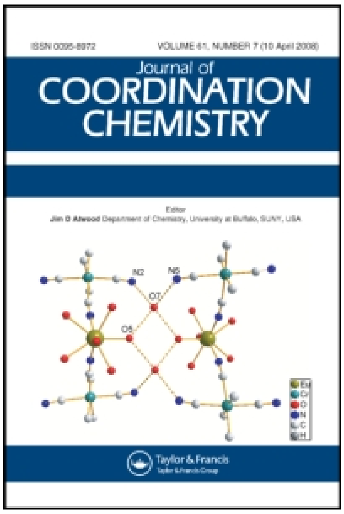

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COPPER(II) COORDINATION COMPOUNDS: CLASSIFICATION AND ANALYSIS OF CRYSTALLOGRAPHIC AND STRUCTURAL DATA IV. TRIMERIC AND OLIGOMERIC COMPOUNDS

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Review

COPPER(II) COORDINATION COMPOUNDS: CLASSIFICATION AND ANALYSIS OF CRYSTALLOGRAPHIC AND STRUCTURAL DATA IV. TRIMERIC AND OLIGOMERIC COMPOUNDS*

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This review summarizes data for over two hundred and thirty trimeric and oligomeric copper(II) coordination compounds. Included are trimeric (73), tetrameric (135), pentameric (5), hexameric (12), octameric (5), nonameric (2) and even dodecameric (1) derivatives. In most complexes, the copper(II) is four-, five- and six-coordinate. The structures are discussed in terms of the coordination about the copper(II) atoms, and correlation's are drawn between donor atom, bond length and interbond angles. There are several examples of distortion isomerism.

Keywords: Review; copper(II); crystallography; structures; trimeric; oligomers

CONTENTS

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[†] Corresponding author.

ABBREVIATIONS

ac	acetate
acac	2,4-pentadionate
ade	adenine
ae	7-amino-4-methyl-5-aza-3-hepten-2-onate
ahd	β-alaninhydroxamate
ain	7-azaindole
amat	4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-diolate
amp	2-amino-2-methyl-1-propanolate
amo	8-amino-5-aza-4-methyl-3-octane-2-onate
ap	3-aminopropanolate
apae	[(3-aminopropyl)amino]ethanolate
at	8-amino-5-aza-4-methyl-3-octen-2-onate
bapa	bis(3-aminopropyl)amine
bc	3,5-di-tertbutyl-1,2-catecholate
bibo	3-(benzylimino)butanone-2-oximate
bipyam	bipyridilamine
bipyamH	bis(2-pyridyl)amide
5B6map	5-bromo-6-methyl-2-aminopyridinium
bpen	1,5-bis[1-(pyridin-2-yl)ethylideneamino]pentan-3-ol
bpim	4,5-bis[2-(2-pyridyl)ethyliminomethyl]imidazole
bpy	2,2′-bipyridine
4-Brbz	4-bromobenzoate
bsmnp	2,6-bis{(salicylideneamino)methyl}-4-nitrophenole
bta	benzotriazolate

bttt	13,26-di-tert-butyl-3,9,17,23-tetraazatetracyclo [23.3.1.1^{11,15}]tiaconta-1(29),2,9,11,13,15(30), 16,23,25,27-decaene-6,20,29,30-tetraol
bz	benzoate
bzac	benzoylacetonate
c	cubic
cdp	product of condensation of 2,3-dihydroxy-benzaldehyde with aminoalkylpyridine
$C_8H_{11}NO_3$	product of condensation of 3-ethoxymethylene-2,4-pentadione and 2-aminoethanol
$C_9H_9NO_2$	product of condensation of 2-oxyethylamine and 2-oxy-1-benzaldehyde
$C_{11}H_{19}N_2O_2$	condensation product of 2,4-pentadione and 3-amino-1-propanol
$C_{12}H_{22}N_2O_2S_4$	dithiooxamid-S-ethanol-propylamine
$C_{12}H_{24}N_2O_4$	4,10-bis(2-hydroxyethyl)-1,7-dioxa-4,10-diazacyclodecane
$C_{12}H_{24}N_4O_2$	N,N′-dipropylamine-2,2′-dimethyl-oxamidate
$C_{13}H_{13}N_2O_3$	3-[(2-pyridyl)methyliminomethyl]benzene-1,2-diolate
$C_{15}H_{13}N_4O_2$	1,2-diphenyl-2-(methylimino)ethanone-1-oxime
$C_{16}H_{14}N_2O_3$	3-hydroxy-4-[4′-(3″,4″-dichlorophenyl)-4′-hydroxy-2′-azabut-1′-en-1′-yl)]5-hydroxymethyl-2-methylpyridine
$C_{16}H_{16}N_2O_3$	3-hydroxy-5-hydroxymethyl-4-(4′-hydroxy-4′-phenyl-2-azabut-1′-en-1′-yl)-2-methylpyridine
$C_{17}H_{18}N_2O_3$	3-hydroxy-5-hydroxymethyl-4-(4′-hydroxy-3′-methyl-4′-phenyl-2′-azabut-1′-en-1′-yl)-2-methylpyridine
$C_{18}H_{42}N_4O_2$	N,N-diethyl-N′-(3-hydroxypropyl)ethylene-diaminate
$C_{18}H_{42}N_6O_3$	tritopic hexa aza macrocycle
$C_{19}H_{21}N_6O$	2,6-bis{N-[2-(4-imidazolyl)ethyl]iminomethyl}-4-methylphenol
$C_{20}H_{24}N_2O$	4,7-bis(2-hydroxybenzyl)-1-oxa-4,7-diazacyclononane
2-Clpr	2-chloropropionate
Clac	chloroacetate
Cl_2ac	dichloroacetate
Cl_3ac	trichloroacetate
cpa	2-carboxypentonate
$dapdH_2$	2,6-diacetylpyridine dioxime
dapo	1,3-diamino-2-propanolate
dapoH	1,3-diamino-2-propanol
dbae	2-dibutylaminoethanolate

dbm	dibenzoylmethanate(1,4-diphenyl-1,3-propanedionate)
dea	2-(diethylamino)acetamidoxime
deae	2-diethylaminoethanolate
dfmph	2,6-diformyl-4-methylphenol dibenzoylhydrazone
dip	2,6-diacetylpyridinebis(picolinoylhydrazonate)
dmae	2-dimethylaminoethanolate
dmap	1,3-bis(dimethylamino)-2-propanolate
dmcpz	3,5-dimethoxycarbonylpyrazole
dmf	dimethylformamide
dmg	dimethylglyoximate
dmppz	3,4-dimethyl-5-phenylpyrazole
dmpz	3,5-dimethylpyrazole
dpae	2-dipropylaminoethanolate
dpg	diphenylglyoximate
dpm	2,2,6,6-tetramethyl-3,5-hepta7dionate
edta	ethylenediaminetetraacetate
eha	N,N′-ethylenebis(o-hydroxyacetopheniminate)
eia	7-hydroxy-4-methyl-5-azahept-4-en-2-an
en	ethylenediamine
es	N,N′-ethylenebis(salicylaldiminate)
Etac	ethylacetate
ettmd	4-ethyl-1,1,7,7-tetramethyldiethylenetriamine
Ettmio	4-ethyl-2,2,5,5-tetramethyl-3-imidazoline-1-oxyl
Et_2dtc	bis(diethyldithiocarbamate)
Et_2na	N,N-diethylnicotiamide
Fac	fluoroacetate
F_3ac	trifluoroacetate
fptsc	2-formylpyridinetiosemicarbazone
gmp	guanosine-3′-monophosphate
hfac	1,1,1,5,5,5-hexafluoro-2,4-pentadionate
hmt	hexamethylenetetraamine
hsd	hexa Schiff base macrocycle
hx	hexagonal
im	imidazole
imp	N,N′-imidopicolinyloxamylhydrazine
inicNO	isonicotinato N-oxide
inp	5′-inasinemonophosphate
ipe	β-diketonate
ipte	2-(isopropylthio)ethanole
m	monoclinic

30m	30-membered macrocyclic ring
mal	malonate
3-mapH	3-methyl-2-aminopyridinium
4-mapH	4-methyl-2-aminopyridinium
md	macrocycle derived from 2-hydroxy-5-methylisopthalaldehyde and 3-dimethylamino-1-propylamine
me	methoxyethanole
Meacpz	1-(1-ethanoyl)-5-methylpyrazolate
Meim	N-methylimidazole
1,2-Me$_2$im	1,2-dimethylimidazole
2-Mepy	2-methylpyridine
4-MepyH	4-methylpyridinium
Mepz	3(5)-methylpyrazolate
Me$_2$pba	2,2-dimethyl-1,3-propanediyl-bis(oximato)
Me$_3$pzH	1,1,4-trimethylpiperazinium
metz	3-methyl-4-ethyl-1,2,4-triazole
mob	1,3-bis(2-methyl-4,6,8-octanetrion-8-yl)benzenate
mor	morpholine
mpd	N-methyl-2-pyrrolidine
mpi	1,3-bis{2-(4-methylpyridyl)imino}isoindoline
mppc	3,6-bis{(4-methylpiperazino)methyl}-pyrocatecholate
msp	N-methyl-N′-(4-methoxysalicylidene)-1,3-propanediamine
mttt	13,26-dimethyl-3,9,17,23-tetraazatetracyclo [23.3.1.1.^{11,15}]triaconta-1(29),2,9,11,13,15(30),16,23,25,27-decaene-6,20,29,30-tetraol
N(2-amet)pipzH$_3$	N-(2-ammonioethyl)piperazinium
nicNO	nicotinato-N-oxide
nitet	ethyl nitronyl nitroxide
nitppy	2-(4-pyridyl)-4,4,5,5-tetramethylimidazoline-1-
oxy-	3-oxide
nmpH	methylphenethylammonium
nmpzH	N-methylpiperazinium
or	orthrombic
oxpn	N,N′-bis(3-aminopropyl)oxamide
paa	pyridoxic acid
pambo	2-propylamino-2-methyl-3-butanone oximate
pba	1,3-propanediyl-bis(oximato)
phen	phenanthroline
phoac	phenoxyacetate

phtmio	4-phenyl-2,2,5,5-tetramethyl-3-imidazoline-1-oxyl
pibo	3-(phenylimino)butanone-3-oximate
pi	piperidine
pip	2-[2-(2-pyridyl)ethyliminomethyl]pyridine
pmd	N,N,N′,N″,N″-pentamethyldiethylenetriamine
pp	1-(2-pyridinyl)-2-propanonate
ppt	3-(pyridin-2-yl)-5-(pyrazin-2-yl)-1,2,4-triazolate
$\mathrm{Pr^i}$tmio	4-isopropyl-2,2,5,5-tetramethyl-3-imidazoline-1-oxyl
pte	2-(propylthio)ethanole
py	pyridine
pyco	pyridine-2-carbaldehyde oximate
pym	5-methylpyrimidine
pysad	N-2-pyridulsalicylaldimine
pz	pyrazole
qo	4-chloro-1-benzoquinone-2-oximate
qu	quinoline
3-quin	3-quinuclidinone
rh	rombohedral
R,S-Hpa	R,S-2-aminopropan-1-ol
R,S-pa	R,S-2-aminopropan-1-olate
salen	N,N′-ethylenebis(salicylideneiminate)
salpd	N,N′-disalicylidene-1,3-propanediamine
sed	N,N′-[4-methyl-4-azaheptane-1,7-diyl]bis(salicylaldiminate)
sl	1,2-bis(benzimidazol-2-yl)-1-hydroxyethane
tac	1,4,7-triazacyclononane
tcp	2,4,6-trichlorophenolate
tde	thiodiethanole
tepz	thioether-pyrazine
terpy	2,2′:6′,2′-terpyridine
tftbd	4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionate
tg	tetragonal
thf	tetrahydrofurane
tmso	tetramethylsulfone
tmtac	1,4,7-trimethyl-1,4,7-triazacyclononane
tnl	1,4,6,9-tetrakis{2-(2-pyridil)amino}benzodi pyridazine
tpa	tris(2-pyridyl)amine
tr	triclinic
trg	trigonal
tris	tris(hydroxymethyl)methylamine
urid	uridine

1 INTRODUCTION

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 crystallographic studies of transition metal compounds are of copper compounds. Although copper in oxidation state +2 is the most common by far, other known oxidation states observed include +1, +3 and +4, and of these copper(I) is the most common. The structural chemistry of almost one thousand published copper(I) structures has been reviewed recently.[1] The structural chemistry of mixed-valence, Cu(I)–Cu(II) compounds has also been reviewed.[2] We reported on the structural aspects of copper(II), finding over two thousand monomeric copper(II) compounds.[3,4] There are over nine hundred dimeric copper(II) compounds for which structural data were analyzed in our review article.[5]

To date there has not been a comprehensive overview of trimeric and oligomeric copper(II) structural chemistry, and this report is aimed at providing such a survey up to 1992.

This review includes over two hundred and thirty published oligomeric copper(II) structures which have been analyzed and classified in order to assist in understanding the stereochemical interactions in the coordination sphere of copper(II) oligomeric species.

The compounds discussed have been sorted by increasing number of copper(II) atoms; trimeric, tetrameric, pentameric, hexameric, octameric, nonameric and dodecameric.

2 TRIMERIC COPPER(II) COMPOUNDS

Crystallographic and structural data for trimeric copper(II) compounds are gathered in Table I. There are over seventy examples mostly green and blue, but some red/purple and even yellow and black, for which crystallographic data are available. From the structural point of view, these compounds are very complex. Structures of $[Cu_3(\mu\text{-bipyamH})_4X_2]$ ($X = Cl$ or Br)[6] are isomorphores. The $Cu_3N_{12}X_2$ complexes involve nearly linear Cu_3 units, Cu–Cu–Cu 178.4° (mean), terminated by the two halide anions. The four separate bipyamH ligands act as tridentate ligands, involving coordination to the three Cu(II) atoms, with Cu–Cu distances of 2.461(1) and 2.471(1) Å for $X = Br$ and $X = Cl$, respectively. These distances are the shortest found in the series of trimeric copper(II) derivatives. The central Cu atom in both structures involves a four-coordinate, rhombic, coplanar CuN_4 center generated by the central amido nitrogens of the four bipyamH ligands. The two terminal Cu atoms involve a square-based pyramidal CuN_4X structures, generated by the terminal pyridine nitrogens of the four bipyamH ligands and an apical halide anion.

The structure of the blue sample[7] was considered as a cryptate of a cationic cluster $[Cu_3(OH)_2]^{4+}$ held inside the macrocyclic cavity of the ligand. The complex cation, $[Cu_3(OH)_2(C_{18}H_{42}N_6O_3)]^{4+}$, has three-fold symmetry. This cluster is composed of three equivalent Cu(II) atoms, bridged by two triply bound N-hydroxo groups, each Cu(II) atom is coordinated to an ethylenediamine subunit and is held inside the cavity of the macrocycle in a cryptate fashion, with a Cu–Cu distance of 2.808(3) Å. The coordination polyhedron of each copper is a very elongated octahedron with two long range interactions along d_z^2, Cu–O (ethers of macrocycle) = 2.605 Å (mean).

There are nine examples[8–16] with a Cu_3OH core held by peripheral bridging ligands. In five of these examples[8,9,11,14,15] the geometry at each copper(II) atom is a distorted square-based pyramid. In another two,[10,11] one Cu(II) atom is in a square-planar arrangement and the remaining two copper(II) atoms are square-based pyramids. In one,[13] a Cu(II) atom has a trigonal-bipyramidal environment and another two Cu(II) atoms form a tetragonal-bipyramidal. Finally, in the remaining structure[16] two copper(II) atoms are square-pyramidal and the other is *pseudo*-octahedral. The Cu–Cu separation in the series of these nine examples ranges from 3.1935(8) to 3.351(1) Å (mean values). There is interdependence between Cu–Cu distances and Cu–OH–Cu bridge angles, with the angle opening when length increases. For example, 3.1935(8) Å and 105.1(1)°,[8] 3.220(3) Å and 108.2(4)°;[14] 3.246(3) Å and 110.9(3)°;[14] 3.351(1) Å and 114.5(1)°.[16] The Cu–O(H) bond distance long ranges from 1.946 to 2.045 Å with a mean value of 2.00 Å.

There are twenty-one examples[17–34] which contain a linear or almost linear trimeric array of copper atoms doubly bridged. This type of bridging, with a pair of two bridging ligands, is the most common. In twelve derivatives[17–27] four O-bridging ligands, and in the remaining derivatives four chlorine[28–31,33,34] or four bromine atoms[32] held together a linear trimeric array of copper atoms.

In violet-blue[17] three copper atoms are arranged linearly with Cu–Cu separations of 2.902(1) Å, the shortest in this series. The geometry around the two terminal copper atoms was described as a slightly distorted square pyramid with the deviation of copper in the direction of the axial site by 0.08 Å. The central copper atom has a square-planar environment (Table I).

A blue compound[18] is formed of trimeric $[Cu_3(\mu\text{-ap})_4(dmf)]^{2+}$ cations and hexanuclear $[Cu_6I_{10}]^{4-}$ anions. The copper(II) atom in the middle of the trimer has a tetrahedrally distorted coordination. The four alkoxy oxygen atoms with the copper atom form a CuO_4 structure with the mean Cu–O, (bridge) distance of 1.914(7) Å. The two structural copper(II) atoms differ, one has square-planar and the other a square-pyramidal geometry. The Cu–Cu distances in the trinuclear cation are 2.914(1) and 2.945(1) Å. In the hexanuclear anion the Cu(I)–Cu(I) distances vary from 2.537(2) to 2.730(2) Å. The structure of another mixed valence derivative[19] is similar.

The trimer, $Cu_3(\mu\text{-pp})_6$,[20] has a distorted octahedrally-coordinated central Cu(II) atom and distorted square-pyramidal terminal Cu(II) atoms. The molecule $Cu_3(\mu\text{-}C_{12}H_{24}N_2O_4)_2$[21] contains a linear trimeric array of copper atoms in which the central copper has a square-planar environment and the two terminal copper atoms are *pseudo*-octahedral.

In another two derivatives[22,25] all copper(II) atoms are four-coordinate with mean Cu–Cu separations of 2.938(1)[22] and 3.017(1) Å,[25] respectively.

In $[Cu_3(\mu\text{-eha})_2(H_2O)](ClO_4)_2$ and $[Cu_3(\mu\text{-es})_2(H_2O)_2](ClO_4)_2 \cdot H_2O$[23] a pair of Cu(eha) and Cu(es) chelate complexes act as bidentate ligands to the central copper atom, bonding through the oxygen atoms which act as bridges (Table I). Significantly, the Cu–Cu separation and especially Cu–Cu–Cu angle are different, with the values 2.963(5) Å mean and 156.2° in the former and 3.023(2) Å (mean) and 97.3(4)° in the latter.

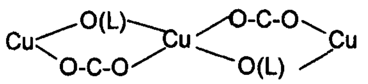
The structure of a dark blue derivative[24] is formed of almost linear alkoxo-bridged copper(II) trimers in which the Cu–Cu–Cu angle is 175.04(2)° and the Cu–Cu distances are 2.9516(5) and 3.0106(5) Å. In a red-brown complex[26] the values are 138(1)° and 3.09(1) Å, while in a green complex[27] the copper(II) atoms exhibit octahedral and square-pyramidal coordination. One octahedron is connected to two pyramids leading to formation of a cluster of stoichiometry Cu_3O_{12} with a Cu–Cu distance of 3.372(1) Å. There is interdependence between the Cu–Cu distances and the Cu–O–Cu bridge angles. When the distance is elongated the angle is opened. For example, 2.902(1) Å and 98.9(3)°;[17] 2.938(1) Å and 100.9(2)°;[22] 3.017(1) Å and 102.4(6)°;[25] and 3.372(1) Å and 104.2(1)°.[27]

When chlorine or bromine serve as bridges[28–34] the Cu–Cu separations vary from 3.331(4) to 3.686 Å and the Cu–X–Cu bridge angles vary from 89.8° to 94.5° (Table I).

Structures of the blue[35] and green[36] derivatives consist of linear trimers of copper(II) atoms which are triply bridged by O donor ligands (Table I). The central and terminal copper atoms are nonequivalent, while the coordination sphere of the central copper atom, CuO_6, has a symmetry close to D_{4h}

in both derivatives.[35,36] The two outer copper atoms which are five-coordinate differ in the blue complex,[35] CuO_4N is square-pyramidal while in the green complex[36] CuO_3N_2 is trigonal-bipyramidal. The Cu–Cu separation is 3.126(1) Å in the former and 3.319(1) Å in the latter.

There are four derivatives[37–40] in which three copper(II) atoms are doubly bridged by two O donor ligands and two carboxylate groups in the manner.



The central and terminal copper atoms are nonequivalent. While in one complex[37] the central copper(II) atom has a square-planar coordination (CuO_4), the terminal copper(II) atoms are square-pyramidal (CuO_5). In another two derivatives,[38,39] the central copper has a tetragonal-bipyramidal configuration (CuO_6) with the terminal copper square-planar (CuO_3N). In another[40] each copper(II) is penta-coordinate (CuO_5), an elongated square-pyramid for the central copper atom and a tetrahedrally-distorted square-pyramid for the terminal copper atoms. The Cu–Cu separations are 3.035,[37] 3.188(1),[38] 3.211(6)[39] and 3.365(1) Å.[40]

The structure of dark green, $Cu_3(\mu\text{-dmap})_2Cl_4$[41] is shown in Figure 1. The oxygen atom O(1) in one of the dmap ligands is bonded to three Cu(II) atoms with the mean Cu–O(1) distance of 2.05(1) Å. The oxygen atom O(2) in the other dmap ligand bridges two copper(II) atoms with a mean Cu–O(2) distance of 1.905(10) Å. The geometry of Cu(1) is a distorted square-pyramid and geometries around the remaining two copper(II) atoms Cu(2) and Cu(3) is square-planar with different degrees of distortion. The separations between these three metal centers span a considerable range: Cu(1)–Cu(2) = 3.378(4) Å, Cu(1)–Cu(3) = 3.027(4) Å and Cu(2)–Cu(3) = 3.200(3) Å.

The three copper(II) atoms in the $[Cu_3(\mu\text{-dapo})_3(\mu\text{-}O_2NO)]^{2+}$ cation[42] form an exact equilateral triangle with one of the bridging oxygens on the three-fold axis. The Cu–Cu separations are 3.321(2), 3.458(3) and 3.657(3) Å with a Cu–Cu–Cu angle of 55.6(1)°. The Cu–O–Cu bridge angles are 117.2(3)°, 125.4(6)° and 139.5(3)°. The coordination spheres of the two copper atoms are square-pyramidal (CuO_3N_2) and that of the remaining copper is square-planar (CuO_2N_2).

The structure of a dark blue derivative[43] is similar to that above,[42] with Cu–Cu separations of 3.420(3), 3.450(3) and 3.694(3) Å and Cu–O–Cu bridge angles of 121.0(5)°, 123.5(5)° and 139.0(5)°.

There are four derivatives[44–46] in which two tetradentate ligands act as two-atom bridges between three copper(II) atoms. In one[44] each copper

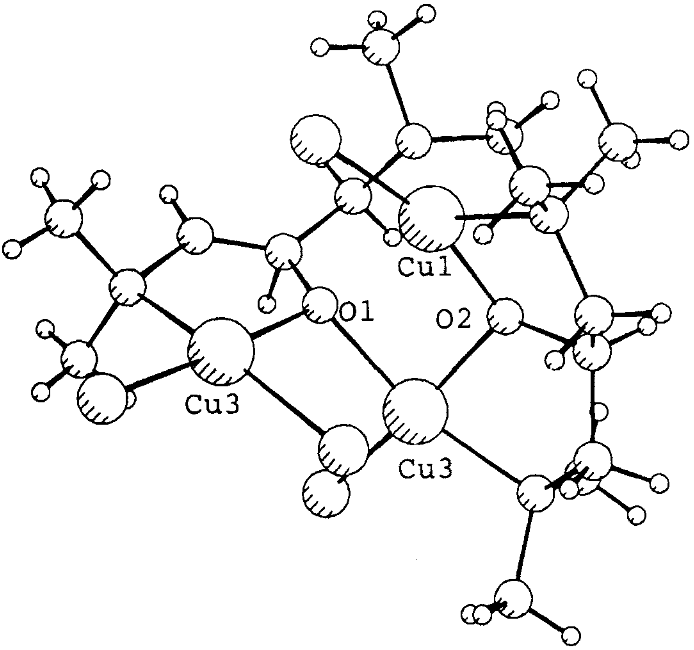


FIGURE 1 Structure of $Cu_3(\mu\text{-dmap})_2Cl_4$.[41]

atom is in a distorted square-pyramidal environment with a Cu–Cu separation of 3.381(4) Å. In another[45] each copper atom is roughly square-planar with a Cu–Cu separation of 3.490(1) Å (mean). In the remaining two species[46] the central coppers are *pseudo*-octahedrally coordinated and the outer two are penta-coordinate (square-pyramidal) with Cu–Cu separations of 3.741(2) and 3.754(2) Å.

The $[Cu_3(\mu\text{-metz})_6(H_2O)_4]^{6+}$ cation[47] consists of linear trimeric clusters positioned on the crystallographic three-fold axis, and the copper(II) atoms are bridged by triple N^1,N^2-coordinating triazole ligands. The terminal copper atoms are in addition coordinated by two water molecules, and thus have a distorted square-pyramidal geometry. The central copper atom is located at a three-fold inversion center and thus should exhibit dynamic Jahn–Teller behavior. The Cu–Cu separation is 3.719(7) Å.

In a green derivative[48] four guanosine-3′-monophosphate ligands act as three-atom bridges (O–P–O) between the three copper atoms. Each copper atom displays a square-pyramidal geometry.

There are six species[49–52] which contain "oxalate" type bridges between three copper(II) atoms. In one[49] the monoclinic unit cell contains a $[CuN_2(C_2)O_2CuO_2(C_2)N_2Cu]$ bridging network, and the copper(II) atoms are square-pyramidal with a Cu–Cu separation of 5.159 Å. Two trimeric units are related through an inversion center to form a bis trimeric entity.

A pale blue derivative[50] consists of tricopper and tetracopper dications packed together in a 1 : 1 ratio and placed around inversion centers. The tricopper cation contains a central CuO_4 and two outer CuN_4 square units. In the $[N_2CuN_2(C_2)O_2CuO_2(C_2)N_2CuN_2]$ unit the Cu–Cu separation is 5.190(1) Å. The tetracopper cation will be discussed in Section 3.

A trimeric cation[51] which consists of the $[CuN_2(C_2)S_2CuS_2(C_2)N_2Cu]$ bridging network contains the central copper atom in a square-planar environment (CuS_4) and the terminal copper atoms in $CuO_2N_2S_2$ structures with tetragonal-bipyramidal geometry. The mean Cu–Cu separation is 5.699(1) Å.

The remaining three species[52] contain a $[CuO_2(C_2)ONCuNO(C_2)O_2Cu]$ bridging network. The central copper(II) atoms in two of the species are square-pyramidal and in the third one the central copper(II) atom is square-planar. The terminal copper(II) atoms in all three species are penta-coordinate with geometries that are intermediate between square-pyramidal and trigonal-bipyramidal (Table I).

There are four derivatives[53–56] in which three copper(II) atoms are singly bridged by μ-oxygen ligands and another three species[57–59] in which a single halogen atom serves as a bridge (chloride,[57,58] or bromide[59]). In the deep blue trimer[53] $[Cu_3(dapo)_2(dapoH)_2]^{4+}$ the cation contains a central four-coordinate copper(II) chelated to the two deprotonated ligands through the oxygen and one nitrogen of each ligand with a *cis* arrangement. Each of the deprotonated ligands is also coordinated to a terminal copper(II) through the oxygen (bridging) and the remaining nitrogen. The square-planar coordination of each terminal copper(II) is completed by two nitrogens of a neutral ligand.

In another deep blue derivative[54] the oxygen atoms of two tridentate 1,3-diamino-2-propanolato ligands act as bridging atoms between the copper(II) atoms; the nitrogen atoms of each of the ligands are coordinated to different copper(II) atoms. The two 1,3-diamino-2-propanol ligands are bidentate to Cu(II) through the nitrogens. Two thiocyanate groups complete the penta-coordination sphere of copper(II) atoms (Table I).

Similar coordination of 1,3-diamino-2-propanol ligands exists in a nitrite trimeric derivative.[55] The bridging oxygen atoms of eddta link the vertices of the coordination polyhedra into a trimeric system.[56] Each copper(II) atom is *pseudo*-octahedrally coordinated, with Cu–Cu separation of 3.840(1) Å and Cu–O–Cu bridge angles of 121.5(2)°.

The structure of a dark green derivative[57] consists of two $Cu(dapdH_2)Cl^+$ cations singly bridged by two chlorides and the $CuCl_4^{2-}$ anion, with

Cu–Cl–Cu bridge angles of 130.84(9)°. A structure of a red complex[58] contains a $Cu_3Cl_{14}^{8-}$ anion, two unequally flattened $CuCl_4^{2-}$ tetrahedra, and $\{N(2amet)pipzH_3\}^{3+}$, cations which are hydrogen bonded to the anions. The structure of $Cu_3Cl_{14}^{8-}$ is a linear array of three Cu atoms singly bridged with two chlorides with Cu–Cl–Cu bridge angles 179.38(2)° and Cu–Cu separation of 5.690(1) Å.

In a dark red derivative[59] iodine atoms serve as bridges between three copper(II) atoms $[(qo)_2Cu–I–Cu(qo)_2–I–Cu(qo)_2]^{2-}$ with Cu–I–Cu bridge angles of 114.3(2)°.

The structure[60] of $[Cu_3(ac)_4(H_2O)(bpy)_3]^{2+}$ is shown in Figure 2. In the trimeric unit the geometry around the copper(II) centers is square-pyramidal CuO_3N_2. The Cu(1), Cu(2) unit is bridged by three acetato ligands displaying different bridging modes. Atom Cu(3) is bonded to a unidentate and a bridging acetato ligand. The Cu(1)–Cu(2), Cu(1)–Cu(3) and Cu(2)–Cu(3) separations are 3.196(1), 6.277(1) and 4.568(1) Å, respectively. In a blue complex[61] the three moieties are held together by a μ_3-carbonate group which lies on a crystallographically required six symmetry axis.

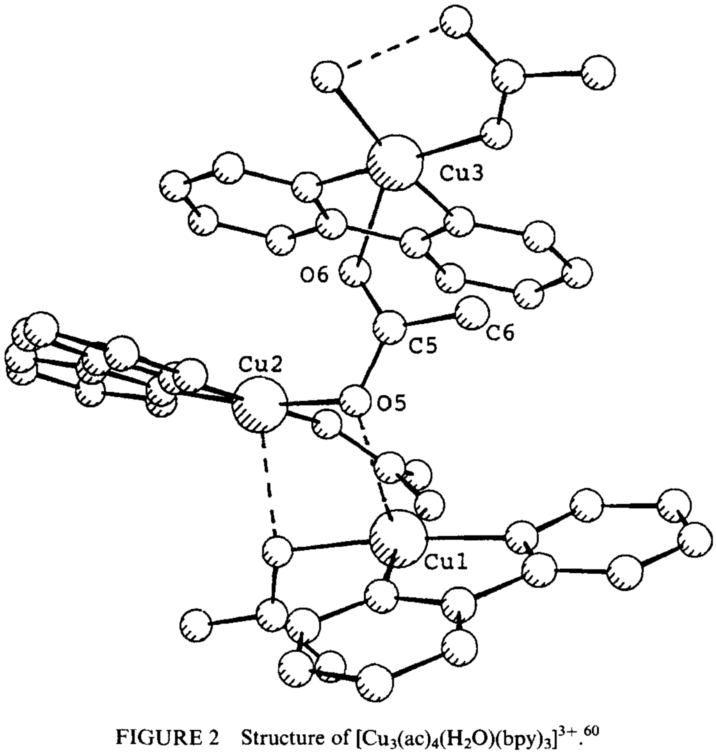


FIGURE 2 Structure of $[Cu_3(ac)_4(H_2O)(bpy)_3]^{3+}$.[60]

Three hexa-coordinate copper(II) atoms with CuO_4N_2 and two with CuO_3N_3 structures are connected only by unique O···H··· hydrogen bonds, with the distances 2.43(2) and 2.37(2) Å.[62]

In another trimeric species[63] each of three Cu(tmtac) moieties is bridged *via* two imidazolate anions to two remaining Cu(tmtac) moieties, yielding three distorted square-pyramidal CuN_5 polyhedra. The three copper(II) atoms are arranged at the corners of an equilateral triangle with a Cu–Cu separation of 5.92 Å.

There are six examples[64–68] of composition $Cu_3(\mu\text{-L})_2(hfac)_6$ where each of the three $Cu(hfac)_2$ moieties is bridged by two bidentate ligands to two remaining $Cu(hfac)_2$ moieties, yielding a *pseudo*-octahedrally coordinated central copper(II) atom and penta-coordinated (square-pyramidal) outer copper(II) atoms (Table I).

The structure of $Cu_3(\mu\text{-tepz})_2Cl_6$[69] is shown in Figure 3. The structure is unique in that it contains a trimeric arrangement of copper(II) centers in which the central Cu(1) bridges two ligands that encompass one copper each. The molecule has a center of symmetry at Cu(1) with the result that the three coppers are linear. The Cu(1)–Cu(2) separation is 7.360(2) Å.

