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

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Review

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

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This review summarizes the data for over nine hundred dimeric Cu(II) coordination compounds. There are several types of the bridges, from which doubly bridges by far prevail. The most common ligands are O- and N- donors. From the stereochemical point of view, a square-pyramidal arrangement with different degrees of distortion about Cu(II), is the most common. Several relationships were found between the Cu–Cu distances and the Cu–L–Cu bridge angle and the type of bridging, between the intra-ligand L–Cu–L ring angles and coordination numbers.

Keywords: Review; Cu(II); crystallography; structures; dimers

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0. ABBREVIATIONS

aamt	4-amino-3,5-bis(aminomethyl)-1,2,4-triazole
aanp	ligand involving two deprotonated amide, two izomethine nitrogen and two phenoxide donors
aapen	tetraanionic ligand derived from the condensation of 1,2-diaminoethane with <i>o</i> -acetoacetylphenol
ac	acetate
acacha	acetylacetonate-mono-(<i>o</i> -hydroxyanile)
acachfacac	acetylacetonate hexafluoro acetylacetonate
acacP(O)	<i>o</i> -(diphenylphosphino)benzoylpinacolone
acgly	N-acetylglycinate
acm	5-acetamido-1,3,4-thiadiazole-2-sulfonamide
acr	acridine
ad	adenine
ae	7-amino-4-methyl-5-aza-3-heptene-2-one
aett	3,4-bis(2-aminoethylthio)toluene
ahm	N,N'-bis(5-amino-3-hydroxypentyl)malonamide
β -ala	β -alanine

amazph	2,6-bis(5'-amino-1'-methyl-2'-azapent-1'-enyl)-4methylphenolate
ambt	α -aminoisobutyrate
2-amepy	2-aminomethylpyridine
ammph	ammoniomethyl(methyl)phosphine
amoc	8-amino-5-aza-4-methyl-3-octene-2-onate
amp	2-aminopyrimidine
5'-amp	5'-monophosphate of adenosine
6-ampur	6-aminopurine
2-ampy	2-aminopyridine
3-ampy	3-aminopyridine
3-ampyH	3-aminopyridinium
4-ampyH	4-aminopyridinium
amsbph	2,6-bis(4-amino-2-thiabutyl)-4-methylphenolate
amzh	7-amino-4-methyl-5-azahept-3-en-2-onate
[12]-aneS ₂	5,8-dithiadodecane
[20]-aneN ₄	20-membered N ₄ binucleating macrocycles ligand
[24]-aneN ₂ O ₆	polyaza-polyoxamacrocyclic ligand
[24]-aneN ₂ S ₄	1,3-diaza-4,10,16,22-tetrathiacyclotetracosane
[24]-aneN ₆	1,5,9,13,17,21-hexaazacyclotetradecane
[24]-aneN ₆ O ₂	cryptate macrocyclic ligand
[30]-aneN ₁₀	1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane
apcs	Schiff base ligand derived from the condensation of 3-aminopropanol with 5-chlorosalicylaldehyde
apha	6-amino-1-(2'-hydroxyphenyl)-3-methyl-4-azahept-2-en-1-one
aples	Schiff base ligand derived from the condensation of 3-aminopropanol with 5,6-benzosalicylaldehyde
apns	Schiff base ligand derived from the condensation of 3-aminopropanol with 3-nitrosalicylaldehyde
arg	L-arginine
asp	aspirinate
2-ath	2-aminothiazole
athal	N-(2-aminoethyl)thiophen-2-aldimine
baa	1-phenyl-1,3,5-hexanetrione
baaep	Schiff base derived from 2,3-butanedione-2-oxime and 2-(2-aminoethyl)pyridine
2-bae	2-dibutylaminoethanolate
bba	N-n-butyl(5-chloro- α -phenyl-2-hydroxybenzylidene)aminatate

2-bbenz	2-benzoylbenzoate
bbi	5-tert-butyl-m-xylene bis(acetylacetone imine)(3,3'-[5-(1,1-dimethylethyl)-1,3-phenylene bis(methylene)]) bis (4-amino-3-penten-2-one)
bbo	3,3'-(trimethylenedinitrilo)bis(butan-2-one-oximate)
bdd	2,3-butanedione dioximate
bdhe	bis(2-(diethylamino)ethyl)-2-hydroxyethylamine
bdo	N,N di (n-butyl)diaminoalcohol
bddo	1,8-bis-(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane
bdta	1,4-butanediaminetetraacetate
bedao	N,N'-bis(6-ethyl-3,6-diazaoctyl)oxamidate
bi-dptmd	4,16,20,32-tetraethyl-5,15,21,31-tetramethyl-8,12,24,28,33,34,35,36-octaazapentacyclo [28.2.1.1 ^{3,6}] ^{14,17}] ^{19,22}]hexatriconta-1,3,5,7,12,14(35),15,17,19,21,23,28,30(33),31-tetradecane
bilm	2,2'biimidazolate
bim	benzimidazole
bimp	2,6-bis{bis[(1-ethylimidazol-2-yl)methyl]amino)methyl]-4-methylphenol
bimpr	1,3-bis(benzimidazol-2-yl)propane
bistren	7,19,30-trioxa-1,4,10,13,16,22,27,33-octaazabicyclo-[11.11.11]pentriacontane
biu	biuretate
bmpp	2,6-bis{bis[2-(methylthio)ethyl]aminomethyl}-4-methylphenole
bmpc	2,6-bis((N-methylpiperazino)methyl-4-chlorophenol
bmpi	1,3-bis(2-(4-methylpyridyl)imino)isoindoline
boaep	Schiff base derived from 2,3-butanedione-2-oxime and 2-(2-aminoethyl)pyridine
botb	1,4-bis[(1-oxa-4,10 dithia-7-azacyclododecane-7-yl)-methyl]-benzene
bpap	1,4-bis[(2-pyridyl)amino]phthalazine
bpc	bis(2-pyridylcarbonyl)amide
bpden	N,N'-bis(3'-pyridazinecarboxamido)-1,2-ethane
bpep	2,5-bis[N,N-bis(2'-pyridylethyl)aminomethyl]pyrazine
bpim	4,5-bis[(2-(2-pyridyl)ethylaminomethyl]imidazolate
bpip	2,2'bipiperidine
bpm	2,2'-bipyrimidine
bpmab	1,3-bis[bis(2-pyridylmethyl)amino]benzene
bpmb	1-[bis(2-pyridylmethyl)amino]-3-[(2-pyridylmethyl)amino]benzene

bpmp	2,6-bis[bis(2-pyridylmethyl)-aminomethyl]-4-methylphenolate
bpmpp	2,5-bis[N,N-bis(2'-pyridylmethyl)aminomethyl]pyrazine
bpsp	[(R)-1,1-bis(2-butoxy-5-tert-butylphenyl)-3-phenyl-2-salicylideneamino-1-propanolate
bpy	2,2'-bipyridine
bpyH	4,4'-bipyridilium
bpyo	2,2'-bipyridine-N,N'-dioxide
bpt	3,5-bis(pyridin-2-yl)-1,2,4-triazolate N',N ¹ ,N ² ,N''
bptp	3,6-bis(2-pyridylthio)pyridazine
Br ₃ ac	tribromoacetate
2-Brbz	2-bromobenzoate
3-Brbz	3-bromobenzoate
4-Br-3-CO ₂ mepz	4-bromo-3-carboxylatomethylpyrazole
4-Brdmpz	4-bromodimethylpyrazole
bsda	N,N'-bissalicylidene-1,5-diimino-3-azapentane
btim	1,2,4,5-tetrakis(4,5-dihydroimidazol-2-yl).benzene
Bu-nso	2-[2-(di n-butylamino)ethylthio]ethanol
bu ¹ py	4-tert-butylpyridine
bz	benzoate
bzacac	benzoylacetate
bz- α -ala	N-benzoyl- α -alaninate
bzcarb	N-benzimidazolyl-2-carbamin acid
bz-15-crown-5	benzo-15-crown-5
bzd	benzidine(4,4'-diaminobiphenyl)
bzmh	benzoyltrimethylhydrazine
4-bzpipH	4-benzylpiperidinium
2-bzpy	2-benzoylpyridine
bzsmph	2,6-bis[4-(2-benzimidazolyl)-2-thiabutyl]-4-methylphenole
bztz	benzotriazolate
c	cubic
ca	dianion of chloranile acid
caf	caffeine (3,7-dihydro-1,3,7-trimethyl-1H-purine-2,6-dione)
cha	cyclohexylamine
car	β -alanyl-L-histidine (carnosine)
CH ₂ Cl ₂	monomethylenedichloride
C ₆ H ₆	benzene
C ₇ H ₇ N ₄ S	2-pyridinecarbaldehyde-thiosemicarbazone

$C_7H_{18}N_2$	N'-isopropyl-2-methyl-1,2-propanediamine
$C_8H_{13}NOCO_2$	2,2,5,5-tetramethylpyrrolin-1-oxyl-3-carboxylate
$C_8H_{16}N_3O$	2-(N,N-dimethyl-2-aminoethyl)imino-3-butanone oximate
$C_8H_{16}N_3O_2$	2-(N-(2-hydroxyethyl)-2-aminoethyl)imino-3-butanone oximate
C_5H_4NO	α -pyridone(2-hydroxypyridine)
$C_7H_5N_2$	7-azaindolate
$C_{11}H_{13}NO_2$	2-hydroxy-N-3-hydroxypropyl- α -methylbenzylideneaminat
$C_{12}H_{10}NO$	N-methyl-2-hydroxy-1-naphthaldiminate
$C_{12}H_{14}NO_2$	(4S)-4,5-dihydro-4-isopropyl-2-(2'-oxidophenyl)oxazole
$C_{12}H_{14}N_2O_4$	N,N'-bis(1-methyl-3-oxo-2-butenyl)oxamidate
$C_{12}H_{15}N_2O$	condensation product of 1,4-diazacycloheptane and salicylaldehyde
$C_{12}H_{21}N_4O_2$	2-oximino-11-oximinato-3,10-dimethyl-4,9-diazadodeca-3,9-diene
$C_{13}H_9F_3NCO_2$	N-3-trifluoromethylphenylanthranilate
$C_{13}H_{32}N_4S_4$	ligand prepared from 5,5-bis(4-amino-2-thiabutyl)-3,7-dithianonane-1,9-diamine and lithium dithionate
$C_{14}H_{33}N_3$	N,N-bis(diethylaminoethyl)-ethylamine
$C_{14}H_{26}N_6$	5,12-dimethyl-3,7,10,14,15,16-tetraazapentacyclo-[7.5.1 ^{2,8} .1 ^{5,16} .1 ^{12,15}] octadecane
$C_{14}H_{29}N_4O_2$	4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione dioxime
$C_{15}H_{10}N_2O_4$	2-hydroxy-N-3-hydroxypropyl-5-nitrobenzylideneaminat
$C_{15}H_{20}N_3O_2$	bis(1-N'-(N-2-aminoethylmorpholine)-1-phenylpropane-2-oxime
$C_{17}H_{20}F_{12}N_2O_2$	Schiff base prepared by condensation of 5,5,5-trifluoro-4-hydroxy-4-(trifluoromethyl)-2-pentanone with diamine
$C_{17}H_{22}N_4O$	2,6-bis(N,N'-dimethylethylenamineformimidoyl)-4-methylphenolate
$C_{17}H_{27}N_4O$	2,6-bis(N,N'-dimethylethylenamine formimidoyl)-4-methylphenolate
$C_{17}H_{30}N_6$	3,5-bis[(2-diethylamino)ethylaminomethyl]pyrazole
$C_{19}H_{23}N_3O_2$	Schiff base derived from 1,1'-(2,6-pyridyl)-bis-1,3-butane-dione and 3-amino-1-propanole
$C_{22}H_{21}N_4O_2$	2,6-bis[N-2-(2'-pyridylethyl)formimidoyl]-4-hydroxy-1-phenolate

$C_{24}H_{28}N_4O_4$	ligand derived by template condensation of 2,6-diformyl-4-R-phenol with 1,3-diamino-2-hydroxypropane
$C_{24}H_{36}N_4O_2$	ligand derived by template condensation of 4-methyl-2,6-diformylphenol with 1,3-diaminopropane
$C_{24}H_{48}N_4O_2S_4$	1,7,13,19-tetraza-4,16-dioxa-10,22,32,-tetrathiatricyclo [17.5.5.5 ^{7,13}] tetratriacontane
$C_{32}H_{46}N_8$	7,7'-ethylene bis[2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(17),2,11,13,15-pentaene
$C_{34}H_{34}N_4O_2$	N,N'-bis(2-((o-hydroxybenzhydrylidene)-amino)ethyl)piperazine
$C_{36}H_{40}N_6$	ligand synthesized by the reaction of bis(20(-pyridyl)-ethyl)amine with α,α' -dibromo-p-xylene
$C_{37}H_{36}N_2O_3$	2-hydroxypropane-1,3-diylbis(3'-t-butyl-5'-methyl-salicylideneimine)
$C_{74}H_{88}N_8$	porphyrine
Clac	chloroacetate
Cl ₃ ac	trichloroacetate
2-Clbz	2-chlorobenzoate
ClC ₆ H ₄ CH ₂ OCO ₂	2-chlorophenoxyethanolate
2-Cl-5-NO ₂ py	2-chloro-5-nitropyridine
2,4-Cl ₂ pac	2,4-dichlorophenoxyacetate
2,4,5-Cl ₃ pac	2,4,5-trichlorophenoxyacetate
2,4,6-Cl ₃ ph	2,4,6-trichlorophenolate
2-Clpr	2-chloropropanoate
3-Clpr	3-chloropropanoate
4-Clpt	p-chlorophenylthio
2-Clpy	2-chloropyridine
3-Clpy	3-chloropyridine
2,5-Cl ₂ py	2,5-dichloropyridine
3,5-Cl ₂ py	3,5-dichloropyridine
4,7-Cl ₂ qu	4,7-dichloroquinoline
cmp	cytidine-5'-phosphate
3-CNbz	3-cyanobenzoate
3-CNpy	3-cyanopyridine
4-CNpy	4-cyanopyridine
C ₄ O ₄	squaric acid
cpc	3-chlorophenylcyanamide
15-crown-5	macrocyclic polyethers
crot	crotonate
C ₂ S ₄	tetrathiooxalate

csmmp	2-(2-chlorophenylthio)-2-methylpropanoate
cychol	trans-1,2-cycloheptanediol
cycol	1,2-cyclohexanediol
dabco	1,4-diazabicyclo[2.2.2]octane
dacado	diacetylazine dioxime
dacpd	20 membered Schiff base derived from 2,6-diacetylpyridine and 1,3-diamino-2-hydroxyallane
daea	di-(2-aminoethyl)amine
dalthc	dialyldithiocarbamate
damet	2-diethylaminoethanolate
damol	diaminoalcohole
damp	N(2-dimethylaminoethyl) 3-aminopropanolate
dana	1,5-bis(p-methoxyphenyl)-1,3,5-pentanetrionate
dapsc	2,6-diacetylpyridine disemicarbazone
dapo	1-(N,N-dimethyl-2-aminoethyl)-1-phenyl-2-oximopropane
dapp	α -dithionaphthothionate hydroxyalkane
dbta	2,3-dioxybutan-1,4-diamin-N,N,N',N'-tetraacetate
dbz-18-crown-6	dibenzo-18-crown-6
dbztsf	dibenzotetrathiafulvalene
dbztsfH	dibenzotetrathiafulvalenium
dcp	3,5-dicarboxypyrazolate
dcpmta	(2,4-dichloro-5-methylphenylthio)acetate
dd	5,5-bis(3,7-diazanonane-1,9-diamine
ddd	5,5'-bis(3,7-dehydro-3,7-diazanonane-4,6-dione-1,9-diamine)
deamp	2,6-bis[N-(2-diethylaminoethyl)-N-ethyl-aminomethyl]-4-methylphenol
deapo	3-diethylaminopropan-1-olate
deha	disubstituted aminoalcohole
dempz	3,5-diethyl-4-methylpyrazole
den	di-(2-aminoethyl)amine
denc	N,N-diethylnicotinamide
desc	diethyldithiocarbamate
dfpp	ligand derived from 2,6-diformyl-4-chlorophenol and polyamine
dhnq	dianion of 5,8-dihydroxy-1,4-naphthoquinone
dhph	1,4-dihydrazinophthalazine
dien	diethylenetriamine
[14]-4,11-dieneN ₄	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene

dio	1,4-dioxane
diimH	Schiff base formed by the condensation of 2-aminoethanol with 2,4-pentanedione
dma	dimethylamine
dmaeoxd	N,N'-bis[2-(dimethylamino)ethyl]oxamide
dmaep	2-(2-dimethylaminoethyl)pyridine
dmapr	1,3-bis(dimethylamino)-2-propanol
dmb	2,6-dimethoxybenzoate
dmda	N,N-dimethyldiaminoalcohol
dmdc	3,4-dimethoxy- α - β -dihydrocinnamate
dmf	dimethylformamide
dmg	dimethylglyoxime
dmpa	ligand prepared by the condensation of 1,3-diaminopropan-2-ol with methyl acetoacetate
dmp	5,7-dimethyl[1,2,4]triazolo[1,5-a]pyrimidine
2,4-dnph	2,4-dinitrophenolate
2,6-dnph	2,6-dinitrophenolate
dp-7	hexyldiporphyrin-7
dpa	2,2'-dipyridylamine
dpa	2-dipropylaminoethanolate
dpba	ligand prepared by the condensation of 1,3-diaminopropan-2-ol with benzoylacetone
dpce	dipyridine crown ether
dpepd	ligand prepared by the condensation of 1,3-diaminopropan-2-ol with 3-ethoxymethylenepentane-2,4-dione
dpma	ligand prepared by the condensation of 1,3-diaminopropan-2-ol with methyl acetoacetate
dpp	3,6-di(2-pyridyl)pyridazine-N,N',N'',N'''
dppn	N,N'-dipicolinoyl-1,3-propanediamine
dpr	di(3-aminopropyl)amine
1,3-dpt	1,3-diphenyltriazene
dptd	2,5-di-(2'-methylpyridylthio)thiadiazole
dpy	di-2-pyridylmethane
dpyam	2,2'-N,N'-bispyridylamine
dpye	1,1-di-2-pyridylethanol
dtbsq	3,5-di-tert-butyl-o-semiquinate
dtic	5-(3,3-dimethyl-1-triazenyl)-imidazole-4-carboxamide
dtma	4-diethylenetriamineacetic acid
dt(metome) ₂	N,N'-(1,2-dithioxoethane-1,2-diyl)bis(methyl methionate)
dzcyc	1,4-diazacycloheptane
eaep	2-(2-ethylaminoethyl)pyridine

eap	N,N'-ethylene bis(2-hydroxyacetophenimine)
ebdta	ethylene bis(oxyethylene)diamine-N,N,N',N'-tetraacetate
ebs	N,N'-ethylene bis(salicylideneiminate)
edta	ethylenediaminetetraacetate
egta	octadentate ligand
ehmpr	2-ethyl-2-hydroxymethyl-1,3-propanediol
enaOH	2,2'-(1,2-diaminoethane)bis(2-methyl-3-butanone)oximate
enbpa	N,N'-ethylene bis(pyrrol-2-ylmethyleneaminato)
epma	N,N'-ethanediylidene bis(1-isopropyl-2-methyl-propylamine)
epthscarb	ethyl pyruvate thiosemicarbazone
etap	N-(2-ethylthioethyl)-3-aminopropanol
etapds	3-diethylamino-5-phenyl-1,2,4-dithiazolium
Etbitp	3,6-bis(N-ethyl-2-benzimidazolylthio)pyridazine
Etbzi	N-ethyl-2-hydroxybenzideniminate
Et ₅ dien	N,N,N',N'',N''-pentaethyldiethylenetriamine
Et ₂ NCO ₂	N,N-diethylcarbamate
Et ₂ NH	diethylimine
ete	2-(ethylthio)ethanol
Et ₃ en	N,N,N'-triethylenediamine
Et ₄ en	N,N,N',N'-tetraethylenediamine
Et-nso	2-[2-(diethylamino)ethylthio]ethanol
EtO	ethoxy
EtOH	ethanol
2-Etpy	2-ethylpyridine
Fac	fluoroacetate
F ₃ ac	trifluoroacetate
F ₃ acac	1,1,1-trifluoro-2,4-pentanedionate
F ₃ acpt	2,5-bis(trifluoroacetyl)cyclopentanone
F ₅ bz	pentafluorobenzoate
2-Fbzth	2-fluorobenzothiazole
fbb	difluoro{3,3'-(trimethylenedinitrilo)bis(butan-2-one oximate)}
fbo	perfluoro-tert-butoxy
F ₆ clobzim	1,1,1,5,5,5-hexafluoro-2,4-pentanedionato(N-ethyl-5-chloro-2-hydroxybenzylideneiminate)
fdmen	ligand derived from the condensation of 2,6-diformyl-4-methylphenol with 1,1-dimethylene diamine
fluf	flufenamate
fm	formiate

fmclaph	Schiff base derived from the condensation of 2,6-diformyl-4-chlorophenol and (+)1-aminoethanephosphonic acid
F ₆ mobzim	1,1,1,5,5,5-hexafluoro-2,4-pentanedionato-(N-(2-methylethyl)-2-hydroxybenzylideneimine)
fmp	ligand formed by template condensation of 2,6-diformyl-4-methylphenol with 3,6-bis((aminoethyl)thio)pyridazine
4-Fpac	4-fluorophenoxyacetate
fpb	2,6-diformyl-4-tert-butyl-phenyl di(benzoylhydrazone)
F ₆ pd	1,1,1,5,5,5-hexafluoropentane-2,4-dionate
F ₆ pdhb	1,1,1,5,5,5-hexafluoro-2,4-pentanedionato-(N-(2,2-dimethylethyl)-2-hydroxybenzylideneimine)
F ₅ pho	(pentafluorophenyl)oxy
F ₆ phobzim	1,1,1,5,5,5-hexafluoro-2,4-pentanedionato(N-phenyl-2-hydroxybenzylideneimine)
fpts	deprotonated 2-formylpyridine thiosemicarbazone
fsaen	3,3'-[1,2-ethanediyl-bis(nitrilomethylidene)-bis(2-hydroxybenzoate)]
F ₃ sbmobzim	4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionate-(N-(2-methylethyl)-2-hydroxybenzylideneimine)
fum	fumarate
gggly	glycylglycylglycine
3'-gmp	guanosine monophosphate
glth	glutathione
glu	glutarate
glygly	glycylglycinate
glyhgly	glycyl-L-histidylglycine
guan	guanine
hadt	1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane
(H)-apenol	2-(((o-hydroxy- α -methylbenzylidene)amino)ethyl)amino)ethanole
H ₂ atp	nucleoside polyphosphate
HB(3,5-i-Pr ₂ pz) ₃	hydrotris(3,5-isopropyl-1-pyrazolyl)borate
HB(pz) ₃	hydrotris-(pyrazol-1-yl)borate
H ₂ B(pz) ₂	dihydrobis(1-pyrazolyl)borate
Hbz	benzoic acid
hbzoct	3'-hydroxybenzo[1',2'-b]-1,4-diazabicyclo[2.2.2]octane
hdN ₆ O	heptadentate macrocyclic ligand N ₆ O

hebd	N,N'-bis(2-hydroxy-3-carboxybenzilidene)-1,2-diaminoethane
heioh	2-(2-hydroxyethyl)imino-3-oximobutanate
hem	chemically modified hemocyanin derivatives
hemnim	1-(2-hydroxyethyl)-2-methyl-5-nitroimidazole
hepk	N-(2-hydroxyethyl)-2-pyridinecarboxaldimine
hepra	di-(2-hydroxyethyl) n-propylamine
hesc	N,N-bis(2-hydroxyethyl)dithiocarbamate
hfc	9-hydroxy-9H-fluorene-9-carboxylate
Hfpts	2-formylpyridine thiosemicarbazone
him	hexaimidazole ligand
hip	hippurate
hmit	1,3-bis(hydroxymethyl)-2-imidazolidinethione
hmtam	hexamethylenetetramine
hnimet	2-[[[(2-hydroxy-1-naphthyl)methyl]imino]-ethanolate
hphen	2-(2-hydroxyphenyl)-1,10-phenanthroline
htr	heptanetrionate
hx	hexagonal
hxa	dihydroxamic acid
ia	iodanilate
ibpd	3,3'-imino bis(propanamidoxime)
idaH	iminodiacetate
im	imidazole
imiph	2,6-bis[[(4-imidazolylethyl)imino)methyl]-4-methylphenolate
5'-imp	inosine 5' monophosphate
impyae	1-(imidazol-4-yl)-2-[(2-pyridylmethylene)amino]ethane
ipr ₃ ph	triisopropylphosphite
ips	(N-isopropyl-2-hydroxybenzylidene)aminatate
Kbz-15-crown-5	benzo-15-crown-5 complexed potassium
L-Et	N,N,N',N'-tetrakis(2-(1-ethylbenzimidazolyl))-2-hydroxy-1,3-diaminopropane
LS	2,6-bis(4'-cyclohexyl-4'-hydroxy-2',3'-diazabuta-1',3'-dien-1'-yl)-4-methylthiophenolate
L2py	2-[2-(α -pyridyl)ethyl]imino-3-butanone oxime
maepy	2-(2-methylaminoethyl)pyridine
mal	malonate
maldpr	ligand prepared by condensation of 2-hydroxy-5-methylisophthaldehyde with 1-amino-3-N,N-dimethylaminopropane

mapycarb	bis(2-N,N-dimethylaminoethyl)pyridine-2,6-dicarboxamide 1-oxide
mapyNO	2-methylaminopyridine 1-oxide
mbrsalpr	N-methyl-N'-(5-bromosalicylidene)-1,3-propanediamine
mdd	5,7,7-trimethyl-4,8-diazaundec-4-ene-1,11-diolate
mddc	2,9-bis(methoxymethyl)-2,9-dimethyl-4,7-dioxadecanedionate
mdmsp	N-methyl-N'-(4,6-dimethoxysalicylidene)-1,3-propanediamine
Me ₃ ac	trimethylacetate
Me ₃ (9-aneN ₃)	trimethyl 1,4,7-triazacyclononane
Me ₆ -22-aneN ₄	22 membered homoleque of curtis type
Me ₂ bcen	N,N'-bis(β-carbamoylethyl)-N,N'-dimethylethylenediamine
2-Mebz	2-methylbenzoate
Me ₂ CO	acetone
Me ₃ dien	1,1,4,7,7-pentamethyldiethylenetriamine
Meen	N-methylenediamine
Me ₂ en	N,N-dimethylethylenediamine
Me ₄ en	N,N,N',N'-tetramethylethylenediamine
megt _b	1,8-bis[bis(1'-methylbenzimidazol-2'-ylmethylamino)]-3,6-dioxaoctane
Me ₄ hd	2,2,6,6-tetramethylheptane-3,5-dionate
1-Me-im	N-methylimidazole
2-Me-im	2-methylimidazole
5-Me-imH	5-methylimidazole
Menic	methyl nicotinate
Me-nso	2-[2-(dimethylamino)-ethylthio]ethanol
MeO	methoxy
MeOH	methanol
4-MeOpyNO	4-methoxypyridine-1-oxide
4-Meox	4-methyloxazole
mep	mepirizole (4-methoxy-2-(5-methoxy-3-methyl-pyrazol-1-yl)-6-methylpyrimidine
mepH	2-amino-2-methyl-1-propanol
3-Mephpz	3-methyl-5-phenylpyrazole
3,4-Me ₂ phpz	3,4-dimethyl-5-phenylpyrazole
4,5-Me ₂ phpz	4,5-dimethyl-3-phenylpyrazole
Me ₄ pip	(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)-pivaloylacetate
Me ₄ pn	N,N,N',N'-tetramethyl-1,3-propanediamine

