr,μBr	89.81(5)	
							Br,μBr	111.2(1,2.6)	
$[Cu_3(Bu_2dtc)_6]\cdot$	tr	12.629(4)	95.84(4)	$Cu^{III}S_5$	S	2.22(1,1)		Not given	35
$[Cd_2(\mu\text{-}Br)_2Br_4]$	P-1	13.706(4)	91.45(4)	(×2)	μS	2.88(1)			
(dark violet black)	1	12.506(4)	86.06(3)						
				$Cu^{II}S_6$	S	2.33(1,3)			
				(×1)	μS	3.19(1)			
				CdS_4	S	Not given			

TABLE I (*Continued*)

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore*	*Cu–L* [Å]		*L–Cu–L* [°]		*Ref.*
$[Cu_2Au(Bu_2dtc)_6 \cdot [Hg_2Br_6]$	tr	12.614(4)	96.37(4)	$Cu^{III}S_5$	S	2.27(1,2)	S,S	76.7(3,1)[f]	36
(dark green)	P-1	13.691(4)	91.47(4)	$(Au^{III}S_5)$		3.15(1)		3.15(1)	
	1	12.502(4)	85.43(4)						
				$Cu^{II}S_6$	S	2.30(1,3)	S,S	77.5(3)[f]	
						3.20(1)			
				$HgBr_4$	Br	2.517(5,5)	Br,Br	122.3(1)	
					μBr	2.724(4,7)	Br,μBr	106.6(1,1)	
							μBr,μBr	90.0(1,9)	
$[Cu_3Co_4(CO)_8(dmpm)_4] \cdot$	m	10.767(2)		$Cu^{III}Co_4$	Co	2.458(4)	Co,Co	168,1(1)	37
BF_4	$P2_1/c$	20.092(2)	92.13(1)	(×1)		2.474(4)		178.0(1)	
(black)	4	22.370(3)							
				$Cu^{I}C_2PCu$	Cu	2.624(3)			
				(×2)		2.683(3)			

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these columns. [c] There are two crystallographically independent molecules. [d] Five-membered metallocyclic ring. [e] Six-membered metallocyclic ring. [f] Four-membered metallocyclic ring.

copper in the order: 1.88 Å [Cu(III)] < 1.97 Å [Cu(II)][3] < 2.055 Å [Cu(I)],[1] as expected.

There are two colorless derivatives[11,12] in which four unidentate C donor ligands create a square-planar environment about copper(III). The mean Cu(III)–C bond distance of 1.955 Å is about 0.025 Å shorter than that of Cu(I)–C bond distance (1.980 Å).[1] Significantly, there are no examples of Cu(II) derivatives[3] with a CuC_4 core.

In another thirteen derivatives,[13–24] S-donor bidentate chelating ligands created a square-planar environment about copper(III) atoms with differing degrees of distortion. The mean Cu–S bond distance elongated with decreasing oxidation state of copper in the sequence: 2.34 Å [Cu(I)][1] > 2.29 Å [Cu(II)][3] > 2.21 Å [Cu(III)].

An X-ray structure of a yellow-brown derivative shows that the copper(III) is coordinated by peptide nitrogens, and the carboxylate oxygen of the tri-α-aminoisobutyrate peptide in a square-planar geometry. The copper(III) and four donor atoms are coplanar with the largest deviation being 0.06 Å. The Cu(III)–N(amino), –N(peptide), and –O(carboxyl) bond distance are 0.13, 0.12 and 0.17 Å shorter than those of the analogous copper(II) bonds.[3]

In a purple derivative[26] the tetradentate 1,2-bis(2-hydroxy-2-methylpropanamido) benzene created a square-planar environment about copper(III) with the chromophore CuO_2N_2 (Table I).

Reaction between trifluoromethylcadmium and $Cu(Et_2dtc)Br_2$ in dimethylformamide at −30°C yields stable $Cu(CF_3)_2(Et_2dtc)$ complex.[27] The structure of the complex shows[27] a distorted quadratic-planar configuration for the copper(III) atom with the chromophore, CuC_2S_2. Structure of dark-violet $Cu(Bu_2dtc)Br_2$[28] is similar to $Cu(Et_2dtc)(CF_3)_2$ (Table I).