In spite of the fact that trimeric copper(II) compounds are much less common than mono- or dimeric derivatives, they have a rich variety of structural types. As seen above, there are a variety of coordination geometries observed: square-planar, tetrahedral, square-pyramidal, trigonal-bipyramidal and tetragonal-bipyramidal, from which, by far, the most common are square-planar and square-pyramidal. The ligands involved are mono- through hexadentate and even octa- and nonadentate. The most common ligands are O and N donors. The multidentate ligands include both homo- and hetero-donor atoms with O and N-donors by far the most common. Bidentate ligands include those with two O, two N, two S donor atoms, and those with O plus N-donor sites. Tridentate ligands include those with three O, three N, one O plus two N-donor sites. Tetradentate ligands include those with two O plus two N-donor sites. Pentadentate ligands involve those with three O plus two N-donor sites. Hexadentate ligands include those with four O plus two N, and two O plus four N-donor sites. Octadentate ligands include those with six O plus two N, two O plus two N plus four S-donor sites. Nonadentate ligand includes three O plus six N-donor sites.

Metal–ligand distances are generally shorter for terminal groups than equivalent bridging ones, and both increase as the coordination number increases and as the donor atom covalent radius increases.

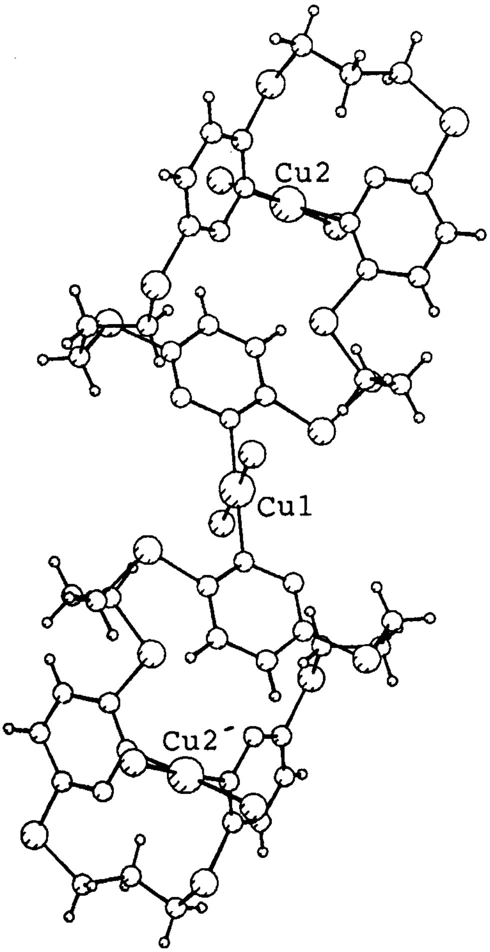


FIGURE 3 Structure of $Cu_3(\mu\text{-tepz})_2Cl_6$.[69]

The mean Cu–L bond distances (Å) as well as the mean intra-metallocyclic ring angles (°) for four-, five- and six-coordinate Cu(II) atoms in trimeric derivatives are summarized in Table IA.

There are examples, which contain with trimers in the same crystal hexameric,[18] polymeric,[19,32] tetrameric[50] or monomeric[56,58] units. Two crystallographically independent molecules, differing by degree of distortion, have been found to be present in one crystal in two cases.[52,55] The coexistence of two or more species, differing only by degree of distortion, is typical of the general class of distortion isomerism.[70]

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

Compound (*colour*)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*	*Cu–L* (Å)	*Cu–Cu* (Å) *Cu–L–Cu* (°)	*L–Cu–L* (°)	*Ref.*
[Cu_3(μ-bipyam)$_4$$Br_2$] · H_2O	or	14.186(3)		CuN_4 (×1)	N[b] 1.967(9,31)	2.468(1)	N,N[b] 89.2(2)	6
(dark purple)	Pnn2	13.040(3)						
	2	11.313(2)						
				CuN_4Br (×2)	N 2.068(8,23)		N,N 88.0(3)	
					Br 2.640(1)		98.3(2,8)	
[Cu_3(μ-bipyam)$_4$$Cl_2$] · H_2O	or	14.092(3)		CuN_4 (×1)	N 1.965(4,12)	2.471(1)	N,N 90.1(1)	6
(purple)	Pnn2	12.895(3)						
	2	11.190(2)						
				CuN_4Cl (×2)	N 2.061(4,11)		N,N 88.5(1)	
					Cl 2.465(1)		N,Cl 98.6(1,1.6)	
[Cu_3(μ_3-OH)$_2$($C_{18}H_{42}N_6O_3$] ·	hx	12.519(5)		CuO_4N_2	μ_3HO 2.019(15,31)	2.808(3)	O,O 73.1(4)	7
(ClO_4)$_4$ · H_2O (blue)	P6_3				O 2.605(13,5)	Not given	N,N 87.3(5)[c]	
	4	29.573(9)			N 1.964(12,14)		O,N 102.0(5,8)	
[Cu_3(μ_3-OH)(μ-ae)$_3$](ClO_4)$_2$	tr	12.448(1)	90.26(1)	CuO_3N_2	μ_3HO 2.012(3,16)	3.1935(8,50)	O,O 84.5(1,11.9)	8
(deep blue)	P-1	12.698(1)	113.36(1)		N 1.963(4,37)	105.1(1,4)	N,N 85.4(2,5)[c]	
	2	11.765(1)	80.66(1)		μaeO 1.910(3,6)		O,N 94.0(1,4)[d]	
					2.400(3,19)		98.3(1,11.1)	
							175.8(1,4.5)	
[Cu_3(μ_3-OH)(μ-at)$_3$](NO_3)$_2$	tr	11.918(2)	98.04(2)	CuO_3N_2	μ_3HO 2.031(5,15)	3.206(1)	O,O 82.9(2,13.6)	9
(emerald green)	P-1	14.478(2)	117.72(2)		μatO 1.916(5,3)	Not given	N,N 97.6(3,4)[d]	
	2	11.501(3)	99.80(1)		2.404(6,68)		O,N 94.6(2,6)[d]	
					N 1.983(7,31)		95.7(2,10.6)	
							168.0(2,11.2)	
[Cu_3(μ_3-OH)(μ-Cl)(μ-pz)$_3$(py)$_2$ ·	or	19.883(3)		CuN_2OCl (×1)	pzN 1.942(4)	3.217(1,105)	N,N 159.6(3)	10
Cl]py (green)	Pnma	15.063(3)			μ_3HO 1.976(4)	μ_3O 107.8(2,5.6)	N,O 90.6(1)	
	4	9.495(2)			Cl 2.257(2)	μCl 70.93(5)	N,Cl 95.0(1)	
							O,Cl 147.5(2)	
				CuN_3OCl (×2)	pzN 1.962(4,6)		N,N 92.3(2,9)	
					pyN 2.028(4,0)		163.7(2)	

					μ_3HO	2.000(3,0)		N,O	88.2(2,1.9)	
					μCl	2.682(2,0)			175.4(2)	
								N,Cl	98.2(1,1)	
								O,Cl	78.1(1)	
$[Cu_3(\mu_3\text{-}OH)(\mu\text{-pyco})_3(\mu_3\text{-}SO_4)]\cdot$	trg	18.05(1)		CuO_3N_2	O	1.987(5)	3.220(3)	O,O	92.3(5,6.7)	11
$16.3H_2O$ (light green)	P-3				N	1.975(2,6)	108.2(4)	N,N	82.7(5)^c	
	2	7.25(1)			O_3SO	2.159(9)		O,N	96.9(5,2.2)	
					μ_3HO	1.987(5)			166.9(5,3.2)	
$[Cu_3(\mu_3\text{-}OH)(\mu\text{-pibo})_3\cdot$	m	15.630(8)		CuO_2N_2 (×1)	O	1.938(5)	Not given	O,O	92.7(2)	12
$(\mu\text{-}O_2ClO_2)](ClO_4)$ (green black)	$P2_1/n$	14.354(3)	93.39(5)		N	1.959(8,5)	μ_3HO 108.8(3,1.7)	N,N	79.7(3)^c	
	4	17.255(4)			μ_3HO	1.946(6)		O,N	93.8(3,4.1)	
									169.1(3)	
				CuO_3N_2 (×2)	O	1.920(6,9)		O,O	95.6(4,14.4)	
					N	1.976(6,23)		N,N	80.2(3,3)^c	
					μ_3HO	1.974(6,5)		O,N	92.3(5,15.0)	
					μ_3O_3ClO	2.490(16,62)			171.7(4,7.2)	
$[Cu_3(\mu_3\text{-}OH)(\mu\text{-bibo})_3(\mu_3\text{-}ClO_4)_2\cdot$	m	15.350(1)		CuO_3N_2 (×1)	O	1.933(6)	3.245(2)	O,O	93.2(2,7.8)	13
$(H_2O)]$ (green black)	$P2_1/c$	12.508(1)	96.81(1)		N	1.965(7,4)	111.1(3,1.3)	N,N	81.0(3)^c	
	4	21.439(2)			μ_3HO	1.963(6)		O,N	92.3(3,5.9)	
					μO_3ClO	2.489(7)			172.2(3,6.9)	
				CuO_4N_2 (×2)	O	1.936(6,3)		O,O	88.7(3,6.7)	
					N	1.970(8,6)		N,N	80.9(3,3)^c	
					μ_3HO	1.970(5,2)		O,N	91.4(3,7.5)	
					μO_3ClO	2.575(8,198)			172.0(3,6.6)	
$[Cu_3(\mu_3\text{-}OH)_{0.5}(\mu\text{-pambo})_3\cdot$	trg	14.44(1)		CuO_3N_2	O	1.94(1)	3.246(3)	O,O	89.4(3,5.7)	14
$(H_2O)_3](ClO_4)_{3/2}\cdot 4H_2O$ (dark green)	R-3				N	1.99(1,4)	110.9(4)	N,N	79.8(3)^c	
	6	35.05(4)			μ_3HO	1.97(1)		O,N	95.0(3,6.8)	
					H_2O	2.69				
$[Cu_3(\mu_3\text{-}OH)(\mu\text{-amo})_3](ClO_4)_2$	tr	11.720(1)	71.78(1)	CuO_3N_2	N	1.983(6,28)	3.283(–,34)	O,O	82.3(2,15.0)	15
(emerald green)	P-1	12.283(2)	81.07(1)		μO	1.917(5,2)	μ_3O 106.7(2,1.6)	N,N	97.6(2,4)^d	
	2	14.252(2)	65.69(1)			2.375(4,39)	μO 60.0(–,1.0)	O,N	94.2(2,6)^d	
					μ_3HO	2.045(5,2)			96.5(2,17.8)	
									168.6(2,3.9)	

TABLE I (*Continued*)

Compound (colour)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	*α* (°) *β* (°) *γ* (°)	*Chromophore*	*Cu–L* (Å)		*Cu–Cu* (Å) *Cu–L–Cu* (°)	*L–Cu–L* (°)		*Ref.*
$[Cu_3(\mu_3\text{-}OH)(pz)_3(pzH)_2(NO_3)_2]\cdot$	m	7.756(2)		CuO_4N_2 (×1)	pzN	1.943(3,17)	3.351(1,27)	O,O	75.0(1,14.9)	16
H_2O (deep blue)	$P2_1$	17.639(3)	91.18(1)		O_2NO	2.042(3)	114.5(1,2.5)	N,N	92.2(1,1.5)	
	2	8.883(1)				2.683(4,187)			171.9(1,8)	
					μ_3HO	1.969(3)		O,N	89.4(1,9.3)	
									173.1(1,2.4)	
				CuN_3O_2 (×2)	pzN	1.946(3,29)		O,O	49.0(1)	
					pzHN	2.007(4,14)		N,N	174.7(1)	
					O_2NO	2.547(4,135)		O,N	88.5(1,3.1)	
					μ_3HO	2.006(3,16)				
$[Cu_3(\mu\text{-}OH)_2(\mu\text{-}C_{18}H_{42}N_4O_2)_2]\cdot$	m	7.759(6)		CuO_4 (×1)	μHO	1.922(7)	2.902(1)	O,O	79.0(3)	17
$(ClO_4)_2$ (violet blue)	$P2_1/c$	13.21(1)	103.95(6)		μO	1.904(7)	98.9(3,3)			
	2	15.00(1)								
				CuO_3N_2 (×2)	N	2.018(9,41)		O,O	79.3(3)	
					O	1.910(7)		N,N	85.2(3)[c]	
					μHO	1.904(7)		O,N	97.4(3,2.4)	
					O_3ClO	2.63(1)				
$[Cu_3(\mu\text{-}ap)_4(dmf)]_2\cdot$	tr	10.294(2)	77.89(2)	CuO_4 (×1)	O	1.914(7,7)	2.930(1,16)	O,O	79.2(3,1)	18
$[Cu^I_6(\mu\text{-}I)_8(I)_2]$ (blue)	P-1	11.342(2)	76.60(2)				99.3(3,1.2)		104.9(3,3.8)	
	1	15.612(3)	82.22(2)						157.7(3,4.1)	
				CuO_2N_2 (×1)	μO	1.921(6,9)		O,O	78.3(3)	
					N	2.005(8,6)		N,N	92.1(3)	
								O,N	94.9(3,1.2)[d]	
									168.2(3,6.1)	
				CuO_3N_2 (×1)	μO	1.925(7,8)		O,O	78.6(3)	
					N	2.002(8,2)			92.3(3,3.0)	
					dmfO	2.601(7)		N,N	90.6(3)	
								O,N	95.7(3,20)[d]	
									91.1(3,3.7)	
									170.8(3,2.4)	
				$CuI_{3/4}$	see Table VI					

$[Cu_3(\mu\text{-ap})_4][Cu^I_3I_5]$ (dark green)	m C2/c 8	14.350(4) 16.046(2) 13.183(3)	101.30(2)	CuO_4 (×1)	μO 1.903(7,4)	Not given 99.3(3,0)	O,O 79.3(3) 103.1(4) 157.7(4)	19
				CuO_4N_2 (×2)	μO 1.930(7,3) N 1.995(10,5)		O,O 77.9(3) N,N 94.2(4) O,N 94.0(4,1.3)^d 169.5(5,3.5)	
$Cu_3(\mu\text{-pp})_6$ (not given)	tr P-1 3	10.667(4) 10.553(4) 9.964(4)	105.2(2) 97.8(2) 87.9(2)	CuO_4N_2 (×1)	N 2.038(5) μO 1.916(4) 2.826(5)	Not given	O,O 79.4(2) 100.6(2) O,N 94.5(2,6.1) 177.1(2)	20
				CuO_3N_2 (×2)	N 2.043(5,4) O 1.894(4) μO 1.912(4) 2.649(5)		O,O 87.3(2,3.0) N,N 91.3(2) O,N 93.4(2,3.2) 173.5(2,3.6)	
$[Cu_3(\mu\text{-}C_{12}H_{24}N_2O_4)_2](PF_6)_2$ (green)	m $P2_1/c$ 2	7.112(2) 18.507(5) 14.106(4)	101.44(3)	CuO_4 (×1)	μO 1.910(5,8)	Not given	O,O 77.6(2)	21
				CuO_4N_2 (×2)	O 2.563(5,119) N 2.094(5,8) μO 1.911(5,7)		O,O 77.6(2) 118.8(2) N,N 116.8(2)	
$[Cu_3(\mu\text{-amat})_2](ClO_4)_2$ (kakki) (at 138(1)K)	m $P2_1/c$ 4	15.945(4) 17.860(5) 14.191(5)	104.84(2)	CuO_4 (×1)	μO 1.912(4,4)	2.938(1,3) 109.9(2,7)	O,O 79.1(2) 110.0(2) 150.9(2)	22
				CuO_2N_2 (×2)	N 1.980(4,7) μO 1.898(4,7)		O,O 79.5(2,2) N,N 87.5(2,3)^c O,N 97.4(2,7)^d 169.1(2,2.2)	

TABLE I (*Continued*)

Compound (colour)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*	*Cu–L* (Å)	*Cu–Cu* (Å) *Cu–L–Cu* (°)	*L–Cu–L* (°)	*Ref.*
$[Cu_3(\mu\text{-eha})_2(H_2O)](ClO_4)_2$	or	26.884(4)		CuO_5 (×1)	μO 1.98(1,8)	2.963(5,13)	O,O 76.7(6,1)	23
(not given)	Pbca	19.093(4)			H_2O 2.18(2)	100.1(7,2.5)	96.6(7,8.2)	
	8	15.740(2)					120.0(7,6.2)	
							178.0(6)	
				CuO_2N_2 (×2)	μO 1.89(11)		O,O 81.5(2,1.3)	
					N 1.91(22)		N,N 89.7(8,2)[c]	
							O,N 94.3(7,1.6)[d]	
							173.7(7,4.5)	
$Cu_3(\mu\text{-ap})_4(\mu\text{-}O_2NO)(NO_3)$	m	20.828(8)		CuO_5 (×1)	μO 1.936(3,26)	2.981(1,29)	O,O 78.5(1,1.3)	24
(dark blue)	C2/c	13.064(2)	119.87(2)		μO_2NO 2.480(4)	100.8(2,3.1)	98.2(1,19.0)	
	8	19.337(8)					160.2(1,9.4)	
				CuO_3N_2 (×1)	μO 1.926(3,11)		O,O 77.5(1)	
					O_2NO 2.538(3)		95.7(1,6.7)	
							N,N 91.7(2)	
							O,N 95.6(1,3)[d]	
							170.3(2,2.4)	
				CuO_4N_2 (×1)	μO 1.939(3,13)		O,O 79.7(1)	
					μO_2NO 2.703(4)		87.9(1,1.4)	
					O_2NO 2.691(4)		N,N 89.3(1)	
					N 1.998(4,3)		O,N 95.5(1,4)[d]	
							91.9(1,3.7)	
							174.5(1,2)	
$Cu_3(\mu\text{-}C_{11}H_{19}N_2O_2)_2$	tr	7.564(2)	111.83(10)	CuO_4 (×1)	μO 1.92(2,1)	3.017(1)	Not given	25
(green)	P-1	9.547(8)	96.32(8)			102.4(6,3)		
	1	9.575(8)	100.25(9)					
				CuO_2N_2 (×2)	μO 1.96(2,0)		Not given	
					N 1.93(2,1)			

$[Cu_3(\mu\text{-es})_2(H_2O)_2](ClO_4)_2 \cdot H_2O$	m	15.488(2)		CuO_6 (×1)	μO	2.037(6,14)	3.023(2,30)	O,O	72.0(2,1)	23
(not given)	$P2_1/n$	21.883(4)	94.28(1)			2.326(6,2)	95.2(2,5.6)		93.7(2,8.0)	
	4	10.884(1)			H_2O	1.975(6,25)			169.3(2,1.4)	
				CuO_2N_2 (×2)	μO	1.910(5,15)		O,O	84.8(2,5)	
					N	1.909(7,15)		N,N	85.6(3,2)^c	
								O,N	94.8(3,8)^d	
									176.6(3,4.2)	
$[Cu_3(\mu\text{-}C_{20}H_{24}N_2O)_2(H_2O)] \cdot$	tg	16.12(1)		CuO_5 (×1)	μO	1.84(2)	3.09(1)	O,O	74(1)	26
$(ClO_4)_2 \cdot 2H_2O$ (red brown)	$P4_2bc$					2.08(2)	105(1,1)		107(1,18)	
	4	18.48(1)			H_2O	2.52(1)			178(2)	
				CuO_3N_2 (×2)	μO	1.94(3,2)		O,O	76(1)	
					O	2.29(3)			107(1,3)	
					N	2.04(4,7)		N,N	88(1)^d	
								O,N	80(1,1)^c	
									97(1)^d	
									172(1,1)	
$[Cu_3\{\mu\text{-}CH_2(PO_3)CH_2COO\}_2 \cdot$	m	5.022(5)		CuO_6 (×1)	O	1.915(2)	3.372(1)	O,O	67.2(1)	27
$(H_2O)_2] \cdot 6H_2O$ (green)	$P2_1/c$	12.340(5)	109.7(1)		μO	1.995(3)	104.2(1)		90.0(1,5.6)	
	2	16.390(8)				2.948(3)			112.8(2)	
				CuO_5 (×2)	O	1.927(3,7)		O,O	85.5(2,1.0)	
					μO	2.010(2)			94.6(2,10.6)	
						2.219(3)				
					H_2O	1.997(3)				
$[Cu_3(\mu\text{-}Cl)_4(H_2O)_2Cl_4](tmso)_2$	m	23.978(10)		$CuCl_4$ (×1)	μCl	2.278(4,18)	3.331(4)	Cl,Cl	90.0(2,3.1)	28
(golden yellow)	C2/c	10.142(5)	127.00(2)				93.3(2,5)			
	4	18.956(10)								
				$CuCl_3O$ (×2)	Cl	2.239(4)		Cl,Cl	89.6(2,3.1)	
					μCl	2.295(4,4)		Cl,O	90.3(3,9)	
					O	1.973(9)				

TABLE I (*Continued*)

Compound (colour)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*	*Cu–L* (Å)	*Cu–Cu* (Å) *Cu–L–Cu* (°)	*L–Cu–L* (°)	*Ref.*
$[Cu_3(\mu\text{-}Cl)_4Cl_3(EtOH)](nmpH)$	m	11.843(4)		$CuCl_4$ (×1)	μCl 2.273(3,19)	3.366	Cl,Cl 90.0(1,4.6)	29
(red)	$P2_1/n$	7.626(3)	79.61(3)			94.0(1,1.2)	177.8(1,5)	
	4	23.840(12)						
				$CuCl_4$ (×1)	μCl 2.349(3,30)		Cl,Cl 90.0(1,6.1)	
					Cl 2.274(3,19)		170.0(1,4.1)	
				$CuCl_3O$ (×1)	μCl 2.309(3,21)		Cl,Cl 87.9(3,2.7)	
					Cl 2.246(3)		171.6(1)	
					EtHO 1.968(8)		Cl,O 91.4(2,2.5)	
							169.1(3)	
$Cu_3(\mu\text{-}Cl)_4Cl_2(dmf)_2$	m	19.190(6)		$CuCl_4$ (×1)	μCl 2.275(2,8)	3.370	Cl,Cl 90.0(2,3.5)	30
(not given)	$P2_1/n$	6.084(4)				94.5(2,2)		
	2	6.975(4)	98.87(5)					
				$CuCl_3O$ (×2)	μCl 2.317(2,2)		Cl,Cl 87.5(2,2.9)	
					Cl 2.248(2)		Cl,O 92.3(2,4.6)	
					O 1.950(6)			
$[Cu_3(\mu\text{-}ade)_2(\mu\text{-}Cl)_4Cl_4]\cdot$	m	11.134(4)		$CuCl_4N_2$ (×1)	N 2.027(5)	3.377(3,103)	Cl,Cl 91.7(1)	31
$4H_2O$ (green)	$P2_1/c$	12.726(2)	119.49(3)		μCl 2.313(3)	Not given	Cl,N 88.8(2,1.5)	
	2	10.404(3)			2.768(3)			
				$CuCl_4N$ (×2)	N 2.028(7)		Cl,Cl 94.0(1,8.1)	
					Cl 2.282(3,10)		165.4(1)	
					μCl 2.324(3)		Cl,N 87.4(2,2.7)	
					2.743(3)		177.0(2)	
$[Cu_3(\mu\text{-}Cl)_4Cl_4](3\text{-}mapH)$	m	26.05(1)		$CuCl_4$ (×1)	μCl 2.261(6,37)	3.382	Cl,Cl 90.0(2,5.4)	29
(orange brown)	C2/c	13.687(4)	117.95(3)		2.411(5)	93.6(2,2.5)	171.2(2,4.2)	
	4	7.099(3)						
				$CuCl_4$ (×2)	μCl 2.326(5)		Cl,Cl 90.0(3,4.2)	
					Cl 2.251(6)		177.4(2,0)	

$[Cu_3(\mu\text{-}Cl)_4Cl_4](nmpzH)$	m	6.840(3)		$CuCl_4$ (×1)	μCl	2.245(3,10)	3.456	Cl,Cl	90.0(1,3.6)	29
(orange)	$P2_1/n$	14.321(9)	102.90(5)				94.2(1,8)		178.2(1,2)	
	4	9.890(5)								
				$CuCl_4$ (×2)	μCl	2.322(3,11)		Cl,Cl	90.0(1,6.3)	
					Cl	2.223(3,13)			168.2(1,5.1)	
$(Et_2NH_2)_2[Cu_3(\mu\text{-}Br)_4Br_4]\cdot$	m	25.043(8)		$CuBr_4$ (×1)	μBr	2.407(6,13)	3.582(6,13)	Br,Br	90.0(2,4.1)	32
$[CuBr_2]\cdot EtOH$ (deep purple)	C2/m	6.4691(14)	102.84(2)				94.4(2,1.3)		179.8(1,1)	
	4	19.009(5)								
				$CuBr_4$ (×2)	μBr	2.476(6,25)		Br,Br	90.0(2,5.7)	
					Br	2.380(6,15)			175.8(2,1.1)	
				$CuBr_4$ (polymer)	μBr	2.410(5,17)	3.235(10,21)	Br,Br	95.5(2,2)	
							84.3(2,1)		116.8(2,3.2)	
$Cu_3(\mu\text{-}Cl)_4Cl(Et_2na)_6$	m	16.618(1)		$CuCl_4N_2$ (×1)	μCl	2.302	3.686	Cl,Cl	87.8	33
(pale blue)	$P2_1/c$	8.253(2)	117.3(4)			2.982	89.8(–,2.4)	Cl,N	89.7(–,1.1)	
	2	28.194(1)			N	2.021				
				$CuCl_3N_2$ (×2)	Cl	2.264(2)		Cl,Cl	95.2(1,2.7)	
					μCl	2.304(1)		N,N	174.0(2)	
						2.790(1)		Cl,N	90.8(2,3.9)	
					N	2.016(4,12)				
$(Me_3pzH)[Cu_3(\mu\text{-}Cl)_4Cl_4]$	m	7.227(1)		$CuCl_4$ (×1)	μCl	2.269(1,6)	Not given	Cl,Cl	90.0(1,4.0)	34
(red orange)	$P2_1/n$	19.356(3)	98.29(1)				94.4(1,3)		177.2(1,6)	
	4	13.421(2)								
				$CuCl_4$ (×2)	Cl	2.240(1,30)		Cl,Cl	90.0(1,6.8)	
					μCl	2.356(1,21)			167.9(1,8.0)	
$(4\text{-}MepyH)_2[Cu_3(\mu\text{-}Cl)_4Cl_4]$	m	24.578(5)		$CuCl_4$ (×1)	μCl	2.063(1)	Not given	Cl,Cl	90.0(1,5.4)	34
(red orange)	C2/c	12.278(2)	95.01(1)			2.272(1,14)	94.1(1,6)		179.0(1)	
	4	7.106(1)								
				$CuCl_4$ (×2)	Cl	2.248(1,17)		Cl,Cl	90.0(1,5.8)	
					μCl	2.339(1,12)			171.2(1,4.4)	

TABLE I (*Continued*)

Compound (colour)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*	*Cu–L* (Å)	*Cu–Cu* (Å) *Cu–L–Cu* (°)	*L–Cu–L* (°)	*Ref.*
$(4\text{-MepyH})_2[Cu_3(\mu\text{-Br})_4Br_4]^e$	m	28.207(5)		$CuBr_4$ (×1)	μBr 2.415(3,8)	Not given	Br,Br 90.0(1,3.0)	34
(red orange)	C2/c	12.779(2)	116.71(1)			93.3(1,1)	179.5(1)	
	8	14.735(2)						
				$CuBr_4$ (×2)	Br 2.348(3,13)		Br,Br 90.0(1,4.7)	
					μBr 2.464(3,5)		170.7(1,5.1)	
				$CuBr_4$ (×1)	μBr 2.402(3,21)	Not given	Br,Br 90.0(1,2.3)	
						93.8(1,1)		
				$CuBr_4$ (×2)	Br 2.383(3,5)		Br,Br 90.0(1,5.6)	
					μBr 2.483(3,19)		171.8(1,7)	
$[Cu_3(\mu\text{-Br})_4Br_4(5B6map)$	m	13.216(3)		$CuBr_4$ (×1)	μBr 2.391(5,3)	Not given	Br,Br 90.0(1,3.1)	29
(dark purple)	$P2_1/n$	4.076(1)	91.65(2)		2.464(5,16)	94.3(1,9)	180	
	2	24.614(6)						
				$CuBr_4$ (×2)	μBr 2.389(3)		Br,Br 90.0(2,5.5)	
					Br 2.425(3)		174.0(2,1.1)	
$Cu_3(\mu\text{-deae})_2(\mu\text{-Fac})_2(Fac)_2\cdot$	tr	7.963(6)	76.16(5)	CuO_6 (×1)	μdetO 1.946(3)	3.126(1)	O,O 89.2(2,3.0)	35
$(EtOH)_2$ (blue)	P-1	8.443(7)	81.82(5)		2.525(5)			
	1	13.553(6)	87.62(6)		FacO 1.954(4)			
				CuO_4N (×2)	μO 1.903(4)		O,O 89.9(2,5)	
					N 2.030(4)		178.7(2)	
					EtHO 2.623(5)		O,N 86.9(1)^c	
					FacO 1.946(5,21)		93.7(2)	
							161.1(1)	
$Cu_3(\mu\text{-ac})_4(msp)_2$	tr	10.865(3)	88.03(2)	CuO_6 (×1)	acO 1.943(6)	3.319(1)	O,O 74.2(2)	36
(green)	P-1	10.852(3)	95.86(2)		μO 2.533(7)	96.8(2,1.5)	91.8(2,2.5)	
	1	7.768(3)	97.49(2)		2.000(5)			
				CuO_3N_2 (×2)	acO 2.076(6)		O,O 79.3(2)	

					mspN	2.014(8,7)			90.7(2,2)	
					μO	1.923(5)		N,N	97.1(3)[d]	
						2.377(7)		O,N	93.7(2)[d]	
									84.0–162.6(2)	
$Cu_3(\mu\text{-}OH)_2(\mu\text{-}nicNO)_4(H_2O)_2$	tr	7.881(9)	97.32(9)	CuO_4 (×1)	O	1.954(1)	3.055	O,O	90.0(1,2.7)	37
(dark bluish green)	P-1	9.658(11)	110.38(9)		μHO	1.912(2)	Not given			
	1	10.368(12)	109.53(9)							
				CuO_5 (×2)	O	1.961(2,18)		O,O	84.7(1,2)	
						2.426(2)			95.1(1,8.5)	
					H_2O	1.925(1)			167.5(1,8.8)	
					μHO	1.876(1)				
$Cu_3(\mu\text{-}deae)_2(\mu\text{-}bz)_2(bz)_2\cdot$	tr	14.793(3)	73.84(1)	CuO_6 (×1)	O	1.982(3)	3.188(1)	O,O	90.6(1,2.5)	38
$(MeOH)_2$ (blue)	P-1	10.533(3)	84.40(1)		μO	1.944(3)	112.2(1)			
	1	8.127(2)	69.15(1)		MeHO	2.478(4)				
				CuO_3N (×2)	O	1.930(3,11)		O,O	90.5(1,1.9)	
					μO	1.897(3)			176.6(2)	
					N	2.028(4)		O,N	85.2(1)[c]	
									94.7(2)	
									165.9(2)	
$Cu_3(\mu\text{-}dbae)_2(\mu\text{-}bz)_2(bz)_2\cdot$	m	8.210(9)		CuO_6 (×1)	μO	1.96(2,0)	3.211(6)	O,O	90.6(7,1.6)	39
$(EtOH)_2$ (blue)	$P2_1/c$	29.77(5)	113.90(5)		μbzO	1.98(1,0)	111(1)			
	2	12.71(1)			EtHO	2.52(2)				
				CuO_3N (×2)	μO	1.93(1)		O,O	91.1(6,8)	
					N	2.04(2)			176.5(7)	
					μbzO	1.97(1)		O,N	84.8(7)[c]	
					bzO	1.93(2)			94.0(7)	
									159.8(9)	
$[Cu_3(\mu\text{-}OH)_2(\mu\text{-}inicNO)_2\cdot$	m	12.051(4)		CuO_5 (×1)	O	1.979(3)	3.365(1)	O,O	90.0(1,4.5)	40
$(inicNO)_2(H_2O)_5]\cdot 2H_2O$	$P2_1/c$	7.043(2)	98.51(2)		μHO	1.895(2)	Not given		167.3(1,3.7)	
(bright green)	2	19.825(6)			H_2O	2.260(4)				
				CuO_5 (×2)	O	1.966(2,12)		O,O	92.0(1,12.4)	
					μHO	1.909(3)			164.8(1,3.8)	

TABLE I (*Continued*)