2,2-Me ₂ pr	2,2-dimethylpropanoate
2-Mepy	2-methylpyridine
3-Mepy	3-methylpyridine
4-Mepy	4-methylpyridine
2,3-Me ₂ py	2,3-dimethylpyridine
2,5-Me ₂ py	2,5-dimethylpyridine
3,4-Me ₂ py	3,4-dimethylpyridine
3,5-Me ₂ py	3,5-dimethylpyridine
1-MepyH	1-methylpyridinium
1,2-Me ₂ pyH	1,2-dimethylpyridinium
4-MepyNO	4-methylpyridine 1-oxide
2,2,5,5-Me ₄ pyNO	2,2,5,5-tetramethylpyridine N-oxide
5-Mepz	5-methylpyrazole
3,5-Me ₂ pz	3,5-dimethylpyrazole
3,4,5-Me ₃ pz	3,4,5-trimethylpyrazole
4-Mequ	4-methylquinoline
7-Mequ	7-methylquinoline
mesalpr	N-methyl-N'-(5-methoxysalicylidene)- 1,3-propanediamine
MeSbpy	2-(3,3-dimethyl-2-thiabutyl)pyridine
Me ₂ SO	dimethylsulphoxide
Mesprp	N-methyl-N-salicylidene-1,3-propanediaminate
4-Meth	4-methylthiazole
mhbi	N-methyl-2-hydroxybenzylideneimine
mhsalim	N-(1,1-dimethyl-2-hydroxyethyl)salicylaldimine
mip	1,4-bis(1-methyl-2-imidazolyl)phthalazine
mmfp	4-methyl-2,6-bis[N-(2-methylthioethyl)- formimidoyl]phenolate
[30]-mN ₆ O ₄	30-membered 'N ₆ O ₄ ' macrocyclic Schiff base ligand
[20]-mN ₆	20-membered macrocycle tetraimine ligand
mnsalpr	N-methyl-N'-(5-nitrosalicylidene)- 1,3-propanediamine
[28]-mN ₈	28-membered 'N ₈ ' macrocyclic Schiff base ligand
mnthc	12-methyl-12-nitro-1,4,7,10-tetra-azacyclotridecane
mor	morpholine
mpp	2-methyl-1,3-di-2-pyridyl-2-propanole
mprph	2,6-bis[3-(dimethylamino)propyliminomethyl]- 4-methylphenolate
4-mpt	p-methylphenylthio
mpzdad	1,1'-(4-methylpyrazole-3,5-diyl)diacetaldehyde dioxime

msimp	N-trimethylsilyl-iminotriphenylphosphoran
mtbne	2-[7-(methoxymethyl)-1,3,5,7-tetraazabicyclo[3.3.1]-nonan-3-yl]ethanolate
naa	nicotinic acid amide
α -nac	α -naphthylacetate
napr	naproxen (6-methoxy- α -methyl-2-naphthaleneacetic acid
nba	bis(β -diketone) ligand based on the larger 2,7-naphthalenediyl bis(methylene) bridge
N ₃ bz	benzotriazole
N-chsalim	N-cyclohexylsalicylideneaminat
N-Etsala	N-ethylsalicylaldimine
nmedtb	N,N,N',N'-tetrakis[(1-methyl-2-benzimidazolyl)methyl]- 1,2-ethanediamine
N-Mesala	N-methylsalicylaldimine
2-NH ₂ pm	2-aminopyrimidine
nic	nicotinamide
nipr	3-[1-(4-nitroimidazolyl)]propionate
NMe ₄	tetramethylammonium
[24]-N ₆ O ₂	1,13-dioxa-4,7,10,16,19,22-hexaazacyclotetracosane
2-NO ₂ bz.	2-nitrobenzoate
4-NO ₂ bz	4-nitrobenzoate
npsalim	N-n-nitrophenylsalicylaldiminate
NPr ₄	tetrapropylammonium
nthy	1,8-naphthyridine
Obim	deprotonated form of 2- α -hydroxybenzylbenzimidazole
2-Obza	o-hydroxybenzylamine
2-O-6-Clpy	6-chloro-2-hydroxypyridine
ocoxb	cyclo-octahydroooxooctacosa-oxooctadecaborate
oct	octanoate
N-oed	1-(2-hydroxyethyl)-3,5-dimethylpyrazole
odt	2-oxo-1,3-dithiole-4,5-dithiolate
OHbim	2- α -hydroxybenzylbenzimidazole
3-OHbz	3-hydroxybenzoic acid
6-OHpur	6-hydroxypurinate
8-OHqu	8-hydroxyquinolate
ophsalim	N-(2-hydroxy-2-phenylethyl)salicylideneiminate
2-Opy	2-pyridonate
2-O-3-Etpy	3-ethyl-2-pyridonate
or	orthorhombic
ox	oxalate

oxd	oxamidate
oxpn	N,N'-bis(3-aminopropyl)oxamide
otbzb	2-oxyethylimino-2-oxy-1-benzaldehydate
pa	tetradentate phthalazine
paaan	2,2-dimethyl-7-(phenylimino)-3,5,7-octanetronate
paaet	2,2-dimethyl-7-(ethylimino)-3,5-octanedionate
paapnan	2,2-dimethyl-7-(4-nitrophenyl(imino))-3,5,7-octanetronate
paapr	2,2-dimethyl-7-(n-propylimino)-3,5-octanedionate
pamph	2,6-bis(bis(2'-pyridylethyl)aminomethyl)phenol
pan	1-(2-pyridylazo)-2-naphtholate
pap	1,4-di(2'-pyridyl)aminophthalazine
papfs	1,4-di-(4',6-dimethylpyridin-2'-ylamino)-phthalazine
paphy	pyridine-2-carbaldehyde 2'-pyridylhydrazone
pap4me	1,4-bis(2-pyridylamino)phthalazine
pap6me	1,4-bis((6-methylpyrid-2-yl)amino)phthalazine
pap46Me	1,4-bis(4,6-dimethyl-2-pyridylamino)phthalazine
pbsalim	Schiff base prepared from salicylaldehyde and m-phenylenediamine
pca	phenylcyanamide
pcdp	Schiff base derived from pyrrole-2-carboxaldehyde and 3-aminopropanole
pcib	p-chlorophenoxyisobutyrate
pcdno	2,6-dicarboxylate-N-oxide
pdnm	phenyldinitromethanate
pdta	m-phenylenediamine-N,N,N',N'-tetra-acetic acid
pdtb	N,N,N',N'-tetrakis(benzimidazol-2-ylmethyl)-1,3-propane- diamine
pea	bis(2-(2-pyridyl)ethyl)amine
penas	D-penicillamine disulfide
pfpac	(pentafluorophenoxy)acetate
Ph	phenyl
phac	phenylacetate
phba	N-phenyl(2-hydroxybenzylidene)aminatate
phbi	N-n-propyl-2-hydroxybenzylideneiminatate
PhCN	benzonitrile
phed	diphenylethanedione dioxime
phen	1,10-phenanthroline
Ph ₄ mdP	tetraphenylmethylenediphosphine
Ph ₃ mgly	N-triphenylmethylglycine
PhOH	phenol
Ph ₂ P	diphenylphosphine

Ph ₃ P	triphenylphosphine
Ph ₃ PO	triphenylphosphine oxide
4-phpyNO	4-phenylpyridine-1-oxide
pht	phthalate
phtN ₆	1,4-dihydrazinophthalazine-bis(2-pyridine)acetalimine
pia	N(CH ₂) ₃ OH
p-Ian	p-iodoaniline
piapr	N-(picolinoyl)-3-amino-1-propoxide
pib	phenoxyisobutyrate
piol	2,3-dimethyl-2,3-butanediol (pinacol)
pipcl	ligand derived from 2,6-dipiperazine and p-chlorophenol
pipH	piperidinium
pkph	di-2-pyridylketone[phenyl(semicarbazono)acetyl]hydrazone
plamph	N-pyridoxylideneaminomethyl-phosphonic acid
pmaH	analogue of bleomycin
pmp	2,6-bis(N-(2-pyridylmethyl)formidoyl)-4-methylphenol
pmk	<i>trans-trans</i> bis(2-pyridylmethyl)ketazine
1,3-pn	1,3-diaminopropane
pN ₆ O	phenoxo bridged binucleating ligand
pnthpy	2,7-bis(2-pyridyl)-1,8-naphthyridine
poapH	4-(phosphonomethyl)-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinane
poh	5-phosphopyridoxylidenehistaminatate
por	disubstituted porphyrine
ppd	3,6-bis(1-pyrazolyl)pyridazine
ppdn	N,N'-dipicolinoyl-1,3-propane)-bis(sulphate)
ppdme	3,6-bis(3,5-dimethyl-1-pyrazolyl)pyridazine
pprz	2,5-bis(2'-pyridyl)pyrazine
pr	propionate
prahmft	tetra Schiff base macrocycle formed by condensation of propane-1,3-diamine with 2-hydroxy-5-methylisophthalaldehyde
pramcres	2,6-bis[(bis[2-(1-pyrazolyl)ethyl]amino]methyl-p-cresolate
prl	pyrrolidone
Pr-nso	2-[2-(di n-propylamino)ethylthio]ethanol
2-PrOH	2-propanol
proxyl	2,2,5,5-tetramethylpyrrolinyl-1-oxy
(prp) ₂ en	N,N'-ethylene bis(2-hydroxypropiofenoneiminate)
ptp	o-phospho-DL-threonine-pyridoxal Schiff base
py	pyridine
pyaa	N-(2-pyridinyl)-acetoacetamide

pyames	2-[(2-pyridylmethyl)amino]ethylsulphinate
3-pycac	3-pyridylcarbinol
pycaro	N,N'-bis(2'-pyridinecarboxamide 1'-oxide)-1,2-ethane
pydca	pyridine-2,6-dicarboxylate
pydiox	2,2-bis(2-pyridyl)-1,3-dioxolane
pyeth	2-[2-(2-pyridyl)ethylthio]ethanol
pymcres	2,6-bis[(2-pyridyl)methyliminomethyl]-p-cresolate
pyNO	pyridine 1-oxide
pypep	ligand related to bleomycin
pyqux	2-(2'-pyridyl)quinoxaline
pyra	pyrazine
4-pyx	4-pyridoxic acid
pz	pyrazole
pzc	pyrazine-2-carboxylate
pzdad	pyridazine-3,6-dicarbalddehyde dioximate
qu	quinoline
qpy	quinquepyridine
rib	riboflavin
sal	salicylate
sal- β -ala	N-salicylidene- β -alaninate
salal	salicylaldehyde
salapr	3-(salicylideneamino)-1-propanolate
(salim) ₂ pr	N,N'-propylene bis(salicylideneiminate)
salpa	N-(2-hydroxypropyl)salicylaldimine
salphala	N-salicylidene-L-phenylalaninate
salqu	8-(salicylideneamino)quinoline
sata	1,2,3,4-tetrakis(salicylideneamino)-2,3-dimethylbutane
sb	Schiff base ligand derived from 1,3-diaminopropane-2-ol and acetylacetone
sbm	dinucleating Schiff base macrocycle
sbN ₆ O	ligand was prepared by a template reaction from 2,6-diacetylpyridine and 1,3-diamino-2-hydroxypropane
sbzph	Schiff-base ligand involving sulphides and benzimidazoles in addition to phenoxide
scsal	semicarbazone of salicylaldehyde
sd	ligand formed by the condensation of salicylaldehyde with 1,3-diamino-2-propanol
sdap	1,3-bis(salicylideneamino)propan-2-ol
sdb	Schiff base formed from the condensation of salicylaldehyde and 1,4-diamino butane-2-ol

sdp ₃	ligand formed by the condensation of salicylaldehyde with 1,5-diamino-3-pentanol
shbr	N-salicylidene-2-hydroxy-5-bromobenzylamine
smp	6-thio-9-methylpurine
spca	N ³ -salicyloylpyridine-2-carboxamidrazone
S ₄ tp	2,5,9,12-tetrathia[13](2,5)thiophenophane
S ₅ tp	pentathia-thiophenophane
suc	succinate
suqn	5-sulphonic-8-quinolate
tabm	5,5-bis(4'-amino-2-azabutyl)-1,9-diamino-3,7-diazanonane
tacac	1,4,7-triazacyclononane-1-acetic acid
tach	1,5,9,13-tetra-azacyclohexadecane
taec	N,N',N'',N'''-tetrakis(2-aminoethyl)-1,4,8,11-tetra-azacyclotetradecane
taet	N,N',N'',N'''-tetra(2-aminoethyl)-1,1,2,2-ethanetetraamide
taep	1,4,8,12-tetra-azacyclopentadecane
tart	dl-tartrate
tba	thiobenzamide
tbi	thiobenzimide
tbne	2-(1,3,5,7-tetraazabicyclo[3.3.1]nonan-3-yl)ethanolate
tbnp	3-(1,3,5,7-tetraazabicyclo[3.3.1]nona-3-yl)propanolate
tcb	tetracarboxylatobenzene
tcc	tetrachloro-o-catecholate
tcnq	7,7,8,8-tetracyanoquinodimethane
tcoa	1,5,8,12,15,22,26-octaazatricyclo[17.9.2.2 ^{5,15}]dotriaconta
tempo	2,2,6,6-tetramethylpiperidiny-1-oxy
terpy	2,2':6',2''-terpyridine
tetac	1,4,7-trimethyl-1,4,7-triazacyclononane
tetb	(μ)-5,5,7,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
tfmd	8,8,8-trifluoro-7-(trifluoromethyl)-5-methyl-4-azaoct-4-ene-1,7-diolate
tfmd'	9,9,9-trifluoro-8-(trifluoromethyl)-6-methyl-5-azanon-5-ene-1,8-diolate
tgly	N-tosylglycinate
thf	tetrahydrofuran
thp	2(1H)-tetrahydropyrimidinone
tlma	di-p-tolylmethylamide
tmsfs	tetra(methylthio)tetrathiafulvalene
tms	tetramethylene sulfoxide
tmp	2,4-diamino-5-(3',4',5'-trimethoxybenzyl)pyrimidine (trimetho-prim)

tmtacd	2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene
tol	toluene
tolm	tolmetin (1-methyl-5-(<i>p</i> -toluoyl)-1H-pyrrole-2-acetic acid)
topcb	ligand derived from 1,4,7,10-tetraoxa-13-azacyclopentadecane with 5'-chlorocarbonyl-2,2'-bipyridine
tos	1,3-propanediyl ditosylate
tp	binucleating ligand containing μ -alkoxo backbones amido-pyridyl "end" groups
tpe	1,1,2,2,-tetrakis(2-pyridyl)ethylene
tped	N,N,N',N'-tetrakis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]-1,2-ethylenediamine
tpma	tris[(2-pyridyl)methyl]amine
tpmc	N,N',N'',N'''-tetrakis(2-pyridylmethyl)-1,4,8,11-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane
tpmta	1,4,8,11-tetrakis(2-pyridylmethyl)-1,4,8,11-azacyclopentadecane
tpt	teraphthalate
tpydax	N,N,N,N'-tetrakis[2-(2-pyridyl)ethyl]- α,α' -diamino- <i>m</i> -xylene
tr	triclinic
tren	2,2',2''-triaminoethylamine
trienMe6	N,N-bis(dimethylaminoethyl-N,N'-diethyl)-1,2-diaminoethane
trg	trigonal
tris	tris(hydroxymethyl)methylamine
tsval	N-tosylvalinate
ttc	cystamine-N,N,N',N'-tetraacetate
ttc6	tropocoronand ligand
ttha	triethylenetetra-aminehexa-acetate
5'-ump	uridine-5'-monophosphate
upm	macrocyclic ligand derived by condensation of 4-methyl-2,6-diformylphenol with 1,3-diaminopropane
vlp	valproate (2-propyl-ethanoic acid)
xba	3,3'-[1,3-phenylene bis(methylene)] bis(2,4-pentanedione)

1. INTRODUCTION

Copper is a tough, soft and ductile reddish metal. The dipositive state is the most important one for copper. Most Cu(I) compounds are fairly readily

oxidized to Cu(II) compounds, but further oxidation to Cu(III) is more difficult. The d^9 configuration makes Cu(II) subject to Jahn-Teller distortion if placed in an environment of cubic symmetry, and this has a profound effect on all its stereochemistry.^{1,2} The chemistry of copper compounds has been extensively investigated, and the relationship between structure and reactivity, ranging from industrial catalysis to biochemical activity, is of major importance.

Dimeric Cu(II) compounds, especially Cu(II) acetate type compounds constitute a class of compounds with long history. The earliest quotation to copper acetate is from the year 1594.³

In spite of this fact, attempts to specify the magnetic interaction in detail of Cu(II) acetate have been plagued by controversy and there are still differences of opinion.³⁻⁸ In a recent, extensive review article only some ten Cu(II) acetate type dimers were mentioned.^{9,10}

Many structural studies of copper compounds have been carried out, and have been sporadically summarized in annual reports.^{11,12} There are complete reviews of the crystallographic and structural data of mixed-valence, Cu(I)-Cu(II),¹³ and Cu(I) compounds.¹⁴ To our knowledge, no complete review of the crystallographic and structural data of Cu(II) compounds exists. A comprehensive overview of mononuclear Cu(II) structural chemistry has also been reviewed recently by us.^{15,16} Complete review of the crystallographic and structural data of dimeric Cu(II) compounds has not yet appeared. This review includes nine hundred published dimeric Cu(II) structures which have been analyzed and classified in order to assist in understanding the stereochemical interactions in the coordination sphere of the Cu(II) species.

The structures have been classified according to the type of bridge between two Cu(II) atoms. The referencing is in the order of increasing copper-copper separation. Under varying conditions Cu(II) has been isolated with coordination number from four to six, with five being by far the most common.

