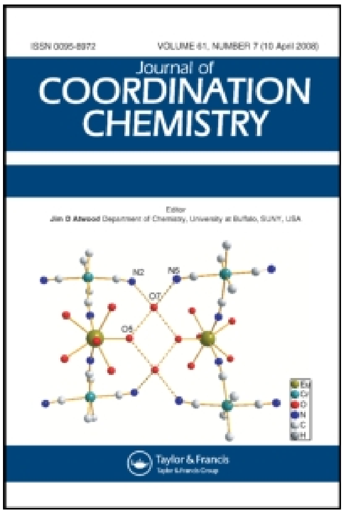

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COPPER(II) COORDINATION COMPOUNDS: CLASSIFICATION AND ANALYSIS OF CRYSTALLOGRAPHIC AND STRUCTURAL DATA. V. POLYMERIC COMPOUNDS

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Review

COPPER(II) COORDINATION COMPOUNDS: CLASSIFICATION AND ANALYSIS OF CRYSTALLOGRAPHIC AND STRUCTURAL DATA
V. POLYMERIC COMPOUNDS*

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This review classifies almost 600 polymeric Cu(II) compounds. The various geometries are found in increasing number in the order: four- (mostly square-planar) ≪ five- (mostly square-pyramidal) ⋘ six-coordinate (mostly tetragonal-bipyramidal). The most common ligands are oxygen and nitrogen atoms. The ligands range from mono- to undecadentate. In most examples, apical positions are occupied by oxygen-donor ligands. In general, the mean Cu–L(equatorial) bond length is shorter than the respective Cu–L(apical) bond length. The shortest Cu–Cu distance in the series of four-coordinate derivatives is 2.95 Å, five-coordinate 2.652(2) Å and six-coodinate 2.977(2) Å. Several relationships between the various structural parameters were found and are discussed.

Keywords: Review; copper(II); crystallography; structures; polymers

CONTENTS

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0. ABBREVIATIONS

abhpH	2-amino-4-bromohydroxy-pyridinium
abpo	azobispyridine-4,4′-di-N-oxide
ac	acetate
acac	acetylacetonate
acval	N-acetyl-DL-valinate
$(ae)_2a$	bis(2-aminoethyl)ammonium
aebg	1-(2-aminoethyl)biquanide
aeim	4-(2-aminoethyl)imidazole
aep	2-(2-aminoethyl)pyridine
ala	D,L-alaninate
β-alaH	β-alaninium
α-alaha	α-alaninehydroxamate
4-ambp	4-aminobenzoylphenone
am-1,2,4-trz	4-amino-3-methyl-1,2,4-triazole
ambz	2-amino-3-methylbenzoate
amoxa	N,N′-bis(2-aminoethyl)-2-methylpropyl oxamidate
amp	aminomethylphosphonate
2-amp	2-(2-aminomethyl)pyridine
4-amp	4-methyl-2-aminopyridinium
6-amp	6-methyl-2-aminopyridinium
amtzt	4-amino-3-methyl-1,4-dihydro-1,2,4-triazole-5-thiane
ampr	(R,S)-1-amino-2-propanol
anH	anilinium
ap	allopurinol
3-ap	3-aminopropanolate
apae	[2-(3-aminopropyl)amino]ethanolate
3-apH	3-aminopropanol
apox	N,N′-bis(3-aminopropyl)oxamide
aud	1,1-aminoudecane

ba	bromazepam
bdmap	1,3-bis(dimethylamino)propan-2-ol
bhben	N,N′-bis(2-((o-hydroxybenzhydrylidene)amino)ethyl)-1,2-ethanediamine
bhedto	N,N′-bis(2-hydroxyethyl)dithiooxamide
bheg	N,N-bis(2-hydroxyethyl)glycinate
bim	benzimidazolium
bimd	benzimidazole
bistrien	1,4,7,10,16,19,22-octaazacyclotetracosane
bmima	bis[2-(1-methylimidazolyl)methyl]amine
bmpcb	N,N′-bis(6′-methylpyridine-2′-carboxamido)-1,2-benzene
bpepc	N,N′-bis[2-(2-pyridyl)ethyl]-2,3-pyrazine-dicarboxamidate
bpca	bis(2-pyridylcarbonyl)amide
4-bpipH	4-benzylpiperidinium
bpm	2,2′-bipyrimidine
2,2′-bpy	2,2′-bipyridine
4,4′-bpy	4,4′-bipyridine
bpydc	2,2′-bipyridine-3,3′-dicarboxylate
2-Brpy	2-bromopyridine
4-Brpy	4-bromopyridine
bsala	N-benzenesulphonyl-DL-alaninate
but	butyrate
$bzNH_3$	benzylammonium
2-bzpy	2-benzoylpyridine
cab	5-[(2-carboxyphenyl)azo]-1,3-dimethylbarbiturate
caf	caffeine
cba	carbamide
cdta	cyclohexane-1,2-diamine-N,N,N′,N′-tetraacetate
ceidac	((2-carboxyethyl)imino)diacetate
cg	cyanoquanidine
chd	1,2-cyclohexanediol
$C_6Cl_2O_4$	3,6-dichloro-2,5-dihydroxo-1,4-benzoquinonate
CH_6N_3	quanidium
$C_2H_6O_2$	1,2-ethanediole
$C_6H_2(COO)_4$	1,2,4,5-benzoltetracarboxylate
$(C_6H_{13})PO_2$	di-*n*-hexylphosphinate
$C_{11}H_7N_2$	1,2,6,7-tetracyano-3,5-diimino-3,5-dihydropyrrolizinide
$C_{32}H_{54}N_2O_8$	(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)pivaloylacetate

C_4O_4	squarate
C_5O_5	croconate
cim	cimetidine
cit	citrate
4-Clan	p-chloroanilin
Cl_3ac	trichloroacetate
cma	9,10-dihydro-9-oxo-10-acridine acetate
cmval	N-carboxymethyl-L-valinate
CNacac	3-cyano-2,4-pentanedionate
cpa	cyclopentylammonium
cpidac	N-(*o*-carboxyphenyl)iminodiacetate
cpo	2-C-carboxypentane
5-crown-5	pentaoxa-1,4,7,10,13-cyclopentadecane
15-crown-5	crown ether
cy	tetraprotonated 1,4,8,11-tetraazacyclotetradecane
cyt	cytosine
daca	diacetatamide
dap	1,3-diammonium-2-propanole
dbap	3-N,N-di-n-butylamino-1-propanolate
2,6-dbh	2,6-dihydroxybenzoate
dcap	diacetoamidopropionate
dcb	1,3-dimethyl-5-((2-carboxyphenyl)azo)barbiturate
dds	dodecylsulphate
dddo	3,9-dimethyl-4,8-diaza-3,8-undecadiene-2,10-dionedioxime
deae	2-diethylaminoethanolate
deap	3-N,N-diethylamino-1-propanolate
degly	N,N-diethylglycinate
den	di-(2-aminoethyl)amine
dien	diethylenediamine
dio	1,4-dioxane
dmae	2-dimethylaminoethanolate
dmap	3-N,N-dimethylamino-1-propanolate
dmbp	N,N′-dimethyl-4,4′-bipyridilium
dmcan	dimethylcantharate
dmf	dimethylformamide
dmhx	7,9-dimethylhypoxanthine
dmso	dimethylsulfoxide
dota	1,4,7,10-tetra-azacyclododecane-N,N′,N″,N‴-tetra-acetate

dpae	2-dipropylaminoethanolate
dpg	diphenylethanedione dioxime
dppo	bis(1,2-diphenylphosphinyl)ethane
dppz	3,6-di(2-pyridyl)pyridazine
dpt	di-(3-aminopropyl)amine
dtac	3,13-dimethyl-3,13-dinitro-1,5,11,15-tetraazaeicosane-8,18-diol
2,2′-dtdp	dithiopropionate
4-dtma	diethylenetriaminemonoacetate
dtmp	4-diethylenetriamine mono-3-propionate
dto	3,6-dithiaoctane
ea	ethanolamine
edta	ethylendiaminetetraacetate
egl	ethylene glycol
en	ethylenediamine
enbs	N,N′-ethylenebis(salicylideneiminate)
Et_2nia	N,N′-diethylnicotinamide
$(EtO)_2PS_2$	diethylthiophosphate
Et_2PO_2	diethylphosphate
Et_4todit	4,5,6,7-tetrathiocino[1,2-b:3,4-b′]diimidazolyl-1,3,8,10-tetraethyl-2,9-dithione
fa	formamide
fu	5-(aminosulphonyl)-4-chloro-2-[(2-furanylmethyl)-amino]benzoate (furisemide)
gh	glycyl-L-histidinate
glt	glycyl-L-leucyl-L-tyrosine
glu	glutamate
gly	glycinate
gly-L-ala	glycyl-L-alaninate
glygly	glycylglycinate
gly-L-met	glycyl-L-methionate
gmp	quanosine 2′-monophosphate
gp	quanosine 5′-phosphate
hfacac	hexafluoroacetylacetonate
his	L-histidine
hist	histamine
hmta	hexamethylenetetramine
hyxa	hypoxanthine
ida	iminodiacetate
im	imidazole

imH	imidazolate
i-pa	isopropylammonium
iptac	(isopropylthio)acetate
L-asp	L-aspartate
L-leu-L-tyr	L-leucyl-L-tyrosine
L-lys	L-lysinate
L-lys-L-tyr	L-lysyl-L-tyrosine
L-met-cys	methionyl-S-methylcysteine
L-prl	L-prolinate
L-tryp	L-tryptophane
L-tyr-L-his	L-tyrosine-L-histidine
L-val-L-tyr	L-valine-L-tyrosine
D-lys	D-lysinate
maep	2-(2-methylaminoethyl)pyridine
mal	maleate
map	9-methylallopurinol
mapm	1-methyl-4-aminopyrazolo[3,4-d]pyrimidine
mapox	N,N-bis[(3-methylamino)propyl]oxamide
mbp	tetraisopropylmethylene bisphosphonate
mcim	cimetidine modified by solvolysis of the nitrile function
mdap	2-methyl-1,2-diaminopropane
Me_2CNO_2	propane-2-nitronate
Me_2cys	D,L-β,β-dimethylcysteate
Me_2en	N,N′-dimethylenediamine
Me_4en	N,N,N′,N′-tetramethylenediamine
1-Meim	1-methylimidazole
2-Meim	2-methylimidazole
mel	mellitate
melH	melaminium
meppz	3-methyl-4-ethyl-5-phenylpyrazole
2-Mepy	2-methylpyridine
2-MepyNO	2-methylpyridine-N-oxide
3-Mepy	3-methylpyridine
4-Mepy	4-methylpyridine
4-Mepz	4-methylpyrazolate
2,4-Me_2py	2,4-dimethylpyridine
mgu	9-methylguanine
mpa	N-methylphenethylammonium
mpym	mepirizole
mpu	9-methylpurine

ms	methanesulphonate
msa	N-methylsalicylaldiminate
msc	S-methyl-N-(salicylidene)isothiosemicarbazidate
mtactd	2-methyl-1,4,8,11-tetraazacyclotetradecane-1-ene
nac	nitroacetate
nbteta	(6-p-nitrobenzyl)-1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetraacetate
nbtfac	(p-nitrobenzoyl)trifluoroacetonate
nic-NO	nicotinate-N-oxide
nitme	2,4,4,5,5-pentamethyl-1-oxyimidazoline-3-oxide
oadp	oxalamide-N,N′-di-3-propionate
$oaoH_2$	oxamidedioxime
ocidac	β-oxyethyliminodiacetate
odac	oxydiacetate
4-OHbz	hydroxybenzoate
2-OH-1,3-pn	2-hydroxy-1,3-propanediamine
8-OHqu	8-hydroxyquinoline
oro	ororate
oth	1,4-oxathiane
ox	oxalate
oxH	oxalic acid
oxd	oxamidoximate
paphy	pyridine-2-carboxaldehyde 2-pyridylhydrazone
pcpci	N-(2′-pyridylethyl)pyridine-2-carboximidate
pepci	N-(2′-pyridylcarbonyl)pyridine-2-carboximidate
pgly	5′-phosphoridoxylidene-glycinate
phen	1,10-phenanthroline
$Ph(Me)PO_2$	phenylmethylphosphinate
Ph_2PO_2	diphenylphosphate
o-pht	o-phthalate
o-phhH	dihydrogen-diphthalate
picr	picrate
pipH	piperidinium
pipzH2	piperazinium
piz	piperazine
pl-o-phen	N,N′-(1,2-phenylene)bis(pyridoxal-hydrochloride-iminate)
placc	Schiff base formed between 1-aminocyclopropane-carboxylic acid and pyridoxal
pmim	1-(2-pyridylmethyl)imidazole

pmsh	N′-pyridylmethylene-N″-salicyloylhydrazinate
1,2-pn	1,2-propanediamine
pp	4-(phosphomethyl)-2-hydroxo-2-oxo-1,4,2-oxaphosphoridinate
ppala	5′-phosphopyridoxylidene-DL-phenylalaninate
pptyr	pyridazolphosphate-DL-tyrosinate
ppzH	5-phenylpyrazole
pq	N,N′-dimethyl-4,4′-dipyridilium
ptyr	5′-phosphopyridoxylidene-DL-tyrosinate
Pu	purine
pur	purinium
px	pyridoxine
pxH	deprotonated pyridoxin
py	pyridine
pydc	pyridinium
pyNO	pyridine N-oxide
pyvgly	pyruvylideneglycinate
pyx	pyridoxylidene
pz	pyrazolate
pzH	pyrazole
pzc	pyrazinecarboxylate
pzdc	2,3-pyrazinedicarboxylate
pys	pyridine-3-sulphonate
pyz	pyridazine
pz	pyrazine
sal	salicylate
sbc	6,6′-spiro-bi(1,4,8,11-tetraazacyclotetradecane)
sc	semicarbazide
schb	Schiff base between(1*R*)-3-hydroxymethylenecamphor and (*S*)-phenylalanine
ser	L-serinate
sgly	N-salicylideneglycinate
sglu	N-salicylidene-(*S*)-(+)-glutamate
styr	N-salicylidene-L-tyrosinate
suc	succinate
ta	terephthalate
tace	tetraacetylethanate
tandp	3N,7N-(1,3,5,7-tetraazabicyclo[3,3,1]nonyl)-dipropionate
tart	meso-tartrate

D-tart	D-tartrate
taz	tenuazonate
tcb	1,2,4,5-tetracyanobenzene
tda	thiodiacetate
terpy	2,2′:6′,2″-terpyridine
tet	tetrathionate
teta	1,4,8,11-tetra-azacyclotetradecane-N,N′,N″,N‴-tetraacetate
tgly	N-tosylglycinate
th	tetrazolyl-1-acethydrazide
thf	tetrahydrofuran
4-tl	4-toluidine
tmpo	4-hydroxy-2,2,6,6-tetramethylpiperidinyl-N-oxy
tmso	tetramethylene sulphoxide
tp	[1,2,4]triazolo[1,5a]pyrimidine
tpmb	1,3,5-tris(pyrazol-1-ylmethyl)benzene
tppr	3,3′-thiopropionatopropionate
trien	diethylenetriamine
tt	trithionate
ttcd	1,5,9-trithiacyclododecane
1,2,4-trz	1,2,4-triazole
tsa	N-p-tolylsalicylideneaminate
tscac	thiosemicarbazideacetate
ttt	4,16-dioxa-1,7,13,19-tetrathia[7,7]-(2,5)-1,3,4-thiadiazolophane
tz	thiazole
val	(±)valine

1. INTRODUCTION

The chemistry of Cu(II) 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 X-ray studies of transition metal compounds are of copper compounds. Many structural studies of Cu(II) compounds have been carried out and have been classified and analyzed, mononuclear four- and five-coordinate,[1] six-, seven- and eight-coordinate[2] dimeric derivatives,[3] trimeric and oligomeric derivatives.[4] To date there has not been a comprehensive overview of polymeric Cu(II) structural chemistry, and this present report is aimed at providing such a survey up to 1992. This includes over 600 published polymeric Cu(II) structures which have been analyzed and classified in order to assist in the understanding of the stereochemical interactions in the coordination sphere of the Cu(II) species.

The systems discussed have been sorted by the coordination number of the Cu(II) atom. Within each coordination number, the compounds are listed in order of increasing covalent radius of the principle coordinating ligand atom and increasing complexity of the coordination sphere.

2. POLYMERIC COMPOUNDS

2.1. Four-Coordination

Crystallographic and structural data for polymeric four-coordinate Cu(II) compounds are gathered in Table I. There are 23 derivatives, mostly blue or green with some yellow compounds. In a dark blue derivative[5] the Cu(II) atom lies on a center of symmetry and is surrounded by O atoms from four phosphate groups in a nearly perfect square-planar arrangement. The Cu(II) atoms are joined by a double phosphate bridge. These bridges are linked in polymeric chains running along *b*. The distance between the bridged Cu(II) atoms is 4.9 Å which ruled out a bond.

A structure of another deep blue derivative[6] consists of well-separated infinite chains of centrosymmetric spiro-fused eight-membered rings extending along the crystallographic (110) direction. Each of the eight-membered rings consists of two Cu(II) atoms bridged by two phosphinate groups. The two crystallographically independent rings have qualitatively similar conformations which can be described as distorted chairs. The Cu(II) atoms have D_{2d} flattened tetrahedral coordination geometry. The Cu–Cu separation is 4.9555(8) Å.

The structure of $Cu(\mu\text{-}Bu_2PO_2)_2$[7] is very similar to that of $Cu(\mu\text{-}Et_2PO_2)_3$,[6] which also contains double phosphinate bridges. The copper atoms have the same D_{2d} flattened tetrahedral coordination geometry observed previously for $Cu(\mu\text{-}Et_2PO_2)_2$.[6] The Cu–Cu separation of 4.938(2) Å is slightly shorter that the value of 4.9555(8) Å in the ethyl analog.[6]

The structure of $Cu(\mu\text{-}Ph_2PO_2)$[8] also consists of infinite chains of centrosymmetric eight-membered rings formed by two copper atoms bridged by two phosphinato groups, but the Cu(II) atom resides on a crystallographic center of symmetry having a nearly square-planar coordination geometry.

TABLE I Crystallographic and structural data for polymeric Cu(II) coordination compounds: four-coordination[a]

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore*	*Cu–L* [Å]		*Cu–Cu* [Å]	*L–Cu–L* [°]		*Ref.*
Cu(μ-amp)$_2$	m	7.571(2)		CuO$_4$	μampO[b]	1.933(3,5)	4.94	O,O[b]	90.1(1,1.4)	5
(dark blue)	P2$_1$/n	4.943(1)	105.84(2)							
	2	11.212(3)								
Cu(μ-Et$_2$PO$_2$)$_2$	tr	7.700(1)	90.48(1)	CuO$_4$	μEt$_2$PO$_2$O	1.918(1,4)	4.9555(8)	O,O	94.2(5,1.8)	6
(deep blue)	P-1	9.807(1)	104.77(1)						148.5(6,1.3)	
	2	10.101(1)	112.21(1)							
Cu(μ-Bu$_2$PO$_2$)$_2$	tr	12.245(6)	101.18(4)	CuO$_4$	μBr$_2$PO$_2$O	1.920(4,6)	4.938(2)	O,O	94.8(2,1.2)	7
(blue)	P-1	9.863(5)	105.78(5)						146.5(2,7)	
	2	9.819(5)	93.77(4)							
Cu(μ-Ph$_2$PO$_2$)$_2$	m	16.618(2)		CuO$_4$	μPh$_2$PO$_2$O	1.914(3,3)	5.081(1)	O,O	90.0(1,7)	8
(blue)	C2/c	5.081(1)	96.39(2)							
	4	25.582(2)								
Cu{μ-(C$_6$H$_{13}$)$_2$PO$_2$}$_2$	tr	9.800	88.53(3)	CuO$_4$	μPO$_2$O	1.909(3,23)	4.9310(8)	O,O	94.13(12,1.83)	9
(blue)	P-1	12.336(6)	74.02(4)							
	2	13.352(8)	82.33(3)							
Cu(μ-acva1)$_2$	tr	5.687(4)	95.48(1)	CuO$_4$	μacva1O	1.935(3,27)	Not given	O,O	90.0(1,4)	10
(blue)	P-1	6.224(1)	89.80(4)							
	1	12.634(2)	98.46(4)							
(CN$_3$H$_6$)$_2$[Cu(μ-CO$_3$)$_2$]	tg	9.068(2)		CuO$_4$	μCO$_3$O	1.956(3,0)	Not given	O,O	93.6(1)	11
(not given)	P-4n2				O	1.968(3,0)			151.0(1)	
	8	12.583(3)						O,O	90.0(1,2.1)	
									174.2(1)	
[Cu(μ-taz)$_2$]·H$_2$O	m	13.77(1)		CuO$_4$	μtazO	1.87(2,1)	Not given	O,O	94.5(10,5)	12
(light blue)	P2$_1$	15.51(1)	109.5(2)							
	4	11.14(1)								
				CuO$_5$	μtazO	1.86(2,1)		O,O	95.5(10,3.5)	
						2.56(—)			93.3(—,6.8)	

TABLE I (*Continued*)

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore*	*Cu–L* [Å]	*Cu–Cu* [Å]	*L–Cu–L* [°]	*Ref.*
$Cu_3(\mu\text{-}OH)_2(\mu\text{-}nicNO)_2\text{-}$ $(H_2O)_2 \cdot (nicNO)_2$ (bluish green)	tr P-1 1	7.881(9) 9.658(11) 10.368(12)	97.32(9) 110.38(9) 109.53(9)	CuO_4 (×1)	μnicNO 1.933(2,21)	3.035	O,O 90.00(7,2.72)	13
				CuO_5 (×2)	μnicNO 1.979(2) 2.426(2) nicNO 1.943(2) H_2O 1.925(1) μHO 1.876(1)		O,O 90.95(7,6.40) 103.56(7) 158.73(7) 176.28(6)	
$Cu(\mu\text{-}4\text{-}Mepz)_2$ (green)	or Ibam 4	9.7436(6) 12.6106(8) 7.7482(6)		CuN_4	μMepzN 1.962(2)	Not given	N,N 96.8(1,3.1) 139.7(1)	14
$Cu(\mu\text{-}pz)_2$ (green) (at 294 K)	or Ibam 4	7.917(1) 11.491(2) 7.778(1)		CuN_4	μpzN 1.957(2,0)	Not given	N,N 96.2(1,2.6) 139.5(1)	15
$Cu(\mu\text{-}pz)_2$ (not given) (at 116 K)	or Ibam 4	7.870(2) 11.259(2) 7.807(3)		CuN_4	μpzN 1.959(2,0)	Not given	N,N 96.5(5,2.7) 140.72(5)	15
$[Cu_2(\mu\text{-}Cl)_4](pq)$ (black)	tg $P4_2/n$ 4	16.28(3) 5.90(2)		$CuCl_4$	μCl 2.36(2,2)	2.95	Cl,Cl 108(1.1,5)	16
$\{(ae)_2a\}[CuCl_4]Cl$ (yellow)	or Pnma 4	7.117(4) 23.78(1) 7.342(4)		$CuCl_4$	μCl 2.274(9,2) 2.876(4)	Not given	Cl,Cl 89.4(2,1.1)	17
$[Cu_2(\mu\text{-}Cl)_4Cl_2] \cdot$ $[Cu(mbp)_2(\mu\text{-}Cl)_2]$ (yellow brown)	tr P-1 1	10.799(1) 11.129(1) 11.509(1)	99.56(1) 115.24(1) 94.69(1)	$CuCl_4$	μCl 2.267(1,56) 2.1939(8)	3.3570(4)	Cl,Cl 96.94(3,1.50) 86.04(2) 147.90(3,1.34)	18
				CuO_4Cl_2	mbpO 1.944(2,10) μCl 2.865(1)		Cl,Cl 180.0(—) Cl,O 90.00(4,2.10) O,O 180.0(—) 90.00(7,2.64)	

α-Cu(μ-msa)$_2$	or	24.71(2)		CuO$_2$N$_2$	O	1.901(—,0)	3.33	O,N	91.1	19
(green)	Ibam	9.25(1)			N	1.989(—,0)				
	4	6.66(2)								
Cu(μ-ambz)$_2$	or	9.580(2)		CuO$_2$N$_2$	O	1.954(3)	Not given	N,O	88.0(4)	20
(dark green)	Pbca	7.213(1)			N	2.054(3)				
	4	21.867(3)								
Cu(μ-ttt)(NO$_3$)$_2$	m	8.674(2)		CuO$_2$N$_2$	O$_2$NO	1.988(2)	Not given	N,O	89.69(7)	21a
(not given)	P2$_1$/n	7.7115(6)	94.47(2)		μtttN	1.978(2)				
	2	17.143(2)								
Cu(μ-L-glu)(im)	or	24.286(2)		CuO$_2$N$_2$	μgluO	1.942(6,15)	Not given	O,N	84.4(2)[c]	21b
(violet)	P2$_1$2$_1$2$_1$	8.604(1)			μgluN	1.989(6)			91.9(2,3.4)	
	4	5.075(1)			imN	1.957(6)		O,O	176.3(2)	
								N,N	172.6(2)	
Cu(μ-dppo)Cl$_2$	m	12.206(2)		CuO$_2$Cl$_2$	μdppoO	1.960(—,0)	Not given	Cl,O	97.1(—)	22
(greenish blue)	C2/c	20.172(4)	97.26(2)		Cl	2.195(—,0)			140.1(—)	
	4	10.559(1)						O,O	90.6(—)	
								Cl,Cl	100.5(—)	
Cu(H$_2$O)$_2$Cl$_2$(5-crown-5)	or	15.667(3)		CuO$_2$Cl$_2$	H$_2$O	1.93(2)	Not given	Cl,Cl	151.5(6)	23
(light green)	Cmcm	8.004(2)			Cl	2.21(1,4)		Cl,O	93.2(9,1.5)	
	8	27.304(9)						O,O	154.4(18)	
				CuO$_2$Cl$_2$	H$_2$O	1.92(2)		Cl,Cl	180	
					Cl	2.19(1,7)		Cl,O	90.0(9,1.9)	
								O,O	176.1(18)	
Cu(H$_2$O)$_2$Br$_2$(5-crown-5)	m	8.698(4)		CuO$_2$Br$_2$	H$_2$O	1.98(3,3)	Not given	Br,Br	148(1)	24
(not given)	P2$_1$	13.740(7)	116.31(3)		Br	2.358(4,9)		O,Br	94(1,6)	
	2	8.019(4)						O,O	150(1)	
[Cu(μ-Et$_4$todit)Cl$_2$]·thf	or	32.674(6)		CuCl$_2$S$_2$	μtoditS	2.340(7,1)	7.601(4)	S,S	155.1(3)	25
(green)	Fdd2	34.547(6)			Cl	2.198(6)	9.185(5)	Cl,S	92.0(2,5.7)	
	16	10.162(3)				2.235(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 a maximum deviation from the mean value. [b] The chemical identity of coordinated atom/ligand is specified in these columns. [c] Five-membered metallocyclic ring.

The Cu–Cu separation of 5.081(1) Å is longer than found for the other Cu(II) phosphinates.[5–7]

A structure of blue $Cu\{\mu\text{-}(C_6H_{13})_2PO_2\}_2$[9] consists of well-separated infinite chains of centrosymmetric spiro-fused eight-membered rings propagating along the crystallographic *c*-axis. The Cu(II) atoms have the same D_{2d} flattened tetrahedral coordination geometry observed for the ethyl[6] and *n*-butyl[7] derivatives. The CuO_4 chromophores in the *n*-butyl and *n*-hexyl derivatives are slightly less compressed than in the ethyl derivative ($\alpha = 74.3°$, $73.3°$ and $73.0°$ for the ethyl, *n*-butyl, and *n*-hexyl derivatives, respectively). The Cu–Cu separation found in the *n*-hexyl derivative is 4.9310(8) Å.

In another blue derivative[10] the Cu(II) atom lies on the symmetry center and displays a square-planar geometry arising from coordination of one carboxylic O and one peptide O belonging to different N-acetyl-DL-valinato ligands, giving rise to a polymeric structure.

In polymeric $[Cu(\mu\text{-}CO_3)_2]^{2-}$[11] two independent copper atoms are present. One lies on a site of 222 symmetry $(\frac{1}{2}, 0, \frac{1}{4})$, while the other is on a site of −4 symmetry at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. In both cases, the environment of the Cu(II) atom comprises four oxygen atoms drawn from nearby carbonate groups, only one oxygen atom about each copper atom being independent, as the remaining are generated from it by the site symmetry. One Cu(II) atom is *pseudo*-tetrahedrally coordinated and the other Cu(II) atom is square-planar (Table I).

The asymmetric unit of a light blue derivative[12] contains four chemically equivalent tenuazonate ligands chelated to two Cu(II) atoms. Each ligand is chelated to a Cu(II) atom through its acetyl oxygen and the amide-(2-carbonyl)oxygen of the pyrolidene ring. The Cu(II) atoms differ from each other; one is in a square-planar arrangement (CuO_4) and the other is square-pyramidal (CuO_5). The dimers are hydrogen-bonded into sheets by water molecules.

The structure of one unit of the polymer[13] is shown in Figure 1. In one structural unit of the polymer there are three Cu(II) atoms (Cu1, Cu2 and Cu2′) quite close to each other. The distance between them is 3.035 Å. Four nicotinate N-oxide groups, two hydroxide groups and two water molecules are coordinated with the copper atoms. The structural units are connected with each other through two N-oxide oxygen atoms which are coordinated to Cu2 and Cu2′ atoms in separate units. The coordination around Cu1 is square-planar and around Cu2 (Cu2′) is distorted square-pyramidal (Table I).

There are three green derivatives[14,15] where structures involve extended chains of pyrazolate-bridged Cu(II) atoms extending along the *c* crystallographic axis. The coordination geometry about the Cu(II) atoms is

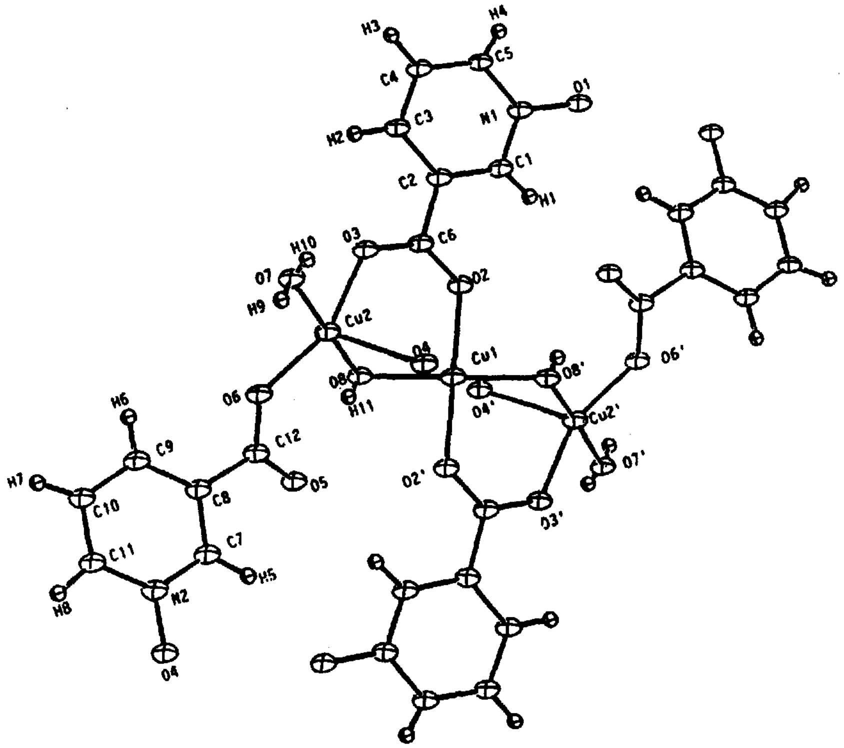

FIGURE 1 Structure of one $Cu_3(\mu\text{-}OH)_2(\mu\text{-}nicNO)_2(H_2O)_2(nicNO)_2$.[13]

distorted tetrahedral with Cu–N distances of 1.962(2), 1.961(5) and 1.957(2) Å in 4-Mepz, 4-Clpz and pz structures. The three unique N–Cu–N angles correspond to N atoms related to one another by three mutually perpendicular twofold axes intersecting at the copper (D_2 symmetry): those within the planar six-membered $Cu(N\text{–}N)_2Cu$ rings are 99.4(1)° (pz), 99.9(1)° (4-Mepz) and 100.5(3)° (4-Clpz), and the others are 94.3(1) and 139.5(1)° (pz); 93.7(1) and 139.7(1)° (4-Mepz); 92.4(2) and 140.8(3)° (4-Clpz), respectively.

The structure of a black derivative[16] contains planar paraquat cations and two crystallographically distinct types of chemically similar $[CuCl_2]_n^{n-}$ chain anions which extend parallel to the (001) axis of the crystal. Each Cu(II) atom is surrounded by a tetrahedron of chlorine atoms, each chlorine bridges two copper atoms. The tetrahedra about the copper atoms are significantly flattened along the –4 axis parallel to the fourfold crystal

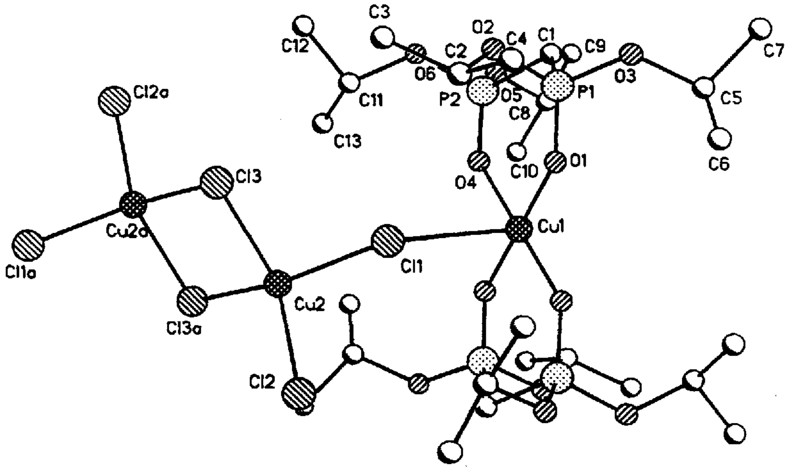

FIGURE 2 Structure of alternating $Cu(mbt)_2^{2+}$ and $Cu_2Cl_6^{2-}$ ions.[18]

axis. The flattening gives mean μCl–Cu–μCl angles of 113° and 103°, very acute Cu–Cl–Cu angles are 77°, and reduces the Cu–Cu distance within the chain to 2.95 Å.

A yellow derivative[17] exhibits a network of planar $CuCl_4^{2-}$ anions, and thermochromism was observed both above and below room temperature.

The structure of a yellow brown derivative[18] is comprised of essentially linear chains of alternating $Cu(mbp)_2^{2+}$ cations and $Cu_2Cl_6^{2-}$ anions which are linked together by singly-bridging chlorine atoms of the anion (Figure 2). Two such bridges result in a tetragonal geometry about the Cu(II) in the centrosymmetric cation, with the chlorine bridges forming elongated bonds to the axial positions of the cation. The $Cu_2Cl_6^{2-}$ anions are centrosymmetric with the two copper centers in the dimer linked together by a double chlorine bridge. The geometry of the Cu(II) in the anion is *pseudo*-tetrahedral (dihedral angle = 44.34(2)°). The Cu–Cu separation in the anion is 3.3570(4) Å and Cu–Cl–Cu bridge angles are 93.96(3)°.

The planar molecules of $Cu(\mu\text{-msa})_2$[19] form chains along the *c*-axis with a Cu–Cu separation of 3.33 Å. In a dark green derivative[20] the coordination of the Cu(II) atom is square-planar, with four methyl-amino-benzoate ligands acting as bridging bidentate ligands. Each Cu(II) atom is bonded to two carboxylate O atoms of two different ligands and to two N atoms of two other ligands. The O and N atoms are in *trans* positions. The bridging ligands lead to the (010) plane.

In a crystal structure of $Cu(\mu\text{-ttt})(NO_3)_2$[21] the macrocyclic ligand 4,16-dioxa-1,7,13,19-tetrathia[7,7]-(2,5)-1,3,4-thiadiazolophane, does not encapsulate a Cu(II) atom to form a discrete complex, but coordinates externally through the nitrogen atom to form linear polymers. The centrosymmetric square-planar Cu(II) atom is coordinated in *trans* fashion by an N atom from each of two macrocycles (Cu–N = 1.978(2) Å) and by two nitrate ions (Cu–O = 1.988(2) Å). The macrocycles are themselves centrosymmetric, yielding infinite chains of alternating macrocycles and metal centers along the *a*-axis of the crystal.

In a greenish blue derivative[22] the Cu(II) atom lies on a twofold axis and the bis(1,2-diphenylphosphinyl)ethane ligand lies on a center of symmetry. The crystal consists of infinite chains of $CuCl_2$ units linked by the phosphine oxide which is functioning as a bridging ligand (Table I). In a light green derivative[23] the $CuCl_2(H_2O)_2$ structural fragments are situated between two 15-crown-5 molecules, forming a polymeric chain with the inorganic and organic parts of the molecule alternating by hydrogen bonds.

The structure of $CuBr_2(H_2O)_2$(15-crown-5)[24] is similar to that of the chlorine adduct.[23] Coordination around the Cu(II) atom[25] involves two chlorine atoms and two S-thioamide atoms of two Et_4todit molecules related by a screw axis, and is nearer to a square-planar than to a tetrahedral arrangement. The bridging Et_4todit ligands form helical chains running parallel to the *c*-axis. The Cu–Cu distances in and between the chains are 7.601(4) and 9.185(5) Å, respectively.

Inspection of the data in Table I reveals two limiting coordination geometries are generally observed, square-planar and tetrahedral, from which the former prevails. In the series of four-coordinated derivatives the following chromophores are found: CuO_4,[5–11] CuN_4,[14,15] $CuCl_4$,[16–18] CuO_2N_2,[19–21] CuO_2Cl_2,[22,23] CuO_2Br_2[24] and $CuCl_2S_2$.[25] There are two examples[12,13] which contain are two non-equivalent Cu(II) atoms with the chromophores CuO_4 (square-planar) and CuO_5 (square-pyramidal). In[18] a tetrahedral $CuCl_4$ and a tetragonal-bipyramidal (CuO_4Cl_2)moieties are present.

In general, the mean Cu–L bond distances elongate with the covalent radius (in parenthesis) of the coordinated atom in the order: 1.95 Å (OL, 0.73 Å) < 2.20 Å (Cl, 0.99 Å) < 2.36 Å (Br, 1.14 Å) for monodentate; and 1.92 Å (OL, 0.73 Å) < 1.98 Å (NL, 0.75 Å) < 2.34 Å (SL,1.02 Å) for bidentate ligands. The mean Cu–Cl (terminal) bond distance of 2.20 Å is shorter by about 0.10 Å than that of the Cu–Cl (bridge) bond distance. In the series of hetero-bidentate ligands (O and N donor atoms), the mean Cu–L bond distances are 1.93 Å (O) and 2.02 Å (N), respectively. The Cu–Cu distances range from 2.95 Å[16] to 7.601 Å.[25]

2.2. Five-Coordination

Crystallographic and structural data for these compounds is presented in Table II. There are over 150 such derivatives in which Cu(II) atoms have primarily a square-pyramidal configuration and quite complex chain structures. For example, in $[Cu_2(\mu\text{-dota})(H_2O)_2]\cdot 3H_2O$[26] the Cu(II) atoms are in completely different environments. The two Cu(II) atoms are bridged by four carboxylate groups which come from four different macrocycles (Cu–Cu distance is 2.652(2) Å) and each Cu(II) additionally binds a water molecule. Another Cu(II) atom is coordinated by two carboxylate oxygens and four nitrogen atoms of the macrocycle which is folded to give a *cis*-octahedral geometry (CuN_4O_2).