The crystal system of twenty-two copper(III) compounds are for the most part monoclinic (16), but there are triclinic (3), tetragonal (2) and orthorhombic (1) examples. The ligands involved are mono-, bi- and tetradentate. The mean Cu(III)–L bond distances for monodentate ligands are 1.955 Å for C-donor ligands and 2.31 Å for bromine. The bidentate ligands are only S-donor with mean Cu(III)–S bond distance of 2.21 Å. The tetradentate ligands include both homo- and hetero-donor atoms, include those with two O plus two N, one O plus three N, and those with four N-donor sites.

The effects of both electronic and steric factors are observed in the values of the L–Cu–L bond angles of the metallocyclic rings. In four-membered rings the mean S–Cu–S intra-ligand angle is 78.5° (range 75.9°–77.3°). For the five-membered rings the values are 82.4°–87.1° (mean 84.7°, N-donor), 87.6° (O + N-donor), and 91.5°–92.7° (mean 92.0°, S-donor). For six-membered rings the value is 96°.

2.2 Coordination Number Five

Blue $Cu(bz)_2(py)_2Cl$ complex[29] is the only example of a monomeric derivative, in which copper(III) is five coordinate. X-ray analysis of the complex shows, that the five monodentate ligands have a square-based pyramidal arrangement about the Cu(III) atom. The basal sites of the square-pyramid are occupied by two benzoate and two pyridine ligands in a *trans*-configuration, while the chlorine atom is situated axially (Figure 2) (Table I).

2.3 π-Sandwich Configuration

There are two colored, dark red[30] and deep blue[31] derivatives, in which the copper(III) atoms are π-sandwiched by bis{(3)-1,2-dicarollyl} in the former and bis(dicarbollide)-pyrazole in the latter. The structure of $Cu(C_2B_9H_{11})_2^-$ anion[30] is distorted from a π-sandwich configuration by slippage of the carborane moieties parallel to one another so that the primary coordination sphere of copper is six borons, three from each carborane cage.

A structure of the diamagnetic meso-isomer, Cu(vfc)[31] is shown in Figure 3. Each of the bonding faces of the dicarbollide structural

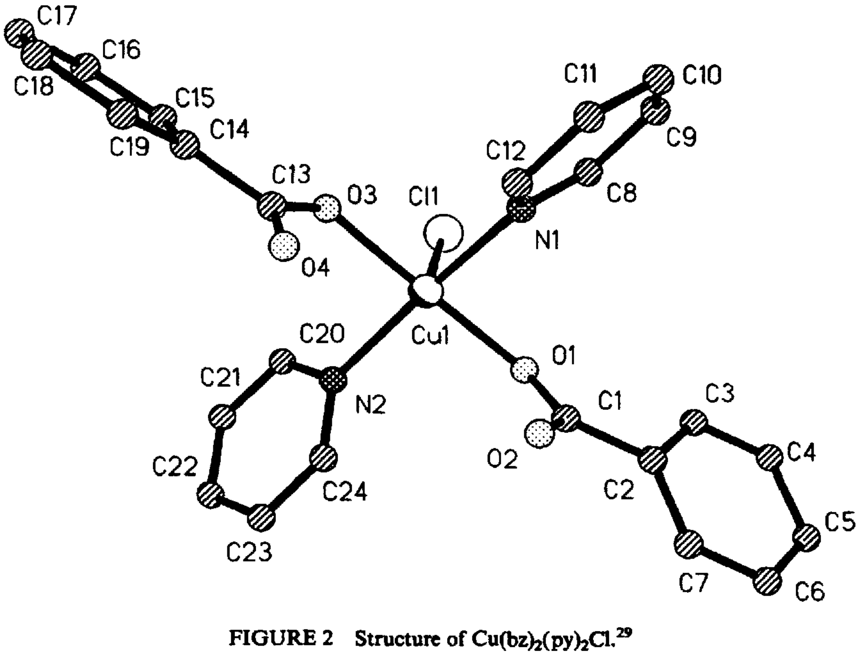

FIGURE 2 Structure of $Cu(bz)_2(py)_2Cl$.[29]