2. DIMERIC Cu(II) COMPOUNDS

2.1 Cu(II) Acetate Type

Crystallographic and structural data for two hundred Cu(II) acetate type dimers are gathered in Table I. A survey of green (blue-green) Cu(II) acetate type dimeric complex units containing either a CuO₅ (Table IA), CuO₄N (Table IB), CuO₄P (Table IC), CuO₄N, CuN₄Cl, CuO₃N₂, CuN₄, or

TABLE I Crystallographic and structural data for copper(II)acetate type dimers^a

Compound (color)	Cryst. cl. space Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å] Cu - out of the plane [Å]	L-Cu-L [°]	Ref.
A: CuO₅								
[Cu(pr) ₂ -0.5dio] ₂ (blue green)	m P2 ₁ /c 4	9.009(2) 8.137(2) 15.121(4)	109.92(5)	CuO ₅	O _{eq} ^b dioO _{ap}	2.5634(4) not given	O,O ^b not given	17
[Cu(but) ₂] ₂ ^c (bright green)	tr P-1 2	9.004(5) 11.736(5) 5.162(5)	94.7(5) 71.3(5) 95.2(5)	CuO ₅	O _{eq} O _{ap}	2.565 not given	O,O not given	18
[Cu(bz) ₂ -0.5dio]idio (blue green)	tg P ₄₁ /ncc 8	14.6786(15) 19.3689(28)		CuO ₅	O _{eq} dioO _{ap}	2.569(3) not given	O,O not given	19
[Cu(pr) ₂ H ₂ O] ₂ (blue green)	m P2 ₁ /c 4	15.102(7) 17.186(5) 15.190(4)	94.24(3)	CuO ₅	O _{eq} H ₂ O _{ap}	2.575(4) 0.185	O,O 92.5(6, 6.3) 169.0(6, 4)	20
[Cu(tgly) ₂] ^c (green)	m P2 ₁ /n 4	24.655(3) 7.697(2) 12.378(3)	87.34(8)	CuO ₅	O _{eq} H ₂ O _{ap} O _{ap}	2.589(5) 0.188(4) 2.577(3) 0.171	O,O O _{eq} ,O _{eq} O _{eq} ,O _{ap}	21
[Cu(Me ₃ PhSi(CO ₂) ₂ H ₂ O) ₂] (blue green)	tr P-1 2	14.067(6) 11.952(3) 14.147(9)	90.33(4) 130.80(4) 68.91(2)	CuO ₅	O _{eq} H ₂ O _{ap}	2.578(1) 0.13	O _{eq} ,O _{eq} 169.8(2, 3.6)	22
[Cu(pr) ₂] ₂ ^c (green)	tr P-1 2	5.19(2) 8.58(5) 9.69(5)	87.5(3) 90.0(3) 75.5(3)	CuO ₅	O _{eq} O _{ap}	2.578(4) 0.22	O,O 83.2(4, 7)	23
[Cu(fm) ₂ -0.5dio] ₂ ^d (not given)	tr P-1 4	6.62(1) 9.05(2) 13.31(2)	112.5 98.5 112.5	CuO ₅	O _{eq} dioO _{ap}	2.58(1) 0.17 2.58(1) 0.20	not given not given	24

[Cu(piv) ₂] ₂ (green)	tr P-1 2	10.078(5) 11.516(2) 11.895(2)	70.87(2) 89.49(3) 75.64(3)	CuO ₅	O _{eq} O _{ap}	1.95(2, 7) 2.34(2, 2)	2.580(2) not given	O _{eq} ·O _{eq} O _{eq} ·O _{ap}	89.5(8, 1.4) 169.4(8, 2.7) 95.2(8, 15.6)	25
[Cu(ac) ₂ acH] ₂ (blue green)	m P ₂ /n 2	15.153(2) 7.772(1) 8.229(1)	103.08(1)	CuO ₅	O _{eq} HacO _{ap}	1.967(2, 31) 2.197(2)	2.581(1) 0.118	O _{eq} ·O _{eq} O _{eq} ·O _{ap}	89.5(1, 4) 95.2(1, 6.0)	26
[Cu(but ¹) ₂] ₂ ^c (green)	tr P-1 1	5.178(1) 8.497(2) 14.415(5)	88.25(2) 85.95(2) 75.58(2)	CuO ₅	O _{eq} O _{ap}	1.95(2, 5) 2.26(2)	2.582(5) not given	O _{eq} ·O _{eq} O _{eq} ·O _{ap}	89.4(9, 1.7) 168.4(9, 7) 95.6(9, 15.4)	25
[Cu(val) ₂] ₂ ^c (green)	tr P-1 1	5.176(1) 9.356(8) 11.183(7)	74.18(5) 89.69(3) 89.69(4)	CuO ₅	O _{eq} O _{ap}	1.964(3, 44) 2.216(2)	2.5822(6) not given	O _{eq} ·O _{eq} O _{eq} ·O _{ap}	89.5(1, 1.1) 169.6(1, 0) 95.2(1, 15.6)	25
[Cu(2-C ₆ H ₄ CH ₂ OCO) ₂] ₂ ^c (not given)	m P ₂ /c 2	11.587(3) 5.084(2) 29.600(6)	103.76(2)	CuO ₅	O _{eq} O _{ap}	1.965(5, 59) 2.169(5)	2.583(2) not given	O _{eq} ·O _{ap} O _{ap}	92.2(2, 16.5) 169.7(2, 2)	27
[Cu(but ²) ₂] ₂ ^c (not given)	tr P-1 1	9.035(2) 5.192(2) 11.695(3)	85.88(2) 95.04(2) 109.32(2)	CuO ₅	O _{eq} O _{ap}	1.964(2, 46) 2.223(2)	2.584(1) not given	O _{ap}	92.4(1, 18.8) 167.0(1, 4.8)	28
[Cu(but ¹) ₂] ₂ ^c (green)	tr P-1 1	5.179(2) 10.548(1) 12.355(2)	101.64(1) 97.76(2) 96.71(2)	CuO ₅	O _{eq} O _{ap}	1.94(1, 6) 2.24(1)	2.584(5) not given	O _{eq} ·O _{eq} O _{eq} ·O _{ap}	89.4(2, 4) 168.3(2, 2) 95.7(2, 15.7)	29
[Cu(Me ₂ acr) ₂ (EtOH)] ₂ ^d (not given)	tr P-1 2	10.484(2) 12.296(2) 14.303(3)	65.97(1) 71.69(1) 68.93(1)	CuO ₅	O _{eq} EtHO _{ap}	1.962(3, 15) 2.154(4)	2.586(1) 0.185	O _{eq} ·O _{eq} O _{eq} ·O _{ap}	89.5(1, 1.0) 169.4(1, 1) 95.3(1, 8)	30
[Cu(mptp) ₂] ₂ ^c (dark green)	m C ₂ /c 4	39.71(2) 5.268(2) 21.68(1)	114.66(2)	CuO ₅	O _{eq} O _{ap}	1.965(3, 22) 2.156(4)	2.601(2) 0.185	O _{eq} ·O _{ap} O _{eq} ·O _{eq}	169.0(2, 0) 95.5(1, 2.1)	31
[Cu(ac) ₂ (iph)] ₂ (brown)	tr P-1 1	13.616(4) 8.193(3) 8.140(3)	87.54(3) 97.32(3) 96.17(3)	CuO ₅	O _{eq} ihpO _{ap}	1.963(2, 27) 2.175(2)	2.587(1) 0.183	O _{eq} ·O _{ap} O _{eq} ·O _{eq}	95.6(5, 16.9) 89.5(1, 1.2) 169.3(1, 1)	32
[Cu(i-val) ₂] ₂ ^c (blue)	tr P-1 1	5.191(1) 10.840(2) 11.063(2)	83.12(1) 86.92(2) 85.60(2)	CuO ₅	O _{ap} O _{ap}	1.959(5, 51) 2.227(4)	2.588(2) not given	O _{ap} O _{ap}	88.7(2, 9.5) 169.6(2, 4)	33

TABLE I (Continued)

Compound (color)	Cryst. cl. space Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	$Cu-L$ [Å]	$Cu-Cu$ [Å] Cu - out of the plane [Å]	$L-Cu-L$ [°]	Ref.
[Cu(ac) ₂ MeOH] ₂ (blue green)	m P2 ₁ /n 2	8.129(2) 7.447(1) 13.332(1)	92.21(1)	CuO ₅	O _{eq} MeHO _{ap}	2.596(1) 0.18	O _{eq} O _{eq} O _{eq} O _{ap} 89.5(1,4) 95.3(1,1.5)	26
[Cu(ptiba) ₂ (EtOH)] ₂ ^d (dark green)	tr P-1 2	13.313(4) 14.281(4) 15.446(4)	116.64(2) 99.63(2) 101.16(2)	CuO ₅ CuO ₅	O _{eq} EtHO _{ap} O _{eq} EtHO _{ap}	2.596(1) not given 2.616(1) not given	O _{eq} O _{eq} O _{eq} O _{ap} O _{eq} O _{eq} O _{eq} O _{eq} O _{eq} O _{ap} O _{eq} O _{ap} 89.5(2,1.6) 169.5(2,2.3) 95.2(2,2.3) 89.4(2,1.8) 168.5(2,1) 95.7(2,2.9)	31
[Cu(piv) ₂ (pivH)] ₂ (green)	m I2/c 4	19.352(5) 11.704(2) 19.521(2)	116.02(2)	CuO ₅	O _{eq} HpivO _{ap}	2.596(2) not given	O _{eq} O _{eq} O _{eq} O _{eq} 89.5(5,1.2) 168.7(4,3) 95.5(3,6.8)	29
[Cu(dmb)(ac)(H ₂ O)] ₂ (blue)	m P2 ₁ /a 2	7.898(2) 20.334(6) 8.148	101.31(3)	CuO ₅	O _{eq} H ₂ O _{ap}	2.597(1) ~ 0.0	O _{eq} O _{eq} O _{eq} O _{eq} O _{eq} O _{ap} O _{eq} O _{ap} 89.51(9,86) 169.33(9,24) 95.3(1,2.0)	34
[Cu(dmpa) ₂ dmf] ₂ (red)	tr P-1 1	12.747(1) 14.596(8) 8.6135(4)	80.05(2) 87.39(2) 74.55(1)	CuO ₅	O _{eq} dmfO _{ap}	2.598(1) 0.19	O _{eq} O _{eq} O _{eq} O _{eq} 89.5(2,8) 168.9(2,1) 95.6(2,6.4)	35
[Cu(2-Clbz) ₂ (H ₂ O)] ₂ (green)	m P2 ₁ /n 2	7.214(2) 19.554(4) 10.877(4)	103.82	CuO ₅	O _{eq} H ₂ O _{ap}	2.599(1) not given	O _{eq} O _{ap} O _{eq} O _{eq} 89.4(1,2.5) 168.6(1,0) 95.6(1,1.2)	36
[Cu(dmfa) ₂ (dmf)] ₂ (olive green)	m P2 ₁ /c 2	10.710(1) 10.4430(5) 29.222(3)	98.08(1)	CuO ₅	O _{eq} dmfO _{ap}	2.601(3) 0.18	O _{eq} O _{ap} O _{eq} O _{eq} 89.5(4,2.4) 169.1(4,1) 95.4(4,2.9)	37
[Cu(2-phbz) ₂ (2-phbzH)] ₂ (dark green)	m P2 ₁ /c 2	12.333(2) 15.392(2) 17.327(2)	98.55(1)	CuO ₅	O _{eq} HphbzO _{ap}	2.602(1)	O _{eq} O _{eq} O _{eq} O _{eq} 85.9(1,1.2) 169.2(1,2) 95.4(1,6.3)	38
[Cu(C ₃ H ₅ COO) ₂ (C ₃ H ₅ COOH)] ₂ (brown)	m P2 ₁ /c 2	9.015(2) 19.704(4) 9.034(2)	116.96	CuO ₅	O _{eq} O _{ap}	2.602(2) not given	O _{eq} O _{ap} O _{eq} O _{eq} 89.5(2,8) 169.0(2,1) 95.5(1,4.7)	39

[Cu(bz) ₂ MeOH] ₂ ·2MeOH (not given)	ig R3 18	25.967(5) 13.628(8) 26.924(8)	CuO ₅	O _{eq} MeHO _{ap} 2.24(1)	1.95(2, 2) 2.24(1)	2.606(3) not given	O,O	not given	40
[Cu(but) ₂ H ₂ O] ₂ (blue green)	m C2/c 8	14.615(5) 25.15(18)	CuO ₅	O _{eq} H ₂ O _{ap}	1.939(5) 2.16(1)	2.608(3) not given	O,O	not given	20
[Cu(ac) ₂ (cp)] ₂ ·C ₆ H ₁₂ (dark green)	tr P-1	11.103(4) 11.865(6)	CuO ₅	O _{eq} cpI _o _{ap}	1.958(6, 6) 2.138(5)	2.609(2) 0.207	O _{eq} O _{eq}	89.5(3, 1.0) 168.6(2, 2)	41
[Cu(ac) ₂ (EtOH)] ₂	1	9.912(3)	CuO ₅	O _{eq}	1.963(8, 23)	2.609(1)	O _{eq} O _{ap}	95.7(2, 3.5)	42
[Cu(ac)(mdmsp)] ₂ (blue green)	tr P-1 2	11.470(3) 11.202(3) 10.771(3)	CuO ₅	O _{eq} EtHO _{ap}	2.198(9)	not given	O _{eq} O _{eq}	89.5(3, 1.8) 168.9(4, 7)	42
			CuO ₃ N ₂	O N O _{br} O _{br}	1.910(8) 1.990(9, 65) 1.980(7) 2.570(7)	3.475(1)	O _{eq} O _{ap}	not given	43
[Cu(pr) ₂ H ₂ O] ₂ (not given)	m P2 ₁ /b 8	15.314(7) 15.109(7) 17.443(8)	CuO ₅	O _{eq} H ₂ O _{ap}	1.92-2.01 2.11-2.18	2.61 not given		not given	43
[Cu(suc) ₂ H ₂ O] ₂ ·2H ₂ O (not given)	tr P-1 2	6.437(11) 7.623(4) 8.081(5)	CuO ₅	O _{eq} H ₂ O _{ap}	1.975(7, 15) 2.102(9)	2.610(1) 0.197	O _{eq} O _{ap}	90.0(3, 5) 168.5(3, 1)	44
[Cu(bz) ₂ (Hbz)] ₂ (blue green)	m P2 ₁ /n 2	15.283(2) 11.716(2) 10.783(1)	CuO ₅	O _{eq} HbzO _{ap}	1.965(4, 37) 2.197(2)	2.610(1) 0.188(2)	O _{eq} O _{ap}	92.5(3, 2.1) 89.5(1, 6) 169.0(1, 1)	45
[Cu(dmdc) ₂ MeOH] ₂ (green)	tr P-1 1	15.084(2) 11.820(1) 7.5253(7)	CuO ₅	O _{eq} MeHO _{ap}	1.963(2, 8) 2.206(2)	2.612(5) 0.1883	O _{eq} O _{ap}	95.4(1, 5.4) 89.48(9, 84) 168.95(8, 4)	46
[Cu(ac-β-ala) ₂ (H ₂ O)] ₂ ·2H ₂ O (green)	m P2 ₁ /c 2	9.120(1) 18.527(3) 8.978(3)	CuO ₅	O _{eq} H ₂ O _{ap}	1.968(4, 11) 2.156(4)	2.613(1) not given	O _{eq} O _{ap}	89.5(2, 1.0) 168.6(2, 1)	47
[Cu(2,3-C ₁₄ H ₁₄ NCO ₂) ₂ ·dmf] ₂ (dark green)	m P2 ₁ /c 2	8.940(2) 14.870(2) 23.394(3)	CuO ₅	O _{eq} (dmf)O _{ap}	1.97(1, 1) 2.16(1)	2.613(2) not given	O _{eq} O _{ap}	95.7(1, 5.5) 89.4(3, 6) 168.5(3, 1)	48

TABLE I (Continued)

Compound (color)	Cryst. cl. space Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	$Cu-L$ [Å]	$Cu-Cu$ [Å] Cu - out of the plane [Å]	$L-Cu-L$ [°]	Ref.
$[Cu(ac)_2dmf]_2$ (blue green)	tr P-1 1	8.002(1) 8.140(1) 9.394(2)	105.85(2) 92.31(2) 113.84(1)	CuO ₅	O _{eq} dmfO _{ap}	2.614(1) 0.20	89.4(1, 1.1) 95.8(1, 3.2)	26
$[Cu(dimpa)_2(dmef)]_2$ (green)	m P2 ₁ /n 2	22.549(2) 16.598(1) 8.4222(2)	95.865(8)	CuO ₅	O _{eq} dmfO _{ap}	2.614(1) 0.20	89.4(1, 7) 168.5(1, 3) 95.6(1, 9.4)	35
$[Cu(ac)_2(H_2O)]_2$ (green)	m C2/c 4	13.167(4) 8.563(2) 13.862(7)	117.019(2)	CuO ₅	O _{eq} H ₂ O _{ap}	2.6143 not given	88.7(1, 2.3) 168.70(7)	49
$[Cu(4-NO_2bz)_2(H_2O)]_2 \cdot 4H_2O$ (green)	tr P1 2	6.716(3) 11.797(4) 12.479(2)	99.44(4) 103.71 96.32(3)	CuO ₅	O _{eq} H ₂ O _{ap}	2.615 not given	O,O not given	50
$[Cu(ac)_2(H_2O)]_2(acH)_2$ (green)	tr P-1 2	7.530(1) 8.118(2) 8.657(2)	94.29(4) 94.34(7) 105.59(4)	CuO ₅	O _{eq} H ₂ O _{ap}	2.616(1) not given	O,O not given	51
$[Cu(F_3bz)_2(dio)_0.5]_2 \cdot 2dio$ (not given)	tr P1 1	8.926(1) 12.175(2) 11.636(2)	96.49(1) 100.51(1) 111.22(1)	CuO ₅	O _{eq} (dio)O _{ap}	2.616(1) 0.192	O,O not given	52
$[Cu(ac)_2(H_2O)]_2$ (dark green)	m C2/c 4	13.168(2) 8.564(2) 13.858(2)	117.02(1)	CuO ₅	O _{eq} H ₂ O _{ap}	2.616(1) not given	89.5(2, 1.6) 168.8(2, 2) 95.6(2, 2.8)	53
$[Cu(asp)_2]_2^c$ (blue)	m P2 ₁ /c 4	8.208(3) 10.39(2) 21.56(1)	104.74(5)	CuO ₅	O _{eq} O _{ap}	2.617(3) not given	O _{eq} O _{ap} 89.5(4, 1.6) 95.5(3, 1.7)	54
$[Cu(2,4-Cl_2pac)_2dio]_2 \cdot 3dio$ (not given)	tr P1 2	12.557(1) 14.391(2) 9.537(11)	112.56(3) 99.62(3) 92.77(3)	CuO ₅	O _{eq} dioO _{ap}	2.620 not given	89.5(-, 1.1)	55
$[Cu(dmb)_2(H_2O)]_2$ (green)	or Cmca 4	27.890(7) 7.098(3) 19.691(5)	92.77(3)	CuO ₅	O _{eq} H ₂ O _{ap}	2.620(1) 0.37	89.981, 1.9) 168.5(1) 95.8(1, 6)	34

[Cu(phac)urea] ₂ ^d (green)	tr P-1 4	11.854(5) 15.524(4) 19.794(6)	106.82(2) 87.64(3) 81.32(3)	CuO ₅	O _{eq} ureaO _{ap}	1.964(4, 22) 2.148(5)	2.623(1) 0.202	O,O	not given	56
[Cu(α-nac) ₂ (dmf) ₂ ·(dmf) ₂ ·H ₂ O (green)	tr P-1 1	11.912(4) 13.626(2) 10.040(3)	95.03(2) 114.8(3) 73.58(3)	CuO ₅	O _{eq} ureaO _{ap} dmfO _{ap}	1.964(5, 14) 2.155(5) 1.969(8, 28) 2.147(7, 16)	2.630(1) 0.196 2.623(1) 0.20	O,O	not given	57
[Cu(C ₁₃ H ₉ F ₃ NCO ₂) ₂ dmf] ₂ (dark green)	m P ₂ /i/a 2	26.955(4) 12.736(2) 9.252(2)	102.82(2)	CuO ₅	O _{eq} dmfO _{ap}	1.97(2, 1) 2.15(2)	2.623(3) not given	O _{eq} O _{eq} O _{eq} O _{ap}	89.4(5, 2.5) 168.0(4, 2.3) 94.3(4, 7.8)	48
[Cu(ac)urea] ₂ ·2H ₂ O (dark green)	m P ₂ /i/c 2	8.758(1) 14.152(2) 8.502	109.01(1)	CuO ₅	urcaO _{eq} O _{ap}	1.970(2, 14) 2.135(1)	2.624(1) 0.200	O,O	89.4(1, 1.3) 168.0(1, 0) 96.0(1, 1.3)	58
[Cu(csmpr) ₂ (H ₂ O)] ₂ (green)	tr P-1 2	7.340 14.863(5) 22.963(8)	104.33(2) 98.18(2) 102.18(2)	CuO ₅	O _{eq} H ₂ O _{aq}	1.971(7, 16) 2.169(7, 14)	2.624(2) not given	O _{eq} O _{eq}	89.5(2, 3.2) 167.8(3, 1.4)	59
[Cu(2-Brbz)2(H ₂ O)] ₂ (green)	m P ₂ /i/n 2	7.384(6) 20.02(2) 11.04(1)	105.4(1)	CuO ₅	O _{eq} H ₂ O _{aq}	1.99(2, 3) 2.17(2)	2.624(7) 0.20	O _{eq} O _{eq}	90(1, 2) 168.5(1, 0.5) 96(1, 1)	60
[Cu(mdde)H ₂ O] ₂ (green)	tr P-1 1	11.506(4) 7.149(2) 13.085(3)	101.01(1) 114.06(2) 90.85(2)	CuO ₅	O _{eq} H ₂ O _{ap}	1.953(4, 16) 2.144(3)	2.626(2) not given	O _{eq} O _{eq} O _{eq} O _{eq}	89.5(2, 1.0) 95.7(2, 2.6)	61
[Cu(bz) ₂ Me ₂ SO] ₂ (dark green)	m C ₂ /c 4	19.030(8) 15.494(9) 23.828(11)	103.73(4)	CuO ₅	O _{eq} Me ₂ SO _{ap}	1.96(1, 4) 2.17(1, 1)	2.627(2) 0.202	O _{eq} O _{eq}	89.4(4, 2.8) 168.2(4, 2.8)	62
[Cu(napr) ₂ (Me ₂ SO)] ₂ (green)	m P ₂ 2	17.166(2) 10.518(2) 18.184(3)	118.69(1)	CuO ₅	O _{eq} Me ₂ SO _{ap}	1.966(4, 29) 2.139(5, 11)	2.629(1) 0.203	O _{eq} O _{ap} O _{eq} O _{eq}	95.9(4, 5.9) 89.4(2, 1.7) 168.1(2, 3.2)	63
[Cu(β-ala) ₂ H ₂ O] ₂ (NO ₃) ₄ ·4H ₂ O (green)	tr P-1 1	12.499(1) 8.717(1) 8.070(1)	77.74(2) 82.44(1) 71.48(1)	CuO ₅	O _{eq} H ₂ O _{ap}	1.975(4, 14) 2.124(3)	2.639(1) not given	O _{eq} O _{eq} O _{eq} O _{ap}	89.5(2, 1.1) 168.6(1, 1) 95.7(2, 1.2)	64

TABLE I (Continued)

Compound (color)	Cryst. cl. space Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	$Cu-L$ [Å]	$Cu-Cu$ [Å] <i>Cu - out of the plane</i> [Å]	$L-Cu-L$ [°]	Ref.
$[Cu(p-OHC_6H_4CO_2)_2$ $Me_2SO]_2 \cdot 4Me_2SO$ (not given)	or Pbca 8	18.623(4) 18.867(4) 15.019(3)		CuO ₅	O _{eq} Me ₂ SO _{ap}	2.639(3) not given	not given	40
$[Cu(2,4-Cl_2pac)_2H_2O]_2 \cdot 2H_2O$ (turquoise)	m C2/c 4	36.98(3) 7.582(2) 14.972	105.52(6)	CuO ₅	O _{eq} H ₂ O _{ap}	2.639(5) 0.24	O _{eq} O _{eq} O _{eq} O _{ap}	65
$[Cu(depmta)_2H_2O]_2 \cdot 2Me_2CO$ (not given)	tr P-1 1	8.140(3) 9.501(5) 18.58(1)	90.73(5) 99.56(5) 108.72(4)	CuO ₅	O _{eq} H ₂ O _{ap}	2.639(5) not given	O _{eq} O _{eq} O _{eq} O _{ap}	66
$[Cu(ac)_2H_2O]_2$ (dark green)	m C2/c 4	13.15 8.52 13.90	117.0	CuO ₅	O _{eq} H ₂ O _{ap}	2.64 not given	O,O not given	67
$[Cu(sal)_2H_2O]_2 \cdot H_2O$ -dio (pale green)	m P2 ₁ /c 2	11.65 6.90 22.36	104.42	CuO ₅	O _{eq} H ₂ O _{ap}	2.64 0.206	O,O not given	68
$[Cu(2-bbenz)_2H_2O]_2$ (green)	m P2 ₁ 2	11.02(1) 17.86(2) 13.06(2)	105.69(3)	CuO ₅	O _{eq} H ₂ O _{ap}	2.64(1) 0.22(-,5)	O _{eq} O _{eq} O _{eq} O _{ap}	69
$[Cu(C_8H_{15}NOCO)_2(EtOH)]_2$ H ₂ O (not given)	tr P-1 1	12.924(41) 13.441(11) 8.033(9)	82.82(8) 90.51(9) 115.01(6)	CuO ₅	O _{eq} EtHO _{ap}	2.644 not given	O _{eq} O _{eq} O _{eq} O _{ap}	70
$[Cu(pfac)_2H_2O]_2$ (not given)	m P2 ₁ /c 4	7.635(5) 12.958(4) 37.45(3)	94.45(4)	CuO ₅	O _{eq} H ₂ O _{ap}	2.644(4) not given	O _{eq} O _{eq} O _{eq} O _{ap}	71
$[Cu(2,4-depmta)_2(Me_2CO)]_2$ (light green)	tr P-1 1	8.357(1) 12.502(2) 13.721(2)	107.20(1) 96.09(1) 104.94(1)	CuO ₅	O _{eq} Me ₂ CO _{ap}	2.646(1) not given	O _{eq} O _{eq} O _{eq} O _{ap}	72
$[Cu(nipr)_2H_2O]_2 \cdot 2H_2O$ (green)	or Pbca 4	13.450(2) 14.403(3) 19.619(3)		CuO ₅	O _{eq} H ₂ O _{ap}	2.647(1) not given	O _{eq} O _{eq} O _{eq} O _{ap}	73