Compound (*colour*)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	*α* (°) *β* (°) *γ* (°)	*Chromophore*	*Cu–L* (Å)	*Cu–Cu* (Å) *Cu–L–Cu* (°)	*L–Cu–L* (°)	*Ref.*
					H_2O 1.978(3)			
					2.247(3)			
$Cu_3(\mu$-dapo$)_2Cl_4$	m	16.45(2)		CuN_2O_2Cl (×1)	μ_3O 2.20(1)	3.289(4,89)	O,O 77.5(5)	41
(dark green)	$P2_1/a$	10.445(7)	101.52(8)		μO 1.90(1)	105.3(5)	N,N 128.3(7)	
	4	16.47(1)			N 2.15(2,13)		O,N 80.8(6,2.7)^c	
					Cl 2.214(6)		91.5(6)	
							138.2(6,9.8)	
				$CuCl_2ON$ (×1)	μ_3O 1.93(1)		Cl,Cl 95.4(2)	
					N 2.08(2)		O,N 84.4(5)^c	
					Cl 2.237(5,40)		Cl,O 86.3(3)	
							176.6(4)	
							Cl,N 94.6(5)	
							163.0(5)	
				CuO_2NCl (×1)	μ_3O 2.02(1)		O,O 82.1(5)	
					μO 1.91(1)		O,N 80.5(6)^c	
					N 2.01(1)		161.3(6)	
					Cl 2.211(6)		O,Cl 97.7(4)	
							158.4(4)	
							N,Cl 94.6(5)	
$[Cu_3(\mu$-dapo$)_3(\mu$-$O_2NO)] (NO_3)_2$	m	13.131(6)		CuO_2N_2 (×1)	μO 1.940(10,12)	3.479(3,178)	O,O 98.7(4)	42
(blue)	$P2_1/n$	15.204(5)	125.66(2)		N 1.981(8,5)	127.4(3,12.1)	N,N 91.5(5)	
	4	13.313(6)					O,N 84.8(5,1)^c	
				CuO_3N_2 (×2)	μO 1.950(8,21)		O,O 93.4(4,1.3)	
					N 2.003(10,27)		N,N 94.6(5,1.2)	
					O_2NO 2.507(10,35)		O,N 85.4(4,7)^c	
$[Cu_3(\mu$-dapo$)_3($dapoH$)_{0.5}\cdot$	m	18.435(16)		CuO_2N_2 (×1)	μO 1.959(10,6)	3.521(3,173)	O,O 97.4(4)	43
$(SO_4)(H_2O)]SO_4\cdot 5H_2O$ (dark blue)	$P2_1/n$	15.072(14)	97.03(9)		N 2.017(12,4)	127.7(5,11.3)	N,N 90.5(5)	
	4	10.611(14)					O,N 85.8(4,5)^c	
							174.4(5,1.8)	

				CuO_3N_2 (×1)	μO	1.962(10,1)		O,O	96.5(4,5.7)	
					N	2.033(14,6)		N,N	94.6(5)	
					H_2O	2.347(12)		O,N	86.0(5,3)^c	
									93.2(5,1.8)	
									167.6(5,2.8)	
				CuO_3N_2 (×1)	μO	1.974(9,18)		O,O	97.5(4,3.3)	
					N	2.007(13,19)		N,N	91.8(5)	
					O_3SO	2.496(13)		O,N	84.7(5,2.2)^c	
									89.8(4)	
									175.0(5,1.2)	
$[Cu_3(\mu\text{-dmg})_2(tmtac)_2Br]ClO_4 \cdot$ MeOH (black)	or	14.006(7)		CuN_4Br (×1)	N	1.960(12,6)	3.381(4)	N,N	80.6(7,5)^c	44
	Pnam	15.972(8)			Br	2.571(4)			94.5(5,0)	
	4	19.27(1)							156.2(5,0)	
								N,Br	101.9(4,1.7)	
				CuN_3O_2 (×2)	N	2.068(18,14)		N,N	84.0(8,2.5)^c	
						2.252(13)		O,O	93.8(4)	
					O	1.909(10,2)		N,O	95.5(6,8.4)	
									172.8(6,1.2)	
$Cu_3(\mu\text{-dmcpz})_4(dmcpz)_2$ (not given)	m	17.286(3)		CuN_4 (×1)	N	2.009(3,6)	3.490(1,10)	N,N	90.0(1,9.6)	45
	$P2_1/c$	20.649(4)	114.51(1)						165.9(1,5)	
	4	16.498(2)								
				CuN_3O (×2)	N	1.960(3,30)		N,N	95.1(1,6.7)	
					O	2.093(3,9)			169.1(1,1.1)	
								N,O	80.0(1,2)^c	
									90.4(1,4)	
									173.2(1,1.3)	
$[Cu_3(\mu\text{-dpg})_2(bpy)_2(MeOH)_2] \cdot$ $(NO_3)_2$ (black purple)	tr	12.114(7)	82.31(4)	CuN_4O_2 (×1)	N	1.998(3,1)	3.741(2)	N,N	80.9(1)^c	46
	P-1	12.757(8)	100.54(3)		O_2NO	2.565(4)			99.1(1)	
	1	9.817(2)	119.09(5)							
				CuO_3N_2 (×2)	O	1.909(3,0)		O,O	97.4(1,5.5)	
					MeHO	2.296(3)		N,N	79.5(1)^c	
					bpyN	2.034(3,6)		O,N	87.8(1,5)	
									163.9(1,1.4)	

TABLE I (*Continued*)

Compound (*colour*)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	*α* (°) *β* (°) *γ* (°)	*Chromophore*	*Cu–L* (Å)	*Cu–Cu* (Å) *Cu–L–Cu* (°)	*L–Cu–L* (°)	*Ref.*
[$Cu_3(\mu\text{-metz})_6(H_2O)_4](F_3CSO_3)_6 \cdot$	hx	14.075(3)		CuN_6 (×1)	N 2.14(5)	3.719(7)	N,N 90.0(1.6,1.0)	47
$4H_2O$ (not given)	R-3							
	3	34.655(8)						
				CuN_3O_2 (×2)	N 2.14(5)		N,N 93.3(1.6)	
					H_2O 1.99(4)		O,O 80.6(1.6)	
							N,O 92.7(1.4,5)	
[$Cu_3(3'\text{-gmp})_2(3'\text{-gmpH})_2(H_2O)_5] \cdot$	m	29.140(7)		CuO_5 (×1)	O 1.925(5)	Not given	Not given	48
$7H_2O$ (green)	C2	6.865(5)	90.31(3)		2.01(2)			
	2	16.980(7)			2.55(2)			
					H_2O 1.87(1)			
					2.55(2)			
				CuO_4N (×2)	O 1.95(–,3)		Not given	
					H_2O 1.982(7)			
					2.26			
					N 1.998(6)			
[$Cu_3(\mu\text{-oxpn})_2(ClO_4)_2]_2$	m	12.257(2)		CuO_5 (×1)	O 1.936(4,16)	5.159	O,O 85.7(2,2)^c	49
(not given)	$P2_1/c$	14.697(5)	104.62(2)		2.518(5)	92.3(2)	92.3(2,5.3)	
	4	15.872(6)					174.6(2,4)	
				CuN_4O (×2)	N 1.984(5,25)		N,N 83.7(2,0)^c	
					O_3ClO 2.646(8,18)		93.2(2,5)	
							90.9(2,1)	
							171.0(2,4.9)	
							N,O 91.4(2,8.6)	
[$Cu_3(C_{12}H_{24}N_4O_2)_2] \cdot$	tr	12.426(1)	102.35(1)	CuO_4 (×1)	O 1.925(4,14)	5.190(1)	O,O 86.4(1)^c	50
[$Cu_4(C_{12}H_{24}N_4O_2)_3$]	P-1	13.405(1)	105.34(1)					
$(NO_3)_4 \cdot 2H_2O$ (pale blue)	1	15.605(2)	113.74(1)					
				CuN_4 (×2)	N 1.985(5,16)		N,N 82.5(1)^c	
							93.2(2,1.8)	
							165.1(2,8.0)	
				CuN_4	see Table III			
				CuO_3N_2	(tetramer)			

$[Cu_3(\mu\text{-}C_{12}H_{22}N_2O_2S_4)_2](ClO_4)_2$	or	15.638(6)		CuS_4 (× 1)	S	2.261(3,6)	5.699(1,16)	S,S	90.9(1,2)^c	51
(green)	Pbca	18.254(9)							89.2(1,9)	
	8	29.437(7)							178.2(2,6)	
				$CuO_2N_2S_2$ (× 2)	N	1.98(1,1)		O,O	158.1(6,1)	
					O	2.39(1,3)		N,N	81.2(4,1)^c	
					S	2.361(5,35)		S,S	86.2(2,8)	
$\{[(bapa)Cu]_2[\mu\text{-}Cu(Me_2pba)]\}\cdot$	or	40.492(4)		CuO_2N_2 (× 1)	O	1.982(7,12)	Not given	O,O	96.2(3)	52
$(ClO_4)_2$ (dark blue)	Pcba	16.363(3)			N	1.931(11,32)		N,N	91.0(4)^d	
	8	10.944(3)						O,N	86.4(4,1.5)^c	
									176.5(3,1.7)	
				CuN_3O_2 (× 2)	N	2.028(8,37)		N,N	93.1(4,3.7)^d	
					O	2.019(6,38)			156.3(3,6.4)	
						2.298(7,12)		O,O	79.9(3,1)^c	
								N,O	94.9(3,17.1)	
									174.0(3,2.6)	
$\{[(pmd)Cu]_2[\mu\text{-}Cu(Me_2pba)]\cdot$	tr	19.610(4)	115.75(3)	CuO_3N_2 (× 1)	O	1.986(9,5)	Not given	O,O	96.9(4)	52
$(ClO_4)\}ClO_4\cdot 3H_2O^e$ (dark blue)	P-1	16.626(4)	89.97(3)		N	1.939(11,1)		N,N	94.4(5)	
	4	16.007(3)	100.86(4)		O_3ClO	2.448(12)		O,N	84.1(4,2)^c	
									173.8(3,1)	
				CuN_3O_2 (× 2)	N	2.040(13,38)		N,N	87.3(5,7)^c	
					O	1.951(10,20)			149.7(6,2.6)	
						2.273(11,23)		O,O	79.8(4,4)^c	
								N,O	99.6(5,12.3)	
									176.3(6,8)	
				CuO_3N_2 (× 1)	O	1.973(11,1)	Not given	O,O	96.5(4)	
					N	1.927(19,3)		N,N	94.5(5)	
					O_3ClO	2.673(7)		O,N	84.6(4,4)^c	
									178.4(4,1)	
				CuN_3O_2 (× 2)	N	2.033(13,19)		N,N	86.7(5,1.6)^c	
					O	1.942(10,6)			149.1(6,3.0)	
						2.231(11,5)		O,O	81.1(4,2)^c	
								N,O	99.6(5,8.0)	
									176.6(5,1.5)	

TABLE I (*Continued*)

Compound (*colour*)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*	*Cu–L* (Å)	*Cu–Cu* (Å) *Cu–L–Cu* (°)	*L–Cu–L* (°)	*Ref.*
{[(ettmd)Cu]$_2$[μ-Cu(pba)] ·	m	18.463(4)		CuO$_3$N$_2$ (×1)	O 1.965(10,5)	Not given	O,O 89.4(8,10.8)	52
(ClO$_4$)$_2$} (dark blue)	P2$_1$/c	14.402(3)	109.00(3)		N 1.91(1,0)		N,N 94.9(6)	
	4	16.537(4)			O$_3$ClO 2.52(3)		O,N 85.4(5,1.4)^c	
							96.7(11,13.4)	
							175.0(6,3.7)	
				CuN$_3$O$_2$ (×2)	N 2.06(2,5)		N,N 86.9(7,1.2)^c	
					O 1.97(1,1)		148.5(7,8.9)	
					2.215(10,25)		O,O 79.9(5,1)^c	
							N,O 100.1(7,10.6)	
							175.7(7,3.1)	
[Cu$_3$(μ-dapo)$_2$(dapoH)$_2$]I$_4$ ·	m	12.255(4)		CuN$_2$O$_2$ (×1)	N Not given	Not given	Not given	53
MeOH (deep blue)	P2$_1$/c	12.999(5)	97.45(2)		μO 1.98(1,2)	116.3(6,1.9)		
	4	19.873(5)						
				CuN$_3$O (×2)	N Not given		Not given	
					μO 2.01(1,1)			
3(μ-dapo)$_2$(dapoH)$_2$(μ-SCN) ·	m	9.992(7)		CuN$_4$O	N 2.011(16,43)	3.348(3,52)	N,N 88.8(6)^d	54
(NCS)](SCN)$_2$ (dark blue)	P2$_1$/n	20.186(13)	98.00(5)		μO 1.997(1)	O 116.6(5,2.4)	96.0(6,8.9)	
	4	15.179(9)			SCN 2.696(9)	S 70.6(2)	159.8(5)	
							O,N 84.9(5)^c	
							92.0(5,9)	
				CuO$_2$N$_2$S	μO 1.945(10,4)		O,O 92.1(4)	
					N 2.042(5,36)		N,N 97.8(6)	
					μCNS 2.885(7)		O,N 86.0(5,6)^c	
							169.2(6,2.3)	
							O,S 90.4(3,8.7)	
							N,S 90.2(5,3.5)	
				CuN$_3$OS	N 2.010(15,22)		N,N 93.6(6,3)	

					μO	1.985(9)			148.2(6)	
					μCNS	2.816(8)		N,O	83.9(5)[c]	
									92.6	
									171.5(5)	
								N,S	99.9(5,9.9)	
								O,S	86.4(3)	
[Cu_3(μ-dapo)$_2$(dapoH)$_2$(NO_2)$_4$][e] (not given)	m	14.902(28)		CuN_4O_2	N	2.026(22,56)	3.44(5,1)	N,N	91.9(8,8)[d]	55
	Cc	16.598(20)	102.52(14)		O_2N	2.755(35,105)	121.9(7,1)	N,O	86.2(8,2.4)[c]	
	8	22.772(33)			ONO	2.564(19,82)				
					μO	1.968(14,56)				
				CuN_4O_2	N	2.014(22,44)	3.453(6,40)	N,N	91.7(9,1)[d]	
					O_2N	2.748(25,98)	121.3(6,2.7)	N,O	85.1(8,1.5)[c]	
					ONO	2.553(26,231)				
					μO	1.981(14,23)				
[Cu_3(en)$_2$(μ-edta)$_2$] · [Cu(en)$_2$(H_2O)$_2$] · 10H_2O (blue)	tr	8.88(2)	95.4(2)	CuN_4O_2 (×1)	enN	2.023(4,4)	3.840(1)	N,N	84.5(2)[c]	56
	P-1	10.93(1)	104.3(1)		μedtaO	2.437(4)	121.5(2)	N,O	89.3(2,5)	
	2	14.20(1)	101.5(1)							
				CuO_4N_2 (×2)	edtaN	2.014(4,6)		O,O	94.9(2,9.9)	
					edtaO	1.965(4)		N,N	89.4(2)[c]	
						2.342(4,14)		O,N	82.0(2,2.7)[c]	
					μedtaO	2.434			94.3(2,3.4)	
									167.3(2)	
				CuN_4O_2 (monomer)	enN	2.015(4,9)		N,N	85.4(2)[c]	
					H_2O	2.562(5)		N,O	91.6(2,2.3)	
[{Cu(μ-dapdH$_2$)Cl}$_2$CuCl$_4$] (dark green)	or	10.463(2)		$CuCl_4$ (×1)	Cl	2.2201(21)	Not given	Cl,Cl	98.8(2,4)	57
	Pccn	12.514(12)			μCl	2.2730(20)	130.84(9)		133.85(11)	
	4	20.275(3)								
				CuN_3Cl_2 (×2)	N	1.930(6)		N,N	77.9(3,3)[c]	
						2.042(7,2)			153.94(27)	
					Cl	2.1931(20)		Cl,Cl	93.61(8)	
					μCl	2.6042(12)		N,Cl	100.6(2,6.4)	
									162.70(18)	

TABLE I (*Continued*)

Compound (colour)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*	*Cu–L* (Å)	*Cu–Cu* (Å) *Cu–L–Cu* (°)	*L–Cu–L* (°)	*Ref.*
$\{N(2amet)pipzH_3\}_4\cdot$	or	16.697(5)		$CuCl_6$ (×1)	Cl_{eq} 2.294(3,24)	5.690(1)	Cl,Cl 90.0(1,6.8)	58
$[Cu_3(\mu\text{-}Cl)_2Cl_2][CuCl_4]$ (red)	Ibam	14.479(3)			μCl_{ap} 2.971(3)	179.38(2)	180	
	4	23.757(7)						
				$CuCl_5$ (×2)	Cl_{eq} 2.312(3,47)		Cl,Cl 91.9(1,6.8)	
					μCl_{ap} 2.719(3)		172.2(1,2)	
				$CuCl_4$ (monomer)	Cl 2.245(2)		Cl,Cl 102.05(5,1.43)	
							125.64(5)	
				$CuCl_4$ (monomer)	Cl 2.266(2)		Cl,Cl 96.16(5,29)	
							141.82(5)	
$K_2[Cu_3(\mu\text{-}I)_2(qo)_6]$	m	11.956(8)		$CuO_2N_2I_2$ (×1)	O 2.02(2,2)	Not given	O,O 180	59
(dark red)	$P2_1/c$	15.506(7)	110.97(7)		N 1.96(3,0)	114.3(2)	N,N 180	
	2	13.910(9)			μI 3.202(2,0)		O,N 84.9(4)^c	
							I,I 180	
				CuO_2N_2I (×2)	O 2.00(1,1)		O,O 155.1(3)	
					N 1.99(1,1)		N,N 163.6(4)	
					μI 2.717(2)		O,N 82.0(4,2)^c	
							94.6(4,6)	
							O,I 102.5(3,1.0)	
							N,I 98.2(3,5)	
$[Cu_3(ac)_4(H_2O)(bpy)_3](PF_6)_2$	tr	11.529(1)	82.01(1)	CuO_3N_2 (×1)	acO 1.955(4,17)	3.196(1)	Not given	60
(dark blue)	P-1	12.121(2)	79.42(1)		2.258(4)	4.568(1)		
	2	17.153(2)	89.62(1)		bpyN 1.992(4,12)	6.277(1)		
						95.2(1,2.3)		
				CuO_3N_2 (×2)	μacO 1.950(3,4)		Not given	
					1.980(4,15)			
					2.338(2,62)			
					bpyN 1.991(4,10)			

$[Cu_3(\mu_3\text{-}CO_3)(pip)_3(H_2O)_3]\cdot$	hx	13.414(3)		CuO_3N_3	N	2.00(2,4)	4.63		Not given	61
$(NO_3)_4$ (blue)	P-62c				μ_3O_2CO	1.956(20)				
	2	16.024(2)			$\mu_3O_2CO_{ap}$	2.69(2)				
					H_2O_{ap}	2.25(2)				
$[Cu_3(R,S\text{-}pa)_2(R,S\text{-}Hpa)_6\cdot$	tr	10.345(2)	80.40(2)	CuO_4N_2 (×1)	N	1.990(2,33)	4.90(1,2)	O,O	90.0(6,6.9)	62
$(CF_3SO_3)_2](CF_3SO_3)_2$ (not given)	P-1	10.720(2)	71.41(2)		O	1.915(2,53)			178.9(1,9)	
	1	13.619(2)	85.14(2)			2.647(7,32)		N,N	175.8(9)	
								O,N	$84.8(9,1.7)^{c}$	
									91.7(8,5.3)	
				CuO_3N_3 (×2)	O	1.956(5)		O,O	96.7(2,2.1)	
						2.461(5,1)			160.3(2)	
					N	2.022(6,13)				
								N,N	94.5(2,2)	
									169.9(2)	
								O,N	79.7(2,28)	
									93.2(2,5.8)	
									174.4(2)	
$[Cu_3(\mu\text{-}im)_3(tmtac)_3](ClO_4)_3$	or	21.337(3)		CuN_5	imN	2.035(25,59)	5.92	N,N	$82.8(11,3.3)^{c}$	63
(deep blue)	$Pmn2_1$	18.160(5)			tmtacN	2.258(33,16)			97.3(11,11.5)	
	4	13.742(2)							170.5(11,3.9)	
$Cu_3(\mu\text{-}5\text{-}pym)_2(hfac)_6$	tr	11.875(1)	91.28(1)	CuO_4N_2 (×1)	O	2.100(6,92)	5.976(1)	O,O	$88.7(2)^{d}$	64
(green)	P-1	13.714(1)	116.51(1)		N	2.050(6)		O,N	89.6(2,7)	
	1	11.411(1)	64.59(1)							
				CuO_4N (×2)	O	1.949(6,15)		O,O	$92.0(2,2)^{d}$	
					N	2.282(5)				
$Cu_3(\mu\text{-}nitet)_2(hfac)_6$	m	19.22(1)		CuO_6 (×1)	hfacO	1.923(5,2)	Not given	O,O	$87.2(2)^{d}$	65
(not given)	$P2_1/c$	9.074(9)	91.60(2)		nitetO	2.452(4)			83.6(1,1.2)	
	4	19.71(1)								
				CuO_5 (×2)	hfacO	1.937(5,26)		O,O	90.3(2,1.8)	
					nitelO	2.180(5)			93.8(2,13.7)	
									165.9(2,2.3)	

TABLE I (*Continued*)

Compound (*colour*)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	*α* (°) *β* (°) *γ* (°)	*Chromophore*	*Cu–L* (Å)	*Cu–Cu* (Å) *Cu–L–Cu* (°)	*L–Cu–L* (°)	*Ref.*
$Cu_3(\mu\text{-nitppy})_2(hfac)_6$ (light green)	m C2/c 8	36.540(9) 23.484(7) 21.292(6)	 118.90(2)	CuO_6 (×1)	hfacO 1.93(1,1) nitppyN 2.47(1,1)	Not given	O,O 91.6(5,1)^d 89.7(4,6.6) 177.9(4,1.2)	66
				CuO_5N (×2)	hfacO 2.01(1,18) nitppyO 2.70(1,1) nitppyN 2.01(1,2)		O,O 91.6(4,2)^d 82.7(4,17.1) 174.4(4,5.9) O,N 92.6(4,9.1) 162.1(4,1.3)	
$Cu_3(\mu\text{-Pr}^i\text{tmio})_2(hfac)_6$ (dark green)	tr P-1 1	12.211(7) 9.142(4) 16.109(6)	96.12(3) 90.24(4) 96.20(4)	CuO_6 (× 1)	O 1.92(1,0) 2.58(3)	Not given	O,O 926(6)^d	67
				CuO_4N (×2)	O 1.93(1,21) 2.18(1) N 2.02(1)		O,O 89.7(6,9)^d 89.6(6,4.6) 177.5(8) O,N 89.2(6,3) 112.4(5)	
$Cu_3(\mu\text{-Ettmio})_2(hfac)_6$ (dark green)	m $P2_1/c$ 2	8.948(3) 25.120(2) 15.983(6)	 103.92(3)	CuO_6 (×1)	O 1.93(2,1) 2.48(2)	Not given	O,O 92(1)^d	67
				CuO_4N (×2)	O 1.92(2,4) 2.21(2) N 1.99(3)		O,O 90(1,2)^d 90(1,6) 176(2) O,N 90(1,11) 162(1)	
$Cu_3(\mu\text{-phitmio})_2(hfac)_6$ (green)	tr P1 1	15.507(10) 8.338(4) 14.644(7)	75.30(4) 93.88(4) 96.03(4)	CuO_6 (×1)	O 1.96(5,5) 2.53(4,1)	Not given	O,O 91(2,3)^d 85;105(2) 175(2,2)	68

				CuO$_4$N (×2)	O	2.03(4,11)		O,O	91(2,7)[d]	
					N	2.04(5,3)				
[Cu$_3$(μ-tepz)$_2$Cl$_6$] · 2CHCl$_3$	tr	13.661(2)	101.08(2)	CuN$_2$Cl$_2$ (×1)	N	1.99(1,0)	7.360(2)	N,N	180.00	69
(blue green)	P-1	14.174(3)	96.94(2)		Cl	2,246(24,0)		Cl,Cl	180.00	
	2	9.412(2)	75.76(2)					N,Cl	90.0(3,1.5)	
				CuN$_2$Cl$_2$ (×2)	N	2.01(1,1)		N,N	87.7(4,0)	
					Cl	2.218(4,12)		Cl,Cl	94.3(2,0)	
								N,Cl	89.1(3,2)	
									176.1(4,2)	

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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 parenthesis is e.s.d., the second is maximum deviation from the mean value.

[b] The chemical identity of coordination atom/ligand is specified in these columns.

[c] Five-membered metallocyclic ring.

[d] Six-membered metallocyclic ring.

[e] There are two crystallographically independent molecules.

TABLE IA

	Cov. rad.	*Four-coordination*	*Five-coordination*	*Six-coordination*
Coord. atom				
$\mu_3O(H)$	0.73	1.96	2.00	1.99
$\mu O(H)$		1.91	1.90	
O(L)		2.24	2.33	2.485
2-dent		1.955	2.115	2.03
3-dent			2.32	2.39
N(L)	0.75		2.185	2.02
2-dent		2.00	2.03	2.03
3-dent		1.965	2.07	2.00
Cl	0.99	2.24	2.29	2.30
μ-Cl		2.28	2.58	2.67
Br	1.14	2.39	2.605	
μ-Br		2.43		
μ-I	1.33		2.72	3.20
Ring				
5-O		86.4	81.3	
5-N		80.3	83.4	81.7
5-S		90.9		
5-O,N		83.9	84.2	84.6
6-O			90.5	90.7
6-N		91.0	94.0	90.0
6-O,N		95.2	95.0	

3 TETRAMERIC COPPER(II) COMPOUNDS

3.1 $Cu_4(\mu_4\text{-}O)$ Tetrahedron

Crystallographic and structural data for tetrameric copper(II) compounds are gathered in Table II. X-ray analysis of the green derivative[71] shows the cation $[Cu_4(\mu_4\text{-}OH)(\mu\text{-bttt})(H_2O)_2]^{3+}$ and NO_3^- groups. The cation is centrosymmetric, with the central oxygen atom on a center of symmetry (Figure 4). Within the macrocyclic ring, only the saturated carbon atoms show significant deviation from planarity. Four copper(II) atoms are bound within the bttt macrocycle, each coordinated to one imine nitrogen, one phenoxide oxygen, one alkoxide oxygen, the central hydroxide anion and to one axial water. The macrocyclic oxygen donors are all deprotonated and each bridges two copper(II) atoms, so that the square plane about each copper shares two edges with the equivalent planes of the two neighboring copper atoms with two sets of Cu–Cu distances 2.953(1) and 3.000(1) Å (Table IIA). Structural data for derivatives which contain a $Cu_4(\mu_4\text{-}O)$ tetrahedral core are summarized in (Table IIB). The structures are in order of increasing mean Cu–Cu distance.

There are twenty-nine complexes[72–96] which contain a μ_4-oxo group tetrahedrally-coordinated to four copper(II) centers. Each pair of copper(II)

TABLE II Crystallographic and structural data for tetrameric copper(II) compounds[a]

Compound (colour)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	*α* (°) *β* (°) *γ* (°)	*Chromophore*	*Cu–L* (Å)		*Cu–Cu* (Å) *Cu–L–Cu* (°)	*L–Cu–L* (°)		*Ref.*
A: $Cu_4(\mu_4\text{-}OH)$ planar core										
$[Cu_4(\mu_4\text{-}OH)(\mu\text{-}bttt)H_2O)_2]\cdot$	m	10.384(2)		CuO_4N (×2)	μ_4HO^b	2.127(1)	2.976(1,24)	O,O^b	88.4(2,6.2)	71
$(NO_3)_3$ (green)	$P2_1/a$	18.515(5)	107.48(2)		μbtttO	1.890(5,26)	HO^a 90.0(1,9)		163.6(2)	
	2	11.264(2)			μbtttN	1.937(5)	180.0	O,N	98.5(2,4.1)	
					H_2O	2.249(5)	O 103.1(2)		167.3(2)	
				CuO_3N (×2)	μ_4HO	2.082(1)		O,O	83.7(2,2)	
					μbtttO	1.899(4,16)			167.1(2)	
					N	1.940(6)		O,N	96.5(2,2.0)	
									175.4(1)	
B: $Cu_4(\mu_4\text{-}O)$ tetrahedron core										
$Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(Et_2na)_4$	tg	15.213(3)		$CuCl_3ON$	μ_4O	1.903(–,28)	3.093^d	O,Cl	84.3(–,3.1)	72
(red brown)	$I4_1$				dencN	1.953(12,23)	O 109.0(–,3)	Cl,N	95.5(4,2.8)	
	4	22.864(4)			μCl	2.411(4,93)	Cl 80.3(1,1.7)	Cl,Cl	104.7(1,7)	
									126.2(1,8.9)	
$Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(Et_2SO)_4$	or	10.436(2)		$CuCl_3O_2$	μ_4O	1.895(7,16)	$3.094(2,26)^d$	Cl,Cl	119.3(1,10.1)	73
(orange)	$P2_12_12_1$	11.092(2)			Et_2SO	1.922(8,13)	O 109.5(4,1.6)	O,O	177.3(4,1.1)	
	4	29.679(7)			μCl	2.408(3,43)	Cl 80.0(1,1.3)	O,Cl	90.0(3,7.3)	
$[Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(Me_2SO)_4]\cdot$	or	10.582(2)		$CuCl_3O_2$	μ_4O	1.896(9,21)	$3.095(3,23)^d$	Cl,Cl	119.33(19,5.84)	74
Me_2SO (orange)	$P2_12_12_1$	10.571(2)			Me_2SO	1.928(11,15)	O 109.5(5,2.1)	Cl,O	85.3(3,1.2)	
	4	28.255(5)			μCl	2.412(5,52)	Cl 79.8(1,1.4)		95.3(4,3.1)	
								O,O	177.7(5,1.4)	
$Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(mpd)_3\cdot$	m	9.062(2)		$CuCl_3O_2$ (×3)	μ_4O	1.895(4,7)	3.095(1,42)	Cl,Cl	119.80(9,8.83)	75
$(mpdH_2O)$ (brown)	$P2_1/n$	22.051(5)	96.65(1)		mpdO	1.918(5,5)	O 109.5(2,1.3)	O,Cl	85.02(14,1.74)	
	4	17.278(3)			μCl	2.406(2,95)	Cl 80.1(7,9)		94.96(18,5.76)	
								O,O	175.37(22,2.14)	
				$CuCl_3O_2$ (×1)	μ_4O	1.936(6)		Cl,Cl	119.38(9,2.11)	
					H_2O	1.936(6)		O,Cl	85.44(14,81)	
					μCl	2,404(2,2)			94.54(22,4.10)	
								O,O	175.23(26)	

TABLE II (*Continued*)

Compound (colour)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*	*Cu–L* (Å)		*Cu–Cu* (Å) *Cu–L–Cu* (°)	*L–Cu–L* (°)		*Ref.*
$[Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(2\text{-}Mepy)_4]\cdot$	m	12.73(2)		$CuCl_3ON$	μ_4O	1.90(2,4)	3.097(6,109)	Cl,Cl	104.0(4,9.0)	76
H_2O (dark olive green)	$P2_1/c$	12.07(2)	90.7(2)		pyN	1.99(2,3)	O 109.4(8,6.4)		137.9(4,3.1)	
	4	21.54(3)			μCl	2.374(8,84)	Cl 78.6(3,1.9)		152.7(4,2.7)	
						2.639(8,46)		N,Cl	96.6(7,5.9)	
								O,N	177.0(9,1.3)	
								O,Cl	83.5(6,7.3)	
$[Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(Ph_3PO)_4]\cdot$	c	24.437(6)		$CuCl_3O_2$	μ_4O	1.897(1)	3.098(2)	Cl,O	90.0(4,5.3)	77
$0.7MeNO_2$ (orange)	F-43c				Ph_3PO	1.929(3)	Not given	O,O	180.0	
	8				μCl	2.381(1)				
$Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(py)_4$	m	11.29(2)		$CuCl_3ON$	μ_4O	1.90(2,2)	3.10(–,1)	O,Cl	84.8(6,2.1)	78
(golden yellow)	$P2_1/n$	21.40(4)	92.20(2)		pyN	1.96(2,2)	O 109.5(–,1.5)	N,Cl	95.2(7,4.7)	
	4	11.96(2)			μCl	2.408(9,78)	Cl 80.2(–,1.4)	Cl,Cl	116.2(3,8.3)	
									134.0(3,3.9)	
$Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(Ph_3PO)_4$	c	24.405(18)		$CuCl_3O_2$	μ_4O	1.900(3)	3.102(2)	Cl,O	90.0(1,5.3)	79
(orange)	F-43c				Ph_3PO	1.88(3)	O Not given			
	8				μCl	2.387(5)	Cl 81.0(2)			
$[Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(MeCN)_4]\cdot$	m	8.795(2)		$CuCl_3ON$	μ_4O	1.897(2,1)	3.102(1,20)	Cl,Cl	119.19(4,5.51)	80
2MeCN (brown)	C2/c	24.411(3)	95.24(3)		N	1.943(4,11)	O 109.5(1,1.1)	Cl,N	95.2(1,29)	
	4	12.414(3)			μCl	2.325(1,59)	Cl 80.8(1,1.0)	O,N	177.4(2,4)	
						2.418(1,18)		Cl,O	84.82(9,61)	
$Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(dmf)_4$	m	40.665(8)		$CuCl_3O$	μ_4O	1.923(9,28)	3.103(3,16)		Not given	81
(green) (at 100 K)	I2/a	15.742(5)			dmfO	1.933(11,22)	Not given			
	8	8.538(4)	79.21(2)		μCl	2.398(4,39)				
$Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(dmf)_4$	m	40.940(8)		$CuCl_3O_2$	μ_4O	1.901(8,38)	3.104(3,21)		Not given	81
(yellow) (at 260 K)	I2/a	15.878(6)			dmfO	1.951(11,27)	Not given			
	8	8.656(5)	79.40(2)		μCl	2.398(5,40)				
$Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(1\text{-}Meim)_4{}^c$	or	18.985(7)		$CuCl_3ON$	μ_4O	1.902(5,9)	3.104(2,13)	O,Cl	85.9(2,1.6)	82
(yellow)	Pbca	33.197(7)			imN	1.934(7,6)	O 109.5(9,1.2)	N,Cl	95.1(2,3.8)	
	16	18.917(5)			μCl	2.415(3,41)	Cl 79.7(10,3.0)	Cl,Cl	116.4(1,7.5)	
									127.8(1,5.8)	
								O,N	177.6(3,1.1)	