The structure of a blue $Cu_4(\mu\text{-ac})_8(bpy)_2$ complex[27] (Figure 3) is composed of one-dimensional, well-separated polymeric chains, containing two different types of Cu_2 units, each at a crystallographic center of symmetry. The chains are formed by alternating $Cu_2(\mu\text{-ac})_4$ and $[Cu_2(\mu\text{-ac})_2(bpy)_2]^{2+}$ units that are linked by syn–anti bridging acetates. The Cu–Cu vectors are not colinear but form a zig-zag line, with Cu(2′)–Cu(2)–Cu(1) and Cu(2)–Cu(1)–Cu(1′) angles of 166.0(1)° and 135.9(1)°, respectively. The $Cu_2(\mu\text{-ac})_4$ unit contains four bidentate bridging acetates with Cu(2)–Cu(2′) distance of 2.669(1) Å and Cu(2) lies 0.216 Å above the O_4 least-squares plane fowards O_2 apical. The other dimeric unit, $[Cu_2(\mu\text{-ac})_2(bpy)_2]^{2+}$ has a centrosymmetric structure with two acetate groups providing mono-atomic bridges,

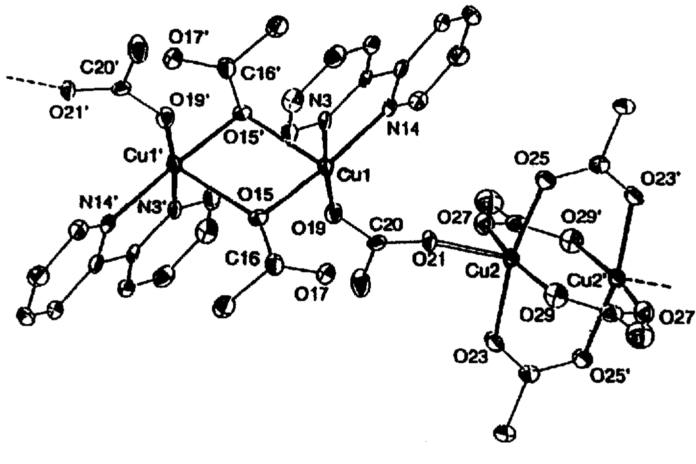

FIGURE 3 Structure of $Cu_4(\mu\text{-ac})_8(2,2'\text{-bpy})_2$.[27]

TABLE II Crystallographic and structural data for polymeric Cu(II) compounds; five-coordination[a]

Compound *(color)*	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	*α* [°] *β* [°] *γ* [°]	*Chromophore Cu-out of plane* [Å]	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°] *μL–Cu–μL* [°]	*L–Cu–L* [°]	*Ref.*
$[Cu_2(\mu\text{-dota})(H_2O)_2]\cdot 3H_2O$ (not given)	m $P2_1/c$ 4	11.607(5) 16.953(5) 12.986(2)	110.82(3)	CuO_5 Not given	μdotaO[b] 1.961(8,8) H_2O 2.164(8)	2.652(2)	O,O[b] Not given	26
$Cu_4(\mu\text{-ac})_8(2,2'\text{-bpy})_2$ (blue) (at 118 K)	tr P-1 1	9.272(2) 14.718(3) 8.023(1)	102.66(1) 103.89(1) 94.00(1)	CuO_5 0.216	μacO[b] 1.976(4,6) 2.162(3)	2.669(1)	O,O[b] 92.8(2,6.5) 167.5(2,2)	27
				CuO_3N_2 0.029	μacO 1.949(3) acμO 1.968(3) 2.353(3) bpyN 2.011(4,8)	3.358(1) 101.6(1) 78.4(1)	O,O 91.2(1,1.8) O,N 95.6(2,3.9) 173.6(2,5) N,N 80.6(2)[c]	
$Cu_4(\mu_4\text{-ac})_2(\mu\text{-ac})_2\text{-}(\mu\text{-MeO})_4$ (green)	m B2 4	11.328(2) 18.169(3) 9.846(2)	94.28(1)	CuO_5 Not given	μMeO 1.92(3,10) μacO 1.92(3,7) $\mu_4$acO 1.95(4,7) 2.61(4,9)	2.959(4,31)	O,O 76.8(9,2.4) 89.3(9,10.7) 107.2(9,2.7) 170.5(9,4.4)	28
$Cu_2(ac)(\mu\text{-}As_3O_6)$ (green)	m $P2_1/m$ 2	9.93 9.40 5.48	102.0	CuO_5 Not given	acO 1.92(2) $As_3O_6\mu O$ 1.94(2,2) 2.34(1)	3.014(4,4) 101.8(8,3)	O,O 92.3(9,4.7) 165(5,5)	29
$Cu_2(\mu_3\text{-cit})(H_2O)_2$ (green)	m $P2_1/a$ 4	14.477(9) 9.718(6) 6.890(5)	91.27(5)	CuO_5 0.14	μcitO 1.932(11,22) 2.277(11) citμO 1.925(8)	3.242(6) 115.2(1)	O,O 90.4(5,7.0) 106.1(5) 159.7(6) 173.8(6)	30
				CuO_5 0.33	μcitO 1.916(11,2) citμO 1.916(8) H_2O 2.096(11) 2.284(11)		O,O 89.0(4,8.2) 136.0(5,1.9) 170.1(6)	
$Cu(\mu\text{-HCOO})_2$ (royal blue)	or Pbca 8	14.195(5) 8.955(5) 6.218(5)		CuO_5 Not given	μHCOO 1.950(10,36) μO 2.397(8)	3.435(4)	O,O 90(1,5)	31

TABLE II (*Continued*)

Compound (*color*)	*Crystallographic classification* *space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore* *Cu-out of plane* [Å]	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°] μ*L–Cu–*μ*L* [°]	*L–Cu–L* [°]	*Ref.*
Cu(μ-sal)$_2$(H$_2$O)$_2$ (green)	or Pca2$_1$ 8	7.730(4) 11.795(9) 31.547(19)		CuO$_5$ Not given	μsalO 1.969(16,47) 2.264(11,1) H$_2$O 1.955(11,25)	5.114(3)	O,O 90.7(6,4.3) 175.6(5,3.0)	32
Cu(μ-sal)$_2$(H$_2$O)$_2$	m P2$_1$/a 8	7.730(4) 11.795(9) 31.783(19)	 96.98(1)	CuO$_5$ Not given	μsalO 1.969(5,41) 2.266(5) H$_2$O 1.956(5,1)		O,O 90.7(3,6.3) 175.6(2,2.4)	32
Cu{μ-Ph(Me)PO$_2$}$_2$- (dmf) (blue)	tr P-1 2	10.104(11) 11.110(2) 9.998(1)	112.47(3) 102.01(3) 90.97(2)	CuO$_5$ 0.16	O 1.96(1,3) dmfO 2.316(8)	5.190(5,9)	O,O 92.1(5,5.6) 170.8(5,4.3)	33
[Cu(4-OHbz)$_2$(H$_2$O)$_3$] · 5H$_2$O (not given)	or Cmc2$_1$ 4	24.47(2) 11.47(1) 7.265(5)		CuO$_5$ 0.21	OHbzO 1.947(5,0) H$_2$O 1.973(6,10) 2.341(12)	Not given	O,O 89.5(4,4.1) 116.0(4) 154.2(4) 168.7(4)	34
[Cu$_2${μ_4-C$_6$H$_2$(COO)$_4$}] · 10H$_2$O (blue)	m A2/a 4	9.679(5) 18.17(2) 12.18(1)	 113.32(5)	CuO$_5$ Not given	O 1.957(—,15) 2.259(—)	Not given	O,O 91.3(—,4.7) 126.7(—) 175.2(—)	35
Cu(μ_3-mal)(H$_2$O) (not given)	m P2$_1$ 2	8.78(2) 7.88(2) 5.35(1)	 125.1(5)	CuO$_5$ 0.08	$\mu_3$malO 1.99(2,2) H$_2$O 2.26(2)	Not given	O,O 91(1,3) 176(1,1)	36
[Cu$_{3.5}$(μ_4-mel)(H$_2$O)$_{10.5}$] · 4.5H$_2$O (blue)	or Iba2 8	19.277(3) 21.054(7) 12.956(4)		CuO$_5$ Not given	$\mu_4$melO 1.953(10,46) H$_2$O 2.201(8) 2.382(10) 2.425(8)	Not given	O,O 90.2(3,4.7) 102.4(4,2.5)	37
[Cu$_5$(μ-mel)(H$_2$O)$_{16}$] · 6H$_2$O (not given)	m Ia 4	25.757(1) 9.533(1) 18.540(1)	 97.96(1)	CuO$_5$ Not given	μmelO 1.94(1,6) H$_2$O 1.98(1,4) 2.39(1,4)	Not given	O,O 80.2(6,1) 91.0(7,6.8) 101.4(5) 173.2(7,7.0)	38

				CuO_6	μmelO 2.32(1) 2.51(1) H_2O 2.00(2,6)		O,O 81.3(6,1.2) 90.6(5,7.2) 106.9(5,5.5) 172.0(7,5.0)	
Cu(picr)(acac)$(H_2O)_2$ (not given)	m $P2_1(P2_1/m)$ 2	11.36 14.95 4.71	103	CuO_5 Not given	Not given		Not given	39
$Cu(urea)_4(\mu\text{-}SO_4)$ (not given)	or Pcan 4	9.289(1) 13.029(1) 8.891(1)		CuO_5 Not given	Not given		Not given	40
$(Cu(\mu\text{-}NO_3)_2(MeNO_2)$ (blue green)	or Pnma 4	12.41(4) 8.30(3) 7.08(3)		CuO_5 Not given	μNO_3O 1.95(2,1) MeONO 2.31(2)	Not given	O,O 88(—,6) 104(—)	41
$Cu(\mu\text{-}MePO_3)(H_2O)$ (not given)	m $P2_1/c$ 4	8.530(2) 7.602(2) 7.321(2)	90.11(3)	CuO_5 Not given	$\mu MePO_3O$ 1.955(2,22) 2.313(2) H_2O 1.999(2)	3.199(5)	O,O 89.7(5,5) 110.5(1) 166.2(5,3.8)	42
$Cu(\mu\text{-}1,1\text{-}N_3)$- $(\mu\text{-}1,1,3\text{-}N_3)\cdot$(2-Mepy) (black)	m $P2_1/a$ 4	8.237(2) 13.038(4) 8.953(3)	112.23(2)	CuN_5 Not given	$N_3\mu N$ 2.010(2,10) μN_3N 1.987(2) 2.273(2) MepyN 1.992(2)	3.095(1) 100.8(2,2.3)	N,N 79.4(1) 94.9(1,5.1) 129.8(1) 164.3(1,4.2)	43
$Cu(\mu\text{-}1,1\text{-}N_3)(\mu\text{-}1,3\text{-}N_3)\cdot$ (3-Mepy) (black)	m C2/c 8	23.120(9) 13.751(4) 6.663(2)	100.43(2)	CuN_5 Not given	$N_3\mu N$ 1.990(10,30) μN_3N 1.993(9) 2.436(10) MepyN 1.999(9)	Not given 108.5(7,7.6)	N,N 76.9(5) 92.7(4,2.6) 102.7(3,1.7) 153.2(3) 170.5(4)	44
$Cu(\mu\text{-}1,1\text{-}N_3)_2$(2-Brpy) (black)	tr P-1 2	5.808(2) 8.628(3) 10.256(3)	81.77(2) 75.25(3) 88.09(2)	CuN_5 Not given	$N_3\mu N$ 2.007(8,13) 2.332(9) BrpyN 2.076(8)	3.216(4,2.1) 100.0(4,2.1)	N,N 80.0(3,2.0) 95.6(3,3.0) 149.1(3) 170.3(4)	45

TABLE II (*Continued*)

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore Cu-out of plane* [Å]	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°] μ*L–Cu–*μ*L* [°]	*L–Cu–L* [°]	*Ref.*
[Cu_2(μ-1,3-N_3)(N_3)$_2$-	m	12.713(1)		CuN_5	μN_3N 2.04(1,2)	4.433(2)	N,N 86.2(5,2)^c	46
(Me_4en)$_2$]·(PF_6)	P2$_1$/c	31.240(4)	102.17(2)	0.20	N_3N 1.99(1,1)		93.3(5,8.2)	
(dark green)	8	13.259(6)			2.31(1,3)		168.6(5,4.3)	
					Me_4enN 2.04(1,3)			
				CuN_5	μN_3N 2.05(1,1)	4.444(2)	N,N 86.4(4,2)^c	
					N_3N 2.00(1,1)		93.3(6,9.2)	
					2.31(2,3)		168.4(6,4.8)	
					Me_4enN 2.05(1,3)			
Cu(μ-NCO)$_2$(2,4-Me_2py)	tr	10.20(3)	73.6(2)	CuN_5	OCNμN 2.044(20,56)	3.33(—,11)	N,N 95.7(7,4.8)	47
(not given)	C-1	10.08(8)	107.5(2)	0.209	2.458(18)	79.3(8,9)	109.3(6)	
	2	10.10(2)	145.8(2)		Me_2pyN 2.043(15)		151.6(7)	
							172.4(6)	
Cu(μ-hmta)$_2$(NCO)$_2$	tr	13.731(9)	91.05(4)	CuN_5	OCN 1.894(3,5)	Not given	N,N 89.6(1,4.7)	48
(green)	C-1	20.831(9)	90.54(6)	Not given	hmtaN 2.167(2,40)		107.2(1)	
	4	6.426(3)	107.39(6)		2.712(3)		135.3(9)	
							169.5(1)	
[Cu(μ-im)(dien)ClO_4	m	14.341(4)		CuN_5	dienN 2.098(7,57)	Not given	N,N 81.9(3,2)^c	49
(pale blue)	P2$_1$/c	15.473(2)	114.11(2)	Not given	μimN 2.061(6,4)		93.4(3,2.8)	
	8	12.822(2)					119.7(3,6.9)	
							170.8(3)	
				CuN_5	dienN 2.090(8,84)		N,N 82.5(3,10)^c	
				Not given	μimN 2.024(6,40)		93.8(3,1.3)	
							107.9(3)	
							125.2(3,2.3)	
							173.5(3)	
(cpa)[Cu(μ-Cl)$_2$Cl]	m	10.560(6)		$CuCl_5$	Cl 2.576(1)	3.084(1)	Cl,Cl 95.41(6,2.71)	50
(red)	P2$_1$/n	6.089(1)	106.06(4)	0.258	μCl 2.297(1,1)	84.11(5,2)	166.73(3,10)	
	4	15.274(4)			2.307(2,2)	85.49(6,22)		

(4-amp)[Cu(μ-Cl)$_2$Cl] (red)	or Pnma 4	11.854(4) 6.663(2) 12.561(5)		CuCl$_5$ 0.353	Cl 2.468(2) μCl 2.322(1,2)	3.405(1) 94.35(4) 85.65(4)	Cl,Cl 95.21(5,3.68) 162.53(3)	50
(6-amp)[Cu(μ-Cl)$_2$Cl]	or Pnma 4	11.407(6) 6.637(2) 12.785(6)		CuCl$_5$ 0.406	Cl 2.471(1) μCl 2.317(1,6)	3.419(1) 95.11(3) 84.90(3)	Cl,Cl 95.84(4,5.51) 159.81(3)	50
(pipH)[Cu(μ-Cl)$_2$Cl] (not given)	m C2/c 4	18.385(7) 8.439(4) 11.878(5)	103.63(5)	CuCl$_5$ Not given	Cl 2.250(1) μCl 2.273(2,29) 2.612(1)	3.440(2,51) 91.3(1,4.2) 85.8(4,1.3)	Cl,Cl 91.90(4,1.90) 104.65(4,3.67) 150.43(4) 177.35(5)	51
(pipzH$_2$)[Cu$_2$(μ-Cl)$_4$Cl$_2$] (not given)	tr P-1 1	7.984(4) 7.054(4) 6.104(3)	111.23(8) 99.95(9) 81.26(7)	CuCl$_5$ Not given	Cl 2.272(2) μCl 2.325(3,1) 2.271(3) 2.622(3)	3.446(3,4) 92.5(2,3.4) 87.6(1,3.4)	Cl,Cl 92.1(1,2.3) 101.5(4,3.4) 156.8(1) 173.1(1)	51
(i-pa)[Cu(μ-Cl)$_2$Cl] (not given)	tr P-1 2	11.692(8) 7.804(4) 6.106(3)	79.00(4) 122.60(4) 116.47(4)	CuCl$_5$ Not given	Cl 2.273(2) μCl 2.295(2,26)	3.462(2,45) 92.4(6,3.1) 99.5(7,2.1)	Cl,Cl 90.3(6,5.5) 160.53(8) 175.10(9)	52
(4-bpipH)[Cu(μ-Cl)$_2$Cl] (not given)	m C2/c 2	28.877(8) 8.440(2) 12.023(2)	101.9(1)	CuCl$_5$ Not given	Cl 2.261(3) μCl 2.300(3,23) 2.687(3)	3.487(2,72) 86.0(1,1.2)	Cl,Cl 91.8(1,2.3) 104.2(1,4.2) 151.0(1) 177.5(1)	53
(mpa)[Cu(μ-Cl)$_2$Cl] (red brown)	m P2$_1$/c 4	6.193(1) 8.365(1) 25.435(2)	104.71(1)	CuCl$_5$ Not given	Cl 2.257(1) μCl 2.295(1,12) 2.372(1) 2.528(1)	3.502(1,49) 85.0(1,1)	Cl,Cl 92.6(—,7) 101.6(1) 124.4(1) 132.9(1)	54
(dmbp)[Cu$_2$(μ-Cl)$_4$Cl$_2$] (not given)	m P2$_1$/n 2	6.30(1) 12.94(1) 10.63(1)	97.25(8)	CuCl$_5$ Not given	Cl 2.238(—) μCl 2.305(—,25)	Not given 95.8(—,1.8) 84.3(—,1.8)	Cl,Cl 92.6(—,3.3) 105.7(—,3) 148.3(—) 172.5(—)	55
(bim)$_2$[Cu$_2$(μ-Cl)$_6$] (dark brown)	m P2$_1$/n 4	18.567(6) 6.443(2) 16.810(2)	92.93(4)	CuCl$_5$ Not given	μCl 2.275(2,30) 2.316(2,71) 2.828(1,11)	3.607(1,170) 97.2(6,2)	Cl,Cl 82,8(6,2) 92.3(6,8) 101.4(5,1.3) 169.5(6,5.6)	56

TABLE II (*Continued*)

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore Cu-out of plane* [Å]	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°] *μL–Cu–μL* [°]	*L–Cu–L* [°]	*Ref.*
(melH)[Cu$_2$(μ-Cl)$_6$]	m	6.6600(1)		CuCl$_5$	μCl 2.294(2,53)	Not given	Cl,Cl 84.4(1)	56
(not given)	P2$_1$/c	10.0598(2)	96.011(3)	Not given	2.767(2)	96.7(1,2.2)	92.1(1,4.1)	
	4	19.2691(12)					173.4(1,2.1)	
				CuCl$_5$	μCl 2.300(2,38)		Cl,Cl 84.0(1)	
				Not given	2.692(2)		92.7(1,5.1)	
							170.5(1,1.4)	
(piz)[Cu$_2$(μ-Cl)$_6$]	tr	6.081(3)	81.14(6)	CuCl$_5$	μCl 2.293(2,28)	Not given	Not given	58
(not given)	P-1	7.041(3)	79.80(3)	Not given	2.606(2)			
	2	7.971(3)	68.951(7)					
(PMe)$_4$[Cu$_2$(μ-Cl)$_5$]	m	10.967(1)		CuCl$_5$	μCl 2.2509(8)	3.6693(5,2310)	Not given	59
(reddish brown)	P2$_1$/n	12.023(1)	109.86(7)	0.31	2.3165(8,155)			
	4	10.211(1)			2.5734(8)			
				CuCl$_5$	μCl 2.2605(8)		Not given	
				Not given	2.3106(8,99)			
					2.6810(8)			
(NMe$_4$)[Cu$_2$(μ_3-Cl)-	m	6.073(1)		CuCl$_5$	μCl 2.2685(6,99)	Not given	Cl,Cl 93.91(2,4.04)	60
(μ-Cl)$_3$Cl]	P2$_1$/c	19.58(1)	99.46(5)	Not given	2.6855(7)		177.49(2)	
(green)	4	10.62(1)			μ_3Cl 2.3099(5,53)			
				CuCl$_5$	Cl 2.2158(6)		Cl,Cl 90.59(2,4.65)	
				Not given	μCl 2.2723(6,195)		106.73(2)	
					2.3474(6)		173.12(2)	
					μ_3Cl 2.8880(6)			
(mapm)[Cu$_2$(μ-Cl)Cl$_3$]	m	26.319(4)		CuCl$_5$	Cl 2.285(2,12)	Not given	Cl,Cl 89.6(1,6.7)	61
(not given)	C2/c	8.352(2)	128.41(1)	Not given	μCl 2.317(2)	94.7(1)	100.9(1,2.8)	
	8	22.116(3)			2.812(2)		166.8(1,8.7)	
Cu(pur)(μ-Cl)$_4$Cl$_2$	m	12.723(3)		CuCl$_5$	Cl 2.270(2)	Not given	Cl,Cl 92.5(1,7.8)	62
(green)	P2$_1$/c	6.110(1)	100.11(1)	0.218	μCl 2.287(2,37)	92.4(1,7.0)	168.3(1,2.5)	
	4	17.234(4)			2.754(1)			
				CuCl$_5$	Cl 2.257(2)		Cl,Cl 89.9(1,6.0)	

					μCl 2.304(2,51) 3.072(2) purN 2.563(4)		173.3(1,1.6) N,Cl 90.4(1,6.9) 175.1(1)	
[Cu{15-C-15(MeCN)$_2$}] · [Cu$_3$(μ-Cl$_8$] (brown)	tr P-1 1	9.762(2) 9.644(2) 9.353(2)	95.02(2) 97.80(2) 122.53(2)	CuCl$_5$ Not given	μCl 2.271(4,13) 2.598(3)	Not given 72.6(1)	Cl,Cl 90.0(1,5.2) 107.4(2)	63a
				CuCl$_6$	μCl 2.255(3) 2.572(5) 2.787(4)		Cl,Cl 89.0(2,4.9) 103.1(1,1.5) 169.1(2,2)	
(i-pa)[Cu(μ-Br)$_2$Br] (not given)	tr P-1 2	12.135(6) 8.199(4) 6.397(3)	78.79(3) 124.72(2) 117.22(3)	CuBr$_5$ Not given	Br 2.414(3,16) μBr 2.435(2,23) 2.822(2)	3.629(3,16) 91.54(7,3.68)	Br,Br 92.84(7,7.09) 159.75(8) 174.42(8)	63b
[Cu(μ-pgly)(H$_2$O)] 3H$_2$O (not given)	tr P-1 2	8.394(4) 9.819(8) 10.884(7)	101.85(6) 97.48(5) 112.68(5)	CuO$_4$N 0.15	O 1.935(7,33) 2.317(8) N 1.935(9) H$_2$O 1.924(8)	Not given	N,O 84.6(3)^c 92.3(4)^d 91.8(3,3.9) 165.6(3,3.0) O,O 93.4(3,3.0) 170.0(3)	64
[Cu(μ-pptyr)(H$_2$O)] 4H$_2$O (green)	tr P-1 2	8.616(2) 11.843(3) 12.177(3)	103.40(2) 112.32(2) 76.50(21)	CuO$_4$N 0.2457(5)	O 1.941(3,40) 2.265(3) N 1.933(4) H$_2$O 1.955(3)	Not given	O,O 94.4(1,8.8) 164.9(1) O,N 83.5(1)^c 93.0(1)^d 96.6(1) 166.0(1)	65
[Cu(μ-ptyr)(H$_2$O)] 3.5H$_2$O (not given)	tr P-1 2	8.634(2) 11.827(2) 11.981(1)	94.07(1) 109.57(1) 103.40(1)	CuO$_4$N Not given	O 1.944(2,39) 2.263(2) N 1.930(2) H$_2$O 1.956(2)	Not given	O,O 94.3(1,9.1) 165.0(1) O,N 83.6(1)^c 92.9(1)^d 166.0(1)	66
[Cu(μ-ppala)(H$_2$O)] 2.5H$_2$O (not given)	tr P-1 2	8.777(3) 11.736(4) 12.188(4)	97.55(2) 108.72(2) 103.36(2)	CuO$_4$N Not given	O 1.947(7,34) 2.269(7) N 1.923(9) H$_2$O 1.972(8)	Not given	O,O 94.5(3,8.4) 164.6(3) O,N 83.5(3)^c 92.3(3)^d 165.7(3)	66

TABLE II (*Continued*)

Compound *(color)*	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore Cu-out of plane* [Å]	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°] μ*L–Cu–*μ*L* [°]	*L–Cu–L* [°]	*Ref.*
Cu(μ-ppala)(H_2O) (not given)	tr P-1 2	8.670(10) 12.925(12) 12.493(12)	111.7(4) 109.0(4) 65.5(2)	CuO_4N Not given	O 1.935(—,45) 2.13(—) N 1.89(—) H_2O 1.98(—)	Not given	Not given	67a
Cu(μ-pp)(H_2O) (not given)	m $P2_1/n$ 4	9.977(7) 7.801(8) 14.615(11)	108.54(5)	CuO_4N Not given	O 1.963(—,24) N 2.064(—) H_2O 1.939(—)	Not given	Not given	67b
Cu(μ-dcb)(H_2O) (not given)	or $P2_12_12_1$ 4	8.171(1) 10.302(3) 17.006(5)		CuO_4N 0.184(2)	O 1.937(3,58) N 1.949(3) H_2O 2.359(3)	4.962(9)	O,O 89.9(1,6.1) 102.3(1) 162.4(1) O,N 92.8(1,6)[d] 173.9(1)	68
[Cu(μ-sgly)(H_2O) · $0.5H_2O$ (dark green)	m C2/c 8	17.16(3) 6.84(2) 17.57(1)	111.29(5)	CuO_4N 0.227	O 1.941(6,13) 2.344(6) N 1.949(6) H_2O 2.016(6)	Not given	O,O 89.5(7,1.5) O,N 83.4(7)[c]	69a
[Cu(μ-sgly)(H_2O)] · nH_2O (green)	or $Pca2_1$ 4	20.21(2) 13.11(1) 7.19(1)		CuO_4N Not given	N 2.05(1) O 1.96(1,7) H_2O 2.22(1)	Not given	O,O 95(—) 171(—) O,N 105(—) 159(—)	69b
[Cu(μ-placc)(H_2O)]- (NO_3) · H_2O (dark green)	m $P2_1/a$ 4	13.222(3) 10.820(2) 11.821(3)	110.51(2)	CuO_4N Not given	O 1.915(4,29) 2.354(3) N 1.947(4) H_2O 1.968(5)	Not given	Not given	69c
[Cu(μ-placc)(H_2O)]$_2$ · $4H_2O$ (green)	tr P-1 2	15.700(2) 11.738(1) 9.281(1)	98.61(1) 97.34(1) 98.16(1)	CuO_4N Not given	O 1.927(3,18) 2.294(3) N 1.951(3) H_2O 1.968(3)	Not given	Not given	69c

				CuO_4N Not given	O 1.942(3,20) 2.321(3) N 1.958(3) H_2O 1.945(3)	Not given	Not given	
[Cu(μ-sglu)(H_2O)$_2$] · H_2O (dark green)	m $P2_1$ 2	11.305(8) 10.919(9) 5.991(4)	 104.31(5)	CuO_4N 0.193(1)	O 1.913(8,12) N 1.908(8) H_2O 2.007(8) 2.315(7)	Not given	O,N 85.2(3)^c 94.9(3)^d 94.4(3,9.2) 162.2(3) O,O 91.3(3,4.6) 172.2(3)	70
[Cu_2(μ-edta)(H_2O)] · $2H_2O$ (blue)	m B2/b 4	16.901(4) 19.132(4) 6.067(3)	 119.63(1)	CuO_4N Not given	O 1.932(4,7) N 2.012(5) H_2O 1.936(4)	Not given	O,N 85.0(2,6)^c 175.6(2) O,O 95.2(2,1.2) 168.9(2)	71
[Cu_3(μ-gp)$_3$(H_2O)$_8$] · $4H_2O$ (light green)	or $P2_12_12$ 4	20.813(4) 23.356(3) 11.392(1)		CuO_4N 0.26	O 2.035(23) N 2.301(23) H_2O 1.996(23,45)	Not given	N,O 97.9(9,6.1) O,O 89.0(9,7.3) 163.9(9,3.4)	72
				CuO_4N 0.22	O 1.963(22,12) N 2.346(23) H_2O 2.006(22,5)		N,O 96.2(9,2.4) O,O 89.4(9,4.5) 167.0(9,1.5)	
				CuO_4N 0.26	O 1.952(23) N 2.205(23) H_2O 2.030(23,69)		N,O 98.0(9.2.0) O,O 89.0(9,5.0) 164.1(10,6)	
[Cu_3(μ-gp)$_3$(H_2O)$_8$] · $5H_2O$ (not given)	or $P2_12_12_1$ 4	23.369(5) 20.711(5) 11.305(3)		CuO_4N Not given	O 1.962(10,46) N 2.241(10,46) H_2O 1.948(10,30)	Not given	Not given	73
[Cu(μ-$EtCO_2$)$_2$(μ-tsa)$_2$ (dark green)	tr P-1 2	12.565(2) 13.040(2) 12.230(2)	107.73(1) 115.72(1) 100.18(1)	CuO_4N Not given	$\mu EtCO_2O$ 1.941(3) μtsaO 1.960(2) tsaμO 1.917(3) 2.371(3) μtsaN 1.979(3)	3.172(1,50)	O,O 88.7(1,4.0) 175.7(1) O,N 92.0(1,6) 102.5(1) 167.5(1)	74
				CuO_4N Not given	$\mu EtCO_2O$ 1.949(2) μtsaO 1.929(3)		O,O 87.6(1,2.5) 174.6(1)	

TABLE II (*Continued*)

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore* *Cu-out of plane* [Å]	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°] μ*L–Cu–*μ*L* [°]	*L–Cu–L* [°]	*Ref.*
					tsaμO 1.901(3)		O,N 92.2(1,3)	
					2.519(3)		100.6(1)	
					μtsaN 1.968(3)		173.1(1)	
Cu(μ-EtCO$_2$)$_2$(4-tl)	tr	12.466(7)	116.03(3)	CuO_4N	μEtCO$_2$O 1.923(15,6)	3.270(6,73)	O,O 89.9(6,9.7)	75
(dark green)	P-1	12.183(6)	91.73(3)	Not given	EtCO$_2$$\mu$O 1.948(14)	99.5(6,3)	176.9(6)	
	—	11.598(6)	73.82(3)		2.318(13)		O,N 89.7(6,5.8)	
					tlN 2.318(13)		174.7(6)	
				CuO_4N	μEtCO$_2$O 1.939(14,18)		O,O 80.7(6)	
				Not given	EtCO$_2$$\mu$O 1.893(13)		91.4(6,5.4)	
					2.465(14)		174.0(6)	
					tlN 2.065(15)		O,N 87.7(6,5.9)	
							171.5(6)	
Cu(μ-but)$_2$(4-Clan)	m	12.586(3)		CuO_4N	butμO 1.941(8)	3.283(3,36)	O,O 92.2(6,5)	76
(green)	$P2_1/a$	12.883(2)	104.73(5)	Not given	2.405(8)		O,N 87.8(6,5.0)	
	8	21.532(4)			μbutO 1.940(8,11)			
					ClanN 2.068(8)			
				CuO_4N	butμO 1.923(8)		O,O 91.8(7,1.4)	
					2.442(8)		O,N 87.8(6,4.7)	
					μbutO 1.940(8,14)			
					ClanN 2.063(9)			
[Cu(μ-px)(pxH)]NO$_3$ ·	m	14.839(2)		CuO_4N	μpxO 1.974(6,59)	Not given	O,O 89,8(2,2.1)^d	77
2.5H$_2$O	$P2_1/n$	10.977(5)	99.78(1)	Not given	pxHN 2.011(6)		103.1(2)	
(green)	4	13.028(2)					178.6(2)	
							O,N 90.1(2,2.7)	
							103.3(2)	
							153.5(2)	

$Cu(\mu\text{-gly})(NO_3)(H_2O)$ (not given)	m $P2_1/n$ 4	9.278(1) 5.183(1) 13.982(1)	103.26(1)	CuO_4N Not given	μglyO 1.943(5) 2.373(5) μglyN 1.982(6) O_2NO 1.995(5) H_2O 1.965(5)	Not given	Not given	78
$[Cu_4(\mu\text{-ac})_4(\mu\text{-bdmap})_2\text{-}(ac)_2\cdot(H_2O)_2]\cdot 4H_2O$ (blue)	tr P-1 1	10.554(5) 11.611(3) 9.406(3)	102.87(2) 99.87(3) 101.88(3)	CuO_4N Not given	μacO 1.964(4) acμO 1.950(4) 2.460(5) bdmapμO 1.912(4) μbdmapN 2.064(5)	3.496(2) 5.435(3)	O,O 170.0(2,5.5) N,O 171.1(2)	79
				CuO_4N Not given	acO 1.959(4) μacO 1.973(5) bdmapμO 1.930(6) μbdmapN 2.065(6) H_2O 2.336(5)		O,N 179.0(2)	
$Cu(\mu\text{-cmva1})$ (not given)	m $P2_1$ 2	9.84(1) 7.26(1) 6.63(1)	107.12(4)	CuO_4N Not given	O 1.93(2,7) 2.26(2) N 2.00(2)	Not given	Not given	80
$Cu(\mu\text{-styr})$ (dark green)	or $P2_12_12_1$ 4	12.310(8) 5.830(5) 20.357(11)		CuO_4N Not given	O 1.930(9,56) μO 1.915(8) 2.490(8) N 1.938(8)	4.358(2) 163.1(4)	O,O 92.0(3,4.2) 177.9(3) O,N 83.2(3)^c 94.8(4)^d 115.9(3) 169.0(3)	81
$Cu(\mu\text{-schb})$ (green)	or $P2_12_12_1$ 4	19.903(5) 13.835(3) 6.968(1)		CuO_4N Not given	O 1.956(6) N 1.916(7)	Not given	O,N 83.5(2)^c 96.7(3)^d O,O 92.3(3,5)	82
$Cu(\mu\text{-CNacac})_2$ (dark blue)	m $P2_1/n$ 4	10.005(1) 12.149(1) 11.246(1)	96.748(4)	CuO_4N 0.114(1)	O 1.920(2,8) N 2.468(3)	Not given	O,O 87.3(1,1) 92.3(1,1)^d 173.2(1,15) O,N 93.4(1,4.6)	83

TABLE II (*Continued*)

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore Cu-out of plane* [Å]	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°] *μL–Cu–μL* [°]	*L–Cu–L* [°]	*Ref.*
$[Cu_9(\mu_3\text{-}Br)_2(\mu\text{-}cpo)_6]_n \cdot xH_2O$ (blue)	trg P321 —	21.273(10) 8.0168(11)		CuO_4Br Not given	μcpoO 1.91(2) cpoμO 193(4,6) μ_3Br 3.058(3) H_2O 1.92(3)	3.332(5) 119.2(10)	O,O 85.5(12,1.0)[c] 94.2(10,4.5) 171.3(8,3.9) BrO 84.8(4,1.0) 94.2(7,4.2) 168.8(6,2)	84
				CuO_6 Not given	μcpoO 1.93(2) 2.31(1) H_2O 1.99(2)		O,O 79.6(6,3.1)[c] 94.2(7,4.2) 168.8(6,2)	
[Cu(μ-α-alaha)-(α-alaha)] · $2H_2O$ (not given)	m $P2_12_12_1$ 4	5.073(2) 11.463(3) 20.198(5)	95.48(3)	CuN_4O Not given	alahaN 1.959(3,35) μalahaN 1.974(3,34) alahaO 2.878(3)	Not given	N,N 81.5(1,1)[c] 98.3(1,6) 176.6(1,1.1) O,N 91.7(1,4.1)	85
$Cu_2(\mu\text{-}apox)(\mu\text{-}NCO)_2$ (blue)	m $P2_1/n$ 2	13.237(3) 7.715(3) 7.161(3)	94.02(1)	CuN_4O Not given	μapoxN 1.975(4,19) μapoxO 1.989(3) NCOμN 1.945(4) 2.620(4)	3.212(1) 6.153(1) 88.1(3) 91.8(2)	N,O 84.0(1)[c] 90.1(2) 175.2(2) N,N 95.2(2)[d] 92.2(2,4.4) 169.4(2)	86
$Cu_2(\mu\text{-}1,3\text{-}N_3)_2$-(μ-mapox) (dark green)	m $P2_1/n$ 2	11.439(3) 10.522(1) 7.376(1)	106.47(4)	CuN_4O 0.006	μmapoxN 1.988(9,36) μmapoxO 1.980(5) μN_3N 1.976(8) 2.542(9)	Not given 95.3(3) 84.7(3)	N,N 95.7(3)[d] 93.8(3,3.2) 172.6(3) N,O 83.6(2)[c] 91.1(3,2.0) 174.1(4)	87
$[Cu_3(\mu\text{-}1,1\text{-}N_3)_5\text{-}(\mu_3\text{-}1,1,1\text{-}N_3) \cdot (2\text{-}bzpy)_2]$ (black)	or Pbca 8	14.803(3) 11.282(2) 39.31(1)		CuN_4O Not given	μN_3N 1.992(9,3) μ_3N 2.017(9) bzpyN 2.037(9) bzpyO 2.296(9)	Not given 103.1(4,15.0)	N,N 91.5(4,5.0) 160.8(4,5.8) N,O 76.3(4)[c] 98.7(4,8.4)	88

				CuN_6 Not given	μN_3N 2.001(9,26) 2.370(9) μ_3N_3N 2.627(7)		N,N 75.0(4,7.2) 96.0(4,8.9) 167.5(4,6.9)	
				CuN_5O Not given	μN_3N 2.008(9,9) 2.386(9) μ_3N 2.010(9) bzpyN 2.020(9) bzpyO 2.336(9)		N,N 72.6(4) 92.8(4,6.3) 170.1(4,2) N,O 75.8(4)^c 94.7(4,3.9) 162.4(4)	
$[Cu(NH_3)_4(H_2O)$- (18-crown-6)$]_n(PF_6)_{2n}$ (not given)	or Cmcm 4	19.275(2) 10.018(1) 14.672(1)		CuN_4O Not given	H_3N 2.04(1,1) H_2O 2.29(1)	Not given	Not given	89
[Cu(terpy)(μ-CN)]- $(NO_3)\cdot H_2O$ (blue green)	m $P2_1/c$ 4	12.230(11) 7.742(6) 17.160(15)	90.93(5)	CuN_4C 0.26	terpyN 2.016(12,76) μNC 1.920(16) N 2.207(14)	Not given	N,N 78.9(5)^c 97.6(4,4.6) 156.7(5) N,C 99.0(5,1.2) 159.9.(5)	90
$[Cu_2(\mu$-sbc)(μ-Cl)]- $(ClO_4)_3\cdot$EtOH (blue)	m I2/a —	15.730(9) 14.368(6) 16.434(4)	101.51(3)	CuN_4Cl 0.15	sbcN 2.01(—) μCl 2.627(2)	5.25(—) 6.41(—)	Not given	91
Cu(μ-im)(imH)$_2$Cl (light blue)	or $P2_1mn$ 2	7.243(1) 13.726(1) 6.096(1)		CuN_4Cl 0.25	μimN 2.058(4) imHN 1.975(5,12) Cl 2.559(2)	Not given	Cl,N 99.6(3,3.1) N,N 162.0(3,3.8)	92
$(NEt_4)_8[Cu_{14}Cl_{28}O_4]$ (red orange)	tr P-1 1	13.184(4) 13.292(4) 17.993(6)	77.09(3) 87.56(3) 72.08(2)	Cu^1Cl_4O	μ_4O 1.920(11) μ_3Cl 2.314(7,19) 2.553(4) μCl 2.307(6)	Not given O 109.4(5,3.1) Cl 78.7(2,5.0) 155.5(3,10.9)	O,Cl 87.5(4,5.3) 178.9(4) Cl,Cl 92.6(2,6.3) 138.7(2) 110.7(2,2.1)	93
				Cu^2Cl_4O	μ_4O 1.908(11) μ_3Cl 2.355(5) 3.100(7) Cl 2.312(7) Cl 2.175(7)		O,Cl 82.3(4,10.5) 165.6(4) Cl,Cl 96.5(3,2.1) 139.6(2) 119.0(3)	

TABLE II (*Continued*)

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore Cu-out of plane* [Å]	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°] *μL–Cu–μL* [°]	*L–Cu–L* [°]	*Ref.*
				Cu^3Cl_4O	μ_4O 1.920(13) μ_3Cl 2.560(5) μCl 2.395(6) 2.391(5)		O,Cl 83.2(3,5) 177.5(4) Cl,Cl 96.8(2,2.2) 107.1(2) 124.4(2,1.8)	
				$Cu^4Cl_3O_2$	μ_4O 1.920(9) μ_3O 1.933(8) μ_3Cl 2.353(7,8) 2.465(6)		O,O 176.8(4) O,Cl 90.0(4,4.5) Cl,Cl 119.9(2,7.8)	
				$Cu^{11}Cl_4O$	μ_3O 1.907(9) μ_3Cl 2.804(4) μCl 2.336(9,11) Cl 2.196(9)		O,Cl 84.3(4,5.1) 151.3(2) 178.2(4) Cl,Cl 99.3(3,6.8)	
				$Cu^{12}Cl_4O$	μ_3O 1.903(11) μCl 2.313(6,6) 2.828(5) Cl 2.196(7)		O,Cl 83.3(4,1.1) 176.3(2) Cl,Cl 97.9(3,4.8) 112.0(2) 141.4(3)	
				$Cu^{13}Cl_4O$	μ_3O 1.890(11) μCl 2.358(6,11) 2.712(5) Cl 2.189(9)		O,Cl 82.5(3,1.2) 179.5(3) Cl,Cl 98.8(3,4.7) 112.5(2) 138.8(2)	
Cu(μ-Cl)Cl_2(ap) (not given)	or Pbca 8	7.197(1) 24.900(1) 10.269(1)		$CuCl_4N$ Not given	Cl 2.252(1,4) μCl 2.296(1) 2.657(1) apN 2.047(2)	Not given	N,Cl 88.0(1,4.2) 176.9(1) Cl,Cl 92.0(1,3.1) 113.1(1) 153.9(1)	61

$Cu_2(\mu\text{-}Cl)_4(4\text{-ambp})_2$-	m	29.903(4)		$CuCl_4N$	μCl 2.294(4)	3.419(13,16)	Cl,Cl 91.6(2,6)	94
(EtOH)	$P2_1/a$	6.202(2)	92.88(4)	Not given	2.451(6,1)	88.5(2,6)	170.4(4)	
(red orange)	4	8.195(2)			2.593(5)		Cl,N 88.8(3,4)	
					ambpN 2.030(10)			
				$CuCl_4ON$	μCl 2.294(4)		Cl,O 85.5(5,5.7)	
				Not given	2.451(6,1)		O,N 92.2(5)	
					2.593(5)			
					EtHO 2.059(17)			
					ambpN 2.030(10)			
$\{Cu(\mu\text{-}Cl)_2\}_3(\mu\text{-oth})_2$	tr	9.375(5)	112.17(12)	$CuCl_4S$	μCl 2.284(2,9)	Not given	Cl,Cl 85.3(1,5)	95
(red)	P-1	7.370(5)	112.56(11)	Not given	2.339(2)		93.3(1,1.9)	
	1	7.821(4)	76.18(5)		2.496(2)		111.1(1)	
					μothS 2.339(2)		176.9(1)	
							Cl,S 91.5(1,5.8)	
							112.1(1)	
							136.5(1)	
				$CuCl_4O_2$	μCl 2.261(2)	Not given	Cl,Cl 90.0(1,1.3)	
				Not given	2.347(2)		Cl,O 92.6(1,1.1)	
					μothO 2.664(6)			
$[Cu_2(\mu_3\text{-}OH)(\mu\text{-}OH)$-	tr	9.281	98.68	CuO_3N_2	μHO 1.941(15)	2.782(5)	O,O 92.4(—,1.7)	96
$(MeNH_2)_4\cdot(H_2O)]SO_4$	P-1	11.311	92.94	Not given	μ_3HO 2.000(—)	3.107(—)	O,N 90.7(—,2.9)	
(dark blue)	2	7.425	113.19		2.403(15)	78.9(8,3)	104.5(—)	
					MeH_2N 2.014(19,7)	89.3(7)	N,N 97.8(—)	
						127.9(—)		
				CuO_3N_2	μHO 1.961(15,23)		O,O 98.4(—,1.0)	
				Not given	H_2O 2.365(15)		O,N 90.7(—,4.0)	
					MeH_2N 2.018(19,7)		N,N 91.9(—)	
$[\{Cu(\mu\text{-}OH)(2,2'\text{-bpy})\}_2\cdot$	tr	9.022(2)	103.51(2)	CuO_3N_2	μHO 1.927(2,4)	2.870(1)	O,O 98.06(9,2.33)	97
$(\mu\text{-}C_4O_4)]\cdot 4H_2O$	P-1	9.040(2)	103.42(3)	0.150(1)	μC_4O_4 2.380(2)	7.882(2)	83.74(9)	
(blue)	1	8.409(2)	103.37(2)		bpyN 2.011(3,15)	96.4(2)	O,N 93.89(10,6.47)	
							151.54(9)	
							171.98(10)	
							N,N 80.62(10)	

TABLE II (*Continued*)

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore Cu-out of plane* [Å]	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°] μ*L–Cu–*μ*L* [°]	*L–Cu–L* [°]	*Ref.*
$Cu_3(\mu\text{-}OH)_2(\mu\text{-}CO_3)_2$-	m	13.430(5)		CuO_3N_2	μHO 1.95(—,3)	2.879(—)	N,N 80.3(—,1)^c	98
(2,2′-bpy)$_3$	$P2_1/b$	17.100(5)		Not given	μO_2CO 2.24(—,1)	95.40(—,1.20)	O,N 95.4(—,2.4)	
(green)	4	22.270(8)	128.30(2)		bpyN 2.02(—,1)			
				CuO_4N_2	μOCO_2 1.95(—)		N,N 80.1(—)^c	
				Not given	2.60(—)		O,N 93.2(—,1)	
					$CO_3\mu O$ 2.24(—)		O,O 97.4(—,2)	
					2.46(—)		117.6(—,6)	
					bpyN 2.01(—,2)			
$[Cu_2(\mu\text{-}msc)_2(\mu\text{-}ClO_4)]\cdot$	m	7.463(1)		CuO_3N_2	mscμO 1.947(5,19)	2.946(1)	O,N 90.6(2)^d	99
ClO_4	$P2_1/n$	12.535(2)		0.137	μmscN 1.934(7,7)	98.5(3,3)	107.8(3)	
(dark green)	4	29.408(5)	106.11(1)		μClO_4O 2.518(5)	78.1(2,2)	N,N 82.6(3)^c	
				CuO_3N_2	mscμO 1.942(5,10)		O,N 90.7(2)^d	
				0.003	μmscN 1.930(7,7)		109.2(3)	
					μClO_4O 2.691(5)		N,N 82.1(3)^c	
$[Cu_2(\mu\text{-}OH)(\mu\text{-}msb)$-	or	42.153(8)		CuO_3N_2	μHO 1.958(8)	3.014(2)	O,O 92.1(5,2.7)	100
$(\mu\text{-}ClO_4)\cdot(H_2O)]\cdot$	Ccc2	18.258(3)		0.05	msbμO 1.969(7)	101.1(4,2)	O,N 92.2(5,2.9)^d	
$0.5H_2O$	8	7.534(1)			N 1.9719(11,42)	78.7(3,6)	171.0(4,2.1)	
(green)					H_2O 2.574(12)		N,N 95.1(5)^d	
				CuO_4N_2	μHO 1.939(8)		O,O 90.1(6,8.4)	
				Not given	msbμO 1.939(6)		173.5(5)	
					N 1.981(10,20)		O,N 91.0(6,4.1)^d	
					μClO_4O 2.644(17)		172.3(4,2.1)	
					2.712(13)		N,N 94.7(4)^d	
$[Cu(\mu\text{-}hfc)(\mu\text{-}4,4'\text{-}bpy)_2]\cdot$	m	10.404(4)		CuO_3N_2	μhfcO 1.942(6)	3.018	O,O 81.3(2,1.9)^c	101
$dmf\cdot H_2O$	$P2_1/n$	16.454(5)	103.99(3)	0.329	hfcμO 1.941(5)	100.6(2)	157.7(2,1.3)	
(dark green)	2	13.539(5)			μbpyN 1.985(6,0)		O,N 96.6(2,4.9)	
							N,N 105.7(3)	

Cu(μ-dmap)(μ-NCO) (blue green)	m $P2_1/c$ 4	9.426(2) 7.356(2) 13.696(3)	117.35(1)	CuO_3N_2 Not given	dmapμO 1.930(1,23) dmapμN 2.066(2) μNCO 2.581(3) μOCN 1.919(2)	3.024(1) O,76.8(1)	O,N 96.8(1,2.8)^d 168.2(1,4) N,N 93.6(1) O,O 95.5(1,5.0)	102
Cu(μ-3-ap)(μ-3-apH) (blue)	m $P2_1/c$ 4	8.944(2) 13.689(5) 10.309(2)	113.31(2)	CuO_3N_2 Not given	μapHO 2.461(9) μapHN 2.001(8) apμO 1.932(6,4) apμN 1.975(11)	3.034(1) 103.5(3) 76.5(3)	O,N 94.4(3,3.7)^d 168.5(4,1) O,O 96.2(3,9) N,N 91.8(4)	103
Cu_2(μ-ac)$_2$(μ-amoxa) (blue)	m $P2_1/n$ 4	6.633(5) 21.146(7) 7.698(4)	100.1(2)	CuO_3N_2 0.13	acμO 1.97(2) 2.31(7) μamoxaO 1.998(8) μamoxaN 1.98(2,4)	3.261(1) 5.24(5) 99.0(1) 80.9(1)	N,N 96.2(1)^d N,O 87.0(1,2.8) 111.2(1) 171.4(3,4.6) O,O 92.8(1,3.4)	104
[Cu_2(μ-ac)$_2$(μ-bhben)] · 2MeOH (green blue)	tr P-1 1/2	8.080(3) 8.166(3) 16.688(4)	91.33(2) 113.86(2) 107.29(2)	CuO_3N_2 0.015	μacO 1.952(6) 2.495(6) μbhenN 1.985(9,41) μbhenO 1.882(7)	3.383(2) 7.352(2)	O,O 87.7(3,6.0) O,N 91.5(3,7.6) 93.4(3)^d 175.6(4.3) N,N 86.7(3)^c	105
Cu(μ-CO_3)$(NH_3)_2$ (dark blue)	m $P2_1/c$ 4	5.640(2) 10.579(3) 7.462(3)	97.49(1)	CuO_3N_2 Not given	μCO_3O 1.988(2,2) 2.303(2) H_3N 1.978(2,7)	3.500(1)	O,O 66.38(8)^e 92.57(8,58) O,N 96.29(10,1.91) N,N 97.80(12)	106
[Cu(μ-ta)(3-Mepy)$_2$] · (3-Mepy)$_{0.5}$ · 0.5MeOH (light blue)	m $P2_1/c$ 4	9.703(4) 13.184(8) 19.825(4)	115.12(2)	CuO_3N_2 Not given	μtaO 1.970(4,21) 2.386(6) MepyN 2.018(6,6)	4.414(2)	O,O 87.6(1) 113.8(2) 158.3(3) O,N 89.9(2,4.3) N,N 178.9(3)	107
[Cu_2(μ-ac)(2,2′-bpy)$_2$] · $2H_2O$ (at 130 K) (blue)	tr P-1 1	8.842(2) 12.266(2) 7.708(1)	98.71(1) 106.35(1) 109.68(1)	CuO_3N_2 0.186	acO 1.974(2) μacO 1.936(2) 2.294(2) bpyN 2.02(2,2)	4.554(1)	O,O 91.4(1,5.8) O,N 91.6(1,5.2) 110.3(1) 168.3(1,6.5) N,N 80.4(1)^c	27