[Cu(3-Clpr) ₂ (Ph ₃ PO)] ₂ (green)	tr P-1 1	8.603(6) 12.605(4) 12.624(5)	76.94(3) 71.74(4) 74.42(4)	CuO ₅	O _{eq} Ph ₃ PO _{ap}	1.969(2, 7) 2.097(2)	2.649(1) 0.2063(4)	O,O	not given	74
[Cu(Clac) ₂ urea] ₂ (green)	m not given 2	7.816(2) 7.677(3) 18.425(7)	107.9(13)	CuO ₅	O _{eq} ureaO _{ap}	1.97(-, 1) 2.08	2.651 0.21	O,O	not given	75
[Cu(Me ₂ NCH ₂ CO ₂) ₂ (ClO ₄) ₂] ₂ (not given)	m C2 4	12.186 12.652 12.857	100.00	CuO ₅	O _{eq} O ₃ ClO ₄ _{ap}	1.96(2) 2.29(3)	2.652(7) not given	O,O	not given	76
[Cu(fm) ₂ urea] ₂ (green)	tr P-1 1	6.797(2) 6.687(1) 9.088(1)	116.46(1) 76.64(2) 113.01(1)	CuO ₅	O _{eq} ureaO _{ap}	1.977(2, 12) 2.120(1)	2.655(1) 0.213	O,O O,O _{ap}	89.3(1, 8) 167.9(1, 1) 96.2(1, 2.6)	58
[Cu(bz)(Ph ₃ PO)] ₂ (blue)	m A2/a 4	24.337(3) 10.566(1) 21.579	93.18(1)	CuO ₅	O _{eq} Ph ₃ PO _{ap}	1.968(2, 9) 2.143(2)	2.657(1) 0.210	O _{eq} O _{eq} O _{eq} O _{ap}	89.3(1, 1.8) 167.7(1, 0) 96.1(1, 9)	77
[Cu(Fac) ₂ urea] ₂ (green)	tr P-1 2	8.156(3) 8.735(5) 13.61	81.42(6) 90.12(5) 92.25(4)	CuO ₅	O _{eq} ureaO _{ap}	1.971(7, 15) 2.099(7)	2.657(3) 0.209	O,O	not given	79
[Cu(fm) ₂ (urea)] ₂ (green)	tr P-1 2	6.677(13) 6.822(14) 9.093(18)	78.44(10) 116.20(10) 113.0(1)	CuO ₅	O _{eq} ureaO _{ap}	1.975(7, 13) 2.105(7)	2.674(3) 0.215	O,O	not given	78
[Cu(tolm) ₂ (Me ₂ SO)] ₂ (green)	tr P-1 1	9.008(2) 12.902(4) 14.446(4)	97.98(2) 81.52(2) 108.94(2)	CuO ₅	O _{eq} Me ₂ SO _{ap}	1.952(16, 13) 2.114(13)	2.657(7) 0.22	O _{eq} O _{ap} O _{eq} O _{eq}	89.3(1, 4) 167.2(2, 0) 96.4(1, 1.6)	63
[Cu(bz-α-ala) ₂ (H ₂ O)] ₂ (blue green)	tr P-1 1	9.421(2) 9.549(2) 12.618(3)	74.31(2) 79.21(2) 88.69(2)	CuO ₅	O _{eq} H ₂ O _{ap}	1.968(3, 10) 2.138(4)	2.6621 0.21	O _{eq} O _{ap} O _{eq} O _{eq}	89.3(1, 1.5) 167.2(2, 2) 96.4(1, 5.6)	80
[Cu(aegly) ₂ H ₂ O] ₂ (not given)	m P2 ₁ /c 4	7.288(2) 8.892(2) 19.473	103.04(3)	CuO ₅	O _{eq} H ₂ O _{ap}	1.971(3, 17) 2.108(3)	2.666(1) not given	O _{eq} O _{eq} O _{eq} O _{ap}	89.3(1, 1.7) 167.5(1, 2) 96.3(1, 4.7)	81

TABLE I (Continued)

Compound (color)	Cryst. cl. space Gr. Z	<i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]	α [°] β [°] γ [°]	Chromophore	<i>Cu-L</i> [Å]	<i>Cu-Cu</i> [Å] <i>Cu-out of the plane</i> [Å]	<i>L-Cu-L</i> [°]	Ref.
[Cu(Fac) ₂ H ₂ O] ₂ (light green)	m C2/c 4	12.736(4) 9.537(3) 13.683(4)	118.09(2)	CuO ₅	O _{eq} H ₂ O _{ap}	2.674(1) 0.314	89.3(1, 1.7) 167.5(1, 1) 96.2(1, 6.2)	82
[Cu(Fac) ₂ (deha) ₂ (not given)	tr P-1 1	7.825 8.816(7) 12.986(6)	74.28(5) 86.57(4) 85.18(6)	CuO ₅	O _{eq} O _{ap}	2.685(0) 0.219	89.3(1, 7) 167.3(1, 1) 96.4(1, 3.9)	82
[Cu(β -ala) ₂ (Ph ₃ P) ₂ (Ph ₂ P) ₂ ·H ₂ O (dark green)	tr P-1 1	9.781(3) 14.247(4) 13.809(4)	94.59(5) 94.73(5) 114.67(5)	CuO ₅	O _{eq} Ph ₃ PO _{ap}	2.688(1) 0.229	89.2(2, 2.9) 166.7(2, 3) 96.5(2, 3.6)	83
[Cu(2-Clpr) ₂ (Ph ₃ PO)] ₂ (dark green)	m P2 ₁ /n 2	11.191(8) 17.161(8) 13.102(4)	91.69(3)	CuO ₅	O _{eq} Ph ₃ PO _{ap}	2.696(2) 0.230	89.5(2) 95.5(2, 2.1)	84
[Cu(2-NO ₂ bz) ₂ (Me ₂ SO)] ₂ (green)	m P2 ₁ /n 2	10.621(4) 10.480(3) 17.567(10)	96.15(8)	CuO ₅	O _{eq} Me ₂ SO _{ap}	2.702(1) 0.225	167.0(1, 1) 96.5(1, 4.1)	85
Cu(H ₂ O) ₄ [Cu ₂ (pib) ₅] ₂ (dark green)	tr P-1 1	14.32(1) 10.950(8) 19.67(1)	99.17(4) 90.32(4) 117.22(4)	CuO ₅ CuO ₄ (monomer)	O H ₂ O	2.85(1) not given	90(1, 6) 89(2)	86
Cu(H ₂ O) ₄ [Cu ₂ (pib) ₅] ₄ ·4H ₂ O (dark green)	m C2/c 4	41.90(1) 12.135(4) 21.501(3)	91.13(2)	CuO ₅	O 2.211(9, 10)	2.929(1) not given	90.8(4, 4.9) 164.2(4, 17.6) 94.3(4, 26.5)	86
[Cu(Cl ₃ ac) ₂ (proxyl)] ₂ (dark green)	tr P-1 2	9.826(3) 13.216(4) 18.022(2)	94.02(2) 114.99(2) 100.45(2)	CuO ₅	H ₂ O O _{eq} O _{eq} proxyl(O _{ap})	3.197(2)	74.1(3) 89.2(3) 90.9(2, 11.2) 130.3(2, 1) 177.0(2, 1) 93.5(2, 8.6) 119.2(8.4)	87

[Cu(Cl ₃ ac) ₂ (tempo)] ₂ (deep green)	m P2 ₁ /n 4	12.134(3) 22.465(5) 16.693(3)	100.43(2)	CuO ₅	O _{eq} O _{eq} tempoO _{ap}	1.910(9, 14) 2.1946(8, 4) 1.946(8, 4)	3.256(2)	O _{eq} , O _{eq} O _{eq} , O _{ap}	89.7(4, 3.8) 125.7(4, 9) 175.3(4, 2.4) 93.4(4, 7.5) 120.8(4, 8.3)	87
[Cu(2,4-dcpmta) ₂ (Me ₂ CO) H ₂ O] ₂ (green)	tr P-1 1	8.140(3) 9.501(5) 18.58(1)	90.78(5) 99.56(5) 108.72(4)	CuO ₅	not given	not given				72
B: CuO₄N										
[Cu(ac) ₂ pyra] ₂ (at 100 K)	m C2/m not given	7.9156(9) 14.024(3) 7.3022(9)	100.99(2)	CuO ₄ N	O _{eq} N _{ap}	1.965(4, 2) 2.167(5)	2.576(1) 0.26	O,O O,N	89.3(1, 1.2) 95.1(1, 1.4)	89
[Cu(ac) ₂ pyra] ₂ (at 300 K)	m C2/m not given	7.967(9) 14.211(1) 7.3210(8)	101.23(2)	CuO ₄ N	O _{eq} N _{ap}	1.964(5, 4) 2.171(6)	2.583(1) 0.28	O,O O,N	89.6(2, 1.0) 95.4(2, 1.5)	89
[Cu(ac) ₂ (Menic)] ₂ (not given)	m P2 ₁ /c 2	8.710(2) 18.823(5) 8.059(2)	92.56(2)	CuO ₄ N	O _{eq} N _{ap}	1.974(3, 10) 2.173(3)	2.607(1) 0.179(1)	O,O O,N	not given 95.7(1, 1.2)	90
[Cu(pr) ₂ py] ₂ ^d (green)	tr P-1 4	16.204(9) 8.442(5) 11.618(7)	103.9(1) 121.0(1) 90.4(1)	CuO ₄ N	O _{eq} N _{ap}	1.97(1, 2) 2.13(1)	2.619(2) not given	not given	not given	91
[Cu(ac) ₂ (tm ₂ tam)] ₂ (green)	or Cmma 4	15.616(4) 15.459(5) 8.066(5)		CuO ₄ N	O _{eq} N _{ap}	1.96(1, 0) 2.17(1)	2.642(2) not given	not given	not given	92
[Cu(ac) ₂ py] ₂ (green)	m A2/a 4	12.520(2) 17.310(4) 9.930(2)	96.73(2)	CuO ₄ N	O _{eq} N _{ap}	1.975(2, 6) 2.212(2)	2.624(1) not given	O,O O,N	90.0(1, 2.3) 145.1 98.9(1)	58
[Cu(2-bbenz) ₂ (p-1am)] ₂ (green)	tr P-1 1	13.429(3) 12.999(5) 10.192(2)	103.85(2) 107.95(2) 106.51(2)	CuO ₄ N	O _{eq} N _{ap}	1.974(5, 9) 2.163(4, 7)	2.628(1) 0.207	O,O O,N	89.4(1, 1.9) 168.1(1.3) 95.9(1, 2.2)	93

TABLE I (Continued)

Compound (color)	Cryst. cl. space Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å] Cu-out of the plane [Å]	L-Cu-L [°]	Ref.
[Cu(vip) ₂ py] ₂ (green blue)	tr P-1 1	10.5074(4) 11.5436(6) 10.4440(7)	95.126 103.373(5) 74.771(4)	CuO ₄ N	O _{eq} N _{ap} 1.963 2.165(9)	2.630(2) 0.205	not given	94
[Cu(pr) ₂ (3-Mepy)] ₂ (not given)	m C2/c 8	20.702(4) 7.306(2) 18.957	107.78	CuO ₄ N	O _{eq} N _{ap} 1.971(2, 10) 2.167(2)	2.6312(4) not given	not given	95
[Cu(ac) ₂ dabco] ₂ (blue green)	m A2/m 2	7.709(7) 15.490(8) 8.172(3)	105.51(5)	CuO ₄ N	O _{eq} N _{ap} 1.975(6, 3) 2.193(8)	2.632(2) 0.21	O,O O,N 89.8(2, 1.4) 96.1(2, 3)	26
[Cu(ac) ₂ (2-ampy)] ₂ (green)	m C2/c 4	15.126(3) 13.709(1) 8.659(2)	93.79(1)	CuO ₄ N	O _{eq} N _{ap} 1.967(5, 17) 2.218(5)	0.633(2) not given	O,O O,N 89.4(3, 3) 167.8(2, 2) 96.1(2, 2.8)	96
[Cu(ac) ₂ (3-pycar)] ₂ ·CH ₂ Cl ₂ ^d (green)	m P2 ₁ /c 4	16.778(13) 19.853(14) 8.384(4)	97.38(5)	CuO ₄ N	O _{eq} N _{ap} 1.970(4, 10) 2.152(5)	2.634(1) 0.205	O,O O,N 89.4(2, 1.3) 168.1(2, 1) 89.3(2, 9)	97
[Cu(pr) ₂ (nic)] ₂ (light green)	tr P-1 2	9.895(7) 11.204(7) 13.509(7)	87.36(5) 89.17(5) 74.25(5)	CuO ₄ N	O _{eq} N _{ap} 1.978(6, 27) 2.18(8, 5)	2.635(2) 0.20	O,O O,N 90.5(3, 3.5) 168.2(3, 3)	98
Cu ₂ (pr) ₄ (pycac) ₂ (green)	or Pbca 4	19.350(4) 15.390(3) 10.725(2)		CuO ₄ N	O _{eq} N _{ap} 1.972(2, 21) 2.167(2)	2.6396(8) 0.211(1)	O,O O,N 89.1(1, 5) 96.1(1, 6)	100
[Cu(ac) ₂ ppy] ₂ (green)	or Pbca 4	13.079(21) 8.594(1) 19.572(5)		CuO ₄ N	O _{eq} N _{ap} 1.972(3, 12) 2.191(2)	2.641(1) 0.208	O,O O,N 89.4(1, 9) 167.9(1, 1) 96.1(1, 8)	58
[Cu(ac) ₂ (NCS)] ₂ (Me ₄ N) ₂ (green)	tg 14/mmm 2	8.873 — 18.087		CuO ₄ N	O _{eq} N _{ap} 2.03(1) 2.08(2)	2.643(3) not given	not given	99

[Cu(ac) ₂ (naa)] ₂ ·2H ₂ O (dark green)	tr P-1 2	10.974(4) 8.132(3) 7.899(4)	96.55(4) 110.75(3) 89.12(9)	Cu ₄ O ₄ N	O _{eq} N _{ap}	1.980(4, 29) 2.168(4)	2.644(2) 0.209	O,O O,N	89.4(2, 1.2) 167.9(2, 2) 96.1(2, 1.3)	101
[Cu(pr) ₂ (3,5-Me ₂ py)] ₂ (green)	tr P-1	8.6652(14) 8.7357(6)	77.31(8) 67.67(13)	Cu ₄ O ₄ N	O _{eq} N _{ap}	1.975(2, 4) 2.168(2)	2.6447(6) not given	O,O O,N	89.3(1, 7) 167.9(1, 1) 96.1(1, 1.2)	102
[Cu(bz) ₂ (caf)] ₂ (green)	m P ₂ /n 2	12.922(2) 22.122(2) 10.898(1)	99.42(1)	Cu ₄ O ₄ N	O _{eq} N _{ap}	1.967(2, 11) 2.222(3)	2.647 0.204(2)	O,O O,N	89.4(1, 7) 168.1(1, 1) 95.9(1, 7.2)	45
[Cu(pr) ₂ (2-Mepy)] ₂ (not given)	tr P-1 2	8.080(7) 8.290(7) 12.444(10)	111.9(1) 75.7(1) 119.4(1)	Cu ₄ O ₄ N	O _{eq} N _{ap}	1.97(1, 1) 2.21(2)	2.647(4) not given	O,O O,N	not given	103
[Cu(2,2-Me ₂ pr) ₂ (4-Mepy)] ₂ C ₆ H ₆ (green)	rh R-3m 9	31.902(4) 11.111(2)		Cu ₄ O ₄ N	O _{eq} N _{ap}	1.971(8, 2) 2.125(13)	2.648(5) not given	O,O O,N	89.4(3, 3.1) 168.4(4, 1) 95.9(4, 1)	104
[Cu(oct) ₂ (py)] ₂ (dark green)	tr P-1	8.379(3) 10.921(6) 13.286(6)	108.42(4) 96.21(4) 92.06(4)	Cu ₄ O ₄ N	O _{eq} N _{ap}	2.007(3, 31) 2.194(4)	2.651(1) 0.209(3)	O,O O,N	89.4(2, 1.1) 168.1(1, 2) 96.0(2, 1.4)	105
[Cu(ac) ₂ -ampy] ₂ -dio (green)	tr P-1	7.356(2) 8.122(2) 12.293(2)	74.26(2) 82.31(2) 82.88(2)	Cu ₄ O ₄ N	O _{eq} N _{ap}	1.970(9, 14) 2.185(11)	2.651(2) 0.22	O,O O,N	89.3(4, 8) 167.3(4, 3) 96.4(4, 2.3)	106
[Cu(ac) ₂ qu] ₂ (not given)	or Pbca 4	21.17(1) 14.319(6) 8.852(5)		Cu ₄ O ₄ N	O _{eq} N _{ap}	1.977(6, 20) 2.224(6)	2.652(2) 0.227	O,N	not given	107
[Cu(mdde) ₂ py] ₂ (green)	tr P-1	11.230(4) 9.940(4) 10.954(4)	112.16(3) 107.26(3) 81.22(3)	Cu ₄ O ₄ N	O _{eq} N _{ap}	1.969(5, 7) 2.179(6)	2.655(1) not given	O,O O,N	89.3(2, 5) 96.2(2, 1.4)	61
[Cu(pr) ₂ (4-Mepy)] ₂ (green)	or Cocm 8	20.300(3) 14.244(3) 20.479(6)		Cu ₄ O ₄ N	O _{eq} N _{ap}	1.970(9, 3) 2.143(9)	2.655(3) not given	O,O O,N	not given	108
				Cu ₄ O ₄ N	O _{eq} N _{ap}	1.972(9, 22) 2.148(9)	2.659(3) not given	O,N	not given	

TABLE I (Continued)

Compound (color)	Cryst. cl. space Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	$Cu-L$ [Å]	$Cu-Cu$ [Å] Cu-out of the plane [Å]	$L-Cu-L$ [°]	Ref.
$[Cu(2,2-Me_2pr)_2(3-Mepy)]_2$ C_8H_6 (green)	trg $P3_121$ 3	18.246(2) — 11.303	— — —	CuO_4N	O_{eq} 1.972(11,52) N_{ap} 2.176(20)	2.657(3) not given	O,O O,N	104
$[Cu(bz)_2(py)]_2$ (blue)	m $P2_1/n$ 2	10.036 10.467(1) 17.344(2)	98.66(1)	CuO_4N	O_{eq} 1.972(2,12) N_{ap} 2.170(3)	2.658(1) 0.217(1)	O,O O,N	109
$[Cu(Et_5NCO)_2(Et_2NH)]_2$ (turquoise)	tr P-1 1	11.182(3) 11.004(4) 8.872(3)	81.36(4) 99.02(2) 70.08(3)	CuO_4N	O_{eq} 1.961(6,15) N_{ap} 2.23(2)	2.658(2) 0.22	O,O O,N	110
$[Cu(ac)_2(2-ath)]_2$ (green)	m $P2_1/n$ 2	9.144(2) 8.467(2) 14.546(2)	106.91(2)	CuO_4N	O_{eq} 1.975(3,7) N_{ap} 2.156(3)	2.658(1) 0.22	O,O O,N	111
$[Cu(crot)_2qu]_2$ (not given)	m $P2_1/n$ 2	14.594(1) 10.863(1) 10.581(1)	99.52	CuO_4N	O_{eq} 1.970(7,6) N_{ap} 2.219(6)	2.660(3) 0.216(5)	O,O O,N	112
$[Cu(ac)_2(bim)]_2$ (green)	or Pbca 2	21.63(5) 14.411(4) 8.037(2)	—	CuO_4N	O_{eq} 1.979(5,8) N_{ap} 2.145(5)	2.663(1) 0.215(5)	O,O O,N	113
$[Cu(ac)_2(demc)]_2$ (not given)	or Pcab 4	8.731(3) 12.685(4) 30.83(1)	—	CuO_4N	O_{eq} 1.973(6,15) N_{ap} 2.175(6)	2.663(3) 0.184	O,O O,N	114
$[Cu(bz)_2(3-Mepy)]_2$ (green)	m $P2_1/n$ 2	17.326(2) 10.554(1) 10.655(2)	95.56(1)	CuO_4N	O_{eq} 1.973(4,8) N_{ap} 2.151(4)	2.664(1) 0.217	O,O O,N	45
$[Cu(3-CNbz)_2]^c$ (green blue)	tr P-1 2	6.545(4) 10.235(5) 12.174(6)	74.40(3) 85.02(4) 78.64(3)	CuO_4N	O_{eq} 1.965(3,10) N_{ap} 2.191(4)	2.664(2) not given	O,O O,N	115

[Cu(bz) ₂ (4,7-Cl ₂ qu)] ₂ (green)	tr P1	10.657(2) 11.047(2) 10.640(2)	97.79(1) 115.08(1) 69.13	CuO ₄ N	O _{eq} N _{ap}	1.972(2, 12) 2.235(2)	2.665(1) 0.215(1)	O,O O,N	89.3(1, 4) 167.5(1, 1) 96.3(1, 5.8)	45
[Cu(ac) ₂ (2-ampy)] ₂ (green)	m P2 _i /c 2	7.433(3) 19.563(4) 8.101(3)	114.28(3)	CuO ₄ N	O _{eq} N _{ap}	1.974(3, 8) 2.218(3)	2.669(1) 0.22	O,O O,N	89.3(1, 3) 167.0(1, 1) 96.5(1, 1.5)	106
[Cu(bz) ₂ qu] ₂ (not given)	or Pcab 4	16.940(5) 19.684(7) 11.482(5)		CuO ₄ N	O _{eq} N _{ap}	1.969(6, 12) 2.186(8)	2.671(2) not given	O,O O,N	89.4(3, 3.2) 95.9(3, 4.9)	116
[Cu(ac) ₂ (2-Mepy)] ₂ (green)	m P2 _i /c 4	7.675(4) 20.008(6) 8.207(4)	115.99(3)	CuO ₄ N	O _{eq} N _{ap}	1.976(10, 27) 2.240(12)	2.671(4) 0.23	O,O O,N	89.3(4, 7) 166.8(4, 3) 96.6(5, 3.5)	117
[Cu(3-Clpr) ₂ (4-Mepy)] ₂ (light green)	tr P-1 1	8.475(3) 8.903(3) 10.204(5)	97.27(3) 92.45(4) 93.721(3)	CuO ₄ N	O _{eq} N _{ap}	1.972(2, 10) 2.170(2)	2.675(1) 0.221	O,O O,N	89.3(1, 1.7) 167.1(1, 0) 96.5(1, 2.2)	118
[Cu(2-Clbz)] ₂ (green)	m P2 _i /a 4	23.365(3) 10.688(1) 20.542(2)	100.03(1)	CuO ₄ N	O _{eq} N _{ap}	1.974(5, 17) 2.149(6, 3)	2.679(1) not given	O,O O,N	89.3(2, 7) 167.2(2, 2.0) 96.4(2, 3.2)	36
[Cu(ac) ₂ (tmp)] ₂ ·(C ₄ H ₆) ₂ · MeOH (green)	m C2/c 4	24.109(5) 15.256(3) 16.532(3)	116.89(2)	CuO ₄ N	O _{eq} N _{ap}	1.972(6, 22) 2.170(5)	2.679(1) 0.23	O,O O,N	89.3(2, 5) 166.6(2, 2) not given	119
[Cu(bz) ₂ py] ₂ ·2H ₂ O (green)	m P2 _i /n 2	10.134(10) 10.530(5) 17.460(16)	98.45(8)	CuO ₄ N	O _{eq} N _{ap}	1.978(5, 6) 2.184(7)	2.681(1) not given	O,O O,N	89.2(2, 6) 167.7(2, 0) 96.1(2, 3.0)	120
Cu ₂ (ac) ₄ (bdodo) (green)	tr P-1 2	8.501(1) 8.590(1) 10.854(2)	84.54(2) 82.10(2) 84.73(2)	CuO ₄ N	O _{eq} N _{ap}	1.973(4, 5) 2.230(5)	2.682(2) not given	O,O O,N	89.3(2, 1.0) 166.8(2, 2) 96.7(2, 4)	121
[Cu(Clac) ₂ (3-Mepy)] ₂ (dark green)	m P2 _i /b 2	8.282(3) 8.308(4) 21.057(6)	114.61(3)	CuO ₄ N	O _{eq} pyN _{ap}	1.973(-, 7) 2.269(4)	2.685(2) 0.228	O,N not given	not given	122
[Cu(bz) ₂ (7-Mecu)] ₂ (green)	m P2 _i /n 4	18.029(3) 20.427(2) 11.673(3)	97.76(2)	CuO ₄ N	O _{eq} quN _{ap}	1.973(5, 3.5) 2.231(5, 6)	2.688(1) 0.189(3)	O,O O,N	89.3(2, 1.4) 166.5(2, 4.0) 96.7(2, 8.5)	45

TABLE I (Continued)