				$CuCl_3ON$	μ_4O	1.903(5,13)	3.107(2,36)	O,Cl	85.8(2,2.0)	
					imN	1.930(7,18)	O 109.5(11,1.7)	N,Cl	95.0(2,2.2)	
					μCl	2.419(3,59)	Cl 79.7(10,3.0)	Cl,Cl	117.0(1,8.4)	
									130.5(1,3.2)	
								O,N	176.8(3,8)	
$[Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(Ph_3PO)_4]\cdot$	c	Not given		$CuCl_3O_2$	μ_4O	1.902(2)	3.107(1)	Cl,O	90.0(1,5.1)	79
$0.75CH_2Cl_2$ (orange)	F-43c				Ph_3PO	1.95(1)	O Not given			
	8				μCl	2.398(2)	Cl 80.8(1)			
$Cu_4(\mu\text{-}O)(\mu\text{-}Cl)_6(dmppz)_4$	m	20.836(1)		$CuCl_3ON$	μ_4O	1.909(4,4)	3.108(1,65)	Cl,Cl	119.3(1,2.0)	83
(brown)	I2/a	11.161(1)	104.54(1)		pzN	1.962(7,2)	O 109.0(4,3.4)	O,N	176.1(2,3)	
	4	22.996(1)			μCl	2.412(3,87)	Cl 80.8(1,2.0)			
$Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(Meim)_4$	or	18.946(1)		$CuCl_3ON$	μ_4O	1.905(7,19)	3.110(3,36)[d]	Cl,Cl	115.7(1,6.9)	84
(yellow green)	Pbca	19.043(1)			imN	1.939(9,28)	O 109.5(3,1.1)		126.3(1,7.9)	
	16	33.256(2)			μCl	2.418(4,75)	Cl 80.1(1,7)	Cl,O	85.0(2,1.6)	
								Cl,N	95.1(3,4.0)	
								O,N	177.5(3,2.2)	
$Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(Ph_3PO)_6$	c	12.22(2)		$CuCl_3O_2$	μ_4O	1.905(3)	3.110(3)	Cl,O	95.6(7)	85
(orange)	P-43m				Ph_3PO	1.89(2)	Not given			
	1				μCl	2.38(1)				
$[Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(Mein)_4]\cdot$	or	14.637(1)		$CuCl_3ON$		Not given	3.117(3,7)[d]		Not given	84
$[Cu(Meim)_4Cl]Cl$ (dark green)	$Pca2_1$	13.233(1)								
	4	26.490(2)								
$Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(hmt)_4$	m	19.417(9)		$CuCl_3ON$	μ_4O	1.909(5,3)	3.117(2,29)	Cl,Cl	119.1(1,4.9)	86
(brown)	A2/a	9.788(6)	116.08(3)		hmtN	2.001(8,3)	O 109.2(2,1.8)	Cl,N	95.6(2,6)	
	4	22.792(9)			μCl	2.412(3,45)	Cl 80.5(1,9)	Cl,O	84.3(2,3)	
								N,O	178.3(3,7)	
$Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(pi)_4$	tr	11.749(3)	106.2(1)	$CuCl_3ON$	μ_4O	1.91(1,5)	3.119(3,26)	Cl,Cl	115.5(3,6.4)	87
(brown)	P-1	11.807(2)	115.5(1)		piN	1.99(2,4)	O 109.3(5,3.0)		126.7(3,3.4)	
	2	14.205(3)	97.45(5)		μCl	2.416(6,43)	Cl 80.4(2,1.0)	O,Cl	85.0(6,2.3)	
								N,Cl	95.2(7,5.6)	
								O,N	175.1(6,2.4)	
$(Me_4N)[Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6Cl_4]$[c]	c	19.361(6)		$CuCl_4O$	μ_4O	1.921(2)	3.137(3,1)	Cl,Cl	119.12(15)	88
(not given)	P-43n				Cl	2.268(4)	Not given			
	8				μCl	2.398(4,33)				

TABLE II (*Continued*)

Compound (*colour*)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	*α* (°) *β* (°) *γ* (°)	*Chromophore*	*Cu–L* (Å)		*Cu–Cu* (Å) *Cu–L–Cu* (°)	*L–Cu–L* (°)		*Ref.*
				$CuCl_4O$	μ_4O	1.958(2)	3.198(3)	Cl,Cl	118.89(8)	
					Cl	2.203(4)	Not given			
					μCl	2.420(5)				
$(Me_4N)[Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6Cl_4]^c$ (red)	c	19.30(2)		$CuCl_4O$	μ_4O	1.92(1)	3.14(1)	O,Cl	84.6(5,1.0)	89
	P-43n				Cl	2.25(2)	O 109.4(4,4)		177.0(7)	
	8				μCl	2.41(2)	Cl 81.3(9,1)	Cl,Cl	95.4(7,2.8)	
									119.1(5,1.4)	
				$CuCl_4O$	μ_4O	1.95(1)	3.18(1)	O,Cl	84.5(6)	
					Cl	2.17(2)	O 109.5(–)		180.0(–)	
					μCl	2.43(3)	Cl 81.5(–)	Cl,Cl	95.5(8)	
									119.1(2)	
$(Et_2NH_2)_4[Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6Cl_4]$ (red)	m	11.099(1)		$CuCl_4O$	μ_4O	1.913(5,10)	3.121(1,53)	O,Cl	84.4(2,3.8)	90
	$P2_1/c$	9.744(1)	111.56(1)		Cl	2.243(3,7)	O 109.4(2,3.3)		177.5(2,1.7)	
	4	36.977(2)			μCl	2.361(3,26)	80.4(1,9)	Cl,Cl	95.5(1,1.8)	
						2.443(2,29)			114.4(1,9.9)	
						2.581(2,7)			133.6(1,4.7)	
$[Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(1,2\text{-}Me_2im)_4]\cdot 0.25H_2O$ (not given)	m	22.582(5)		$CuCl_3ON$	μ_4O	1.909(9,14)	3.122(3,30)	O,Cl	84.6(3,1.8)	91
	$P2_1/c$	11.829(2)	128.46(2)		N	1.945(4,6)	O 109.5(4,1.8)	O,N	178.0(4,2.6)	
	4	16.114(4)			μCl	2.416(5,50)	Cl 80.4(2,1.4)	Cl,Cl	113.0(2,8.9)	
									127.6(2,11.1)	
								Cl,N	95.5(4,4.5)	
$Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(Et_3PO)_4$ (red brown)	rh	12.8971(26)	90.55(2)	$CuCl_3O_2$	μ_4O	1.913(4,17)	3.123(2,7)	Cl,Cl	119.22(16,10.49)	92
	R3c				Et_3PO	1.934(6,2)	O 109.5(3,1.2)	O,O	177.61(35,2.39)	
	2				μCl	2.422(2,53)	Cl 80.3(1,7)	O,Cl	90.06(24,9.54)	
$[Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(ain)_4]\cdot 0.5Etac$ (brown)	m	11.661(2)		$CuCl_3ON$	μ_4O	1.919(5)	$3.132(-,72)^d$	Cl,Cl	101.85(7)	93
	$P2_1/c$	22.415(7)	109.85(2)		ainN	1.996(7,20)	O 109.5(2,3.7)		114.8(8,4.44)	
	4	15.077(4)			μCl	2.349(3,38)	Cl 81.2(1,1.4)		126.99(8,3.1)	
						2.453(2,26)			141.53(8)	
						2.619(2)		Cl,O	84.2(1,3.1)	
								Cl,N	95.9(2,4.6)	

								O,N	177.7(2,3.5)	
$Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(3\text{-quin})_4$	m	11.877(4)		$CuCl_3ON$	μ_4O	1.919(5,6)	3.133(1,22)	Cl,Cl	119.2(1,3.7)	94
(yellow)	$P2_1/c$	19.106(3)	122.28(2)		quinN	2.025(7,7)	O 109.5(2,8)	O,Cl	84.8(2,1.1)	
	4	21.975(5)			μCl	2.413(3,22)	Cl 80.98(8,47)	N,Cl	95.3(2,1.3)	
								O,N	179.5(2,6)	
$Cu_4(\mu\text{-}O)(\mu\text{-}Br)_6(py)_4$	m	30.64(1)		$CuBr_3ON$	μ_4O	1.92(1,1)	3.142(6,19)[d]	O,N	175.9(7,2.5)	95
(dark brown)	C2/c	12.43(2)	129.56(20)		pyN	2.02(2,5)	O 109.5(6,1.1)	N,Br	93.9(5,6.2)	
	8	20.17(1)			μBr	2.534(4,76)	Cl 76.7(2,1.0)	O,Br	86.6(4,1.4)	
								Br,Br	111.8(2,7.0)	
									130.7(2,7.5)	
$[Cu_4(\mu_4\text{-}O)(\mu\text{-}Br)_6(mor)_4]\cdot$	m	11.128(2)		$CuBr_3ON$	μ_4O	1.933(8,23)	3.155(2,12)	Br,Br	119.5(1,6.1)	96
$2H_2O$ (black)	P2/b	13.356(2)			morN	2.0(2,0)	O 109.5(4,1.7)	O,N	179.1(5)	
	2	12.608(2)	106.02(5)		μBr	2.535(3,48)	Cl 76.96(8,73)			
$[Cu_4(\mu_4\text{-}O)(\mu\text{-}pz)_2(dpm)_4]$	m	21.430(9)		CuO_3N	μ_4O	1.930(6)	3.285(6,132)[d]	O,O	82.9–92.5(6)	96b
(blue)	A2/a	24.70(8)	111.24(3)		dpmO	1.930(6)	107.7(1,8.4)			
	4	13.759(6)			μpzN	1.930(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 parenthesis is e.s.d., the second is maximum deviation from the mean value.

[b] The chemical identity of coordination atom/ligand is specified in these columns.

[c] There are two crystallographically independent molecules.

[d] Calculated by us.

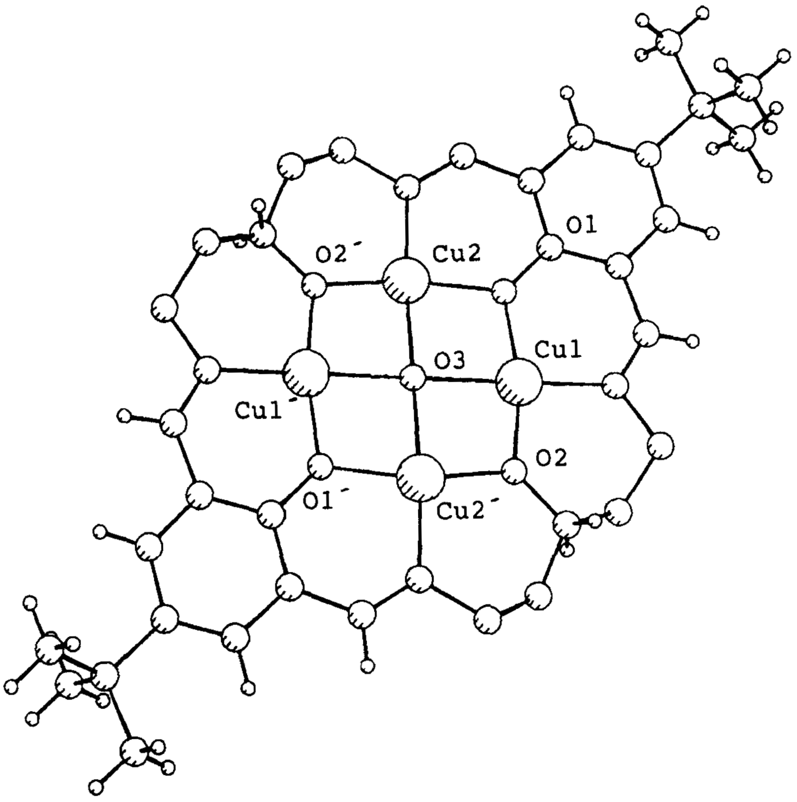

FIGURE 4 Structure of $[Cu_4(\mu_4\text{-}OH)(bttt)]^{3+}$.[71]

centers is bridged by a single chlorine[72–94] or bromine[95,96] atom. The structure of the orange complex, $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)(Et_2SO_4)$,[73] is shown in Figure 5 as an example. The coordination sphere about each copper(II) is trigonal-bipyramidal, with three chlorine or bromine atoms in the equatorial plane. There are four types of core structural units, $CuCl_3ON$,[72,76,78,80,82–84,86,87,91,93] $CuCl_3O_2$,[73–75,77,79,81,85,92,94] $CuCl_4O$[88–90] and $CuBr_3ON$.[95,96] The Cu–Cu separation in these tetrahedral cores ranges from 3.093 to 3.155 Å (mean values), suggesting an absence of metal–metal bonding. The mean Cu–O–Cu bridge angle is 109.5(6.0)°. The mean Cu–Cl–Cu bridge angle of 80.5° is about 4.0° more open than that of a Cu–Br–Cu bridge (76.5°).

The mean values of both Cu–L (terminal) and Cu–L (bridge) bond distances increase with covalent radius of coordinated atoms (in parenthesis)

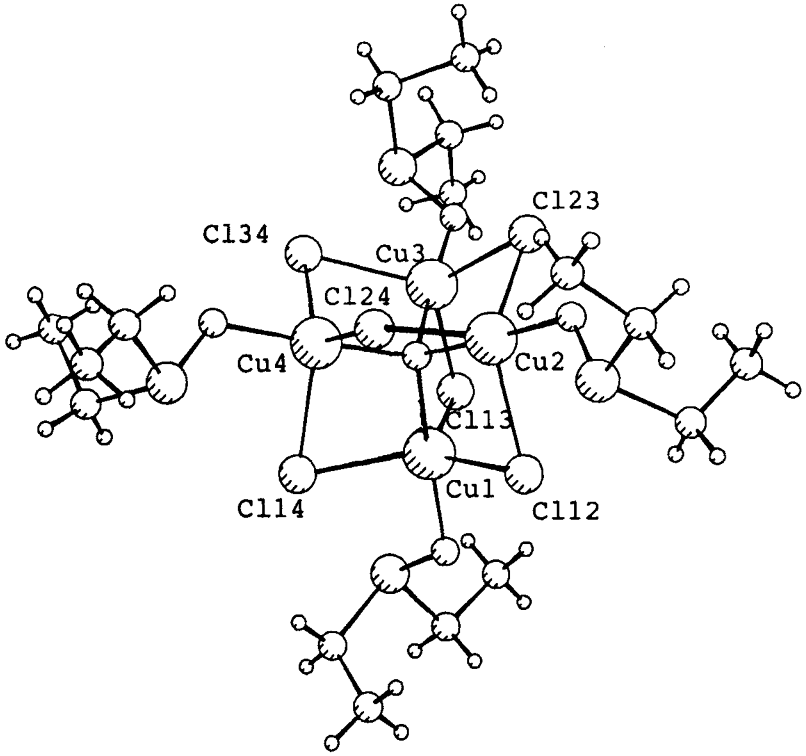

FIGURE 5 Structure of $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)(Et_2SO)_4$.[73]

in the sequences: 1.96 Å (OL, 0.73 Å) < 1.97 Å (NL, 0.74 Å) < 2.24 Å (Cl, 0.99 Å) and 1.915 Å (μ_4O) < 2.42 Å (μ-Cl) < 2.535 Å (μ-Br).

Most derivatives (12) are red-brown in color, but there are orange (5), green (4) and yellow (4) complexes. There are three derivatives[82,88,89] which contain two crystallographically independent tetramers, differing mostly by degree of distortion and provide other examples of distortion isomers.[70]

3.2 Cubane Type

The essentially green and blue compounds of this type are given in Table IIIA. There are over forty examples[97–134] which possess a central Cu_4O_4 cubane-type structure. The structure of $[Cu(\mu_3\text{-deae})(NCO)]_4$[108] is shown in (Figure 6) as an example. Structures are reported in the order of increasing mean Cu–Cu separation. Copper(II) displays considerable flexibility in the cubic framework, with five-coordinate,[97,98,100–110,112–121,124,125,131]

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

Compound (colour)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	*α* (°) *β* (°) *γ* (°)	*Chromophore*	*Cu–L* (Å)	*Cu–Cu* (Å) *shortest* *longest* *average* *Cu–L–Cu* (°)	*L–Cu–L* (°)	*Ref.*
A: Cubane								
[Cu(μ_3-pte)Cl]$_4$ (not given)	tg	14.740(5)		CuO$_3$SCl	μ_3O[b] 1.961(4,19)	2.964(1)	O,O[b] 80.9(1,2)	97
	I-4				2.422(4)	3.340(1)	O,S 84.9(1)[c]	
	2	8.028(1)			S 2.329(2)	3.089	95.1(1)	
					Cl 2.205(2)	98.4(1,6)	165.8(1)	
							O,Cl 98.0(1)	
							115.0(1)	
							163.6(1)	
							S,Cl 96.03(6)	
[Cu(μ_3-OMe)(tcp)(MeOH)]$_4$	m	18.014(9)		CuO$_5$	μ_3O 1.95(–,6)	2.964(–)	O,O 86.1(–,6.3)	98
(light green)	P2$_1$/b	14.795(8)			2.31(,25)	3.187(–)	95.5(–,4.2)	
	16	18.083(11)	94.01(15)		tcpO 2.06(–,2)	3.104	169.5(–,5.7)	
					MeO 2.06(–,2)	84.8(–,6.1)		
[Cu(μ_3-me)(hfacac)]$_4$	m	17.046(5)		CuO$_6$	μ_3O 1.942(6,7)	2.936(2)	O,O 77.6(3,3.4)[c]	99
(dark green)	C2/c	17.211(5)	93.50(2)		2.424(6,22)	3.234(2)	83.4(2,5.6)[d]	
	4	17.634(3)			hfacacO 1.956(6,20)	3.108	93.8(3,2.0)	
					O 2.560(8)	Not given	106.8(3,5.7)	
					2.672(8)		162.8(3,10.0)	
α-[Cu(μ_3-C$_7$H$_{11}$NO$_2$)]$_4$	tg	14.46(2)		CuO$_4$N	μ_3O 1.99(2,1)	3.006(8)	O,O 81.5(8,3)	100
(not given)	P42$_1$c				2.32(2)	3.259(8)	98.4(9)	
	8	7.63(2)			O 1.91(2)	3.133	O,N 86.0(10)[c]	
						97.8(8)	95.0(11)[d]	
							120.3(8)	
							153.1(8)	
[Cu(μ_3-ipte)Cl]$_4$	tg	13.170(4)		CuO$_3$SCl	μ_3O 1.964(5,25)	3.148(1)	O,O 75.0(2)	97
(not given)	P-42$_1$c				2.343(5)	3.191(1)	83.8(2,1.1)	
	2	9.872(2)			S 2.321(3)	3.162	O,S 85.3(2)[c]	

					Cl	2.218(3)	94.4(2,1.6)		112.2(1)	
							106.5(2)		167.0(2)	
								O,Cl	98.0(2,2)	
									177.3(2)	
								S,Cl	92.0(1)	
[Cu(μ_3-OEt)(tftbd)]$_4$	or	14.071(5)		CuO$_5$	μ_3O	1.946(6,1)	2.977(2)	O,O	81.7(3,1.8)[d]	101
(not given)	Fddd	14.294(9)				2.411(7)	3.281(2)		94.4(3,2.9)	
	8	49.93(3)			O	1.927(6,8)	3.173		101.6(3)	
							97.7(3,2.1)		172.8(3,1.9)	
[Cu(μ-dbae)(NCS)]$_4$	tr	12.34(2)	73.8(1)	CuO$_3$N$_2$	μ_3O	2.01(1,10)	3.034(4)	O,O	78.6(4,8)	102
(not given)	P-1	13.53(2)	107.6(1)			2.25(1,4)	3.253(3)		81.8(5,1.5)	
	2	20.33(3)	109.0(1)		SCN	1.91(2,2)	3.173	O,N	85.7(7,1.1)[c]	
					N	2.05(2,4)	98.6(6,4.7)		97.1(7,3.4)	
									130.9(6,8.9)	
									150.3(6,6.9)	
									176.7(6,3.1)	
								N,N	96.5(8,2.2)	
[Cu(μ_3-OMe)(hfacac)(thf)]$_4$	or	14.00(1)		CuO$_6$	μ_3O	1.937(3,8)	2.932(3)	O,O	82.5(1,3.2)[d]	99
(dark green)	Fddd	27.75(2)				2.441(3)	3.318(3)		92.5(1,6.5)	
	8	29.16(1)			hfacacO	1.944(3,10)	3.177		103.2(1)	
					thfO	2.547(4)	97.6(1,1.2)		142.2(1)	
									173.0(1,8)	
[Cu(μ_3-C$_8$H$_{11}$NO$_3$)]$_4$	tr	12.330(2)	97.44(2)	CuO$_4$N	μ_3O	1.952(4,31)	3.092(1)		Not given	103
(not given)	P-1	13.766(1)	92.05(2)			2.403(4,74)	3.337(1)			
	2	11.109(3)	85.09(2)		O	Not given	3.178			
					N	Not given	105.3(2,8)			
[Cu(μ_3-dpae)(NCO)]$_4$	or	12.83(1)		CuO$_3$N$_2$	μ_3O	1.923(8,10)	3.155(4)	O,O	80.4(4,3.7)	104
(light green)	Pnna	19.03(2)				2.154(8,4)	3.208(2)	O,N	91.7(6,6.3)	
	4	19.28(2)				2.229(8,15)	3.182		139.0(4,2.0)	

TABLE III (*Continued*)

Compound (*colour*)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*	*Cu–L* (Å)		*Cu–Cu* (Å) *shortest* *longest* *average* *Cu–L–Cu* (°)	*L–Cu–L* (°)		*Ref.*
					OCN	1.862(14,14)	98.8(2,5.7)		174.0(5,5)	
					N	2.072(13,13)		N,N	98.7(6,0)	
β [Cu(μ_3-eia)]$_4$ · 2C$_6$H$_6$	tr	16.72(2)	95.3(1)	CuO$_4$N	μ_3O	1.948(8,41)	3.064(2)	O,O	90.1(–,3.5)	105
(blue)	P-1	12.19(1)	95.0(1)			2.408(8,97)	3.311(2)	O,N	84.7(–)^c	
	2	11.68(1)	107.6(1)		N	1.927(7,11)	3.183		95.1(–)^d	
							97.9(29,7.6)			
[Cu(μ_3-deae)Cl]$_4$	tg	11.334(3)		CuO$_3$NCl	μ_3O	1.966(6,31)	2.931(2)	O,O	81.1(2,2)	106
(dark green)	P4$_1$2$_1$2					2.472(6,49)	3.450(2)	O,N	85.1 (3,6)^c	
	16	27.791(8)			N	2.065(7,8)	3.185	O,Cl	96.0(2,2)	
					Cl	2.230(3,5)	96.7(3,1.0)	N,Cl	97.1(2,6)	
[Cu(μ_3-dbae)(NCO)]$_4$	tr	12.14(1)	72.2(1)	CuO$_3$N$_2$	μ_3O	2.02(2,12)	3.051(4)	O,O	78.6(9,7)	102
(not given)	P-1	13.09(1)	103.5(1)			2.27(1,4)	3.265(4)		81.9(6,1.7)	
	2	16.69(2)	106.5(1)		OCN	1.87(2,5)	3.189	O,N	85.5(7,2.2)^c	
					N	2.08(2,2)	98.5(7,5.1)		96.6(8,5.2)	
									133.6(7,10.8)	
									152.2(6,2.6)	
									175.6(8,3.0)	
								N,N	97.1(9,3.4)	
[Cu(μ_3-deae)(NCO)]$_4$ · CHCl$_3$	m	12.861(3)		CuO$_3$N$_2$	μ_3O	1.927(6,3)	3.154(3)^e		Not given	107
(dark green)	P2$_1$/c	14.039(3)	100.39(1)			2.170(6,14)	3.238(3)			
	4	24.236(5)				2.206(6,10)	3.193			
					OCN	1.903(11,14)	99.0(2,5.5)			
					N	2.043(9,25)				
[Cu(μ_3-deae)(NCO)]$_4$	tr	13.478(3)	84.020(5)	CuO$_3$N$_2$	μ_3O	1.925(4,8)	3.153(1)	O,N	85.3(2,1.0)^c	108
(dark green) (form B)	P-1	12.873(3)	80.263(5)			2.170(5,22)	3.254(1)		175.5(3,1.6)	
	2	11.542(3)	86.863(5)			2.215(4,5)	3.194	N,N	97.5(3,1.2)	
					OCN	1.896(8,14)	98.9(2,6.7)			
					N	2.046(7,31)				

[Cu(μ_3-deae)(NCO)]$_4$	tg	17.85(1)		CuO$_3$N$_2$	μ_3O	1.936(6)	3.193(2)	O,O	79.9(3,3.6)	109
(light green)	I42d					2.113(6)	3.194(2)	N,N	98.1(4)	
	4	11.92(1)				2.243(6)	3.194	O,N	85.0(3)^c	
					OCN	1.903(9)	99.2(2,5.0)		96.9(3)	
					N	2.066(8)			139.2(3,3.1)	
									174.0(3)	
[Cu(μ_3-me)(bzac)]$_4$	tr	20.062(2)	69.156(8)	CuO$_5$	μ_3O	1.955(5,22)	3.020^e	O,O	80.5(1,2.3)	110
(green blue)	P-1	14.970(1)	74.597(9)			2.346(5,1)	3.436		91.9(1,6.5)^d	
	2	10.658(2)	65.637(8)			2.526(5,7)	3.195		103.6(1,1.6)	
					bzacO	1.920(6,8)	97.5(2,6.3)		173.83(10)	
[Cu$_4$(μ_3-OH)$_4$(μ-SO$_3$CF$_3$)$_2$(tpa)$_4$] ·	m	18.848(7)		CuO$_4$N$_2$	μ_3O	1.967(7,21)	2.967(2)	O,O	81.1(4,2.1)	111
SO$_3$CF$_3$ · Me$_2$CO (deep blue)	P2$_1$/n	13.804(5)	99.29(3)			2.387(7,8)	3.371(2)		90.5(4,4.1)	
	4	29.491(10)				2.475(7)	3.207		168.3(3,1.4)	
					μO	2.531(10,45)	98.2(4,2.5)	N,N	85.1(2,3)	
						2.682(9)		O,N	89.5(3,4.9)	
					tpaN	2.010(6,18)			103.8(2,3)	
[Cu(μ_3-amp)Cl]$_4$ (green)	tg	12.604(8)		CuO$_3$NCl	μ_3O	1.965(7,6)	3.036(2)	O,O	81.8(3,3.1)	112
	P4$_2$/n					2.461(9)	3.302(2)	O,Cl	101.3(2,1.3)	
	2	8.998(3)			N	1.984(9)	3.213		174.0(3)	
					Cl	2.230(3)	97.6(3,3.6)	O,N	81.1(3)^c	
									98.8(4)	
									159.3(3)	
								Cl,N	99.6(3)	
[Cu(μ_3-amp)Br]$_4$ (light green)	tg	12.954(13)		CuO$_3$NBr		Not given	Not given		Not given	112
	P4$_2$/n									
	2	9.248(6)								
[Cu(μ_3-C$_{16}$H$_{16}$N$_2$O$_3$)]$_4$ ·	tg	18.193(4)		CuO$_4$N	μ_3O	1.978(4,20)	3.124(1)	O,O	76.4(2)	113
9MeOH (dark green)	P4$_2$/n					2.475(4)	3.412(2)		105.9(2)	
	2	12.615(4)			O	1.884(5)	3.220		173.1(2)	
					N	1.924(6)	93.9(2,5.1)	Cl,N	82.4(2,1.4)^c	

TABLE III (*Continued*)

Compound (*colour*)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*		*Cu–L* (Å)	*Cu–Cu* (Å) *shortest* *longest* *average* *Cu–L–Cu* (°)		*L–Cu–L* (°)	*Ref.*
							104.4(2)		93.2(2)[d]	
									109.7(2)	
									169.5(2)	
[Cu(μ_3-dpae)Cl]$_4$ (green)	or	15.965(4)		CuO_3NCl	μ_3O	1.955(13,8)	3.190(5)	O,O	80.5(5,3.9)	114
	Pbcn	14.941(1)				2.158(12,18)	3.238(5)	O,N	84.8(6)[c]	
	8	19.305(2)				2.236(14,24)	3.221		87.0(6)	
					N	2.029(20,4)	98.7(5,5.6)	N,Cl;	96.3(6,1.0)	
					Cl	2.228(6,8)		O,Cl	94.7(3,1.0)	
[Cu(μ_3-tde)Cl]$_4$ (green)	m	20.836(3)		CuO_3ClS	μ_3O	1.963(7,29)	3.158(2)	S,Cl	92.3(1,0)	115
	C2/c	9.963(2)	122.57(2)			2.440(8,9)	3.364(2)	O,Cl	94.6(2,2.3)	
	4	17.793(3)			Cl	2.280(3,3)	3.230		173.8(2)	
					S	2.336(3,6)	95.0(3,3.7)	O,S	83.2(2,3.1)[c]	
							107.6(3,1)		109.1(2,1.1)[d]	
									170.3(2,1)	
								O,O	73.8(3,1)	
									88.2(3,8.1)	
									166.9(3,1.0)	
[Cu(μ_3-ipe)(acac)]$_4$ (blue)	m	24.432(4)		CuO_5	μ_3O	1.948(3,13)	2.9970(6)	O,O	81.6(1,2.5)	116
	C2/c	10.771(5)	115.98(2)			2.463(3,8)	3.3396(9)		94.2(1,4.7)[d]	
	8	21.300(4)			acacO	1.910(3,11)	3.2347		101.6(1,1.6)	
							97.8(1,3.0)		171.0(1,9)	
[Cu(μ_3-dbae)Cl]$_4$ (green)	tr	15,563(10)	93.49(10)	CuO_3NCl	μ_3O	1.972(9,42)	3.128(2)	Cl,O	95.3(3,6.0)	117
	P-1	16.280(11)	100.32(10)			2.424(9,66)	3.417(2)		172.5(3,5.0)	
	8	11.659(8)	112.51(10)		N	2.054(11,41)	3.240	Cl,N	97.3(4,1.3)	
					Cl	2.234(4,9)	90.9(3,10)	O,N	84.5(5,1.2)[c]	
							104.0(4,4.2)		128.9(4,5.1)	
									152.4(4,4.4)	
								O,O	79.4(3,6.7)	

[Cu(μ_3-$C_{16}H_{14}N_2O_3$)]$_4$·	m	27.062(5)		CuO_4N	μ_3O	1.983(5,66)	3.021(1)	O,O	75.7(2,2.9)	118
9MeOH (dark green)	12/c	25.062(5)	92.39(1)			2.360(5,33)	3.492(2)		86.2(3.7.0)	
	8	26.390(5)				2.631(6,59)	3.254		93.9(4,2.1)	
					O	1.890(6,8)	89.9(1,3.5)		109.9(4,7.5)	
					N	1.927(7,12)	104.1(1,6.8)		170.4(4,7.0)	
								O,N	84.0(4,1.4)^{c}	
									93.2(4,3)^{d}	
									108.6(4,6.4)	
									169.7(4,7.0)	
[Cu(μ_3-dbae)Br]$_4$ (green)	tr	15.539(10)	94.58(10)	CuO_3NBr	μ_3O	1.963(10.42)	3.134(3)	Br,O	94.8(3,5.4)	117
	P-1	16.452(11)	100.65(10)			2.480(10,85)	3.477(3)		171.1(3.5.5)	
	8	11.766(8)	111.67(10)		N	2.066(13,8)	3.268	Br,N	97.3(4,1.4)	
					Br	2.382(3,13)	90.7(4,1.8)	O,N	84.7(5,1.4)^{c}	
							104.6(5,6.5)		127.2(5,4.0)	
									155.1(5,3.4)	
								O,O	78.9(4,8.1)	
[Cu(μ_3-deae)Cl]$_4$ (green)	tg	11.342(4)		CuO_3NCl	μ_3O	1.971(4,24)	2.935(–)	O,O	79.2(3,3.1)	119
	P4$_1$2$_1$2					2.463(7,48)	3.459(–)	O,Cl	95.2(3,1.1)	
	4	27.861(11)			N	2.076(9,26)	3.274		102.8(3,1)	
					Cl	2.236(3,14)	99.7(3,4.4)		175.5(9,1.4)	
								O,N	85.7(3,5)^{c}	
									116.3(3,4.6)	
									157.8(3,3.9)	
								Cl,N	97.5(3,7)	
[Cu(μ_3-$C_9H_9NO_2$)]$_4$ (green)	tg	13.967(7)		CuO_4N	μ_3O	1.960(4,7)	3.155(–)	O,N	84.9(3)^{c}	120
	P4$_2$/n					2.421(4)	3.343(–)		93.7(3)^{d}	
	8	9.726(6)			O	1.894(5)	3.280		115.7(3)	
					N	1.918(7)	99.5(3,7.8)		164.9(3)	
								O,O	74.0(3)	
									83.0(3,2.5)	
									97.3(3,9)	
									177.3(3)	

TABLE III (*Continued*)