TABLE II (*Continued*)

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore Cu-out of plane* [Å]	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°] *μL–Cu–μL* [°]	*L–Cu–L* [°]	*Ref.*
[Cu_2(μ-teta)(H_2O)]·	tr	9.254(4)	92.01(2)	CuO_3N_2	O 1.940(6,3)	4.776	Not given	26
$5H_2O$	P-1	10.220(3)	100.01(2)	0.17	2.243(7)	5.532		
(not given)	2	15.937(2)	113.71(2)		N 2.022(7,1)			
				CuO_3N_2	O 1.938(7,11)			
				0.22	N 2.033(7,6)			
					H_2O 2.236(6)			
[Cu_2(μ-nbeta)(H_2O)]·	m	10.501(3)		CuO_3N_2	μtetaO 1.970(7,23)	4.828(—)	N,N 98.0(4)^d	108
$7H_2O$	Pc	9.216(3)	92.06(2)	Not given	μtetaN 2.023(9,1)		N,O 85.1(3,1)^c	
(deep blue)	2	17.640(4)			H_2O 2.274(8)		95.6(3,2)	
							168.6(3,1.1)	
							O,O 95.0(3,1.0)	
				CuO_3N_2	μtetaO 1.928(7,6)		N,N 96.3(3)^d	
				Not given	2.312(7)		N,O 85.6(3,5)^c	
					μtetaN 2.030(9,22)		93.8(3,5)	
							171.7(3,4.3)	
							O,O 93.3(3,4.7)	
Cu(μ-SO_4)(μ-hyxa))-	m	4.955(1)		CuO_3N_2	μO_2SO_2 1.916(3)	4.955(1)	N,N 162.4(1)	109
(H_2O)	$P2_1$	12.948(3)	92.15(1)	0.18	2.244(3)		N,O 90.4(1,4.9)	
(blue)	2	7.241(1)			μhyxaN 2.018(3,22)		103.3(1)	
					H_2O 1.978(3)		O,O 92.0(1,1.6)	
							175.5(1)	
Cu(μ-dtdp)$(py)_2$(H_2O)	or	22.268(15)		CuO_3N_2	μdtdpO 1.95(1,0)	5.700(4)	O,O 96.9(6)	110
(blue)	$Pna2_1$	14.855(12)		0.21	H_2O 2.23(1)		156.4(7,3.5)	
	4	5.670(4)			pyN 2.04(1,2)		O,N 90.4(6,1.5)	
							N,N 174.6(6)	
[Cu(μ-cab)(py)]·$3H_2O$	m	15.070(8)		CuO_3N_2	μcabO 1.904(6,38)	6.322(3)	O,O 101.1(2,3.1)	111
(green)	$P2_1/n$	7.230(4)	96.86(1)	0.177(3)	2.462(4)		157.8(2)	
	4	19.165(10)			μcabN 2.000(7)		O,N 89.7(2,1.2)^d	
					pyN 2.092(8)		N,N 177.4(3)	

Cu(μ-tace)(Me$_4$en)$_2$-	m	15.598(2)		CuO$_3$N$_2$	μtaceO 1.888(2,1)	7.257(1)	O,O 92.5(1)^d	112
(ClO$_4$)$_2$·(H$_2$O)	P2$_1$/c	8.748(1)	106.22(1)	0.0608(5)	H$_2$O 2.855(4)	8.002(1)	95.9(1)	
(purple)	4	26.508(3)			Me$_4$enN 2.030(3,3)	8.748(1)	O,N 92.7(1,3.0)	
							172.0(1,3.7)	
							N,N 87.0(1)^c	
				CuO$_4$N$_2$	μtaceO 1.900(3,3)		O,O 78.6(1,2.1)	
				0.0873(5)	H$_2$O 2.496(3)		92.6(1)^d	
					O$_3$ClO 2.988(5)		88.5(1,3.5)	
					Me$_4$en 2.040(3,2)		161.2(1)	
							O,N 94.8(1,3.5)	
							169.5(1,8.3)	
							N,N 86.0(1)^c	
[Cu(μ-NO$_3$(trien)]NO$_3$	or	9.050(4)		CuO$_3$N$_2$	μNO$_3$O 2.123(4)	Not given	N,O 94.0(1,1.1)	113
(blue)	Pmnb	9.066(4)		Not given	2.287(3)		123.8(1)	
	4	12.944(4)			2.579(4)		149.8(2)	
					trienN 1.996(5,3)		O,O 50.7(1,3.1)^e	
							86.3(3)	
							N,N 85.1(1)^c	
							168.8(1)	
[Cu(μ-HCOO)(HCOO)-	or	9.731(1)		CuO$_3$N$_2$	HCOO 1.951(3)	Not given	N,N 170.87(11)	114
(py)$_2$]·H$_2$O	Pnma	14.351(1)		0.066	μHCOO 1.967(3)		O,O 89.16(12,4.38)	
(blue)	4	10.302(1)			2.313(3)		178.7(13)	
					pyN 2.025(3,0)		N,O 92.83(8,1.42)	
[Cu(μ-C$_4$O$_4$)(mpym)-	or	18.592(3)		CuO$_3$N$_2$	μC$_4$O$_4$ 2.054(3,55)	Not given	O,O 91.2(1,9)	115
(H$_2$O)]·2H$_2$O	Pbcn	14.723(2)		Not given	H$_2$O 1.935(3)		109.5(1)	
(brown)	8	13.755(3)			mpymN 2.026(4,7)		O,N 92.8(1,3.4)	
							115.4(1)	
							134.3(1)	
							175.9(1)	
							N,N 79.7(1)^c	
Cu(μ-ox)(2-Meim)$_2$	or	8.235(2)		CuO$_3$N$_2$	oxO 1.973(4,12)	5.395(1)	O,O 82.7(1)^c	116
(blue)	Pbc2$_1$	19.565(5)		0.0596(1)	μO 2.276(4)		86.7(2,1.7)	
	4	7.994(2)			MeimN 1.984(4,1)		O,N 92.0(2,3.9)	
							114.1(2)	
							163.8(2,7.1)	
							N,N 95.3(2)	

TABLE II (*Continued*)

Compound *(color)*	*Crystallographic* *classification* *space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore* *Cu-out of plane* [Å]	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°] *μL–Cu–μL* [°]	*L–Cu–L* [°]	*Ref.*
Cu(μ-dap)(ox) (light blue)	tr P-1 2	9.693(2) 11.039(2) 7.441(2)	91.33(2) 78.32(3) 112.83(2)	CuO_3N_2 Not given	oxO 1.971(5,11) dapO 2.394(4) N 1.986(5,11)	Not given	O,O 83.5(2)^c 95.7(2,2.4) O,N 93.7(2,9.0) 168.2(2,5.1) N,N 90.9(2)^d	117
Cu(μ-pht)(py)$_2$ (green blue)	m P2$_1$/c 8	18.199(6) 11.991(14) 17.923(8)	 119.98(2)	CuO_3N_2 0.343	μphtO 1.945(5,23) 2.316(4) pyN 2.070(6,55)	Not given	O,O 60.6(2)^e 103.4(2) 163.192) O,N 95.2(2,4.7) 139.7(2) N,N 114.3(2)	118
				CuO_3N_2 0.265	μphtO 1.938(5,17) 2.285(4) pyN 2.106(5,78)		O,O 61.4(2)^e 104.1(2) 161.9(2) O,N 94.9(2,4.0) 150.1(2) N,N 106.2(2)	
[Cu(μ-pht)(phen)- $(H_2O)]\cdot 0.5H_2O$ (blue)	or Pbcm 4	11.670(3) 11.175(3) 14.073(3)		CuO_3N_2 0.035(2)	μphtO 1.930(4,0) H_2O 2.411(6) phenN 2.0145(5,0)	Not given	O,O 86.7(2)^c 91.7(2) O,N 93.0(2,2.7) N,N 82.0(2)^c	119
Cu(μ-pyx)(val) (green)	trg R-3 18	25.53 13.32		CuO_3N_2 0.14	μpyxO 1.93(—) 2.28(—) N 1.93(—) valN 1.99(—)	Not given	O,O 92.3 O,N 83.1^c 91.4^d 92.3	120
[Cu(μ-L-asp)(im)]· $2H_2O$ (blue)	or P2$_1$2$_1$2$_1$ 4	16.049(2) 9.622(1) 7.465(1)		CuO_3N_2 0.086	μaspO 1.97(2,3) 2.37(2) imN 1.98(2)	Not given	O,O 92.3(7) 101.6(8) 166.0(9)	121

							O,N 80.4(7) 85.6(7)^c 93.3(7,3.9) N,N 170.5(9)	
Cu(μ-D-ala)$_2$ (blue)	or P$2_12_12_1$ 4	11.63(1) 8.77(1) 8.43(1)		CuO$_3$N$_2$ 0.13	μalaO 1.947(7,3) 2.390(7) μalaN 1.979(8,0)	Not given	O,N 84.2(3,6)^c 171.7(3.6) O,O 92.1(3) N,N 98.6(3)	122
[Cu(μ-L-leu-L-tyr)- (H$_2$O)]·2H$_2$O·EtOH (deep blue)	or P$2_12_12_1$ 4	15.545(1) 16.121(2) 8.6838(5)		CuO$_3$N$_2$ Not given	O 1.986(3,20) N 1.958(3,47) H$_2$O 2.291(3)	Not given	N,N 83.9(1)^c N,O 82.4(1)^c 103.2(1,5.2) 164.8(1,1.1) O,O 83.7(1) 91.4(1,1.5)	123
Cu(μ-tandp) (blue)	or P$2_12_12_1$ 4	12.370(4) 6.358(3) 26.029(4)		CuO$_3$N$_2$ 0.364(4)	O 1.95(2,0) 2.13(2) N 2.03(2,3)	Not given	O,O 96.4(7,7) O,N 85.3(7,5)^c 101.8(7,5.2) N,N 87.7(7)^d	124
Cu(μ-pl-o-phen) (black)	tr P-1 2	12.028(31) 20.378(6) 11.378(3)	113.10(2) 84.13(2) 95.99(2)	CuO$_3$N$_2$ 0.132	O 1.912(5,1) 2.336(6) N 1.950(6,3)	Not given	O,O 77.4(2) 89.6(2,5.6) 161.1(2) O,N 83.6(2) 94.0(2,2.2) 102.2(2) 175.8(2,1.0)	125
				CuO$_4$N$_2$ Not given	O 1.933(5,1) 2.480(6) 2.641(6) N 1.956(6,5)		O,O 90.7(2,2.9) O,N 94.6(2,2.5) 171.9(3,1.1) N,N 84.4(2)	
Cu{(μ-L-met-cys)- (MeO)} (not given)	m P2_1 4	10.535(2) 8.836(2) 14.188(2)	99.08(2)	CuO$_3$N$_2$ Not given	O 1.99(—,4) 2.34(—) N 1.97(—,7)	Not given	N,N 83(—)^c N,O 86(—,4)^c 103(—,3) O,O 93(—)	126

TABLE II (*Continued*)

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore Cu-out of plane* [Å]	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°] μ*L–Cu–*μ*L* [°]	*L–Cu–L* [°]	*Ref.*
Cu(μ-gly-L-met) (blue)	or $P2_12_12_1$ 4	10.354(6) 11.471(7) 8.872(5)		CuO_3N_2 0.235	O 2.005(3,15) 2.237(3) N 1.992(4,72)	Not given	O,O 90.2(1,1.7) 106.6(1) O,N 83.8(2,1.8)^{c} 104.0(1,1.3) 162.8(2,6) N,N 83.89(2)^{c}	127
[Cu(μ-gly-L-ala)]· $2H_2O$ (blue)	or $P2_12_12_1$ 4	9.18(1) 9.75(1) 8.94(1)		CuO_3N_2 0.136	O 1.991(6,32) 2.352(6) N 1.954(8,53)	Not given	O,N 82.3(8)^{c} O,O 92.8(8) N,N 84.1(8)^{c}	128
[Cu(μ-L-val-L-tyr)]· $4H_2O$ (blue)	or $P2_12_12_1$ 4	8.33(1) 14.28(2) 16.23(2)		CuO_3N_2 0.068	O 1.976(2,7) 2.795(2) N 1.950(2,22)	Not given	N,O 80.3(1.8)^{c} 121.2(1.8) 158.2(1.8) 171.1(1.8) O,O 121.5(1.8)	129
[Cu(μ-enbs)]·$CHCl_3$ (red)	m $P2_1/c$ 4	13.42(2) 7.54(3) 17.88(2)	 96.0(3)	CuO_3N_2 0.049	μenbsN 1.94(1,9) μenbsO 1.90(9) enbsμO 1.929(9) 2.79(9)	Not given	O,N 92.5(4,1.1)^{d} O,O 90.2(4) N,N 84.7(4)^{c}	130
[Cu(μ-glt)]Et_2O· $4H_2O$ (blue)	or $P2_12_12_1$ 4	9.316(2) 25.76(2) 21.05(1)		CuO_3N_2 Not given	O 1.95(2) 2.57(2) N 1.96(2,4)	Not given	O,N 85(1,6) 109(1,6) O,O 87(1,3)	131
				CuO_3N_2 Not given	O 1.97(2,3) 2.32(2) N 2.00(22)	Not given	O,N 85(1,4) 100(1,2) O,O 92(1,3)	
Cu(μ-abpo)$_2$(abpo)Cl_2 (not given)	tr P-l 1	11.185(5) 10.410(5) 7.862(8)	97.8(1) 81.6(1) 103.7(1)	CuO_3Cl_2 0.29	μabpoO 2.010(10,21) abpoO 2.27(1) Cl 2.199(6,5)	3.274(4)	O,O 70.9(—) 95.7(—,1.2) O,Cl 95.0(—,5.7) Cl,Cl 102.4(—)	132

Cu(μ-L-prl)(H_2O)Cl (blue)	m $P2_1$ 2	9.509(2) 5.206(2) 8.189(2)	109.40(2)	CuO_3NCl 0.18	μprlO 1.948(3) 2.286(5) μprlN 1.994(5) H_2O 1.987(5) Cl 2.261(2)	Not given	O,O 89.7(2,2.3) O,N 84.9(1)^c 92.4(1) Cl,O 93.3(1,1.5) 165.23(7) Cl,N 94.9(1)	133
Cu(μ-degly)Cl (blue)	or $P2_12_12_1$ 4	9.978(2) 12.624(3) 7.129(1)		CuO_3NCl Not given	μdeglyO 1.961(3) deglyμO 1.947(4) 2.801(4) N 2.044(3) Cl 2.199(1)	4.72(—) O 167.0(2)	O,O 51.5(1)^e 92.0(1,5.2) O,N 84.3(1)^c 120.6(1) 167.1(1) Cl,O 95.5(1,1.5) 162.4(1) Cl,N 97.3(1)	134
[{Cu_2(μ-bhedto)- (H_2O)$_2$}·(μ-SO_4)] (dark green)	m C2/c 4	21.47(5) 7.49(1) 9.75(2)	111.93(10)	CuO_3NS 0.09	O 2.002(4) N 1.935(5) S 2.265(5) H_2O 1.967(5) μSO_4O 2.442(2)	5.18(1) 6.75(1)	O,O 90.6(2.4.8) O,N 81.5(2)^c 97.7(2) O,S 97.0(2,1.0) S,N 87.7(2)^c	135
Cu(μ-tscac) (green)	m $P2_1/n$ 8	14.04(3) 14.46(3) 9.47(3)	105.5(5)	CuO_3NS Not given	O 2.04(—,9) N 2.08(—) S 2.28(—)	Not given	O,O 169(—) S,O 150(—)	136
[Cu(μ-L-lys-L-tyr)- (H_2O)]·H_2O (deep blue)	m $P2_1$ 2	8.787(5) 9.753(5) 10.525(5)	101.69(5)	CuN_3O_2 0.070(1)	N 1.895(7) 2.023(8,22) O 1.981(6) H_2O 2.348(8)	Not given	O,O 89.3(3) O,N 83.6(3)^c 91.9(3,3.8) 168.0(3) N,N 84.6(3)^c 101.6(3) 168.2(3)	137
Cu(μ-4-dtma)(NCS) (not given)	m C2/m 4	20.036(3) 8.271(3) 6.655(2)	96.85(2)	CuN_3O_2 Not given	SCN 1.962(7) μdtmaN 2.047(5,20) μdtmaO 2.191(4) 2.749(5)	Not given	N,N 90.2(2,6.2) 154.0(2) 178.8(2) O,N 81.4(2)^c 92.2(2,5.2) O,O 168.3(2)	138

TABLE II (*Continued*)

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore Cu-out of plane* [Å]	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°] *μL–Cu–μL* [°]	*L–Cu–L* [°]	*Ref.*
Cu(μ-glu)(2,2′-bpy)	or	7.674(1)		CuN_3O_2	bpyN 2.019(11,8)	Not given	N,N 81.2(4)^{c}	21b
(deep blue)	$P2_12_12_1$	17.738(4)		0.289	μgluO 1.960(8)		100.4(4)	
	8	21.761(5)			2.245(9)		173.5(4)	
					μgluN 1.987(10)		N,O 83.4(4)^{c}	
							96.1(4,10.6)	
							151.7(4)	
							O,O 100.6(4)	
				CuN_3O_2	bpyN 2.014(12,6)		N,N 80.8(5)^{c}	
				0.238	μgluO 1.926(9)		98.4(5)	
					2.160(10)		158.8(5)	
					μgluN 1.999(10)		N,O 85.5(4)^{c}	
							96.3(5,5.3)	
							172.0(5)	
							O,O 95.3(5)	
[Cu(μ-L-tryp)(phen)]-	or	28.430(4)		CuN_3O_2	phenN 2.00(1,1)	Not given	N,N 83.0(6)^{c}	139
$ClO_4 \cdot 2.5H_2O$	$P2_12_12_1$	11.085(2)		Not given	μtrypN 2.02(1)		99.8(6)	
(not given)	4	8.162(3)			μtrypO 1.93(1)		160.4(5)	
					2.29(1)		O,O 89.7(5)	
							N,O 84.0(5)^{c}	
							90.4(6,3.2)	
							112.3(5)	
							176.2(6)	
[Cu(μ-ida)(terpy)] ·	m	23.41(1)		CuN_3O_2	terpyN 1.997(6,54)	Not given	O,O 103.3(2)	140
$Me_2CO \cdot H_2O$	$P2_1/n$	10.538(7)	91.3(1)	0.04	μidaO 1.966(5)		O,N 95.9(2,4.0)	
(blue green)	4	8.372(6)			2.175(6)		102.3(2)	
							154.4(2)	
							N,N 80.0(2,4)^{c}	
							159.9(2)	

Cu(μ-tda)(terpy) (bright green)	m C2/c 4	10.551(6) 21.23(1) 8.633(5)	 112.0(2)	CuN_3O_2 Not given	terpyN 1.998(4,36) μtdaO 2.095(3,0)	Not given	O,N 97.9(1,1.9) 134.0(1) O,O 91.9(1) N,N 79.2(1)^c 158.4(1)	141
[Cu(μ-HCOO)(trien)]- HCOO (blue)	or Pnam 4	8.954(13) 11.640(14) 9.676(13)		CuN_3O_2 Not given	trienN 2.016(7,7) μHCOO 2.035(5) 2.169(5)	Not given	N,N 85.2(1)^c 168.8(2) N,O 93.8(1,9) 111.8(3) 152.6(2) O,O 95.6(2)	142
[Cu(μ-ac)(bmima)]ClO_4 (blue)	tr P-1 1	5.176(5) 8.489(3) 10.066(3)	95.09(5) 95.72(3) 102.37(4)	CuN_3O_2 0.085	mimaN 1.996(3,51) μacO 1.928(2) 2.415(2)	5.176(2)	O,O 102.41(8) O,N 92.2(8,10.8) 173.9(1) N,N 81.4(2,1)^c 162.0(1)	143
Cu(μ-L-tyr-L-his) (violet)	or $P2_12_12_1$ 4	17.388(5) 6.560(1) 13.060(2)		CuN_3O_2 0.06	N 1.971(4,51) O 1.938(4) 2.601(4)	6.725(2)	N,N 83.6(2)^c 93.9(2)^d 177.0(2) O,N 90.0(1,4.7) O,O 85.3(3) 174.8(1)	144
[Cu_2(μ-pht)(trien)$_2$- (ClO_4)]·ClO_4 (dark blue)	m $P2_1$ 2	12.101(6) 7.805(4) 15.415(7)	 109.82(4)	CuN_3O_2 0.11	trienN 1.999(7,17) μphtO 1.927(5) O_3ClO 2.46(5)	4.180(3) 6.704(4) 109.0(3)	N,N 84.1(4,3)^c 163.2(5) N,O 92.2(6,1.4) 174.2(4)	145
				CuO_3N_3 Not given	trienN 1.993(9,11) μphtO 2.010(7) 2.318(8) 2.800(8)		O,O 52.0(3) 94.0(3) 145.8(4) N,N 84.5(4,1)^c 166.5(4) N,O 98.8(3,1.7) 116.8(3) 168.0(4)	

TABLE II (*Continued*)

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore Cu-out of plane* [Å]	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°] *μL–Cu–μL* [°]	*L–Cu–L* [°]	*Ref.*
Cu(pmsh)(μ-NCS) (green)	m $P2_1/n$ 4	16.46(1) 15.72(1) 5.63(1)	92.4(1)	CuN_3OS 0.18	pmshN 1.925(4) 2.038(3) pmshO 1.990(3) μSCN 1.930(5) μNCS 2.709(2)	Not given	N,N 80.5(1)^c 90.6(1,10.1) 170.1(1) N,O 78.9(1)^c N,S 94.9(1,6) O,S 96.1(1)	146
[Cu(paphy)(μ-Cl)]- $(PF_6)\cdot H_2O$ (green)	m $P2_1/c$ 4	16.245(6) 15.731(8) 6.698(2)	99.19(3)	CuN_3Cl_2 0.109(2)	paphyN 1.98(1,4) μCl 2.217(4) 2.805(4)	3.919(3) 102.0(2) 73.1(1)	N,N 80.1(1,1.1)^c 160.1(4) N,Cl 94.1(3,6.4) 167.6(4) Cl,Cl 103.2(1)	147
Cu(pcpci)(μ-Cl) (blue)	m Pc 2	3.963(2) 8.48(3) 18.21(12)	94.9(2)	CuN_3Cl_2	Not given		Not given	148
$[Cu(\mu\text{-pmim})_2]\cdot H_2O$ (blue)	tr P-1 2	7.75(2) 9.81(2) 14.63(1)	74.50(5) 80.15(5) 87.77(5)	CuN_3Cl_2 Not given	μmimN 1.976(6,0) 2.290(6) Cl 2.350(2,6)	Not given	N,N 87.9(2,4) 175.5(3) N,Cl 90.8(2,1.4) 104.6(2) 119.9(2) Cl,Cl 135.5(1)	149
$Cu_2(\mu\text{-bpepc})(\mu\text{-Cl})Cl_2$ (dark green)	m $P2_1/c$ 4	7.95(1) 27.00(3) 10.25(1)	92.1(1)	CuN_3Cl_2 Not given	μbpepcN 2.006(7,50) Cl 2.363(3) μCl 2.384(4)	Not given 106.9(1)	N,N 78.2(3)^c 95.0(3)^d 170.0(3) Cl,N 92.6(2,3.4) 110.2(2) 142.0(2) Cl,Cl 106.4(1)	150

				CuN_3Cl_2 Not given	μbpepcN 1.991(7,37) Cl 2.239(4) μCl 2.622(4)	Not given 103.0(1)	N,N 79.5(3)[c] 95.0(3)[d] 172.2(3) Cl,N 91.1(2,4.7) 110.5(2) 145.3(2) Cl,Cl 103.0(1)	
Cu(pcpci)(μ-Br) (blue)	m Pc 2	3.888(3) 8.641(3) 17.944(1)	92.63(6)	CuN_3Br_2 0.19	pcpciN 1.906(11) 2.023(12,4) μBr 2.409(2) 2.887(2)	3.888(3)	N,N 82.4(5,2)[c] 88.0(5,1.5) 164,4(5) Br,Br 94.0(2) N,Br 96.1(4,4.5) 168.3(4,3.0)	148
[Cu(pepci)(μ-Br)]PF_6 (blue)	or $Pc2_1b$ 16	7.904(3) 24.816(3) 34.289(4)		CuN_3Br_2 Not given	pepciN 1.99(2,4) μBr 2.417(3,16) 2.861(3,5)	4.846(4) 7.58(2) 134.1(1)	Not given	151
				CuN_3Br_2 Not given	pepciN 1.99(2,7) μBr 2.400(3,19) 2.879(3,8)	4.851(4) 7.59(2) 134.9(1)	Not given	
[Cu($C_2H_6O_2$)(μCl)$_2$]· 0.5H_2O (light green)	or Pcnb 8	10.198(1) 18.769(1) 7.043(1)		$CuCl_3O_2$ 0.113(1)	O 1.986(3,18) μCl 2.251(1,16) 2.712(1)	3.821(1)	Cl,Cl 98.14(3) Cl,O 90.9(1,4) 168.1(1,3.0) O,O 79.9(1)[c]	152
Cu(dmf)$_2$(μ-Cl)$_2$ (light green)	m $P2_1/a$ —	11.720 11.641 9.012	103.28	$CuCl_3O_2$ Not given	μCl 2.266(2) 2.464(2) 2.794(2) dmfO 1.984(4,31)	Not given	Cl,Cl 89.4(1,6.2) Cl,O 90.5(3,1.9) 149.7(1) 171.2(1) O,O 84.6(2)	153 120.9(3)
Cu(μ-pyNO)$_2$(μ-Cl)Cl (green)	Not given	Not given		$CuCl_3O_2$ Not given	Cl 2.206 μCl 2.217 2.836 μpNO 2.01(—,3)	Not given O 72(—) Cl 86(—)	Not given	154

TABLE II (*Continued*)

Compound *(color)*	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore* *Cu-out of plane* [Å]	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°] *μL–Cu–μL* [°]	*L–Cu–L* [°]	*Ref.*
$Cu_3(\mu$-$Cl)_4Cl_2$- (μ-2-MepyNO)$_2\cdot(H_2O)_2$ (green)	tr P-1 1	9.732(7) 7.380(5) 9.596(7)	104.26(5) 119.21(5) 68.15(5)	$CuCl_3O_2$ (×2) 0.23	μCl 2.221(4) 2.654(1) Cl 2.244(4) pyNO 2.00(4,2)	3.255(3) 3.581(2) O 70.7(4) 109.3(5) Cl 92.9(1,2)	Cl,O 93.8(3,3.7) Cl,Cl 84.4(1)	155
				$CuCl_4O_2$ Not given	μCl 2.2649(3) 2.955(3) H_2O 1.99(1,0)		Cl,Cl 96.4(2,3.6) Cl,O 95.8(3,3.5) 160.9(3,3.7)	
Cu(im)$_2$(μ-Cl)Cl (green)	or Pbn2 4	12.969(1) 10.796(1) 6.803(1)		$CuCl_3N_2$ 0.182	Cl 2.321(4) μCl 2.365(4) 2.751(6) imN 1.983(12,10)	Not given	Cl,Cl 96.6(3,6) 166.9(3) Cl,N 90.7(8,2.6) N,N 174.3(10)	156
Cu(maep)(μ-Cl)Cl (blue green)	or $P2_12_12_1$ 4	19.627(9) 8.288(3) 6.520(2)		$CuCl_3N_2$ 0.16	Cl 2.267(1) μCl 2.300(2) 2.785(2) maepN 2.032(4,13)	4.263(2) Cl 113.58(5)	Cl,Cl 92.6(1,1.7) Cl,N 89.0(1,2.2) 101.2(1) 170.9(2,5.2) N,N 90.9(1)	157
[Cu(μ-Cl)Cl(MeCN)]$_2$- (μ-S_2N_2) (brown red)	m $P2_1$/c 2	9.635(4) 7.270(4) 10.009(9)	 93.16(6)	$CuCl_3N_2$ Not given	Cl 2.271(3) μCl 2.313(2) 2.670(2) μS_2N_2,N 1.959(7) MeCN 1.963(8)	Not given 92.5(2)	Cl,Cl 93.6(1,6.1) 168.8(1) Cl,N 91.8(2,6.7) N,N 167.6(3)	158
Cu(oxd)(μ-Cl)Cl (green)	m Pc 2	7.708(7) 3.751(1) 13.377(2)	 105.97(4)	$CuCl_3N_2$ Not given	Cl 2.271(5) μCl 2.265(6) 3.223(20) oxdN 1.950(20,23)	4.342(1)	Cl,Cl 95.6(2,9) Cl,N 92.3(2,3.4) 167.7(6,2.1) N,N 79.3(3)^e	159
Cu(μ-Cl)Cl(H_2O)(map) (not given)	m $P2_1$ 2	3.762(1) 16.757(2) 8.356(1)	 94.34(1)	$CuCl_3ON$ Not given	Cl 2.286(1) μCl 2.287(1) 2.729(1)	Not given	N,Cl 93.1(1,4.6) N,O 174.0(1) Cl,Cl 95.4(1,1.5)	61

					H_2O 1.965(2) mapN 2.032(2)		168.8(1) Cl,O 88.4(1,1.0)	
Cu(μ-Cl)Cl(H_2O)(caf) (green)	or $P2_12_12_1$ 4	16.370(9) 13.432(7) 5.814(6)		$CuCl_3ON$ 0.15	Cl 2.248(2) μCl 2.319(2) 2.788(2) H_2O 1.96(1) cafN 1.98(1)	4.60(—) 128.1	Cl,O 90.3(4,2.4) Cl,N 90.6(2,3.0) 106.7(2) Cl,Cl 89.7(1,2) 178.8(1) O,N 161.0(4)	160
Cu(μ-dto)(μ-Cl)Cl (green)	tr P-1 2	7.832(4) 7.929(5) 9.803(6)	69.71(4) 71.36(4) 77.84(4)	$CuCl_3S_2$ Not given	Cl 2.230(1) μCl 2.264(1) 3.234(1) dtoS 2.311(1,8)	4.046(1) 4.679(1)	Cl,Cl 86.9(1) 105.5(1,6.1) Cl,S 74.7(1) 90.1(1,7.3) 159.8(1,7.7) S,S 70.7(1)^c 80.1(1,9.4)	161
Cu(μ-pzdc)Cl (green)	or $Pna2_1$ 4	9.552(2) 10.888(2) 7.719(11)		CuO_2N_2Cl Not given	μpzdcN 2.01(—,1) μpzdcO 1.99(—) 2.19(—) Cl 2.23(—)	4.812(—) 6.678(—)	O,O 94.6(—) N,N 172.3(—) N,O 80.0(—)^c 97.6(—,5.0) O,Cl 115.4(—) 150.0(—) N,Cl 93.7(—,1.1) 122.9(—)	162
[Cu(L-lys)(D-lys)Cl_2] · $2H_2O$ (blue)	m $P2_1/n$ 2	5.152(1) 17.394(2) 11.325(2)	96.81(1)	CuO_2N_2Cl Not given	lysO 1.937(1) lysN 1.970(1) Cl 3.047(1)	Not given	N,O 84.6(1)^c N,Cl 90.5(1) O,Cl 85.7(1)	163
[Cu_2(μ_3-OH)(H_2O)- (μ-dppz)Cl_2] · Cl · $2H_2O$ (green yellow)	or Pbca 8	22.519(3) 23.318(3) 7.703(1)		CuO_2N_2Cl 0.124	μ_3HO 1.884(11) 2.772(11) μdppz 1.982(12,5) Cl 2.200(5)	3.387(3) 100.9(6,1.4) 122.5(6)	Cl,O 92.6(3,3.5) Cl,N 97.1(4) 175.8(4) O,N 90.5(5,3.6) 161.3(5) O,O 102.2(5)	164

TABLE II (*Continued*)

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore Cu-out of plane* [Å]	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°] *μL–Cu–μL* [°]	*L–Cu–L* [°]	*Ref.*
				CuO_2N_2Cl 0.133	μHO 1.977(10) μdppzN 2.013(14,45) H_2O 2.370(11) Cl 2.216(6)		N,N 79.3(6)[c] Cl,O 99.3(3,7) Cl,N 97.4(4) 172.1(4) O,N 87.2(5,3.1) 161.6(5) O,O 95.9(4) N,N 78.7(5)[c]	
Cu(μ-dmae)(μ-NCS) (green)	m $P2_1/c$ 8	11.95(4) 8.954(3) 16.805(6)	107.5(1)	CuO_2N_2S Not given	dmaeμO 1.911(3,1) dmaeμN 2.037(3) μSCN 1.913(4) μNCS 2.884(2)	2.950(—) 5.375(—) 100.9(1,7) 77.5(1,3)	O,N 85.1(1)[c] 98.2(1) 164.5(1,4.6) O,S 91.5(1,7) N,N 97.6(1) N,S 98.5(1,9)	165
Cu(μ-dpae)(μ-NCS) (dark green)	m $P2_1/c$ 2	11.737(2) 7.936(1) 21.174(3)	140.16(1)	CuO_2N_2S Not given	dpaeμO 1.916(10,14) dpaeμN 2.066(12) μSCN 1.925(7) μNCS 2.84(6)	2.956(2) 101.0(5) 79.0(5)	O,N 83.5(4)[c] 97.9(5) 149.5(3) 175.2(5) N,N 100.8(5) O,S 91.5(4,6.5) S,N 98.5(5,6.7)	166
Cu(μ-ea)(μ-NCS) (dark green)	m $P2_1/c$ 4	7.564(1) 8.910(1) 9.390(2)	105.60(1)	CuO_2N_2S Not given	eaμO 1.942(5) eaμN 1.983(6) μSCN 1.976(6) μNCS 2.872(5)	2.974(4)	O,S 101.9(2) N,O 98.9(3) 156.2(2) N,S 91.0(2,9.2) N,N 93.4(3)	167

Cu(μ-deae)(μ-NCS) (not given)	m P2_1/n 4	12.058(2) 7.821(3) 11.316(1)	 101.57(14)	CuO$_2$N$_2$S Not given	deaeμO 1.925(8,12) deaeμN 2.089(11) μSCN 1.941(12) μNCS 2.851(4)	2.981(2) 101.5(3) 78.5(3)	N,O 84.9(4)^{c} S,N 101.6(4,8.0) S,O 89.8(3,4.7)	168
Cu(μ-dbap)(μ-NCS) (blue green)	tr P-1 2	8.131(2) 9.102(2) 12.120(3)	72.400(5) 70.930(5) 68.840(5)	CuO$_2$N$_2$S Not given	dbapμO 1.924(3,25) dpapμN 2.074(4) μSCN 1.934(4) μNCS 3.013(2)	3.030(1) 76.1(2)	O,N 94.0(1)^{d} 164.2(2,6.6) N,N 94.9(2) S,O 94.2(1,5.1) S,N 96.0(1,4.8)	102
Cu(μ-dmap)(μ-NCS) (blue green)	m P2_1/c 4	7.403(2) 17.317(4) 8.702(2)	 124.605(5)	CuO$_2$N$_2$S Not given	dmapμO 1.932(2,25) dmapμN 2.069(3) μSCN 1.936(3) μNCS 2.893(1)	3.033(1) 76.6(1)	O,N 95.2(1)^{d} 167.1(1,3) N,N 92.5(1) S,O 92.2(1,1.8) S,N 97.6(1,1.2)	102
Cu(μ-deap)(μ-NCS) (blue green)	tr P-1 2	9.186(2) 8.840(2) 7.910(2)	66.32(1) 75.84(1) 88.23(1)	CuO$_2$N$_2$S Not given	deapμO 1.927(2,22) deapμN 2.072(3) μSCN 1.939(3) μNCS 2.887(1)	3.035(1) 76.1(1)	O,N 95.3(1)^{d} 165.2(1,5.5) N,N 93.1(1) S,O 91.8(1,2.6) S,N 98.5(1,5.6)	102
[Cu(μ-2,2′-dtdp)- (2,2′-bpy)] · 3H$_2$O (blue)	tr P-1 2	8.598(5) 10.378(6) 11.205(6)	96.43(5) 94.34(4) 91.16(5)	CuO$_2$N$_2$S 0.1	μdtdpO 1.953(5,28) μdtdpS 2.678(2) bpyN 2.003(6,5)	Not given	O,O 94.4(2) O,S 80.6(2)^{c} 86.5(2) O,N 92.1(2,5) 170.7(2,1.5) S,N 103.4(6,1) N,N 81.0(2)^{c}	169
[Cu$_2$(μ-apae)$_2$(μ-I)]I · 2H$_2$O (blue)	tr P-1 2	8.105(7) 11.294(10) 11.931(12)	83.34(8) 74.36(7) 78.83(7)	CuO$_2$N$_2$I 0.28 CuO$_2$N$_2$I 0.29	apaeμO 1.976(5,7) apaeμN 2.006(7,12) μI 2.996(—) apaeμO 1.971(5,10) apaeμN 2.012(6,15) μI 3.026(—)	2.976 97.5(2) 82.6(2) 2.969 98.1(2) 81.9(2)	N,N 93.3(3)^{d} N,O 85.4(2)^{c} N,N 94.0(2)^{d} N,O 84.7(2)^{c}	170

TABLE II (*Continued*)

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore* *Cu-out of plane* [Å]	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°] μ*L–Cu–*μ*L* [°]	*L–Cu–L* [°]	*Ref.*
Cu(μ-MeO)(μCl)-(2-Mepy) (green)	m $P2_1/c$ 2	8.79(3) 6.01(1) 17.59(3)	104.4(2)	CuO_2Cl_2N Not given	MeOμO 1.93(1,2) μCl 2.265(4) 2.944(4) MepyN 2.01(1)	3.025(3) Cl 98.8(2) O 103.3(5) 76.7(5)	O,N 93.5(5) 158.7(5) N,Cl 94.3(4,2.2) O,Cl 98.2(4,7.3) 174.3(4) Cl,Cl 87.2(2)	171
Cu(μ-MeO)(μ-Cl)(py) (green)	tr P-1 2	8.280(3) 6.089(2) 9.302(5)	62.67(2) 94.67(3) 70.81(2)	CuO_2Cl_2N Not given	MeOμO 1.936(6,4) μCl 2.279(3) 2.820(3) pyN 2.012(5)	3.037(2) 3.736(3) 103.2(1) O 76.7(2) Cl 93.62(8)	Cl,O 99.5(2,6.0) 173.9(1) N,Cl 94.0(2,4) N,O 92.0(3) 157.9(3) Cl,Cl 86.38(8)	172
[Cu_2(μ-tpmb)$_2$(μ-Cl)$_2$-(H_2O)$_4$]·(ClO_4)$_2$·$2H_2O$ (pale green)	m $P2_1/c$ 2	11.288(2) 13.633(3) 15.173(3)	104.635(15)	CuN_2Cl_2O Not given	μtpmbN 2.017(6,8) μCl 2.276(2) 2.685(2) H_2O 1.978(5)	3.437(2) 87.31(6)	Cl,Cl 92.69(7) Cl,N 92.46(18,1.16) Cl,O 95.06(14) 171.73(4) N,N 172.87(2,3) N,O 87.25(22,1.83)	173
Cu(gly)(1-Meim)(μ-Cl) (blue)	or $Pca2_1$ 4	24.97(2) 4.009(1) 9.116(7)		CuN_2Cl_2O Not given	MeimN 1.946(15) glyN 1.946(16) glyO 1.963(13) μCl 2.296(5) 2.883(5)	Not given	Cl,Cl 100.8(2) N,Cl 91.5(5,4.6) Cl,O 94.4(4) 163.8(4) N,N 172.9(7) N,O 84.0(6)[c] 89.1(6)	174

$Cu_2(\mu\text{-}OH)(\mu\text{-}dppz)\text{-}$	m	13.691(5)		CuN_2Br_2O	Br 2.378(9)	3.398(8)	Br,Br 115.6(2)	175
$(\mu\text{-}Br)_2Br$	$P2_1/n$	6.245(3)	103.92(5)	0.47	μBr 2.666(6)	Br 107.5(2)	Br,O 95.2(11,1.8)	
(green)	2	10.298(4)			μdppzN 2.019(36,14)	O 128.1(17)	Br,N 97.7(10,6.3)	
					μHO 1.916(35)		O,N 83.2(4)	
							161.9(13)	
							N,N 79.6(14)[c]	
				CuN_2Br_2O	Br 2.814(6)		Br,Br 108.0(2)	
				0.29	μBr 2.515(6)		Br,O 94.4(11,5.6)	
					μdppzN 2.017(33,32)		Br,N 94.6(10,7.0)	
					μHO 1.862(36)		158.4(8)	
							O,N 84.6(12)	
							163.9(13)	
							N,N 81.3(12)[c]	

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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 a maximum deviation from the mean value. [b] The chemical identity of coordinated atom/ligand is specified in these columns. [c] Five-membered metallocyclic ring. [d] Six-membered metallocyclic ring. [e] Four-membered metallocyclic ring.

a terminal bipyridine molecule and an oxygen atom from a syn–anti bridging acetate complex with square-pyramidal coordination at each copper atom. The Cu(1)–Cu(1′) separation is 3.358(1) Å and Cu(1)–Cu(2) is 5.441(1) Å.

The structure of a green derivative[30] consists of a three-dimensional array of Cu(II) atoms linked by alkoxo and three types of carboxylate bridges of citrates. The asymmetric unit contains two water molecules, one heptadentate citrate ligand, and two crystallographically unique Cu(II) atoms with O_5-ligand sets. An alkoxo and syn–syn carboxylate group bridge the Cu(II) atoms within this unit. An anti–syn carboxylate group joins these units into zig-zag chains, which in turn are joined by a second type of anti–syn carboxylate bridge to form the three-dimensional network.

$Cu(\mu\text{-sal})_2(H_2O)_2$ crystallizes with a disordered OD structure.[32] The two structures, orthorhombic and monoclinic, have been determined from single-crystal X-ray diffractometer data. The complex contains chains, parallel to *b*, in which one of the salicylate ligands acts as a bridge between two Cu(II) atoms. Each Cu(II) atom is square-pyramidally coordinated by O atoms. The Cu–Cu separation is 5.114(3) Å.

The structure of blue $Cu\{\mu\text{-Ph(Me)PO}_2\}_2(dmf)$[33] consists of infinite chains of centrosymmetric eight-membered rings formed by two metal atoms belonging to four different $O_2PPh(Me)$ groups, forming a roughly square-planar array. One molecule of dimethylformamide with a Cu–O distance of 2.316(8) Å completes a square-pyramidal environment about the Cu(II) atom. The deviation of the copper atom from square-planar is 0.16 Å.

Square-pyramidal environment about Cu(II) atom in $Cu(\mu_3\text{-mal})(H_2O)$[36] is created by a water molecule at the apex ($Cu{-}OH_2 = 2.26(2)$ Å), a chelating maleate group forming a seven-membered chelate ring, and two oxygen atoms of two other maleate groups with the average Cu–O(equatorial) bond distance of 1.99(2) Å. Each maleate group is bound to three Cu(II) atoms to form a polymeric sheet.

In $Cu(\mu\text{-MePO}_3)(H_2O)$[42] each Cu(II) atom is surrounded by five O atoms in a trigonal-bipyramidal arrangement. The pyramids are connected by a common edge to form Cu_2O_8 clusters in which the Cu–Cu distance is 3.139(5) Å. These clusters are associated with methylphosphonate tetrahedra to form infinite layers of polyhedra parallel to (100).

In the series of derivatives with CuO_5 framework,[26–42] only the last example[42] contains Cu(II) in a trigonal-bipyramid in all other compounds a square-pyramidal environment exists. The Cu(II) atoms are displaced from their basal-plane toward the apical O donor in the range from 0.08 Å[36] to 0.33 Å.[30]

The mean Cu–O apical bond distance of 2.30 Å is about 0.34 Å longer than the mean Cu–O equatorial bond distance (1.96 Å), which is typical for Cu(II) complexes.

There are seven derivatives[43–49] in which five-coordination about Cu(II) is created only by N donor ligands. In black $Cu(N_3)_2(2\text{-}MePy)$,[43] the Cu(II) atom has a distorted square-pyramidal environment; one-half of the azide groups act as $\mu(1,1)$ bridging ligands to form centrosymmetric dimers. These dimeric units are further connected by the remaining $\mu(1,3)$ bridging azido groups to form layers within the *a–b* plane. These layers are separated by the basal coordinated 2-methylpyridine ligands. The average Cu–N-(equatorial) bond distance of 2.000(2) Å is shorter than that of Cu–N-(apical) distance (2.273(2) Å). The Cu–Cu separation is 3.095(1) Å.

In another black complex, $Cu(N_3)_2(3\text{-}Mepy)$,[44] two azido ligands lying on a crystallographic diad bridge a pair of Cu(II) atoms to form a planar Cu_2N_2 ring. The rings are linked alternately by pairs of a third type of azido ligand which asymmetrically bridges copper atoms related by the *c* glide, giving rise to a composite column structure. The coordination geometry about the copper atom is distorted trigonal-bipyramidal, with the 3-methylpyridine ligand occupying one of the axial positions (Cu–N = 1.999(9) Å).

In another black $Cu(N_3)_2(2\text{-}Brpy)$[45] the Cu(II) has a distorted square-pyramidal coordination geometry, where both azido ligands function as $\mu(1,1)$ bridges to form chains along the crystallographic *a*-axis.