Compound (color)	Cryst. cl. space Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	$Cu-L$ [Å]	$Cu-Cu$ [Å] $Cu-out$ of the plane [Å]	$L-Cu-L$ [°]	Ref.
$[Cu(bz)_2(4-Mequ)]_2$ (not given)	tr	10.684(3)	92.55(2)	CuO_4N	O _{eq} 1.968(2.8)	2.688(1)	O,O 89.2(1.7)	45
$[Cu(pcb)_2(4-apm)]_2$ (dark green)	P-1	10.780(2)	109.78(3)	CuO_4N	quN _{ap} 2.207(2)	0.230(1)	166.6(1.1) 96.7(1.5,0)	86
	P-1	10.207(2)	68.44(2)		apmO _{eq} N _{ap} 1.969(7, 10) 2.198(7)	2.689(2)	not given	
$[Cu(2-ClC_6H_4CH_2OCO)_2]$ (2-ampy) ^d (not given)	tr	17.543(5)	77.89(3)	CuO_4N	O _{eq} 1.970(9, 5)	2.700(3)	O,O 89.2(5, 2.2)	27
	P-1 2	13.344(5) 8.459(3)	81.43(3) 87.61(3)	ampyN _{ap} ampyN _{ap} 1.975(9, 11) 2.243(9)	2.730(3)	not given	O,N 96.7(5, 3.8) O,O 89.1(5, 5) 165.3(5, 4) O,N 97.4(5, 4.2)	
$[Cu(Me_3ac)_2(acr)]_2$ (green)	tr	9.448(4)	105.61(3)	CuO_4N	O _{eq} 1.968(1, 5)	2.702(1)	not given	123
	P-1	11.463(5) 11.963(4)	103.40(3) 105.92(3)	acrN _{ap} 2.371(5)	0.24	not given		
$[Cu(4-Fpac)_2(2-NH_2pm)]_2$ (dark green)	tr	12.688(2)	78.74(1)	CuO_4N	O _{eq} 1.977(3, 10)	2.710(1)	O,O 89.1(1, 3.1)	124
	P1	11.422(2)	107.51(1)	pmN _{ap} 2.176(3)	not given	not given	166.0(2, 1) 96.4(1, 3.3)	
$[Cu(Clac)_2caf]_2$ (green)	tr	7.932(2)	93.19(6)	CuO_4N	O _{eq} 1.97(4, 2)	2.711(3)	O,O 89.2(4, 9)	125
	P-1	12.798(2) 9.078(5)	109.95(3) 96.92(6)	cafN _{ap} 2.23(4)	0.236	not given	166.2(4, 1) 96.9(4, 8.3)	
$[Cu(2,4,5-Cl_3pac)_2py]_2$ (green)	tr	12.184(8)	99.69(5)	CuO_4N	O _{eq} 1.973(12, 11)	2.716(7)	O,O 89.2(10, 2.1)	65
	P-1	13.719(7) 8.687(6)	99.15(5) 114.01(4)	pyN _{ap} 2.142(12)	0.23	not given	166.2(10, 1) 96.8(11, 1.1)	
$[Cu(fm)_2(NCS)_2]_2 \cdot (NMe_4)_2$ (green)	tg 14/mmm 2	8.917 — 15.800	— — —	CuO_4N	O _{eq} 1.983(4) SCN _{ap} 2.093(9)	2.716(2)	not given	99
$[Cu(Clac)_2qu]_2$ (not given)	tr	7.622(1)	73.30(1)	CuO_4N	O _{eq} 1.974(6, 13)	2.724(2)	not given	107
	P-1	9.145(2) 11.297(2)	96.61(1) 92.78(1)	quN _{ap} 2.211(7)	0.248	not given		

[Cu(Fac)2qu]2 (not given)	m P2 ₁ /b 2	8.284(9) 20.218(14) 8.188(13)	79.37(5)	CuO ₄ N	O _{eq} quN _{ap}	1.977(2, 10) 2.210(3)	2.725(1) 0.239	not given	126
[Cu(Cl ₃ ac) ₂ (PhCN)] ₂ ^d (green)	tr P-1 2	12.780(1) 16.064(1) 10.130(1)	108.39(1) 113.34(1) 81.07(1)	CuO ₄ N	O _{eq} PhCN _{ap}	1.964(6, 9) 2.141(9)	2.731(1) 0.251	O,O O ₁ N O,O	127
[Cu(Cl ₃ ac) ₂ caf] ₂ ·2tol (pale green)	tg P4 ₃ /ncm 4	15.731(2) 19.115(3)		CuO ₄ N	O _{eq}	1.957(7, 12) 2.11(1)	2.736(1) not given	O,O O ₁ N	128
[Cu(Clac) ₂ (2-Mepy)] ₂ (green)	tr P-1 1	7.881(15) 8.913(9) 10.995(19)	115.53(5) 87.7(5) 87.42(6)	CuO ₄ N	O _{eq} cafN _{ap}	1.975(9, 23) 2.1611(10)	2.747(3) 0.26	not given O ₁ N	129
[Cu(Cl ₃ ac) ₂ (2-Fbzth)] ₂ (green)	tr P-1 1	10.336(2) 11.381(3) 9.272(2)	107.30(1) 94.63(2) 66.53(2)	CuO ₄ N	O _{eq} thN _{ap}	1.970(4, 9) 2.153(5)	2.761(1) not given	O,O O ₁ N	128
[Cu(Cl ₃ ac) ₂ (2-Clpy)] ₂ (light green)	tr P-1 1	9.316(9) 10.707(10) 10.493(11)	57.22(2) 107.02(3) 100.01(3)	CuO ₄ N	O _{eq} pyN _{ap}	1.957(5, 16) 2.145(5)	2.766(3) 0.28	O,O O ₁ N	130
[Cu(Br ₃ ac) ₂ (2-Clpy)] ₂ (not given)	tr P-1 1	10.452(4) 9.767(4) 10.697(4)	69.87(2) 116.44(3) 98.57(3)	CuO ₄ N	O _{eq} pyN _{ap}	not given not given	2.766(3) not given	not given not given	131
[Cu(Cl ₃ ac) ₂ (4-CNpy)] ₂ (pale green)	m P2 ₁ /a 4	20.788(5) 17.951(4) 9.693(2)	99.45(2)	CuO ₄ N	O _{eq} pyN _{ap}	1.977(6) 2.134(6, 8)	2.769(1) not given	O,O O ₁ N	128
[Cu(Cl ₃ ac) ₂ (3-Clpy)] ₂ (pale green)	tr P-1 1	10.246(1) 10.739(1) 9.598(1)	103.27(1) 111.23(1) 62.36(1)	CuO ₄ N	O _{eq} pyN _{ap}	1.976(3, 5) 2.120(4)	2.774(1) not given	O,O O ₁ N	128
[Cu(Cl ₃ ac) ₂ (4, 7-Cl ₂ qu)] ₂ (green)	tr P-1 1	10.201(1) 11.688(2) 9.301(1)	107.37(1) 100.45(1) 73.99(1)	CuO ₄ N	O _{eq} quN _{ap}	1.971(3, 10) 2.161(4)	2.785(1) not given	O,O O ₁ N	128

TABLE I (Continued)

Compound (color)	Cryst. cl. space Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å] Cu - out of the plane [Å]	L-Cu-L [°]	Ref.
[Cu(F ₃ ac)qu] ₂ ·2H ₂ O (light green)	m C2/c 4	14.886(24) 16.707(29) 13.694(23)	111.26(5)	CuO ₄ N	O _{eq} quN _{ap}	2.886(4) 0.32	O,O 88.5(3,1.7) 161.2(3,2) 99.4(3,2.4)	132
[Cu(Cl ₃ ac) ₂ (2,5-Cl ₂ py)] ₂ (pale green)	tr P-1 2	11.359(1) 17.928(2) 9.324(1)	97.35(1) 103.04(1) 92.66(1)	CuO ₄ N	O _{eq} pyN _{ap}	2.951(1) not given	O,O 89.1(2,1.6) 145.5(2,1) 174.0(2,5) 92.5(2,2.4) 122.4(2,2.0)	128
[Cu(Cl ₃ ac) ₂ (3,5-Me ₂ py)] ₂ ·2C ₆ H ₆ (pale green)	m C2/c 4	19.547(3) 14.990(1) 17.181(3)	106.93(3)	CuO ₄ N	O _{eq} pyN _{ap}	3.031(1) not given	O,O 88.8(2,2.3) 141.5(1) 172.6(2) 95.7(2,4.0) 118.8(2)	128
[Cu(Cl ₃ ac) ₂ (2-Cl-5-NO ₂ py)] ₂ (pale green)	tr P-1 2	13.683(2) 14.122(2) 9.796(2)	98.269(1) 93.762(1) 80.286(1)	CuO ₄ N	O _{eq} pyN _{ap}	3.054(3) not given	O,O 89.4(5,2.5) 136.9(5,3) 175.1(5,6) 91.3(5,2.5) 131.0(5,6)	128
[Cu(Cl ₃ ac) ₂ caf] ₂ (pale green)	m C2/c 4	20.048(2) 17.575(2) 12.350(7)	106.01(2)	CuO ₄ N	O _{eq} cafN _{ap}	3.062(1) not given	O,O 89.0(1,3.3) 138.2(1) 174.5(1) 91.9(1,2.0) 131.4(1)	128
[Cu(Cl ₃ ac) ₂ (3-CNpy)] ₂ (pale green)	tr P-1 2	10.952(1) 16.338(2) 10.833(1)	106.80(1) 97.02(1) 71.90(1)	CuO ₄ N	O _{eq} pyN _{ap}	3.066(1) not given	O,O 89.5(2,2.2) 137.4(2,1) 177.3(2,1) 92.7(2,13.3)	128
[Cu(Cl ₃ ac) ₂ (2,5-Cl ₂ py)] ₂ ·C ₆ H ₆ (pale green)	m P2 ₁ /a 4	20.370(2) 18.296(3) 11.585(2)	100.35(1)	CuO ₄ N	O _{eq} pyN _{ap}	3.113(3) not given	O,O 89.2(4,2.8) 134.7(4,7) 175.3(4,7)	128

[Cu(Cl ₃ ac) ₂ (3,5-Cl ₂ py)] ₂ ·tol (green)	tr P-1 2	10.859(2) 19.225(2) 10.692(2)	91.01(1) 97.89(2) 81.11(1)	CuO ₄ N	O _{eq} pyN _{ap}	1.941(6, 43) 2.026(5, 7)	3.177(1) not given	O,N O,O O,N	91.0(4, 2.1) 133.9(4, 1) 89.6(2, 3.4) 131.0(2, 1) 176.99(2, 5) 89.0(2, 3.6) 143.0(2, 8)	128
[Cu(Cl ₃ ac) ₂ (3,4-Me ₂ py)] ₂ (pale green)	m P ₂ /c 4	20.567(2) 10.414(2) 18.231(2)	106.13(1)	CuO ₄ N	O _{eq} pyN _{ap}	1.979(6, 100) 2.014(7, 7)	3.186(2) not given	O,O O,O	89.0(2, 2.0) 132.3(2, 4) 174.7(2, 1) 94.9(2, 6.9) 128.3(2, 2.0)	128
[Cu(Cl ₃ ac) ₂ (2,3-Me ₂ py)] ₂ ·tol (pale green)	m P ₂ /n 4	21.544(4) 18.099(4) 11.423(2)	99.49(2)	CuO ₄ N	O _{eq} pyN _{ap}	1.966(9, 66) 2.212(9, 14) 2.019(8)	3.206(2) not given	O,O O,O	88.8(4, 2.6) 131.8(4, 1) 173.9(3, 1) 94.2(4, 3.6) 131.2(4, 7)	128
[Cu(Cl ₃ ac) ₂ (2,5-Me ₂ py)] ₂ ·tol (pale blue)	m P ₂ /a 4	21.010(1) 18.725(2) 11.574(1)	104.90(1)	CuO ₄ N	O _{eq} pyN _{ap}	1.951(6, 69) 2.233(6, 16) 2.012(6, 5)	3.226(1) not given	O,O O,O	89.0(2, 2.2) 131.0(2, 1) 174.4(2, 3) 93.7(2, 6.0) 132.1(2, 2.8)	128
[Cu(Cl ₃ ac) ₂ (2-Et ₂ py)] ₂ (pale green)	tr P-1 2	11.144(1) 18.291(2) 9.206(1)	97.56(1) 100.53(1) 84.05(1)	CuO ₄ N	O _{eq} pyN _{ap}	1.958(4, 54) 2.306(4, 22) 2.032(4, 1)	3.261(1) not given	O,O O,N	88.8(2, 2.2) 129.6(2, 2) 173.8(2, 4) 92.2(2, 3.7) 137.9(2, 1.1)	128
C: CuO₄P										
[Cu(mddc) ₂ Ph ₃ P] ₂ (dull green)	tr P-1 1	14.593(1) 10.747(1) 11.894(2)	75.025(6) 115.011(6) 99.567(6)	CuO ₄ P	O _{eq} Ph ₃ P _{ap}	1.967(3, 12) 2.570(2)	2.676(1) not given	O,O O,P	89.3(2, 1.9) 96.6(2, 9.1)	61
[Cu(ac) ₂ (Ph ₃ P)] ₂ (green)	tr P-1 1	9.149(7) 9.559(3) 14.709(3)	61.00(2) 72.67(5) 90.34(5)	CuO ₄ P	O _{eq} Ph ₃ P	1.956(6, 22) 2.570(2)	2.709(1) 0.245	O,O O,P	89.1(2, 2.0) 165.6(2, 1) 97.1(2, 7.1)	133

TABLE I (Continued)

Compound (color)	Cryst. cl. space Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å] Cu-out of the plane [Å]	L-Cu-L [°]	Ref.
D:								
[Cu(1,3-dpt) ₂] ₂ (olive green)	tr P-1 2	10.373(3) 15.916(5) 13.612(3)	99.51(2) 94.85(3) 102.33(2)	CuN ₄	N 2.020(6,47)	2.441(2) 0.2	N,N 89.8(3,2.8)	134
[Cu(2-O-6-Clpy) ₂] ₂ (deep red) (at 150 K)	or P2 ₁ 2 ₁ 2 ₁ 8	15.394(2) 15.892(2) 18.497(2)		CuO ₂ N ₂	O N 2.014(-,14)	2.499(1)	O,O 178.3(9) N,N 90.0(2,1.8) 167.3(2)	135
[Cu(2-O-3-Etpy) ₂ (dmf) ₂] ₂ (dark)	m P2 ₁ /n 4	9.906(1) 13.494(3) 14.029(2)	103.8(1)	CuO ₃ N ₂	O _{eq} N _{eq} dmf(O _{ap}) 1.959(6,3) 2.000(6,3) 2.283(6)	2.550(1) not given	O _{eq} O _{eq} O _{eq} N _{eq} O _{eq} O _{ap} 88.3(3) 90.5(2,1.0) 172.1(2,3) 89.8(2)	136
[Cu(C ₅ H ₄ NO) ₂ (Me ₂ SO)] ₂ (black green)	m P2 ₁ /n 2	9.452(2) 9.183(1) 15.849(3)	101.34(2)	CuO ₃ N ₂	O _{eq} N _{eq} dmsO _{ap} 1.95(1,0) 2.01(1,0) 2.26(1)	2.587(4) 0.152(8)	O _{eq} O _{eq} N,N 88.5(6) O _{eq} N 90.2(5,4) 171.2(5,4)	137
[Cu(C ₇ H ₅ N ₃) ₂ (dmf) ₂] (not given)	m P2 ₁ /n 2	9.377(6) 13.854(3) 12.928(4)	94.10(4)	CuN ₄ O	N _{eq} dmfO _{ap} 2.003(4,19) 2.325(3)	2.782(1) not given	N,N 89.4(1,1.4) 167.7(1,1)	138
[Cu(6-ampur) ₂ (H ₂ O)] ₂ (blue violet)	tr P-1 2	9.458(2) 10.452(2) 9.410(3)	102.98(2) 116.58(2) 79.81(2)	CuN ₄ O	N _{eq} H ₂ O _{ap} 2.03(-,1) 2.20	2.947(2) 0.27	N,O 96.1(1,4.1) N,N 88.0(-,1.1) N,O not given	139
[Cu(ad) ₂ H ₂ O] ₂ (ClO ₄) ₂ ·2H ₂ O (purple)	m P2 ₁ /c 4	12.212(6) 12.240(6) 17.635(9)	130.27(3)	CuN ₄ O	N _{eq} H ₂ O _{ap} 2.020(8,18) 2.166	2.951(4) 0.269(2)	N,N N,O 82.4(1,5.2) 97.7(2,4.1)	140
[Cu(MeO)(C ₇ H ₅ N ₃) ₂ (dmf) _{0.5}] ₄ (not given)	tr P-1 1	9.189(3) 9.511(2) 12.704(2)	88.09(2) 83.26(3) 66.75(3)	CuO ₂ N ₂ CuO ₃ N ₂	N MeO 1.966(2,1) 1.921(2,6) N 1.985(2,9)	- - 3.007(1,8)	O,O N,N 93.6(1) O,N 94.5(1,9) O,O 97.2(1,4)	138

[Cu(6-OHpur) ₂ Cl] ₂ ·3H ₂ O (turquoise)	tr P-1 2	9.858(2) 10.259(4) 9.717(3)	102.53(3) 89.36(2) 102.21(3)	Cu ₂ N ₄ Cl	dmfO N _{eq} Cl _{ap}	2.422(3) 1.998(-, 90) 2.431	103.0(1, 5) 3.024 0.29	N ₁ N N ₁ N N ₁ Cl	92.4(1) 88.8(-, 1.2) 98.2(-, 1.0)	141
[Cu(ad) ₂ Cl] ₂ ·Cl ₂ ·6H ₂ O (blue green)	or Cmca 4	23.92 13.44 11.262		Cu ₂ N ₄ Cl	N _{eq} Cl _{ap}	2.025(11, 17) 2.429(6)	3.066(4) 0.33	N ₁ N N ₁ Cl	88.4(4, 1.6) 99.4(4, 9)	142
E:										
Cu ₂ (fluf) ₄ (cof)(H ₂ O) (blue)	m P2 ₁ /n 4	4.772(2) 23.156(5) 12.502(3)	95.67(3)	CuO ₅	O _{eq} H ₂ O _a	1.956(3, 1) 2.141(5)	2.633(1) 0.0.189	O _{eq} , O _{eq}	89.5(2, 2.0) 168.9(1)	143
				CuO ₄ N	O _{eq} calN _{ap}	1.960(3, 4) 2.239(5)	N, 0.223	O _{eq} , O _{ap} O _{eq} , O _{eq} O _{eq} , N _{ap}	95.6(2, 2.5) 89.3(2, 1.5) 166.9(1) 96.5(2, 6.4)	

^a Where more than one chemically equivalent distance or angle is present the mean value is tabulated. The first number in parenthesis is l.s.d., the second is a maximum deviation from the mean value. ^b The chemical identity of coordinated atom. ^c Dimers in polymeric chain. ^d There are two crystallographically independent molecules.

CuO_2N_2 (Table ID) chromophores. In the complexes (Table IA–C) two Cu(II) atoms are bridged by four carboxylate groups in a syn–syn arrangement (Figure 1). The apical positions are occupied usually either by oxygen, nitrogen or phosphorus containing ligands. Except,⁹¹ where the coordination polyhedron can be described as trigonal bipyramidal, all other (Table IA–C) about each Cu(II) displays a distorted square pyramidal geometry. There is usually a center of symmetry within a dimeric unit. However, there are twelve complex units, where there is only C_i symmetry element involved. Selected bond distances and angles for CuO_5 and CuO_4N chromophores are summarized in Table IF.

While the Cu–O(basal) bond distances were in the range of 1.943–1.987 Å (average 1.965 Å) and 1.955–1.985 Å (average 1.97 Å) for the CuO_5 and CuO_4N chromophores, respectively, the remaining three distances, Cu–L(apical), Cu–Cu and out of O4 plane, show wide ranges. There are strong correlations between the Cu–Cu distance and out of plane deviation, the Cu(II) atoms to be pushed out from the basal O4 plane upon elongation of the Cu–Cu distance. The correlations are 0.887 and 0.977 for the CuO_5 and CuO_4N types, respectively.^{6,8}

There is also strong correlation of -0.929 between the average angle Cu–O–C and O–C–O for the CuO_5 type dimers. When the former opens the

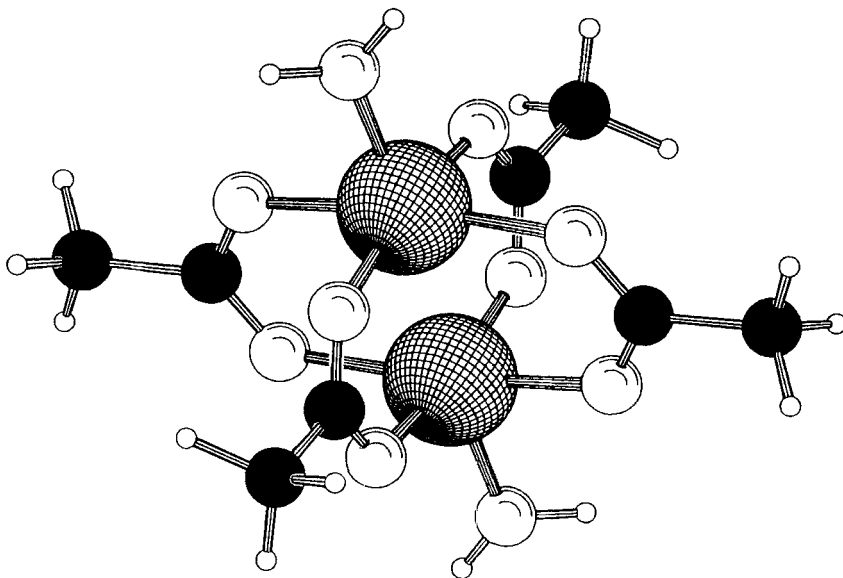


FIGURE 1 A schematic structure of Cu(II) acetate type dimer.

TABLE IF Summary of selected bond distances and angles for CuO_4O and CuO_4N chromophores type^a

	CuO_4O	CuO_4N
<i>Distances</i> [Å]		
Cu–O (basal)	1.943–1.987(1.965)	1.955–1.985(1.97)
Cu–L (apical)	2.074–2.238(2.15)	2.11–2.269(2.18)
Cu–Cu	2.563–3.256	2.576–3.261
Cu – out of O_4 plane	0.13–0.24	0.184–0.322
<i>Angles</i> [°]		
Cu–O–C	119.8–130.2(123.2)	121.5–125.0(123.5)
O–C–O	111.6–132.0(125.0)	122.4–129.3(125.8)
^b	0.719–15.852	0–12.733

^a The mean values are given in parenthesis. ^b Values for the apical deviation angle between Cu–L (apical) line and the perpendicular to the basal O_4 plane.

latter closes. Surprisingly, the correlation is not so good for the CuO_4N type dimers. The structural parameter showing the greatest coefficient of variation is the apical deviation angle for both type of chromophores (Table IF). This indicates that the data depart significantly from a normal distribution. Because the range values are wide, this may indicate a weakness in the chemical bonding in the apical direction.

There are also some structures where the equatorial ligand is the same whereas the apical ligand is changed. The apical ligand influence on the Cu–O(basal) distances range is wider for the CuO_5 structure type. The sum for the bond lengths in a coordination polyhedron is almost constant for each chromophore type, 10.01 Å for CuO_5 and 10.06 Å for CuO_4N . This illustrates nicely the plasticity effect in Cu(II) compounds.¹⁴⁴

There are two green examples^{61,133} (Table IC) in which apical positions are occupied by PPh_3 molecules. The mean Cu–P bond distance of 2.570(2) Å is longer than those of Cu–N (apical) and Cu–O (apical) with the values of 2.18 and 2.15 Å, respectively, as expected.

In Table ID are examples, in which two Cu(II) atoms are bridged by four bidentate N-donor; ligands in a syn–syn configuration. In olive green $\text{Cu}_2(\text{dpt})_4$ ¹³⁴ pairs of very closely separated metal atoms (2.441(2) Å) are bridged by four dpt groups in a syn–syn arrangement such that the environment of each Cu(II) atom is almost square-planar with the mean Cu–N bond distance of 2.020(6) Å. The Cu–Cu distance of 2.441(2) Å is the shortest found in the series of Cu(II) acetate type structure.