Compound (*colour*)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	*α* (°) *β* (°) *γ* (°)	*Chromophore*	*Cu–L* (Å)		*Cu–Cu* (Å) *shortest* *longest* *average* *Cu–L–Cu* (°)	*L–Cu–L* (°)		*Ref.*
[Cu(μ_3-deae)Br]$_4$ · 4CCl$_4$	tg	19.47(2)		CuO$_3$NBr	μ_3O	1.953(5,29)	3.176(2)	O,O	78.1(3,8.6)	121
(light green)	I4$_1$/a					2.524(5)	3.523(2)	ON	85.1(3)[c]	
	4	15.78(1)			N	2.052(8)	3.291		126.8(3)	
					Br	2.390(2)	88.8(3)		156.4(3)	
							106.5(3,2.4)	O,Br	93.9(2,18)	
									166.5(2)	
								N,Br	97.6(2)	
[Cu(μ_3-apae)(μ-NO$_3$)]$_4$ · 2H$_2$O[e]	m	27.312(15)		CuO$_4$N$_2$	μ_3O	1.964(9,36)	3.224(3)	O,O	71.6(4,1.2)	122
(not given)	C2/c	20.936(13)	128.82(3)			2.594(13,39)	3.443(2)		84.8(4,3.5)	
	8	17.510(9)			N	2.02(1,4)	3.298			
					μO$_2$NO	2.69(2,11)	98.9(5,13.5)			
[Cu$_4$(μ_3-sl)(μ-NO$_3$)(NO$_3$)(EtO) ·	or	28.663(9)		CuO$_4$N$_2$ (×1)	μ_3O	1.96(1,1)	3.069(4)	O,O	76.7(16,8)	123
(NO$_3$)$_2$ · 3EtOH · 2H$_2$O (purple)	P2$_1$2$_1$2	18.599(4)				2.65(2)	3.732(4)		89.7(6,2.3)	
	4	15.509(8)			N	1.99(2,0)	3.306		153.7(5)	
					O$_2$NO	2.93(2)	103.6(7,2.0)	O,N	72.1(7)	
									92.9(7,1.7)	
									104.4(7)	
									114.4(6)	
								N,N	99.6(8)	
				CuO$_4$N$_2$ (×1)	μ_3O	1.98(1,1)		O,O	77.6(7,3.3)	
						2.74(1)			90.3(7,1.5)	
					N	2.00(2,1)			156.9(6)	
					EtO	2.58(2)		O,N	72.2(6)	
									93.7(8,1.2)	
									106.7(7,3.2)	
								N,N	98.6(6)	
				CuO$_4$N$_2$ (×2)	μ_3O	1.97(2,4)		O,O	76.2(7,2.1)	
						2.76(1,2)			86.0(7,6.5)	

					N	1.98(2,5)			157.5(6,4.0)	
					μO_2NO	2.56(2)		O,N	71.0(7,3)	
						2.76(2)			92.6(8)	
									112.1(7,3.7)	
								N,N	99.0(8,4)	
$[Cu(\mu_3\text{-apae})]_4Br_4 \cdot 3H_2O$ (blue)	m	18.648(8)		CuO_3N_2	μ_3O	1.962(7,14)	3.186(2)	O,Br	95.4(2,5.8)	124
	$P2_1/n$	22.013(8)	90.08(4)			2.583(7,62)	3.555(2)		166.0(2,1.3)	
	4	9.237(5)			N	2.008(10,35)	3.307	O,O	79.6(3,9.1)	
							88.3(3,1.1)	O,N	91.9(3,7.8)	
							105.1(3,6.8)		118.5(3,1.9)	
									170.3(4,6.4)	
								N,Br	81.9(3,6.5)	
								N,N	94.4(4,7)[d]	
$[Cu(\mu_3\text{-}C_{17}H_{18}N_2O_3)]_4 \cdot$	tg	17.991(4)		CuO_4N	μ_3O	1.964(4,22)	3.258(1)	O,O	70.7(2)	113
8EtOH (dark green)	$P4_2/n$					2.749(4)	3.412(2)		91.8(2,7.5)	
	2	14.296(4)			O	1.899(4)	3.309		175.6(3)	
					N	1.937(5)	90.3(2,4.2)	O,N	83.8(2)[c]	
							112.0(2)		92.2(2)[d]	
									118.4(2)	
									168.6(2)	
$[Cu(\mu_3\text{-}C_{17}H_{18}N_2O_3)]_4 \cdot 8MeOH$	tg	17.226(4)		CuO_4N	μ_3O	1.961(4,16)	3.259(1)	O,O	70.5(2)	125
(dark green)	$P4_2/n$					2.734(4)	3.481(1)		87.3(2,2.8)	
	2	14.667(3)			O	1.880(4)	3.333		95.8(2,2.6)	
					N	1.941(5)	90.3(3,3.7)		176.1(2)	
							112.4(3)	O,N	83.7(2)[c]	
									92.6(6)[d]	
									118.9(2)	
									168.0(2)	
$Cu_4(\mu_3\text{-dbae})_4(\mu\text{-}Cl_2ac)_3(Cl_2ac)$	tr	13.293(13)	96.32(5)	CuO_5N (×3)	μ_3O	1.94(2,6)	3.134(5)	O,O	70.8(6,6.5)	126
(not given)	P-1	14.130(6)	97.37(6)			2.79(2,18)	3.824(5)		95.9(8,11.8)	
	2	18.471(13)	106.42(6)		μacO	1.94(2,2)	3.372		144.7(6,2.1)	
						2.52(2)	84.0(7,2.0)		172.2(7,5.0)	

TABLE III (*Continued*)

Compound (*colour*)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*	*Cu–L* (Å)	*Cu–Cu* (Å) *shortest* *longest* *average* *Cu–L–Cu* (°)	*L–Cu–L* (°)	*Ref.*
					2.85(3,12)	108.5(7,9.5)	O,N 89.8(8,4.3)^{c}	
					N 2.13(2,2)		113.0(7,2.9)	
							173.1(8,2.4)	
				CuO_4N (× 1)	μ_3O 1.92(1,3)		O,O 85.2(8,13.3)	
					2.60(2)		168.1(7)	
					acO 1.90(2)		O,N 86.9(8,3.0)^{c}	
					N 2.10(2)		123.9(6)	
							162.6(8)	
[Cu(μ_3-deae)(μ-F_3ac)]$_4$	tg	17.903(6)		CuO_5N	μ_3O 1.940(4,7)	3.206(1)	O,O 75.6(1,6.4)	127
(dark blue)	$I4_1/a$				2.721(4)	3.714(1)	94.4(2,5.0)	
	4	14.534(4)			μacO 1.949(4)	3.375	172.1(2)	
					2.756(5)	111.4(2)	N,O 86.0(2)^{c}	
					N 2.100(5)		87.9(2,6.2)	
							109.5(2,4.2)	
							143.1(1)	
							173.7(2)	
[Cu(μ_3-dmae)(μ-F_3ac)]$_4$ (blue)	m	14.073(3)		CuO_5N	μ_3O 1.924(10,12)	3.154(2)	O,O 76.3(4,8.2)	128
	$P2_1/c$	21.379(5)	104.65(2)		2.755(9,64)	3.813(2)	98.6(4,8.2)	
	4	14.201(3)			μacO 1.952(11,18)	3.376	140.4(3,2.0)	
					2.686(12,23)	83.7(3,2)	171.7(5,9)	
					2.846(12,1)	108.7(5,6.0)	O,N 85.9(5,1.2)^{c}	
					N 2.058(13,4)		90.5(5,3.1)	
							116.0(5,1.3)	
							172.7(5,2.5)	
[Cu(μ_3-deae)(Clac)]$_4$ (blue)	tg	18.115(6)		CuO_5N	μ_3O 1.942(7,14)	3.200(–)	O,O 71.6(2,2.2)	129
	$I4_1/a$				2.720(6)	3.746(–)	84.5(3,5.0)	
	4	14.262(7)			acO 1.933(9)	3.382	100.5(4,5.7)	
					2.663(10)	111.0(–)	142.3(3)	

					N	2.101(9)		O,N	89.8(4,4.1)^{c}	
									113.1(3)	
[Cu$_4$(μ_3-apae)$_4$(μ-mal)$_2$]·5H$_2$O (blue)	tg	15.749(16)		CuO$_4$N$_2$	μ_3O	1.973(7,23)	3.222(2)	O,O	75.3(2,5.2)	130
	I4$_1$/a					2.606(6,65)	3.623(2)		89.3(3,6.6)	
	8	34.407(19)			μmalO	2.433(7)	3.385		158.0(3,2)	
						2.871(11)	105.3(3,6.5)	O,N	83.5(3,4.5)^{c}	
					N	2.005(9,34)			94.5(3,2.5)	
									117.7(3,2.1)	
								N,N	94.6(4,2)^{d}	
[Cu(μ_3-C$_{13}$H$_{13}$N$_2$O$_3$)(NO$_3$)]$_4$ (green)	m	20.47(5)		CuO$_3$N$_2$	μ_3O	1.95(4,5)	3.301(12)	O,O	75(2,3)	131
	P2$_1$/n	21.27(5)	93.93(7)			2.13(4,7)	3.541(12)		95(2,5)	
	4	14.31(7)			N	1.95(6,8)	3.387	N,N	84(2,3)	
					O$_2$NO	2.22(4,10)	110(2)	O,N	95(2,16)	
									172(2,2)	
Cu$_4$(μ_3-deae)$_4$(μ-Cl$_3$ac)$_3$(Cl$_3$ac) (blue)	m	14.772(7)		CuO$_5$N (×3)	μ_3O	1.96(2,1)	3.094(4)	O,O	77.3(7,10.3)	132
	P2$_1$/n	19.442(8)	106.87(3)			2.90(2,11)	3.996(4)		97.2(7,8.2)	
	4	20.085(8)			μacO	1.95(2,1)	3.433		143.1(5,4.5)	
						2.51(2,9)	83.2(6,3.2)		173.3(7,2.6)	
					N	2.10(2,1)	109.0(8,10.9)	O,N	85.6(7,1.6)^{c}	
									101.9(8,10.9)	
									175.1(8,2.5)	
				CuO$_4$N (×1)	μ_3O	1.95(2,1)		O,O	77.4(6,3.5)	
						2.52(2)			93.7(7,3.0)	
					acO	1.93(1)			166.2(6)	
					N	2.04(2)		O,N	88.0(7,2.0)^{c}	
									142.5(6,12.0)	
Cu$_4$(μ_3-deae)$_4$(μ-Cl$_2$ac)$_3$(Cl$_2$ac) (blue)	tr	12.370(6)	94.41(1)	CuO$_5$N (×3)	μ_3O	1.94(2,9)	3.176(6)	O,O	71.5(8,8.4)	133
	P-1	12.808(4)	119.97(2)			2.85(2,14)	4.024(6)		90.0(10,4.8)	
	2	20.163(6)	107.80(1)		μacO	1.97(3,1)	3.435		103.3(10,7.6)	
						2.71(3,19)	114.0(10,6.0)		139.8(8,3.6)	
					N	2.09(2,2)			172.7(10,3.3)	
								O,N	93.4(10,4)	
									115.2(10,2.8)	
									173.5(10,2.0)	

TABLE III (*Continued*)

Compound (*colour*)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*	*Cu–L* (Å)	*Cu–Cu* (Å) *shortest* *longest* *average* *Cu–L–Cu* (°)	*L–Cu–L* (°)	*Ref.*
				CuO_4N (×1)	μ_3O 1.89(2,2)		O,O 72.9(9,3.4)	
					2.73(2)		93.9(10,4.9)	
					acO 1.92(3)		125.0(9,5.9)	
					N 2.05(3)		167.3(7)	
							O,N 90.0(11,3.9)	
							121.1(7)	
							166.4(6)	
$Cu_4(\mu_3\text{-dmae})_4(\mu\text{-}Cl_2ac)_2(Cl_2ac)_2$	m	18.675(9)		CuO_5N (×2)	μ_3O 1.954(7,12)	3.124(2)	O,O 69.3(2,1.9)	134
(blue)	C2/c	15.109(8)	101.33(7)		2.858(6)	3.935(2)	90.2(3,4.7)	
	4	16.403(8)			μacO 1.947(8)	3.481	108.5(3)	
					2.517(7)	110.5(3,3.3)	144.5(2)	
					N 2.061(8)		O,N 84.8(3)[c]	
							93.0(4,2.0)	
							110.8(3)	
				CuO_4N (×2)	μ_3O 1.931(6,7)		O,O 75.4(3,3.4)	
					2.633(7)		95.5(3,3.6)	
					acO 1.949(7)		112.9(3)	
					N 2.043(9)		137.5(2)	
							O,N 86.9(3,1.4)[c]	
							91.1(3)	
							118.5(3)	
B: Cu–(X)$_2$–Cu–(X)$_2$–Cu								
$Cu_4(\mu\text{-salen})_2(\mu\text{-}Cl)_2Cl_2$ (black)	m	7.791(6)		CuO_2N_2 (×2)	μO 1.91(1,2)	3.109	O,O 85.1(7)	135
	$P2_1/n$	16.780(6)	100.80(9)		N 1.90(1,1)	O 100.5(7,5.2)	O,N 95.1(7,1.0)[d]	
	2	10.536(5)					175.3(7,4)	
							N,N 85.1(7)[c]	
				$CuCl_3O_2$ (×2)	μO 1.99(1)	3.439	Cl,Cl 88.9(4,4.1)	
					2.30(1)	Cl 95.2(5)	153.6(4)	

					μCl	2.328(4,38)		Cl,O	92.8(6,2.9)	
					Cl	2.239(6)			107.4(6,2.8)	
									174.3(6)	
								O,O	73.3(7)	
$Cu_4(\mu\text{-}Cl)_6(terpy)_2Cl_2$ (green)	tr	11.146(7)	97.13(5)	$CuCl_5$ (×2)	μCl	2.255(1,16)	3.456(1)	Cl,Cl	85.2(1,3.1)	136
	P-1	8.365(4)	93.60(5)			2.344(1)	Not given		95.5(1,2.4)	
	2	9.263(5)	88.82(5)			3.033(1)			169.1(1,2.4)	
					Cl	2.234(1)				
				CuN_3Cl_2 (×2)	μCl	2.221(1)	3.595(1)	Cl,Cl	95.5(1)	
						2.613(1)	90.1(1,5.2)	N,Cl	96.1(1,3.7)	
					N	1.991(4,53)			172.1(1)	
								N,N	79.8(1,2)^c	
									157.8(1)	
$(Me_3NH)_2[Cu_4(\mu\text{-}Cl)_6Cl_4]$ (dark brick red)	m	6.114(3)		$CuCl_4$ (×2)	μCl	2.288(3,27)	Not given	Cl,Cl	89.8(1,3.6)	137
	$P2_1/c$	10.253(4)	97.88(3)						172.4(1,1.0)	
	2	19.05(1)								
				$CuCl_4$ (×2)	μCl	2.306(3,15)	Not given	Cl,Cl	90.1(1,5.7)	
									170.2(1,4.8)	
$(Me_4N)_2[Cu_4(\mu\text{-}Cl)_6Cl_4]$ (red)	m	6.072(2)		$CuCl_4$ (×2)	μCl	2.290(1,30)	Not given	Cl,Cl	90.0(1,5.8)	138
	$P2_1/c$	19.574(1)	99.46(2)				93.5(1,1)		167.6(1,5.4)	
	2	10.610(3)								
				$CuCl_4$ (×2)	μCl	2.318(1,28)	Not given	Cl,Cl	90.0(1,4.5)	
					Cl	2.234(1,19)	93.5(1)		171.6(1,3.3)	
$(4\text{-map})_2[Cu_4(\mu\text{-}Cl)_6Cl_4]$ (reddish brown)	m	3.847(2)		$CuCl_4$ (×2)	μCl	2.272(7,35)	Not given	Cl,Cl	90.0(3,3.7)	138
	$P2_1/n$	21.276(2)	96.44(3)				93.7(3)		178.0(3,6)	
	2	15.336(6)								
				$CuCl_4$ (×2)	μCl	2.372(7,1)	Not given	Cl,Cl	90.0(3,7.4)	
					Cl	2.229(7,3)	99.9(2)		168.9(3,2.3)	
$(Et_4N)_4[Cu_4(\mu\text{-}Cl)_6Cl_6]$ (red)	m	13.779(3)		$CuCl_5$ (×2)	μCl	2.316(2,4)	Not given	Cl,Cl	88.6(1.66)	139
	$P2_1/c$	11.316(2)	106.04(2)			2.662(2)	91.9(1,3.6)		105.6(1,2.3)	
	2	17.883(3)			Cl	2.320(2)			148.8(1)	
									171.4(1)	
				$CuCl_4$ (×2)	μCl	2.287(2,37)	Not given	Cl,Cl	90.0(1,8.4)	
					Cl	2.214(2,2)	96.2(1)			

TABLE III (*Continued*)

Compound (*colour*)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	*α* (°) *β* (°) *γ* (°)	*Chromophore*	*Cu–L* (Å)	*Cu–Cu* (Å) *shortest* *longest* *average* *Cu–L–Cu* (°)	*L–Cu–L* (°)	*Ref.*
$(Me_3NH)_2[Cu_4(\mu\text{-}Br)_6Br_4]$	m	9.556(3)		$CuBr_4$ (×2)	μBr 2.240(6,20)	Not given	Br,Br 90.0(2,4.0)	140
(dark violet)	$P2_1/c$	14.703(4)	99.75(3)			94.0(2,1.8)	174.2(2,4.8)	
	4	18.173(5)						
				$CuBr_4$ (×2)	μBr 2.472(6,39)		Br,Br 90.0(2,6.6)	
					Br 2.378(6,17)		170.0(2,4.5)	
$Cu_4(\mu\text{-}OCMe_3)_6\{OC(CF_3)_3\}_2$ (green)	tr	10.609(3)	100.69(3)	CuO_4 (×2)	μO 1.947(4,31)	Not given	O,O 79.9(2,1.9)	141
	P-1	10.667(3)	95.37(3)			98.9(2,6)	108.5(2,2.8)	
	1	11.151(3)	99.65(3)				148.8(2,3.8)	
				CuO_3 (×2)	μO 1.861(4,5)		O,O 83.3(2)	
					O 1.797(5)		138.2(2,6.7)	
C: **Chain**								
$[Cu_4(\mu\text{-}OH)_3\{(mpi)_4O\}]\cdot 2.5C_6H_6\cdot$	tr	14.586(1)	105.48(1)	CuN_3O_2 (×2)	μHO 1.992(–,53)	Not given	N,N 89.2(–,7)^d	142
H_2O (not given)	P-1	14.925(1)	105.48(1)		2.200(–,68)		177.1(–,2.2)	
	2	20.781(2)	80.24(1)		N 2.002(–,75)		O,O 101.4(–,5.2)	
							O,N 90.3(–,4.4)	
							122.4(–,8.6)	
							150.0(–)	
				CuN_3O (×2)	μHO 1.873(–,10)		N,N 89.7(–,1.0)^d	
					N 1.968(–,87)		154.5(–,2.2)	
							O,N 96.0(–,3.0)	
							153.2(–,2.1)	
$[Cu_4(\mu\text{-}sed)_2(hfacac)_4]\cdot 0.6CHCl_3$	tr	17.370(6)	93.14(5)	CuO_4N (×2)	μO 1.903(6)	Not given	O,O 88.9(3,73)^d	143
(deep green)	P-1	13.374(5)	99.54(5)		2,398(6)	O 94.3(2)	175.0(3)	
	2	8.553(4)	104.33(5)		N 1.966(9)		O,N 92.1(4,4.2)	
					O 1.976(7,39)		104.8(3)	
							168.0(4)	

				CuO$_3$N$_2$ (×2)	μO	2.024(9)		O,O	84.4(3,6)^d	
						2.276(9)			95.1(3)	
					N	1.892(9)		O,N	89.1(4,3.9)	
					O	2.012(11,38)			101.7(4,1.4)	
								N,N	96.1(4)	
[Cu$_2$(μ-C$_{14}$H$_{12}$N$_2$O$_2$)(μ-ac)$_2$]$_2$	tr	8.365(2)	98.40(2)	CuO$_5$ (×2)	μacO	1.913(4)	3.303(1)^c	O,O	83.6(1)^c	131
(brown)	P1	9.667(1)	103.97(5)			2.181(5)	115.3(2)		102.1(2,13.2)	
	2	12.556(1)	94.26(2)		μO	1.958(4,2.4)			163.4(2)	
				CuO$_3$N$_2$ (×2)	μacO	2.077(4,19)		O,O	97.6(2,13.1)	
					μO	1.933(3)		N,N	92.2(2)^d	
					N	2.010(4,1)		O,N	89.6(2)^d	
									100.6(2,15.2)	
									133.9	
									177.1(2)	
[Cu$_2$(μ-salpd)(μ-ac)(μ-OMe)]$_2$	m	11.826(2)		CuO$_5$ (×2)	μMeO	1.922(3,5)	3.027(1)	O,O	73.1(1,3.0)	144
(dark green)	P2$_1$/n	17.192(4)	94.08(2)		μsalpdO	2.027(3)	3.123(1)		93.9(1,1.2)	
	2	9.836(2)				2.323(3)	3.075			
					μacO	1.926(3)	94.2(1)			
							103.4(2,3)			
				CuO$_3$N$_2$ (×2)	μacO	2.235(4)		O,O	80.5(2)	
					μsalpdO	1.944(4,2.0)		O,N	91.2(2)	
					salpdN	1.985(5,7)		N,N	95.7(2)	
[Cu$_2$(μ-cdp)(μ-ac)$_2$]$_2$ · H$_2$O	tr	8.365(2)	98.40(2)	CuO$_5$ (×2)	μO	1.958(4,24)	3.053(1)	O,O	80.3(2,3.4)	145
(pale brown)	P-1	9.667(1)	103.97(2)		μacO	1.913(4)	3.303(1)		96.2(2,2.5)	
	2	12.556(1)	94.26(2)			2.181(5)	3.178		101.6(2,1.0)	
							103.1(−)		160.0(2,3.4)	
				CuO$_3$N$_2$ (×2)	μO	1.933(3)		N,N	92.2(2)^d	
					μacO	2.077(4,19)		N,O	88.6(2,3.2)	
					N	2.010(4,1)			115.4(2)	
									133.9(2)	
									177.1(2)	
								O,O	91.1(2,7)	
									110.7(2)	

TABLE III (*Continued*)

Compound (*colour*)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*	*Cu–L* (Å)		*Cu–Cu* (Å) *shortest* *longest* *average* *Cu–L–Cu* (°)	*L–Cu–L* (°)		*Ref.*
D: **Step-like**										
$Cu_4(\mu_3,\mu\text{-tris})_2Cl_4$ (green)	tr	9.182(1)	99.85(1)	CuO_3NCl (×2)	μ_3O	1.983(6,38)	2.841(1)	O,N	83.8(3)[c]	146a
	P-1	9.120(2)	87.01(1)			2.407(6)	3.233(2)	O,Cl	98.8(2)	
	1	8.817(1)	84.13(1)		N	1.984(7)	2.919	N,Cl	97.9(2)	
					Cl	2.253(2)	92.7(2,14)	O,O	79.8(2)	
				CuO_2NCl (×2)	μO	1.947(5,8)		O,N	84.8(2)[c]	
					N	1.985(7)		O,Cl	98.9(2)	
					Cl	2.260(2)		N,Cl	95.1(2)	
$[Cu_2(\mu_3,\mu\text{-dbm})(\mu\text{-me})_2(\mu\text{-dbm})_2$	tr	13.823(1)	91.699(5)	CuO_5	$\mu_3$dbmO	1.954(2)	2.965[e]	O,O	78,26(10)	110
(green)	P-1	12.473(2)	123.216(5)		μdbmO	1.926(2)	99.3(1,1.6)		88.94(11,7.9)	
	1	12.978(1)	110.723(5)		meO	1.903(2,0)			102.04(11)	
					μmeO	2.697(3)			173.83(10)	
				CuO_5	$\mu_3$dbmO	1.985(2)		O,O	84.6(11,5.20)	
						2.312(3)			101.84(11,3.38)	
					μdbmO	1.925(2)				
					meO	1.927(3)				
					μmeO	1.928(2)				
$[Cu_4(\mu_3\text{-OH})_2(\mu\text{-dfmph})_2]\cdot 2dmf$	tr	11.653(2)	106.23(1)	CuO_4N	μ_3HO	1.926(4,9)	2.938(1)	O,O	81.3(2,2.2)	146b
(dark green)	P-1	12.765(2)	104.68(1)			2.322(5)	3.282(1)		98.2(2,7.5)	
	2	9.318(2)	88.32(1)		μO	1.933(4,11)	3.135	O,N	82.4(2,2)	
						2.718(6)	99.0(2,2.6)		91.4(2,0)	
					O	1.901(5)	88.0(2)		104.4(2,2)	
					N	1.911(5,2)				
$Cu_4(\mu_3\text{-PhCH}_2O)_2(\mu\text{-PhCH}_2O)_2\cdot$	m	11.53(3)		CuO_5	μ_3O	1.88(1,1)	2.995(3)	O,O	94.3(1,4.1)	147
$(\mu\text{-acac})_2(acac)_2$ (blue)	$P2_1/c$	22.68(5)	112.0(3)			2.42(1)	5.399(3)		103.3(1,2.5)	
	2	10.19(3)			μO	1.95(1,1)	3.745			
					μacacO	1.92(1)	104.9(1,1.0)			
						2.71(1)				

					acacO	1.91(1,2)				
$[Cu_2(\mu_3\text{-}N_3)(\mu\text{-}N_3)(N_3)(\mu\text{-md})\cdot(ClO_4)_2]_2$ (dark brown)	tr	14.104(2)	83.79(1)	CuN_4O_2 (×2)	μ_3N	1.973(6)	3.120(1)	O,N	76.5(3)	148
	P-1	12.199(2)	74.19(1)			2.858(6)	5.573(1)		92.4(2)	
	2	10.908(2)	65.32(1)		μN	1.969(7)	3.983		166.1(2)	
					mdN	1.965(6)	O 102.9(3)	N,N	95.3(3,1)	
					μmdO	1.987(5)	N 104.5(4)		168.8(3)	
					O_3ClO	2.563(7)				
				CuN_4O (×2)	μ_3N	1.927(7)		O,N	76.1(2)	
					μN	2.466(7)			92.3(2)	
					N	1.972(7)			166.5(3)	
					mdN	1.973(7)		N,N	95.5(3,2.7)	
					μmdO	2.003(4)			168.3(3)	
$[Cu_2(\mu\text{-}Cl)(\mu\text{-}Cl)(\mu\text{-}Et_2dtc)_2]_2$ (dark)	m	11.203(1)		$CuCl_3S_2$ (×2)		Not given	Not given		Not given	149
	$P2_1/n$	18.989(2)	98.83(1)							
	4	9.043(2)								
				$CuCl_3S_2$ (×2)		Not given			Not given	
$[Cu_4(\mu_3\text{-}OH)(\mu\text{-bpen})_2(H_2O)]\cdot(ClO_4)_2\cdot H_2O$ (green)	or	27.287(14)		CuO_3N_2 (×1)	μ_3HO	1.949(3)	2.928(1)	N,N	81.3(2)[c]	150
	Pbca	12.000(6)			μO	1.903(3)	3.1	N,O	97.8(2,3.4)	
	—	15.487(8)			N	1.984(5,20)	3.019	O,O	80.2(1)	
					H_2O	2.234(4)	HO 97.1(1) 100.4(2)			
				CuO_3N_2 (×3)	μ_3HO	1.956(3)		N,N	82.0(2)[c]	
						2.420(4)		N,O	98.4(2,3.4)	
					μO	1.907(4)		O,O	79.9(1)	
					N	1.985(4,21)				
$[Cu_4(\mu_3\text{-}OMe)_2(\mu\text{-}OMe)_2(dpm)_4]$ (light blue)	m	10.110(2)		CuO_5 (×2)	μ_3MeO	1.958(5,24)	2.9677(8)[e]	O,O	78.7(2,1.0)	96b
	$P2_1/a$	30.162(9)	103.20(2)		μMeO	1.898(5,19)			93.5(2,1.8)	
	2	9.657(2)			dpmO	1.911(5,12)				
						2.379(6)				

TABLE III (*Continued*)

Compound (*colour*)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	*α* (°) *β* (°) *γ* (°)	*Chromophore*	*Cu–L* (Å)	*Cu–Cu* (Å) *shortest* *longest* *average* *Cu–L–Cu* (°)	*L–Cu–L* (°)	*Ref.*
E: **Unique**								
$Cu_4(\mu_3\text{-}OH)_2(\mu\text{-inicNO})_4(\mu\text{-}SO_4)\cdot$	m	19.809(8)		CuO_5 (×2)	μ_3HO 1.98(2,1)	2.855(6)	O,O 89.9(7,7.5)	151
$(H_2O)_4$ (green)	C2	6.844(3)	140.9(3)		μinicO 1.92(2,0)	HO 92.1(5)	164.8(9,4)	
	2	19.533(12)			μO_3SO 1.92(4)	117.9(9)		
				CuO_5 (×2)	μ_3HO 1.95(1)		O,O 86.9(8)	
					μinicO 1.96(2,1)		165.2(6,1.0)	
					H_2O 2.08(1,9)			
$Cu_4(\mu\text{-OMe})_4(\mu\text{-ain})_4(dmf)_2$	tr	9.189(3)	88.09(2)	CuO_2N_2 (×2)	μMeO 1.920(2,6)	2.999(1)	O,O 75.30(9)	152
(not given)	P-1	9.511(2)	83.26(3)		μainN 1.966(2,1)	3.0141(8)	97.2(1,4)	
	1	12.704(2)	66.75(3)			3.006	O,N 94.3(1,2.0)	
						O 102.9(1,6)	166.5(1,4)	
							N,N 92.4(1)	
				CuO_3N_2 (×2)	μMeO 1.933(2,6)		O,O 75.88(9)	
					μainN 1.985(2,20)		O,N 95.2(1,2)	
					dmfO 2.422(3)		170.4(1,2)	
							N,N 93.6(1)	
$[Cu_4(\mu\text{-mob})_2(py)_4]\cdot$	m	19.33(2)		CuO_4N	μmobO 1.890(8,5)	3.021(2)	O,N 96.8(4,2.3)	153
2py (violet)	$P2_1/c$	19.831(6)	97.64(8)		1.905(9,3)	6.9	O,O 77.2(3,0)	
	2	9.809(8)			1.933(8,4)	102.8(4,2)	93.3(3,2.6)^d	
					pyN 2.31(1,2)		164.4(4,1.5)	
$[Cu_4(\mu\text{-}OH)_2(\mu\text{-tnl})(H_2O)_6\cdot$	m	11.907(3)		CuO_3N_2	μHO 1.881(5)	3.190(2)	O,O 92.6(4,3.7)	154
$(EtOH)_2](CF_3SO_3)_6$ (green)	I2/m	19.858(3)	105.31(2)		H_2O 1.968(6)	116.0(5)	O,N 89.5(3,1.9)	
	2	15.965(4)			μtnlN 1.986(7,23)		176.3(4,2.1)	
							N,N 90.3(2)^d	
$[Cu_4(\mu\text{-}OH)_2(\mu\text{-tnl})(H_2O)_8)\cdot$	m	10.813(9)		CuO_3N_2	μHO 1.885(3,0)	3.202(2)	O,O 92.0(2,1.1)	154
$(CF_3SO_3)_6\cdot 6H_2O$ (green)	I2/m	26.204(15)	98.73(8)		μtnl 2.008(5,22)	116.3(3)	O,N 90.8(2,5.4)	
	2	13.489(15)			H_2O 1.962(4)		175.5(2,4.2)	
					2.473(5)		N,N 89.0(2)^d	

$[Cu_4(\mu\text{-}N_3)_2(\mu\text{-bttt})(N_3)_2]\cdot$	m	8.559(3)		CuO_2N_2 (×2)	ubtttO	1.919(4,3)	3.045(1)	O,N	78.2(2)	71
2MeOH (green)	$P2_1/a$	18.719(6)	97.29(4)		N	1.964(4)	3.460(1)		95.8(2,2.4)	
	2	13.485(7)			μN_3N	1.978(2)	3.253	O,O	158.6(2)	
							Not given	N,N	161.9(2)	
				CuN_3O_2 (×2)	μbtttO	1.957(4)		O,N	80.9(2,3.4)	
						2.341(4)			91.7(2,8)	
					N	1.977(5)		O,O	109.5(1)	
					μN_3N	1.978(5)		N,N	96.7(2,1.1)	
					N_3N	1.993(5)			166.0(2)	
$[\{Cu(\mu\text{-fptsc})\}_4(\mu\text{-}P_2O_7)]\cdot$	m	29.074(6)		CuN_2S_2O	μP_2O_7O	1.910(7,6)	3.231(2)	S,S	95.1(1,1.3)	155
nH_2O (dark green)	C2/c	28.021(3)	102.93(2)		N	1.984(8,64)	3.288(2)	S,O	97.8(3,5.0)	
	8	13.374(3)			S	2.273(3,7)	3.260	S,N	88.2(3,4.1)	
						2.881(3,29)			163.4(2,3.2)	
								O,N	95.3(3,1.6)	
									173.5(3,2.6)	
								N,N	81.2(3,3)	
$[Cu_2(\mu_3\text{-OH})(\mu\text{-}F_3ac)(F_3ac)(qu)_2]_2$	tr	10.401(16)	58.07(5)	CuO_4N (×2)	μ_3HO	1.977(6,13)	2.996(4)	O,O	90.3(3,8.9)	156
(green)	P-1	12.773(20)	124.22(4)		μF_3acO	1.936(7)	3.502(5)		100.6(3)	
	1	15.237(24)	113.81(4)			2.174(6)	3.282		166.7(2)	
					quN	1.989(4)	98.6(2)	O,N	92.4(3,5.4)	
							116.9(3)		171.2(4)	
							124.8(3)			
				CuO_4N (×2)	μ_3HO	1.963(6)		O,O	91.7(3,1.3)	
					μF_3acO	1.968(7)			102.4(3)	
						2.200(7)			166.6(2)	
					F_3acO	1.990(6)		O,N	89.4(3,3.7)	
					quN	2.004(6)			174.2(2)	
$[Cu_2(\mu_3\text{-bc})(\mu\text{-bc})(py)_2]_2$	m	16.074(6)		CuO_4N (×2)	μ_3O	2.00(2)	3.08(1)	O,O	87.8(1.0,3.3)	157
(not given)	$P2_1/n$	25.187(8)	95.96(3)			2.74(2,12)	3.68(1)	O,N	93.3(1.0,4.3)	
	4	21.167(6)			μO	1.96(2,1)	3.34			
					O	1.89(2,1)	111.5(1,7.5)			
					pyN	2.01(3,1)	131.5(1,4.5)			