The structure of a dark green derivative[46] consists of zig-zag chains of dimeric cations, $[Cu_2(N_3)_3(Me_4en)_2]^+$ parallel to the *c*-direction and non-coordinated PF_6^- anions. Within the dimeric unit, the copper atoms are bridged by a single azido group in a symmetrical end-to-end fashion with a Cu–Cu mean separation of 4.439 Å. The dimeric units are linked to each other by a double dissymmetrical end-to-end azido bridge with a Cu–Cu mean separation of 5.131 Å. Each Cu(II) atom has a slightly distorted square-based pyramid.

The structure of $Cu(\mu\text{-}NCO)_2(2,4\text{-}Me_2py)$[47] consists of infinite polymeric chains, mutually bonded by van der Waals bonds. The nitrogen atoms in the cyanate groups fulfill the function of bridges between the Cu(II) atoms, while the oxygen atoms remain free. The approximately square-planar coordination around the Cu(II) atom is formed by three N atoms of NCO^- groups with an N atom of 2,4-dimethylpyridine, and the N atom of NCO group completing a distorted square-pyramidal environment. The Cu–Cu separations of 3.22 and 3.44 Å ruled out a direct metal–metal bond.

The Cu(II) atom in the green derivative[48] is bonded to two terminal NCO groups (Cu–N = 1.894(3) Å) and to two hexamethylenetetramine molecules

(Cu–N = 2.167(2) Å). There is an additional, rather long bond to one of the hexamethylenetetramine molecules of the neighboring complex unit (Cu–N = 2.712(3) Å), resulting in the formation of chains.

A pale blue crystal is built up of polymeric [Cu(μ-im)(dien)]ClO_4 units.[49] The geometry around each Cu(II) atom is trigonal-bipyramidal, comprising the tridentate diethylenetriamine ligand and two imidazole molecules. The Cu(II) atoms are bridged by imidazole rings in two alternating orientations, leading to two polymeric units in each unit cell.

Noticeably, while the mean values Cu–N_{eq} *vs.* Cu–N_{ap} of 2.063 *vs.* 2.080 Å are almost identical for trigonal-bipyramidal environments; the values 2.027 *vs.* 2.399 Å for a square-pyramid differ from each other.

There are 17 examples[50–63] in which five chlorine atoms created a square-pyramidal[50–53,55–61] or trigonal-bipyramidal environment around Cu(II) atoms. Two derivatives[62,63] contain a square-pyramidal and tetragonal-bipyramidal coordination about the copper atoms.

Dibridged linear chains are most common in this series. The mean Cu–Cl bond distances elongate in the order: 2.335 Å (Cl) < 2.422 Å (μ-Cl) < 2.503 Å (μ_3-Cl). The Cu–Cu separations range from 3.084(1)[50] to 3.669(1) Å.[59] Deviation of the Cu(II) atom from the basal plane towards an apical chlorine atom range from 0.218 to 0.406 Å.

The structure of (ipa)[$CuBr_3$][63b] consists of linear chains of symmetrically bi-bridged $Cu_2Br_6^{2-}$ anions. Bridging distances are 2.433(2) and 2.458(2) Å with a bridging angle of 95.21(7)°. The asymmetric bridges between dimers have lengths 2.413(2) and 2.823(2) Å. The average Cu–Cu separation of 3.629(3) ruled out a metal–metal bond.

There are 22 derivatives[64–83] in which a square-pyramidal coordination around each Cu(II) atom is created by four O donor atoms and one N donor atom (CuO_4N). In eight of them[64–69] a tetradentate ligand and water molecule built up such a coordination. For example, in [Cu(μ-pgly)(H_2O)] · $3H_2O$[64] the square-pyramidal geometry around Cu(II) is created with phenolic oxygen, imine nitrogen, and carboxylate oxygen atoms of the Schiff-base ligand and a water molecule as basal donors. The compound is a one-dimensional polymer due to the axial coordination of one of the phosphole oxygens of a neighboring molecule (Table II). The Cu(II) atom deviates from a basal plane towards an apical ligand from 0.114(1) Å[83] to 0.26 Å.[72] The Cu–Cu separation ranges from 3.172(1) Å[74] to 5.435(3) Å,[79] excluding a metal–metal bond.

Blue [$Cu_9(\mu_3\text{-}Br)_2(\mu\text{-}cpa)_6]_n$ · xH_2O[84] contains copper in two distinct environments, one located near the threefold axis with a square-pyramidal coordination polyhedron of four O atoms and an apical bromine atom, and the other located on a twofold axis with a tetragonally distorted octahedral coordination polyhedron of six O atoms. The bromine atom bridges three copper atoms which are part of a six-membered alternating Cu–O ring. The cpa^{3-} is a heptadentate ligand to the three copper atoms. Channels of disordered water occupy a major fraction of the cell volume. The Cu–Cu separation is 3.332(5) Å and Cu–O–Cu bridge angle is 119.2(10)°.

In $[Cu(\alpha\text{-alaha})_2]\cdot 2H_2O$[85] the Cu(II) atom is coordinated by four nitrogens of the amino and hydroxamate groups, and by an oxygen of the carbonyl group from a neighboring molecule. These nitrogens and the Cu(II) atom are coplanar. An oxygen atom is bound in the apical position, with Cu–O distance of 2.878(3) Å.

The structure of blue $Cu_2(\mu\text{-apox})(\mu\text{-NCO})_2$[86] consists of neutral one-dimensional chains of Cu(II) atoms bridged alternatively by the oxamidato and cyanato groups. The former acts as a bis-terdentate bridge whereas the latter is bound through nitrogen in an end-on fashion. The equatorial plane around Cu(II) is defined by the oxygen and nitrogen atoms of the amide, the nitrogen atom of the amine group, and the nitrogen atom of the cyanato ligand whereas the apical position is filled by a nitrogen atom of another cyanato group (CuN_4O). The Cu–Cu separation through $apox^{2-}$ and cyanato bridges are 5.240(1) and 3.212(1) Å. The shortest Cu–Cu separation is 6.153(1) Å.

In a dark blue derivative[87] neutral one-dimensional chains of Cu(II) atoms are bridged alternatively by the oxamidato and azido groups. The former acts as a bis-terdentate ligand whereas the latter is bound through a nitrogen in an asymmetrical end-on fashion. The Cu(II) environment is square-pyramidal (CuN_4O).

In a black complex $[Cu_3(N_3)_6(2\text{-bzpy})_2]$,[88] bidentate 2-benzoylpyridine molecules each coordinate to a Cu(II) atom to form a five-membered metallocycle ring and all six independent azido groups serve to bridge neighboring metal centers in the $\mu(1,1)$ mode, yielding infinite composite chains which pack laterally to constitute a polymeric structure, with CuN_4O, CuN_6 and CuN_5O chromophores (Table II).

The structure of another derivative[89] reveals that the $[Cu(NH_3)_4(H_2O)]^{2+}$ cation forms a chain copolymer with 18-crown-6 in which each individual crown molecule is involved in no fewer than 10 hydrogen bonds with four amine ligands coordinated to the Cu(II) centers in adjacent ions.

In a blue green derivative[90] a distorted square-pyramid around Cu(II) atom is created by three nitrogen atoms of the terpyridine ligand (Cu–N = 1.94(1), 2.05(1) and 2.06(1) Å) with the fourth position of the basal plane occupied by cyanide group (Cu–C = 1.92(2) Å). The Cu(II) atom is displaced 0.26 Å from the basal plane toward the nitrogen and (Cu–N = 2.21(1) Å) of cyanide bonded to a symmetry-related Cu(II) atom. This extended interaction involving non-linear (Cu–N–C = 164(1)°) cyanide bridges between Cu(II) atoms extends through the lattice along the crystallographic twofold screw axis.

The crystal structure of polymeric chains of $[Cu_2(\mu\text{-sbc})(\mu\text{-Cl})]^{3+}$ cations is shown in Figure 4. The zig-zag propagation of the chain results primarily from the ligand structure where the quarternary carbon in the ligand plays a crucial role and controls the relative orientation of each macrocyclic plane defined by the CuN_4 unit. The angle between these planes is 86.9° and the distance between the copper atoms that are not bridged through a chlorine atom is 6.41 compared to 5.25 Å between the chloro-bridged copper atoms. The polymeric structure results from the alternate linkages formed by the bridging chlorine and the quarternary carbon in the ligand structure.

In the light blue $Cu(\mu\text{-im})(imH)_2Cl$[92] the imidazolato ring is in a mirror plane ($y = 0$) with both nitrogens bonded to equatorial Cu(II) atoms in the same plane, forming a bridge between the copper atoms in successive unit cells in the z-direction. The two imidazole rings are coordinated to the copper atoms on either side of the mirror plane through one of the nitrogen atoms. The chlorine atom lies in the mirror plane with the Cu–Cl bond in the x-direction. The polymeric chains are held together by hydrogen bonds between adjacent chains. The distance $NH \cdots Cl = 3.223(6)$ Å. The Cu(II) atom lies 0.25 Å over the N_4 plane toward the apical chlorine atom (Cu–Cl = 2.559(2) Å).

The red orange derivative[93] contains a centrosymmetric $Cu_{14}Cl_{28}O_4^{8-}$ anion and eight tetraethylammonium cations per unit cell. There are five crystallographically independent cations in the structure. The anion can be visualized as being built up from parent $Cu_4Cl_{10}O^{4-}$ clusters in a two-step process. First, two of these units are fused together, showing a common $CuCl_3$ face on the inner chloride octahedron. This defines a hypothetical intermediate $Cu_7Cl_{15}O_2^{5-}$ cluster. The Cu(II) atom in the shared face is coordinated to two oxygen atoms in axial positions, while each of the other copper atoms has one oxygen and one chlorine atom in these positions. The second step involves dimerization of two $Cu_7Cl_{15}O_2^{5-}$ clusters with one of the non-bridging (exo) ligand sites from each cluster being occupied by one of the bridging chlorine atoms from the other cluster. The centrosymmetric linkage yields the final cluster (Figure 5). While Cu(1), Cu(3) and Cu(4) have trigonal-bipyramidal geometry, Cu(2), Cu(11), Cu(12) and Cu(13) have square-pyramidal geometry (Table II).

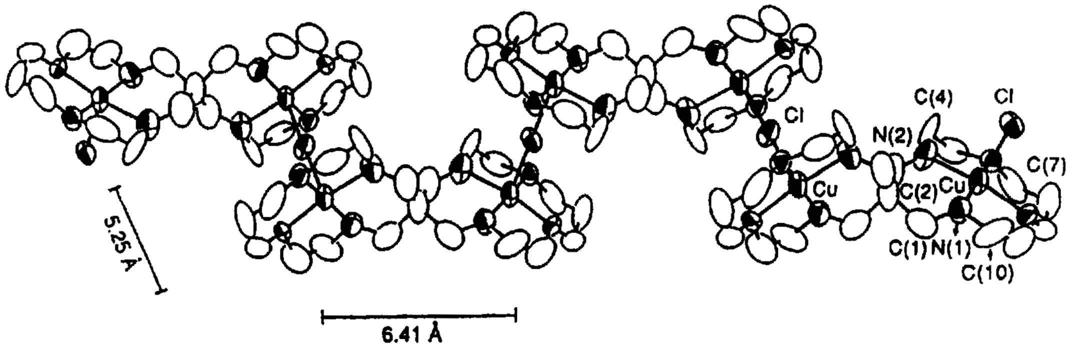

FIGURE 4 Structure of $[Cu_2(\mu\text{-sbc})(\mu\text{-Cl})]^{3-}$.[91]

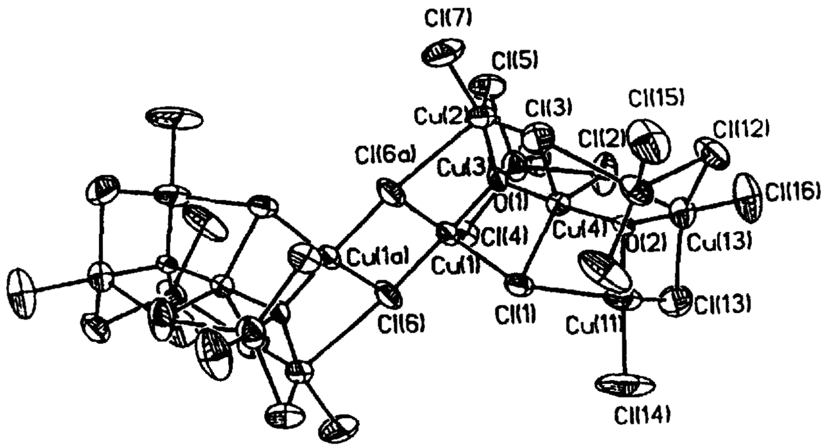

FIGURE 5 Structure of $[Cu_{14}Cl_{28}O_4]^{8-}$.[93]

The structure of another red orange derivative[94] consists of infinite chains of chlorine bridged Cu(II) atoms along the *b*-axis; the repeating unit is (4-ambp-$CuCl_2$-EtOH-$CuCl_2$-4-ambp)$_n$. Although the two coppers are related through crystallographic inversion centers, they have different coordination geometries owing to the positioning of the ethanol molecule. One has a square-pyramidal geometry ($CuCl_4N$) and the second is a *pseudo*-octahedral coordination ($CuCl_4ON$) (Table II).

In a red derivative[95] stepped chains $(CuCl_2)_n$ are crosslinked by (S–O) bridging 1,4-oxathiane ligands to give five-coordinate ($CuCl_4S$) and six-coordinate ($CuCl_4O_2$) environments.

There are almost 40 derivatives[26,27,96–131] which contain five-coordination around the Cu(II) atom with a CuO_3N_2 chromophore (Table II). The structures are very complex. For example the structure of a dark blue derivative[96] contains two crystallographically independent Cu(II) atoms having square-pyramidal coordination, joined together with one of the edges of each polyhedron in common to form a dimer. The dimers are piled up along the *c*-axis, and sulfate ions are attached to them through hydrogen bonds.

A structure of $\{Cu(\mu\text{-}OH)(bpy)\}_2(\mu\text{-}C_4O_4)$[97] contains squarato-$O^1$,$O^3$-bridge bis($\mu$-hydroxo)bis[(2,2′-bipyridyl)copper(II)] units forming zigzag one-dimensional chains. Each copper atom is in a square-pyramidal environment.

The crystal structure of a dark green derivative[99] is built up from $[Cu_2(\mu\text{-}msc)_2(\mu\text{-}ClO_4)]^+$ cations and ClO_4^- anions. The approximately planar $Cu_2(\mu\text{-}msc)_2$ dimers in the cations are joined in chains by tetrahedral

μ-bridging perchlorate ions. The coordination polyhedron of each Cu(II) atom is square-pyramidal. The deviations of the Cu atoms from the O_2N_2 plane are 0.137 and 0.003 Å.

In a green derivative[100] the dimeric units are linked by perchorate groups to one-dimensional infinite chains along the *c*-axis. The coordination polyhedra around the copper atoms are square-pyramidal and tetragonal-bipyramidal, respectively.

In a dark green derivative[101] two CuO_3N_2 square pyramids are combined by sharing an O–O edge, forming dimeric units. All dimeric units are connected through N atoms of the 4,4′-bipyridyl ligands, resulting in an infinite network.

The structure of a dark green Cu(μ-dmap)(μ-NCO)[102] complex consists of an infinite two-dimensional network of alkoxo-bridged dimers connected by cyanato-groups in the plane (100).

The crystal structure of blue $Cu_2(\mu\text{-ac})_2(\mu\text{-amoxa})$[104] consists of zig-zag chains of Cu(II) atoms bridged by amoxa and acetate groups. The Cu–Cu distance for the atoms separated by the amoxa ligand is 5.24(5) Å while that for the atoms bridged by acetate is 3.261(1) Å.

In a green blue derivative[105] zig-zag chains of Cu(II) atoms are bridged by bhben and acetate groups with Cu–Cu separation of 7.325(2) and 3.383(2) Å, respectively.

The structure of a dark blue derivative[106] consists of infinite polymeric chains of $Cu(\mu\text{-}CO_3)(NH_3)_2$ units; the polymeric linkages are formed through the terminal oxygen atom of one carbonate moiety bonding to an adjacent copper atom, whose terminal carbonate oxygen atom continues the chain.

The structure of a green derivative[111] is shown in Figure 6. The Cu(II) atoms are bridged sequentially by the barbituric ring with a Cu–Cu separation of 6.322(3) Å. The environment of each copper atom is square-pyramidal, with a deviation of copper from the basal plane of 0.177(3) Å.

A brown derivative[115] has infinite chains parallel to (001) built up of 1-bis-(monodentate)squarate-O^1O^3 C_4O_4 anions bridging $[Cu(mpym)(H_2O)]^{2+}$ units. The Cu(II) atoms display distorted trigonal-bipyramidal geometry.

The structure of a green blue derivative[118] consists of two crystallographically independent, square-pyramidal $Cu(\mu\text{-pht})(py)_2$ complexes linked in polymeric chains by bridging phthalate anions which also act as chelating ligands through two O atoms from one carboxylate group. Each Cu(II) atom has a square-pyramidal environment with the deviation of the Cu(II) atom from the basal plane of 0.265 Å.

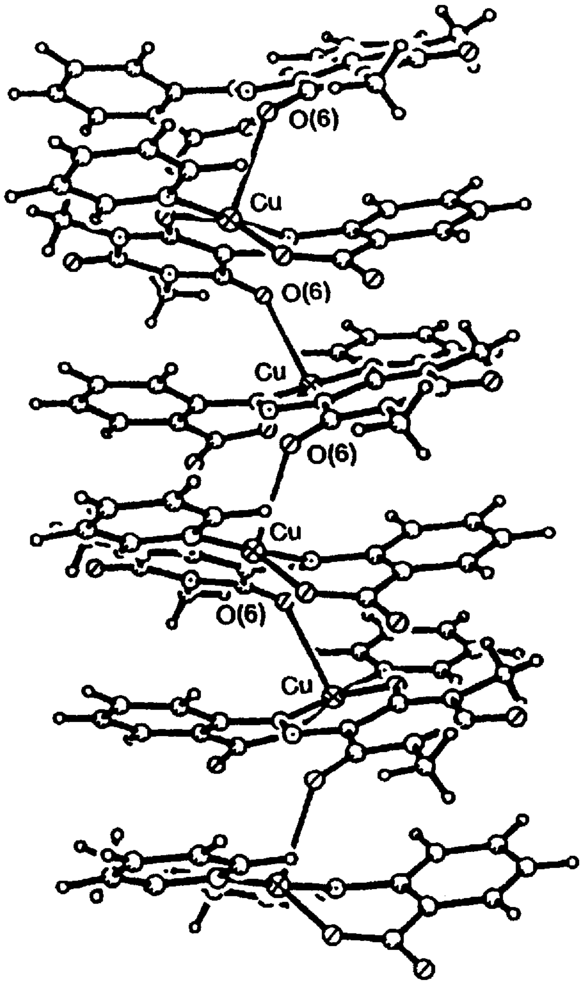

FIGURE 6 Structure of Cu(μ-cab)(py).[111]

A structure of a blue derivative[121] consists of a polymeric two-dimensional network in which each Cu(II) atom is coordinated in a distorted square-pyramidal geometry by three asparate ions and one imidazole molecule. The asparate ion acts as a bidentate ligand bridging in an extended configuration, with three metal atoms.

There are several examples[124–131] in which one multidentate ligand, frequently peptide, created a square-pyramidal environment around each Cu(II) atom (CuO_3N_2) in polymeric chains.

In the series of polymeric Cu(II) complexes where Cu(II) atoms are surrounded by three O and two N donor atoms (CuO_3N_2) a distorted square-pyramidal geometry dominates, except for one example[115] in which a trigonal bipyramidal environment around Cu(II) was found. The deviation of Cu(II) atom from the basal plane towards the apical (by far prevails O donor atom) ligand is in the range from 0.003 to 0.364 Å. There are four examples[98,100,112,125] which contain non-equivalent Cu(II) atoms, CuO_3N_2 (square-pyramidal) and CuO_4N_2 tetragonal-bipyramidal). The shortest Cu–Cu distance found in this series is 2.782(5) Å.[96]

In Cu(μ-abpo)$_2$(abpo)Cl_2[132] each Cu(II) atom has a slightly distorted square-pyramidal environment (CuO_3Cl_2). The two oxygen and two chlorine atoms form the base, with an oxygen at the apex. The Cu(II) atom sits 0.29 Å above the basal plane. Two Cu(II) atoms share the two basal oxygen atoms and a center of symmetry requires the four-membered ring (Cu_2O_2) to be planar with Cu–Cu distance of 3.274(4) Å. The second N-oxide oxygen atom of each bridging ligand bridges a second pair of copper atoms forming an infinite polymer.

There are two blue derivatives[133,134] in which the oxygen with one nitrogen donor atom and a chlorine atom (CuO_3NCl) created a distorted square-pyramidal environment around each Cu(II) atom. A one-dimensional polymer chain is bridged by a carboxylate group of a L-prolinato in a syn–anti configuration.[133] The Cu(II) atom deviates from the O_2NCl plane by 0.18 Å toward the apical O atom ($Cu-O_{ap} = 2.286(5)$ Å).

In two green derivatives[135,136] each Cu(II) atom with a chromophore CuO_3NS has a distorted square-pyramidal geometry (Table II).

There are nine derivatives, mostly green,[21b,137–140,142–145] in which three O and two N donor atoms (CuO_3N_2) build up a distorted square-pyramidal environment about Cu(II). In all of them an apical position is occupied by an oxygen donor atom with $Cu-O_{(apical)}$ bond distances ranging from 2.160(10)[21b] to 2.749(5) Å.[138] The Cu(II) atom deviates from the basal plane (N_3O) toward an apical O donor atom from 0.04 Å[140] to 0.289 Å.[21b] In Cu(μ-tda)(terpy)[141] the coordination polyhedron (CuN_3O_2) was described as distorted trigonal-bipyramidal. A green complex, Cu(pmsh)(μ-NCS), shows[146] a distorted square-pyramidal environment around each Cu(II) atom, involving a tridentate (N_2O) pmsh anion, and a thiocyanate nitrogen ($Cu-N = 1.930(5)$ Å and sulfur ($Cu-S = 2.709(2)$ Å) from an adjacent thiocyanate group. This group bridges the coordination polyhedra in zig-zag chains along (001). The Cu(II) atom is out of the plane (N_3O) by 0.18 Å in the direction of the top of the pyramid (S).

In a green derivative[147] the $[Cu(paphy)(\mu\text{-}Cl)]^+$ unit is stacked in columns oriented in the (001) direction with chlorine atoms building a linear chain between CuN_3 moieties. The Cu(II) atom deviates from the N_3Cl plane by 0.109(2) Å toward the apical chlorine atom (Cu–Cl(apicai) = 2.805(4) Å).

In other blue[149] and dark green[150] derivatives polymeric chains of copper centers are linked by attachment of the pyridyl group to the adjacent Cu(II) atom. The copper is in a roughly trigonal-bipyramidal environment CuN_3Cl_2 (Table II).

There are two blue complexes[148,151] which contain mono-μ-bromocopper(II) chains. Each Cu(II) atom is in a *pseudo*-square-pyramidal environment (CuN_3Br_2). Two green derivatives[152,153] with di-μ-chlorocopper(II) chains and again each Cu(II) atom is in a *pseudo*-square-pyramidal arrangement with a chromophore $CuCl_3O_2$.

The structure of a green complex $Cu(\mu\text{-}pyNO)(\mu\text{-}Cl)Cl$[154] contains oxygen-bridged dimers held together in infinite chains by chloride bridges. Three chlorine atoms with two oxygen donor atoms form around each Cu(II) atom a *pseudo*-square-pyramidal environment.

Another green derivative[155] consists of $Cu_2(\mu\text{-}Cl)_2(\mu\text{-}2MepyNO)_2Cl_2$ dimers bridged by $Cu(\mu\text{-}Cl)_2(H_2O)_2$ groups with Cu–μ–Cl distances 2.654(1) and 2.955(3) Å to form infinite chains. The Cu(II) atoms are found in square-pyramidal and distorted octahedral environments (Table II).

Another three derivatives, green[156,159] and blue green,[157] consist of square-pyramids ($CuCl_3N_2$) which are linked by single chloride bridges, the axial chloride on one Cu(II) atom being in the basal plane of an adjacent copper. The copper atom lies 0.182 Å[156] and 0.16 Å[157] out of the N_2Cl_2 planes.

Polymeric chains[61,160] are also linked by single Cu–Cl–Cu bridges from distorted square-pyramidal $CuCl_3ON$ chromophores. Formula units of the green $Cu(\mu\text{-}dto)(\mu\text{-}Cl)Cl$[161] are catenated in two directions to neighboring units, forming a chain comprised of alternating sulfur and chlorine bridges with Cu–Cu separation in the Cu_2Cl_2 planar units of 4.046(1) and in the Cu_2S plane of 4.679(1) Å with a Cu–Cl–Cu bridging angle of 93.1(1)° and with a Cu–S–Cu bridging angle of 109.3(1)°.

In another three derivatives, green,[162] blue[163] and green yellow[164] a distorted square-pyramid around each Cu(II) atom is created by O_2N_2Cl donors with chlorine[162,163] or O donor atoms[164] in an apical position.

There are seven green deriviatives[102,165–168] of general formula $Cu(\mu\text{-}L)(\mu\text{-}NCS)$ which are isostructural. These compounds essentially consist of alkoxo-bridged dimeric units. Each Cu(II) atom is coordinated by amino and thiocyanate nitrogens and two alkoxo-oxygen atoms. In addition to this coordination, a thiocyanate S atom of a neighbouring dimeric unit approaches the copper atom forming a distorted square-pyramid (CuO_2N_2S), thereby dimeric units are linked in chains parallel to the *b*-axis throughout the crystal. The Cu–Cu distance in the dimeric units range from 2.950(2) to 3.035(1) Å.

The structure of a blue derivative[169] consists of crystallographically equivalent $Cu(bpy)^{2+}$ units linked by 2,2′-dithiodiproponate ligands into infinite chains. Each Cu(II) atom has a distorted square-pyramidal coordination geometry with the two bpy nitrogen and two carboxylate oxygen atoms in equatorial positions. An apically bound disulfide completes the coordination sphere (Table II).

The structure of another blue derivative[170] consists of $[Cu_2(\mu\text{-apae})_2]^{2+}$ dimers where Cu–Cu distances are 2.969 and 2.976 Å. Each Cu(II) atom has a distorted square-pyramidal coordination with O_2N_2 atoms in the basal plane, and an iodide ion in the apical position. The iodide ion lies between two dimers, giving rise to polymeric chains.

The structures of two green derivatives[171,172] are isostructural and consist of methoxy-bridged dimers connected to each other through asymmetric chlorine bridges, forming a one-dimensional chain. Each Cu(II) atom is in a distorted square-pyramidal environment (CuO_2Cl_2N).

In a pale blue derivative[173] each Cu(II) atom is bridged by two 1,3,5-tris-(pyrazol-1-ylmethyl)benzene ligands and two chloride ions to form a polymeric structure. The coordination around each Cu(II) atom is distorted square-pyramidal (CuN_2Cl_2O).

Molecules of blue Cu(gly)(1-Meim)(μ-Cl)[174] are linked through μ-Cl atoms forming polymeric zig-zag chains. Each Cu(II) atom has four close, equatorial ligating atoms (N_2OCl) and an axial chlorine ligand at 2.883(5) Å.

The structure of green $[Cu_2(OH)(bppz)Br_3]_n$[175] is shown in Figure 7. It consists of dimeric units joined to each other through bridging bromine atoms to form a polymeric array. The two independent Cu(II) atoms of the dimeric moiety are five-coordinate with a geometry which is intermediate between square-pyramidal and a trigonal-bipyramidal. The Cu–Cu distance within the dimer is 3.398(8) Å, excluding a direct metal–metal bond.

Inspection of the data in Table II reveals that there are over 160 derivatives in which Cu(II) atoms are five-coordinate. Square-pyramidal is prevalent, with a few trigonal-bipyramidal examples.[44,49,145,149,150] There are 26 different types of chromophores from which CuO_3N_2 are most common. Several cases contain non-equivalent Cu(II) atoms, five- and six-coordinated.[26,38,62,63,84,88,94,95,98,100,112,125,145,155] Cu(II) atoms[27] exist with CuO_5 and CuO_3N_2 chromophores. The shortest Cu–Cu distance found

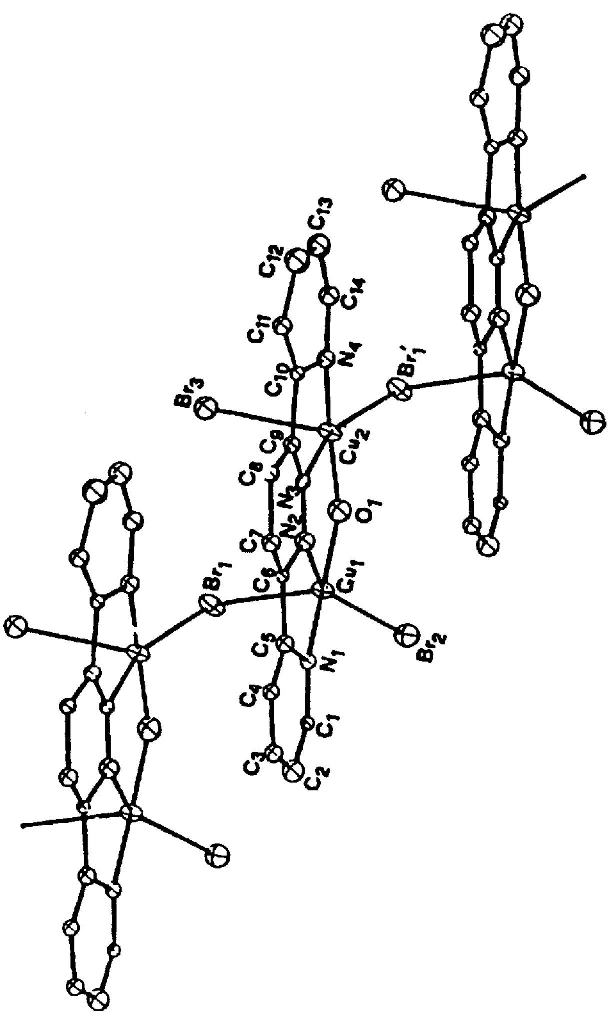

FIGURE 7 Structure of $[Cu_2(OH)(bppz)Br_3]_n$.[175]

in this series is 2.652(2) Å.[26] In the series of Cu(II) derivatives with a square-pyramidal configuration, deviation of Cu(II) from the basal plane toward on apical donor atom range from 0.08 to 0.406 Å.

A summary of the copper–ligand(atom) bond lengths for Cu(II) compounds with coordination number five is given in Table IIA. In general, the Cu–L bond distances increase with covalent radius of the respective donor atoms. The mean Cu–L(equatorial) bond lengths are somewhat shorter than those of Cu–L(apical). The mean Cu–L(bridge) bond distances are longer than those of the non-bridging bonds. In the series of chelating ligands, the effect of both electronic and steric hindrance of the coordinated atom can be seen in the opening of the L–Cu–L bond angles of the respective metallocycles. For example, in the five-membered metallocyclic rings, the L–Cu–L angles range from 77° to 81°, when L is an N-donor with unsaturation, and from 82° to 86.5° when the N-donor is saturated, but from 80° to 85.5° when L is an O-donor.

TABLE IIA Summary of the Cu(II)–L bond distances for five-coordinated derivatives[a]

Coord. atom[b]	*Cov. rad.* [Å]	*Cu–L (equatorial)* [Å]	*Cu–L (apical)* [Å]
LO	0.73	2.01(9,28)	2.37(14,48)
μLO		1.95(8,10)	2.39(8,7)
μOH		1.93(7,15)	—
μ_3O		1.90(1,1)	—
μ_3OH		2.00	2.43
μ_4O		1.92(2,0)	—
L^2O		1.97(12,20)	2.39(15,30)
L^3O		1.98(7,14)	2.37(8,20)
L^4O		1.94(5,6)	2.38(12,32)
L^7O		1.92(2,4)	2.28
LN	0.75	1.97(2,5)	2.32
μLN		1.98(9,8)	2.53(20.18)
L^2N		2.02(8,15)	2.33(6,10)
L^3N		1.99(9,10)	—
L^4N		2.02(4,3)	—
L^8N		2.01	—
Cl	0.99	2.55(8,11)	2.66(19,39)
μCl		2.30(10,6)	2.55(15,65)
μ_3Cl			2.57(26,79)
L^2S	1.02	2.32	
Br	1.14	2.40(2,2)	2.81
μBr		2.43(3,8)	2.39(33,33)
μ_3Br			3.06
μI	1.33	2.99	3.22
$\mathrm{SC\underline{N}}$	0.75	1.93(3,4)	—
$\mathrm{NC\underline{S}}$	1.02	—	2.89(18,18)

[a] The first number in parenthesis is the maximum deviation from the mean of the lowest value observed. The second number in parenthesis is the maximum deviation from the mean of the highest value observed. [b] $L^x = x -$ dentate.

The metallocyclic internal ring angle increases as expected with the number of ring atoms in the order L=O mean value 56(6,6)° for four-membered rings; 83.5(3.5,2) for five-membered and 92.5 for six-membered; for L=N the values are 79(2,2)° for five-membered(unsaturated), 83.5(15,3)° for five-membered(saturated) and 94(6,4)° for six-membered.

2.3. Six-Coordination

Crystallographic and structural data for six-coordinate polymeric Cu(II) compounds are summarized in Table III. The order is in increasing complexity of the coordination sphere and increasing covalent radius of the principal coordinated atom. Structures are very complex. There are 51 examples[36,98,116,176–219] which contain CuO_6 chromophores.

In four complexes, besides O donor organic ligands four molecules of water create a *pseudo*-octahedral configuration about Cu(II).[176–181] The structure of $Cu(\mu\text{-}EtSO_4)(H_2O)_4$[176] consists of chains parallel to the *c*-axis. Adjacent chains are held together by a system of hydrogen bonds from each water oxygen of one chain to ethyl sulfate oxygens of adjacent chains. Monoclinic $Cu\{\mu\text{-}O_3(CH_2)_2SO_3\}(H_2O)_4$[177] shows chains of Cu(II) atoms bridged by the ethanedisulfonato groups. All H atoms of the water molecules are involved in hydrogen bonds (average 2.75 Å). The structure of triclinic $Cu\{\mu\text{-}O_3S(CH_2)_4SO_3\}(H_2O)_4$[178] is similar to that of the 1,2-ethanedisulfonate derivative[177] with hydrogen bonds (average 2.7 Å).

In green $Cu(\mu\text{-}C_4O_4)(H_2O)_4$[179] the $Cu(H_2O)_4^{2+}$ moieties are bridged by bidentate squarate anions. Copper(II) is coordinated to the p-orbital of the squarate oxygen (the torsion angle C(2)–C(1)–O(1)–Cu = −100.2°). The geometry around Cu(II) is characteristic of Jahn–Teller distortion. The Cu(II) to squarate oxygen bond length, Cu–O = 2.469(2) Å, is much longer than the copper to water oxygen length, Cu–O = 1.961(3) and 1.98(2) Å.

Blue $Cu_2(\mu\text{-}cdta)(H_2O)_4$ was studied by two groups.[180,181] The complex exhibits a chain arrangement built up from altering 'hydrated' and 'chelated' *pseudo*-octahedral sites bridged by carboxylate groups of cdta anions.

Brown $Cu(\mu\text{-}C_5O_5)(H_2O)_3$[182] consists of infinite one-dimensional chains of Cu(II) atoms bridged by croconate ligands acting in mono- and bidentate fashion.

Pale green $Cu(\mu\text{-}HCOO)_2(H_2O)_2$ which was studied by two groups[183,184] consists of three-dimensional chains of Cu(II) atoms joined together by formate groups in an anti–syn and anti–anti bridging arrangement. Two Cu(II) atoms in the unit cell are surrounded exclusively by oxygen atoms of formate groups, forming an elongated octahedral coordination. The remaining

TABLE III Crystallographic and structural data for polymeric Cu(II) coordination compounds: coordination number six[a]

Compound (*color*)	*Crystallographic* *classification* *space group 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(μ-EtSO$_4$)(H$_2$O)$_4$ (not given)	or Pbca 4	9.72(—) 7.30(—) 19.70(—)		CuO$_6$	H$_2$O^b 1.97(—,1) μEtO$_3$SO 2.39(—)	Not given	O,O^b 89.2(—,1.6)	176
Cu{μ-SO$_3$(CH$_2$)$_2$SO$_3$}-(H$_2$O)$_4$ (not given)	tr P-1 2	5.974(1) 8.657(1) 10.760(1)	95.07(1) 88.30(1) 109.65(1)	CuO$_6$	H$_2$O 1.967(2,9) μO 2.344(2,10)	Not given	O,O 90.85(7,2.19)	177
Cu{μ-SO$_3$(CH$_2$)$_4$SO$_3$}-(H$_2$O)$_4$ (not given)	m P2$_1$/c 2	6.2125(8) 9.081(2) 11.324(3)	 108.65(1)	CuO$_6$	H$_2$O 1.949(1,1) μO 2.361(1)	Not given	O,O 89.54(6,3.10)	178
Cu(μ-C$_4$O$_4$)(H$_2$O)$_4$ (green)	m P2$_1$/c 2	6.676(2) 7.946(4) 7.688(2)	 110.39(2)	CuO$_6$	H$_2$O 1.955(3,7) μC$_4$O$_3$O 2.469(2)	Not given	O,O 90.0(1,2.7) 180.0	179
Cu$_2$(μ-cdta)(H$_2$O)$_4$ (light blue)	or P2$_1$2$_1$2$_1$ 4	10.863(3) 12.074(4) 14.802(6)		CuO$_6$	H$_2$O 1.983(7,10) 2.351(7) 2.975(8) μcdtaO 1.950(6,5)	Not given	O,O 86.2(3,6.1) 93.3(3,3.6) 171.9(3,2.4)	180
				CuO$_4$N$_2$	μcdtaO 1.962(6,10) 2.383(7,19) μcdtaN 2.016(7,18)		O,O 86.5(3,1.1) 101.8(3,3.0) 168.7(2) N,N 89.6(3)^c O,N 82.0(3,3.7)^c 92.6(3,4) 164.4(3,1.8)	
Cu$_2$(μ-cdta)(H$_2$O)$_4$ (blue)	or P2$_1$2$_1$2$_1$ 4	10.840(3) 12.048(2) 14.802(2)		CuO$_6$	H$_2$O 1.978(7,8) 2.372(7) 2.974(7) μcdtaO 1.932(7,4)	Not given	O,O 85.6(3,5.1) 92.9(3,4.3) 172.1(3,2.2)	181

TABLE III (*Continued*)

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore*	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°]	*L–Cu–L* [°]	*Ref.*
				CuO_4N_2	μcdtaO 1.950(6,29) 2.344(6) 2.425(6) μcdtaN 2.011(7,13)		O,O 98.5(3) 168.2(3) N,N 89.4(3,2.0)^c O,N 81.3(3,2.0)^c 91.7(3) 166.3(3)	
$Cu(\mu\text{-}C_5O_5)(H_2O)_3$ (brown)	or Pbca 8	11.770(2) 8.085(2) 15.571(2)		CuO_6	μC_5O_4O 1.978(2) 2.322(2,13) H_2O 2.002(2,45)	Not given	O,O 80.9(1)^c 89.6(1,4.6) 170.9(1,1.6)	182
$[Cu(\mu\text{-}H_2O)_2(H_2O)_2]$malH (not given)	m I2/m 2	3.594(4) 18.79(2) 9.69(1)	93.25(2)	CuO_6	H_2O 1.959(2) μH_2O 1.933(2) 2.682(2)	Not given	O,O 93.4(1,6.9)	36
$Cu(\mu\text{-}HCOO)_2(H_2O)_2$ (pale green)	m $P2_1/c$ 4	8.54(2) 7.15(1) 9.50(2)	96.18	CuO_6	μHCOO 2.03(—,1) 2.28(—)	Not given	O,O 89(—,2)	183
				CuO_6	μHCOO 2.35(—) H_2O 2.00(—,3)		O,O 89(—,2)	
$Cu(\mu\text{-}HCOO)_2(H_2O)_2$ (pale green)	m $P2_1/c$ 4	8.54(2) 7.15(1) 9.50(2)	96.48	CuO_6	μHCOO 2.003(17,16) 2.304(18)	Not given	O,O 88.2(7,1.4)	184
				CuO_6	μHCOO 2.368(19) H_2O 2.009(16,35)		O,O 87.3(6,4)	
$[Cu(\mu\text{-}HCOO)_2(H_2O)_2]\cdot$ $2H_2O$ (light blue)	m $P2_1/a$ 2	8.18(2) 8.15(2) 6.35(2)	101.5(20)	CuO_6	μHCOO 2.01(—,1) H_2O 2.36(—)	Not given	Not given	185
$[Cu(\mu\text{-}HCOO)_2(H_2O)_2]\cdot$ $2H_2O$ (light blue) (by neutron diffraction)	m $P2_1/a$ 2	8.15(—) 8.18(—) 6.35(—)	101.5	CuO_6	μHCOO 2.00(1,1) H_2O 2.38(1)	Not given	O,O 88.8(4,2.0)	186

[Cu(μ-HCOO)$_2$(H$_2$O)$_2$]· 2urea (green)	m P2$_1$/c 2	8.275(4) 8.346(3) 8.018(3)	96.36(5)	CuO$_6$	μHCOO 1.972(1,5) H$_2$O 2.433(1)	5.79	O,O 89.1(2,2.6)	187
[Cu(μ-dcap)$_2$(H$_2$O)$_2$]· 4H$_2$O (light blue)	m P2$_1$/c 2	7.944(3) 11.267(3) 13.562(5)	103.84(3)	CuO$_6$	H$_2$O 1.995(1) μdcapO 1.996(1) 2.298(2)	Not given	O,O 90.0(1,3.0)	188
Cu(μ-tppr)$_2$(H$_2$O)$_2$ (blue)	or Pbca 4	8.366(2) 9.262(2) 23.221(4)		CuO$_6$	H$_2$O 1.912(4,0) μtpprO 1.946(4) 2.731(5)	Not given	O,O 90.0(2,3.0)	189
[Cu$_2$(μ-L-ala)(μH$_2$O)$_2$]- (SO$_4$)$_2$ (pale blue)	m P2$_1$ 4	6.311(7) 23.119(6) 14.064(3)	93.42(4)	CuO$_6$	μalaO 1.933(—,1) H$_2$O 1.978(—,9) 2.415(—) 2.538(—)	3.153(—,4)	Not given	190
Cu(μ-2,6-dhb)$_2$(H$_2$O)$_2$ (not given)	m P2$_1$/n 2	5.246(1) 10.709(1) 13.134(1)	94.49(1)	CuO$_6$	μdhbO 1.935(2) 2.599(3) H$_2$O 1.966(3)	Not given	O,O 90.0(1,5.1)	191
[Cu(μ-egl)$_2$(H$_2$O)$_2$]SO$_4$ (blue)	m C2/c 4	7.249(1) 15.539(2) 10.027(1)	103.42(1)	CuO$_6$	H$_2$O 1.952(2,0) μeglO 1.979(2,0) 2.378(2,0)	Not given	O,O 89.3(1.5.3)	192
Cu(μ-cma)$_2$(H$_2$O)$_2$ (green)	m C2/c 4	17.700(7) 19.266(8) 7.424(4)	91.88(4)	CuO$_6$	cmaμO 1.921(2) 2.892(3) H$_2$O 1.947(2)	3.976(3) 109.4(1) 70.6(1)	O,O 72.3(1,1.7) 90.6(1,2.8) 107.8(1,8) 177.5(1,8)	193
[Cu(μnicO)$_2$(H$_2$O)$_2$]· 4H$_2$O (green)	m P2$_1$ 2	4.84(1) 27.55(7) 6.77(1)	106.08(17)	CuO$_6$	μnicO 1.942(5,16) 2.522(6,55) H$_2$O 1.933(6,67)	Not given	O,O 90.0(2,4.6) 176.8(3,2.1)	194
[Cu(μ-C$_6$Cl$_2$O$_4$)(H$_2$O)$_2$]· H$_2$O (not given)	tr P-1 2	7.040(4) 7.962(4) 9.364(5)	84.58(3) 89.25(3) 76.53(3)	CuO$_6$	μC$_6$Cl$_2$O$_3$O 1.966(5,1) 2.591(4,7) H$_2$O 2.006(5,10)	4.991(2)	O,O 78.1(2,0)^c 90.0(2,2.5) 101.9(2,2) 178.4(2,1.2)	195

TABLE III (*Continued*)