In deep red $\text{Cu}_2(2\text{-O-6-Clpy})_4$ ¹³⁵ and dark $\text{Cu}_2(2\text{-O-3-Etpy})_4(\text{dmf})_2$ ¹³⁶ two Cu(II) atoms are held together by four bidentate -O,N-donor; anions in a syn–syn arrangements. Each Cu(II) atom in the former is square-planar with the mean Cu–O of 1.928 Å and Cu–N of 2.014 Å. The Cu–Cu

TABLE II Crystallographic and structural data for doubly bridged copper(II) dimers^a

Compound (color)	Cryst. cl. space G. Z	<i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]	<i>α</i> [°] <i>β</i> [°] <i>γ</i> [°]	Chromophore	<i>Cu</i> – <i>L</i> [Å]	<i>Cu</i> – <i>Cu</i> [Å] <i>Cu</i> – <i>L</i> – <i>Cu</i> [°] <i>μL</i> – <i>Cu</i> – <i>μL</i> [°]	<i>L</i> – <i>Cu</i> – <i>L</i> [°]	Ref.
A: Cu(μ-F)₂Cu								
[Cu(μ-F)(3,5-Me ₂ pz) ₂](BF ₄) ₂ (blue)	trg R-3 12	28.649(7) — 17.133(4)	— — —	CuN ₃ F ₂	N ^b μF	2.893(4) 91.1 88.9(3)	87.9(4,27) 103.9(3,4) 179.1(4) 93.6(5,9) 151.2(4)	145
[Cu(μ-F)(3-Me ₂ pz) ₂](BF ₄) ₂ (blue)	m P2 ₁ /c 2	9.912(2) 9.993(2) 21.330(6)	92.69(2)	CuF ₂ N ₂	N μF	2.922(2) 98.9(8) 81.1(1)	102.0(2)	146
[Cu(μ-F)(5-Me ₂ pz)(3,5-Me ₂ pz) ₂] (BF ₄) ₂ (blue)	m P2 ₁ /c 2	9.954(1) 11.862(2) 17.679(4)	99.45(1)	CuN ₃ F ₂	Me ₂ pzN Me ₂ pzN μF	2.9962(9) 93.73(8) 86.27(8)	87.8(1,1,4) 103.5(1,2,4) 175.3(1) 94.1(1,9) 152.0(2)	147
[Cu(μ-F)(3,4,5-Me ₃ pz) ₂](BF ₄) ₂ (tight blue)	m P2 ₁ /n 2	11.514(4) 16.439(3) 13.159(3)	101.82(2)	CuN ₃ F ₂	N μF	3.0141(8) 94.59(7) 85.41(7)	87.0(1,1,9) 103.1(1,2,5) 174.3(1) 95.4(1,6) 151.6(1)	147
[Cu(μ-F)(3,5-Me ₂ pz)(5-Me ₂ pz) ₂] (BF ₄) ₂ (blue)	trg P-1 1	9.578(2) 9.893(1) 10.994(2)	104.27(1) 109.04(2) 99.12(1)	CuN ₃ F ₂	Me ₂ pzN Me ₂ pzN μF	3.131(1) 97.19(8) 82.81(8)	93.8(1,8,7) 172.6(1) 91.9(1,13) 159.9(1)	148
[Cu(μ-F)(tpma) ₂](PF ₆) ₂ (not given)	m P2 ₁ /n 4	11.649(4) 12.942(4) 14.654(4)	110.67(2)	CuN ₄ F ₂	N μF	3.444(1) 88.0(2) 92.0(2)	85.3(2,3,5) 100.2(2,7,4) 159.9(2) 171.8(2) 82.8(2,22) ^c 100.0(2) 167.1(2)	149

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	<i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]	α [°] β [°] γ [°]	Chromophore	<i>Cu-L</i> [Å]	<i>Cu-Cu</i> [Å] <i>Cu-L-Cu</i> [°] $\mu\text{L-Cu-}\mu\text{L}$ [°]	<i>L-Cu-L</i> [°]	Ref.
[Cu(μ -OH)(bpy)(CF ₃ SO ₃) ₂] ^c (blue)	tr	8.165(2)	93.10(1)	CuO ₃ N ₂	N 2.000(4.4)	2.8917(1)	O,O 96.5(1.1,1.1)	156
	P-1	14.265(2)	100.58(2)		O 2.436(4, 18)	97.3(1.4)	O,N 97.5(1.1,1.1)	
	3	18.748(5)	99.17(1)		μ HO 1.926(3, 9)	82.7(1.1)	N,N 171.6(2,2.7) 81.1(2,2) ^c	
[Cu ₂ (μ -OH) ₂ (bpy) ₂ (H ₂ O)(SO ₄) ₂] ^c (blue)	m	9.683(10)		CuO ₃ N ₂	N 1.996(4, 10)	2.920(1)	O,O 96.8(1.7)	157
	P2 ₁ /c	34.52(3)	103.50(5)		O 2.438(3, 0)	98.5(1)	O,N 95.2(2, 5.2)	
	4	7.882(10)			μ HO 1.927(3, 5)	81.5(1)	N,N 170.8(1, 1.9) 81.5(2, 0) ^c	
[Cu ₂ (μ -OH) ₂ (bpy) ₂ (H ₂ O)(SO ₄) ₂] ^c (blue)	m	9.658(12)		CuO ₃ N ₂	N 2.001(6, 20)	2.893	N,N 80.5(3, 6) ^c	158
	P2 ₁ /c	34.29(3)	103.3(1)		H ₂ O 2.247(5)	96.5(2, 6)	O,N 96.8(2, 3.7)	
	4	7.626(10)			O ₃ SO 2.207(5)	83.3(2, 4)	O,O 166.5(2, 3.0)	
[Cu ₂ (aamp)] ₂ ·H ₂ O (brown)	m	16.4854(9)		CuO ₂ N ₂	N 1.875(10, 18)	2.898(2)	O,O 94.4(4, 3)	159
	P2 ₁ /n	7.6005(13)	104.090(5)		μ O 1.895(8, 23)	99.8(4, 8)	O,N 172.4(5, 2.7)	
	4	21.162(11)				80.1(3, 3)	N,N 90.5(5, 3)	
[Cu ₂ (deamp)Cl] ₂ (blue)	or	14.138(4)		CuO ₂ NCl	N 2.046(11, 3)	2.903(3)	Cl,N 99.3(3, 12)	160
	Pbca	19.705(5)			Cl 2.207(5, 1)	97.9(4, 1)	Cl,O 99.6(3, 3)	
	8	14.729(4)			μ O 1.924(10, 16)	76.8(4, 3)	O,N 84.1(4, 13) ^c	
[Cu(μ -tbn)(ClO ₄) ₂ MeOH (purple)]	tr	8.970(4)	101.09(3)	CuO ₃ N ₂	O ₃ ClO 2.441(5)	2.9114(20)	N,N 87.14(16)	155
	P-1	9.974(2)	128.57(3)		N 1.996(4, 0)	96.54(14)	N,O 95.59(20, 9.42)	
	2	10.123(5)	93.93(3)		μ HO 1.951(3, 1)	83.46(14)	O,O 164.76(15, 6.20) 86.17(14) ^c	
[Cu(μ -OH)(eaeap)(ClO ₄) ₂] (violet)	m	9.195(19)		CuO ₃ N ₂	N 2.008(10, 45)	2.917(5)	O,O 95.35(19, 4.04)	161
	P2 ₁	19.290(44)	77.00(7)		O ₃ SO 2.590(9, 28)	99.2(2, 4)	N,N 94.7(5, 1.7) ^c	
	2	7.679(16)			μ HO 1.916(8, 21)	80.9(2, 7)	N,O 93.0(5, 6.8) O,O 170.2(4, 4.6) 92.7(3, 2.0)	

[Cu(μ -OH)(dpyam)] ₂ (BF ₄) ₂ (steel blue)	tr	9.686(2)	69.90(1)	CuO ₂ N ₂	N	1.977(3.0)	2.917(1)	N,O	95.5(1)	162
	P-1	9.429(3)	97.53(2)		μ HO	1.914(2.8)	99.3(2)		161.4(1)	
[Cu ₂ (μ -fpb)(μ -EtO)(MeOH)] (ClO ₄) ₂ (green)	1	7.414(3)	106.97(3)				80.7(2)	N,N	92.7(1)	163
	tr	10.552(1)	72.53(1)	CuO ₃ N	O	1.961(6)	2.924(2)	O, μ O	81.0(3)	
	P-1	13.271(2)	78.46(2)		N	1.923(7)	98.5(3,2,3)		107.1(3)	
	2	14.418(4)	72.83(1)		μ O	1.958(6)	80.6(3,4)		171.8(3)	
				μ EtO	1.886(6)			O,N	86.0(3,2,3) ^c	
				MeHO	2.296(8)			O,O	168.4(3)	
				O	1.964(8)				99.4(3,7,1)	
				N	1.962(8)			O,N	167.6(4)	
				μ O	1.970(6)			O,N	88.5(3) ^e	
				μ EtO	1.908(6)				164.3(3)	
				CuO ₄ N						
				CuO ₃ NCl	O	2.28(1)	2.926(3)	O,O	96.9(4,3,9)	164
	m	19.459(5)			N	2.05(1)	95.8(5)	O,N	83.5(5,1,5) ^c	
	P2/a	18.202(5)			μ O	1.97(2,0)	80.5(6)	O,Cl	97.5(3,1,5)	
	16	13.251(6)	67.21(2)		Cl	2.236(6)		N,Cl	97.8(4)	
				CuO ₃ NCl	O	2.30(1)	2.954(4)	O,O	98.2(4,4,3)	
					N	2.07(1)	97.0(4)	O,N	84.1(5,1,7) ^c	
					μ O	1.97(1,2)	79.6(3)	O,Cl	97.3(3,8)	
					Cl	2.232(4)		N,Cl	97.0(3)	
				CuO ₃ NCl	O	2.30(1)	2.956(4)	O,O	98.6(4,5,6)	
					N	2.07(1)	97.0(4)	O,N	82.9(4,2,0) ^c	
					μ O	1.97(1,2)	79.7(3)	O,Cl	97.4(3,7)	
					Cl	2.236(6)		N,Cl	97.5(4)	
				CuO ₃ NCl	O	2.28(1)	2.973(3)	O,O	99.3(4,3,6)	
					N	2.05(1)	97.5(7)	O,N	83.4(4,1,3) ^c	
					μ O	1.98(1,0)	79.7(5)	O,Cl	96.5(3,1)	
					Cl	2.250(4)		N,Cl	98.0(3)	
				CuO ₃ N ₂			2.929(1)		not given	165
	or	19.704(9)					not given			
	Pbca	12.735(3)								
	8	13.508(4)								
				CuO ₃ N ₂	O	2.292(6)	2.929	O,O	99.2(5)	166
	m	8.4495(6)			N	1.977(8,11)	98.2(6)	O,N	78.9(5) ^c	
	P2 ₁ /c	23.612(5)	115.43(1)		μ O	1.958(6)	81.8(5)		85.0(5) ^f	
	2	8.3041(8)				2.292(6)			103.4(5,36)	
									164.8(6,12,8)	
								N,N	94.3(6) ^g	
[Cu(μ -mdd)] ₂ (ClO ₄) ₂ (dark green)										
[Cu(μ -mdd)] ₂ (ClO ₄) ₂ (dark green)										

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å] Cu-L-Cu [°] μ L-Cu- μ L [°]	L-Cu-L [°]	Ref.
[Cu(μ -OH)(cha) ₂] ₂ (ClO ₄) ₂ (blue)	m C2/c 8	27.77(1) 14.45(1) 17.68(1)	91.7(1)	CuO ₂ N ₂ μ HO	N 2.008(7, 6) 1.941(6, 27)	2.934(8) 98.2(2, 16) 76.1(2, 0)	N,N 96.1(2, 4, 5) O,N 94.1(3, 2, 5)	167
[Cu(μ -OH)(dmaep)(ClO ₄) ₂] (dark blue)	m P2 ₁ /c 2	7.266(3) 16.500(9) 10.851(9)	82.43(3)	CuO ₃ N ₂ O ₃ ClO μ HO	N 2.005(3, 1) 2.721(4) 1.910(3, 10)	2.935(1) not given 79.6(1)	O,N 93.1(1, 7, 9) 171.0(2, 3) 86.9(1, 3, 3) N,N 95.2(1)	168
[Cu(HB(3, 5-i-Pr ₂ p ₂) ₃)(OH)] ₂ 1.5CH ₃ Cl ₂ (not given)	tr P-1 2	16.466(4) 16.904(5) 14.077(3)	112.92(2) 99.21(2) 90.76(2)	CuO ₃ N ₂ N μ HO	N 2.000(8, 16) 2.371(6) 2.640(7) 1.944(6, 10)	2.937(2) not given 79.4(2, 2)	N,O 92.7(3, 11, 8) 118.5(2, 1, 2) 157.7(3, 2, 5) 172.8(3, 1)	169
(pipH) ₂ [Cu(μ -MeOH) (2, 4-dmhp) ₂] ₂ (olive green)	or Pcab 4	13.935(3) 14.725(3) 21.730(5)		CuO ₆ O μ MeO	O 1.948(4, 12) 2.421(4, 3, 1) 1.939(4, 10)	2.939(1) 98.3(1) 81.8(2)	N,N O,O 94.2(2, 9, 8) 174.4(2, 2, 0) 156.8(2)	170
[Cu(μ -dmda)(ClO ₄) ₂] (not given)	m P2 ₁ /a 4	16.435(4) 14.522(3) 11.678(2)	109.98(2)	CuO ₃ N ₂ N μ O O ₃ ClO	N 2.032 1.941 2.590(6, 51)	2.939 98.4	not given	171
Cu ₂ (μ -hebd)(MeOH) (blue black)	m P2 ₁ /n 4	11.456(5) 11.425(3) 14.357(4)	104.15(3)	CuO ₄ O μ -O	O 1.879(3, 6) 1.924(3, 5)	2.942 100.1(1, 2) 79.8(1, 3)	O,O 93.5(2, 2, 0) ^f 171.4(1, 3)	172
[Cu(2-Brbz)(dame) ₂] (not given)	m P2 ₁ /c 2	12.228(9) 8.633(5) 14.297(8)	97.63(6)	CuO ₄ N O N N μ O	MeO 2.266(4) N 1.901(4, 6) μ O 1.913(3, 11)	2.946(2) 101.5(4) 78.5(4)	O,O O,N 167.2(2, 3, 3) N,N 87.5(2) ^c	173

[Cu(etap)Cl(H ₂ O)] ₂ (dark green)	tr P-1 1	8.133(1) 10.459(1) 6.689(1)	94.50(1) 97.86(1) 81.63(1)	CuO ₃ N2Cl	Cl S H ₂ O N μO	2.7792(8) 2.4101(6) 2.792(2) 1.991(2) 1.936(1.17)	2.9461(5) 99.11(6) 80.89(6)	Cl,S S,O S,N Cl,O O,O Cl,N O,N	97.44(2) 74.04(4) 97.89(4) 87.61(5) ^c 96.46(5.2.2) 170.88(4) 90.27(7.1) 90.27(6) 89.37(7.3.1) ^f	174
(pfpH) ₂ [Cu(2,4-dnph) ₂ (MeO)] ₂ 2MeOH (green)	or Pbca 8	13.552(3) 13.874(3) 26.170(5)		CuO ₆	phO μMeO	1.971(5.32) 2.354(6.17) 1.937(5.9)	2.947(2) 99.0(2) 80.9(2)	O,O O,O	77.8(2.0) ^c 94.0(2.4.7) ^f 168.7(2.5.8)	175
[Cu ₂ (dmf)(MeO)] ₂ :fpb (dark green)	tr P-1 2	12.035(2) 15.461(3) 7.614(1)	101.03(1) 101.06(1) 99.55(1)	CuO ₃ N	O N μO μHO	1.906(5.1) 1.902(6.0) 1.934(5.4) 1.898(5.7)	2.947(1) 99.3(2) 79.4(2.0)	O,N O,O	87.4(2.4.2) ^c 105.9(2.3)	176
[Cu(piapr)(H ₂ O)] ₂ :2H ₂ O (dark green)	m C2/c 4	20.328(7) 7.317(3) 16.862(3)	119.58(2)	CuO ₃ N ₂	H ₂ O N μO	2.394(6) 1.965(5.46) 1.949(4.3)	2.948(2) 98.3(2) 80.4(2)	N,N N,O O,O	82.1(2) ^c 95.8(2.5.9) ^f 176.3(2)	177
Cu ₂ (fsaen)(H ₂ O) (deep purple)	m P2 ₁ /n 4	13.961(5) 11.787(3) 11.622(3)	113.09(2)	CuO ₄	O μO	1.877(5.6) 1.912(5.3)	2.949(1) not given	O,O	100.3(2.8.9) not given	178
[Cu(2,4-dnph)(py)(MeO)] ₂ (not given)	m P2 ₁ /b 2	9.652(1) 15.159(2) 9.327(1)	92.21(1)	CuO ₃ N ₂ CuO ₄ N	H ₂ O N μO pyN O	2.557(5) 1.880(6.1) 1.899(5.1) 2.007(4) 1.921(4) 2.351(4) 1.929(4.15)	2.953(1) 99.9(2) 80.1(2)	O,O	80.2(2) ^f 89.8(2.9.6) 173.9(2) 93.0(2.2.2) 109.6(2) 162.2(2)	179
[Cu ₂ (damp) ₂ (H ₂ O)(ClO ₄)](ClO ₄) (not given)	m P2 ₁ /c 4	15.04(1) 12.85(1) 16.24(1)	100.1(1)	CuO ₃ N ₂	H ₂ O O ₃ ClO N μO	2.62(1) 2.32(1) 2.027(8.55) 1.935(6.20)	2.953(3) 99.4(2.1) 79.4(2.5)	N,N N,O	86.2(3.7) 91.1(2.4) 100.9(3.5)	180

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	<i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]	α [°] β [°] γ [°]	Chromophore	<i>Cu-L</i> [Å]	<i>Cu-Cu</i> [Å] <i>Cu-L-Cu</i> [°] μ <i>L-Cu-μL</i> [°]	<i>L-Cu-L</i> [°]	Ref.
[Cu(damet)(3-OHbz)] ₂ (dark blue)	m P2 ₁ /n 4	8.733(5) 21.670(19) 15.270(10)	96.14(5)	CuO ₂ N	bzO aeN μO	2.958(2) 101.7(3.6,4) 159.1(3,4) 84.1(2.4,9) ^f 103.0(2) 93.2(3.1,7) 173.2(3.1,1)	O,N O,N O,O	181
Cu ₂ (aspen)(H ₂ O) (green)	m P2 ₁ /c 4	12.991(5) 8.530(4) 18.546(6)	104.10(4)	CuO ₂ N ₂ CuO ₅	N μO H ₃ O O 1.875(11,0) μO 1.953(10,4)	2.96 99.9(4,3) 80.1(4,8)	N,N O,N O,O	182
N ₄ [Cu ₂ (fmcclaph)(OH)(H ₂ O)] ₂ 11H ₂ O (deep green)	tr P-1 2	17.129(5) 11.558(5) 8.372(5)	95.95(3) 104.72(3) 76.21(3)	CuO ₄ N H ₂ O μO 1.971(4,6) μHO 1.927(4,7)	N O 1.950(4,0) H ₂ O 2.278(4) 2.509(5)	2.964(1) 99.1(2,1.6) 80.7(1,0)	O,O O,N O,N	183
[Cu(Me ₄ m)(OH)] ₂ (ClO ₄) ₂ (burgundy)	m P2 ₁ /c 2	7.707(1) 14.996(2) 11.627(2)	109.13(1)	CuO ₂ N ₂	N μHO	2.966(3) 101.6(4) 78.4(4)	O,N N,N	184
[Cu(μ- <i>m</i> itbne)(Me ₂ SO)] ₂ (ClO ₄) ₂ (blue green)	m P2 ₁ /n 4	12.431(2) 14.251(3) 11.132(2)	108.01(2)	CuO ₃ N ₂ μMe ₂ SOO	O N 2.039(3,24)	2.9662(10) 98.31(10) 81.69(10)	N,N N,O O,O	155
[Cu(bz)(Me ₄ hd)] ₂ (purple)	tr P-1 1	13.462(5) 6.064(2) 12.756(6)	82.13(4) 115.61(2) 90.56(3)	CuO ₄	O μbzO	2.970(2) 102.1(2) 77.9(2)	O,O O,O	185

$[\text{Cu}_2(\text{[20-aneN}_3\text{]})(\text{MeO})_2(\text{MeCN})_2(\text{BPh}_3)_2$ (bright green)	m $\text{P2}_1/\text{n}$ 2	17.697(12) 14.830(13) 12.237(9)	105.0(1)	CuN_3O_2	N MeCN μMeO	2.056(24) 2.232(31) 1.787(42) 1.764(25) 2.070(25)	2.970(7) 101.3 78.7(11)	N,N	94.0(1,6,5) 92.7(1,3,2) 134.6(1,6,7) 173.5(15)	186
$\text{Cu}_2(\text{[20-aneN}_3\text{]})(\text{EtO})_2(\text{NCS})_2$ (green)	m $\text{I2}/\text{c}$ 4	15.356(10) 10.239(9) 18.662(16)	102.5(1)	CuN_3O_2	N SCN μEtO	2.192(19,92) 1.947(17) 1.932(13,29)	3.003(3) 102.73 78.0(5)	N,N O,N	92.6(7,4,1) ^f 93.9(6,1,8) 121.5(6) 140.9(6) 173.7(7)	186 187
$[\text{Cu}(\text{Me}_3(9\text{-aneN}_3)(\text{OH}))_2(\text{ClO}_4)_2]$ (blue)	not given			CuN_3O_2	N	2.072(5,12) 2.238(4)	2.971(1) 100.1(2)	N,O N,N	98.7(2,3,9) 84.7(2,1,1) ^c	188
$[\text{Cu}(\text{Me}_4\text{pip})(\text{EtO})_2]$ (purple)	m $\text{P2}_1/\text{n}$ 2	12.073(2) 11.510(2) 14.78(2)	101.47(2)	CuO_4	μHO O μEtO	1.938(4,1) 1.920(3,23) 1.901(3,2)	2.974(2) 103.0(2) 77.0(2)	O,O	92.8(1) ^f 93.2(1,12,5)	189
$[\text{Cu}(\text{Me}_4\text{em})(\text{OH}))_2(\text{ClO}_4)_2]$ (violet)	m $\text{P2}_1/\text{c}$ 2	7.557(5) 16.025(17) 14.014(9)	103.56(3)	CuO_2N_2	N μHO	2.064(5,40) 1.903(4,4)	2.978(2) 103.0(2) 77.0(2)	O,N N,N	98.2(2,1) 87.8(2) ^c	190
$[\text{Cu}(\text{bimpr})(\text{EtO})_2(\text{ClO}_4)_2]$ ·EtOH (violet)	m $\text{P2}_1/\text{n}$ 4	9.848(2) 13.000(2) 18.750(3)	96.46(1)	CuO_2N_2	N μEtO	1.972(9,2) 1.910(6,2)	2.979(2) ^d 102.46(29) 77.54(27)	N,O N,N	96.8(3,3) 173.1(3,2) 88.5(3) ^c	191
$[\text{Cu}_2(\text{C}_{10}\text{H}_{17}\text{N}_4\text{O})(\text{OH})(\text{MeCN})_2]$ $[\text{Cu}_6\text{fio}]$ (not given)	tr P-1 2	10.476(3) 11.846(6) 13.558(7)	97.77(4) 99.62(3) 96.33(3)	CuO_2N_2	N μO μHO	1.976(7,63) 1.954(6) 1.915(7)	2.980(2) ^d 98.49 102.95 78.8(-,3)	N,N O,N N,N	84.9(3) ^c 96.6(3,4,8) 166.1(3,1,2)	192
$\text{Cu}_2(\text{acacP}(\text{O}))(\text{MeO})(\text{MeOH})$ (blue)	m $\text{P2}_1/\text{n}$ 2	9.750(2) 16.399(2) 16.698(4)	97.25(2)	CuN_3O_2	N μO μHO	1.952(8,40) 2.490(9) 1.988(6) 1.896(7)	2.982(3) 101.6(4) 78.4(4)	N,N O,N O,O	86.0(3) ^c 95.7(3,1,4) ^f 94.2(3,9,5) 170.2(3,4,8)	193