TABLE III (*Continued*)

Compound (colour)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*	*Cu–L* (Å)	*Cu–Cu* (Å) *shortest* *longest* *average* *Cu–L–Cu* (°)	*L–Cu–L* (°)	*Ref.*
				CuO_3N (×2)	μ_3O 1.97(2,1)		O,O 86.6(9,4.9)	
					μO 1.97(2)		O,N 93.5(1.0,1.5)	
					O 1.89(2,2)			
					pyN 2.00(3,1)			
$[Cu_4(\mu\text{-dmap})_2(\mu\text{-ac})_4](PF_6)_2$	m	10.154(5)		CuO_3N	μO 1.879(8,5)	3.305(2)	O,O 92.4(4,2.7)	158
(blue)	$P2_1/n$	12.712(4)	99.05(6)		μacO 1.942(9,23)	3.435(3)	174.7(4,2)	
	2	15.405(9)			N 2.02(1,1)	3.370	O,N 87.8(4,2.1)^c	
						132.1(4)	159.8(4)	
							173.4(4)	
$[Cu_4(\mu\text{-dmap})_3(\mu\text{-ac})_2(\mu\text{-OH})(ac)\cdot$	tr	13.289(6)	97.29(4)	CuO_4N (×1)	μHO 1.92(1)	3.149(3)	O,O 92.5(4,6)	158
$(H_2O)](PF_6)_2$ (dark blue)	P-1	15.737(6)	96.24(4)		μacO 1.97(1)	3.695(3)	173.8(5)	
	2	13.214(5)	103.77(3)		μO 1.970(9)	3.461	O,N 87.6(5,5)^c	
					N 2.02(1)	112.9(5,2.6)	176.4(5)	
					acO 2.68(2)	139.7(5,4)		
				CuO_3N_2 (×2)	μacO 1.97(1,1)		O,O 92.5(5,2.0)	
					μO 1.97(1,2)		169.1(5,3.0)	
					N 2.00(1,1)		O,N 80.0(5,7)	
					2.42(1,1)		89.2(5,6.9)	
							167.2(5,1.8)	
							N,N 112.1(6,2.3)	
				CuO_4N (×1)	μHO 1.92(1)		O,O 92.5(4,1.3)	
					μacO 1.94(1)		173.0(4)	
					μO 1.95(1)		O,N 87.1(5,1.4)^c	
					N 2.01(1)		168.9(5)	
					H_2O 2.47(1)			

$[Cu_4(\mu\text{-dmap})_2(\mu\text{-ac})_3(\mu\text{-OH})\cdot$	tr	13.40(2)	113.65(4)	CuO_4N	μHO	1.91(1,1)	2.998(5)	O,O	87.9(6,1.8)	158
$(\mu\text{-OH}_2)]PF_6$ (blue)	P-1	14.009(7)	95.73(9)		μacO	1.99(1,1)	4.739(4)		95.9(6,10.0)	
	2	11.729(9)	74.81(7)			2.45(2,1)	3.785		168.3(6,1.2)	
					μO	2.00(1,2)	74.4(5,1.9)	O,N	86.6(7,3.0)^c	
					N	2.01(2,2)	105.3(6,1.8)		101.9(7,1.1)	
							136.1(7,5)		170.2(7,6)	
				CuO_4N	μHO	1.93(1,1)		O,O	90.7(6,1.8)	
					μacO	1.99(1,2)			171.2(6,4.0)	
					μO	2.01(1,2)		O,N	87.5(7,2.2)^c	
					μH_2O	2.44(1,7)			100.2(6,1)	
					N	2.00(2,1)			176.7(7,1.0)	
$[Cu(\mu\text{-bc})(py)]_4\cdot 2MeCN$	or	13.395(5)		CuO_3N	μO	1.941(8,22)	3.152(1)	O,O	87.2(4,2.5)^c	159
(brown)	$P2_12_12_1$	24.287(11)			O	1.891(9,42)	3.572(1)		171.0(4,4.4)	
	4	24.918(11)			pyN	2.007(11,17)	3.377	O,N	92.1(4,6.3)	
							Not given		171.3(4,7.8)	
$[Cu(\mu\text{-pysad})(H_2O)]_4(NO_3)_4$	tg	14.83(2)		CuO_3N_2	μO	1.968(6,3)	3.077(2)	O,O	74.4(3)	160
(green brown)	$P4_22_12$				N	2.006(8,31)	4.259(2)		87.1(3)	
	2	13.58(2)			H_2O	2.225(10)	3.502	O,N	96.2(3,5.5)	
							102.9(3)		150.5(3)	
									173.5(2)	
								N,N	96.2(3)	
$[Cu_4(\mu\text{-deaH})_2(\mu\text{-dea})_2](ClO_4)_2\cdot$	m	24.703(14)		CuN_3O (×2)	μdeaN	1.97(1,7)	3.334(3)	N,N	84.9(5)^c	161
H_2O (black green)	C2/c	5.887(5)	126.50(4)		μdeaHO	1.93(1)	3.847(3)	N,O	85.7(5,6)^c	
	4	28.998(15)			μdeaHN	1.90(2)	3.591			
							Not given			
				CuO_2N_2 (×2)	μdeahO	1.89(1)		N,N	82.9(6)^c	
					μdeaO	1.91(1)		O,O	89.7(5)	
					μdeaN	1.99(1,7)		O,N	101.2(6)	
$[Cu_4(\mu\text{-deaH})_2(\mu\text{-dea})_2](ClO_4)_2$	m	12.627(4)		CuN_3O (×2)	μdeaHO	1.873(8)	3.329(1)	N,N	84.8(3)^c	161
(black green)	$P2_1/n$	7.344(2)	90.38(2)		μdeaHN	1.934(7)	3.861(1)	N,O	85.3(3,1.9)^c	
	2	22.250(9)			μdeaN	1.979(8,75)	3.595			
							Not given			

TABLE III (*Continued*)

Compound (colour)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*	*Cu–L* (Å)		*Cu–Cu* (Å) *shortest* *longest* *average* *Cu–L–Cu* (°)	*L–Cu–L* (°)		*Ref.*
				CuO_2N_2 (×2)	μdeaHO	1.9096(7)		N,N	83.1(3)[c]	
					μdeaO	1.917(6)		O,O	90.3(3)	
					μdeaN	2.000(8,9)		N,O	101.1(3)	
[Cu(μ-Mepz)$_2$(μ-Meacpz)(NO_3)$_2$]	m	11.245(3)		CuO_3N_2 (×2)	μacpzO	1.924(3)	3.3174(8)	N,N	99.0(2)	162
(dark blue)	$P2_1/n$	13.690(4)	109.31(3)		μpzN	1.948(4,6)	5.106(1)	O,O	54.0(2)	
	2	13.553(5)			O_2NO	1.991(4)	4.058		90.9(1)	
						2.572(5)	Not given	N,O	88.3(2,1.3)	
									159.7(2,3.9)	
				CuN_3O (×2)	μacpzO	1.926(3)		N,N	95.1(2,1.0)	
					μpzN	1.943(4,12)			169.2(2)	
								N,O	84.9(2,2.9)	
									176.1(2)	
[Cu(μ-imp)(NO_3)]$_4$ · 8H_2O	tg	19.334(4)		CuN_3O_2	impN	1.95(1,0)	3.435(4)	N,N	80.7(5)[c]	163
(dark green)	$I4_1/a$				impO	1.96(1)	4.456(4)		112.6(6,6.6)	
	4	15.257(13)			O_2NO	2.81(2)	4.116		165.7(6,4.8)	
								N,O	86.6(6,6.2)	
								O,O	77.6(6)	
[Cu(μ-ppt)(H_2O)]$_4$(NO_3)$_4$ · 12H_2O	tg	18.868(3)		CuN_4O	μpptN	2.004(2,36)	4.2686(4)	N,N	76.6(1)	164
(dark green)	$I4_1/a$					2.289(2)	4.3195(5)		90.9(1,10.9)	
	16	18.936(2)			H_2O	1.951(2)	4.2941		105.9(1)	
								N,O	92.8(1,9)	
[Cu$_2${μ-S_2C_2(NCH_2CH_2OH)$_2$} ·	m	24.211(6)		CuO_3NS (×2)	O	2.052(3)	3.999(1)	S,N	86.4(1)[c]	165
(H_2O)SO_4](μ-OH)$_2$}$_2$ (green)	C2/c	8.173(5)	110.68(2)		N	1.947(3)	5.648(1)	N,O	80.8(1)[c]	
	8	15.179(6)			S	2.300(1)	4.650		106.0(1)	
					O_3SO	1.949(3)		O,O	87.9(1,8)	
					μH_2O	2.487(3)		O,S	100.9(1,2.2)	
				CuO_3NS (×2)	O	2.061(3)		S,N	87.0(1)[c]	
					N	1.950(3)		N,O	82.5(1)[c]	

					S	2.286(1)			106.9(1)	
					H_2O	1.958(3)		O,O	90.1(1,2.0)	
					μH_2O	2.300(3)		S,O	97.4(1,9)	
[Cu(μ-im)(tac)]$_4$(ClO_4)$_4$ ·	m	15.088(4)		CuN_5	μimN	1.985(14,30)	5.891(3)	N,N	81.4(6,1.6)^c	166
$2H_2O$ (deep blue)	$P2_1/c$	14.430(3)	102.05(2)		tacN	2.064(14,30)	5.987(3)		92.4(6,1.2)	
	2	14.713(5)				2.234(15,1)	5.923		106.2(6,3.1)	
							Not given		169.3(6,4.4)	
[Cu_4(μ-im)$_2$(μ-bpim)$_2$(NO_3)$_3$ ·	tg	27.204(10)		CuN_4O_2 (×2)	μbpimN	2.007(5)	5.911(2)	O,N	84.5(–,5.0)	167
(H_2O)](NO_3) · $2H_2O$ (deep blue)	$I4_1/a$					2.040(5,50)	8.628(2)		95.0(–,5.0)	
	8	14.704(6)			μimN	1.969(5)	6.725	O,O	165.4(–)	
					H_2O	2.428(7)	Not given	N,N	85.5(2,4.0)^c	
					O_2NO	2.734(6)			94.4(2,4)	
									172.0(2,3.7)	
				CuN_4O_2 (×2)	μbpimN	1.992(5)		O,N	83.4(–,2.8)^c	
					bimN	2.028(5,25)			96.0(–,5.5)	
					μimN	1.964(5)		O,O	166.7(–)	
					O_2NO	2.587(6)		N,N	80.9(2)^c	
						2.840(14)			93.1(2,5.0)	
									170.5(21.6)	
[Cu_2(μ_3-OH)(μ-$C_{19}H_{21}N_6O$) ·	m	14.67(1)		CuO_3N_2 (×2)	μ_3HO	1.937(5)	3.047(2)^e	N,N	93.9(2)^d	168
(H_2O)]$_2$(BF_4)$_2$ SiF_6 · 0.84H_2O	C2/c	22.23(1)	125.13(2)			2.516(5)	100.6(2,2.7)	N,O	96.8(2,5.1)	
(not given)	8	19.18(1)			μO	1.969(6)	114.2(2)		165.8(2,3.9)	
					N	1.952(8,13)		O,O	79.2(2,1.6)	
									93.7(2)	
				CuO_3N_2 (×2)	ν_3HO	1.971(5)		N,N	93.5(2)^d	
					μO	1.970(6)		N,O	95.4(2,4.1)	
					N	1.957(7,1)			167.7(2,1.5)	
					H_2O	2.334(8)		O,O	76.8(2)	
									92.0(2,2.6)	
[Cu_2(μ-dip)Cl_2]$_2$ · $2H_2O$	m	11.646(5)		CuN_3OCl (×2)	μdipN	1.990(4,5)	4.423(2)^e	Cl,N	94.8(1)	169
(dark green)	$P2_1/n$	22.831(8)	90.6(2)			2.401(6)			105.6(1)	
	4	9.172(5)			μdipO	1.968(3)			158.8(1)	
					Cl	2.241(2)		N,O	82.0(1,7.9)	
									169.7(1)	
								N,N	80.4(1)	

TABLE III (*Continued*)

Compound (*colour*)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*	*Cu–L* (Å)	*Cu–Cu* (Å) *shortest* *longest* *average* *Cu–L–Cu* (°)	*L–Cu–L* (°)	*Ref.*
							95.4(1)	
							110.2(1)	
							Cl,O 92.9(1)	
				CuN_4Cl (×2)	μdipN 1.990(4,41)		Cl,N 97.1(1,6.4)	
					Cl 2.472(4)		N,N 84.3(1,5.2)	
							104.5(1)	
							163.5(1,6.7)	
$[Cu_4(\mu\text{-paa})_2(bipyam)_4(H_2O)_2\cdot$	tr	13.825(6)	92.23(3)	CuO_3N_2 (×2)	μpaaO 1.95(5)	4.585(2)^e	Not given	170
$Cl_2](NO_3)_2\cdot MeOH\cdot 10H_2O$ (dark green)	P-1	14.034(6)	98.89(5)		2.30(2)			
	2	19.231(5)	98.47(6)		N 2.01(2,4)			
					H_2O 2.29(2)			
				CuO_2N_2Cl (×2)	μpaaO 1.95(5)		Not given	
					2.34(2)			
					N 2.01(2,4)			
					Cl 2.29(1,3)			
$[Cu(\mu\text{-}C_{12}H_{24}N_4O_2)]_3\cdot$	tr	12.426(1)	102.35(1)	CuN_4 (×2)	N 1.980(7,44)	5.395(1)^e	N,N 90.5(2,6.8)	50
$[Cu(\mu\text{-}C_{12}H_{24}N_4O_2)]_4(NO_3)_4$ (pale blue)	P-1	13.405(1)	105.34(1)				167.9(2,5.7)	
	1	15.605(2)	113.74(1)					
				CuO_3N_2 (×2)	N 1.982(7,5)		O,O 78.9(1)^c	
					O 1.994(5,12)		97.4(2,6.3)	
					2.244(5)		N,O 93.7(2,10.7)	
							167.6(2,3.4)	
							N,N 93.3(2)^d	
				CuO_4	see Table I			
				CuN_4	(trimer)			
$[Cu_4(\mu\text{-inp})_2(phen)_4(H_2O)_4]\cdot(NO_3)_2\cdot$	or	18.823(6)		CuN_3O_2 (×2)	μO 1.956(10,3)	Not given	Not given	171a
$14H_2O$ (dark green)	$C222_1$	24.513(10)			μN 2.017(12,4)			
	8	40.253(20)			phenN 2.011(12,13)			
					H_2O 2.183(11,14)			

				CuN_3O_2 (×2)	μO	1.939(13,10)		Not given	
					μN	2.010(13,9)			
					phenN	2.010(14,20)			
					H_2O	2.229(12,7)			
$[Cu_4(\mu\text{-adpH})_2(bpy)_4(H_2O)_2 \cdot$	m	12.705(4)		CuO_3N_2		Not given	Not given	Not given	171b
$(NO_3)_2] \cdot 2NO_3$ (blue)	$P2_1$	25.279(8)	95.58(2)						
	2	12.985(3)							

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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 parenthesis is e.s.d., the second is maximum deviation from the mean value.

[b] The chemical identity of coordination atom/ligand is specified in these columns.

[c] Five-membered metallocyclic ring.

[d] Six-membered metallocyclic ring.

[e] Calculated by us.

[f] Tetrameric unitsare joined by NO_3 groups.

[g] Four-membered metallocyclic ring.

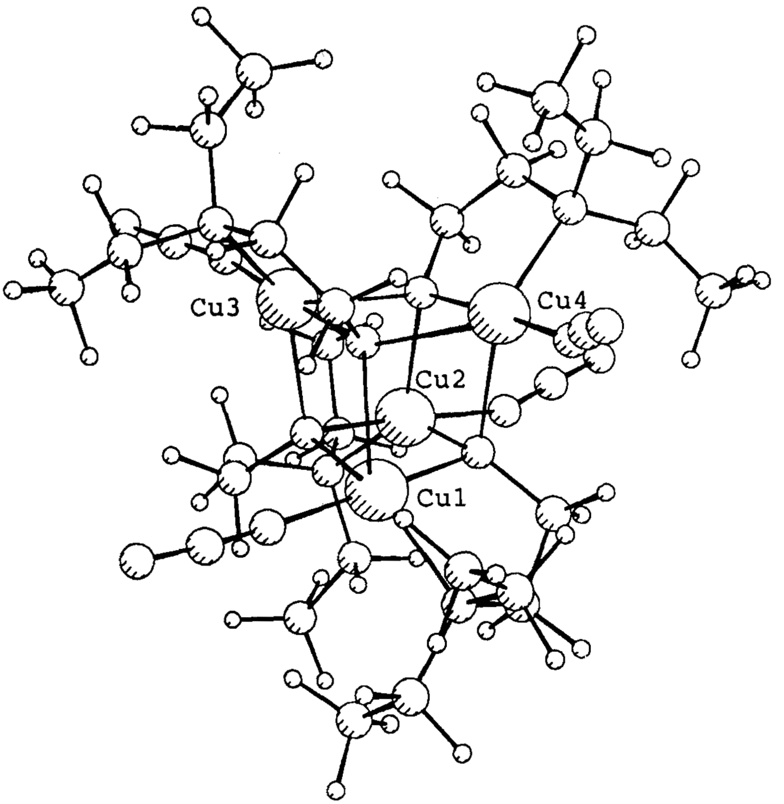

FIGURE 6 Structure of $[Cu(\mu_3\text{-deae})(NCO)]_4$.[108]

six-coordinate[99,111,122,123,127–130] and five- plus six-coordinate sub-site coordination.[126,132–134] The Cu–Cu separations in these cubic frameworks range from 3.094(4) to 4.024(6) Å (mean 3.43 Å) suggesting an absence of metal–metal bonding. The Cu–O–Cu bridge angles range from 85° to 112.5° with a mean of 97.5°. The mean Cu–L terminal bond distance increases in the sequence: 1.915 Å (NL) < 2.16 Å (OL) < 2.24 Å (Cl) < 2.38 Å (Br). The mean Cu–O (bridge) bond distance is 2.21 Å. In the series of hetero donor ligands, O plus N; O plus S; two O plus N; O plus 2N donor sites *only O atoms* serve as bridge with mean Cu–O bond distance 2.23 Å.

3.3 Bifolded Dimers

In Table IIIB are summarized crystallographic and structural data for thirteen tetrameric units formed by bifolded dimers. In a black derivative[135] two chlorine atoms bridge binuclear species Cu(salen)$CuCl_2$. The copper(II) atoms bonded by the organic ligands are four-coordinate (CuO_2N_2) with a planar donor stereochemistry, the remaining copper atoms are five-coordinate with the ligands in a distorted square-pyramidal geometry ($CuCl_3O_2$). The Cu–Cu separations of 3.109 and 3.439 Å ruled out a metal–metal bond. The structure of a green complex, $Cu_4(\mu\text{-}Cl)_6(terpy)_2Cl_2$,[136] consists of a discrete neutral tetrameric unit formed by slightly bifolded $[Cu_2Cl_6]^{2-}$ dimers stacked between two planar $[Cu(terpy)Cl]^+$ entities. The coordination geometry around each copper(II) atom is square-pyramidal (Table IIIB).

In another three examples (red)[137,138] the $Cu_4Cl_{10}^{2-}$ anion exists as a discrete dibridged tetrameter. The structure of another red derivative[139] consists of discrete Et_4N^+ cations and $Cu_4Cl_{12}^{4-}$ anions. The centrosymmetric anions contain copper(II) atoms in two distinct coordination geometries, the central pair of copper(II) atoms have 4 + 1 coordination while the outer pair have a distorted tetrahedral geometry. The central pair are joined by two symmetrical Cu–Cl–Cu bridges with bridging bond angles of 96.35°. One symmetrical Cu–Cl–Cu bridge and one asymmetrical Cu–Cl–Cu bridge link each outer copper(II) atom to a central atom. The bridging angles are 95.51° and 88.30°, respectively.

In a dark violet derivative[140] the $Cu_4Br_{10}^{2-}$ anion exists as a discrete dibridged tetramer where the copper(II) atoms assume a nearly square-planar geometry.

The structure of a green complex, $Cu_4(\mu\text{-}OCMe_3)_6\{OC(CF_3)_3\}_2$,[141] consists of three Cu_2O_2 linked twisted rings with bridging $OCMe_3$ groups and two terminal $OC(CF_3)_3$ groups, where the central Cu(II) atoms are four-coordinate and the two outer Cu(II) atoms are three-coordinate. The CuO_3 moieties are Y-shaped, and the interior CuO_4 moieties are compressed tetrahedra.

3.4 Chain Structures

The molecule $[Cu_4(\mu_3\text{-}OH)_3(mpi)_4O]$[142] contains two square-planar and two trigonal-bipyramidal Cu(II) atoms, each coordinated to three nitrogen atoms of the tridentate mpi ligand and linked in a linear array by three bridging hydroxyl groups. In addition a single oxygen atom, located on a pyridil α carbon of the mpi ligand is distributed nonstatistically over the linear tridentate ligands (Table IIIC).

In a deep green derivative[143] two symmetry independent copper(II) atoms in the centrosymmetric tetrameric complex are five-coordinate with

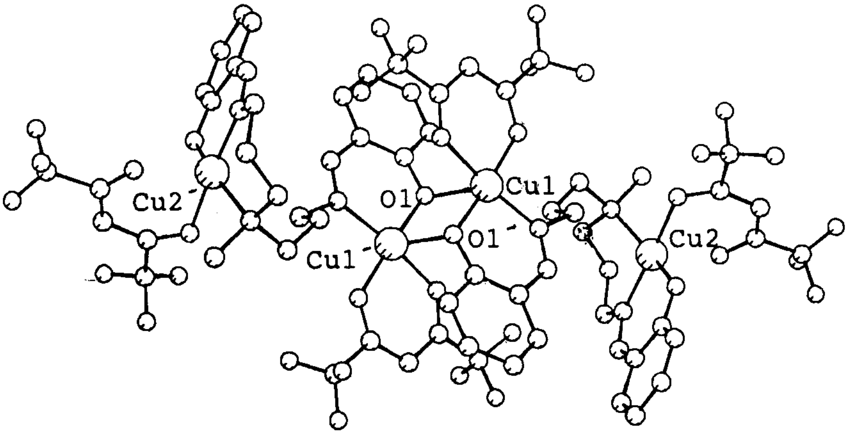

FIGURE 7 Schematic outline of the $Cu_4(\mu\text{-sed})_2(hfacac)_4$.[143]

distorted square-pyramidal geometries. The two inner copper(II) atoms bridged by the salicylaldimine oxygen, are close to each other (3.176(1) Å), whereas the outer copper(II) atoms are separated by considerable distances (> 6 Å) from the other metal centers in the structure (Figure 7).

A dark green complex[144] forms a centrosymmetric molecule made up of two units of $[Cu(\mu\text{-salpd})(\mu\text{-ac})Cu]$ bridged by a pair of methoxo groups. Each terminal copper(II) atom forms four short bonds with N and O donor atoms of sapd and a slightly longer bond with one oxygen of the acetato groups. Each inner copper(II) atom is also pyramidally coordinated by two methoxo oxygens, one of the acetato oxygens, and one of the bridging salpd oxygens (Table IIIC).

The structure of a pale brown complex[145] is composed of two halves related by a center of symmetry located at the center of the CuOCuO parallelogram. Each half of the molecule contains a dicopper unit where the metal atoms are bridged by the ligand and two acetate ions. There are two nonequivalent pairs of Cu(II) atoms, the inner are square-pyramidal (CuO_5) and the outer are trigonal-bipyramidal (CuO_3N_2). The Cu–Cu distance within the dimeric moiety is 3.303(1) Å. The distance is longer than the Cu–Cu distance (3.053(1) Å) between the two dimeric units.

3.5 Step-like Structures

There are seven derivatives[110,146–150] where a step-like structure of the tetramers is formed (Table IIID). A green derivative[146a] consists of two dimeric units related by inversion symmetry and held together by an oxygen-bridging donor atom. Thus the complex should be considered as a tetramer with a step-like geometry of the central core, containing both four- and five-coordinate copper(II) atoms.

In a dark green derivative[146b] two dimeric moieties, $Cu_2(OH)(dfmph)$, related by the center of symmetry are bridged by two hydroxide groups and as a result form a tetrameric structure in a stepped geometry. The molecule of a blue derivative[147] consists of two approximately planar benzoxy-bridged dimers $(acac)Cu(\mu\text{-}OCH_2Ph)_2Cu(acac)$, joined together by apical Cu–O bonds of length 2.42 Å. The coordination of the copper(II) atoms (CuO_5) is approximately square-pyramidal.

A step-like structure of a dark brown complex[148] is formed by two dimeric subunits which are inverted by a center of symmetry (Figure 8). The subunits are asymmetrically bridged dimeric moieties with a phenolate and an arido bridge. There are two pairs of copper(II) atoms, tetragonal-bipyramidal (CuN_4O_2) and square-pyramidal (CuN_4O).

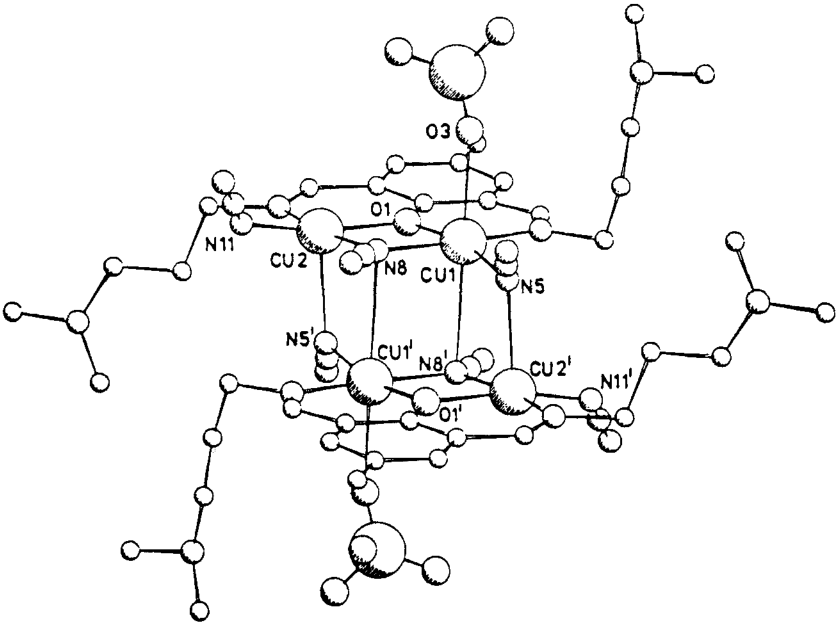

FIGURE 8 Structure of $[Cu_2(N)_3(md)(ClO_4)_2]_2$.[148]

A light blue derivative[96b] is also a step tetramer. The Cu_4O_4 core was described in terms of two interacting methoxy-bridged dimers of $Cu_2(MeO)_2(dpm)_2$ (Table III D).

Another green complex[150] also involves pairs of dimeric units in a stepped geometry. Each copper(II) atom has a square-pyramidal environment (CuO_3N_2) with displacement of the copper(II) atom from the basal plane (O_2N_2) by 0.126 and 0.179 Å.

3.6 Unique Structures

Crystallographic and structural data for unique tetrameric derivatives are summarized in (Table IIIE). In the structure of a green derivative[151] there are four square-pyramidally coordinated copper(II) atoms, which are connected by four bridging carboxylate groups of isonicotinato-N-oxide, by two μ_3-hydroxide groups, and by one bridged bidentate sulfate group, with the Cu_4O_4S cage in the center of the structure and a Cu–Cu distance of 2.855(6) Å.

Another tetrameric derivative[152] contains four methoxide bridges, four 7-azaindolate bridges and two coordinated dimethylformamide molecules. Two kinds of Cu(II) atoms were found in the structure, one with square-pyramidal geometry (CuO_3N_2) and the other with square-planar geometry (CuO_2N_2). The Cu–Cu distances are 2.999(1) and 3.014(1) Å.

Violet $Cu_4(\mu\text{-mob})_2(py)_4$[153] consists of two binuclear copper(II) triketonate-type moieties linked through 1,3-substitutions on phenyl rings. The Cu–Cu separation within a dimeric unit is 3.021(1) Å and the closest Cu–Cu distance between the dimeric units is 6.9 Å. Each copper(II) atom is bounded to four ketonate oxygens and one pyridine nitrogen in typical square-pyramidal geometry. The O–Cu–N angles deviate from 90° (av. 97°) due to the copper(II) atoms residing out of the ligand plane an average of 0.21 Å in the direction of the pyridine.

The structure of $[Cu_4(\mu\text{-tnl})(\mu\text{-OH})_2((H_2O)_8]^{6+}$[154] is shown in Figure 9. The structure represents a unique arrangement in which four square-pyramidal copper(II) atoms are grouped in two pairs on opposite sides of the benzodipyridazine fragment, and within each dimeric unit the coppers are bridged equatorially by the diazine N_2 group and a hydroxide. Two water molecules complete the copper coordination sphere with a O_2N_2 in plane donor set. The copper(II) atom is displaced from the O_2N_2 plane by 0.055(3) Å, towards the axial water molecule.

A green derivative[71] contains a non-planar $Cu_4(\mu\text{-}N_3)_2$ core. The μ-azido ligands lie on either side of the macrocyclic plane. The two independent

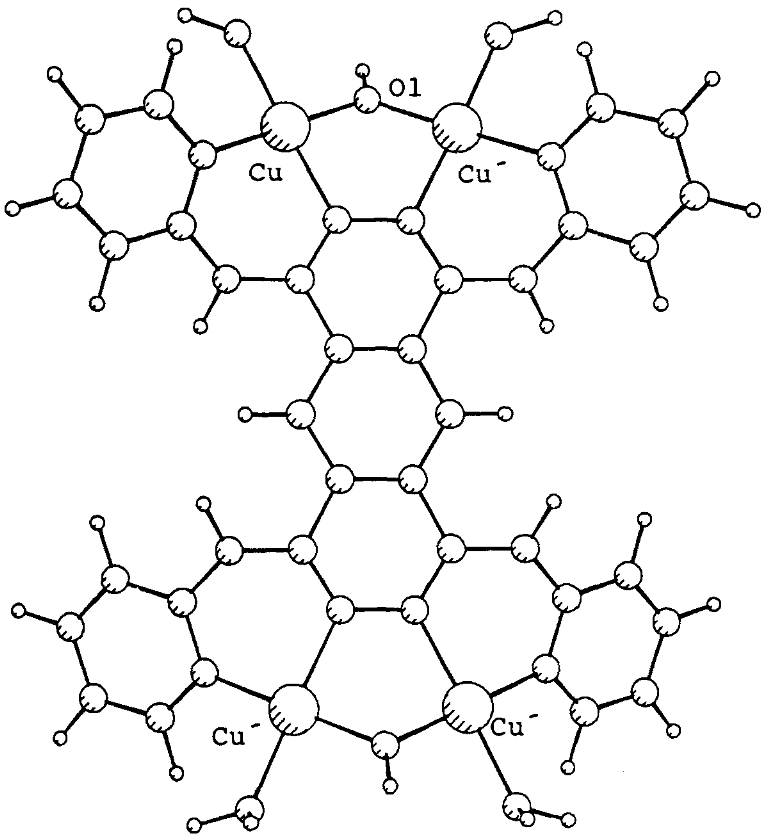

FIGURE 9 Structure of $[Cu_4(\mu\text{-tnl})(\mu\text{-OH})_2(H_2O)_8]^{6+}$.[154]

copper(II) atoms have different coordination environments, square-planar and square-pyramidal with displacement of Cu(II) by 0.2 Å from the mean plane.

The structure of the dark green complex[155] may be considered as a pair of dimeric $\{Cu(\mu\text{-fptsc})^+\}_2$ units linked by a $P_2O_7^{4-}$ anion, $(LCu)_2\text{-}OP(O)_2\text{-}OP(O)_2O\text{-}(CuL)_2$. The dimeric units are further linked by Cu–S axial bonds. These axial bonds range in length from 2.852(3) to 2.895(3) Å and result in a Cu–Cu separation within $(CuL^+)_2$ dimers of 3.231(2) and 3.288(2) Å.

A crystal structure of a green compound[156] is comprised of centrosymmetric tetrameric molecules in which copper(II) atoms are linked by carboxylate bridges and by triply-bridging OH groups. Each of the two crystallographically independent Cu(II) atoms is coordinated to four oxygen atoms and a quinoline nitrogen atom in a distorted square-pyramidal configuration. The displacements of copper(II) atoms from their basal coordination planes are 0.151 and 0.174 Å, respectively.

In $[Cu(bc)(py)]_4$[157] four Cu(II) atoms are connected by μ_3-O and μ-O of bc ligands with Cu–Cu distances ranging from 3.08(1) to 3.68(1) Å. There are two pairs of nonequivalent Cu(II) atoms that are four- and five-coordinate (Table IIIE).