Compound (*color*)	*Crystallographic classification space group 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(μ-C_4O_4)(H_2O)$_2$	m	7.818(2)		CuO_6	C_4O_4μO 1.953(3,7)	Not given	O,O 85.92(16,1.75)	196
(greenish yellow)	P2$_1$/c	11.816(7)	100.30(2)		2.501(4)		94.07(16,3.47)	
	4	6.295(1)			H_2O 1.964(4,13)		177.07(18,2.73)	
					2.696(4)			
[Cu(μ-D-tart)(H_2O)$_2$] ·	m	12.13(2)		CuO_6	tartO 1.95(1,5)	5.42(—)	O,O 93.1(7,6.2)	197
H_2O	P2$_1$	8.37(2)			tartμO 1.97(1)			
(blue)	4	8.74(1)	104.6(4)		H_2O 2.40(2)			
				CuO_6	tartO 1.94(1,5)		O,O 90.6(7,5.5)	
					tatrμO 2.37(2)			
					H_2O 1.95(2)			
Cu(μ-o-pht)(H_2O)$_2$	m	10.263(7)		CuO_6	H_2O 1.980(5)	Not given	O,O 51.2(2)[d]	198
(blue)	P2$_1$	6.540(9)	94.8(1)		1.993(5,13)		86.1(2,2.3)	
	2	6.795(8)			μphtO 1.958(5,8)		94.2(2,4.9)	
					2.154(5)		133.6(2,4.9)	
					2.861(6)		173.3(2,4.7)	
Cu(μ-HCOO)$_2$-	m	7.775(5)		CuO_6	μHCOO 1.970(2,8)	Not given	O,O 87.9(3,1.6)	98
($HCONH_2$)$_2$	P2$_1$/b	7.995(5)			2.368(3)			
(green)	2	7.949(5)	64.83(2)		(NH_2)HCO 1.962(2)			
K_2[Cu(μ-nac)$_2$] · H_2O	m	8.544(1)		CuO_6	H_2O 1.925(5,9)	Not given	O,O 89.6(2,11.9)	199
(green)	P2$_1$/n	9.433(2)	98.07(1)		2.539(—)		92.0(2)[e]	
	4	12.819(2)			μnacO 1.919(4)		173.8(2,4.3)	
					2.891(—)			
Cu(μ-fu)$_2$(MeOH)$_2$	tr	4.749(1)	88.23(1)	CuO_6	μfuO 1.924(2)	4.749	O,O 91.75(9,4.09)	200
(green)	P-1	12.433(2)	83.11(1)		2.720(2)			
	1	13.722(2)	88.58(1)		MeHO 1.941(2,0)			

[Cu(μ-lactate)$_2$(H$_2$O)]· 0.5H$_2$O (blue)	m A2 4	10.53(3) 20.55(5) 5.66(2)	119.3(3)	CuO$_6$	μlactO 1.95(—,2) 2.90(—) H$_2$O 2.30(—)	Not given	O,O 81.6(—,6)^c 94.6(—,4.6)	201
Cu(μ-glycolate)$_2$ (not given)	m P2$_1$/a 2	7.93(2) 5.08(2) 8.68(2)	111.1(3)	CuO$_6$	μglycO 1.92(—,1) 2.54(—)	Not given	O,O 83.4(—)^c 90.4(—,1.5)	201 202
Cu(μ-o-pht)(μ-H$_2$O) (blue)	m B2/b 8	26.10(25) 9.79(1) 6.67(1)	93.9(2)	CuO$_6$	μH$_2$O 1.961(4) phtμO 1.962(4) 2.462(4)	Not given	O,O 88.8(2,3.1)	203
				CuO$_6$	μH$_2$O 2.577(4) phtμO 1.946(4) 1.931(4,0)		O,O 91.3(2,9.6) 168.9(2,1.5)	
Cu(μ-odac)(H$_2$O) (royal blue)	or Pbcn 8	9.263(6) 14.283(5) 9.283(6)		CuO$_6$	μodacO 2.488(7) μodacO 1.947(9,6) H$_2$O 2.73(2)	Not given	O,O 74.4(5,6)^c 91.7(6,4.9) 115.8(3,1.2) 134.7(5) 169.8(4,8)	204
Cu(μ-HCOO)(μ_3-OH) (blue)	m P2$_1$ 2	7.316(1) 5.958(1) 3.279(1)	103.83(1)	CuO$_6$	μHCOO 1.96(1,2) μ_3HO 1.94(2,3) 2.60(2,2)	2.979	O,O 90.0(1,1.1)	205
(Me$_2$NH$_2$)- [Cu(μ-HCOO)$_3$] (turquoise)	m I2/c 4	11.4204(5) 8.7139(5) 8.8502(5)	96.247(5)	CuO$_6$	μHCOO 1.970(—,1) 2.491(—,0)	Not given	O,O 89.69(—,2.16)	206
Cu(μ-HCOO)$_2$ (light blue)	m P2$_1$/a 2	8.195(6) 7.925(6) 3.620(5)	122.21(9)	CuO$_6$	HCOO 1.947(—,19) 2.656(2,0)	Not given	O,O 90.0(—,11.3)	207
Cu(μ-HCOO)$_2$ (blue)	or Pbca 8	14.1900(3) 8.9354(2) 6.2205(2)		CuO$_6$	μHCOO 1.967(6,29) 2.410(5) 2.797(5)	Not given	O,O 92.3(2,3.5) 79.7(2)	208
Cu(μ-HCOO)$_2$ (blue) (at 80 K)	or Pbca 8	14.1791(3) 8.9059(2) 6.1584(3)		CuO$_6$	μHCOO 1.961(5,24) 2.389(5) 2.786(5)	Not given	O,O 92.0(2,3.3) 79.0(2)	208

TABLE III (*Continued*)

Compound (*color*)	*Crystallographic classification space group 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(μ-HCOO)$_2$ (blue) (at 4.2 K)	or Pbca 8	14.1813(4) 8.8988(3) 6.1468(3)		CuO$_6$	μHCOO 1.962(5,25) 2.371(5) 2.781(5)	Not given	O,O 92.2(2,3.7) 79.7(2)	208
Cu(μ-Me$_2$CNO$_2$)$_2$ (not given)	m P2$_1$/a 4	6.792(6) 10.343(8) 13.366(9)	90.76(5)	CuO$_6$	O 1.96(6,8) 2.50(6,10)	Not given	O,O 67(2)^d 91(2)	209
Cu(μ-C$_{32}$H$_{54}$N$_2$O$_8$)$_2$ (green)	tr P-1 2	11.992(1) 12.188(1) 12.912(1)	78.03(2) 78.96(2) 84.06(2)	CuO$_6$	O 1.917(3,13) 2.583(5,0)	Not given	O,O 92.3(1)^e 86.3(1,3.5)	210
				CuO$_6$	O 1.905(4,7) 3.157(5,0)		O,O 92.9(2)^e 83.8(2,5.5)	
[Cu(μ-o-phhH)$_2$]$\cdot$2H$_2$O (not given) (by neutr. diff.)	m P2$_1$/a 2	8.360(2) 14.395(4) 7.086(2)	112.18(5)	CuO$_6$	O 1.929(1) 2.629(2)	Not given	Not given	211
(pyH)[Cu(μ-ox)$_2$]oxH (blue)	tr P-1 1	8.980(6) 14.159(7) 3.697(3)	92.47(7) 101.17(7) 97.69(4)	CuO$_6$	oxHO 1.945(1) μoxO 1.915(2) 2.893(3)	3.697	O,O 85.61(6)^c 88.1(1,6.7)	116
(bzNH$_3$)$_2$[Cu(μ-ox)$_2$] (blue)	or Pbca 4	7.100(2) 8.004(2) 35.444(8)		CuO$_6$	μoxO 1.936(5,3) 2.568(5)	Not given	O,O 85.6(2)^c 96.2(2,1.0)	212
{NH$_3$(CH$_2$)$_3$NH$_3$}- [Cu(μ-ox)$_2$] (royal blue)	m C2/c 4	17.901(3) 4.920(1) 14.002(3)	118.7(2)	CuO$_6$	μoxO 1.934(2,3) 2.883(3)	Not given	O,O 86.73(9)^c 91.3(1,3.6)	212
[Cu(H$_2$O)$_6$]- [Cu(μ-dmcan)$_2$] (green)	tr P-1 1	6.580(1) 8.527(2) 9.859(2)	100.04(2) 101.67(2) 94.75(2)	CuO$_6$	μdmcanO 2.20	5.757	Not given	213
Cu(μ-PhMePO$_2$)$_2$(μ-fa)$_2$ (pale blue)	tr P-1 2	11.550(2) 11.569(1) 8.113(1)	107.98(5) 90.86(4) 91.32(4)	CuO$_6$	O 1.988(9,17) faμO 2.385(10,5)	4.056(1) 116.7(3)	O,O 90.0(4,1.8)	214

Cu(nbtfac)$_2$(μ-dio) (green)	m P2$_1$/n 2	15.753(4) 11.262(3) 7.587(2)	91.72(2)	CuO$_6$	nbtfacO 1.934(4,6) μdioO 2.458(4,0)	Not given	O,O 89.7(1,3.8)	215
Cu(hfacac)$_2$(μ-tmpo) (green brown)	m P2$_1$/n 4	10.482(3) 15.565(5) 16.702(5)	97.75(2)	CuO$_6$	hfacacO 1.947(5,4) μtmpoO 2.427(6,13)	Not given	O,O 89.5(2,6.4) 92.8(2,3)^e 176.6(2,1.5)	216
Cu(hfacac)$_2$(μ-nitme) (not given)	tr P-1 2	8.955(6) 15.915(7) 10.29(4)	71.20(3) 68.24(2) 76.44(3)	CuO$_6$	hfacacO 1.946(4,10) μnitmeO 2.341(6)	Not given	O,O 88.6(2,3.7)	217
				CuO$_6$	hfacacO 1.933(5,6) μnitmeO 2.431(5)		O,O 91.2(2,3.7)	
Cu(μ-acac)(μ-Cl$_3$ac) (blue green)	hx P6$_1$;P6$_5$ —	11.143(2) 17.917(4)		CuO$_6$	μacacO 1.90(—,5) 2.57(—,9) μCl$_3$acO 1.90	3.19	Not given	218
Cu(μ-cba)(cba)$_2$(μ-SO$_4$) (not given)	or Pbcn 4	13.004(6) 9.268(4) 8.873(4)		CuO$_6$	μSO$_3$O 1.974(2) cbaO 1.935(2) μcbaO 2.608(3)	Not given	O,O 93.05(1)	219
Cu{μ-(1,1)-N$_3$}- {μ-(1,3)-N$_3$} (black brown)	or Pnma 4	13.481(2) 3.084(1) 9.076(2)		CuN$_6$	μ(1,1)-N$_3$N 1.975(7) 2.696(12) μ(1,3)-N$_3$N 1.984(8) 2.596(15)	3.084(1) 3.496(4) 84.3(4)	N,N 77.5(4) 87.5(4) 94.3(4,2.6) 102.3(6,3)	220
Cu{μ_3-(1,1,3)-N$_3$}- (N$_3$)(NH$_3$)$_2$ (blue green)	or Pnma 4	6.389(5) 7.454(5) 12.71(1)		CuN$_6$	H$_3$N 1.985(8,0) N$_3$N 1.952(8) μ_3N$_3$N 2.053(8) 2.61(1,6)	4.238(4) 133.4(4)	N,N 90.0(5,3.4) 177.9(4)	221
Cu(py)$_2$)(N$_3$)- {μ-(1,1,3)-N$_3$} (green)	or Cmc2$_1$ 4	13.884(2) 13.646(2) 6.403(2)		CuN$_6$	pyN 2.041(20) N$_3$N 1.979(26) μ_3N$_3$N 2.010(20) 2.496(29) 2.761(25)	Not given	N,N 90.0(10,7.4)	222

TABLE III (*Continued*)

Compound (*color*)	*Crystallographic classification space group 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{μ-(1,1)-N_3}$_2$(4-Mepy)$_2$	m	11.062(3)		CuN_6	MepyN 2.00(2,6)	3.535(5,22)	N,N 81.6(7,4.0)	223
(black)	$P2_1/a$	19.310(6)	90.83(2)		μN_3N 2.00(2,4)	102.1(8,4.3)	101.4(7)	
	12	20.547(5)			2.55(2,3)		92.0(8,6.0)	
					2.73(2,7)		174.9(10,2.4)	
				CuN_5	MepyN 2.00(2,4)		N,N 89.9(9,5.1)	
					μN_3N 2.00(2,2)		106.2(7)	
					2.79(2)		169.5(9,5.4)	
Cu{μ-(1,1)-N_3}-	m	11.366(2)		CuN_6	μN_3N 1.972(8)	3.546(2)	N,N 90.2(3,1.8)	45
{μ-(1,3)-N_3}·(3-Mepy)$_2$	$P2_1/n$	13.902(3)	109.34(1)		2.644(8)	98.3(3)		
(black)	6	14.462(3)			MepyN 2.010(6)			
				CuN_6	μN_3N 1.996(8)		N,N 90.4(3,8.4)	
					2.625(9)		173.5(3,4.1)	
					$N_3\mu N$ 1.970(7)			
					2.679(8)			
					MepyN 2.014(5,17)			
Cu(2,2′-bpy){μ-(1,1)-N_3}$_2$	tr	6.649(2)	86.99(2)	CuN_6	bpyN 2.018(6,2)	Not given	N,N 79.6(2)^c	224
(green)	P-1	8.433(1)	87.77(3)		μN_3N 1.958(4,17)		91.1(2,13.7)	
	2	10.820(2)	78.59(2)		2.681(8,1)		165.9(3,5.5)	
[Cu(en)$_2$(μ-NCS)]Br	or	7.224(5)		CuN_6	enN 2.02(—,1)	Not given	N,N 85.1(—)^c	225
(violet)	Pnam	15.573(12)			μSCN 2.70(—,3)			
	4	10.429(5)						
[Cu(en)$_2$(μ-NCS)]BF_4	or	15.379(4)		CuN_6	enN 2.014(4,5)	Not given	N,N 84.6(2)^c	226
(violet)	Pnam	10.788(2)			μSCN 2.720(2)		91.5(5,3.6)	
	4	7.610(2)					180.0(3)	
[Cu(en)$_2$(μ-NCS)]ClO_4	or	15.60(3)		CuN_6	enN 2.03(2,1)	Not given	N,N 85^c	227
(violet)	Pnam	7.63(2)			μSCN 2.73(3)		89(—,4)	
	4	10.82(2)						
Cu{μ-(2,4)-trz}$_2$(NCS)$_2$	m	10.084(7)		CuN_6	μtrzN 2.002(5)	Not given	N,N 90.0(2,2.5)	228
(not given)	$P2_1/n$	7.682(5)	116.43(7)		2.477(3)		180	
	2	9.126(6)			SCN 1.984(3)			

	m B2_1/c 4	10.151(5) 7.682(5) 16.337(9)	96.37(7)					
α-Cu(μ-tp)(NCS)$_2$ (dark green)	m P2_1/c 2	11.669(2) 8.808(2) 7.951(2)		CuN$_6$	μtpN 2.035(5) 2.633(6) SCN 1.935(6)	8.905	N,N 91.1(2,3.1)	229
Cu{μ-C(CN)$_3$}$_2$ (black)	or Pmna 2	7.176(5) 5.471(5) 10.753(5)		CuN$_6$	N 1.98(1) 2.49(1)	Not given	Not given	230
[Cu{μ-C(CN)$_3$}(pzH)$_4$]- {C(CN)$_3$} (blue)	m P2_1/c 4	9.56894) 16.692(7) 14.957(9)	94.05(4)	CuN$_6$	pzN 1.994(6,15) μC(CN)$_3$N 2.373(7) 2.500(7)	Not given	N,N 90.0(3,3.0) 177.2(3,1.0)	231
[Cu(aebg)(μ-cg)](SO$_4$) $\cdot$ H$_2$O (red violet)	m P2_1/c 4	7.088(7) 15.64(1) 13.43(1)	101.8(2)	CuN$_6$	aebgN 1.96(1,5) μcgN 1.96(1) 3.10(1,4)	Not given	Not given	232
[Cu(μ-C$_{11}$H$_7$N$_2$] $\cdot$ 2thf (purple)	or Pbca —	13.233(2) 10.754(2) 21.411(4)		CuN$_6$	N 1.989(5,6) 2.82	Not given	N,N 92.1(2)^e	233
(Me(NH$_3$)$_2$[Cu(μ-Cl)$_2$Cl$_2$] (brown) (at 297 K)	m P2_1/a 2	7.268(4) 7.367(4) 9.971(3)	110.89(1)	CuCl$_6$	Cl 2.297(1,0) μCl 2.283(1,0) 2.907(1,0)	Not given	Cl,Cl 89.39(10,6.8) 180	234
(Me(NH$_3$)$_2$[Cu(μ-Cl)$_2$Cl$_2$] (brown) (at 100 K)	m P2_1/a 2	7.155(4) 7.424(4) 9.814(3)	109.18(7)	CuCl$_6$	Cl 2.311(1,0) μCl 2.287(1,0) 2.902(1,0)	Not given	Cl,Cl 88.35(4,1.18) 180	234
(Me$_4$N)[Cu(μ-Cl)$_3$] (red) (at 405 K)	hx P6_3/mmc 2	9.160(2) 6.474(2)		CuCl$_6$	Not given	Not given	Not given	235
(Me$_4$N)[Cu(μ-Cl)$_3$] (red) (at 323 K)	tr P-1 2	9.082(5) 9.073(5) 6.442(3)	90.05(4) 92.40(4) 119.99(3)	CuCl$_6$	Not given	Not given	Not given	235

TABLE III (*Continued*)

Compound (*color*)	*Crystallographic classification* *space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore*	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°]	*L–Cu–L* [°]	*Ref.*
$(Me_4N)[Cu(\mu\text{-}Cl)_3]$ (red) (at 213 K)	m $P2_1$ 10	8.948(8) 32.225(10) 8.980(2)	 119.487(18)	$CuCl_6$	Not given	Not given	Not given	235
$\{H_3N(CH_2)_3NH_3\}_2\cdot$ $[Cu(\mu\text{-}Cl)_2Cl_2]$ (yellow)	or Pnma 4	7.200(2) 18.246(6) 7.451(2)		$CuCl_6$	μCl 2.275(1) 2.946(1) Cl 2.314(1)	Not given 165.70(4)	Cl,Cl 88.45(2,1.79)	236
$(aud)_2[Cu(\mu\text{-}Cl)_2Cl_2]$ (green)	tr P-1 2	7.237(1) 7.536(1) 27.605(2)	97.98(8) 92.45(8) 90.02(8)	$CuCl_6$	Cl 2.289(1,17) μCl 2.975(1,0)	Not given	Cl,Cl 90.0(—,3.4) 180(—)	237
				$CuCl_6$	Cl 2.295(1,1) μCl 2.300(1,0)		Cl,Cl 90.0(—,3.4) 180(—)	
$\{H_3N(CH_2)_2NH_3\}$- $[Cu(\mu\text{-}Cl)_2Cl2]$ (brown green)	m $P2_1/b$ 2	8.609(2) 7.130(2) 7.192(2)	 92.69(2)	$CuCl_6$	Cl 2.316(2) μCl 2.308(2) 2.896(2)	Not given 166.46(6)	Cl,Cl 89.95(6,1.88)	238
$\{(H_3NCH_2CH_2)_2NH_2\}\cdot$ $[Cu(\mu\text{-}Cl)_2Cl_2]Cl$ (yellow)	or Pnma 4	7.1109(3) 23.6788(10) 7.3353(3)		$CuCl_6$	Cl 2.3106(6) μCl 2.2821(6) 2.8725(6)	5.108 164.50(2)	Cl,Cl 89.94(2,7)	239
$(anH)_2[Cu(\mu\text{-}Cl)_2Cl_2]$ (yellow brownish)	m $P2_1/c$ 2	15.050(2) 7.443(1) 7.180(1)	 100.7(1)	$CuCl_6$	Cl 2.300(7,5) μCl 2.2804(6) 2.9178(5)	Not given 164.38(2)	ClCl 89.68(2,3.02)	240
$(\beta\text{-alaH})_2[Cu(\mu\text{-}Br)_2Br_2]$ (purple)	m I2/c 4	7.661(1) 8.027(1) 24.295(7)	 92.49(2)	$CuBr_6$	Br 2.429(1) μBr 2.444(1) 3.172(1)	5.354(—) 167.53(4)	Br,Br 90.12(5,1.55)	241
$\{H_3N(CH_2)_2NH_3\}$- $[Cu(\mu\text{-}Br)_2Br_2]$ (not given)	m $P2_1/a$ 2	7.511(1) 7.803(1) 8.334(2)	 92.12(2)	$CuBr_6$	Br 2.444(1) μBr 2.431(1) 3.034(1)	Not given 164.5(1)	Br,Br 90.4(1)	242

$\{H_3N(CH_2)_3NH_3\}$- $[Cu(\mu\text{-}Br)_2Br_2]$ (not given)	m $P2_1/n$ 4	8.036(2) 7.566(2) 17.622(5)	96.75(2)	$CuBr_6$	Br 2.444(3,4) μBr 2.432(3) 3.148(3)	Not given 164.8(1,8)	Br,Br 90.3(1,3)	242
$(abhpH)_2[Cu_2(\mu_3\text{-}Br)$ $(\mu\text{-}Br)_2Br_3]$ (brownish violet)	tr P-1 2	6.301(2) 7.037(2) 8.881(2)	81.47(2) 86.21(2) 86.16(2)	$CuBr_6$	Br 2.398(2,8) μBr 2.458(2,8) μ_3Br 2.466(2) 3.269(2,27)	Not given 97.1(1)	Br,Br 90.0(1,7.1) 172.5(1,1.4)	243
$Cu(pyvgly)(H_2O)_3$ (blue)	m $P2_1/c$ 4	10.489(12) 6.654(7) 14.904(17)	116.25(81)	CuO_5N	pyvglyO 1.999(10,4) pyvglyN 1.917(11) H_2O 1.923(9) 2.451(10) 2.616(10)	Not given	O,O 90.89(40,9.35) O,N 82.11(42,46)^c 96.32(39,3.54)	244
$[Cu(\mu\text{-}Me_2cys)(H_2O)_3]\cdot$ $2H_2O$ (deep blue)	m Cc 4	13.605(2) 11.163(1) 9.560(2)	117.07(2)	CuO_5N	cysO 1.953(3,4) N 1.986(3) H_2O 1.983(3) 2.471(3) 2.572(5)	5.0397(2)	O,O 89.7(1,5.0) 176.1(1,1.7) O,N 83.5(1)^c 86.1(2,3.8) 97.8(1,5) 170.8(2)	245
$Cu(\mu\text{-}opidac)(H_2O)_2$ (green)	m $P2_1/b$ 4	10.571(5) 9.254(6) 12.170(6)	99.00(3)	CuO_5N	O 1.952(5,1) 2.386(7) N 2.041(6) H_2O 1.977(6) 2.566(7)	Not given	O,O 89.7(3,7.5) 168.2(3,5) O,N 84.5(2,2)^c 88.6(2) 106.5(2) 171.2(3)	246
$Cu(\mu\text{-}ida)(H_2O)_2$ (blue)	or Pbca 8	10.228(2) 10.419(2) 13.688(3)		CuO_5N	μidaO 1.953(3,8) 2.494(3) N 2.014(3) H_2O 1.991(3) 2.410(3)	Not given	O,O 90.8(1,6.4) O,N 73.2(1)^c 90.3(1.6.4)	247
$Cu(\mu\text{-}pydc)(H_2O)_2$ (blue)	m $P2_1/c$ 4	7.21(1) 19.02(1) 6.41(1)	107.1(1)	CuO_5N	μpydcO 2.044(4,7) 2.423(3) N 1.898(4) H_2O 1.940(4) 2.396(3)	Not given	O,O 99.6(1,4.0) O,N 80.4(1)^c	248

TABLE III (*Continued*)

Compound (*color*)	*Crystallographic* *classification* *space group 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(μ-ocidac)(H_2O)] · H_2O (blue)	or $P2_12_12_1$ 4	9.70(2) 13.36(2) 6.42(2)		CuO_5N	μocidacO 1.95(1,4) 2.37(1,2) N 2.00(1) H_2O 1.91(1)	Not given	Not given	249
[Cu(μ-cpidac)(H_2O)] · H_2O (not given)	or Pbca 8	22.659(4) 7.5048(9) 15.156(3)		CuO_5N	μcpidacO 1.936(4,37) N 2.058(5) H_2O 2.644(6)	Not given	O,O 90.2(2,6.7) 101.3(2) 171.9(2,4.0) O,N 84.0(2,3.2)^c 90.5(2)^e	250
Cu(μ-ceidac)(H_2O) (dark blue)	m $P2_1/c$ 4	10.559(3) 8.715(2) 11.217(2)	111.85(3)	CuO_5N	μceidacO 1.968(3,5) 2.491(3,3) μceidacN 1.997(3) H_2O 1.924(2)	Not given	O,O 89.9(1,7.4) 102.2(1) 169.0(1,1.5) O,N 84.7(1,7)^c 91.2(1)^e 93.5(1)	251
Cu(μ-bsala)(H_2O) (blue)	m $P2_1/c$ 4	13.533(1) 7.908(1) 12.066(1)	111.04(1)	CuO_5N	μO 1.945(2) 2.838(2) O 1.966(2) 2.648(2) N 1.968(2) H_2O 1.974(2)	Not given	O,O 50.87(7)^d 77.2(7,2.7) 125.2(1,10.3) 169.57(8) O,N 90.0(1,6.2) 111.4(1,4.7) 161.2(9)	252
[Cu(μ-glu)(H_2O)] · H_2O (blue)	or $P2_12_12_1$ 4	11.084 10.350 7.238		CuO_5N	O 1.974(—,7) 2.299(—) 2.588(—) N 1.998(—) H_2O 1.991(—)	Not given	Not given	253

Cu(μ-ox)(NH_3) (pale blue)	or Pbca 8	11.19(1) 9.43(1) 8.38(1)		CuO_5N	O 1.996(6,15) μO 2.376(6.16) H_3N 1.988(7)	Not given	O,O 80.2(2,3.6)[c] 92.4(2.5) O,N 92.5(3,4)	254
Cu(μ-3-ap)(μ-HCOO) (blue)	m $P2_1/c$ 2	8.569(1) 8.877(1) 8.370(1)	99.55(1)	CuO_5N	apμO 1.942(3,4) μapN 1.982(4) μHCOO 1.996(3) 2.548(4) 2.693(4)	2.964(1) 4.622(1) 5.479(1) 99.5(1)	O,O 86.0(1,7.5) 165.2(1) O,N 95.3(2,5.6)[e] 174.3(2)	255
Cu_2(μ-1,1-NCO)$_2$- (μ-1,3-NCO)$_2$ · (bpm) (blue)	m C2/c 4	19.846(1) 7.527(1) 15.252(1)	137.8(2)	CuN_5O	bpmN 2.036(4,9) OCNμN 1.961(4) μOCN 2.456(7) μNCO 1.919(4) 2.724(7)	Not given 93.1(2)	N,N 88.8(2,8.5) 98.7(2,2.1) 169.0(2,2.5) O,N 76.4(2,2.6) 94.0(2) 110.4(2) 162.8(1)	256
Cu(py)(μ-Br)$_2$(μ_3-Br)$_2$ (not given)	tr C-1 2	17.902(21) 3.978(4) 10.776(16)	86.89(11) 101.94(10) 93.28(8)	$CuBr_5N$	μBr 2.412(4) 2.928(4) μ_3Br 2.460(6,4) 3.331(4) pyN 1.996(27)	3.643(9) 95.5(2)	Br,Br 76.6(2) 88.4(2,5.2) 169.6(2) Br,N 92.1(7,4) 174.7(6)	257
Cu(μ-F)$_2$(meppz)$_2$ (pale green)	tr P-1 2	13.888(6) 6.671(3) 15.181(6)	91.95(4) 111.56(3) 92.93(4)	CuF_4N_2	μF 1.916(2,1) 2.424(2,24) N 1.994(2,2)	3.312(2,18) 98.80(6,10)	F,F 83.7(1,5.0) N,N 95.86(9) F,N 88.50(8,1)	258
[Cu(μ-mpu)(H_2O)$_4$]- $SO_4 \cdot H_2O$ (blue)	m $P2_1/n$ 4	7.310(1) 13.117(1) 14.628(2)	100.98(1)	CuO_4N_2	μmpuN 2.049(2,19) H_2O 1.967(2,3) 2.384(—,1)	Not given	O,O 89.99(7,2.08) 178.54(7,1.06) N,N 179.70(7) O,N 90.00(7,1.96)	259
[Cu(μ-pu)(H_2O)$_4$]- $SO_4 \cdot 2H_2O$ (blue)	or Pbca 8	11.912(5) 17.828(2) 12.673(2)		CuO_4N_2	μpuN 1.970(17,67) H_2O 2.015(28,0) 2.349(28,80)	Not given	O,O 89.3(5,3.2) 176.8(5,1.1) O,N 89.9(5,2.7) N,N 178.0(5)	260

TABLE III (*Continued*)

Compound (*color*)	*Crystallographic classification space group 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(μ-H_2O)(H_2O)$_3$(mgu)$_2$]-	m	11.8733(9)		CuO_4N_2	mguN 2.018(12,2)	Not given	O,O 90.0(6,7.4)	261
$SO_4 \cdot 2H_2O$	$P2_1/c$	6.8057(7)	103.423(7)		H_2O 1.992(12,21)		176.0(6,5)	
(green)	4	28.4534(16)			2.371(12)		O,N 90.1(6,3.6)	
					μH_2O 2.704(12)		N,N 176.5(6)	
[Cu(μ-gmp)$_2$(H_2O)$_3$] ·	tr	11.289(2)	107.99(1)	CuO_4N_2	μgmpN 2.032(7,20)	Not given	O,O 90.0(2,5.0)	262
$5H_2O$	P1	10.093(2)	114.40(1)		μgmpO 2.474(8)		175.3(3,4.0)	
(green)	1	11.831(2)	114.97(1)		H_2O 1.966(4,4)		N,O 90.1(3,4.0)	
					2.336(10)		N,N 177.9(2)	
Cu(μ-pzc)$_2$	m	5.0340(4)		CuO_4N_2	O 1.93(1)	3.53(1)	O,O 92.7(2)	263
(green)	$P2_1/c$	15.3316(12)	106.627(9)		2.72(1)	5.037(1)	O,N 84.5(2)^c	
	2	7.0707(9)			N 1.98(1)		87.5(2)	
Cu(μ-pys)$_2$(H_2O)$_2$	m	7.71(5)		CuO_4N_2	μpysN 2.034(16)	Not given	O,O 88.2(5)	264
(blue)	$P2_1/n$	11.00(5)	97.0(5)		μpysO 2.347(13)		O,N 92.1(5,6)	
	2	8.32(5)			H_2O 1.976(12)			
Cu(μ-suc)(bim)$_2$(H_2O)$_2$	m	12.9020(7)		CuO_4N_2	μsucO 1.966(1)	Not given	O,O 83.16(3)	265
(blue)	C2/c	13.0699(7)			H_2O 2.699(1)		O,N 88.44(6,19)	
	4	10.5613(12)			bimN 2.008(1)			
[Cu(μ-β-ala)(H_2O)$_2$] ·	tr	9.164(7)	99.89(9)	CuO_4N_2	μalaO 2.015(3)	Not given	O,O 90.0(1,4.0)	266
$2H_2O$	P-1	10.000(7)	102.21(9)		2.460(4)		O,N 92.9(2)^e	
(blue)	2	7.041(7)	91.42(9)		μalaN 1.967(4)		89.0(2,1.9)	
				CuO_4N_2	μalaO 1.960(4)		O,O 90.0(2,3.4)	
					μalaN 1.987(3)		O,N 93.4(2)^e	
					H_2O 2.596(4)		88.9(2,4.5)	
[Cu(μ-oadp)(H_2O)$_2$-	tr	7.940(1)	107.29(1)	CuO_4N_2	μoadpO 1.937(1,12)	Not given	O,O 91.7(1,5.1)	267
(2,2′-bpy)] · H_2O	P-1	12.622(2)	103.91(1)		H_2O 2.594(2,4)		O,N 90.0(2,6.0)	
(not given)	2	12.568(2)	109.78(1)		bpyN 2.004(2,6)		174.2(1,1.4)	
							N,N 80.9(2)^c	

Cu(μ-SO_4)(H_2O)$_2$- (2,2′-bpy) (pale blue)	m C2/c 4	15.165(—) 12.361(—) 6.960(—)	106.01(—)	CuO_4N_2	H_2O 1.975(7) μO_2SO_2 2.44(1) bpyN 2.005(9)	6.99	O,O 90.2(4,5.6) 176.0(4) O,N 92.1(4,2.4) 171.5(4) N,N 80.9(5)^c	268
Cu(μ-SO_4)(H_2O)$_2$(phen) (not given)	m C2/c 4	14.883(8) 13.843(9) 7.019(4)	108.60(4)	CuO_4N_2	H_2O 1.970(2) μO_2SO_2 2.468(3) phenN 2.009(2)	7.23	O,O 89.8(1,4.4) 178.5(3) O,N 91.3(1,2.5) N,N 82.0(1)^c	269
Cu(μ-SO_4)(H_2O)$_2$(en) (not given)	m C2/c 4	7.233(1) 11.273(3) 10.485(3)	116.13(2)	CuO_4N_2	H_2O 1.976(2) μO_2SO_2 2.492(2) enN 1.990(2)	7.23	O,O 88.7(1,1.9) 175.90(1) O,N 89.5(1,2.4) 173.63(2) N,N 86.43(2)^c	270
Cu(μ-SO_4)(μ-ba) (green)	or Pbcn —	18.681(4) 9.167(3) 19.111(5)		CuO_4N	μbaO 2.27(2) 2.90(2) μbaN 2.00(2,0) μO_3SO 1.95(2,1)	4.172(4) 6.008(5)	O,O 95.8(8,4.5) O,N 90.3(8,5.5) 167.4(8,2.8) N,N 81.2(8)^c	271
Cu(μ-H_2O)(ala)$_2$ (deep blue)	m C2/c 4	12.087(3) 9.583(3) 8.973(3)	110.85(2)	CuO_4N_2	O 1.958(2) N 1.976(3) μH_2O 2.684(2)	4.487(2) 113.4(1)	O,O 89.22(7) O,N 83.35(9)^c 93.20(7)	272
Cu_2(μ-H_2O)(μ-dtac)- (NO_2)$_2$ (blue)	m C2/c 4	14.789(6) 14.560(6) 12.759(9)	99.65(4)	CuO_4N_2	μO 1.929(3,4) ONO 2.532(6) μH_2O 2.995(2) N 2.029(5)	3.031(1) 103.6(2) 76.4(2)	O,O 88.0(2,7.9) 169.0(2) O,N 93.4(2,6.3) 172.7(2,1) N,N 90.5(3)^c	273
Cu(μ-H_2O)(tgly)$_2$- (4-Mepy)$_2$ (pale blue)	m C2/c 4	19.089(10) 15.891(5) 10.883(3)	100.45(1)	CuO_4N_2	tglyO 1.929(4) μH_2O 2.755(1) MepyN 1.977(5)	Not given	O,O 86.2(2) O,N 88.1(2,1.6)	274
Cu(μ-H_2O)(HCOO)$_2$(bim)$_2$ (blue)	m C2/c 4	12.94(4) 12.70(4) 10.40(2)	96.0(3)	CuO_4N_2	HCOO 1.997(5) bimN 2.017(6) μH_2O 2.625(2)	Not given 164.2(5)	O,O 78.8(2) O,N 85.8(2,1.6)	275

TABLE III (*Continued*)

Compound *(color)*	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore*	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°]	*L–Cu–L* [°]	*Ref.*
$[Cu(\mu\text{-}H_2O)(ac)_2(4\text{-}tl)_2]\cdot$ $2H_2O$ (not given)	m C2/c 4	26.04 9.24 9.45	 94.25	CuO_4N_2	acO 1.976(5) μH_2O 2.595(3) tlN 2.052(5)	Not given 131.1(3)	O,O 83.2(2) O,N 92.4(2,5.5)	276
$Cu(\mu\text{-}ta)(H_2O)_2(en)$ (dark blue)	m P2/c 2	5.726(1) 8.806(2) 12.866(4)	 101.12(1)	CuO_4N_2	H_2O 2.644(3) μtaO 1.961(3) 3.083(3) enN 2.008(3)	5.7263(1) 11.1673(6)	O,O 87.0(1,3) 102.5(1) 170.9(1) O,N 88.9(1,4.5) 169.7(1) N,N 84.9(1)^c	277
$[Cu(\mu\text{-}ttac)(ttac)(H_2O)]\cdot$ $2H_2O$ (blue)	m Cc 4	35.222(9) 6.126(4) 15.986(7)	 108.65(4)	CuO_4N_2	μttacN 2.093(25) μttacO 1.991(19) 2.498(20) ttacN 2.062(37) ttacO 1.838(22) H_2O 2.491(20)	Not given	O,O 63.4(13) 115.0(9) O,N 83.5(12,1.9)^c 96.2(12,2.8) N,N 179.4(17)	278
$[Cu(\mu\text{-}ida)(imH)(MeOH)]\cdot$ $0.37H_2O$ (dark blue)	m $P2_1$ 2	9.649(5) 7.772(4) 9.856(2)	 103.10(3)	CuO_4N_2	imN 1.940(7) μidaN 1.977(7) μidacO 1.983(7,4) 2.453(9,15) MeHO 2.468(9)	Not given	O,O 90.2(3,8.2) 169.4(3,4.7) O,N 83.8(3,4)^c 92.1(3,5.3) N,N 176.6(4)	279
$Cu(\mu\text{-}ox)(Me_2en)(H_2O)$ (blue)	m $P2_1/c$ 4	6.855(3) 10.230(5) 14.287(7)	 99.73(4)	CuO_4N_2	μoxO 1.966(5,18) 2.710(7) H_2O 2.450(6) Me_2enN 2.005(6,8)	Not given	O,O 94.1(2,7.2) 167.6(2) O,N 79.9(2,1.0) 92.2(2,5.0) N,N 86.4(2)^c	280

[Cu_2(μ-famp)(μ-1,1-OCN) · $(ClO_4)_2$] (dark green)	m $P2_1$ 2	8.987(3) 14.774(4) 9.664(1)	90.71(2)	CuO_4N_2	fampμO 1.945(7,28) fampμN 1.956(9,63) μNCO 1.980(7,14) μClO_4O 2.604(9,80) 2.747(9,27)	2.977(2)	O,O 80.9(3,1.0) O,N 91.2(3,2)^e 104.5(3,3) N,N 83.7(3,1.0)^c	281
[Cu(dpya)(dtbsq)(μ-ClO_4)] · 0.5thf (green)	tr P-1 4	14.794(4) 19.513(4) 9.766(2)	90.74(2) 105.37(2) 93.79(2)	CuO_4N_2	dtbsqO 1.957(5,23) μClO_4O 2.434(10,14) 2.741(8,54) dpyaN 1.977(6,17)	Not given	O,O 82.9(2,4)^c O,N 92.5(2,8) 169.3(2,5.7) N,N 92.2(3,5)^e	282
[Cu(ac)(dpya)(μ-ClO_4)] · $4H_2O$ (dark green)	m $P2_1/c$ 4	7.309(3) 16.363(4) 13.646(4)	103.085(3)	CuO_4N_2	acO 2.019(3,27) μClO_4O 2.541(4) 2.638(4) dpyaN 1.947(3,7)	Not given	O,O 64.7(1)^d 82.6(1,6.1) O,N 97.5(1,9.9) 163.5(1,1.7) N,N 94.9(1)^e	283
Cu(μ-NO_3)(oba)(4-Mepy) (green)	m $P2_1/n$ 4	7.145(4) 11.431(6) 20.068(7)	87.08(4)	CuO_4N_2	obaO 1.966(5,78) obaN 1.946(6) μNO_3O 2.580(5) 2.772(5) MepyN 2.013(5)	Not given	O,O 175.1(2) O,N 83.2(2)^c 93.4(2)^e 91.8(2,2) N,N 173.3(3)	284
Cu_2(μ-NO_3)$_2$(NO_3)$_2$- (μ-bpym) (blue)	m C2/c 8	19.314(3) 7.914(1) 15.060(2)	137.4(1)	CuO_4N_2	NO_3O 1.952(4) 2.547(2) $NO_3\mu O$ 1.965(3) 2.300(2) bpymN 2.010(4,2)	3.418(1) 106.3(1)	O,O 55.1(1)^d 86.5(1,3.5) 134.7(1) O,N 95.2(2,4.5) 115.3(1,10.9) 175.8(1,2.4) N,N 82.7(2)^c	285
[Cu(μ-NO_3)$_2$(pm)$_2$] · H_2O (green)	tr P-1 2	14.248(2) 8.568(1) 9.319(1)	94.08(1) 89.73(1) 99.13(1)	CuO_4N_2	μO 2.507(3,42) pmO 1.974(3,4) pmN 1.984(3,6)	4.284	O,O 88.7(1,3.8) O,N 92.4(1,2)^e 91.8(1,4)	286
Cu(μ-NO_3)(NO_3)(MeCN)$_2$ (deep blue)	m $P2_1/c$ 4	8.81(2) 7.36(2) 14.73(3)	94(1)	CuO_4N_2	NO_3O 1.89(4) 2.50(1) μNO_3O 2.02(4) 2.31(4) MeCN 1.92(6,1)	Not given	O,O 86(1) O,N 92(2,9)	287

TABLE III (*Continued*)

Compound *(color)*	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore*	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°]	*L–Cu–L* [°]	*Ref.*
$[Cu_2(\mu\text{-}NO_3)_2 \cdot (\mu\text{-}Me_3\text{-}NCH_2COO)_2(\mu\text{-}1,1\text{-}N_3)_2]$ (deep green)	m C2/c 4	19.958(6) 9.103(2) 13.180(1)	 120.00(2)	CuO_4N_2	O 1.978(4,19) μNO_3O 2.432(4,14) μN_3N 1.988(4,4)	3.436(1) 119.5(2)	O,O 87.1(2,6) 105.8(2) 167.7(3) O,N 90.0(2,3.1) 167.9(1) N,N 95.5(2)	288
$Cu(\mu\text{-}pr)(NO_3)_2$ (not given)	or Pnma 2	6.712(1) 5.142(1) 11.732(2)		CuO_4N_2	NO_3O 2.010(4) 2.490(5) μprN 1.984(4)	Not given	O,O 56.11(17)^d O,N 90	289
$[Cu(\mu\text{-}ox)(2,2'\text{-}bpy)] \cdot 2H_2O$ (violet)	tr P-1 2	9.673(3) 8.940(3) 9.103(3)	105.718(3) 110.347(3) 97.539(3)	CuO_4N_2	μoxO 1.988(4,4) 2.320(4,1) bptN 2.007(4,5)	Not given	O,O 77.7(2,3)^c 88.8(2,2.8) 159.5(1) O,N 94.4(2,5) 101.0(2,2.1) 174.7(1,1.0) N,N 80.9(2)^c	290
$[Cu(\mu\text{-}ox)(2,2'\text{-}bpy)] \cdot 2H_2O$ (blue)	tr P-1 2	9.110(1) 9.675(1) 8.922(1)	97.54(1) 105.80(1) 110.26(1)	CuO_4N_2	μoxO 1.988(2,5) 2.313(2,1) bpyN 2.005(2,7)	Not given	O,O 77.7(1,2)^c 88.7(1,3.0) O,N 96.7(1,6.3) 174.6(1,1.0) N,N 80.72(6)^c	291
$[Cu_2(\mu\text{-}ox)_2(\mu\text{-}bpm)] \cdot 5H_2O$ (green)	m C2/m 2	9.445(2) 16.622(3) 6.202(1)	 101.4(1)	CuO_4N_2	μoxO 2.081(3,5) μbpmN 2.129(3)	5.406(1) 11.022(2)	O,O 79.7(1)^c 95.3(1,7) 173.8(1) O,N 93.3(1,3.7) 164.9(1)	292
$[Cu(\mu\text{-}ox)_2(NH_3)_2] \cdot 2H_2O$ (not given)	tr P-1 1	6.293(5) 5.781(8) 5.539(5)	77.53(6) 100.59(9) 104.11(7)	CuO_4N_2	μoxO 2.147(19) H_3N 2.327(18) 1.960(19)	Not given	O,O 76.0(6)^c 97.0(8,7.0) 180.0	293

							O,N 89.6(8,5) N,N 180.0	
Cu(μ-o-pht)(NH$_3$)$_2$ (not given)	m P2$_1$/c 4	6.64(1) 19.91(1) 7.55(1)	109.9(1)	CuO$_4$N$_2$	μphtO 1.971(5) 2.799(5) phtμO 1.988(5) 2.313(5) H$_3$N 1.995(8,2)	3.260(2)	O,O 86.5(2) O,N 89.8(2,1.9) N,N 94.0(3)	294
[Cu(μ-purp)$_2$] · 5H$_2$O (not given)	or Fddd 8	24.610(8) 24.859(9) 8.0119(3)		CuO$_4$N$_2$	μpurpO 2.421(6) N 1.931(9)	Not given	O,O 83.0(2) 103.2(2) 153.4(2) O,N 76.7(7)[c] 103.3(2)	295
[Cu(μ-abz)$_2$] · 2H$_2$O (not given)	m P2$_1$/n 2	8.3(—) 20.0(—) 5.15(—)	107.7(—)	CuO$_4$N$_2$	μabzO 1.96(—) 2.67(—) μabzN 1.98(—)	Not given	O,N 90.0(—,3.6)	296
[Cu(μ-pm)$_2$] · 2H$_2$O (dark green)	or Pbca 4	10.982(1) 13.918(1) 12.095(1)		CuO$_4$N$_2$	μpmO 1.951(2) 2.688(3) μpmN 1.995(3)	Not given	O,O 86.2(2) O,N 92.1(1)[e] 86.7(2)	286
Cu(μ-ams)$_2$ (azure blue)	m P2$_1$/n 2	7.064(3) 7.668(3) 7.256(3)	88.1(5)	CuO$_4$N$_2$	O 1.995(2) 2.506(2) N 1.999(2)	Not given	O,O 92.2(1) O,N 88.2(1,5)[c]	297
Cu(μ-met)$_2$ (blue)	m P2$_1$ 2	9.487(5) 5.061(3) 15.563(8)	92.46(3)	CuO$_4$N$_2$	O 1.957(8,13) 2.676(8) 2.751(7) N 1.99(1,2)	5.338(2)	O,O 90.0(3,5.0) 176.7(4,3.0) O,N 84.0(4,3)[c] 93.3(4,7.6) N,N 175.0(3)	298
[Cu(μ-pyac)$_2$] · 2H$_2$O (blue)	m Pc 4	12.23(5) 7.27(1) 18.00(9)	114.0(3)	CuO$_4$N$_2$	μO 1.945(11,23) 2.68(—,9) N 1.948(17,2) 2.056(16,24)	Not given	O,N 89.8(5,2.2)[e]	299