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å]			α [°]			Chromophore	Cu-L [Å]	Cu-Cu [Å]			L-Cu-L [°]	Ref.
		b	c	β	γ	Cu-L-Cu	Cu-L-Cu			μ				
[Cu(2-bae)Br] ₂ (olive green)	or	21.16(2)						CuO ₂ NBr	N	2.071	2.984(124) ^d	O,N	88.4(3.0,6.29) ^f	194
	P2 ₁ 2 ₁ 1 4	15.15(2)	8.40(1)				Br		2.369	105.2(3.3,7.0)	Br,N	157.4(3.79,1.6)	157.4(3.79,1.6)	
[Cu(pyeth)(NO ₃) ₂] ₂ [Cu(pyeth)- (H ₂ O)] ₂ (NO ₃) ₂ ^e (dark green)	tr	11.234(2)			95.13(2)			CuO ₃ NS	O ₂ NO	2.255(6)	2.986(1)	O,S	85.5(1) ^f	195
	P-1 2	15.605(2)	8.535(2)	121.74(1)	72.90(1)		N		1.964(5)	100.6(2)		110.1(1)	110.1(1)	
							S	2.335(2)	79.4(2)		153.4(2)	153.4(2)		
							μ O	1.941(1.23)			96.6(2,1.3)	96.6(2,1.3)		
											169.6(2)	169.6(2)		
											S,N	93.2(2) ^f	S,N	
											O,O	93.9(2,1.0)	O,O	
											O,S	85.6(2)	O,S	
											101.0(2)	101.0(2)		
											155.8(1)	155.8(1)		
											O,N	96.8(2,1.6)	O,N	
											164.6(2)	164.6(2)		
											S,N	92.5(2) ^f	S,N	
											O,O	99.8(2,4)	O,O	
											O,N	92.2(1.4) ^f	O,N	196
											2.986(1)	2.986(1)		
											—	—		
											76.7(1)	76.7(1)		
											3.005(1)	3.005(1)		
											—	—		
											76.7(1)	76.7(1)		
											101.1(1)	101.1(1)		
											N,N	98.4(1)	N,N	
											Cl,Cl	109.5(1,24.9)	Cl,Cl	

[Cu(acacha) ₂] (green)	tr P-1 2	8.914(10) 10.485(10) 11.733(10)	101.6(3) 110.6(3) 92.5(3)	Cu ₃ N ₂	N O μO	1.988(11.14) 1.890(12.10) 1.967(9.65)	2.989(3) 98.9(4.18) 78.3(4)	O,O O,N 98.0(5.5) ^f	197
[Cu ₂ (pamph)(OMe)](ClO ₄) ₂ 0.5MeOH (not given)	tr P-1 2	13.571(4) 12.316(3) 14.072(3)	91.43(2) 103.59(2) 122.80(2)	Cu ₃ N ₂	N μO μMeO	2.050(9.38) 2.069(7.1) 1.899(7.3)	2.989(3) 98.2(3.5.7) not given	O,N 126.9(3.1) 171.7(3.1) 124.6(4.2)	198
[Tl ₄ Cu ₁ (Cu(ocoxb)) ₂ ·10H ₂ O] (blue)	or Amm2 2	12.836(8) 24.933(9) 7.482(3)		Cu ₄	O	1.942(12.30)	2.990(6) 98.7(9) 81.3(9)	O,O 93.9(8.1) ^f	199
[Cu(C ₂₂ H ₂₁ N ₄ O ₂)(OH)](ClO ₄) ₂ (dark green)	tr P-1 2	9.399(2) 10.469(1) 14.612(4)	102.72(2) 100.71(2) 104.60(2)	Cu ₃ N ₂	O ₃ ClO N μO μHO	2.481(9) 1.967(10.47) 1.971(6) 1.991(2)	2.991(2) 100.6(3.1.4) 78.7(3.1)	O,O O,N 168.9(3.4.7) 96.1(4.2) ^f	200
[Cu(C ₂₂ H ₂₁ N ₄ O)(OH)] ₂ (BF ₄) ₂ (dark green)	tr P-1 2	9.323(4) 10.449(2) 14.179(4)	102.30(4) 102.43(2) 101.84(2)	Cu ₂ N ₂	N μO μHO	1.965(5.32) 1.968(4.1) 1.910(4.1)	2.990(2) not given not given	N,N N,O 169.3(2.3.2) 78.3(2.0)	201
[Cu(tmp)(MeO)Cl] ₂ (violet)	m P2 ₁ /n 2	12.09(2) 7.647(3) 19.815(5)	96.63(2)	CuO ₂ NCl	N Cl μMeO	1.964(4) 2.257(4) 1.917(4.17)	2.992(1) 102.6(2) 77.4(2)	Cl,N Cl,O 169.8(1) 93.2(2)	202
[Cu ₂ (pmp)(OH)](NO ₃) (H ₂ O)]NO ₃ (blue green)	m Pn 2	7.438(2) 14.823(2) 10.399(4)	90.23(2)	Cu ₃ N ₂	H ₂ O N μO μHO	2.213(4) 1.970(6.37) 1.981(3) 1.930(3)	2.992(1) 101.1(2.1.2) 78.5(1.9)	O,O N,N O,N 102.2(2.6.3) 165.3(2.4) 94.0(1.8.9) 165.1(2)	203
[Cu(Pr-nso)Br] ₂ (not given)	m P2 ₁ /a 2	17.765(2) 10.363(1) 7.831(1)	102.71(1)	CuO ₂ NSBr	Br N S μO	2.381(1) 2.443(5) 2.315(2) 1.935(5.5)	2.992(1) 101.3(3) 78.7(2)	O,S S,Br O,Br O,N 99.1(2.4) 84.6(2) ^c 104.7(1)	204

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å] Cu-L-Cu [°] μ L-Cu- μ L [°]	L-Cu-L [°]	Ref.
[Cu(2-Me-im) ₂ (OH) ₂](ClO ₄) ₂ 2H ₂ O (not given)	m C2/a 2	14.920(6) 13.768(7) 7.482(4)	103.2(3)	CuO ₂ N ₂ μ HO	N μ HO	2.993(1) 99.3(2) 80.7(1)	O,N 93.6(1) 168.2(1) 93.9(1)	205
[Cu ₂ (bzsmph)(OH)(ClO ₄) ₂] (not given)	or Fdd2 8	26.30(1) 18.801(8) 14.831(9)		CuO ₂ NS S N μ O 2.001(6) μ HO 1.868(6)	O ₃ ClO S N μ O 1.911(8) 2.335(3) 2.596(10)	2.994(1) 101.7(5,4,8) 78.3(3)	S,O 164.0(2) 91.9(2) 99.1(3) 175.8(3)	206
[Cu(μ -tbnp)(ClO ₄) ₂] (deep blue)	tr P-1 2	9.074(1) 9.971(1) 7.708(1)	82.39(1) 104.77(1) 107.02(1)	CuO ₂ N ₂ N μ O	O ₃ ClO N 2.012(2,13) 1.921(1,8)	2.9949(6) 102.41(6) 77.59(6)	N,N 86.22(7) 96.03(7,3,61) 169.41(7,2,36) 97.35(6) 94.87(6,4,59)	155
[Cu(tfmd)] ₂ (not given)	m P2 ₁ /c 4	9.144(2) 11.564(3) 12.008(2)	97.05(1)	CuO ₃ N μ O	N O μ O	2.995(2) not given 76.80(8)	O,O O,O 169.33(7) 94.59(8,4) 170.74(8)	207
[Cu(2,6-dtpp)(py)(MeO)] ₂ (not given)	m A2/a 4	15.503(2) 15.350(2) 12.609(1)	109.20(2)	CuO ₄ N μ MeO	pyN O μ MeO	2.996(1) 102.7(1) 77.3(1)	O,O O,O 93.2(1,9,1) 173.3(1) 93.8(1,3,7) 168.2(1)	179
[Cu(Me-nso)Cl] ₂ (not given)	tr P-1 1	7.677(1) 9.131(1) 7.564(1)	99.68(1) 69.87(1) 71.79(1)	CuO ₂ N5Cl N S μ O	Cl N S μ O	2.9955(6) 101.6(1) 78.4(1)	O,S 84.72(8) S,Cl 96.62(3) O,Cl 98.00(8) O,N 98.8(1,1,9) S,N 84.94(8) Cl,N 102.87(7)	204
[Cu(Bu-nso)Br] ₂ (not given)	m P2 ₁ /a 2	10.284(1) 19.806(3) 7.955(1)	96.76(1)	CuO ₂ NSBr N S μ O	Br N S μ O	2.998(1) 100.9(2) 79.1(2)	O,S 84.6(1) S,Br 94.63(5) O,Cl 100.0(1) O,N 98.02(2,5)	204

[Cu(Pr-nso)Cl] ₂ (not given)	m P ₂ /a 2	17.829(3) 10.322(2) 7.639(1)	102.73(1)	CuO ₂ N ₂ Cl	Cl N S μO	2.236(2) 2.468(3) 2.330(2) 1.935(4, 10)	2.999(1) 101.6(2) 78.4(2)	O ₂ S S ₂ Cl O ₂ Cl O ₂ N S ₂ N Cl ₂ N	85.0(1) ^c 106.6(1)	204
[Cu(Me ₆ en)(OH) ₂ Br ₂ (burgundy)]	or Fddd 8	17.072(5) 18.482(5) 12.825(5)		CuO ₂ N ₂	N μHO	2.030(10, 0) 1.902(3, 0)	3.000(4) 104.08(17) 75.92(17)	O ₂ N O ₂ N N ₂ N	98.8(27) 86.7(80) ^c	208
[Cu(pcdp)] ₂ (red)	m C2/c 4	25.61(2) 5.46(1) 16.90(2)	136.33(10)	CuO ₂ N ₂	N μO	1.947(13, 5) 1.906(11, 15)	3.001(4) 103.9(4) 76.1(4)	O ₂ N N ₂ N	95.2(4) ^f 100.6(4, 5.4) 83.2(5) ^c	209
Cu(ambt) (red purple)	m P ₂ /n 2	16.661(6) 10.256(4) 5.333(1)	98.69(2)	CuO ₂ N ₂	N μO	1.952(3, 47) 1.912(3, 12)	3.002(1) 103.5(1) 76.5(1)	O ₂ N O ₂ N	99.7(1, 2.6) 97.1(1) ^f 174.4(1, 1.0) 84.2(1) ^c	210
[Cu(2, 4, 6-Cl ₃ ph)(qu)(ac)] ₂ (black green)	m P ₂ /b 4	9.494(3) 11.397(4) 14.705(4)	94.44(7)	CuO ₃ NCl	quN Cl ₃ phO μCl μacO	2.001(14) 1.911(11) 2.983(6) 1.921(11, 4)	3.004(1) 102.9(5) 77.1(7)	N ₂ N N ₂ O Cl ₂ O	95.0(9, 2.9) 72.1(5) ^c 96.2(6, 2.5)	211
[Cu(3-Brbz)(damet)] ₂ (not given)	tr P-1 1	8.263(5) 8.759(5) 10.552(6)	87.54(4) 80.74(5) 87.47(5)	CuO ₄ N	O N N μO	1.895(6) 2.895(7) 1.029(9) 1.907(6, 18)	3.005(2) 104.0(3) 76.0(3)	O ₂ N O ₂ O	91.9(3, 6.9) 159.6(3) 100.1(3) 175.9(3)	173
Cu ₂ (cap)Cl ₂ (not given)	m P ₂ /c 4	7.639(2) 18.527(3) 14.633(3)	116.93(1)	CuO ₂ N ₂	N μO	1.919(8, 9) 1.884(6, 13)	3.006 100.6(3, 3.1) 78.5(3, 3.5)	N ₂ N O ₂ N	89.8(3) ^c 94.2(3, 1.0) ^f 175.7(3, 8) 136.1(2, 3.9)	212
[Cu(damet)] ₂ (dark violet)	tr P-1 2	6.297(3) 8.059(2) 10.464(4)	73.33(3) 76.84(3) 71.57(3)	CuO ₂ Cl ₂	Cl μO	2.181(3, 1) 1.952(7) 2.097(6)	3.007(1) 103.6(1) 76.4(1)	Cl ₂ Cl O ₂ Cl	105.8(1) 103.6(2, 3.5) 103.6(2, 3.5)	213

TABLE II (Continued)

Compound (color)	<i>C_{2v}</i> cl. space G. Z	<i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]	α [°] β [°] γ [°]	Chromophore	<i>Cu-L</i> [Å]	<i>Cu-Cu</i> [Å] <i>Cu-L-Cu</i> [°] $\mu L-Cu-\mu L$ [°]	<i>L-Cu-L</i> [°]	Ref.
[Cu(Et ₂ z)(NO ₃) ₂] (black)	m P2 ₁ /c 2	9.678(6) 9.82(1) 16.267(7)	134.69(4)	CuO ₄ N	O ₂ NO N μO	3.008(1) 101.1(1) 78.9(1)	O,O O,N 158.1(1)	214
[Cu(apns)] ₂ (not given)	m P2 ₁ /c 2	4.597(1) 15.515(5) 16.345(4)	113.28(2)	CuO ₃ N	O N μO	3.009(1) ^d 103.4(2) 76.6(1)	O,N 170.8(2) 92.9(1) ^f 167.7(1)	215
[Cu(OHbim)(Obim)] ₂ (ClO ₄) ₂ 5EtOH (blue)	tr P-1 2	19.380(4) 21.345(6) 9.484(3)	102.52(2) 103.93(2) 105.76(2)	CuO ₃ N ₂	O N μO	3.008(4) 102.6(3,1) 76.7(3,1)	N,O 95.2(3,1,4) 157.1(3,1) 170.8(3,5) 76.6(3) 99.4(3,1,6) 105.3(3,2)	216
[Cu(Me-nso)(NCS)] ₂ (dark green)	m P2 ₁ /a 2	10.025(3) 14.421(3) 8.595(2)	110.49(2)	CuO ₂ N ₂ S	SCN S N μO	3.009(2) 103.0(2) 77.0(2)	S,O 160.8(2) 92.0(2,7,6) ^f 100.6(3,3,5) 159.0(3) 98.7(3)	217
[Cu(dpae)(OCN)] ₂ (dark green)	m P2 ₁ /n 2	10.469(7) 12.742(8) 8.695(6)	95.92(1)	CuO ₂ N ₂	OCN N μO	3.010(1) 104.2(1) 75.8(1)	O,N 100.5(1,1,5) 165.3(1,6,9) 102.0(1)	218
[Cu(Pr-nso)Cl] ₂ (at 120 K) (dark green)	m P2 ₁ /a 2	17.647(3) 10.246(1) 7.636(1)	102.98(1)	CuO ₂ N ₂ NSCl	Cl N S μO	3.010(1) 101.6(1) 78.4(1)	S,O 163.4(1) 95.1(1) 84.4(1) ^c 98.4(1,7) 100.2(1) 156.5(1) 104.3(1)	219

[Cu ₂ (imiph)(OH)(H ₂ O)(ClO ₄)]·ClO ₄ (green blue)	m P2 ₁ /c 4	7.354(4) 21.781(19) 16.175(8)	90.70(4)	CuO ₂ N ₂	H ₂ O	2.185(18)	3.011(4)	N,N	94.81(59, 29) ^f	220
					O ₃ ClO	2.990(14)	102.04	N,O	94.45(62, 2.48) ^f	
					μO μHO	1.938(14, 18) 1.938(13, 5) 1.925(15, 28)	77.96	O,O	90.82(63, 7.98)	
[Cu(mapyNO)Cl ₂] ₂ (amber)	tr P-1 1	11.0483(11) 9.2975(9) 9.4998(9)	124.61(1) 92.85(1) 99.26(1)	CuO ₃ Cl ₂	Cl	2.231	3.011(1)	O,O	88.3(1)	221
					O	2.515	112.4(3)	Cl,O	159.3(1)	
					μO	1.928 1.958(-, 30)	71.1(1)	Cl,Cl	146.4(1)	
Cu ₂ (salen)(F ₃ acac) ₂ ^e (dark)	tr P-1 4	17.03(4) 19.11(4) 9.89(2)	96.58(11) 100.10 107.70(13)	CuO ₂ N ₂	N	1.960(17, 37)	3.011(3)	N,N	83.6(8) ^c	222
					μO	1.934(13, 1)	91.1(6, 8.7)	O,N	92.9(7, 2.5) ^f	
					O	1.959(13, 36)	81.4(6, 9.0)	O,O	174.6(7, 9)	
					μO	2.305(11)			88.8(5, 1.6) ^f	
					μO	2.007(13) 2.576(12)			92.0(6, 13.3) 172.3(6, 5.6)	
[Cu(scal) ₂ NO ₃ ·H ₂ O] (not given)	m P2 ₁ /n 4	18.817(7) 8.689(4) 7.289(5)	104.916(3)	CuO ₃ N	N	1.939(4)	3.012(2)	O,O	105.5(2)	223
					O	1.993(4)	100.2(2)	O,N	80.9(2) ^f	
					μO	1.963(3, 1)	79.7(1)		91.9(2) ^f	
					N	2.008	3.013		not given	
					μO	1.934	102.4			
[Cu(μ-bdo)] ₂ ClO ₄ (not given)	tr P-1 1	9.829(3) 12.431(3) 8.741(3)	104.15(2) 115.77(2) 69.53(2)	CuO ₂ N ₂	N	2.008	3.013		not given	171
					μO	1.934	102.4			
					O	1.980(14, 48)			87.3(5, 3.4) ^f	
					μO	2.260(15) 2.024(11)			92.5(6, 10.7) 175.5(6, 2.5)	
					μO	2.335(12)				
[Cu(tfmd')] ₂ (not given)	or Pbca 4	12.486(3) 19.387(4) 10.754(2)	3.014(2) not given 75.94(9)	CuO ₃ N	O	1.892(2)	3.014(2)	O,O	93.59(8) ^f	207
					N	1.998(2)	not given		169.30(8)	
					μO	1.911(2, 13)	75.94(9)	O,N	95.2(9, 3.4) ^h	
									174.55(9)	
[Cu(hzoc)(NO ₃) ₂] ₂ (green)	tr P-1 2	8.830(4) 9.224(4) 9.230(3)	87.76(3) 113.74(3) 107.41(3)	CuO ₄ N	O ₂ NO	1.940(5)	3.016	O,N	91.7(2, 5.8) ^f	224
					N	2.035(7)	not given	O,O	93.8(2, 10.9)	
					μO	1.945(5, 3)	78.3(2)			

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	<i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å] Cu-L-Cu [°] μ L-Cu- μ L [°]	L-Cu-L [°]	Ref.
[Cu(hfc)(phen)] ₂ (dark blue)	m P2 ₁ /n 2	9.10(2) 20.68(3) 11.101(1)	93.55(2)	CuO ₃ N ₂ phenN O μ O	1.993(3) 2.305(3) 1.962(3) 1.935(2,27)	3.016 102.4(1) 77.6(1)	O,O 151.9(1) 95.9(1,3,6) 113.5(1,6) 169.5(1) 77.5(1) ^c	225
[Cu(OHbim)(Obim)(NO ₃) ₂] 4Me ₂ SO (blue)	m P2 ₁ /n 2	15.932(8) 9.227(1) 21.180(2)	98.51(3)	CuO ₃ N ₂ O ₂ NO OHbimN ObimN μ O	2.447(8) 1.955(7) 1.967(7) 1.938(6,1)	3.017(5) 102.3(4) 77.3(3)	N ₁ O 95.9(3) 170.2(2) 99.5(3) 82.6(3) 105.3(3)	226
[Cu(fmp)](BF ₄) ₂ ·H ₂ O (green)	m C2/c 4	38.80(2) 12.618(6) 18.366(8)	112.42(4)	CuN ₃ O ₂ N μ O	1.98(2,4) 2.64(2,5) 1.94(1,4)	3.017(5) 101.18(6,1,3) 78.3(6,6)	O,N 154.7(7,5,0) 106.5(8,1,4)	227
[Cu ₂ (maidpp)(OH)](ClO ₄) ₂ (violet)	m P2 ₁ /c 4	7.807(1) 23.232(3) 16.215(2)	103.845(4)	CuO ₂ N ₂ N μ O μ HO	1.961(4,53) 1.962(3,4) 1.887(4,14)	3.018(1) 103.5(2,2,9) 76.8(1,0)	O,N 172.6(2,5,2) 87.0(2,1) ^c	228
[Cu(Et-nso)Cl] ₂ (not given)	tr P-1 1	8.694(2) 9.879(2) 7.591(2)	94.03(2) 114.59(2) 83.61(2)	CuO ₂ N ₃ Cl Cl N S μ O	2.229(2) 2.421(4) 2.334(1) 1.934(3,3)	3.018(9) 102.6(1) 77.4(1)	O,S 95.90(6) 99.2(1) 99.7(1,1) 84.66(9) ^c 105.8(1)	204
[Cu(bba)Br] ₂ (black)	m P2 ₁ /c 2	10.895(7) 8.978(5) 19.90(2)	113.46(7)	CuO ₂ NBr Br N μ O	2.304(6) 2.01(2) 1.96(2,1)	3.019(7) 101.2(9) 78.8(8)	O,N 152.1(8) 100.7(6) 152.5(6) 101.0(6)	229

α -[Cu(2-bae)Br] ₂ (not given)	or P ₂ ,P ₂ ,P ₂ ,P ₂ , 4	21.235(13) 15.220(8) 8.390(5)	CuO ₂ NBr	Br N μ O	2.333(4) 2.06(2.1) 1.92(2.1)	3.019(4) 103.8(7.5) 76.2(7.5)	O,Br	99.0(5.2) 171.7(7.1,6) 82.5(7.7) ^c 158.5(7.1) 102.5(6.2)	230
K ₂ [Cu(biu)(OH)] ₂ ·4H ₂ O (not given)	m P ₂ ,/c 2	3.784(1) 14.505(2) 15.035(2)	CuO ₂ N ₂	N μ HO	1.912(5.1) 1.955(4.6)	3.020(1) 101.1(2)	O,N N,N	94.2(2.5) 92.7(2) ^f	231
[Cu ₂ (bmmp)(OH)](ClO ₄) ₂ (not given)	m P ₂ ,/a 4	21.531(6) 18.479(2) 8.177(1)	CuO ₂ S ₂ N	N S μ O μ HO	2.005(8.1) 2.393(3.35) 1.984(7.10) 1.906(8.0)	3.020(2) 102.0(3.2,9) 78.1(3.5)	O,S O,N	97.0(2.3,1) ^f 110.4(2.2,2) 132.1(2.3,9) 92.1(3.7) ^e 169.6(3.5) 88.2(2.1,4) ^c 117.4(1.1,7)	232
[Cu(salapr)] ₂ (violet)	m P ₂ ,/c 2	9.018(5) 10.810(4) 10.233(5)	CuO ₂ N	O N μ O	1.896(14) 1.896(18) 1.924(16.7)	3.021(4) 103.5(4)	O,O	not given 177.2(3.5) 87.0(3.3) ^f 93.5(3.13,0) 172.4(3.5,9)	233
Cu ₂ (F ₆ pd)(ebs) ^f (not given)	tr P-1 4	21.374(6) 17.065(5) 9.938(4)	CuO ₂ N ₂ CuO ₆	N N μ O O	1.927(8.11) 1.916(8.16) 1.959(6.29) 2.269(9)	3.021(3) not given 78.8(3.7,9)	N,N O,N	84.6(4) ^c 94.3(3.6) ^f	234
Cu ₂ (m ₁ prpb)(OH)(H ₂ O)(ClO ₄) (blue)	m C ₂ /c 8	29.924(2) 12.289(1) 15.168(1)	CuO ₂ N ₂	H ₂ O O ₃ ClO N μ O μ HO	1.933(8.7) 1.916(6.20) 1.938(7.46) 2.289(8) 2.031(5) 2.376(7) 2.346(4) 2.544(3)	3.137(2) not given 80.3(3.7,0)	N,N O,N O,O	85.5(4) ^c 93.6(3.4) ^f 177.7(4.1,0) 85.9(3.2,8) ^f 93.6(3.9,5) 175.6(3.2,4)	235

TABLE II (Continued)