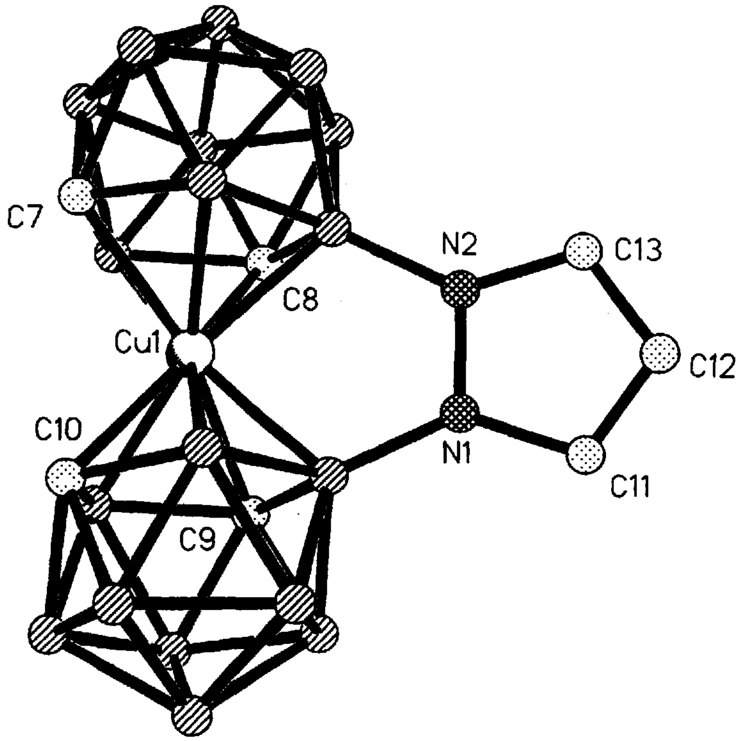

FIGURE 3 Structure of Cu(vfc).[31]

components is planar to within 0.123(7) Å and Cu distances to these planes are 1.670(2) Å (unprimed atoms) and 1.664(2) Å (primed atoms). The dicarbollide bonding faces are eclipsed, and the angle between normals to these faces is 14.1(3)°. The Cu–C distances vary from 2.223(5) to 2.349(6) Å, and Cu–B interactions range from 2.136(6) to 2.182(7) Å (Table I).

3 DOUBLE SALTS

A structure of dark derivative[32] consists of a discrete $[Fe(tpp)(imH)_2]^+$ cation and an $[Cu(mnt)_2]^-$ anion. Of the two occluded tetrahydrofuran molecules in the asymmetric unit, one is hydrogen bonded to the coordinated imidazole. The copper(III) is surrounded by two bidentate *cis*-1,2-dicyanoethylenedithiolate ligands in a square-planar environment, CuS_4, with the mean

Cu–S bond distance of 2.172(2) Å and five-membered metallocyclic ring, S–Cu–S of 92.8(1)°. The Fe(III) atom has an octahedral geometry, created by tetradentate-N_4 tpp in a plane and an apical positions are occupied by imidazole molecules.

4 MIXED-VALENCE, Cu(III)–Cu(II) COMPOUNDS

The structure of dark-violet $[Cu_3(Bu_2dtc)_6][Hg_2Br_6]$ has been studied at 233[33] and 103 K,[34] respectively. The structure at 233 K (Figure 4) is found to be essentially isomorphous with the low-temperature (at 103 K,) form, apart from a significant change of the conformation around C(25)–C(26) from *trans* to gauche. The most drastic changes may be found in the intermolecular contacts of the butyl chains. The structures consist of two centrosymmetric ionic units $[Cu_3(Bu_2dtc)_6]^{2+}$ and $[Hg_2Br_6]^{2-}$. In the cation one copper atom has an apically distorted octahedral S-coordination. The two other equivalent copper(III) atoms have five-fold pyramidal S-coordination (Table I). The $Hg_2Br_6^{2-}$ ion can be described as a distorted edge-condensed bi-tetrahedron.