TABLE III (*Continued*)

Compound (*color*)	*Crystallographic classification space group 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(μ-(L)-leucine)$_2$ (blue)	m P2$_1$ 2	9.725(4) 5.127(1) 14.689(6)	 105.79(2)	CuO$_4$N$_2$	O 1.960(3) 2.629(4) 2.749(4) N 1.992(4,4)	Not given	O,O 90.0(1,2.9) 176.9(8,29) O,N 84.2(2)^{c} 91.9(2,7.6) N,N 174.6(2)	300
Cu(μ-(DL)-abut)$_2$ (blue)	m P2$_1$/c 2	11.138(6) 5.066(1) 9.487(6)	 92.15(6)	CuO$_4$N$_2$	O 1.947(2) 2.758(3) N 1.990(3)	Not given	O,O 90.00(8,3.82) O,N 84.55(9)^{c} 91.8(1,6.5) N,N 180	300
Cu(μ-pys)$_2$ (green)	m P2$_1$/c 2	7.587(2) 10.106(3) 8.373(2)	 114.08(2)	CuO$_4$N$_2$	O 1.957(1) 2.580(2) N 1.972(2)	Not given	O,O 85.39(6) O,N 85.22(6)^{c} 93.25(6)	301
Cu(μ-phala)$_2$ (light blue)	m P2$_1$ 2	16.710(14) 5.217(9) 9.509(7)	 98.40(6)	CuO$_4$N$_2$	O 1.953(4,6) 2.635(4,56) N 1.995(4,5)	Not given	O,N 84.4(2,5)^{c}	302
Cu(μ-dpcop)$_2$ (light green)	m P2$_1$/c 2	10.588(2) 13.395(3) 9.540(5)	 90.32(3)	CuO$_4$N$_2$	O 1.953(7,5) N 2.52(1)	Not given	O,O 87.9(3,6)^{e} O,N 92.5(4,2.8)	303
Cu(μ-γ-abut)$_2$ (blue)	m P2$_1$/c 2	7.097(2) 9.693(1) 7.919(4)	 107.56(4)	CuO$_4$N$_2$	O 1.982(3) 2.641(4) N 2.015(5)	Not given	O,O 54.7(1)^{d} O,N 86.0(2,2.2)	304
[Cu(μ-γ-abut)$_2$] · 2H$_2$O (violet)	m P2$_1$/c 2	5.206(1) 14.406(3) 8.740(2)	 109.20(2)	CuO$_4$N$_2$	O 1.959(6) 2.796(6) N 2.015(5)	Not given	O,O 51.8(2)^{d} O,N 92.3(2,1.7)	304
Cu(μ-o-abnz)$_2$ (dark green)	m P2$_1$/c 2	12.95(1) 5.25(1) 9.39(1)	 93.3(1)	CuO$_4$N$_2$	O 1.973(5) 2.415(5) N 2.024(7)	Not given	O,O 89.4(2) O,N 87.1(2)^{e} 93.8(2)	305

Cu(μ-L-ala)$_2$ (not given)	m P2$_1$ 2	9.24(4) 5.505(2) 9.59(9)	95.2(3)	CuO$_4$N$_2$	O 1.97(2,1) 2.80(5,10) N 2.02(1,1)	Not given	O,N 87^c	306
Cu(μ-D-ala)$_2$ (not given)	m P2$_1$ 2	9.153(2) 5.052(5) 9.500(2)	94.64(2)	CuO$_4$N$_2$	O 1.949(7,1) 2.72(1) 2.86(1) N 1.986(9,5)	Not given	O,O 179.3(3) O,N 84.2(3,1)^c 95.8(3,6) N,N 175.8(3)	307
Cu(μ-mcys)$_2$ (blue)	m P2$_1$ 2	13.265(8) 5.036(3) 9.571(6)	97.55(2)	CuO$_4$N$_2$	O 1.944(6,8) 2.716(7,13) N 1.988(8,3)	Not given	O,O 90.0(3,2.6) 178.1(4,1.3) O,N 84.8(3,3)^c 91.7(3,7.0) N,N 176.3(3)	308
Cu(μ-L-asp)$_2$ (royal blue)	m P2$_1$ 2	5.028(1) 18.928(4) 6.174(1)	96.4(1)	CuO$_4$N$_2$	O 1.951(22,4) 2.529(20) 2.774(25) N 2.020(28,16)	Not given	O,O 90.0(8,3.5) 175.9(10,6) O,N 84.6(9,2.3)^c 90.0(9,3.7)	309
Cu(μ-hpbx)$_2$ (light brown)	m C2/c 4	24.171(4) 3.7609(3) 21.553(3)	98.85(2)	CuO$_4$N$_2$	O 1.937(10) 2.812(9) N 2.016(11)	3.761(—)	O,N 89.2(4)^e	310
Cu(μ-ekim)$_2$ (green)	m P2$_1$ 2	11.939(3) 10.884(2) 11.459(2)	113.76(2)	CuO$_4$N$_2$	O 1.92(1,8) 2.53(1,0) N 2.05(1,1)	Not given	O,O 90.9(6,2.8) 176.6(6) O,N 87.6(6,7.6) N,N 175.6(6)	311
[Cu(μ-pyac)$_2$]·2H$_2$O (not given)	m P2$_1$/c 4	12.196 7.259 18.045	114.05	CuO$_4$N$_2$	O 1.942(2,8) 2.676(2,14) N 1.998(2,6)	Not given	O,N 90.0(1,1)^e	312
{Cu(μ-ahx)$_2$]·2H$_2$O (violet)	m P2$_1$/n 4	8.550(2) 20.068(3) 5.145(1)	106.85(2)	CuO$_4$N$_2$	O 1.967(5) 2.768(6) N 1.994(6)	Not given	O,O 51.8(2)^d O,N 87.9(2,1.1)	313
[Cu(μ-trisH)$_2$]·5H$_2$O (violet)	m P2/n 2	12.926(7) 10.116(3) 6.368(3)	95.8(4)	CuO$_4$N$_2$	O 1.937(5) 2.887 N 1.991(7)	Not given	O,N 85.3(3)^c	314

TABLE III (*Continued*)

Compound (*color*)	*Crystallographic classification space group 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(μ-viol)$_2$(H$_2$O)$_2$] · 2H$_2$O (violet)	tr P-1 1	12.66(1) 15.146(5) 6.36(1)	102.5(1) 111.9(1) 93.4(2)	CuO$_4$N$_2$	H$_2$O 2.06(1) O 2.21(1) N 1.97(1)	Not given	O,O 89(—) O,N 78(—)^c	315
[Cu(μ-suc)(en)] · 4H$_2$O (not given)	m P2$_1$/c 4	15.803(6) 7.129(2) 16.003(10)	112.58(4)	CuO$_4$N$_2$	μsucO 1.986(3,10) 2.622(3,32) enN 2.028(4,32)	Not given	O,O 55.2(1,9)^d 88.7(1,4.0) 131.3(1) O,N 91.8(1) 105.2(1,8.3) N,N 86.5(1)^c	316
Cu(μ-glu)(Me$_4$N) (not given)	or P2$_1$2$_1$2$_1$ 4	8.631(5) 10.438(7) 15.878(6)		CuO$_4$N$_2$	μgluO 1.965(7,24) 2.547(8,47) Me$_4$enN 2.045(9,5)	Not given	O,O 56.7(3,1.2)^d 92.2(3,1.8) 137.8(3) O,N 95.4(4,4.9) 112.5(3,1) N,N 86.0(4)^c	317
[Cu(μ-3,3′-dtdp)-(2,2′-bpy)] · 2H$_2$O (blue)	m P2$_1$/n 4	9.686(4) 9.409(3) 21.231(4)	102.0(2)	CuO$_4$N$_2$	μdtdpO 1.948(3,14) 2.231(4) 2.826(5) bpyN 1.992(4,4)	3.348(3)	O,O 51.3(1)^e 77.5(1) 90.8(1,1.7) 128.5(1) O,N 85.9(1) 96.5(1,4.9) 174.3(1,5) N,N 80.9(1)^c	169
[Cu(μ-L-hprol)$_2$] · 4H$_2$O (blue)	m P2$_1$ 2	10.209(6) 8.071(3) 9.698(3)	100.33(4)	CuO$_4$N$_2$	O 1.949(5,7) 2.612(6) 2.831(6) N 2.006(5,6)	Not given	O,O 93.1(2,7.8) 169.8(3) O,N 85.1(2,1)^c 87.0(2,3.6)	318

							173.0(1,1.1) N,N 97.2(2)	
[Cu(μ-D-ahprol)$_2$] · 2.5H$_2$O (blue)	or P2$_1$2$_1$2$_1$ 8	8.678(5) 17.737(4) 18.686(7)		CuO$_4$N$_2$	O 1.929(7,3) 2.801(9,4) N 1.978(9,1)	Not given	O,O 89.9(4,8.6) 155.6(4) 178.2(2) O,N 85.6(4,7)^{c} 90.0(4,6.0) N,N 173.9(3)	318
[Cu(μ-ee)] · 4H$_2$O (blue)	or P2$_1$2$_1$2$_1$ 4	10.070(1) 18.832(2) 9.425(1)		CuO$_4$N$_2$	O 1.973(4,37) 2.334(3) N 2.088(4) 2.485(4)	Not given	O,O 85.0(2,3.6) 95.6(1,4.3) 102.1(1,6) 177.1(2) O,N 74.8(2,3)^{c} 82.7(2) 103.1(1,5.4) 142.9(1) 168.7(2) N,N 80.7(1)^{c}	319
Cu(hfacac)$_2$(μ-ted) (yellow green)	or Pnnm 2	16.148 8.428 7.743		CuO$_4$N$_2$	hfacacO 1.956(5,2) μtedN 2.566(7)	Not given	O,O 91.9(2)^{e}	320
Cu(hfacac)$_2$(μ-pr)$_2$ (green)	tr P-1 1	11.228(6) 6.821(4) 6.742(7)	109.06(5) 103.27(3) 95.12(2)	CuO$_4$N$_2$	hfacacO 1.964(7,40) μprN 2.529(9)	Not given	O,O 92.4(3)^{e} O,N 90.0(3,5)	321
Cu(μ-gly)(μ-ser) (not given)	m Pb 2	8.71(2) 9.64(1) 5.08(1)	 92.1(2)	CuO$_4$N$_2$	μglyO 1.95(1) 2.70(—) μserO 1.92(1) 2.77(1) μserN 2.03(1,2)	Not given	Not given	322
[Cu$_2$(μ-sal)$_2$(amp)$_2$] · 4PropOH (green)	tr P-1 1	10.085(7) 8.663(4) 13.522(8)	102.78(4) 72.65(5) 108.32(5)	CuO$_4$N$_2$ CuO$_4$	ampO 2.010(3) ampN 1.968(3) μsalO 2.654(4) μsalO 1.902(3,1)	Not given	O,O 91.8(1) O,N 82.8(1)^{c} 99.0(1) O,O 93.8(1)^{e}	323

TABLE III (*Continued*)

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore*	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°]	*L–Cu–L* [°]	*Ref.*
$[Cu_2(\mu\text{-tac})Cl_2]\cdot$	m	16.711(3)		CuO_4N_2	tacμO 1.899(5)	4.627(2,24)	O,O 84.3(3,5.5)	324
MeOH	$P2_1/n$	9.671(2)	111.00(2)		O 1.911(6)		95.8(3,5.0)	
(black)	4	15.829(3)			2.471(8,40)		172.9(2,4.4)	
					μtacN 2.061(8,5)		O,N 76.1(3,1)	
							90.0(3,8.2)	
							104.3(3,3)	
							N,N 176.5(3)[c]	
				CuO_4Cl_2	μtacO 1.979(6,5)		O,O 52.8(2,4)[d]	
					2.275(5)		85.2(3)	
					tacμO 2.759(6)		113.5(2,2)	
					Cl 2.208(4,6)		164.0(2)	
							O,Cl 95.0(2,4.6)	
							148.3(2,8)	
							Cl,Cl 101.1(1)	
Cu(μ-L-prl)(MeOH)Cl	m	9.038(3)		CuO_4NCl	prlμO 1.958(6)	Not given	O,O 54.4(2)[d]	133
(pale blue)	$P2_1$	5.980(1)	101.62(2)		2.656(6)		87.2(2,5.9)	
	2	8.567(2)			μprlO 1.958(6)		144.1(2)	
					μprlN 2.006(6)		O,N 83.8(2)[c]	
					MeHO 2.297(6)		106.0(2,4.5)	
					Cl 2.276(3)		155.8(2)	
							O,Cl 93.5(2,7)	
							101.8(1)	
							176.2(2)	
							N,Cl 93.4(2)	
$[Cu_2(\mu\text{-tedta})(H_2O)_2]\cdot$	or	9.646(4)		CuO_4NS	O 1.964(5,32)	5.180(1)	O,O 88.7(14,7.2)	325
$3H_2O$	$P2_12_12_1$	14.264(5)			2.561(4)	136.38(5)	103.09(14)	
(blue)	4	14.724(5)			N 2.015(4)		165.20(13)	

					μS 2.750(1)		O,N 88.2(15,9.0)	
							O,S 85.6(1,1.7)	
							102.62(11)	
							173.1(15,2.5)	
							N,S 84.51(11)^c	
				CuO_4NS	O 1.944(3,4)		O,O 91.4(15,6.9)	
					N 1.998(4)		169.62(14)	
					μS 2.829(1)		O,N 88.1(15,3.5)	
					H_2O 1.973(3)		177.40(15)	
					2.418(4)		O,S 80.13(12)	
							98.6(11,1.3)	
							164.29(11)	
							N,S 83.94(12)^c	
$[Cu_2(\mu\text{-tbcmc})(H_2O)_2]\cdot$	m	19.479(3)		CuO_4NS	O 1.968(6,5)	4.632(2)	O,O 86.9(3,2)	326
$4H_2O$	C2	7.194(1)	111.43(2)		N 2.024(8)	6.236(2)	96.0(3,2.4)	
(blue)	2	8.492(2)			S 2.721(3)		167.5(3)	
					H_2O 1.956(7)		O,S 84.2(2)^c	
							96.8(2,3.6)	
							167.6(2)	
							O,N 84.4(3,7)^c	
							177.3(3)	
							N,S 86.0(2)^c	
$[Cu(\mu\text{-iptac})_2]\cdot 2H_2O$	m	14.318(2)		CuO_4S_2	O 1.905(2)	Not given	O,O 92.78(8)	327
(black violet)	$P2_1$	10.968(2)	93.74(2)		2.745(2)		O,S 82.2(1,5.3)^c	
	2	4.949(1)			S 2.358(1)			
$[Cu_3(tmso)_4(\mu_3\text{-Cl})_2\text{-}$	tr	8.250(4)	67.59(4)	CuO_4Cl_2	tmsoO 1.952(2,5)	Not given	O,O 89.2(1,0)	328
$(\mu\text{-Cl})_2Cl_2]$	P-1	9.330(5)	73.29(6)		μ_3Cl 2.894(1,0)	93.4(1)	O,Cl 89.2(1,1.7)	
(red)	1	11.131(6)	74.67(6)			112.3(1)		
				$CuCl_4$	μ_3Cl 2.213(1)		Cl,Cl 95.5(1,8.9)	
					μCl 2.278(1)		138.9(1)	
					2.325(1)		146.8(1)	
					Cl 1.183(1)			
$Cu(daca)_2(\mu\text{-Cl})Cl_3$	tr	8.6819(9)	89.05(6)	CuO_4Cl_2	O 1.947(—,22)	Not given	Not given	329
(not given)	P-1	10.1399(7)	102.52(7)		μCl 2.774			
	2	9.5137(7)	91.91(2)					

TABLE III (*Continued*)

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore*	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°]	*L–Cu–L* [°]	*Ref.*
				$CuCl_4$	Cl 2.220(—,32)		Not given	
					μCl 2.724			
$Cu_2(\mu\text{-px})_2(px)_2(\mu\text{-Cl})_2Cl_2$	tr	9.660(2)	81.57(3)	CuO_4Cl_2	μpxO 1.875(9)	3.553(—)	O,O 90.3(4)^e	330
(not given)	P-1	9.920(2)	86.10(4)		pxO 1.980(9)		O,Cl 91.9(3,4.5)	
	2	5.8342(3)	115.25(2)		μCl 2.860(3)			
				$CuCl_4O_2$	μCl 2.320(3)		Cl,Cl 89.7(1)	
					Cl 2.322(4)		Cl,O 88.8(2,5.4)	
					μpyxO 2.545(9)			
$[Cu_3(tmso)(\mu_3\text{-Br})_2\text{-}$	tr	8.448(2)	65.42(1)	CuO_4Br_2	tmsoO 1.941(5,2)	Not given	O,O 90.0(2,2)	328
$(\mu\text{-Br})_2Br_2]$	P-1	9.630(2)	71.59(2)		μ_3Br 3.063(1,0)	91.1(1)	O,Br 88.3(2,2.0)	
(black)	1	11.655(2)	73.52(1)			112.4(1)		
				$CuBr_4$	μ_3Br 2.447(2)		Br,Br 97.0(1,8.1)	
					μBr 2.341(1)		134.9(1)	
					2.410(1)		142.0(1)	
					Br 2.316(1)			
$Cu(5\text{-ppzH})_4(\mu\text{-SiF}_6)$	tr	5.531(7)	121.69(5)	CuN_4F_2	ppzHN 1.997(5,5)	Not given	N,N 90.8(2)	331
(light blue)	P-1	12.211(5)	99.30(4)		μSiF_6F 2.251(3,0)		N,F 91.0(2,8)	
	2	12.140(7)	101.73(3)					
				CuN_4F_2	ppzHN 2.002(5,8)		N,N 89.7(2)	
					μSiF_6F 2.245(3,0)		N,F 90.3(2,9)	
$[Cu(2,2'\text{-bpy})_2(\mu\text{-BF}_4)]\cdot$	tr	11.275(4)	96.44(3)	CuN_4F_2	bpyN 1.986(4,38)	Not given	N,N 82.0(1,2)^c	332
BF_4	P-1	14.760(5)	101.63(4)		μBF_4F 2.560(5)		102.8(1,1.0)	
(not given)	2	7.366(3)	110.25(4)		2.656(5)		156.6(1,3.1)	
$Cu(im)_4(\mu\text{-SO}_4)$	m	9.224(1)		CuN_4O_2	imN 2.011(5,11)	Not given	N,N 90.0(2,1.6)	333
(violet)	C2/c	17.626(1)	93.473(4)		2.843(5,40)		O,N 86.1(2,9)	
	4	10.552(1)			μSO_4O 2.574(4)			

$Cu(NH_3)_4(\mu\text{-}SeO_4)$ (deep blue)	m $P2_1/n$ 4	10.3128(4) 10.2590(3) 7.4046(3)	 104.431(3)	CuN_4O_2	H_3N 2.005(9,13) μSeO_4O 2.451(8) 2.607(7)	Not given	N,N 90.0(3,1.4) 176.6(3,3.4) O,O 177.2(2) N,O 90.0(3,2.7)	334
$Cu(NH_3(\mu\text{-}NO_3)_2$ (deep blue)	or Pnnm 8	10.840(2) 23.693(4) 6.902(2)		CuN_4O_2	H_3N 2.019(5,11) μNO_3O 2.544(5,27)	Not given	N,N 90.8(2,3.4) N,O 90.0(1,6.2) O,O 173.9(2)	335
				CuN_4O_2	H_3N 2.016(5,4) μNO_3O 2.547(5) 2.706(7)		N,N 90.8(2,3.1) N,O 82.9(2,3.4) 97.2(2,2.8) O,O 171.0(2)	
$Cu(Me_2en)_2(\mu\text{-}NO_3)_2$ (not given)	m $P2_1/c$ 2	7.426(4) 8.547(7) 13.144(12)	 105.52(4)	CuN_4O_2	enN 2.054(4,4) μNO_3O 2.520(5,0)	Not given O 127.1(3)	N,N 85.3(2)^c N,O 89.4(2,4.6)	336
$[Cu(en)_2(\mu\text{-}NO_3)]SeCN$ (purple blue)	m Pc 4	9.254(3) 14.018(3) 9.720(5)	 99.20(5)	CuN_4O_2	enN 1.966(21,21) 2.068(25,31) μNO_3O 2.461(15,54) 2.716(20,54)	Not given	N,N 85.2(9,8)^c 92.4(9,8) 175.2(9,3.4) O,O 171.1(7,3.8) N,O 90.0(6,10.5)	337
$Cu(1,2\text{-}pn)_2(\mu\text{-}Cr_2O_7)$ (yellow brown)	m $P2_1/c$ 2	8.986(4) 10.398(5) 8.421(3)	 102.66(4)	CuN_4O_2	pnN 1.96(7) 2.23(5) μCr_2O_7O 2.62(5,0)	Not given	N,N 85(2)^c O,N 91(2,5)	338
$[Cu(2,2'\text{-}bpy)_2(\mu\text{-}ClO_4)]\cdot$ ClO_4 (not given)	tr P-1 2	11.238(4) 14.863(5) 7.403(3)	96.28(3) 99.49(4) 110.21(4)	CuN_4O_2	bpyN 1.993(4,12) μClO_4O 2.512(5) 2.746(5)	Not given	N,N 81.8(2,1)^c 102.8(2,8) 156.8(2,5)	332
$[Cu(2,2'\text{-}bpy)_2(ClO_4)]\cdot$ ClO_4 (not given)	tr P-1 2	7.44(1) 14.93(1) 15.32(1)	136.3(1) 103.7(1) 83.2(1)	CuN_4O_2	bpyN 1.99(2,2) μClO_4O 2.45(2) 2.73(2)	Not given	N,N 82.7(8,1.1)^c 102.2(8,1) 156.1(8,5.1) O,N 76.4(7,9) 88.0(7,10.0) 114.0(7,3.3) O,O 156.2(6)	339

TABLE III (*Continued*)

Compound *(color)*	*Crystallographic classification space group 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(hist)$_2$(μ-ClO$_4$)$_2$ (violet)	m P2$_1$/c 2	8.235(6) 13.676(9) 8.084(6)	100.5(5)	CuN$_4$O$_2$	histN 2.018(9,3) μClO$_4$O 2.617(12,0)	Not given	N,N 91.3(4)^{e} O,N 88.8(4,2.2)	340
Cu(mtactd)(μ-ClO$_4$)$_2$ (blue)	or P2$_1$2$_1$2$_1$ 4	13.896(7) 13.890(6) 9.911(1)		CuN$_4$O$_2$	N 1.99(1,5) μClO$_4$O 2.64(1) 2.71(2)	Not given	N,N 85.2(5,4)^{c} 95.1(5,60)^{e} 174.6(5,1.0)	341
[{Cu$_3$(μ-im)$_2$(im)$_8$(ClO$_4$)$_2$} · (μ-ClO$_4$)$_2$] (dark violet)	m P2$_1$/a 2	16.664(5) 15.524(5) 9.226(1)	94.68(5)	CuN$_4$O$_2$	imN 2.009(6) μimN 1.975(6) μClO$_4$O 2.755(6)	Not given	N,N 90.1(3,6) O,N 89.9(3,7)	342
				CuN$_4$O$_2$	imN 1.988(7,3) μimN 1.976(6) ClO$_4$O 2.581(8) 2.930(7)		N,N 90.6(3,2.7) O,N 90.0(3,11.1) O,O 169.9(3)	
[Cu$_2$(μ-4,4′-bpy)(trien)$_2$ · (μ-ClO$_4$)$_2$] · 2ClO$_4$ (purple)	or Pbca 4	11.189(2) 14.414(2) 16.213(2)		CuN$_4$O$_2$	trienN 2.003(8,10) μbpyN 2.008(6) μClO$_4$O 2.660(13) 2.876(12)	7.283(2) 11.106(2)	N,N 84.6(3,1)^{c} 95.4(3,9) 172.8(3,6.3) N,O 85.2(4,6.6) 103.4(4,3.4) O,O 165.2(4)	343
Cu(2,2′-bpy)(μ-4,4′-bpy)-(ClO$_4$)$_2$ (dark blue)	or Pbcn 4	12.413(3) 14.645(3) 12.287(2)		CuN$_4$O$_2$	bpyN 1.922(4) μbpyN 2.017(4) ClO$_4$O 2.516(7)	Not given	N,N 82.6(2)^{c} 95.9(2) 169.4(2) O,N 90.0(2,7.4) O,O 174.6(2)	344
Cu(2,2′-bpy)$_2$(μ-tt) (blue)	or Pbcn 4	10.29(2) 13.05(2) 16.38(2)		CuN$_4$O$_2$	bpyN 1.99(1,1) μttO 2.82(1,0)	Not given	Not given	345

Cu(2,2′-bpy)$_2$(μ-tet) (royal blue)	or Pbcn 4	11.260(10) 12.839(10) 16.170(11)		CuN$_4$O$_2$	bpyN 1.990(6,5) μtetO 2.627(6)	Not given	N,N 82.2(3)^c 103.2(3,7)	346
Cu(en)$_2$(μ-dds)$_2$ (purple)	tr P-1 1	5.608(1) 8.247(1) 21.381(3)	97.30(3) 95.07(3) 104.17(3)	CuN$_4$O$_2$	enN 2.007(2,1) μddsO 2.517(2,0)	Not given	N,N 84.9(1)^c N,O 89.0(1,2.3)	347
[Cu$_2$(μ-dddo)$_2$(MeOH)]- (ClO$_4$)$_2$ (red)	tr P-1 4	6.897(3) 12.023(4) 22.646(7)	100.81(3) 98.69(3) 106.73(3)	CuN$_4$O$_2$	μdddoN 1.948(5,13) μdddoO 2.493(4) MeHO 2.624(10)	5.122(4)	N,N 81.1(2,5)^c 96.7(2) 100.2(2,4.8) O,N 87.0(3,4.8) 99.0(2,2.6) O,O 173.7(2)	348
				CuN$_4$O$_2$	μdddoN 1.948(5,12) μdddoO 2.491(4) MeHO 2.625(11)	5.129(1)	N,N 80.9(2,5)^c 96.8(2) 100.5(2)^e O,N 87.1(3,4.8) 99.1(2,2.5) O,O 173.4(3)	
Cu(μ-pzn)$_2$(ClO$_4$)$_2$ (not given)	m C2/m 2	14.123(4) 9.781(2) 8.984(2)	147.12(2)	CuN$_4$O$_2$	μpzN 2.062(3) ClO$_4$O 2.373(12)	7.012	N,N 90.0(2,8) 180.0(3) O,N 89.2(2) O,O 180.0(3)	349
Cu(μ-pzn)$_2$(ms)$_2$ (pale blue)	or Pnnm 2	8.199(1) 13.130(1) 6.913(1)		CuN$_4$O$_2$	μpzN 2.058(2) 2.692(2) msO 1.956(1)	Not given	N,N 90 180 O,N 78.92(5) 90 O,O 180	350
[Cu(μ-th)$_2$](ClO$_4$)$_2$ (light blue)	m P2$_1$/a 4	9.850(1) 15.437(2) 11.780(2)	93.08(1)	CuN$_4$O$_2$	N 2.054(6,22) 2.233(6) 2.350(5) O 2.008(4,4)	Not given	N,N 91.8(2) 164.4(2,1.7) O,N 75.7(2)^c 89.6(2,3.0) 104.7(2) O,O 178.0(2)	351

TABLE III (*Continued*)

Compound (*color*)	*Crystallographic classification space group 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(2-OH-1,3-pn)$_2$(μ-ta) (not given)	tr P-1 1	6.681(6) 7.182(4) 9.648(5)	104.74(5) 84.74(6) 91.45(6)	CuN$_4$O$_2$	pnN 2.045(7,14) μtaO 2.482(7,0)	Not given	N,N 89.0(3)^c	352
Cu(μ-OHqu)$_2$(μ-tcb) (black)	tr P-1 1	7.37(1) 7.70(1) 14.29(2)	98.9(1) 96.3(1) 97.3(1)	CuN$_4$O$_2$	quN 1.96(1,1) quO 1.90(1,1) μtcbN 2.95(1)	Not given	N,O 85.0(7)^c	353
Cu(μ-4-dtmp)(NCS) (not given)	m P2$_1$/n 4	11.592(2) 8.271(3) 10.327(2)	 93.75(5)	CuN$_4$O$_2$	SCN 2.178(9) μdtmpN 2.024(8,43) μdtmpO 2.032(6) 2.630(7)	Not given	N,N 84.5(3,6)^c 101.3(3,8.6) 164.6(3) O,N 91.7(3,7.3) 153.3(3,3) O,O 54.5(2)^d	138
Cu(μ-bmpcb) (dark green)	m P2$_1$/c 4	10.44(3) 14.57(4) 11.76(2)	 104.1(2)	CuN$_4$O$_2$	N 2.006(7,79) O 2.693(6) 2.798(6)	Not given	N,N 81.5(2,5)^c 117.3(2) 159.3(2,1.2) O,N 86.4(2,3.0) 104.9(2,1.5) O,O 163.5(2)	354
Cu(μ-tp)Cl$_2$ (blue)	m P2$_1$/c 2	9.546(1) 8.958(1) 8.082(1)	 107.32(1)	CuN$_4$Cl$_2$	μtpN 2.021(4) 2.692(4) Cl 2.297(1)	8.406	N,N 89.3(1) N,Cl 93.6(1,1.9)	229
[Cu(aeim)$_2$(μ-Cl)]Cl · 2H$_2$O (not given)	m P2$_1$/c 4	9.727(2) 10.463(2) 18.022(3)	 114.83(1)	CuN$_4$Cl$_2$	aeimN 2.029(5,17) μCl 2.856(2,0)	Not given	N,N 91.1(2)^e N,Cl 92.2(1,2.4)	355
				CuN$_4$Cl$_2$	aeimN 2.026(4,16) μCl 2.875(2,0)		N,N 90.8(2)^e N,Cl 87.6(1,3.6)	

[Cu_2(μ-bistrien)(μ-Cl)$_2$]- (ClO_4)$_2$ (deep blue)	m $P2_1/m$ 2	11.811(2) 11.352(2) 11.358(2)	99.11(3)	CuN_4Cl_2	N 2.05(1,4) μCl 2.48(1) 3.31(1)	6.138(2) 157.0(2,2.3)	N,N 84.0(4,4)^c 101.8(4) 157.7(5,6.5) N,Cl 100.2(5,8.2)	356
Cu_2(cy)(μ-Cl)$_2$$Cl_2$ (dark brown)	or Panm 4	8.370(2) 12.804(2) 16.791(2)		CuN_4Cl_2	cyN 2.012(8,6) μCl 2.854(2,2)	Not given	N,N 85.7(3)^c 94.3(3,4)^e 178.9(3) Cl,N 90.0(2,3.3) Cl,Cl 177.6(1)	357
				$CuCl_4$	Cl 2.253(3) μCl 2.236(4,1)		Cl,Cl 100.7(1,8) 129.1(1,3.3)	
[Cu(μ-cim)$_2$](ClO_4)$_2$ (green)	m $P2_1/c$ 4	12.264(3) 8.529(3) 15.947(4)	94.45(2)	CuN_4S_2	N 2.004(5,32) S 2.700(1,0)	Not given	N,N 91.7(2) S,N 78.8(1)^c 93.2(1)	358
[Cu(μ-cim)$_2$](NO_3)$_2$ (brown)	m $P2_1/n$ 2	11.597(3) 10.555(1) 12.256(1)	97.07(1)	CuN_4S_2	N 1.942(2) 2.558(2) S 2.419(1)	Not given	N,N 88.7(1) N,S 79.3(1)^c 84.9(1)	359
[Cu(μ-cim)$_2$](SO_4) · $9H_2O$ (green)	m C2/c 4	25.417(4) 13.905(2) 10.677(2)	97.61(1)	CuN_4S_2	N 1.991(3,10) S 2.910(1,0)	Not given	N,N 89.0(1) N,S 77.4(1)^c 87.3(1)	360
[Cu(en)$_2${μ-(EtO)$_2$$PS_2$}]- (NCS) (violet)	m $P2_1/c$ 4	8.529(1) 19.247(6) 13.696(3)	122.67(1)	CuN_4S_2	enN 2.03(1,1) S 3.04(1,5)	Not given	N,N 85.9(—,3)^c	361
Cu(en)(μ_3-NCS)(NCS) (light blue)	or $Pn2_1a$ 8	24.51(8) 6.018(1) 12.413(3)		CuN_4S_2	enN 2.13(3,1) μ_3SCN 2.00(2,1) NCμ_3S 3.05(2,6)	Not given	N,N 83.7(1.0)^c 92.0(1.0,4.8) 172.1(1.9,3) N,S 90.2(2.2,4.4) S,S 176.5(3)	362
				CuN_4S_2	enN 2.14(2,0) SCN 2.03(3,2) μ_3NCμS 3.05(2,4)		N,N 82.1(9)^c 92.1(1.0,1.7) 169.3(20,1.0) N,S 91.0(17,10.4) S,S 170.1(3)	

TABLE III (*Continued*)

Compound *(color)*	*Crystallographic classification space group 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-Brpy)$_2$(μ-NCS)$_2$ (dark green)	tr P1 2	8.568(3) 9.200(3) 10.809(5)	72.64(3) 86.15(3) 80.14(3)	CuN$_4$S$_2$	BrpyN 2.044(20,41) μSCN 1.954(20,5) μNCS 3.068(10,10)	Not given	N,N 90.0(8,3.8) 175.9(8,2) N,S 90.1(7,2.9) S,S 177.8(4)	363
				CuN$_4$S$_2$	BrpyN 1.979(20,60) μSCN 2.036(10,0) μNCS 2.991(10,80)		N,N 90.0(8,3.3) 174.1(9,2.8) N,S 90.0(8,9.0) S,S 178.6(4)	
Cu(4-Mepy)$_2$(μ-NCS)$_2$ (dark green)	m P2$_1$ 6	9.808(6) 26.752(10) 9.927(4)	 107.89(4)	CuN$_4$S$_2$	MepyN 2.021(8,18) μSCN 1.948(8,9) μNCS 3.117(4,8)	Not given	N,N 90.1(4,2.6) 175.9(4,1) N,S 90.0(3,5.0) S,S 173.6(2)	364
				CuN$_4$S$_2$	MepyN 2.064(8,10) μSCN 1.936(8,3) μNCS 2.987(4,19)		N,N 90.0(4,8) 179.0(4,1) N,S 90.0(3,2.4) S,S 177.8(1)	
				CuN$_4$S$_2$	MepyN 2.023(8,1) μSCN 1.963(9,11) μNCS 2.977(4) 3.528(4)		N,N 90.0(4,2) 177.2(4,2) N,S 89.1(3,7.6) S,S 171.6(2)	
Cu(4-Mepy)$_2$(μ-NCS)$_2$ (green) (at 180 K)	m P2$_1$ 6	9.63(1) 26.53(2) 9.84(2)	 106.40(7)	CuN$_4$S$_2$	MepyN 2.01(1,2) μSCN 1.92(1,3) μNCS 3.06(1,5)	Not given	N,N 175.7(7,1.7) N,S 86.8(5)	365
				CuN$_4$S$_2$	MepyN 2.05(1,0) μSCN 1.94(2,1) μNCS 2.94(1,2)		N,N 179.2(8,7) S,S 177.8(1)	
				CuN$_4$S$_2$	MepyN 2.00(1,2) μSCN 1.93(1,3) μNCS 3.21(1,5)		N,N 176.4(8,1) S,S 171.9(1)	

Cu(bpm)(μ-NCS)$_2$ (dark green)	m C2/c 4	11.543(1) 13.948(2) 7.818(1)	93.26(1)	CuN$_4$S$_2$	bpmN 2.009(6) μSCN 1.941(6) μNCS 3.174(2)	5.328(2)	N,N 89.3(2,8.8) 162.6(2) N,S 82.2(2,1.9) 97.8(2,8) S,S 178.3(2)	256
Cu(bpm)(μ-NCS)$_2$ (blue green) (at 153 K)	m C2/c 4	11.403(2) 13.943(3) 7.722(2)	93.93(2)	CuN$_4$S$_2$	bimN 2.004(2) μSCN 1.939(2) μNCS 3.121(1)	Not given	N,N 80.6(1)^c 94.6(1,2) 163.1(1) N,S 82.5(1.20) 97.6(1,1.2) S,S 178.9(1)	366
Cu$_2$(μ-bpm)(μ-NCS)$_4$ (blue green) (at 153 K)	or Fddd 16	12.676(2) 22.171(3) 24.490(3)		CuN$_4$S$_2$	μbimN 2.053(2,6) μSCN 1.933(3,0) μNCS 2.916(1,10)	Not given	N,N 81.0(1,1)^c 93.0(1,2.1) 173.4(1) N,S 89.5(1,7.4) S,S 168.8(1)	366
Cu$_2$(μ-NCS)$_4$(μ-bpm)$_2$ (blue green)	or Fddd 16	12.811(1) 22.473(1) 24.259(1)		CuN$_4$S$_2$	μbpmN 2.052(5) μSCN 1.921(5) μNCS 2.497(1)	5.430(2)	N,N 90.0(2,9.2) 173.3(2) N,S 85.9(2,2.2) 93.7(2,3.2) S,S 169.2(1)	
				CuN$_4$S$_2$	μbpmN 2.060(5) μSCN 1.923(6) μNCS 2.933(1)		N,N 90.0(3,9.7) 172.5(2) N,S 86.2(1,2.1) 93.4(4,3.3) S,S 170.0(4)	256
Cu(NH$_3$)$_4$(μ-I$_4$) (not given)	m C2/m 2	14.172(4) 8.926(2) 6.558(2)	128.65(2)	CuN$_4$I$_2$	H$_3$N 2.013(5,0) μI$_4$I 3.224(1,0)	Not given	N,N 90.00(20,4) 180.0 N,I 90.00(9,6.1) I,I 180.0	367
Cu(den)(μ-NCS)(μ-ClO$_4$) (blue)	tr P-1 2	11.81(2) 7.48(2) 7.48(2)	70.9(3) 89.7(3) 105.4(3)	CuN$_4$OS	denN 2.02(1,1) μSCN 1.95(1) μNCS 2.76(4) μClO$_4$O 2.90(2)	5.51	N,N 84.3(2,2)^c 95.1(2,1.0)	368

TABLE III (*Continued*)

Compound (*color*)	*Crystallographic classification space group Z*	*a* [Å] *b* [Å] *c* [Å]	α [°] β [°] γ [°]	*Chromophore*	*Cu–L* [Å]	*Cu–Cu* [Å] *Cu–L–Cu* [°]	*L–Cu–L* [°]	*Ref.*
$Cu_2(chd)(thf)_2(\mu\text{-}Cl)_4$	m	16.561(3)		$CuCl_4O_2$	μCl 2.288(2,0)	3.525(2)	Cl,Cl 79.8(1)	369
(brown)	C2/c	13.217(2)	134.05(1)		2.726(2,0)	94.5(1,4.6)	99.9(1,9)	
	4	13.290(3)			chdO 1.996(4,0)		179.7(1)	
							Cl,O 90.1(2,1.7)	
							168.6(1)	
							O,O 81.9(2)^e	
				$CuCl_4O_2$	μCl 2.240(2,0)		Cl,Cl 90.0(1,6)	
					2.350(2,0)		180.0(1,0)	
					thfO 2.719(4,0)		Cl,O 90.0(1,6.6)	
							O,O 180.0(2)	
$(Me_3NH)[Cu(\mu\text{-}Cl)_2\text{-}$	m	7.5066(8)		$CuCl_4O_2$	μCl 2.2770(5)	Not given	Cl,Cl 86.33(1)	370
$(H_2O)_2]Cl$	$P2_1/c$	7.8873(5)	91.914(9)		2.9087(5)	93.7(1,2.4)	96.66(1)	
(green)	4	16.758(1)			H_2O 1.971(1)		Cl,O 90.00(4,1.04)	
				$CuCl_4O_2$	μCl 2.3060(5)		Cl,Cl 86.44(1)	
					2.7530(5)		93.56(1)	
					H_2O 2.005(1)		Cl,O 93.00(3,15)	
$Cu(\mu\text{-}tmso)(\mu\text{-}Cl)_2$	or	13.844(10)		$CuCl_4O_2$	μCl 2.254(2)	3.209(6)	Cl,Cl 87.6(2,7.2)	371
(orange)	Pbca	6.418(12)			2.339(5)	Cl 83.9(2,2.9)	104.1(2,4.4)	
	—	17.480(16)			2.663(5)	O 79.7(3)	177.5(2)	
					tmsoμO 1.972(10)		Cl,O 72.2(2,5.2)	
					2.209(11)		88.6(3,4.2)	
							92.8(3)	
							112.5(2)	
							164.3(3,2.0)	
							O,O 88.0(4)	
$Cu(\mu\text{-}dmso)(\mu\text{-}Cl)_2$	m	7.774(1)		$CuCl_4O_2$	μCl 2.343(2,17)	3.238(1)	Cl,Cl 79.06(5)	371
(orange)	$P2_1/c$	13.557(3)	103.83(1)		2.714(2)	Cl 84.2(5,3.3)	91.06(6,8.9)	
	—	6.475(1)			dmsoμO 1.959(4)	O 88.71(16)	103.88(7,3.63)	

					2.901(4)		177.88(7) Cl,O 72.22(9,5.95) 88.56(13,5.50) 94.06(13) 114.24(9) 164.50(14,1.26)	
Cu($C_2H_6O_2$)(μ-Cl)$_2$ (light green)	m P2$_1$/c 4	7.424(1) 10.939(5) 7.518(1)	95.666(9)	$CuCl_4O_2$	μCl 2.234(1,2) 3.020(1,44) O 1.977(4,19)	3.704(1) 4.704(1)	Cl,Cl 95.97(5) 170.03(3) Cl,O 92.6(1,6) 170.8(1,1.4) O,O 79.1(1)^c	152
{Cu(μ-Cl)Cl}$_3$(μ-dio)$_2$ (not given)	m C2/m 2	7.880(6) 12.045(14) 9.208(13)	106.45(2)	$CuCl_4O_2$	μCl 2.296(3) dioμO 2.436(15)	3.120(3) 3.358(3) 89.6(2,4.1)	Cl,Cl 93.7(2) Cl,O 83.7(3)	372
				$CuCl_4O_2$	μCl 2.302(4) Cl 2.302(4) dioμO 2.846(19) μdioO 2.341(17)		Cl,Cl 89.6(2,3.3) Cl,O 95.1(3)	
Cu(μ_3-Cl)Cl(oaoH$_2$) (dark green)	m P2$_1$/m 2	7.804(7) 6.267(3) 8.414(7)	114.14(3)	$CuCl_4N_2$	μ_3Cl 2.253(3) Cl 2.246(4) oaoHN 1.959(12,22)	3.972(2) 93.4(1) 86.6(1)	Cl,Cl 97.2(1) Cl,N 92.6(4,1.7) 170.3(4,1.7) N,N 77.7(4)^c	373
Cu(μ_3-Cl)Cl(en) (blue)	m P2$_1$/m 2	8.219(2) 5.747(1) 6.776(1)	93.72(2)	$CuCl_4N_2$	Cl 2.286(2) μ_3Cl 2.301(2) 2.887(2) enN 2.014(5,4)	Not given	Cl,Cl 92.84(6) N,Cl 91.4(1,3.0) 175.8(1,3.0) N,N 84.4(2)^c	374
Cu(py)$_2$(μ-Cl)$_2$ (not given)	m P2$_1$/n 2	16.967(3) 8.5596(4) 3.8479(7)	91.98(2)	$CuCl_4N_2$	μCl 2.299(2) 3.026(2) pyN 2.004(5)	Not given	Cl,Cl 91.52(5) Cl,N 90.4(1,0)	375
Cu(4-Mepy)$_2$(μ-Cl)$_2$ (greenish blue)	m P2$_1$/c 2	9.745(7) 3.392(4) 19.035(9)	111.8(2)	$CuCl_4N_2$	μCl 2.35(1) 3.19(1) MepyN 2.07(3)	3.932(4) 89.0(4)	Cl,N 90.6(12,4)	376

TABLE III (*Continued*)

Compound *(color)*	*Crystallographic classification space group 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(μ-Cl)$_2$(tz)$_2$ (turquoise blue)	m P2$_1$/c 2	7.332(6) 3.853(4) 17.493(17)	93.70(1)	CuCl$_4$N$_2$	μCl 2.322(1) 2.998(1) tzN 1.990(2)	3.853(4) 91.89(2)	Cl,N 90.18(6,28)	377
Cu(2,2′-bpy)(μ-Cl)$_2$ (not given)	tr P-1 2	7.288(2) 9.640(2) 9.771(2)	55.36(3) 69.29(2) 70.48(3)	CuCl$_4$N$_2$	μCl 2.267(1,0) 3.071(1,36) bpyN 2.053(3,26)	3.839(1,37)	Cl,Cl 94.24(3,6.0) 166.63(3) N,Cl 87.87(8,5.95) 172.09(8,5.2) N,N 80.0(1)^c	378
Cu(μ-Cl)$_2$(dpg) (green)	or Pbcn 4	13.382(2) 19.925(4) 6.901(1)		CuCl$_4$N$_2$	μCl 2.247(2) 2.904(2) dpgN 1.997(7,0)	3.649(—)	Cl,Cl 99.2(1) N,Cl 91.8(2) N,N 77.2(4)^c	379
Cu(μ-Cl)$_2$(μ-pzn) (green)	m C2/m 2	11.971(3) 6.849(3) 3.701(3)	95.96(5)	CuCl$_4$N$_2$	Not given	Not given	Not given	380
Cu(pyz)(μ-Cl)$_2$ (green)	m C2/c 4	9.383(3) 12.429(3) 6.754(4)	128.48(5)	CuCl$_4$N$_2$	μCl 2.300(1) 2.796(1) μpyzN 2.045(3)	3.3785	Cl,Cl 94.9(1) N,Cl 90.0(1)	381
Cu(μ-Cl)$_2$(μ-1,2,4-trz) (pale green)	m I2/c 4	6.81 11.39 7.13	96.58	CuCl$_4$N$_2$	μCl 2.337(—) 2.769(—) μtrzN 1.981(—)	Not given 83.2(—)	N,Cl 86.0(—,3.6)	382
Cu(μ-Cl)$_2$- (μ-am-1,2,4-trz) (not given)	m P2$_1$/c 4	8.700(1) 11.962(1) 7.034(1)	98.35(1)	CuCl$_4$N$_2$	Not given	Not given	Not given	383
Cu$_2$(μ-Cl)$_4$(μ-bpm) (green)	m C2/m 2	6.835(1) 13.321(2) 6.806(1)	90.54(2)	CuCl$_4$N$_2$	μCl 2.252(1) 2.869(1) μbpmN 2.061(2)	3.600(1) 5.528(2) Cl 88.5(1)	Cl,Cl 95.0(1,4.4) 164.3(1) N,Cl 86.9(1,5.8) 172.1(1) N,N 80.1(1)^c	384