In another three blue derivatives[158] a planar twelve-membered ring is formed by four copper(II) atoms, two oxygen atoms from the dmap ligands, and two CO_2 groups. The four copper(II) atoms have an approximate rectangular arrangement.

A brown complex[159] exhibits four square-planar Cu(II) centers, each bonded to two oxygens of a chelating catecholate, a pyridine nitrogen and a bridging oxygen from a neighboring catecholate. The Cu–Cu distances range from 3.152(1) to 3.572(1) Å.

Four copper(II) atoms in a green-brown complex[160] are situated in an almost square arrangement with two independent Cu–Cu distances of 3.077(2) and 3.171(2) Å. The tridentate Schiff base ligand (N-2-pyridilsalicylaldiminate) is coordinated to three different copper(II) atoms, the phenolic oxygen bridging two of the atoms, while the pyridine nitrogen atom is coordinated to the third. A water molecule occupies the axial position of a distorted square-pyramidal coordination sphere about the Cu(II) atom. The copper(II) is located 0.25 Å above the weighted least-squares plane and is displaced towards the axial water molecule.

Two black-green derivatives[161] are basically similar, consisting of centrosymmetric tetrameric complex cations. The Cu(II) atoms have a square-planar coordination environment in which each ligand is bound to Cu(II) through its amino and oxime nitrogen atoms. There are two pairs of crystallographically independent Cu(II) atoms with coordination spheres of CuN_3O and CuO_2N_2, respectively. The complex moieties themselves are nearly planar.

A dark blue derivative[162] appears to be tetrameric with C_i symmetry. The structure is built up by four copper(II) atoms, arranged at the corners of a parallelogram, with side lengths of 3.3174(8) and 3.4159(8) Å and angles of 81.38(2)° and 98.62(2)°. All sides are bridged by 3(5)-methylpyrazolate ligands. The short sides are additionally bridged by oxygen atoms of the 1-(1-ethanoyl)-5-methylpyrazolate ligand.

A dark green cluster[163] consists of four copper(II) atoms at the vertices of a flattened tetrahedron with Cu–Cu separations of 3.435(4) and 4.456(4) Å. Each copper(II) is in a distorted square-pyramidal environment consisting of three nitrogen atoms and one oxygen atom from the N,N′-imidopicolinyloxamylhydrazin, and an apical oxygen from a nitrate group.

The structure of a dark green derivative[164] consists of four copper(II) atoms at the vertices of a slightly distorted tetrahedron with four ligands bridging the edges of the tetrahedron and four coordinated water molecules. The coordination geometry around the copper(II) atoms is a distorted square-pyramid (CuN_4O). The tetrameric unit has two different Cu–Cu distances, 4.2686(4) and 4.3195(5) Å, respectively.

The structure of a green complex[165] consists of dimeric units $[Cu_2\{\mu\text{-}S_2C_2(NCH_2CH_2OH)_2\}(H_2O)(SO_4)]$ doubly bridged by water molecules making tetrameric entities. The coordination of each copper is 4 + 1 in the form of a square pyramid, the apex of which is occupied by an oxygen atom of the bridging water molecule.

In a deep blue derivative[166] each of the four (tac)Cu units is coordinated *via* two imidazolate anions to two (tac)Cu units, yielding four distorted square-pyramidal CuN_5 polyhedra. The four copper(II) atoms which lie on a plane form an approximate parallelogram with sides of 5.891(3) and 5.987(3) Å.

In a deep blue derivative[167] the tetrameric cation of two Cu_2bpim^{3+} units is joined by two bridging imidazole ligands and has a crystallographically required two-fold axis. Three N atoms of the bpim ligand (Cu–N = 1.99–2.09 Å) and one N of the im ion (Cu–N = 1.967(5) Å) form the principal copper coordination plane. Axial sites are occupied by water and nitrate O atoms (Table IIIE). The four Cu(II) atoms lie within ±0.36 Å of the best plane through them and form an approximate parallelogram of sides 6.214(2) Å (within the Cu_2bpim^{3+} group) and 5.911(2) Å (between the Cu_2bpim^{3+} groups).

In another derivative[168] two Cu(II) atoms are bridged by the OH group and by the oxygen atom of the multidentate $C_{19}H_{21}N_6O$ ligand; the four N atoms of the ligand complete a roughly square-planar coordination about the two Cu(II) atoms. Each Cu(II) atom has an additional axial ligand, a water molecule in the case of Cu(B) and, in the case of Cu(A), the hydroxyl oxygen from a neighboring dimeric species related by a diad.

The main features of a dark green derivative[169] are the presence of two nonequivalent copper(II) atoms and the octadentate behavior of the dip ligand. There are two coordination polyhedra quite different in geometry, even though the copper(II) atoms are both five-coordinate in distorted square-pyramidal arrangements. For Cu(1) the basal corners of the pyramid are occupied by a chloride, two nitrogen atoms from dip and an oxygen atom from an adjacent dip molecule, while a nitrogen atom from the same adjacent ligand is at the apex. The Cu(2) environment is more regular and involves four nitrogen atoms from the same dip molecule at the base and a chloride in an apical position. In both cases the atoms forming the base of the pyramid are not coplanar, but tetrahedrally arranged with the copper(II) atoms displaced from the mean plane, forward the apex, by 0.24 and 0.25 Å, respectively.

An X-ray structure of a dark green derivative[170] reveals that the compound is tetrameric with four square-pyramidally coordinated copper(II) atoms, two paa moieties and four bipyam ligands. The basal sites for the two Cu(1) atoms are occupied by two bipyam nitrogens, one phenolic oxygen and one carboxylate oxygen. The axial position is filled by a water molecule. On the other hand, for the two Cu(2) atoms the phenolic oxygen at the basal site is replaced by a chloride and a 5-hydroxymethyl oxygen of the pyridoxic acid occupies the axial position. The pyridoxic acid moiety bridges three copper(II) atoms in both a mono- and bidentate fashion.

A pale blue crystal[50] consists of tricopper and tetracopper dications packed together in a 1 : 1 ratio and placed around inversion centers. The tricopper cation was discussed in Section 2. The tetracopper cation contains two inner square-pyramidal CuO_3N_2 units and two outer CuN_4 square units (Table IIIE).

There are almost thirty tetrameric derivatives (Table IIIE) whose structures are complex. The predominant geometry about copper(II) is square-pyramid, with some examples[158,159,161] of square-planar and one example[167] in which copper(II) atoms are in a *pseudo*-octahedral environment.

A summary of the data in Table IIIB–E reveals that the mean Cu–L lengths increase in the sequences: monodentate L; 2.05 Å (NL) < 2.27 Å (Cl) < 2.315 Å (OL) < 2.38 Å (Br); bidentate L; 1.975 Å (NL) < 2.02 Å (OL); bridging μ-L; 1.95 Å (OH) < 2.03 Å (OL) < 2.22 Å (NL) < 2.33 Å (Cl) < 2.44 Å (Br); bridging μ_3-L; 2.08 Å (OL) < 2.26 Å (NL).

Both steric and electronic factors associated with the donor atom appear to influence the L–Cu–L bond *angles are five-membered* rings, 82.5° (N-donor) < 85.4° (O + N-donor) < 86.5° (N + S-donor) < 87° (O-donor); six-membered rings, 90.5° (O-donor) < 91.0° (N-donor) < 95.0° (O + N-donor).

There are over one hundred and thirty tetrameric Cu(II) derivates (Tables II and III). The predominate geometry about copper(II) is a square-pyramidal. Several distinct type of cores are found with a cubane-type the most common.

A summary of the mean Cu–L bond distances for tetrameric derivatives is given in Table IV. In general the mean Cu–L (monodentate) bond distances are somewhat longer than those of Cu–L (bridge) increasing in the

TABLE IV Summary of the mean Cu(II)–L bond distances for tetrameric derivatives[a]

Coord. atom	*Cov. rad.* (Å)	*Cu–L* (Å)	*Coord. atom*	*Cu–L* (Å)
LO	0.73	2.32(50,53)	$L < \mu_3O$	2.22(20,68)
L^2O		2.02(13,43)	N	2.06(8,5)
L^6O		1.93(4,4)	$L < \mu_3O$	2.18(24,27)
μ OH		1.95(6,5)	S	2.33(1,1)
μ OL		2.03(17,45)	$L < \mu_3(O)_2$	2.28(36,45)
μ_3 OH		2.08(20,44)	N	1.93(1,1)
μ_3 OL		2.21(27,35)	$L < \mu_3O$	2.28(33,26)
μ_4 OH		2.10(2,3)	2N	2.00
LN	0.75	1.99(10,32)	$L < \mu O$	2.04(16,36)
L^2N		1.97(1,4)	2N	2.04(7,38)
L^3N		2.05(10,18)	O	2.05
L^8N		2.00(4,3)	$L \leftarrow S$	1.95
μ_3NL		2.27	N	2.29
Cl	0.99	2.25(4,22)	$L < \mu(O)_2$	2.07
μ Cl		2.39(17,28)	2N	1.90
Br	1.14	2.39(2,2)	$L > \mu O$	1.94
μ Br		2.49(9,9)	4N	1.97

[a] The first number in parentheses is the difference between the shortest value and the mean, the second number is the difference between the highest value and the mean.

order: μ-L < μ_3-L < μ_4-L; and the mean Cu–L (terminal) bond distances are somewhat shorter than those of Cu–L (bridge) bond distances.

4 PENTAMERIC COPPER(II) COMPOUNDS

Crystallographic and structural data for pentameric copper(II) compounds are given in Table V.

The structure of $[Cu_5(OH)_2(ac)_6(H_2O)_2(imH)_4]^{2+}$ is shown in Figure 10. In the centrosymmetric complex, the coordination geometries of the Cu(1), Cu(2) and Cu(3) centers are square-pyramidal, tetragonally elongated octahedral and square-planar, respectively. The Cu(1)–Cu(2), Cu(1)–Cu(3) and Cu(2)–Cu(3) distances are 3.178(1), 3.578(1) and 3.043(1) Å, respectively. While the Cu(1) and Cu(3) centers are bonded to two μ-acetate ligands, the Cu(2) atom is bonded to four such ligands and two μ_3-OH groups. In the Cu_3O moiety, the O(7) atom is displaced 0.579(4) Å from the plane of the copper atoms. The imidazole coordinates as a terminal ligand to the Cu(1) and Cu(3) atoms. The pentameric units are linked symmetrically by μ-aqua bridges to give an intra-chain, inter-unit Cu–Cu separation of 4.507(1) Å.

In another pentameric derivative[173] four peripheral copper(II) atoms form an almost planar structure and the central copper(II) atom is 0.4 Å above this plane. There are twelve five- and six-membered rings with

TABLE V Crystallographic and structural data for pentameric copper(II) compounds[a]

Compound (colour)	*Cryst. cl* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*	*Cu–L* (Å)		*Cu–Cu* (Å) *shortest* *longest* *average* *Cu–L–Cu* (°)	*L–Cu–L* (°)		*Ref.*
$[Cu_5(\mu_3\text{-}OH)_2(\mu\text{-}ac)_6(H_2O)_2\cdot(imH)_4]ClO_4)_2$ (not given)	m	26.889(4)		CuO_6 (×1)	μ_3HO[b]	2.023(2,0)	3.043(1)	O,O[b]	87.5(2,3.1)	172
	C2/c	11.077(3)	134.07(1)		μacO	1.971(5,6)	3.578(1)			
	4	18.936(2)				2.268(6,0)	3.266			
							117.7(1,19.0)			
				CuO_3N (×2)	μ_3HO	1.971(4)		O,O	90.0(1)	
					μacO	1.941(4,19)		O,N	88.0(2,1.3)	
					N	1.972(6)			177.0(2)	
				CuO_4N (×2)	μ_3HO	1.980(2)		O,O	86.3(1,3.6)	
					μacO	1.971(5,6)		O,N	90.8(1,2.9)	
					H_2O	2.425(2)			167.2(2)	
$[Cu_5(ahd)_4](ClO_4)_2\cdot 5H_2O$ (not given)	tr	10.568(2)	94.49(2)	CuO_4 (×1)	μO	1.911(4,32)	3.221(2)	O,O	90.0(2,1.1)	173
	P-1	11.800(2)	110.58(3)				4.368(2)		172.2(2,4.5)	
	2	13.742(3)	99.81(3)				3.935			
							117.7(2,6.1)			
				CuO_2N_2 (×4)	μO	1.922(4,49)		O,O	81.5(2,7)[c]	
					O	1.950(4,12)		N,N	93.6(2,1.4)[c]	
					N	1.971(5,22)		O,N	92.3(2,3.8)	
									171.0(2,7.1)	
$Cu_5(OH)_2(mppc)_2(NO_3)_4\cdot 2.5H_2O$ (green)	m	15.559(3)		CuO_5 (×1)	μO	1.933(5,16)	3.27	O,O	85.2(2,3)[c]	174
	$P2_1/n$	13.417(3)	99.03(1)		O_2NO	2.660(5)	5.78		89.7(2,4.7)	
	4	24.638(3)					3.99		105.5(2,2)	
							120.7(–,9)			
				CuO_4N_2 (×2)	μO	1.987(4,12)		O,O	85.8(2,8.4)	
					N	2.035(7,40)			156.4(2)	
					μHO	1.892(5,7)		N,N	73.4(2,4)[c]	
					μH_2O	2.607(5,91)		O,N	93.5(2,4)[d]	
					O_2NO	2.811(12,124)			98.1(2,10.6)	
									164.9(2,6.3)	

				CuO_4N_2 (×2)	μO	1.980(5,6)		O,O	85.7(2,10.4)	
					N	2.022(7,40)			159.2(2,1.1)	
					μOH	1.895(5,10)		N,N	73.5(2,2)[c]	
					μO_2NO	2.577(7,5)		O,N	95.2(2,1.3)[d]	
					O_2NO	2.724(15,102)			97.9(2,11.9)	
									165.1(2,4.8)	
$[Cu_5(bta)_6(acac)_4]\cdot$	m	16.038(1)		CuN_6 (×1)	$btaN_{eq}$	2.046(9,17)	3.615(2)		Not given	175
$0.5CH_2Cl_2$ (green)	$P2_1/n$	22.836(2)	93.194(6)		N_{ap}	2.305(8)	6.126(2)			
	4	17.497(1)				2.471(9)	5.068			
							109.5(1,7.8)			
				CuN_3O_2 (×4)	acacO	1.932(8,23)			Not given	
					$btaN_{eq}$	2.011(9,33)				
					$btaN_{ap}$	2.20(1,3)				

---

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

[b] The chemical identity of coordination atom/ligand is specified in these columns.

[c] Five-membered metallocyclic ring.

[d] Six-membered metallocyclic ring.

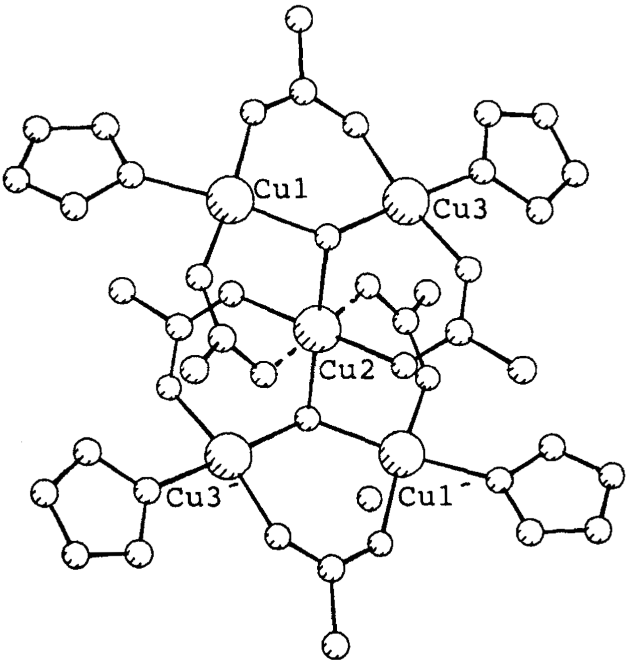

FIGURE 10 Structure of $[Cu_5(OH)_2(ac)_6(H_2O)_2(imH)_4]^{2+}$.[172]

different conformations. The distances between the central and peripheral copper(II) atoms vary from 3.221(2) to 3.315(2) Å. The distances between peripheral copper(II) atoms are in the range 4.565(2)–4.638(2) Å.

In a green derivative[174] five copper(II) atoms are arranged as a rectangular-based pyramid. The overall molecule results from the association of two dimeric units, which are linked by the two OH groups and the fifth copper(II) atom. From the approximate C_{2v} symmetry of the pentameric cluster it follows that the four lateral sites are equivalent while the apical one is unique. Each catechol ligand binds two Cu(II) atoms through two piperazine nitrogens and a catecholate oxygen. The fourth equatorial ligand is a OH group. The coordination of the "apical" copper atom contrasts with the four others since it is roughly a square pyramid with the copper 0.19 Å, out-of the plane of the four catecholate oxygens. This displacement results from the interaction of the copper with a nitrate oxygen (Cu–O = 2.660(5) Å).

The structure of a compound with green prismatic crystals[175] is shown in Figure 11. The pentameric copper(II) assembly consists of a distorted tetrahedral arrangement of four copper atoms (Cu(2)–Cu(5)) centered on the fifth copper (Cu(1)); the cube which envelopes this arrangement is

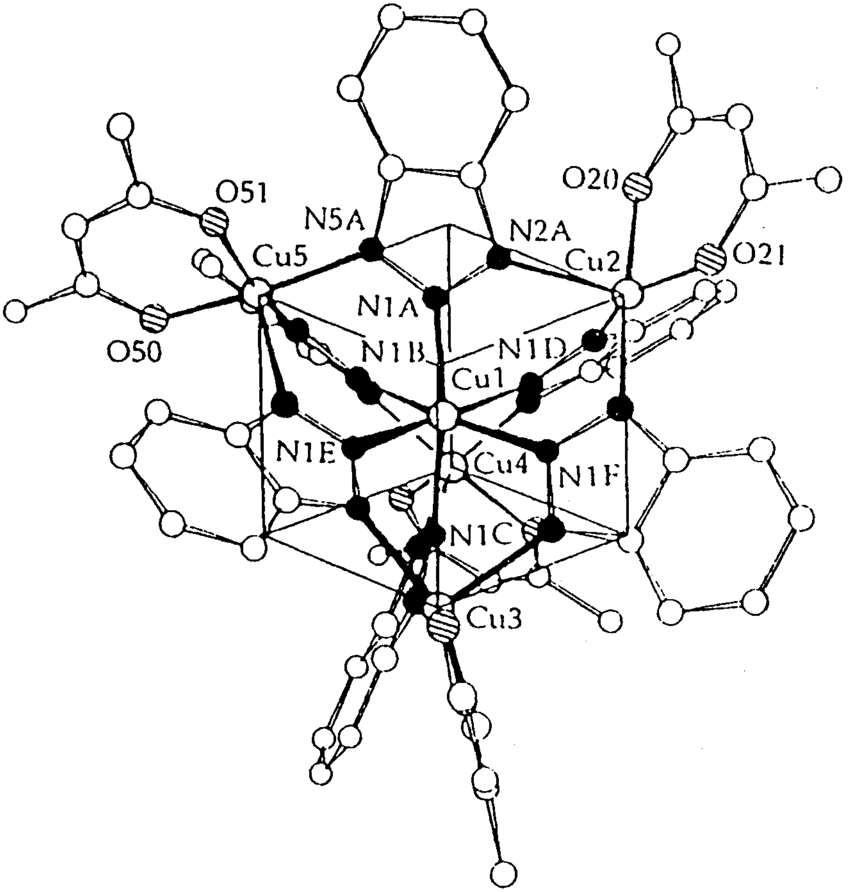

FIGURE 11 Structure of $[Cu_5(bta)_6(acac)_4]$.[175]

identified in the figure. Each of the six bta(−) ligands spans an edge of the Cu_4 tetrahedron and is ligated to the central copper atom (Cu(1)) through its central nitrogen atom. The Cu–Cu distances between the central Cu(1) atom and the peripheral (Cu(2)–Cu(5)) range from 3.165(2) to 3.715(2) Å, and the distances between peripheral copper atoms range from 5.740(2) to 6.126(2) Å.

5 HEXAMERIC COPPER(II) COMPOUNDS

There are twelve hexameric copper(II) compounds for which crystallographic and structural data are summarized in Table VI. A green-black derivative[12] is a centrosymmetric hexameric molecule containing two equivalent Cu_3O units, the central oxygens of which are bonded to a copper from the other Cu_3O. The central oxygens of the Cu_3O groups are very flattened tetrahedra, whose apices point along the Cu–O bonds linking the two Cu_3O units.

The structure of a dark blue derivative[176] is composed of centrosymmetrical hexameric molecules located at the inversion center (0, 0, 0) (Figure 12). The Cu(II) atoms are linked by triply-bridging ethanolato oxygen atoms and OH^- groups, and by carboxylato and ethanolato oxygen bridges. The three independent copper(II) atoms have a square-pyramidal coordination. Cu(2) and Cu(3) are 0.69 and 0.68 Å above their least-squares basal planes towards the apical oxygen atoms as compared to 0.121 Å for Cu(1). All these planes have the triply-bridging oxygen atom of the hydroxo group in common.

The structure of a blue derivative[177] is built up from centrosymmetric complexes and disordered H_2O's which link the hexamers into chains along a. The Cu(II) atoms are linked by triply-bridging ethanolato O atoms and OH groups, and by carboxylato and ethanolato O bridges.

The structure of $Cu_6(4\text{-Brbz})_6(dmae)_6(H_2O)_2$[178] is composed of three dimers, which are bridged into a hexameric unit by carboxyl oxygen atoms. Within the Cu_2O_2 dimeric units the bridging Cu–O–Cu angles are 98.(2)° (mean). The coordination around the four Cu(II) atoms is distorted octahedral, while the remaining two coppers are five-coordinate in a distorted square-pyramidal environment (Table VI).

The overall molecule[179] (Figure 13) has approximate C_2 symmetry in which the different copper(II) atoms associate into pairs: Cu(1) and Cu(4), Cu(2) and Cu(5), Cu(3) and Cu(6). The two tricopper units are linked through the phenoxy oxygen O(4) bridging Cu(1) and Cu(4) and the chloride anion Cl(1) which bridges Cu(2) and Cu(5). Every copper(II) atom is in a tetragonal environment (Table VI).

A molecule of another triclinic derivative[180] consists of three roughly planar methoxo-bridged dimeric units; a centrosymmetric "dimer" with average Cu–O of 1.94(1) Å and Cu–O–Cu of 99.5(3)° within the Cu_2O_2 bridging group, and two different Cu–O–Cu angles, 96.9(3)° and 102.8(3)°. The dimers are joined by axial copper–oxygen bonds. The geometry around the copper atoms is approximately square-pyramidal.

In a blue derivative[181] the complex cation has a Cu_6O_8 core formed by alternating copper(II) and alkoxo oxygen atoms. There is a cubane-like Cu_4O_4 subcore. Two of six faces of the sub-core (the top and bottom) are capped by copper atoms. The capping copper atoms lie on the four-fold

TABLE VI Crystallographic and structural data for hexameric copper(II) compounds[a]

Compound (*colour*)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*	*Cu–L* (Å)		*Cu–Cu* (Å) *shortest* *longest* *average* *Cu–L–Cu* (°)	*L–Cu–L* (°)		*Ref.*
$[Cu_3(C_{15}H_{13}N_4O_2)_3(ClO_4)]_2$	m	14.036(6)		CuO_3N_2 (×4)	μ_3O[b]	1.872(2,18)	2.828(1)	O,O[b]	95.1(1,1.4)	12
(green black)	$P2_1/n$	19.449(5)	97.62(4)		O	1.978(2,22)	3.415(1)	N,N	80.2(1,1.0)[c]	
	2	17.131(9)			N	1.988(3,11)	3.157	O,N	92.5(1,3.0)	
					μO	2.581(3,247)	116.5(1,1.1)		168.1(1,1.2)	
				CuO_3N_3 (×2)	μ_3O	1.860(2)		O,O	92.9(1)	
					O	1.958(3)		N,N	81.3(1)[c]	
					N	1.980(3,9)		O,N	92.8(1,1.8)	
					O_3ClO	2.585(3)			173.1(1,1.4)	
$[Cu_3(\mu\text{-}2\text{-}Clpr)(2\text{-}Clpr)_2(\mu_3\text{-}OH)\cdot$	tr	10.712(7)	73.74(4)	CuO_4N (×2)	N	2.062(12)	2.891	O,O	93.9(4,9.6)	176
$(\mu_3deae)(deae)(H_2O)]_2$ (dark blue)	P-1	12.914(4)	67.57(4)		μ_3O	1.929(8)	6.433		163.8(4)	
	1	13.295(7)	85.35(4)		μ_3HO	2.004(8)	4.151	O,N	84.3(4)[c]	
					ClprO	1.925(10)	μ_3 92.7(3)		90.6(4,2)	
					μO	2.349(9)	107.4(4)		175.1(4)	
							129.8(4)			
							μ 87.5(3)			
							95.1(3)			
							118.9(3)			
							127.2(5)			
				CuO_4N (×2)	N	2.054(10)		O,O	79.7(3)	
					μ_3O	1.922(6)			91.8(3,5.5)	
					μHO	1.984(7)			176.9(3)	
					ClprO	1.931(7)		O,N	94.4(3,5.8)	
					H_2O	2.469(11)			164.9(4)	
				CuO_5 (×2)	O	1.920(9)		O,O	77.3(3)	
					μ_3O	1.995(8)			92.9 (3,2.8)	
						2.301(8)			169.7(3,1.9)	

TABLE VI (*Continued*)

Compound (*colour*)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*	*Cu–L* (Å)		*Cu–Cu* (Å) *shortest* *longest* *average* *Cu–L–Cu* (°)	*L–Cu–L* (°)		*Ref.*
					μ_3HO	2.013(6)				
					ClprO	1.941(9)				
$Cu_6(\mu_3\text{-}OH)_2(\mu\text{-}ac)_2(ac)_4\cdot$	tr	9.070(6)	107.23(5)	CuO_4N (×2)	N	2.063(14)	2.926(4)	O,O	77.4(6,4.2)	177
$(\mu_3\text{-}deae)_2(\mu\text{-}deae)_2(H_2O)$ (blue)	P-1	11.944(6)	96.94(6)		acO	1.923(11)	6.487(6)		99.3(7,7)	
	1	13.081(9)	76.76(5)		μ_3O	1.919(10)	4.147		173.1(5)	
					μ_3HO	1.934(11)	66.2	O,N	87.1(4)^c	
					H_2O	2.274(31)	130.4		96.4(7,3.4)	
									168.5(4)	
				CuO_4N (×2)	N	2.079(14)		O,O	93.6(5,7.8)	
					acO	2.367(13)			164.9(5)	
					O	1.964(14)		O,N	84.2(5)	
					μ_3O	1.937(11)			91.1(5,1.9)	
					μ_3HO	1.999(11)			173.5(5)	
				CuO_6 (×2)	acO	1.938(13)		O,O	77.7(7,2.1)	
					μ_3O	1.968(11,19)			93.8(6,6.8)	
					μ_3HO	2.048(10)			168.2(8,2.9)	
					μO	2.369(10)				
					H_2O	2.595(24)				
$[Cu_6(\mu\text{-}4\text{-}Brbz)_2(4\text{-}Brbz)_4\cdot$	tr	10.897(4)	69.33(4)	CuO_5N (×2)	μO	1.936(5,20)	2.942(2,46)	O,O	49.8(2)^d	178
$(\mu\text{-}dmae)_6(H_2O)_2]$ (not given)	P-1	12.496(6)	95.59(4)		N	2.060(8)	98.8(2,3.3)		78.7(2)	
	1	16.260(11)	102.00(4)		μbzμO	2.575(7)			94.7(2,5.7)	
					μbzO	1.924(5)			132.7(2,7.1)	
						2.922(7)		O,N	85.5(2)^c	
									94.9(4,5)	

				CuO_5N (×2)	μO	1.928(6,8)		O,O	56.2(2)^d	
					N	2.067(9)			79.1(2)	
					μbzO	1.972(5)			96.2(2,18.5)	
						2.571(7)			155.3(2)	
					H_2O	2.700(6)		O,N	84.9(2)^c	
									99.6(2,2.0)	
				CuO_4N (×2)	μO	1.921(7,14)		O,O	54.5(2)^d	
					N	2.017(9)			77.9(3)	
					μbzO	1.942(6)			100.5(2,1.5)	
						2.651(5)		O,N	83.9(3)^c	
									96.9(3,1.4)	
[$Cu_6(\mu_3$-OH$)_2(\mu_3$-dbae$)_2$ ·	tr	10.414(7)	109.96(6)	CuO_4N (×2)	μ_3 HO	2.005(5)	3.037	O,O	83.7(2)	178
(μ-Cl_2ac$)_2$(Cl_2ac$)_2$] (not given)	P-1	13.884(9)	106.76(5)		$\mu_3$dbaeO	1.941(6)	3.608		91.7(2,2.0)	
	1	15.806(9)	78.21(6)		N	2.059(7)	3.265	O,N	87.1(3)	
					μCl_2acO	1.922(7)	μ_3 HO 101.6(3,1.8)		95.8(2,6)	
						2.360(5)	130.4(3)			
							μ_3O 87.7(2,7)			
							118.7(3)			
							μO 120.6(3)			
				CuO_4N (×2)	μ_3 HO	2.003(5)		O,O	88.6(2)	
					μdbaeO	1.935(7)			94.0(2,4.8)	
					N	2.041(6)		O,N	85.9(3)	
					μCl_2acO	2.331(5)			91.0(3,3)	
					Cl_2acO	1.944(7)				
				CuO_5 (×2)	μ_3HO	1.972(5)		O,O	72.3(2)	
					$\mu_3$dbaeO	1.964(5)			92.1(2,3.8)	
						2.438(6)			111.7(2)	
					μCl_2acO	1.982(6)				
[{$Cu_3(\mu_3$-OH)(μ-bsmnp)(dmf)}$_2$ ·	tr	13.288(10)	102.96(6)	CuO_5N (×2)	μ_3HO	1.981(5,12)	2.946(2)	O,O	60.28-135.96(18)	179
(μ-Cl)(μ-bsmnp)] · 2dmf (green)	P-1	14.678(7)	89.07(7)		μO	1.931(5,38)	3.994(3)		167.7(1,4.4)	
	2	22.591(23)	113.15(5)			2.534(6,43)	3.197	O,N	92.1(1,1.1)	
						2.884(6,153)	μ_3HO 100.6(2,5.9)		117.8(1,15.8)	
					N	1.927(7,18)	μO 93.0(2,1)		169.1(1,4.0)	
							126.3(3)			
							Cl 102.13(12)			

TABLE VI (*Continued*)

Compound (*colour*)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	*α* (°) *β* (°) *γ* (°)	*Chromophore*	*Cu–L* (Å)		*Cu–Cu* (Å) *shortest* *longest* *average* *Cu–L–Cu* (°)	*L–Cu–L* (°)		*Ref.*
				CuO_4NCl (×2)	μ_3HO	1.955(5,4)		O,O	64.6(1,1.4)	
					μO	1.941(5,19)			81.8(1,5.5)	
						2.045(5,17)			158.4(1,2)	
						2.742(6,75)		O,N	92.9(1,1.3)	
					N	1.902(7,5)			100.0;164.1	
					μCl	2.568(3,18)		O,Cl	99.0(1,4.1)	
								N,Cl	98.4(1,1.0)	
				CuO_5N (×2)	μ_3HO	1.942(5,5)		O,O	65.38-111.52	
					μO	1.902(6,11)			162.8(1,4.5)	
						2.052(5,19)		O,N	93.3(1,1.2)	
						2.687(6,40)			97.2(1,7.1)	
					N	1.910(7,9)			167.5(1,1.8)	
					dmfO	2.367(7,26)				
$[Cu_2(OMe)_2(tftbd)_2]_3$	tr	11.212(7)	92.71(5)	CuO_5 (×2)	μ_3MeO	1.963(6)	2.964(2)	O,O	81.3(3,3.0)	180
(not given)	P-1	11.079(7)	116.80(5)			2.499(7)	99.7(3,4.7)		92.9(3)^{e}	
	1	15.315(9)	95.56(5)		μMeO	1.898(6)			93.3(3,2.0)	
					O	1.944(6,9)			104.7(3)	
				CuO_5 (×2)	μ_3 MeO	1.942(5,10)		O,O	82.5(3,2.1)	
						2.515(7)			92.8(3)	
					μO	1.948(6)			92.6(3,4.9)	
					O	1.923(6)			103.9(3)	
				CuO_5 (×2)	μ_3 MeO	1.918(6,22)		O,O	80.2(3,2.4)	
					μO	2.843(7)			93.4(3)^{e}	
					O	1.919(6,1)			97.0(3,3.3)	
$[Cu_6(\mu_3\text{-amp})_4(\mu\text{-amp})_4](ClO_4)_4$	tg	13.516(2)		CuO_4N (×4)	μ_3O	1.983(4,28)	3.095(1)	O,O	82.2(2,4.9)	181
(blue)	$P\text{-}42_1/c$					2.269(5)	3.525(1)		95.1(2,3.2)	
	2	16.204(3)			μO	1.916(4)	3.278		174.0(2)	

					N	2.038(6)	μ_3O 97.0(2,6.7)	O,N	85.0(2)	
							μO 133.1(3)		100.7	
									154.2(2)	
				CuO_2N_2 (×2)	μO	1.928(5,0)		O,O	98.1(2)	
					N	1.966(7,0)		N,N	91.8(3)	
								O,N	85.1(2)[c]	
									175.9(3)	
[Cu(μ-phoac)$_2$]$_6$ (pale green)	rh	30.23(3)		CuO_6 (×6)	O	1.95(1,4)	3.531(3)	O,O	87.5(5,2.2)	182
	R-3					2.45(1,2)	5.65		94.4(5)	
	4	8.06(1)					4.59		163.4(5)	
[Cu$_6$(μ_4-O)$_2$(μ-bibo)$_6$(H$_2$O)] · 2ClO$_4$ ·	m	15.622(2)		CuO_2N_2 (×3)	μ_4O	1.86(1,1)	Not given	O,O	94.5(5,1.0)	13
0.5H$_2$O (green)	P2$_1$/n	27.025(2)	97.38(2)		O	1.95(1,2)	91.9(5,2.2)	N,N	80.0(6,1.2)[c]	
	4	18.864(4)			N	1.99(1,6)	111.9(6,7.7)	O,N	92.7(6,3.8)	
				CuO_3N_2 (×2)	μ_4O	1.88(1,1)		O,O	90.0(6,5.3)	
						2.33(1,6)		N,N	79.9(6,7)[c]	
					O	1.97(1,0)		O,N	96.3(6,8.7)	
					N	1.99(1)			167.3(6,1.3)	
				CuO_3N_2 (×1)	μ_4O	1.89(1)		O,O	95.7(6,3.1)	
					O	1.95(1)		N,N	81.4(6)[c]	
					N	1.98(2,1)		O,N	91.5(6,5.5)	
					H$_2$O	2.55(3)			170.2(6,7.4)	
[Cu$_6$(μ-OH)$_2$(μ-ac)$_2$(MeOH)$_2$ ·	tr	11.283(4)	81.65(8)	CuO_5		Not given	Not given		Not given	183
(H$_2$O)(hsb)] (green)	P-1	16.665(8)	80.34(3)							
	2	22.127(6)	74.88(4)							
(PhSiO$_2$)$_6$[Cu$_6$(O$_2$SiPh)$_6$] ·	rh	14.725(1)	65.836(4)	CuO_5 (×6)		Not given	Not given		Not given	184
6EtOH (not given) (at 153 K)	R3									
	1									

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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 parenthesis is e.s.d., the second is maximum deviation from the mean value.