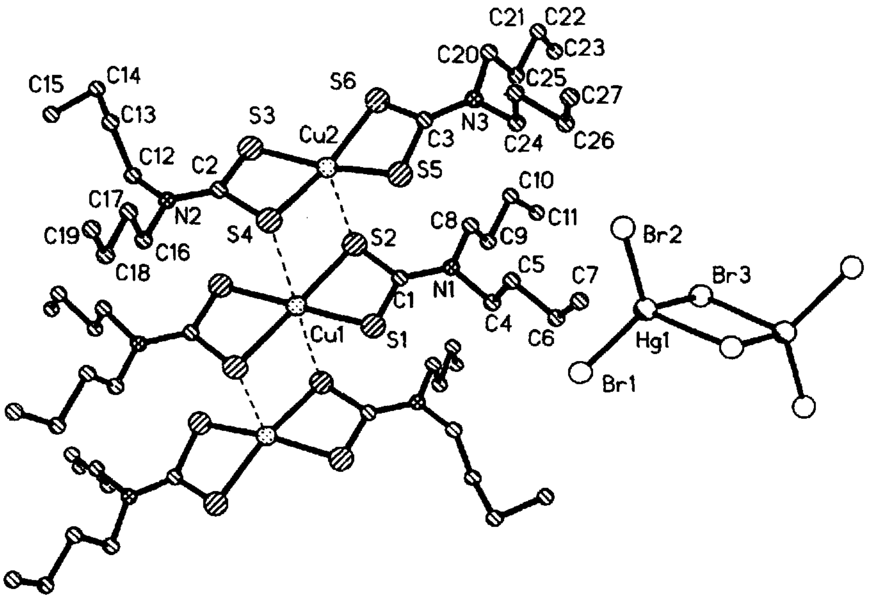

FIGURE 4 Structure of $[Cu_3(Bu_2dtc)_6][Hg_2Br_6]$.[33]

The structure of the dark violet-black $[Cu_3(Bu_2dtc)_6][Cd_2Br_6]$ derivative[35] is isomorphous with the corresponding mercury complex[33] (Table I). In general, the Cu(III)–S bond distances (Table I) are shorter than Cu(II)–S bond distances, as expected.

5 HETEROMETALLIC COPPER(III) COMPOUNDS

A dark-green derivative[36] consists of $[Cu_2Au(Bu_2dtc)_6]^{2+}$ and $[Hg_2Br_2]^{2-}$ and is isomorphous with structures in Section 3. The cation is situated at a centrosymmetric position, with disordered Cu(III) and Au(III) attached to a central Cu(II) atom. The central Cu(II) atom has an apically distorted octahedral S-coordination. The disordered [Cu(III) and Au(III)] positions have five-fold pyramidal S-coordination (Table I).

A black cluster of composition $[Cu_3Co_4(dmpm)_4(CO)_8]BF_4$ was prepared[37] by reaction of $Co_2(CO)_4(dmpm)_2$ with $[Cu(MeCN)_4]BF_4$. X-ray analysis of the cluster shows (Figure 5) that there are two triangles of metal atoms [Co(1) Co(2) Cu(2) and Co(3) Co(4) Cu(3)] bridged by a central