Cu(μ_3-Cl)Cl(hist) (dark green)	tr P-1 2	8.592(3) 9.045(3) 5.893(2)	91.2(1) 98.7(1) 79.9(1)	$CuCl_4N_2$	Cl 2.281(3) μ_3Cl 2.337(3) 2.960(3,11) *hist*N 1.998(9,17)	Not given	Cl,Cl 92.8(1,3.7) 169.4(1) Cl,N 87.3(3,6.6) 174.8(4,1.2) N,N 92.5(3)[e]	385
Cu(μ-Cl)$_2$(sc) (green blue)	m P2$_1$/c 4	6.91(1) 8.30(1) 11.32(1)	 117.1(2)	CuCl$_4$ON	μCl 2.900(5) 3.037(6) scO 1.97(1) scN 1.99(1)	Not given	Not given	386
Cu(μ-Cl)$_2$(sc) (blue)	or Pna2$_1$ 4	6.91(1) 8.30(1) 10.24(1)		CuCl$_4$ON	μCl 2.972(6) 3.144(6) scO 1.97(1) scN 1.99(1)	Not given	Not given	386
Cu(μ-Cl)$_2$(amp) (not given)	m P2$_1$/c 4	8.050(5) 10.930(6) 8.120(6)	 92.20(6)	CuCl$_4$ON	μCl 2.260(1,13) 3.087(1,94) ampO 2.02(2,1) ampN 1.96(2,6)	Not given	Cl,Cl 93.8(1,4.2) 170.46(4) Cl,N 77.0(3,4.2) 90.0(3,5.0) 100.8(3) 167.9(1,7.3) Cl,O 76.4(1,6.0) 92.4(1,1.4) 166.1(1,5.6) N,O 82.5(1,6)[c]	387
Cu(μ-Cl)$_2$(L-his) (not given)	or P2$_1$2$_1$2$_1$ 4	10.01(5) 5.944(6) 17.5469(7)		CuCl$_4$ON	μCl 2.274(4,20) hisO 1.98(1) hisN 1.98(1)	Not given	Cl,Cl 92.8(1) Cl,O 94.4(3) Cl,N 88.1(3) N,O 84.6(4)[c]	388
Cu(μ-Cl)$_2$(μ-Me$_2$NNO) (brown red)	or Pnam 4	6.376(3) 14.685(8) 7.265(6)		CuCl$_4$ON	μCl 2.289(4,0) μMe$_2$NNO 2.09(1) μMe$_2$NON 3.02(2)	3.206(3) 88.74(1)	Cl,Cl 89.60(1,3.54) 171.30(1) Cl,O 93.91(1,0) Cl,N 78.34(3,0) N,O 171.58(6)	389

TABLE III (*Continued*)

Compound *(color)*	*Crystallographic classification space group 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(μ-Cl)$_2$(μ-amtzt)] · H_2O (not given)	m P2$_1$/c 4	10.205(1) 13.277(1) 7.206(1)	101.87(1)	$CuCl_4NS$	Not given	Not given	Not given	383
Cu(μ-ttcd)$_2$Cl$_2$ (red brown)	m C2/c 4	20.213(5) 8.521(5) 16.214(4)	116.29(3)	CuS_4Cl_2	μttcdS 2.4474(9) 3.050(6) Cl 2.2054(8)	Not given	S,S 92.33(3) S,Cl 93.55(3,3.94)	390
Cu(py)$_2$(μ-Br)$_2$ (brown)	m P2$_1$/n 2	8.424(2) 17.599(9) 4.0504(8)	97.12(2)	$CuBr_4N_2$	μBr 2.451(1) 3.240(1) pyN 2.013(5)	Not given	Br,Br 90.36(2) Br,N 90.1(1,1)	375
Cu(2,2′-bpy)(μ-Br)$_2$ (not given)	m C2/c —	16.966(4) 9.287(2) 7.490(2)	111.60(2)	$CuBr_4N_2$	μBr 2.410(1) 3.175(1) bpyN 2.030(6)	3.974(1)	Br,Br 93.23(6,5.09) Br,N 88.33(18,6.12) 173.87(18) N,N 80.22(36)^{c}	378
Cu(μ-Br)$_2$(μ-pz) (brown)	m C2/m 2	12.392(3) 6.859(2) 3.907(3)	96.23(5)	$CuBr_4N_2$	μBr 2.427(2) 3.034(2) μpzN 2.030(15)	3.907(3)	Br,Br 89.4(3) N,Br 90.0	380
Cu$_2$(μ-Br)$_4$(μ-bpm) (brown)	m C2/m 2	7.100(1) 13.504(2) 7.063(1)	90.69(4)	$CuBr_4N_2$	μBr 2.394(1) 3.018(1) μbpmN 2.067(3)	3.749(1) 5.545(2) 86.9(1)	Br,Br 94.9(1,3.4) 163.4(1) Br,N 86.9(1,6.5) 172.9(1) N,N 80.1(1)^{c}	384
Cu(amp)(μ_3-Br)Br (green)	m P2$_1$/m 2	8.222(15) 6.372(13) 9.883(18)	116.3(1)	$CuBr_4N_2$	Br 2.385(5) μ_3Br 2.422(5) 3.260(6) ampN 2.007(9,4)	3.737(6) 80.77(4)	Br,Br 96.02(4,4.6) 155.5(1) Br,N 79.6(1) 89.3(5,8.7) 174.9(8,4.5) N,N 82.8(3)^{c}	391

Cu(mdap)(μ_3-Br)Br (green)	or Pnma 4	20.276(28) 6.208(3) 7.058(3)		$CuBr_4N_2$	Br 2.426(4) μ_3Br 2.435(2) 3.109(2) mdapN 2.017(9,1)	3.866(2) 87.56(3)	Br,Br 92.4(1,8) 173.6(1) Br,N 89.0(4,7.1) 175.1(2,4.4) N,N 83.4(4)^c	391
Cu(μ-Br)$_2$(aep) (blue)	or Pbca 8	8.861(7) 19.896(16) 11.269(9)		$CuBr_4N_2$	μBr 2.400(2,13) 3.637(3,68) aepN 2.005(6,16)	4.006(3)	Br,Br 82.46(3) 94.70(5,6.63) 122.29(5) 152.47(4) Br,N 72.7(2,1.6) 89.9(2,8.6) 161.9(2,1.6) N,N 93.0(2)^e	392
[Cu(μ-dmhx)(glygly)]· $4H_2O$ (dark blue)	or $P2_12_12_1$ 4	14.314(6) 7.741(2) 16.032(6)		CuO_3N_3	glyO 1.992(2) glyN 1.957(3,57) μdmhxN 1.977(3) dmhxμO 2.769(2) 2.970(2)	Not given	O,O 80.9(1,4.1) 133.0(1) O,N 50.9(1)^d 82.9(1)^c 95.2(1,5.7) 116.8(1,9.7) 165.3(1) N,N 83.5(1)^c 96.3(1) 177.3(1)	393
Cu(μ-cyt)(glygly) (purple)	m $P2_1/n$ 4	10.695(4) 8.077(1) 14.756(7)	92.38(3)	CuO_3N_3	glyO 1.983(3) glyN 1.952(3,60) μcytO 2.713(3) 2.819(3) μcytN 1.979(3)	Not given	O,N 83.8(2)^c 97.3(2) 167.6(2) N,N 83.9(2)^c 95.1(2) 171.3(2)	394
[Cu(μ-HCOO)(dien)]- (HCOO) (dark blue)	or Pnam 4	8.954 11.640 9.676		CuO_3N_3	μHCOO 2.030(7) HCOμO 2.614(7) 2.165(7) dienN 2.023(7,5)	Not given	O,O 55.1^d 95.7 O,N 103.0(—,8.6) 152.8 N,N 85.6^c 169.2	395

TABLE III (*Continued*)

Compound (*color*)	*Crystallographic classification space group 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(μ-oro)(NH$_3$)$_2$	m	7.217(5)		CuO$_3$N$_3$	μoroO 1.962(3)	Not given	O,O 96.7(1)	396
(dark purple)	P2$_1$/n	7.617(5)	100.73(6)		2.930(4)		N,O 82.5(1,1)^c	
	4	15.148(11)			μoroN 2.005(3)		92.4(1,4.4)	
					H$_3$N 1.978(3,18)		N,N 90.4(1,1)	
[Cu$_2$(μ$_4$-C$_5$O$_5$)(bpca)$_2$]·	m	19.535(2)		CuO$_3$N$_3$	μ$_4$C$_5$O$_5$O 1.961(2)	5.935(1)	O,O 79.0(1,3.1)^c	397
3H$_2$O	P2$_1$/c	20.189(2)	97.485(8)		2.541(3,45)	7.346(1)	157.93(8)	
(blue)	4	7.5167(6)			bpcaN 1.976(3,49)		N,O 85.7(1,3)	
							97.0(1,2.6)	
							107.6(1)	
							176.2(1)	
							N,N 82.2(1,2)^c	
							164.2(1)	
				CuO$_3$N$_3$	μ$_4$C$_5$O$_5$O 1.973(2)		O,O 77.9(9,5)^c	
					2.474(3)		155.70(8)	
					μO 2.932(3)		N,O 86.1(1,1.0)	
					bpcaN 1.969(3,35)		95.3(1,6.1)	
							117.3(1)	
							165.4(1)	
							N,N 82.2(1,1)	
							164.3(1)	
[Cu(μ-gh)(H$_2$O)]·	tg	11.24(2)		CuO$_3$N$_3$	O 2.007(6)	Not given	O,O 49.4(2)^d	398
0.5H$_2$O	P4$_3$2$_1$2				2.943(8)		87.7(3)	
(blue)	8	17.84(4)			N 2.004(8,39)		129.9(3)	
					H$_2$O 2.458(9)		O,N 73.9(3)	
							91.8(4,5.9)	
							119.1(3,7.9)	
							175.7(3)	
							N,N 83.3(3)^c	
							92.8(3)^e	
							162.7(4)	

$Cu_2(\mu\text{-ghg})_2(H_2O)$ (blue)	m C2 4	19.040(6) 6.943(4) 12.201(4)	103.89(2)	CuO_3N_3	O 1.996(3) 2.817(4) N 1.968(3,29) H_2O 2.784(4)	Not given	O,O 51.1(1)^d 88.2(1) 137.0(2) O,N 77.2(2) 93.0(2,8.8) 134.9(2) 171.3(2) N,N 82.9(1)^c 93.5(1)^e 168.2(2)	399
$[Cu(\mu\text{-L-ala})(\text{L-his})(H_2O)]\cdot$ $3H_2O$ (blue)	m $P2_1$ 2	10.980(4) 7.362(3) 9.700(2)	101.45(3)	CuO_3N_3	hisN 1.986(10,20) μalaN 1.981(10,20) μalaO 2.512(9) H_2O 2.864(9)	Not given	O,O 93.2(3,2.4) 173.4(3) O,N 82.6(4)^c 89.4(4,6.2) 175.2(4) N,N 92.8(4,1)^e 169.6(4)	400
$Cu(\mu\text{-L-ser})(\text{L-his})(H_2O)$ (blue)	m $P2_1$ 2	11.046(2) 7.315(1) 9.737(1)	101.34(2)	CuO_3N_3	hisN 1.991(5,38) μserN 1.972(5,5) μserO 2.895(5) H_2O 2.447(6)	Not given	O,O 91.6(2,4.3) 176.5(2) O,N 83.5(2)^c 89.5(2,6.6) 173.8(2) N,N 92.9(2)^e 168.7(2)	401
$[Cu(\mu\text{-ac})(\text{dpt})]ClO_4$ (blue)	or $Pna2_1$ 4	8.53(1) 18.50(2) 8.74(1)		CuO_3N_3	μacO 2.02(2) μO 2.29(1) μO 2.74(1) dptN 2.00(2,8)	Not given 129.8(8)	O,O 52.5(5)^d 91.0(5) 142.1(5) O,N 93.6(10,2.6) 84.1(7,4.2) 122.9(11) 170.8(8) N,N 91.4(9,7.5)^e 173.0(7)	402

TABLE III (*Continued*)

Compound (*color*)	*Crystallographic classification space group 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(μ-ac)(dien)ClO$_4$ (blue)	m P2$_1$/n 4	10.138(5) 8.063(4) 15.536(10)	99.00(4)	CuO$_3$N$_3$	μacO 1.972(4) μO 2.403(4) 2.646(4) dienN 1.976(5,7)	4.210(4)	O,O 54.7(2)^d 95.5(2) 150.2(1) O,N 93.7(2,7.9) 110.1(2) 164.8(2) N,N 85.1(2,1)^c 166.3(2)	403
[Cu$_2$(μ_3-ter)(dien)$_2$]- (ClO$_4$)$_2$ (dark blue)	m P2$_1$/c 2	8.911(6) 8.022(5) 19.61(2)	90.2(1)	CuO$_3$N$_3$	$\mu_3$terO 1.982(5) 2.485(5) 2.760(5) dienN 2.012(7,32)	4.179(3) 11.006(5) 105.5(2)	O,O 53.0(2)^d 98.8(2) O,N 91.0(3,8.1) 108.9(3,5.1) 166.7(3) N,N 85.1(3,1.5)^c 166.6(3)	404
Cu$_2$(μ-famp)(μ-1,1-N$_3$)· (μ-ClO$_4$)$_2$ (dark green)	m P2$_1$ 2	8.973(3) 14.785(3) 9.650(1)	90.63(2)	CuO$_3$N$_3$	fampμO 1.946(9,13) N 1.95(1,6) μN$_3$N 1.95(1,2) μClO$_4$O 2.60(1,9) 2.76(1,6)	2.993(2) O 100.5(3) N 99.7(3)	O,O 92.6(4,11.1) O,N 87.8(4,7.6) N,N 84.0(5,1)^c 105.4(5,7)	281
Cu(μ-SO$_4$)(H$_2$O)(im)$_3$ (blue)	m P2$_1$/n 4	14.239(1) 8.707(1) 11.717(1)	90.244(5)	CuO$_3$N$_3$	H$_2$O 2.478(3) μSO$_4$O 2.015(2) 2.578(2) imN 1.999(3,4)	Not given	O,O 90.6(1,1.5) 177.6(1) O,N 89.7(1,3.0) 176.7(1) N,N 90.7(1,8) 178.1(1)	405
[Cu(μ-NCS)(bheg)]· H$_2$O (blue)	m Cc 4	14.567(2) 6.970(1) 11.051(2)	93.67(1)	CuO$_3$N$_2$S	bhegO 1.98(1,0) 2.37(1) N 2.01(1)	Not given	O,O 93.6(4,5.8) 164.0(4) O,N 82.7(4,2.5)^c	406

					μSCN 1.93(1) μNCS 3.11(1)		96.6(5,2.1) O,S 85.7(3,1.6) 172.4(4) N,S 91.5(4,1.7) N,N 175.3(5)	
Cu(gly)(μ-Cl)(μ-MeOH) (blue)	m $P2_1/c$ 4	5.192(3) 7.945(5) 16.51(1)	100.24(5)	CuO$_3$Cl$_2$N	glyO 1.964(4) 2.540(5) μMeHO 1.958(4) glyN 1.951(5) μCl 2.249(2) 3.218(2)	Not given Cl 93.6(1)	O,O 91.5(2,4.0) O,Cl 91.7(1,8.7) 104.4(1) 164.9(1,4.5) O,N 84.0(2,8)^c 171.8(2) Cl,N 77.5(2) 93.9(1) Cl,Cl 86.5(1)	174
{[Cu(μ-tampz)$_2$Cl](μ-Cl)}- Cl$_2$ · 2.25H$_2$O (green blue)	or Immm 2	5.76(1) 8.415(1) 17.483(1)		CuN$_3$Cl$_3$	μtampzN 1.991(4,46) Cl 2.243(1) μCl 2.871(1,0)	5.563(1) 6.557(1) Cl 169.2(1)	N,N 81.6(1)^c 163.2(1) Cl,N 90.7(1,7.7) 180.0(0) Cl,Cl 95.4(1) 169.2(1)	407
Cu(μ-I)(dien)I (dark blue)	or $Pnm2_1$ 2	8.837(2) 8.890(3) 6.658(1)		CuN$_3$I$_3$	die N 2.014(7,16) I 2.585(1) μI 3.348(1,23)	6.658(1) I 167.7(1)	N,N 83.9(2)^c 167.8(5) I,N 78.2(6) 91.1(13,5.0) 177.0(7) I,I 96.2(3,3) 167.7(1)	408
[Cu(mcim)(μ-ClO$_4$)]ClO$_4$ (blue)	m $P2_1/c$ 4	11.698(3) 7.387(2) 23.670(4)	94.53(2)	CuN$_3$O$_2$S	mcimN 1.953(6,9) mcimS 2.353(2) μClO$_4$O 2.505(6) 2.805(7)	Not given	O,O 174.1(2) S,N 176.7(2) N,N 163.2(2)	358

TABLE III (*Continued*)

Compound (*color*)	*Crystallographic classification space group 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{μ-gaba(mpy)$_2$}Br] · MeOH (blue)	pr P2$_1$2$_1$2$_1$ 4	10.542(4) 12.197(7) 14.984(6)		CuN$_3$O$_2$Br	N 2.014(8,11) O 1.933(6) 2.770(7) Br 2.741(2)	Not given	O,O 52.33(22)^d O,N 93.8(3,4.3) 117.72(26) 170.04(28) N,N 81.3(3,2)^c O,Br 93.15(18) 145.45(14) N,Br 96.0(2,1.0)	409
Cu(μ-Et$_2$nia)$_2$Cl$_2$ (not given)	tr P-1 —	10.453(5) 12.242(6) 15.476(7)	122.9(1) 116.9(1) 75.8(1)	CuO$_2$N$_2$Cl$_2$	O 2.764(7,4) N 2.025(9,15) Cl 2.270(6,7)	Not given	Cl,O 88.4(6,6) N,O 91.6(6,0) 123(1) Cl,N 91.0(6,7)	410
[Cu(μ-bpydc)(μ-Cl)$_2$] · H$_2$O (green)	or Pbca 8	9.932(1) 17.560(2) 17.065(2)		CuO$_2$N$_2$Cl$_2$	μbpydcN 2.020(2,13) μbpydcO 2.678(2) μCl 2.244(1) 3.117(1)	Not given	N,N 80.5(1)^c Cl,N 95.1(1,1.5) 163.5(1,5) Cl,Cl 93.2(1)	411
Cu(μ-oth)$_2$Cl$_2$ (green)	or Abma 4	10.86(1) 12.63(1) 9.64(1)		CuO$_2$Cl$_2$S$_2$	Cl 2.254(3) μothS 2.372(2) μothO 2.618(6)	Not given	Cl,Cl 180.0 Cl,S 90.0 S,O 90.1(4) Cl,O 90.0	95

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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 a maximum deviation from the mean value. [b] The chemical identity of coordinated atom/ligand is specified in these columns. [c] Five-membered metallocyclic ring. [d] Four-membered metallocyclic ring. [e] Six-membered metallocyclic ring.

two coppers are surrounded by two molecules of water, which form a square-planar coordination. This coordination is completed to the elongated octahedral coordination most typical for Cu(II) atoms by two oxygen atoms from two different formate groups.

X-ray[185] and neutron diffraction[186] analysis of light blue $[Cu(\mu\text{-}HCOO)_2(H_2O)_2]\cdot 2H_2O$ show, that each Cu(II) atom is surrounded by four oxygen atoms of four different formate ions in an approximately square configuration and by two water molecules at a greater distance (Table III); green $[Cu(\mu\text{-}HCOO)_2(H_2O)_2\cdot 2urea$[187] is isostructural. The Cu(II) atom in a light blue complex[188] lies on a center of symmetry and is coordinated to six oxygen atoms in an octahedral-type configuration by pairs of water molecules, monodentate carboxylic groups and two carbonyl-O-of-peptide atoms. Diacetoamidopropionate anions bridge Cu(II) atoms, such that the structure consists of a two-dimensional (sheet-type) polymer. A blue complex[189] has a similar structure.[188]

The structure of pale blue $[Cu_2(\mu\text{-}alaH)(\mu\text{-}H_2O)_2](SO_4)_2$,[190] Figure 8, shows a polymeric chain of Cu(II) atoms bridged by water molecules and by the carboxylate functions (syn–syn) of the alanine molecules, in its zwitterionic form.

There are four derivatives of general formula $Cu(\mu\text{-}L)_2(H_2O)_2$; L = 2,6-dihydrobenzoate,[191] ethylene glycol,[192] 9,10-dihydro-9-oxo-10-acridineacetate,[193] or nicotinate-N-oxide[194] in which two L ligands serve as a bridge between *pseudo*-octahedral (CuO_6) units (Table III).

In another four derivatives of composition $Cu(\mu\text{-}L)(H_2O)_2$, L = 3,6-dichloro-2,5-dihydroxo-1,4-benzoquinonate,[195] squarate,[196] *d*-tartrate[197] or *o*-phthalate[198] one four-oxygen donor ligand serves as a bridge and two

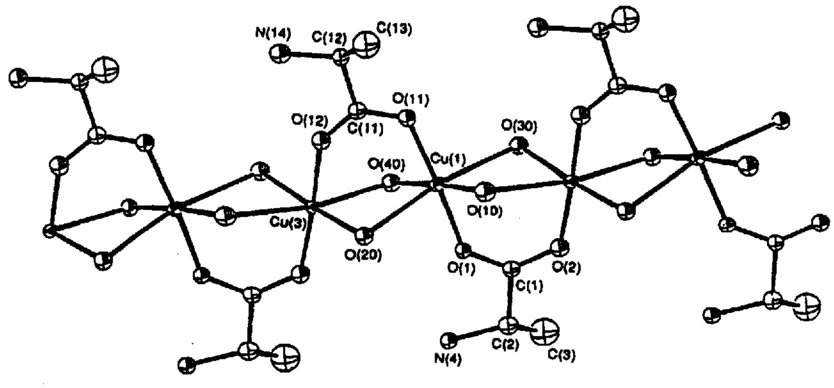

FIGURE 8 Structure of $[Cu_2(\mu - alaH)(\mu - H_2O)_2]_n^{4+}$.[190]

water molecules complete a *pseudo*-octahedral environment about each Cu(II) atom.

A green derivative[199] contains square-planar $[Cu(\mu\text{-nac})_2]^{2-}$ units in which the nitro and carboxyl groups of the two chelate ligands are in *cis* positions. Two of the units form a centrosymmetric dimer with a four-membered CuOCu"O"-ring, the dimers being connected by exo-oxygens of the ligands into two-dimensional layers.

Another green derivative[200] consists of flattened molecules arranged in stacks with a centrosymmetric CuO_6 elongated bipyramid formed around Cu(II) by four oxygen atoms from the carboxylate groups of furosemidate and two from the methanol molecules. The carboxylate groups act as bridges between the Cu(II) atoms with two oxygens in the equatorial plane (Cu–O = 1.924(2) Å) and the other two in apical positions at 2.720(2) Å. The Cu–Cu separation of 4.749 Å excluded a metal–metal bond.

There are two derivatives[201,202] in which *pseudo*-octahedrally-coordinated Cu(II) atoms (CuO_6) are held together by lactate or glycolate anions. A blue derivative[203] contains two types of Cu(II) atoms, one at -1 and the other on the twofold axis, both with distorted octahedral coordination spheres. Each Cu(II) atom is bound to two bridged water molecules and four phthalate groups, and each phthalate group is bound to four Cu(II) atoms through three of its oxygen atoms. The result is a complex sheet polymer extending through the *b–c* plane.

Copper(II) atoms in a royal blue derivative[204] are coordinated by four carboxy-oxygen atoms, two from the two ends of a chelating oxydiacetate ligand and one from each of two neighboring $Cu\{O(CH_2CO_2)\}$ groups, with Cu–O = 1.941(9)–1.952(8) Å. Longer contacts to the ether oxygen of the chelating ligand (Cu–O = 2.488(8) Å) and to a statistically disordered water molecule (Cu–O = 2.73(21) Å) complete a (4 + 1 + 1) arrangement.

In another blue derivative[205] the HCOO group in a syn–syn arrangement with the OH group bridge the neighboring Cu(II) atom, and in this way infinite zig-zag chains are formed along the *b*-axis. The chains are connected by the bonds of Cu(II) atoms and hydroxy groups, and the layers parallel to (100) are formed. In a turquoise derivative[206–208] the HCOO groups act as bridges between Cu(II) atoms forming an infinite anti–anti chain through the crystal.

The Cu(II) atoms and the nitronate groups in the crystals of $Cu(\mu\text{-}Me_2CNO_2)_2$[209] are bound to each other in such a way that the structure consists of chains of bis(propane-2-nitronato)copper(II) units. Each Cu(II) atom is coordinated in a distorted octahedral (4 + 1 + 1) manner to six oxygen atoms from four different propane-2-nitronate ions.

One of the most characteristic features of the $Cu(\mu\text{-}C_{32}H_{54}N_2O_8)_2$ structure[210] is the different conformation of the two molecules in the cell. The coordination geometry about both Cu(II) atoms corresponds to a tetragonally-distorted octahedron with a pair of β-diketonate ligands and two monodentate-O-bonded nitrozyl radicals belonging to other molecules. Significant parameters of the coordinated nitroxides include Cu–O 2.583(5) and 3.157(3) Å and Cu–O–N 158.5(4)° and 139.5(4)°.

There are three blue salts[116,212] containing planar $Cu(\mu\text{-ox})_2^{2-}$ ions in which the oxalate ions act as bidentate ligands. In each salt, the Cu(II) atoms complete their coordination sphere by formation of long Cu–O bonds to non-coordinated oxygen atoms of neighboring anions (Table III).

A pale green derivative[214] consists of one-dimensional polymeric chains in which two phosphinate groups form double bridges and a formamide oxygen atom forms a μ-O bridge between Cu(II) atoms. The intrachain Cu–Cu distance is 4.056(1) Å.

In green complexes[215–217] *pseudo*-square-planar CuO_4 moieties, created by a pair of O,O′-chelating acetylacetonato ligands, are held together by bidentate, 1,4-dioxane molecules of 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-N-oxy,[216] or 2,4,4,5,5-pentamethyl-1-oxyimidazoline-3-oxide[217] in a one-dimensional polymeric array.

In the infinite, left-bonded helical structure of $Cu(\mu\text{-acac})(\mu\text{-}Cl_3ac)$,[218] each Cu(II) atom is surrounded by six oxygen atoms, two from a bidentate acetylacetonato ligand, two from separate trichloroacetato ligands which bridge to neighboring Cu(II) atoms in the spiral, and two atoms of ligands of neighboring Cu(II) atoms.

There are 15 derivatives[45,220–233] where *pseudo*-octahedral environments about Cu(II) atoms are created by six nitrogen donor atoms (CuN_6) (Table III). In black brown crystals, $Cu(N_3)_2$,[220] the CuN_6 octahedra are linked together by sharing edges to form double chains, which are then coupled by azide groups to form a three-dimensional network. In blue green $Cu(N_3)_2(NH_3)_2$[221] and green $Cu(N_3)_2(py)_2$[222] the CuN_6 octahedra are linked to form chains by the sharing of corners. The structure of black $Cu(N_3)_2(4\text{-}Mepy)_2$[223] is built up by oligomeric edge-sharing chains of polyhedra. In green $Cu(N_3)_2(bpy)$[224] each azide takes part in asymmetric bridging through a single nitrogen atom (μ(1,1)) (Table III).

Three violet complexes[225–227] which contain $[Cu(en)_2(\mu\text{-NCS})]^+$ cations are isostructural. The isothiocyanate group forms a bridging unit between two $[Cu(en)]^{2+}$ cations, giving infinite chain structures and complete a tetragonal bipyramidal arrangement about each Cu(II) atom (CuN_6). $Cu(trz)_2(NCS)_2$[228] exhibits two-dimensional networks with 2,4-bridging triazole molecules and NCS^- groups, acting as N donors on either side of the planes. The CuN_6 octahedra clearly show Jahn–Teller deformation with Cu–N(NCS) 1.984(3) Å; and Cu–N(trz) 2.002(5) and 2.477(3) Å bond distances.

X-ray analysis of dark green $Cu(tp)(NCS)_2$[229] shows an essentially layered structure with the Cu(II) atom coordinated in a square-planar by two nitrogen atoms (*trans*) from the N_3-coordinating tp ligand and by two NCS groups. The coordination is completed to octahedral by two nitrogen atoms from adjacent tp molecules which N_1-coordinate axially to a Cu(II) atom, so that two-dimensional system parallel to each other is formed.

In black $Cu\{\mu\text{-}C(CN)_3\}_2$[230] Cu(II) is surrounded by a distorted octahedron of six CN groups belonging to six different molecules. The crystal structure is therefore polymeric consisting of planes of $C(CN)_3^-$ ions intersecting at an angle of about 79° with Cu(II) atoms occupying *pseudo*-octahedral holes.

A blue derivative[231] consists of polymeric one-dimensional chains, formed from $[Cu(pzH)_4]^{2+}$ cations linked by one bridging tricyanomethanide anion. The second tricyanomethanide anion is not bonded to this chain. The Cu(II) atom is *pseudo*-octahedrally coordinated by four pyrazole molecules in the equatorial plane (average Cu–N 1.994(6) Å) and axially by two N atoms from two symmetrically equivalent tricyanomethanide anions (Cu–N 2.373(7) and 2.500(7) Å).

There are 10 derivatives[234–240] in which each Cu(II) atom is coordinated by six chlorine atoms ($CuCl_6$) with a different degree of distortion. The crystal structure[234] of $[CuCl_4]^{2-}$ consists of corner-sharing octahedra which form layers in the *a–b* plane. Two of the four Cu–Cl distances (bridging) are relatively short (CuCl 2.283(1) Å) and two are long (Cu–Cl 2.907(1) Å). The two axial bonds are short with a distance of 2.296(1) Å. At 100 K the two long Cu–Cl distances appear slightly shorter, whereas the four short ones appear longer, in accordance with a riding-atom model (Table III). Other derivatives[236–240] also contain $[CuCl_4]^{2-}$ anions, which are isostructural with that described above[234] (Table III).

Six bromine atoms, create a *pseudo*-octahedral arrangement about each Cu(II) in four derivatives.[241–243] Three[241,242] contain $[CuBr_4]^{2-}$ with a structure which consists of layers of square-planar $[CuBr_4]^{2-}$ anion linked together by semi-coordinate Cu–Br bonds with the latter completing the Jahn-Teller distortion. The structure is strictly isomorphous with the corresponding chloride salt.

A brownish violet derivative[243] consists of the 2-amino-4-bromohydroxypyridinium cations, planar dibridged $Cu_2Br_6^{2-}$ dimers, and water molecules.

The dimers aggregate through the formation of semi-coordination Cu–Br bonds to form stacks parallel to the *a*-axis.

There are 11 blue[244,245,247–255] and one green[246] derivative in which a *pseudo*-octahedral arrangement around each Cu(II) atom is created by five oxygen donor atoms and one nitrogen donor atom (CuO_5N) (Table III). In $Cu(pyvgly)(H_2O)_3$[244] the octahedral coordination is composed of the long bonds ($Cu-OH_2$ 2.451(10) and 2.616(10) Å), and of four short square bonds. The octahedrons in the unit cell are associated with each other by hydrogen bonds (average 2.73 Å).

The structure of $[Cu(\mu\text{-}Me_2cys)(H_2O)_3]2H_2O$[245] contains Cu(II) atoms linked by syn–anti carboxylate bridges to form zig-zag Cu–O–C–O chains parallel to *c*-axis. Each Cu(II) atom is tetragonally coordinated. Equatorial O_3N ligation is provided by the two carboxylate O atoms (1.949(3) and 1.957(3) Å) and the amino N atom (1.986(3) Å) of the tridentate β,β-dimethylcysteate ligand; and one water molecule (1.983(3) Å). Two additional water molecules form axial bonds with copper (2.471(3) and 2.572(5) Å) and complete the O_5N coordination.

There are three derivatives of composition $Cu(\mu\text{-}L)(H_2O)_2$, L = N-oxyphenyliminodiacetate,[246] iminodiaceate,[247] or pyridine-2,6-dicarboxylate.[248] The organic molecule acts as a tridentate O_2N ligand, with one of its O atoms in a bridging position so that the coordination polyhedra are joined in chains running parallel to the *a*-axis.

Five derivatives of general formula $Cu(\mu\text{-}L)(H_2O)$, L = β-oxyethylimino diacetate,[249] N-(*o*-carboxyphenyl)iminodiacetate,[250] N-(*o*-carboxyethyl)-iminodiacetate,[251] N-benzenesulfonyl-DL-alaninate,[252] or glutamate[253] contain tetragonal-elongated octahedral coordination of each Cu(II) atom (CuO_5N). Each ligand molecule links two Cu(II) atoms and each Cu(II) is bonded to two ligands. The related copper complexes share one oxygen atom, thus forming infinite polymeric zig-zag chains.

In the polymeric structure of $Cu(\mu\text{-}ox)(NH_3)$,[254] one oxygen of an oxalate group functions as a bridge between two Cu(II) atoms. Each Cu(II) atom has a tetragonal-bipyramidal arrangement, CuO_5N. The blue crystals of Cu(ap)(HCOO)[255] are centrosymmetric dialkoxy, bridged dimers (Cu–Cu = 2.964(1) Å). The dimers are polymerized along the *c*-axis into chains *via* two NH–O hydrogen bonds (Cu ··· Cu = 5.479(1) Å). These chains are joined along the *b*-axis by CuOCOCu bridges and NH ··· O hydrogen bonds (Cu ··· Cu = 4.622(1) Å) forming layers, which are held together by van der Waals forces.

The structure of blue $Cu_2(bpm)(NCO)_4$[256] consists of a two-dimensional array of Cu(II) atoms bridged by bis-bidentate bpm ligands and end-to-end cyanato groups. The Cu(II) atoms are in a distorted octahedral arrangement with a CuN_5O chromophore. Four nitrogen atoms, two from the bpm ligand and two from the cyanate groups, occupy the equatorial positions, whereas the axial positions have an oxygen and a nitrogen atom of other cyanate groups (Table III).

The structure of $Cu(\mu_3\text{-}Br)_2(\mu\text{-}Br)_2(py)_2$[257] consists of well-defined centrosymmetric dimers which stack on top of one another to form linear chains. Within each dimer, Cu–Br distances range from 2.412(4) to 2.464(6) Å while interdimer distances are 2.928(4) and 3.331(4) Å. The pyridine ring is not coplanar with the Cu_2Br_2 plane but is twisted at an angle of 54° from the dimer plane allowing efficient packing of the pyridine rings.

The structure of pale green $Cu(\mu\text{-}F)_2(meppz)_2$[258] is shown in Figure 9. The structure consists of Cu(II) atoms coordinated by two pyrazole nitrogen atoms and two fluoride ions in a distorted square-planar arrangement. The axial bonds, two fluoride ions of nearby Cu(II) atoms (related to the central

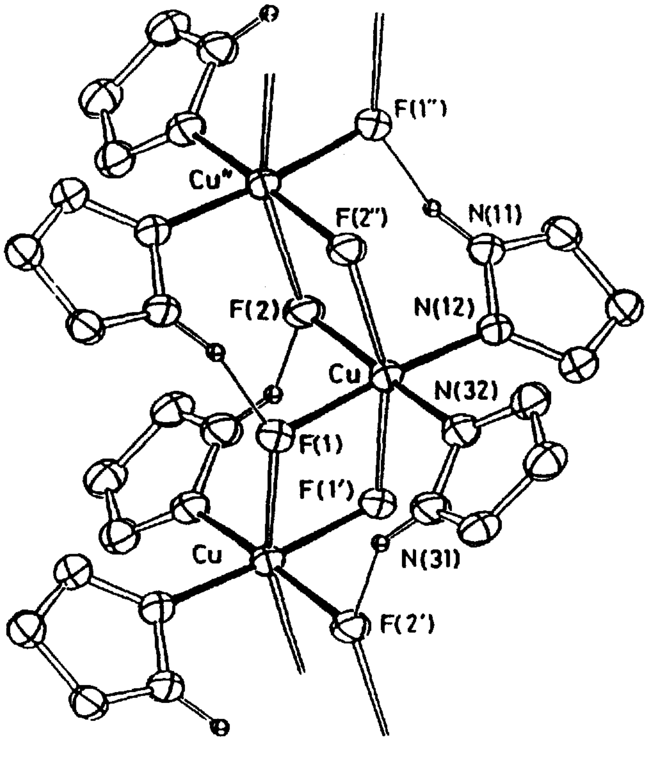

FIGURE 9 Structure of $Cu(\mu\text{-}F)_2(meppz)_2$.[258]

copper by an inversion center), have significantly longer Cu–F bond lengths. The zig-zag chains, consisting of two different CuF_2Cu units, are positioned along the *b*-axis, Cu–Cu distances are 3.330(2) and 3.294(2) Å. The polymeric structure is stabilized further by hydrogen bonding of the pyrazole N–H to fluoride ions of nearby Cu(II) atoms.

There are 70 derivatives[169,259–324] (Table III) in which a distorted octahedral environment (mostly a tetragonal-bipyramid) is created by four oxygen and two nitrogen donor atoms, usually two O donor atoms occupying axial positions. The compounds are mostly blue or green, with some violet. Their polymeric structures are complex. For example, in two derivatives 9-methylpurine[259] or, purine[260] bind equatorially to Cu(II) through two atoms in two symmetry-related purine rings, thus producing polymeric chains. The other positions are occupied by water molecules.

In green $[Cu(\mu\text{-}H_2O)(H_2O)_3(mgu)_2]SO_4 \cdot 2H_2O$[261] the six-coordinate Cu(II) atoms (CuO_4N_2) are linked in an infinite chain by one of the coordinated water molecules. Two 9-methylquanine molecules, binding copper through N(7), are arranged in a syn configuration with a water molecule in the coordination sphere bridging to two carbonyl groups *via* hydrogen bonds.

A green derivative[262] consists of structural units of the type $Cu(\mu\text{-}gmp)_2(H_2O)_3$, which are linked into a polymeric chain by Cu–O bonds involving the ribose O of one of the two gmp group molecules.

There are three monoclinic derivatives of general formula $Cu(\mu\text{-}SO_4)(H_2O)(L)$, L = bpy,[268] phen[269] or en[270] which are isostructural. The *pseudo*-planar CuO_2N_2 units are bridged through the two axial coordination positions by sulfate groups: $O \cdot SO_2 \cdot O[Cu(OH_2)_2L]O \cdot SO_2 \cdot O$, *etc.* to give a linear polymeric array. The five-membered metallocyclic ring, opens in the order of L: 80.9(5)° (L = bpy) < 82.0(1)° (L = phen) < 86.43(2)° (L = en).

The structure of deep green $Cu_2(\mu\text{-}NO_3)_2(\mu\text{-}Me_3NCH_2COO)_2(\mu\text{-}1,1\text{-}N_3)_2$[288] is shown in Figure 10. The structure contains Cu(II) atoms in two crystallographically and chemically different environments, as illustrated in Figure 10. Cu1, located at an inversion center in Wyckoff position 4(a), is *trans*-coordinated by two carboxy oxygens from different betaines, two azido nitrogens, and two nitrato oxygens in a distorted octahedral environment. The other Cu(2), lying on twofold axis in Wyckoff position 4(e), is also *trans*-coordinated. Every pair of adjacent copper atoms, separated by a non-bonded distance of 3.436(1) Å, are simultaneously bridged by an azido group, a nitrato group, and the carboxy group of a betaine ligand to build up a linear zig-zag polymeric chain running parallel to the *c*-axis.

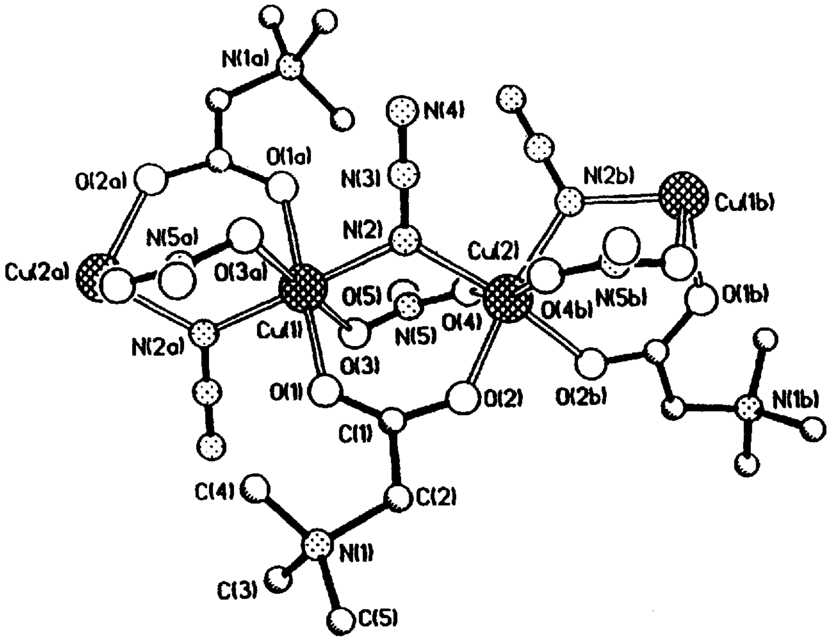

FIGURE 10 Structure of $Cu_2(NO_3)_2(Me_3NCH_2COO)_2(N_3)_2$.[288]

There are several derivatives[295–314,318] in which crystals are built up from *trans*-CuL_2 (L = tridentate O_2N) chelates associated in infinite layers (Table III).

In another three derivatives of composition Cu(μ-L′)(L); μ-L′ = succinate,[316] glutarate[317] or 3,3′-dithiopropionate;[169] and L = en, Me_4en or bpy, the μ-L′ ions join the CuL^{2+} units in chains. Each Cu(II) atom is coordinated with four short bonds (O_2N_2) in nearly square-planar arrangements and two longer bonds (O_2) to complete a tetragonal bipyramidal arrangement (Table III).

A 12-membered heptadentate macrocycle[319] with two pendent acetato groups created a distorted octahedral environment about Cu(II) (CuO_4N_2). One of the features of the structure is that one of the acetato groups is coordinated to two Cu(II) atoms forming a one-dimensional –Cu–O–C–O–Cu– chain.

There are two green derivatives[320,321] in which the Cu(II) and two β-diketonates lie in a plane of symmetry, giving square-planar coordination about the Cu(II) atom (CuO_4). The fifth and sixth positions are occupied by nitrogen atoms of 1,4-diazabicyclo[2,2,2]-octane(ted)[320] or pyrazine (pz)[321] ligands. The ted[320] or pz[321] molecule bridges two copper atoms.

A black derivative[324] contains two non-equivalent Cu(II) atoms, one being coordinated symmetrically to pairs of N, the other O and carbonyl O atoms (CuO_4N_2) and the other to two Cl and four carbonyl atoms of neighboring ligands (CuO_4Cl_2), thus joining the molecules into chains parallel to (101).

In a pale blue derivative,[133] distorted octahedrally coordinated Cu(II) atoms (CuO_4NCl) are linked by bridged prolinate groups.

In another two blue derivatives[325,326] a *pseudo*-octahedral environment about each Cu(II) atom is built up by four oxygen, one nitrogen and one sulfur donor atoms (CuO_4NS). The structure of $[Cu_2(\mu\text{-tedta})(H_2O)_2]\cdot 3H_2O$[325] consists of dimeric units containing two independent Cu(II) atoms. The thioether S atom bridges the copper atoms. The crystal structure is held together by a combination of bridging carboxylate groups and an extended hydrogen-bond network. The Cu–Cu distances across these bridges are 5.387(1) and 5.629(1) Å compared to 5.189(1) Å across the thioether bridge.

In $[Cu_2(\mu\text{-tbcmc})(H_2O)_2]\cdot 4H_2O$[326] one N and two O atoms (from the same bis(carboxymethyl)amino moiety) and one O atom (from one water molecule) approximately define the square base of a distorted octahedral environment for each Cu(II). The octahedron is achieved by longer *trans* axial bonds to one S atom (from a disulfide group) and to one O atom (from the adjacent ligand). Each ligand molecule chelates two Cu(II) atoms and is also bonded *via* a bidentate carboxylate group to two others, thus forming layers linked to each other by water in a hydrogen bonded network.

In a black violet derivative[327] the (isopropylthio)acetato acts as a terdentate ligand, coordinating *via* one S, and one carboxylate O to a copper atom, and *via* the other O to another copper atom. The Cu(II) atom has a deformed octahedral coordination (CuO_4S_2), and the complexes are aligned to form a polymer chain parallel to the *c*-axis.