[b] The chemical identity of coordination atom/ligand is specified in these columns.

[c] Five-membered metallocyclic ring.

[d] Four-membered metallocyclic ring.

[e] Six-membered metallocyclic ring.

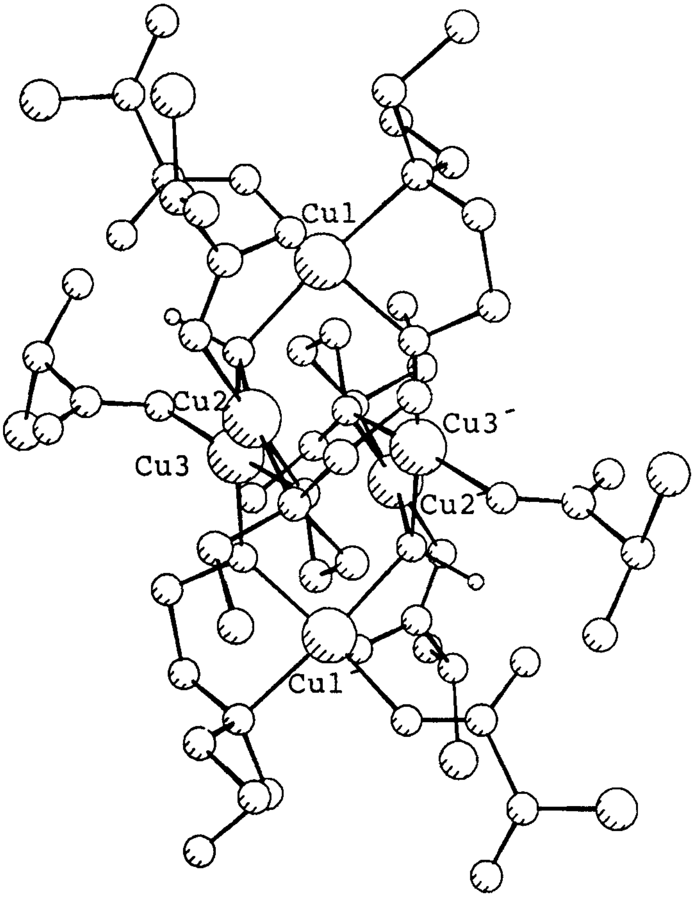

FIGURE 12 Stereoview of $[Cu_3(2\text{-}Clpz)_3(OH)(deae)_2(H_2O)]_2$.[176]

axis. One capping copper atom is joined via oxygen bridges to the two copper atoms in the top face, and the other is likewise joined to the two copper atoms in the bottom face. In the Cu_4O_4 cubane portion of the structure, the Cu–Cu separations are 3.095(1) (× 2) and 3.122(1) Å (× 4). The Cu–Cu separation between the tapping and the cubane copper atoms is 3.525(1) Å (× 4). The cubane copper atoms have a square-pyramidal coordination geometry, which is distorted towards a trigonal-bipyramidal arrangement. The capping copper atoms are planar.

In a pale green complex[182] any one of the Cu(II) atoms, which are at general positions in the unit call, has exactly the same environment as the other five by the C_{3i} symmetry. The Cu atoms together form a compressed

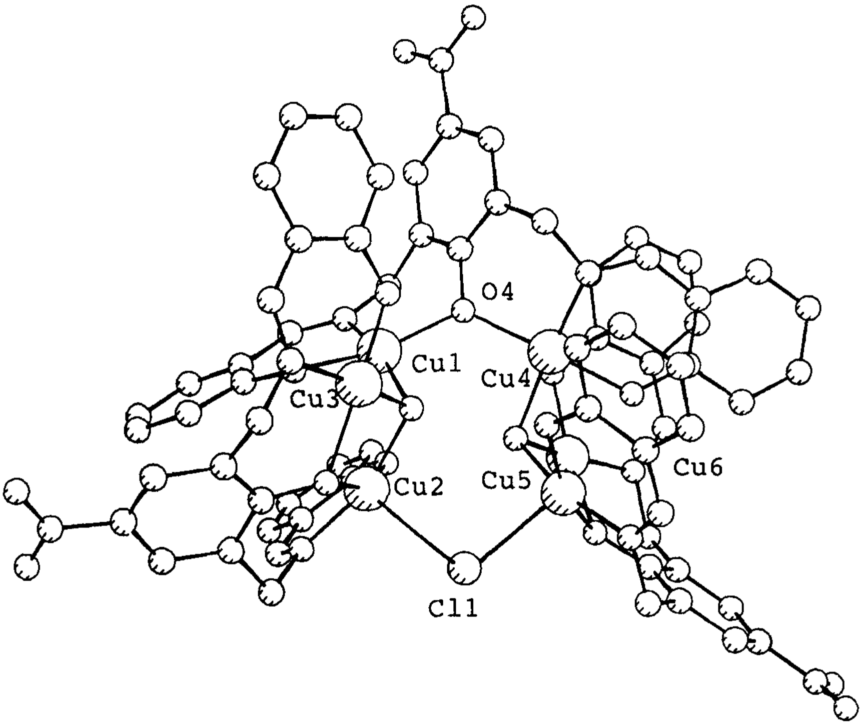

FIGURE 13 Structure of [{Cu_3(OH)(bsmnp)(dmf)}$_2$(Cl)(bsmnp)].[179]

trigonal antiprism with six long edges (Cu–Cu 5.65 Å) bordering the equilateral triangular faces and six short edges (Cu–Cu 3.53 Å). The Cu coordination is distorted octahedral with four short (Cu–O 1.95(1) Å) and two long (Cu–O 2.45(1) Å) distances.

In a green-black derivative[13] the $[Cu_6(\mu_4\text{-}O)_2(bibo)_6]^+$ cation contains two triangular $[Cu_3O]$ units, bridged by their central oxygen atoms. Their are two types of Cu(II) atoms a square-planar (CuO_2N_2) and trigonal-bipyramidal with the core CuO_3N_2.

6 OCTA-, NONA-, AND DODECAMERIC COPPER(II) COMPOUNDS

There are five examples[71,185–188] which contain eight Cu(II) atoms; the structural data for these compounds are given in Table VII. The structure of $Cu_8(O)_2(Pr^iNCO_2)_{12}$[185] is shown in Figure 14. In the asymmetric unit there are four copper(II) atoms and six di(isopropyl) carbamato groups which are

TABLE VII Crystallographic and structural data for octa-, nona- and dodecameric copper(II) compounds[a]

Compound (colour)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*	*Cu–L* (Å)		*Cu–Cu* (Å) *shortest* *longest* *average* *Cu–L–Cu* (°)	*L–Cu–L* (°)		*Ref.*
$[Cu_8(\mu_4\text{-}O)_2(Pr_2{}^iNCO_2)_{12}]\cdot C_7H_{16}$	tr	16.034(4)	110.11(3)	CuO_5 (× 2)	μ_4O^b	1.948(5,3)	2.830(2)	O,O[b]	78.7(2)	185
(green)	P-1	16.353(4)	113.63(3)		μO	1.984(6)	3.081(2)		94.0(2,9.2)	
	1	13.770(3)	94.0(4)			2.357(6)	2.971		169.6(2,8.8)	
					O	1.958(5)	μ_4O^b100.4(3,7.2)			
							123.8(3,2.1)			
							μO 86.0(3,3.2)			
							103.6(3,3.8)			
				CuO_5 (× 4)	μ_4O	1.913(5,7)		O,O	82.1(3)	
					μO	1.999(8,20)			91.1(3,6.3)	
						2.347(8,19)			118.5(3)	
					O	1.948(7,30)			153.4(3)	
									179.3(3)	
				CuO_5 (× 2)	μO	1.948(7)		O,O	79.1(3,3.2)	
						2.399(8)			94.1(3,13.9)	
					O	1.939(7,10)			117.7(3)	
									147.3(3,2.8)	
									168.4(3,3.4)	
$[Cu_4(\mu_5\text{-}O((\mu\text{-}mttt)(ClO_4)]_2\cdot$	tr	11.497(4)	102.92(2)	CuO_3N (× 2)	μ_5O	2.032(6)	2.844(2)	O,O	86.4(2,1.3)	71,186
$(ClO_4)_2\cdot 2H_2O$ (green)	P-1	12.714(3)	113.15(2)		μO	1.907(6,7)	3.241(2)		171.1(3)	
	1	13.546(4)	100.36(3)		N	1.969(8)	2.946	O,N	93.3(3,2.3)	
							93.5(3,6.7)		174.9(2)	
							163.9(4,2.3)			
				CuO_4N (× 4)	μ_5O	2.066(5)		O,O	88.4(2,5.4)	
						2.372(7)			169.8(3)	
					μO	1.931(6,9)		O,N	96.7(3,5.4)	
					N	1.974(7)			171.0(3)	

				CuO_4N (× 2)	μ_5O	2.053(6,1)		O,O	88.3(3,8.0)	
					μO	1.893(6,21)			170.5(3,5)	
					N	1.972(8,4)		O,N	94.3(3,2.4)	
					O_3ClO	2.571(8,53)			174.2(3,2.7)	
$[Cu_4(\mu_5\text{-}O)(\mu\text{-bttt})(ClO_4)]_2 \cdot$	m	15.778(5)		CuO_3N	μ_5O	2.032(11)	2.834(4)	O,O	86.2(5,11)	71
$(ClO_4)_2 \cdot 2H_2O$ (green)	$P2_1/n$	17.384(4)	109.54(3)		μO	1.899(12,7)	3.242(5)		169.3(5)	
	2	15.392(5)			N	1.972(15)	2.948	O,N	93.5(6,1.0)	
							93.3(5,6.7)		176.3(6)	
							164.8(7,3.1)			
				CuO_4N	μ_5O	1.079(11)		O,O	88.1(5,3.6)	
						2.381(12)			169.7(5)	
					μO	1.934(11,8)		O,N	96.9(6,5.3)	
					N	1.962(18)			170.7(6)	
				CuO_4N	μ_5O	2.045(11,4)		O,O	88.4(6,5.2)	
					μO	1.891(13.22)			169.4(6,3)	
					N	1.969(15,14)		O,N	94.3(6,3.3)	
					O_3ClO	2.506(15,19)			173.8(6,3.7)	
$Na_7[Cu_8(urid)_8Na(H_2O)_6] \cdot$	c	23.716(5)		CuO_3N	N	2.00(2)	2.96	O,O	81.8(1)^c	187
$5NaClO_4 \cdot 48H_2O$ (not given)	P432				O	2.04(2,3)			84.5(1)	
	3				μO	1.94(2)		O,N	97.1(1,6)	
$Cu_8(OH)_8(dmpz)_8$	m	10.229(3)		CuO_2N_2	μHO	1.921(8,12)	3.213(3)	O,O	158.8	188
(green)	$P2_1/m$	27.217(2)	98.51(1)		N	1.967(9,21)	3.268(2)	N,N	161.9	
	2	14.532(1)					3.237			
							114.7(5)			
$Cu_9(\mu_3\text{-}OH)_2(\mu_3\text{-dmae})_6 \cdot$	m	14.835(3)		CuO_6 (× 1)	μ_3HO	1.941(7,0)	3.071	O,O	90.2(3,5.2)	189
$(\mu\text{-}Cl_2ac)_8(Cl_2ac)_2$ (dark green)	$P2_1/n$	14.205(4)	97.46(2)		μCl_2acO	2.207(8,0)	3.653		172.9(3,1)	
	2	20.887(5)				2.107(9)	3.299			
				CuO_6 (× 2)	μ_3HO	1.964(8)		O,O	77.1(3,1.2)	
					μ_3dmaeO	1.966(7)			92.7(3,7.1)	
						2.380(8)			167.4(3,1.5)	
					μCL_2acO	1.960(9,17)				
						2.406(8)				
				CuO_4N (× 2)	μ_3HO	2.149(7)		O,O	78.3(3)	
					μ_3dmaeO	1.930(8)			93.5(3,6.0)	
						2.111(8)			167.7(3)	
					N	2.048(11)		O,N	86.2	

TABLE VII (*Continued*)

Compound (*colour*)	*Cryst. cl.* *space gr.* *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Chromophore*	*Cu–L* (Å)		*Cu–Cu* (Å) *shortest* *longest* *average* *Cu–L–Cu* (°)	*L–Cu–L* (°)		*Ref.*
					μCl_2acO	1.936(8)			117.1(3)	
									165.7(3,2.0)	
				CuO_5N (× 2)	μ_3dmaeO	1.957(8,21)		O,O	70.9(3,1.4)	
						2.645(7)			92.2(3,11.5)	
					N	2.035(10)			149.0(3)	
					O	1.924(9)			173.7(4)	
					μCl_2acO	2.431(10)		O,N	94.7(3,9.3)	
									171.9(4)	
				CuO_4N (× 2)	μ_3dmaeO	1.943(9,39)		O,O	93.1(3,10.5)	
					O	2.463(9)			163.2(3)	
					N	2.051(11)		O,N	89.3(4,2.7)	
					Cl_2acO	1.943(9)			172.6(4)	
$Na_2[Cu_9Cl_2(cpa)_6$	trg	21.274(5)		CuO_4Cl (× 6)	μ_3Cl	2.93(2)	3.342(4)	O,O	89.9(6,9.4)	190
$(H_2O)_3] \cdot xH_2O$ (blue)	P321				μO	1.93(2,1)	O 120.4(6)		172.7(6,2.0)	
	—	7.976(6)			O	1.91(2,3)	Cl 69.4(1)	O,Cl	82.7(3,2)	
									104.1(5,2.4)	
				CuO_6 (× 3)	O	1.91(2)		O,O	90.1(5,6.7)	
						1.92(2)			175.8(4,5)	
					H_2O	2.29(2)				
$Cu_9(\mu_3\text{-OHO})(\mu_3OH)_6$	m	15.108(8)		CuO_4 (× 2)	μ_3HO	1.89(1)	not given	not given		96b
$(dpm)_9$ (light blue)	$P2_1/c$	29.437(17)	113.56(3)				96(1)			
	4	30.528(12)					123(1)			
				CuO_5 (× 7)	μ_3HO	2.20(5)		not given		
					O	1.93(1,2)				
$[Cu_6(\mu_3\text{-OH})_2(\mu\text{-OH})(30m)]_2 \cdot$	tr	14.482(7)	95.64(5)	CuO_4N (× 4)	μ_3HO	1.99(1,1)	2.929(3)	not given		191
$(NO_3)_6 \cdot 10H_2O$ (dark green)	P-1	14.72(1)	92.32(4)			2.44(1,1)	6.644(6)			

1	12.193(4)	114.85(4)	μ30mO	1.96(1,1)	4.856
			N	1.94(1,2)	μ_3HO 97.8(5,5)
					μHO 96.3(4)
					μO 97.1(5,8)
					133.3(8,1.7)

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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 parenthesis is e.s.d., the second is maximum deviation from the mean value.

[b] The chemical identity of coordination atom/ligand is specified in these columns.

[c] Five-membered metallocyclic ring.

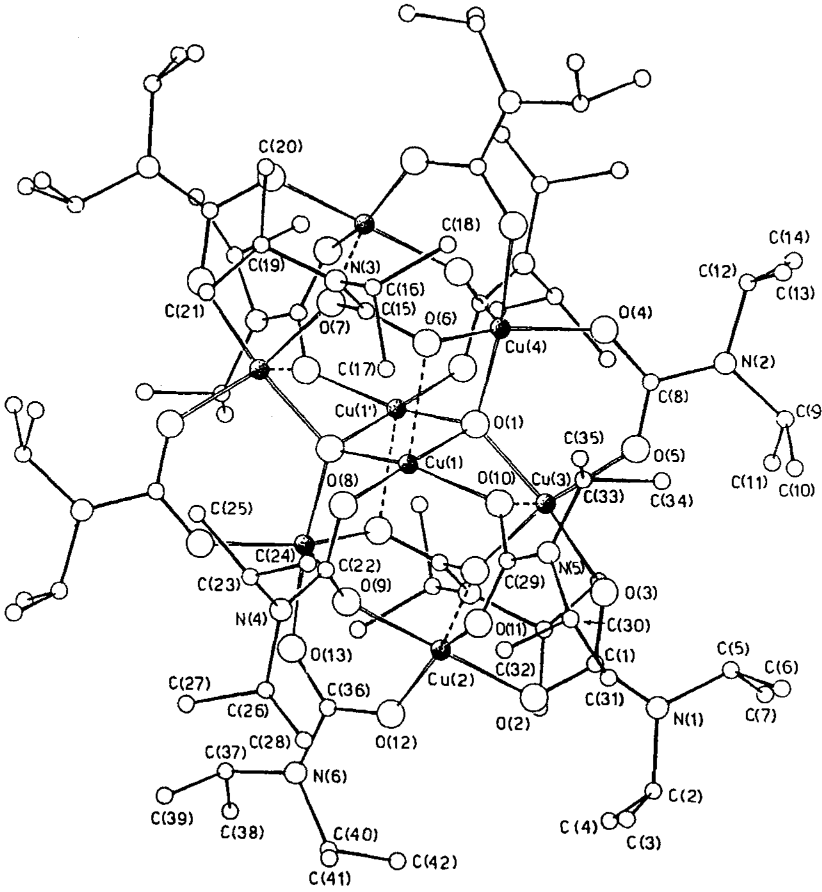

FIGURE 14 Structure of $Cu_8(O)_2(Pr_2^iNCO_2)_{12}$.[185]

crystallographically independent. An important feature of the structure is the presence of a μ_4-O(1), which is coordinated tetrahedrally to four copper(II) atoms with Cu–O distances ranging from 1.906(5) to 1.950(6) Å and with Cu–O–Cu angles (range 93.2(3)°–125.9(3)°) considerably different than the normal tetrahedral angle. The environment around each copper atom is a square pyramid (CuO_5). The Cu–O apical bonds are 0.3–0.5 Å longer than the equatorial Cu–O bonds. The out-of-plane distance of the copper atom varies from 0.07 to 0.22 Å.

Structures of another two green derivatives[71,186] are rather similar. Both structures are centrosymmetric dimers with four copper(II) atoms bound with the macrocycle. The central oxygen donor is a five-coordinate oxo anion which is displaced from the mean plane of the four copper(II) atoms by 0.29 and 0.27 Å, respectively. The coordination sphere of μ_5-O is completed by a copper atom from the second macrocyclic unit of the dimer. This bond holds the dimer together with Cu–O distances of 2.84(1) and 2.72(1) Å for one derivative[71,186] and 2.80(1) and 2.73(1) Å for the other.[186]

The structure of another derivative[187] has two interesting aspects: (1) molecular entities Cu_8urid_8, containing $Na(H_2O)_6$ ions, surrounded by perchlorate groups, and (2) a three-dimensional framework based on sodium atoms, giving rise to the formation of tunnels where the copper entities are located. The uridine ligand is three-coordinate towards three copper(II) atoms by the nitrogen atom of the pyrimidine base and by two oxygen atoms of the ribose, from which one oxygen atom bridges two copper atoms. The copper(II) atoms are in a square-planar configuration and associated in dimers in the Cu_8urid_8 octamer. The Cu–Cu distance within the dimers is 2.96 Å. In the Cu_8urid_8 octamer, the eight copper(II) atoms occupy the vertices of a distorted Archimedian square antiprism (diagonal of the square line is 11.4 Å). The eight interconnected uridine ligands form a kind of toric structure (Figure 15).

$Cu_8(OH)_8(dmpZ)_8$[188] consists of a discute molecule of towidal shape, containing a ring of eight monomeric units. Each molecule lies on a crystallographic mirror plane and possesses idealized D_{4d} symmetry, with an S_8 axis normal to the plane and is topologically equivalent to cyclo-octane. Each of the copper(II) atoms, approximately located at the vertices of a regular octagon, is connected to two OH and two dmpz groups, with almost square-planar coordination geometry (*trans* isomer). All ligands bridge Cu(II) pairs, having an average non-bonding distance of 3.237 Å.

There are three derivatives[96b,189,190] which contain nine Cu(II) atoms. The structure of a green compound[189] is shown in Figure 16. The crystal structure consists of discrete nonameric molecules which possess a two-fold rotation axis passing through a copper atom. The nine copper atoms in the molecule are bridged by ten carboxylate groups, six triply-bridging ethanoltato oxygen atoms and two triply-bridging hydroxo oxygen atoms. The coordination number of copper is five for Cu(3) and Cu(5) and six for the other Cu(II) atoms, the coordination polyhedra being square-pyramidal or *pseudo*-octahedral. The Cu(3) and Cu(5) are displaced from the mean planes towards the apical sites by 0.29 and 0.11 Å, respectively.

The structure of a blue derivative[190] is shown in Figure 17. Two environments for copper were found in the structure. The copper atom in site one, located near a crystallographic three-fold axis, has a square-pyramidal

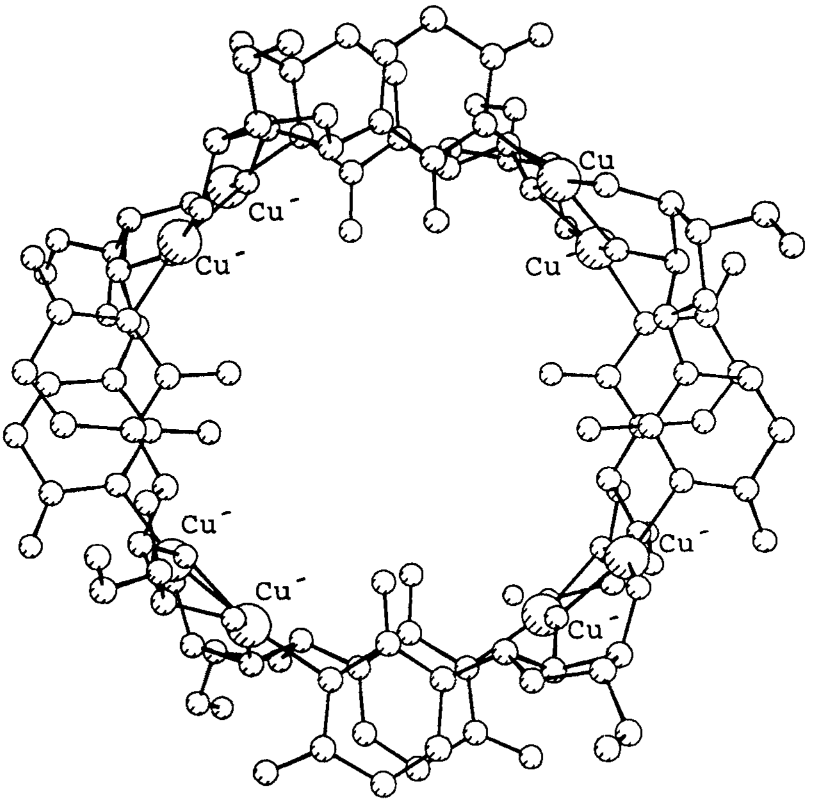

FIGURE 15 Structure of $[Cu_8(urid)_8Na(H_2O)_6]^{7-}$.[187]

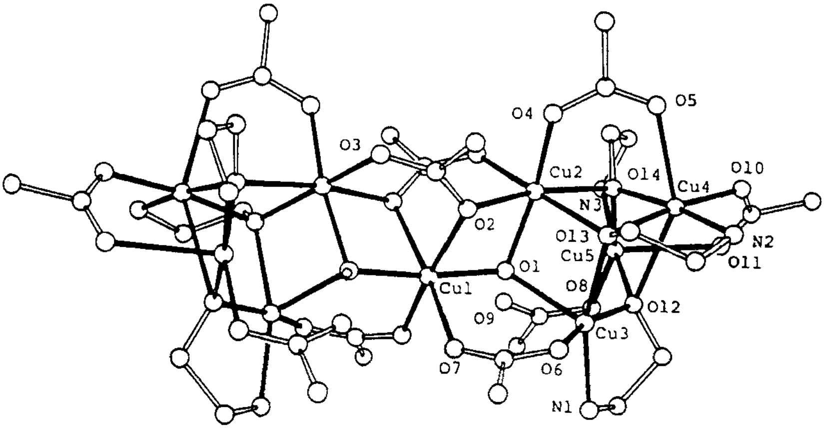

FIGURE 16 Structure of $Cu_9(OH)_2(dmae)_6(Cl_2ac)_{10}$.[189]

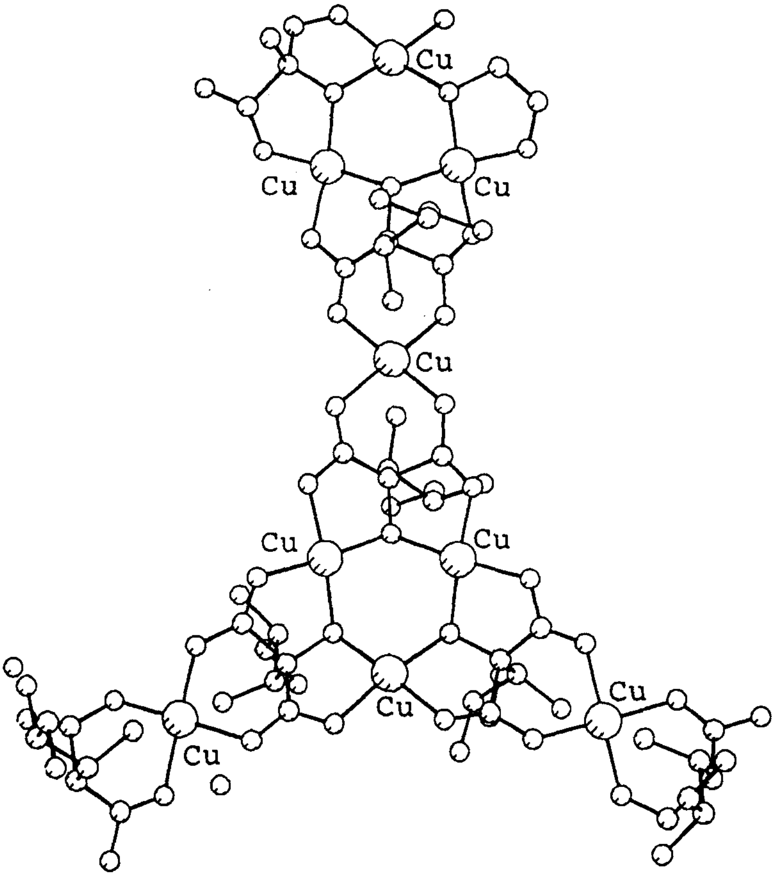

FIGURE 17 Structure of $[Cu_9Cl_2(cpa)_6(H_2O)_3]^{2-}$.[190]

environment (CuO_4Cl). The copper atom in site two is located on a crystallographic two-fold axis and has four relatively short equatorial bonds and two longer axial bonds, all to oxygen donors (Figure 17, Table VII).

The central core in $Cu_9(OHO)(OH)_6(dmp)_9$[96b] contains nine Cu(II) atoms and eight oxygen atoms. Six copper(II) atoms form a trigonal prism with the remaining three copper(II) atoms above the rectangular faces. The Cu(II) atoms of the trigonal prism exhibit square-pyramidal geometry with two oxygen atoms furnished by the chelating dpm, two oxygen atoms furnished by the bridging OH groups and one oxygen furnished by a postulated OHO^- group. The trigonal prism chelate rings are at a 45° angle to the equatorial (facial) chelate rings.

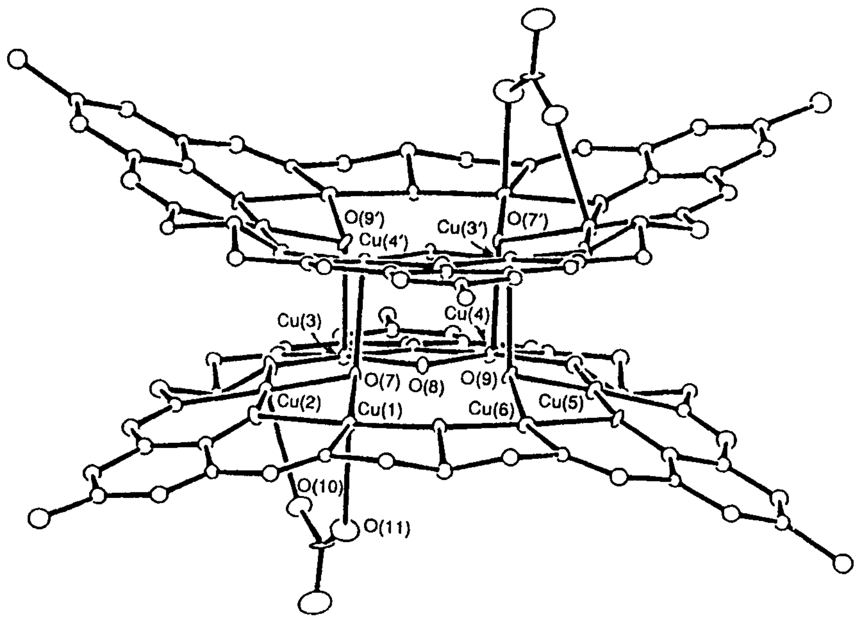

FIGURE 18 Structure of $[Cu_6(OH)_3(30m)]_2^{6+}$.[191]

The structure of a dimeric cation[191] is unique consisting of two almost flat, hexagonal macrocyclic rings, each involving an array of six *pseudo*-square-planar copper(II) centers, which are coupled together by an axial bridging interaction in which hydroxide bridges (O(7) and O(9)) not only bridge copper pairs Cu(1), Cu(2) and Cu(5), Cu(6), respectively, within the same ring, but also provide a bridge to copper atoms Cu(4) and Cu(3), respectively, on the other macrocyclic ring. The molecular symmetry dictates that this inter-macrocycle bridging also involves the symmetry related atoms and so the two rings are held together by four axial hydroxide bridges (Figure 18). The copper(II) atoms are linked within each ring by an alternating single and double bridged arrangement of oxygen atoms (alkoxide and hydroxide plus phenoxide) that resembles a resonance from a benzene. The adjacent Cu–Cu separations alternate between short (2.92–2.96 Å) and long (3.54–3.57 Å) contacts (Table VII).

7 CONCLUSIONS

This review has classified over two hundred and thirty oligomeric copper(II) structures. Copper(II) compounds are for the most part green and blue, but there are many red/orange, yellow, brown and even black complexes. The number of examples decrease in the sequence: tetrameric (135) > trimeric (73) > hexameric (12) > pentameric (5) ≅ octameric (5) > nonameric (2) > dodecameric (1). The most common donor atom ligands are oxygen and nitrogen donors, with oxygen as the most common bridging atom. The ligands range from mono- to octadentate and even dodecadentate. Various geometries are found: four- (square-planar), five- (mostly square-pyramidal) and six- (mostly tetragonal-bipyramidal) coordination.

Pairs of independent molecules with differing degrees of distortion are found in the same crystal in several cases.[52,55,82,88,89]

Relationships between the various structural parameters have been discussed within each section.

This review, together with its precursors dealing with monomeric[3,4] and dimeric[5] complexes of copper(II), represents the first overview of structural data for copper(II).

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 not mentioned at all. This can lead to the overlooking of relevant structural features which should be compared with other derivatives. On the other hand, there are several examples where the same compounds are studied by two or more different groups without any cross referencing, and important discrepancies in the data obtained have gone without comment. In view of the limitations in information retrieval, we believe that it is necessary to make a systematic overall review, and that such reviews serve to delineate areas of both interest and weakness. A related review of the structural chemistry of polymeric copper(II) complexes is currently in progress.

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