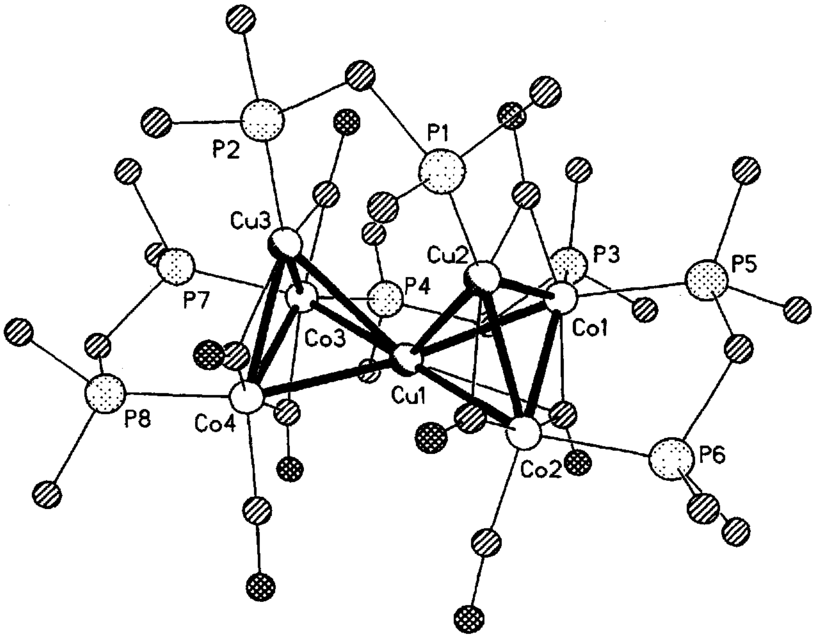

FIGURE 5 Structure of $[Cu_3Co_4(\mu\text{-}dmpm)_4(CO)_8]^+$.[37]

copper(III) atom [Cu(1)]. Each Co_2Cu triangle has three edge-bridging carbonyl ligands of which one [*e.g.*, C(3) O(3)] bridges a Co–Co bond and two [*e.g.*, C(5) O(5) and C(7) O(7)] are semi-bridging between cobalt and copper. The two Co_2Cu triangles are bridged by two dmpm ligands, of which one bridges between equivalent copper(1) atoms [Cu(2)P(1)P(2)Cu(3)] and one bridges between cobalt atoms [Co(1)P(3)P(4)Co(3)], while the remaining dmpm and carbonyl ligands are terminally bound to cobalt. The two Co_2Cu triangles lean towards one another such that the non-bonding distance Cu(2) ··· Cu(3), 3.211(4) Å is much shorter than the corresponding distances Co(1) ··· Co(3), 4.248(4) Å and Co(2) ··· Co(4), 4.241 Å.

The most remarkable feature of the structure is the geometry of the bridging copper atom Cu(1). It does not bridge symmetrically between the faces of the Co_2Cu triangles but is displaced towards the cobalt atoms such that the Cu(1)–Co distances, 2.458(4)–2.474(4) Å are significantly shorter than the Cu(1)–Cu distances, 2.683(4) and 2.624(3) Å.

6 CONCLUSIONS

This review has classified thirty formally, copper(III) containing structures. Copper(III) compounds are mostly black, while copper(I) compounds[1] are for the most part colorless and copper(II) compounds[3–7] blue and green. The most common coordination number for copper(III) compounds is four. A square-planar environment with different degrees of distortion about copper(III) is most common. In general, the mean Cu–L bond distance elongated with decreasing oxidation state of the copper atom in the sequence: Cu(III)–L < Cu(II)–L < Cu(I)–L.

Two independent molecules, differing by degree of distortion, have been found to be present in one crystal in several cases.[8,15,16,20] The coexistence of two or more species, differing only by degree of distortion, is typical of the general class of distortion isomerism.[38]

This review, together with its precursors for copper(I);[1] copper(I)–copper(II);[2] copper(II);[3–7] silver[39] and gold,[40] represents the first overview of structural data for the various oxidation states of the metals of the subgroup 1B. During the collection and organization of the data it became clear that, despite the increasing availability of data retrieval systems, the tracing of relevant material is not always straightforward. Some of the data are only available as supplementary material, and some are not mentioned at all. This can lead to overlooking relevant structural features which should be compared with other derivatives. In view of such limitations in information retrieval, we believe that it is necessary to make a systematic overall review, and that such reviews serve the useful purpose of delineating areas of both interest and weakness.

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