A red derivative[328] consists of alternating chains of dimeric dibridged $Cu_2Cl_6^{2-}$ anions ($CuCl_4$) and monomeric $Cu(tmso)_4^{2+}$ cations (CuO_4Cl_2) extended along the *c*-axis.

In $Cu(daca)_2(\mu\text{-Cl})Cl_3$[329] two non-equivalent Cu(II) atoms, one CuO_4Cl_2 and the other $CuCl_4$ are linked by a single chlorine atoms.

In another derivative[330] two non-equivalent *pseudo*-octahedral units CuO_4Cl_2 and $CuCl_4O_2$ are linked by chlorine atoms. The Cu–Cu distance of 3.553 Å ruled out a direct metal–metal bond; black $Cu_3(tmso)Br_6$[328] is isostructural with its chlorine analogue.[328]

There are two derivatives[331,332] in which approximately planar CuN_4^{2+} units are linked by bridging SiF_6^{2-} [331] or BF_4^- [332] groups as axial ligands completing a tetragonal-bipyramidal arrangement (CuN_4F_2).

There are over 20 derivatives[138,332–354] mostly blue or violet in which a *pseudo*-octahedral environment about Cu(II) is created by four N and two O donor atoms (CuN_4O_2). In the violet complex $Cu(im)_4(\mu\text{-}SO_4)$[333] four imidazole nitrogens create square-planar CuN_4^{2+} units which are linked together by SO_4^{2-} ions, forming symmetry-related chains; these chains form layers parallel to the *a–c* plane. A deep blue complex $Cu(NH_3)_4(\mu\text{-}SeO_4)$[334] is isostructural with that of $Cu(im)_4(\mu\text{-}SO_4)$.[333]

In another three blue derivatives[335–337] nearly square-planar CuN_4^{2+} units are connected by NO_3^- ions as axial ligands, completing a tetragonal-bipyramidal environment about each Cu(II) atom (CuN_4O_2). In yellow brown $Cu(1,2\text{-pn})_2(\mu\text{-}Cr_2O_7)$[338] the dichromate(VI) anions serve as a bridge between square-planar CuN_4^{2+} units.

The structure of $[Cu(bpy)_2(\mu\text{-}ClO_4)]ClO_4$ was studied by two groups.[332,339] The crystal is composed of infinite chains of $[Cu(bpy)_2(\mu\text{-}ClO_4)]^+$ and ClO_4^-. A perchlorate ion in the chain bridges two adjacent Cu(II) atoms through its two oxygen atoms in axial positions. The coordination polyhedron around each Cu(II) atom is a tetragonal-distorted octahedron. In another two derivatives[340,341] nearly square-planar CuN_4^{2+} units are also linked by perchlorate groups (Table III).

The structure of a dark violet derivative[342] is built up of trimeric units, consisting of distorted octahedral environments about each Cu(II) atom (CuN_4O_2) connected through two imidazolato bridges. Each unit is centrosymmetric around the central Cu(II) atom. The trimer units are linked through two perchlorate groups forming a chain running along the *c*-direction.

A purple derivative[343] consists of μ-4,4′-bipyridine Cu(II) dimeric cations and perchlorate anions. Two of the perchlorate anions are not coordinated, whereas the other two link the dimeric units in a bis(monodentate) way, building one-dimensional chains of Cu(II) linked by 4,4′-bipyridine to form ladders. They are arranged in a three-dimensional network. The Cu(II) atom is in a 4 + 2 environment (CuN_4O_2) with O atoms in axial positions (Table III). The Cu–Cu distance through the 4,4′-bipyridine molecule, within a dimeric unit, is 11.106(2) Å, much longer than the Cu–Cu distance through a perchlorate anion between two dimeric units, which is 7.283(2) Å.

In a dark blue derivative[344] only the 4,4′-bipyridine ligand bridges neighboring Cu(II) atoms forming polymeric chains along the *c*-axis in the crystal. Each Cu(II) atom has a 4 + 2 coordination (CuN_4O_2) with O atoms in axial positions.

In a blue derivative[345] $[Cu(bpy)_2]^{2+}$ units are linked by trithionate anions forming chains along (100). In this case, each Cu(II) atom also has a 4 + 2 coordination (CuN_4O_2) with O atoms of trithionate groups on axial positions. A royal blue complex $Cu(2,2'\text{-bpy})_2(\mu\text{-ted})$[346] is isostructural with $Cu(2,2'\text{-bpy})_2(\mu\text{-tt})$.[345] In purple $Cu(en)_2(\mu\text{-dda})_2$[347] two O atoms of the dodecylsulfato ligands occupy axial positions about each Cu(II) atom. In addition to the Cu–O bond, there are two intramolecular hydrogen bonds from each dodecylsulfato ligand to the bis(ethylenediamine) Cu(II) moiety. The dodecyl chains are extended and form a highly ordered interdigitating structure.

A red derivative[348] consists of perchlorate anions and infinite-chain $[Cu_2(\mu\text{-dddo})_2(MeOH)]^{2+}$ cations. Each Cu(II) atom is coordinated to a tetradentate dddo ligand through four coplanar nitrogen atoms (Cu–N distances range from 1.937(5) to 1.961 Å), and each Cu(II) atom is also coordinated to an oxime oxygen of the adjacent unit (Cu–O distances of 2.491(4) and 2.493(4) Å) to form singly-bridged zig-zag chains.

The structure of $Cu(\mu\text{-pz})_2(ClO_4)_2$[349] consists of sheets of Cu(II) atoms bridged by ambidentate pyrazine ligands. The distance between two adjacent sheets is 7.012 Å. The coordination geometry about each Cu(II) atom is that of a tetragonally elongated octahedron, where each Cu(II) atom is bonded strongly (Cu–N = 2.062(3) Å) to four pyrazine ligands and weakly (Cu–O = 2.373(12) Å) to two perchlorate group. The structure of pale blue $Cu(\mu\text{-pz})_2(ms)_2$[350] is isostructural with that of $Cu(\mu\text{-pz})_2(ClO_4)_2$.[349]

Light blue $[Cu(\mu\text{-th})_2](ClO_4)_2$[351] consists of $[Cu(\mu\text{-th})_2]^{2+}$ cations and perchlorate anions; the structure of the $[Cu(\mu\text{-th})_2]^{2+}$ cations is shown in Figure 11. As can be seen the complex cation has a chain structure and tetrazolyl-1-acethydrazide performs the function of a tridentate-bridging ligand bonding adjacent Cu(II) atoms through the chelate hydrazide fragment and the nitrogen atom in position 4 of tetrazole, respectively.

In $Cu(2\text{-OH-}1,3\text{-pn})(\mu\text{-trp})$[352] $[Cu(2\text{-OH-}1,3\text{-pm})_2]^{2+}$ units are linked by the terephthalate groups, resulting in infinite chains.

The crystal of a black derivative[353] is made up of alternating sheets of bis(8-hydroxyquinolinato)Cu(II) molecules and tetracyanobenzene molecules. These sheets extend in the y–z plane, and the molecules in each sheet are inclined to this plane. The sheets are arranged so that alternate copper chelate and tetracyanobenzene molecules stack along the z-axis.

In dark green $Cu(\mu\text{-bmpcb})$[354] the ligand is tetradentate through the four N atoms forming a highly distorted, square plane about the Cu(II) atom. Amide oxygen atoms of neighboring molecules coordinate also to form chains parallel to a, completing a tetragonally distorted six-coordination (CuN_4O_2).

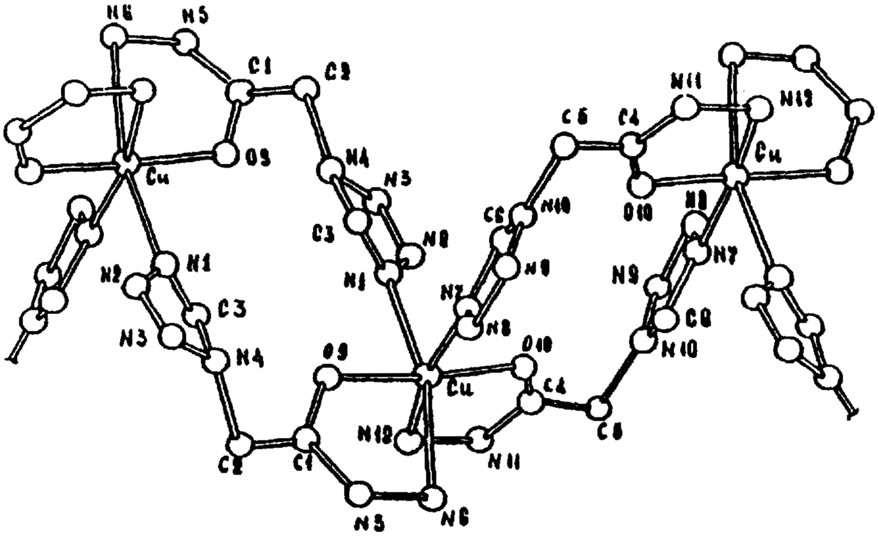

FIGURE 11 Structure of $[Cu(\mu\text{-th})_2]^{2+}$.[351]

There are four derivatives[229,355–357] in which Cu(II) has a *pseudo*-octahedral environment created by four N and two Cl atoms (CuN_4Cl_2). In $[Cu(aeim)_2(\mu\text{-}Cl)]Cl \cdot 2H_2O$[355] the Cu(II) atoms are located at two independent centers of symmetry (000 and 0$\frac{1}{2}$0). Two bidentate histamine ligands form a square-planar environment around the Cu(II) atoms (CuN_4). The coordination sphere is expanded to a tetragonal-bipyramid by bridging chlorine atoms. Polymeric chains are extented along the *y*-axis (Table III).

The structure of a deep blue derivative[356] consists of centrosymmetric dimeric $Cu_2(\mu\text{-bistren})^{4+}$ units held together by chlorine bridges forming pairs of polymeric zig-zag chains parallel to the *b*-axis. Each Cu(II) atom has a $4+1+1$ coordination (Table III). The intramolecular Cu–Cu distance is 6.138(1) Å.

In a dark brown derivative[357] the Cu(II) atoms are not equivalent, one Cu(II) has the tetradentate N_4 atom macrocycle in a square-planar arrangement. In addition, the axial positions are occupied by two chlorine atoms of two $CuCl_4^{2-}$ units, which act as bridges. The other Cu(II) atom is coordinated by four chlorine atoms in a distorted tetrahedral geometry (Table III).

There are 10 derivatives[256,358–366] in which each Cu(II) atom is surrounded by four nitrogen and two sulfur donor atoms (CuN_4S_2). The structures of two green[358,360] and one brown[354] complex are characterized by infinite polymeric chains along (010), constructed from $Cu(\mu\text{-(cimetidine)}_2^{2+}$

entities which are linked through N-cyano groups belonging to symmetry-related molecules. The Cu(μ-cim$_2$)$^{2+}$ cations in the perchlorate,[358] nitrate[359] and sulfate[360] salts are one-dimensional infinite chains characterized by different conformations of the antiulcer drug cimetidine (cation structure isomerism). The Cu(II) atom lies in a strongly distorted octahedral CuN$_4$S$_2$ environment (Table III).

A violet derivative[361] consists of Cu(en)$_2${μ-(EtO)$_2$PS$_2$}$^+$ cations and NCS$^-$ anions. In the complex cation Cu(en)$_2$ moieties are linked by diethyldithiophosphate anions to form polymeric chains. Each Cu(II) atom has a tetragonal-bipyramidal arrangement (CuN$_4$S$_2$) with S atoms in the apical positions.

Light blue Cu(en)(μ_3-NCS)(NCS)[362] contains two symmetrically independent Cu(II) atoms. Each Cu(II) atom is coordinated in plane by the N atoms of ethylenediamine and the N atoms from two NCS groups. The planar coordination is supplemented by the sulfur atom of the NCS group to give a distorted tetragonal-bipyramidal environment (CuN$_4$S$_2$). There are two types of NCS groups, μ_3-SCN and monodentate (N).

The structure of dark green Cu(4-Brpy)$_2$(μ-NCS)$_2$[363] is shown in Figure 12. There are two symmetrically independent Cu(II) atoms, both *pseudo*-octahedrally coordinated (CuN$_4$S$_2$). Both types of Cu(II) polyhedra alternate in the chain and are linked by thiocyanate groups. Another dark green complex Cu(4-Mepy)$_2$(μ-NCS)$_2$[364,365] contains three symmetrically independent Cu(II) atoms and is isostructural with Cu(4-Brpy)$_2$(μ-NCS)$_2$.[363]

The structure of dark green Cu(bim)(μ-NCS)$_2$[256,366] is made up of one-dimensional chains of Cu(bim)$^{2+}$ units linked by thiocyanato groups which act as asymmetrical end-to-end bridges. Blue green Cu$_2$(μ-NCS)$_4$(μ-bpm)$_2$[256,366] is made up of a three-dimensional network of Cu(II) atoms bridged by bis-bidentate bpm ligands and bis-unidentate end-to-end thiocyanate groups Figure 13.

In Cu(NH$_3$)$_4$I$_4$[367] four nitrogen atoms and two axial iodine atoms form a tetragonal-bipyramidal environment about Cu(II) (CuN$_4$I$_2$). A connection of the Cu(II) atoms by linear, centrosymmetric I$_4^{2-}$ polyiodide ions results in infinite chains of [Cu(NH$_3$)$_4^{2+}$I$_4^{2-}$] units.

In the blue complex[368] perchlorate groups link the [Cu(den)(μ-NCS)]$_2^+$ dimers along the *b*-axis. Each Cu(II) atom is coordinated by four N atoms in the plane and an S atom of the NCS group and an O atom of the perchlorate group complete a tetragonal-bipyramidal environment (CuN$_4$OS) (Table III). The Cu–Cu distance in the dimeric unit is 5.51 Å.

There are six derivatives[152,369–372] in which each Cu(II) atom is coordinated by four chlorine and two oxygen donor atoms (CuCl$_4$O$_2$). The structure of a

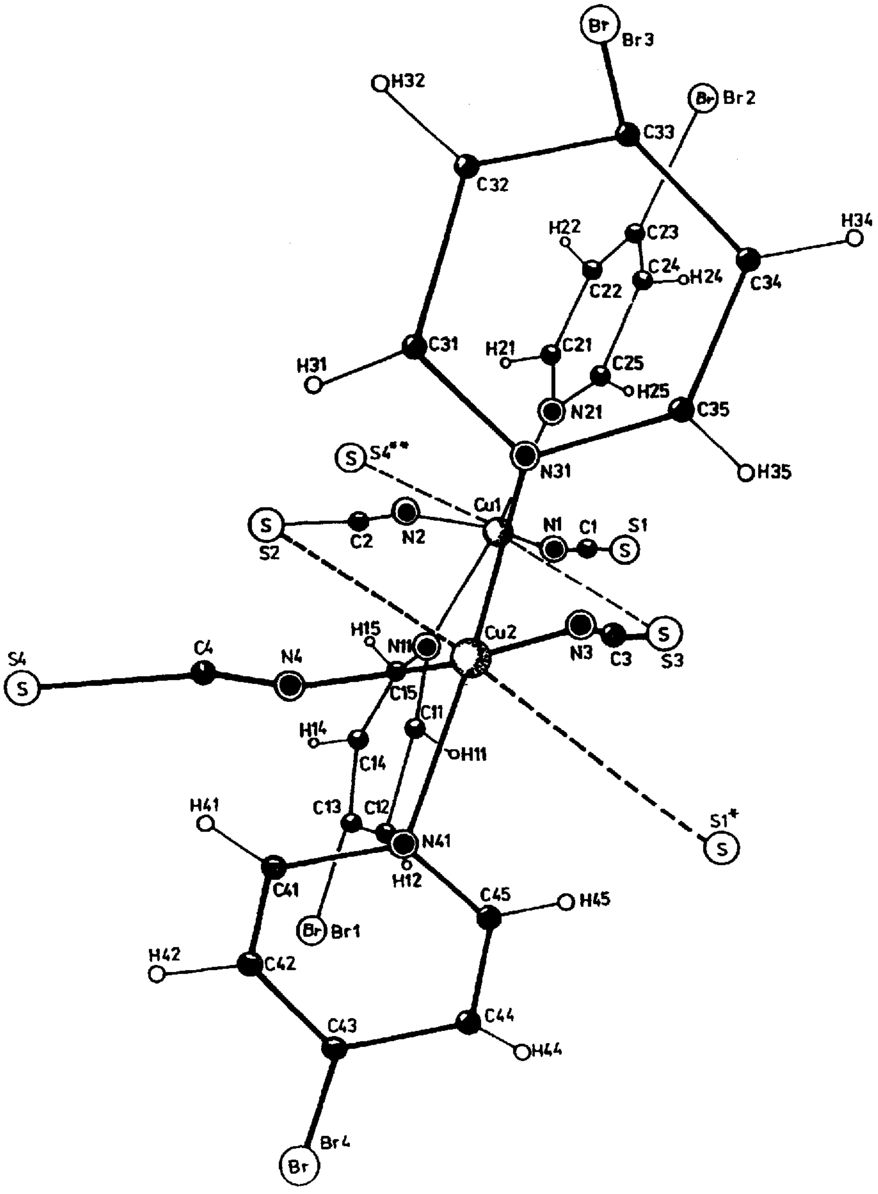

FIGURE 12 Structure of $Cu(4\text{-}Brpy)_2(\mu\text{-}NCS)_2$.[363]

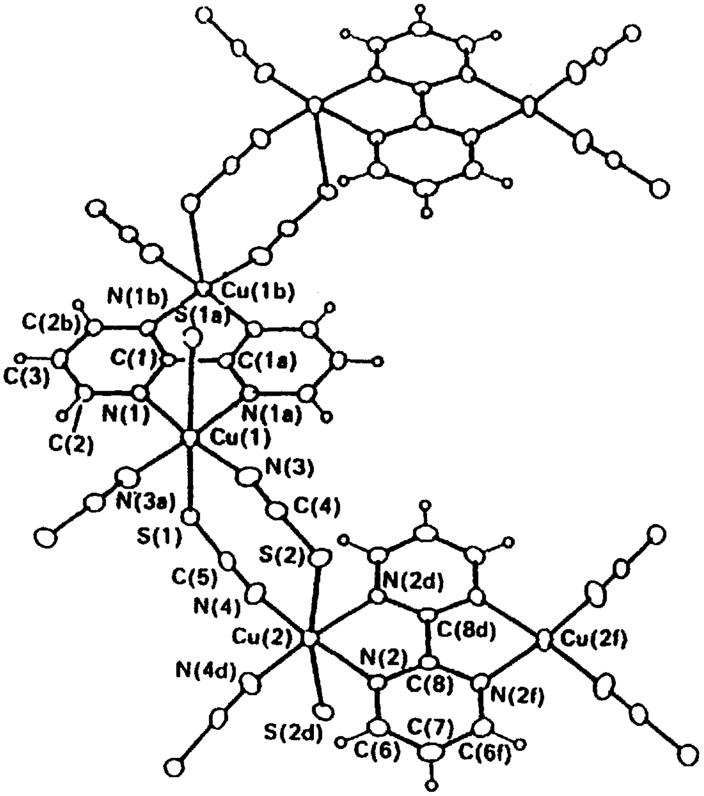

FIGURE 13 Structure of $Cu_2(\mu\text{-}NCS)_4(\mu\text{-}bpm)_2$.[366]

brown derivative[369] is formed of nearly planar ($CuCl_2$(*trans*-chd) and $CuCl_3(thf)_2$ units which are alternatingly tied together by two chloro-bridges and one hydrogen bond, forming an infinite chain along the *c*-axis. In this chain there are three copper atoms on the same line. These lines form a zig-zag type trace. Each Cu(II) atom has tetragonal-bipyramidal geometry, in the former with two chlorine atoms and in the latter units two oxygen atoms (thf) in apical positions (Table III).

The structure of a green derivative[370] contains square-planar $CuCl_2(H_2O)_2$ subunits stacked along the *a*-axis. Distorted octahedral coordination at Cu(II) is completed by two rather long Cu–Cl bonds with the next layers. The octahedral units form one-dimensional chains by edge-sharing (Table III). There are two orange derivatives[371] of composition $Cu(\mu\text{-}Cl)_2(\mu\text{-}L)$ (L = tetramethylsulfoxide or dimethylsulfoxide). Each contains linear chains of Cu(II) atoms with three bridging ligands (2Cl, 1O) between each pair of Cu(II) atoms with Cu–Cu distances of 3.209(6) and 3.238(1) Å, respectively. In each salt, the copper coordination geometry is severely distorted from octahedral with four short Cu–ligand bonds (Cl_3O) and two long Cu–ligand bonds (OCl).

The structure of $(CuCl_3)(dio)_2$[372] contains zig-zag $(CuCl_2)_n$ chains along the *c*-axis. Each Cu(II) atom is also bonded to two O atoms of 1,4-dioxane molecules, which cross-link the chains in the *a*–*c* plane. The Cu–Cu distances of 3.120(3) and 3.358(3) Å alternately ruled out a direct metal–metal bond.

There are 13 derivatives[373–385] in which a square plane about each Cu(II) atom is created by pairs of chlorine and nitrogen atoms (N_2Cl_2) and another pair of chlorine atoms completed a square-bipyramidal coordination ($CuCl_4N_2$). A polymeric chain structure of dark green $CuCl_2(oaoH_2)$[373] is formed where a chlorine atom bridges three Cu(II) atoms. This leads simultaneously to bent and to nearly linear Cu–Cl–Cu chains, and to zig-zag chains of copper atoms with a Cu–Cu distance of 3.972(2) Å.

The structures of another five derivatives[375–379] (Table III) consist of infinite chains of doubly chloride-bridged Cu(II) atoms, with Cu–Cu distance ranging from 3.649 to 3.932(4) Å.

The crystal structure of green $CuCl_2(pz)$[380,381] reveals that $CuCl_2$ units are bonded by pyrazine to form linear chains. These chains are cross-linked by doubly-bridged chlorine atoms.

The structural unit of $CuCl_2(tz)$[382] and $CuCl_2(amtz)$[383] is an infinite chain parallel to the *c*-axis, in which coordination octahedra are joined by sharing edges containing two chlorine atoms. The octahedra are also linked along the chain through vertices from the N atoms, since vertices of adjacent octahedra are occupied by adjacent N'atoms of one triazole[382] or 4-amino-3-methyl-1,2,4-triazole[383] molecule.

A green derivative[384] consists of $Cl_2Cu(bpm)CuCl_2$ dimeric units doubly bridged by chlorine atoms. The bpm ligand bridges two copper atoms in a planar arrangement with the intermolecular Cu–Cu distance of 5.528(2) Å. While in $Cu(Cl)_2Cu$ moieties the intermolecular Cu–Cu distance is only 3.600(1) Å.

There are five derivatives[386–389] in which a *pseudo*-octahedral environment about each Cu(II) atom is created by four chlorine, one oxygen and one nitrogen atoms ($CuCl_4ON$).

$CuCl_2(sc)$, exists in two isomeric forms a blue green monoclinic and blue orthorhombic.[386] In the monoclinic compound, the two semicarbazide molecules, which are present in two adjacent octahedra along the chain, have the oxygen and nitrogen atoms in the *trans* configuration, one with respect to the other, and are correlated by a center of symmetry. In the orthorhombic compound, the two semicarbazide molecules are in the *cis* configuration and there is no center of symmetry. In both compounds packing is determined by the NH···Cl and NH···O hydrogen bonds which join the chains together.

In $CuCl_2(amp)$[387] all chlorine atoms are shared between different coordination octahedra, which form slabs parallel to (100). The octahedra in a slab alternately share edges and corners. The Cu–L bonds are not colinear (deviation 10°) and the total coordination of Cu(II) can be seen as a Jahn–Teller distortion octahedron (Table III). $CuCl_2$(L-his)[388] is isostructural with $CuCl_2(amp)$.[388]

The structure of brown red $CuCl_2(Me_2NNO)$[389] consists of slightly folded $CuCl_2$ chains parallel to (100). The chlorines surround the copper in an almost perfect square. Perpendicular to the chlorine plane two adjacent coppers in the chain are connected by the O and the nitroso N of one dimethylnitrosamine alternating on both sides of the $CuCl_2$ chain.

The structure of [$CuCl_2$(amtzt) · H_2O[383] is isostructural with the brown red derivative.[389] Two adjacent coppers in the chain are connected by the N and the S of the amtzt molecule alternating on both sides of the $CuCl_2$ chain.

A centrosymmetric coordination sphere of Cu(II) atom in red brown $Cu(\mu\text{-tted})_2Cl_2$[390] is comprised of an S atom from each of two 1,5,9-trithiacyclododecane ligands and two chlorine atoms at distances of 2.447(1) and 2.205(1) Å, respectively. In addition, each copper interacts weakly with an S atom of a neighboring unit to yield a severe tetragonal elongation geometry (CuS_4N_2) (Table III).

There are seven derivatives[375,378,380,384,391,392] in which a tetragonal-bipyramidal arrangement about each Cu(II) atom is built up by four bromine and two N donor atoms, with two bromine atoms at apical positions. Structures of four of them[375,378,380,384] are isostructural with their chlorine analogue.

Structures of two green derivatives[391] consist of infinite dibromo-bridged chains, in which one bromine ligand serves to propagate the chain in both directions while the others are not involved in the chain, thus one bromine is coordinated to three copper atoms while the others are coordinated to only one. The geometry about each Cu(II) center is distorted octahedral, with two *cis* nitrogen atoms and two bromines in the plane, and the weaker chain-propagating bromine interactions out of the plane. The Cu–Cu separation in the two chains are 3.737(6) and 3.866(2) Å for the aminomethylpyridine and diaminopropane complex, respectively, with associated Cu–Br–Cu bridging angles of 80.77(4)° and 87.56(3)°, respectively.

Blue $CuBr_2(aep)$[392] consists of infinite Cu–Br–Cu chains which are joined by doubly-bridged Cu–Br–Cu–Br linkages, where the bromine atoms involved in these pairwise linkages are not involved in the chain propagation. Both types of bromine bridges are asymmetric (Table III).

In another 14 derivatives[281,393–405] a *pseudo*-octahedral arrangement about each Cu(II) atom is created by three O and three N donor atoms (Table III). Their structures are very complex. For example, in dark blue $[Cu(\mu\text{-dmhx})(glygly)] \cdot 4H_2O$[393] the primary coordination sphere about the copper is approximately square-planar with the tridentate glycylglycine dianion and an N atom of the 7,9-dimethylhypoxanthine ligand. In addition to the strongly coordinated equatorial plane, the copper also forms two weak, axial interactions with an O atom of the 7,9-dimethylhypoxanthine ligand; one intramolecular Cu–O = 2.970(2) Å, and one intermolecular Cu–O = 2.769(2) Å. The structure of purple $Cu(\mu\text{-cyt})(glygly)$[394] is very similar to that of $Cu(\mu\text{-dmhx})(glygly)$.[393]

The structure of blue $Cu_2(\mu\text{-ghg})_2(H_2O)$[399] is shown in Figure 14. Each tripeptide binds two copper atoms and, therefore produces a polymeric chain of Cu-tripeptide–Cu-tripeptide units extending approximately along the crystallographic *a*-axis. The four closest donor atoms, which form an approximate square-plane about the copper, are the amino, peptide and

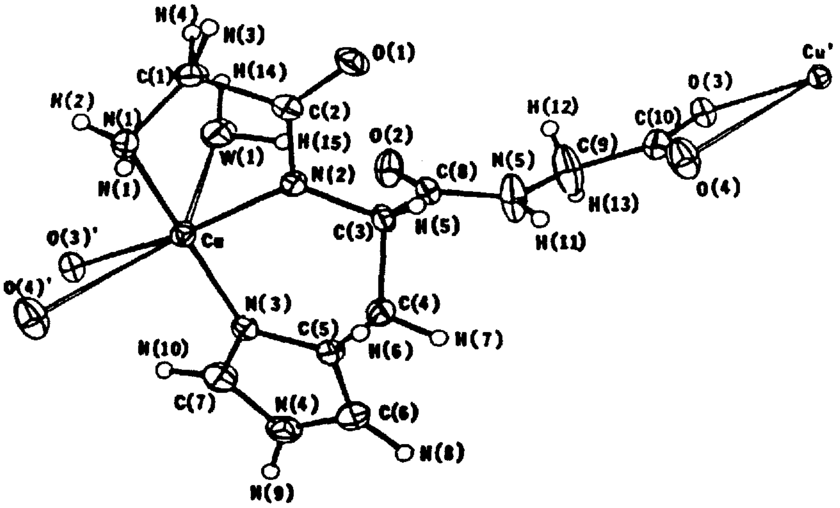

FIGURE 14 Structure of $Cu_2(\mu\text{-ghg})_2(H_2O)$.[399]

imidazole N atoms of one ligand and a carboxyl O of another. The distorted octahedral geometry about the Cu(II) atom is completed by the second O atom of the carboxyl group, and by a water molecule (Table III).

A dark blue derivative[404] contains perchlorate anions and the dicationic centrosymmetric dimeric $[(\mathrm{dien})\mathrm{Cu}(\mu\text{-tp})\mathrm{Cu}(\mathrm{dien})]^{2+}$ complex. The crystallographic inversion center is located at the center of the benzene ring of the terephthalate anion (tp) bridging ligand. Within the dimeric unit the Cu(II) atoms are bridged by the tp ligand in a bis-unidentate fashion with a Cu–Cu separation in each dimeric entity of 11.006(5) Å. Moreover, two Cu(II) centers of two different dimeric units are bridged by an oxygen atom of a carboxylate group. Thus, chains along the *b*-direction and layers parallel to (100) are formed.

In another blue derivative[405] the sulfate group forms a bridge between *pseudo*-hexacoordinate Cu(II) atoms ($\mathrm{CuO_3N_3}$) leading to infinite chains along the twofold screw axes. Blue $[\mathrm{Cu}(\mu\text{-NCS})(\mathrm{bheg})]\mathrm{H_2O}$[406] forms a one-dimensional polymer chain through the isothiocyanato group. The polymer chains are parallel to the *c*-axis. Each Cu(II) atom is at the center of the typical tetragonal-bipyramidal geometry ($\mathrm{CuO_3N_2S}$) (Table III).

The structure of green blue $[\mathrm{Cu_2(tampz)Cl_2}]\mathrm{Cl_2} \cdot 2.25\mathrm{H_2O}$[407] is shown in Figure 15. The dimeric complex cations are linked by two parallel Cu–Cl(2)–Cu bridges to form a ladder-type polymer structure with an intermolecular Cu–Cu distance of 5.716(1) Å. In the crystal the ladders stack up the *a*-axis with an interladder Cu–Cu distance of 5.536(1) Å. Each Cu(II) is *pseudo*-octahedrally coordinated, ($\mathrm{CuN_3Cl_3}$) (Table III).

A deep blue derivative[408] consists of chains of iodine-bridged Cu(II) atoms along the crystallographic *c*-direction. Each Cu(II) atom has a tetragonal-bipyramidal environment ($\mathrm{CuN_3I_3}$). The equatorial plane consists of three nitrogen atoms from the diethylenetriamine ligand and one iodine, while the axial sites are occupied by the other (chain-propagating) iodine ligands. The intrachain Cu–Cu separation is 6.658(1) Å, and the bridging Cu–I–Cu angle is 167.7(1)°.

The structure of blue $\mathrm{Cu\{gaba(mpy)_2\}Br}$[409] is shown in Figure 16. The bis(2-pyridylmethyl)amino moiety binds in a meridional fashion. There is no crystallographically imposed symmetry around the copper atom, but there is a *pseudo*-mirror plane through N(1)–Br–O(1)–O(2), ignoring the carboxylate tail. The dihedral angle between N(1)–N(2)–N(3) and O(1)–C(16)–O(2) is 87.6(4)°. Each Cu(II) atom is tetragonal-bipyramidally coordinated ($\mathrm{CuN_3O_2Br}$) (Table III).

In triclinic $\mathrm{CuCl_2(et_2nia)_2}$[410] all the N,N-diethylnicotinamide molecules are bridging, and are coordinated *via* the nitrogen atom of a pyridine ring to

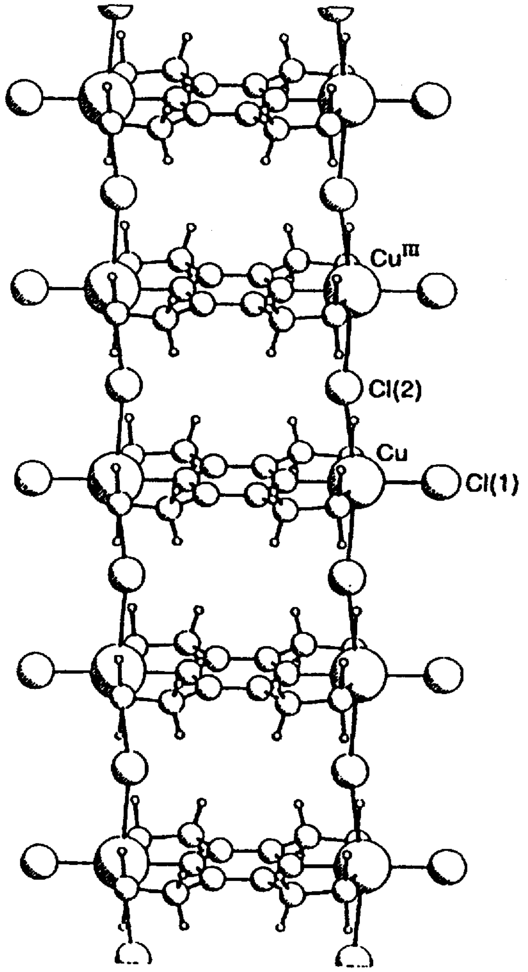

FIGURE 15 Structure of $[Cu_2(tampz)Cl_2]Cl_2$.[407]

a copper atom situated in one system of centers and *via* the oxygen atom to a copper atom lying in another system of centers. This leads to the production of a three-dimensional framework. Each Cu(II) atom is tetragonal-bipyramidally coordinated ($CuO_2N_2Cl_2$) with two O atoms in the axial positions.

In green $[Cu(\mu\text{-bpydc})(\mu\text{-Cl})_2] \cdot 2H_2O$[411] *pseudo*-octahedrally coordinated Cu(II) atoms ($CuO_2N_2Cl_2$) are bridged by bpydc molecules as well as by chlorine atoms. Finally, in another green derivative[95] tetragonal-bipyramids ($CuO_2Cl_2S_2$) are linked by 1,4-oxathiane molecules (Table III).

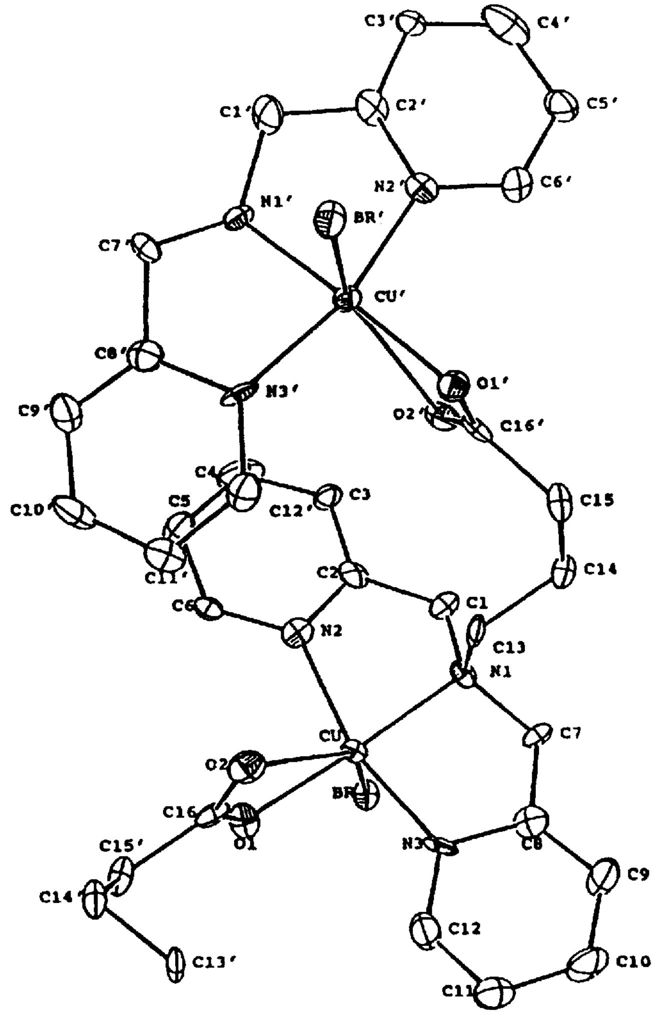

FIGURE 16 Structure of Cu{gaba(mpy)$_2$}Br.[409]

Inspection of the data in Table III reveals that there are over 270 Cu(II) derivatives, in which Cu(II) atoms are six-coordinated, with tetragonal-bipyramidal geometry the most common. From 36 different types of chromophores around Cu(II) atoms, the CuO_4N_2 (70×) and CuO_6 (51×) are the most common. There are several derivatives which contain non-equivalent Cu(II) atoms: CuO_4N_2 and CuO_4,[323] CuO_4Cl_2 and $CuCl_4$,[328,329] CuO_4Br_2

and $CuBr_4$,[328] CuN_4Cl_2 and $CuCl_4$,[357] CuN_6 and CuN_5,[222] CuO_6 and CuO_4N_2,[18,181] CuO_4N_2 and CuO_4Cl_2,[324] and CuO_4Cl_2 and $CuCl_4O_2$.[330]

The Cu–Cu distances range from 2.977(2) to 11.0229(2) Å which excludes direct metal–metal bonding. The mean Cu–L distances found in the six-coordinate polymeric Cu(II) compounds are summarized in Table IIIA. In general Cu–L(equatorial) bond distances are shorter than Cu–L(apical) bond distances. The Cu–L bond distance elongated with increasing covalent radius of the coordinated atom. The mean Cu–L bond distances obtained for six-coordinate derivatives (Table IIIA) compared to those obtained for five-coordinate derivatives (Table IIA) show that, in mostly cases, the mean Cu–L bond distance is longer for six- than for five-coordinate species. But when $L = LO_{eq}$, L^3O_{eq}, Cl_{eq}, Br_{ap}, μ-LN or μ-Cl_{eq}, the opposite is true, and finally, when $L = L^2N_{eq}$, L^3N_{eq} or μ-LO_{eq}, the mean Cu–L bond distances are equal.

Multidentate ligands include both mono- and hetero-donor atoms, with O and N donors being by far the most common. Hetero-bidentate ligands

TABLE IIIA Summary of the Cu(II)–L bond distances for six-coordinate derivatives[a]

Coord. atom[b]	*Cov. rad.* [Å]	*Cu–L (equatorial)* [Å]	*Cu–L (apical)* [Å]
LO	0.73	1.98(6,8)	2.54(24,45)
μLO		1.95(3,4)	2.57(22,34)
L^{2}O		2.01(11,11)	2.61(31,39)
L^{3}O		1.96(5,7)	2.57(24,33)
L^{4}O		2.01(9,31)	2.66(31,27)
L^{5}O		1.94(4,6)	2.48(11,6)
LN	0.75	2.00(9,8)	2.70(14,14)
μLN		1.97(1,2)	2.57(11,11)
L^{2}N		2.02(11,13)	2.65(18,30)
L^{3}N		1.99(8,4)	2.65(38,47)
L^{4}N		2.05(11,8)	—
L^{8}N		2.05(4,4)	—
Cl	0.99	2.28(8,3)	—
μCl		2.29(8,6)	2.88(40,42)
μ_3Cl		2.28(3,2)	2.86(1,4)
L^{2}S	1.02	2.45	3.04(4,5)
μ_3S			2.57(26,79)
Br	1.14	2.43(4,2)	2.74
μBr		2.42(3,3)	3.20(27,50)
μ_3Br		2.44(2,2)	3.21(15,12)
μI	1.33	2.585	3.22
SC$\underline{\text{N}}$	0.75	1.95(5,8)	—
NC$\underline{\text{S}}$	1.02	—	3.05(29,22)

[a] The first number in parenthesis is the maximum deviation from the mean of the lowest value observed. The second number in parenthesis is the maximum deviation from the mean of the highest value observed. [b] $L^x = X$ – dentate.

include those with O plus N; O plus S and N plus S donor sites. Hetero-tridentate ligands include those with two O plus one N, two N plus S, and one O plus two N donor sites. The hetero-tetradentates are either three O plus N, three N plus S, or two O plus two N donor sites. The hetero-pentadenta-ligands include four O plus N, two O plus three N, one O and four N donor sites. The hetero-hexadentate ligands include four O plus two N, four O plus S, two O plus four N donor sites. The hetero-heptadenate ligands have five O plus two N donor sites, hetero-nonadentate ligand has six O plus two N and one S; and hetero-undecadentate has seven O plus four N donor sites as the only examples.

The effects of both electronic and steric factors of the coordinated atoms can be seen in the opening of the L–Cu–L bond angles of the respective metallocycles. In four-member rings the mean L–Cu–L intra-ligand angles are: 49.9°–56.7° (mean 53.2°, O–C–O) and 64.7°–67.0° (mean 65.8°, O–Cl–O). For the five-member rings the values are: 77.0°–81.2° (mean 80.0°, N donor with unsaturation); 82.0°–89.5° (mean 84.5°, N donor with saturation); 74.4°–85.7° (mean 81.0°, O donor); 73.6°–85.7° (mean 83.3°, O + N donor); 82.2°–84.2° (mean 83.2°, O + S donor); 77.4°–78.8° (mean 78.0°, N + S donor, unsaturation and 86.0° N + S donor saturation. For six-member rings the values are: 87.5°–93.8° (mean 91.5°, O donor); 91.2°–95.3° (mean 93.0°, O + N donor) and 89.0°–100.50° (mean 93.8°, N donor).

3. CONCLUSIONS

The review has classified almost 500 polymeric Cu(II) compounds. The various geometries are found in increasing number in the order : four- ≪ five- ⋘ six-coordination. In the series of four-coordinate complexes there are square-planar, tetrahedral and intermediate square-planar ⇔ tetrahedral derivatives. In the series of five-coordination, by far the most prevalent is square-pyramidal geometry with differing degrees of distortion. The Cu(II) atom is displaced from the basal plane toward an apical donor atom from 0.003 to 0.406 Å. In the series of six-coordination, an elongated tetragonal-bipyramidal environment with differing degrees of distortion prevails.

Two symmetrically independent copper units, differing by degree of distortion, have been found in several cases.[21b,23,26,30,46,49,56,59,60,62,74–76,79,96,99,108,118,131,150,151,164,170] In one case[72] three such units and in one case[93] seven such units are present. There are several examples which contain non-equivalent Cu(II) atoms: four- and five-coordinate,[12,13] four- and six-coordinate,[18,321,328,329,357] five- and six-coordinate.[38,63a,84–88,94,95,98,100,112,125,155,222] In two cases five-coordinate Cu(II) atoms differ by chromophores; CuO_5 and CuO_3N_2,[27] $CuCl_4O$ and $CuCl_3O_2$,[93] and in another four derivatives six-coordinate Cu(II) atoms also differ by chromophores; CuO_6 and CuO_4N_2,[180,181] CuO_4N_2 and CuO_4Cl_2;[324] CuO_4Cl_2 and $CuCl_4O_2$.[330]

Copper(II) compounds are for the most part blue or green, but there are examples of violet, red, yellow or even black.

The 'borderline' behavior of the Cu(II) atom is evident from the nature of the ligands most commonly found, and in particular the nature of the binding. The most common ligands are oxygen and nitrogen donors, and chlorine atoms. The ligands range from mono- to undecadentate. In mostly examples, an apical positions are occupied by oxygen-donor ligands.

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

In general, the mean Cu–L bond length increases with coordination number of the metal atom and with covalent radius of the donor atom. In general, the mean Cu–L(equatorial) bond length is shorter than the respective Cu–L(apical) bond length. The shortest Cu–Cu distance found in the series of four-coordinate derivatives is 2.95 Å,[16] five-coordinate 2.652(2) Å[26] and six-coordinate 2.977(2) Å.[281]

Table IV summarizes the intra-metallocyclic ring angles for the five- and six-coordinate derivatives. The angle opens with increasing covalent radius of the donor atom and with increasing number of atoms in the ring as expected. The angle opens with decreasing coordination number, except of 5-N and 5-O + S.

TABLE IV Summary of the mean intra-metallocyclic ring angles (°)

Ring	*5-Coord.*	*6-Coord.*
4-O	56.0	53.0
5-O	83.7	81.0
5-N	80.0[a]	80.3[a]
	83.7[b]	84.5[b]
5-O + N	83.7	83.3
5-O + S	80.6	83.2
5-N + S	87.7	80.7
6-O	92.4	91.5
6-N	94.0	93.8
6-O + N	93.7	93.2

[a]Unsaturation. [b]Saturation.

This review together with its precursors of Cu(II) for monomers[1,2] 1800× dimers[3] 900× trimers and oligomers[4] 250× represents the first overview of structural data for over 3500 Cu(II) coordination compounds.

These reviews for Cu(II) coordination compounds, together with the review[412] which classified over 1000 Cu(I) structures and the review[413] which classified 40 mixed-valence Cu(I)–Cu(II) coordination complexes show the wide range of stereochemistry around copper atoms with different degree of distortion and the enormous interest in copper chemistry.

During the collection and organization of the data it became clear, despite the increasing availability of data retrieval systems, the tracing of relevant material is not always a straightforward task. Some of the data are only available as supplementary material, and some are not mentioned at all. This can lead to overlooking of relevant structural features which should be compared with other derivatives. In view of such limitations in information retrieval, we believe, that it is necessary to make a systematic overall review, and that such reviews serve the useful purpose of delineating areas of both interest and weakness. Related reviews of the structural chemistry of heterometallic Cu(II) compounds as well as of Cu(III) compounds are currently in progress.

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