Compound (color)	<i>C</i> ₁ <i>cryst. cl.</i> <i>space G.</i> <i>Z</i>	<i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]	α [°] β [°] γ [°]	Chromophore	<i>Cu-L</i> [Å]	$\frac{Cu-Cu}{Cu-L-Cu}$ [Å] $\frac{\mu L-Cu-\mu L}{\mu L-Cu-\mu L}$ [°]	<i>L-Cu-L</i> [°]	Ref.
Cu ₂ (bpsp) (dark green)	m P2 ₁ 2	17.657(1) 25.573(2) 9.165(1)	91.58(1)	CuO ₂ N	N O μ O	3.023(1) 101.2(2, 8) 78.5(1, 4)	O,O 173.0(2, 1.9) O,N 86.1(2, 1) ^c 92.8(2, 4) ^f 169.7(2, 1.2)	236
[Cu(tpcs)] ₂ (brown)	m P2 ₁ /c 2	9.475(1) 11.251(3) 9.875(2)	102.84(2)	CuO ₂ N	O N μ O	3.026(1) ^d 103.6(1) 76.4(1)	O ₂ N 169.1(1) 93.1(1) ^f 164.4(1)	215
[Cu(pia)] ₂ (brown)	m P2 ₁ /c 4	5.98(1) 10.97(2) 14.42(2)	106.75(10)	CuO ₂ N	N O μ O	3.026(6) 106.4(6) 73.6(6)	O ₂ N 97.3(7, 2.3) 173.1(6) O,O 91.8(6)	237
[Cu(damet)Br] ₂ (green)	m P2 ₁ /n 4	8.579(2) 12.062(3) 8.919(1)	102.72(2)	CuO ₂ NBr	Br N μ O	3.026(2) 104.5(4) not given	N ₂ O Br,N Br,O 100.9(2) 104.5(4) 172.4(3)	238
[Cu ₂ (bimp)(MeO)](ClO ₄) ₂ 2MeOH (green)	m C2/c 4	23.221(3) 12.903(2) 17.681(3)	125.34	CuN ₃ O ₂	N N μ O μ MeO	3.026(1) 102.1(1, 3.4) 77.9(1)	N ₂ O 114.7(1) 130.4(1) 169.9(1) 82.0(1, 1.6) ^c 113.1(1)	239
[Cu(phb)(NO ₃) ₂] (not given)	tr P-1 1	10.420(3) 8.489(8) 11.687(2)	107.38(6) 90.96(2) 131.19(8)	CuO ₄ N	O ₂ NO N μ O	3.027(1) 100.05(6) 79.95(6)	O,O 87.97(6) 105.1(6, 4.8) 161.4(7)	240
[Cu(ete)Br] ₂ (not given)	tr P-1 1	7.320(3) 8.544(3) 6.181(2)	103.88(2) 99.61(3) 88.15(3)	CuO ₂ SBr	Br S μ O	3.028(2) 102.9(4) 77.1(4)	O ₂ S 161.7(3) 99.9(3) 167.7(2) 95.9(1)	241

[Cu ₂ (ahm)]·3H ₂ O (not given)	m P ₂ ₁ /n 4	22.613(21) 8.890(7) 9.496(5)	93.00(8)	CuO ₂ N ₂	N μO	1.960(8, 30) 1.925(6, 15)	3.029(3) 103.8(3.5) 76.3(2.5)	O,N N,N	95.1(3, 8) ^f 93.6(3.2, 0) ^f	242
[Cu(paaan)] ₂ ·C ₆ H ₆ (not given)	m C ₂ /c 2	19.001(9) 6.516(3) 15.802(6)	113.36(3)	CuO ₃ N	N O μO	1.924(4) 1.928(3) 1.908(3, 38)	3.030(1) 103.7(1) 76.3(1)	O,O O,N	93.4(1) ^f 95.2(2, 1.0) ^f	243
[Cu(aples)] ₂ (not given)	m P ₂ ₁ /c 2	10.982(8) 8.799(2) 12.322(2)	90.68(3)	CuO ₃ N	O N μO	1.887(3) 1.935(4) 1.923(3, 6)	3.030(2) ^d 104.0(1) 76.0(1)	O,N O,O	95.1(1, 1.9) ^f 170.9(1) 92.8(1) ^f 168.4(1)	215
[Cu ₂ (Me ₂ [(9)-aneN ₃](H ₂ O))]· (ClO ₄) ₂ (green)	not given	not given	not given	CuN ₃ O ₂	N μO μH ₂ O	2.069(7, 5) 2.221(7) 2.199(5) 2.220(5)	3.032(1) 88.6(2) 91.4(2)	N,O N,N	91.0(2, 2) 107.8(2) 85.2(3, 1.2) ^f	188
Cu ₂ (Fe ₆ pd) ₂ (ppp) ₂ en (not given)	m P ₂ ₁ /c 4	13.702(3) 20.010(8) 12.579(3)	96.81(1)	CuO ₂ N ₂ CuO ₆	μO μO O μO	2.092 1.981 2.305 1.985 2.210 2.400	3.032 95.6(-, 6.2)	not given	not given	244
[Cu(damet)Br] ₂ (not given)	m P ₂ ₁ /n 2	8.946(9) 12.188(12) 8.576(9)	102.45(18)	CuO ₂ NBr	Br N μO	2.356(3) 2.021(11) 1.911(13, 38)	3.033(5) 105.0(6) 75.0(6)	Br,O Br,N O,N	100.7(4) 171.3(4) 101.7(3) 83.1(5) ^f 157.4(5)	245
[Cu ₂ (Me ₂ [[22]-aneN ₄](MeO)] ₂ · (ClO ₄) ₂ (blue green)	m P ₂ ₁ /a 2	16.734(3) 8.549(1) 13.103(2)	111.05(1)	CuO ₂ N ₂	N μMeO	2.013(3, 6) 1.945(2, 7)	3.034(1) 102.50(8) 77.50(8)	not given	not given	246
[Cu(Me ₂ N(CH ₂) ₃ NH(CH ₂) ₂ O)] ₂ · (MeOH)] ₂ (ClO ₄) ₂ (deep green)	or P _{bc} a 8	14.760(5) 16.441(5) 11.911(4)		CuO ₃ N ₂	MeHO N μO	2.348(10) 2.031(10, 21) 1.930(7, 4)	3.034(2) 103.6(2) 76.3(3)	O,N N,N O,O	94.5(4, 10.7) 83.8(3) ^f 94.7(3) ^f 96.8(4, 3.5)	247

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å]			Chromophore			α [°] β [°] γ [°]	$Cu-L$ [Å]	$Cu-Cu$ [Å] $Cu-L-Cu$ [°] $\mu L-Cu-\mu L$ [°]	$L-Cu-L$ [°]	Ref.
		b [Å]	c [Å]									
[Cu ₂ (Cl) ₂] (not given)	tr P-1 1	7.243(3) 8.459(3) 6.068(2)			CuO ₂ SCl	Cl S μO	2.230(2) 2.319(2) 1.925(4, 2)	3.034(1) 103.9(2) 76.1(2)	O,S O,Cl S,Cl	85.8(1) ^f 161.6(1) 100.3(1) 168.3(1) 96.91(6)	241	
[Cu(dana)(py)] ₂ (blue)	m P2 ₁ /c 2	8.413(2) 22.791(5) 11.109(2)			CuO ₄ N	pyN O μO	2.298(3) 1.899(2, 9) 1.947(2, 16)	3.0351(9) 102.44(9) 77.56(9)	N,O N,O O,O	93.9(9, 2.0) 105.76(9) 92.4(8, 7) ^f 93.1(9, 1.4) 163.1(11, 3, 7)	248	
[Cu ₂ (C ₃₄ H ₄₀ N ₆ O)(OH)](PF ₆) ₂ (not given)	or P2 ₁ P2 ₁ P2 ₁ 4	11.205(2) 23.261(5) 16.333(4)			CuN ₃ O ₂	N μO μHO	2.028(31, 34) 2.209(19, 11) 2.015(21, 0)	3.037(5) 100.8(9, 3, 0) 77.6(8, 1)	O,N O,N N,N	90.4(10, 7, 7) ^f 101.8(8, 3, 8) 157.6(10, 6, 5) 97.2(11, 5, 8)	249	
[Cu(H ₂ O) ₂ (4-NO ₂ bpz)(py)] ₂ (blue)	tr P-1 1	6.943(4) 13.942(8) 12.979(9)			CuO ₃ N	bpzO H ₂ O μH_2O	1.91(1, 1) 2.44(1) 79.1(1)	3.04 100.4(1) 79.1(1)	O,O O,N	89.4(1, 7, 0) 174.9(1, 1, 9) 92.5(1, 6, 7) 173.3(1)	250	
[Cu(N-Mesala)Cl] ₂ (not given)	tr P-1 1	6.998(2) 10.165(2) 7.189(1)			CuO ₂ NCl	Cl N μO	2.202(4) 1.94(1) 1.954(7, 39)	3.041(1) 102.2(2) 77.8(2)	O,N N,Cl O,Cl	94.5(4) ^f 97.5(3) 149.1(1)	212	
[Cu(N-ocd)Br] ₂ (dark green)	tr P-1 1	4.5213(6) 8.484(1) 13.052(7)			CuO ₂ NBr	Br O μO	2.348(4) 1.94(2) 1.92(2, 0)	3.042(4) not given 74.1(7)	Br,N Br,O N,O	99.3(6) 159.3(5) 92.1(7)	251	
[Cu(bdhe)] ₂ (ClO ₄) ₂ (deep green)	m P2 ₁ /n 2	9.349(2) 17.676(4) 11.720(3)			CuN ₃ O ₂	N μO	2.050(6, 57) 2.504(7) 1.944(6, 30)	3.044(2) 103.1(3) 76.9(2)	O,N O,N N,N	84.0(3) ^f 107.4(3, 2, 6) 118.5(3) 84.3(3, 3, 4) ^f 109.1(3)	252	

[Cu(deapo)(NCO)] ₂ (blue green)	m P ₂ /c 4	7.363(3) 12.422(5) 11.117(5)	96.37(2)	Cu ₂ N ₂	OCN N μO	1.913(2) 2.058(2) 1.922(2, 22)	3.044(1) 104.7(1) not given	O,N N,N	168.0(1, 6) 95.8(2) 92.6(1)	253
[Cu(diamo)(EtOH)] ₂ ·BF ₄ (not given)	m P ₂ /a 2	16.004(2) 9.579(2) 9.410(1)	103.16(1)	CuO ₃ N ₂	μO μO EtHO	2.008 1.922 2.448	3.045 104.8		not given	171
[Cu(phba)Cl] ₂ (dark brown)	tr P-1 1	12.236(3) 7.658(3) 7.312(3)	114.39(2) 77.04(2) 105.56(2)	CuO ₂ NCl	Cl N μO	2.192(2) 1.949(2) 1.943(3, 19)	3.045(1) ^d 103.3(1) 76.7(1)	Cl,O Cl,N O,N	101.7(1) 151.6(1) 100.5(1) 92.2(1) 151.0(1)	254
[Cu(paapan)] ₂ ·2C ₆ H ₆ (not given)	m C2/c 4	15.312(3) 10.399(2) 23.743(4)	91.82(1)	CuO ₃ N	N O μO	1.926(3) 1.918(2) 1.903(2, 29)	3.046(1) 103.9(1) 76.1(1)	O,O O,N	93.7(1) ^f 95.1(1, 8) ^f	243
[Cu(Bu-nso)Cl] ₂ (not given)	m P ₂ /a 2	15.109(2) 9.915(1) 11.529(1)	109.70(1)	CuO ₂ N ₂ NSCl	Cl N S μO	2.229(1) 2.448(3) 2.3446(8) 1.930(2, 3)	3.0463(5) 104.22(9) 75.78(8)	O,S S,Cl O,Cl	84.95(6) ^e 96.82(3) 98.38(7)	204
[Cu(C ₁₂ H ₁₅ N ₂ O)(ac)(EtOH)] ₂ (dark green)	m P ₂ /a 2	20.867(3) 10.168(3) 7.960(1)	94.12(2)	CuO ₄ N	acO EtO N μO	1.936(3) 2.267(4) 2.023(4) 1.968(3, 19)	3.050(1) 101.6(1) 78.4(1)	O,O O,N	95.1(2, 3, 6) 173.5(1) 94.9(1, 6, 8) ^f 157.7(1)	255
[Cu(N-Etsala)Cl] ₂ (not given)	tr P-1 1	9.989(1) 7.441(1) 8.396(1)	122.56(1) 98.74(1) 104.28(1)	CuO ₂ NCl	N Cl μO	1.950(4) 2.202(1) 1.945(3, 22)	3.051(1) 103.3(2) 76.7(2)	O,N N,Cl O,Cl	92.1(2) ^f 99.2(1) 154.0(1)	212
[Cu(htr)(py)] ₂ (black)	tr P-1 1	9.60(3) 9.94(3) 8.61(3)	123.7(3) 91.6(3) 108.2(3)	CuO ₄ N	pyN O μO	1.91(2, 3) 2.32(2) 1.95(2, 3)	3.051(3) 103(1) 77(1)	O,O N,O	96(1, 8) ^f 95(1, 4)	256
[Cu(N-Etsala)Br] ₂ (not given)	tr P-1 1	10.169 7.674 8.380	121.40 97.92 106.43	CuO ₂ NBr	N Br μO	1.95(2) 2.34(3) 1.93(1, 4)	3.05(1) 104.6(2) 75.4(2)	O,N N,Br O,Br	92.6(5) ^f 99.8(4) 150.7(4)	212
[Cu ₂ (pramcres)(OH) ₂ (BF ₄) ₂ (brown black)]	m P ₂ /c	22.32(1) 9.551(5)	95.76(3)	Cu ₂ N ₃ O ₂	N	2.007(11, 48) 2.075(10, 26)	3.053(4) 102.8(4, 9)	N,O	92.2(4, 11, 2) ^f 139.6(4)	257

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	<i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]	α [°] β [°] γ [°]	Chromophore	<i>Cu-L</i> [Å]	<i>Cu-L-Cu</i> [Å] <i>Cu-L-Cu</i> [°] $\mu L-Cu-\mu L$ [°]	<i>L-Cu-L</i> [°]	Ref.
	4	16.715(8)			μO μHO	77.1(3.9)	164.2(4.9,3) 95.6(5.2) ^f 102.4(5.11.3)	
[Cu ₂ (C ₂₉ H ₃₇ N ₁₀ O)](BF ₄) ₂ (not given)	m P2 ₁ /c 4	22.329(1) 9.552(1) 16.715(1)	95.70(2)	CuN ₃ O ₂	N μO μHO	3.054(4) 102.1(5.3) 77.8(4.1.1)	N,N N,N N,O	258
[Cu(baa)(py)] ₂ ·2py (reddish brown)	or Pbca 4	8.473(3) 25.377(15) 19.000(10)		CuO ₄ N	pyN O μO	3.055(3) 103.5(3) 76.5(3)	O,O N,O N,O	259
[Cu ₂ (paater)] ₂ ·0.5 C ₆ H ₆ (black)	tr P-1 2	9.438(4) 13.323(2) 11.384(1)	75.68(1) 89.68(2) 82.34(2)	CuO ₃ N	N O μO	3.060(1) 104.3(1.2) 75.7(1.1)	N,O O,O O,O	260
[Cu(C ₁₂ H ₁₅ N ₂ O)(ac)(MeOH)] ₂ (dark green)	m P2 ₁ /a 2	20.627(3) 9.987(3) 7.839(3)	92.41(2)	CuO ₄ N	acO MeOH N μO	3.061(1) 102.4(1) 77.6(1)	O,O O,O O,N 157.9(1)	255
[Cu(F ₃ acpt)(H ₂ O)] ₂ ·H ₂ O (not given)	or Pbca 4	10.721(10) 24.634(10) 17.739(16)		CuO ₅	H ₂ O O μO	3.064(8) 103.8 85.8	O,O O,O O,O	259
[Cu ₂ (fmp)](BF ₄) ₂ ·MeOH (green)	tr P-1 2	14.194(3) 15.887(3) 12.240(3)	107.54(2) 113.22(2) 82.44(2)	CuN ₃ O ₂	N N μO	3.066(2) 102.8(3.2.6) 77.2(3.5)	O,N O,N N,N	227
[Cu(dapp)(ac)] ₂ (dark green)	m P2 ₁ /c 2	12.585(11) 8.421(8) 18.175(16)	121.30(7)	CuO ₄ N	acO N μO	3.067(1) 103.84(16) 76.16(4)	O,O O,O O,N	261

[Cu(dapp)(ac)(MeOH)] ₂ (dark green)	or Pbna 4	7.423(7) 24.444(28) 19.142(7)	Cu ₂ O ₄ N	acO	1.932(5) 2.421(6) 2.044(6) μO 1.986(5, 1)	3.067(2) 101.1(3) 78.89(10)	O,O O,N	95.4(1, 4, 1) 163.65(12) 92.4(1, 1, 5) 172.54(11)	261
[Cu(ips)Cl] ₂ (dark black)	tr P-1 2	7.432(4) 7.867(9) 10.740(4)	CuO ₂ NCl	Cl N μO	2.209(1) 1.965(1) 1.952(1, 24)	3.067(1) 103.56(4) 76.44(4)	Cl,O Cl,N O,N	99.32(3) 148.16(4) 104.31(4) 92.97(5) ^f	262
[Cu(2-Mebz)(hmtt)] ₂ (dark green)	m P ₂ /c 2	12.48(2) 9.228(8) 14.444(1)	CuO ₃ S	bzO S μO	1.908(5) 2.308(3) 1.928(5, 10)	3.069(3) 105.5(2) 74.5(2)	O,S O,O	94.2(2, 1, 3) ^f 169.9(2) 97.0(2) 170.1(2)	263
[Cu(F ₃ acac)(μ-F ₃ pho)] ₂ (moss green)	tr P-1 2	9.670(2) 10.054(2) 10.776(3)	CuO ₅	O μO	1.905(4, 3) 2.279(5) 1.928(4, 26)	3.070(2) 103.4(1) 76.6(1)	O,O	94.8(2, 3, 5) 166.3(2, 5) 94.4(2) ^f	264a
[Cu ₃ (μ-ac) ₂ (pea)](ClO ₄) ₂ (green)	m P ₂ /m 2	8.182(4) 13.912(7) 17.245(6)	CuN ₃ O ₂	N μacO	1.998(14, 6) 2.363(13) 1.934(9, 0)	3.070(2) 105.07(2, 1) 77.8(5)	O,N	95.5(5, 1, 4) 108.5(6, 6, 8) 160.3(6, 8, 1) 90.2(6, 1, 5)	264b
Cu ₂ {(salim) ₂ pr}Cl ₂ (not given)	m P ₂ /c 4	11.15(2) 8.438(8) 18.17(2)	CuO ₂ N ₂	N μO	1.955(10, 5) 1.95(1, 1)	3.07(1) ^d 102.2(5, 8) 76.9(5, 8)	N,N N,N O,N	100.3(5) ^f 91.1(5, 1, 7) ^f 168.2(5, 1, 5)	265
[Cu(bpy)(dbeat)] ₂ (purple)	or Pbca 8	15.731(4) 14.204(3) 19.449(3)	CuO ₃ N ₂	bpyN O μO	2.007(3, 11) 1.909(2) 1.908(2) 2.330(2)	3.0742(8) 87.5(1)	O,O N,N O,N	95.9(1, 8, 6) 79.8(1) 96.2(1, 1) 166.0(1, 6, 8)	266
[Cu(shbr)(Me ₃ SO)] ₂ (Me ₃ SO) ₂ (dark green)	m P ₂ /n 2	17.095(12) 8.547(1) 16.074(8)	CuO ₄ N	Me ₃ SO N shbrN μO	2.480(11) 1.912(11) 1.911(9) 1.986(9, 16)	3.077(2) 101.6(4)	O,O N,N O,N	not given	267a
[Cu ₂ (C ₂₀ H ₁₉ N ₆ O)(OH)](PF ₆) ₂ (green)	m P ₂ /c 4	18.221(3) 13.323(3) 18.643(4)	CuN ₃ O ₂	N μO μHO	2.024(14, 18) 2.204(15, 55) 1.976(11, 4) 1.950(10, 12)	3.081 ^d 103.5(5, 1, 0) 76.5(4, 2)	N,N N,O	97.0(6, 5, 4) 95.2(6, 6, 4) 160.9(5, 3, 8)	267b

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å] Cu-L-Cu [°] μ L-Cu- μ L [°]	L-Cu-L [°]	Ref.
[Cu ₂ (C ₃₆ H ₃₀ N ₆ O)(OH)](PF ₆) ₂ (green)	m P2 ₁ /c 4	18.221(3) 13.323(3) 18.643(4)	102.39(2)	CuN ₃ O ₂	N μO μHO	3.082(1) 2.204(15, 55) 103.5(5, 3.8) 76.5(4, 2)	O,N O,N O,N	268
[Cu(paaapr)] ₂ (deep green)	m P2 ₁ /c 2	11.274(6) 6.249(1) 19.237(3)	94.47(3)	CuO ₃ N	N O μO	3.083(1) 105.2(1) 74.83(9)	O,O O,N O,N	260
[Cu ₂ (ump)(MeOH) ₂] (ClO ₄) ₂ (brown)	m P2 ₁ /n 2	8.6516(7) 11.6832(9) 16.7205(6)	92.596(5)	CuO ₃ N ₂	MeOH N μO	3.088(1) 103.88(12) 76.12(10)	O,N O,N O,N	269
[Cu ₂ (C ₂₄ H ₃₈ N ₄ O ₄)(MeOH)- (ClO ₄) ₂](ClO ₄) (green)	m P2 ₁ /c 4	12.139(6) 17.051(4) 14.457(3)	93.51(2)	CuO ₃ N ₂	O ₃ ClO N μO MeOH	3.089(2) 103.8(1) 75.8(3, 0) 2.311(9)	N,N O,N O,N O,N	270
[Cu(F ₆ pdhb)] ₂ (not given)	m P2 ₁ /c 2	8.918(3) 12.776(3) 16.674(4)	103.57(2)	CuO ₄ N	N O μO	3.089(1) 101.3(1) 78.7(1)	O,O O,N O,N	240
[Cu ₂ (upm)(H ₂ O) ₂](ClO ₄) ₂ [Cu ₂ (upm)(H ₂ O) ₂](ClO ₄) ₂ (green)	m P2 ₁ /a 4	14.7242(5) 12.3816(3) 16.5571(6)	105.681(3)	CuO ₃ N ₂	H ₂ O N μO	3.096(3) 103.6(3) 76.4(3)	O,N O,N O,N	271
				CuO ₄ N ₂	H ₂ O O ₃ ClO N μO	3.091(3) 102.3(3) 77.7(3)	O,N O,N O,N	
						170.1(3, 2) 88.2(4, 7.0) 168.9(4) 97.2(4) ^f	O,O O,O N,N N,N	

$\text{Cu}_3(\text{C}_{15}\text{H}_{10}\text{N}_2\text{O}_4)_2$ (not given)	m $\text{P}2_1/c$ 2	10.988(5) 5.444(5) 17.455(7)	96.49(5)	CuO_3N	N O μO	2.04(2) 1.93(2) 1.90(2.2)	3.1 106.1(10) 73.9(10)	O,O	95.4(9) 168.8(8)	272
$[\text{Cu}_3(\text{upm})_3] \cdot \text{H}_2\text{O}$ (brown)	m $\text{P}2_1/a$ 4	8.2826(8) 16.7383(8) 9.6470(12)	99.107(14)	$\text{CuO}_2\text{N}_2\text{I}$	I N μO	3.0264(15) 1.962(8.6) 1.975(6.1)	3.104(2) not given 76.34(24)	I,O I,N O,N	93.83(19, 1.56) 96.28(24, 14) 92.6(3, 1) ^f 165.4(3, 2.1) 96.8(3) ^f	273
$[\text{Cu}_2(\text{Qpy}2(\text{OH}))(\text{BPh}_4)_2 \cdot \text{Me}_2\text{CO}]$ (not given)	tr P-1 2	13.089(4) 15.146(3) 21.971(5)	101.13(2) 96.46(2) 103.35(2)	CuN_3O_2	N N μO μHO	2.026(9, 39) 2.222(9, 3) 1.969(7, 16) 1.959(7, 1)	3.108 104.7(3, 4) 75.4(3, 4)	N,N N,O	96.4(4, 3.1) ^f 95.9(3, 6.1) ^f 160.9(3, 1.6)	274
$[\text{Cu}_2(\text{ump})(\text{tcnq})]$ (violet black)	tr P-1 1	11.592(2) 14.232(3) 6.971(3)	90.45(3) 98.52(1) 112.84(2)	CuO_2N_2	N μO	1.957(4, 11) 2.378(5) 1.971(3, 6)	3.110(2) 104.2(2) 75.8(2)	O,N	94.1(2, 3.0) ^f 166.2(2, 4) 94.9(2, 2.7) ^f	275
$\text{Cu}_2(\text{ebs})\text{Cl}_2$ (not given)	m $\text{P}2_1/n$ 4	9.791(6) 16.781(6) 10.536(5)	100.80(1)	CuO_2N_2	N μO	1.91(1.1) 1.905(10, 15)	3.11(1) ^d 100.5(5, 5.2) 79.0(5, 6.8)	N,N O,N	85.8(5) ^e 94.8(5, 9) ^f 175.0(5, 6)	265
$[\text{Cu}(\text{Famobzim})_2]$ (not given)	m $\text{P}2_1/c$ 2	12.142(3) 16.104(6) 8.835(1)	94.88(1)	CuO_4N	Cl μO	2.264(5, 24) 1.98(1) 2.30(1)	3.119(1) 95.43(5) 84.57(5)	O,O	91.8(6, 7.2) ^f 174.14(5) 94.4(6, 4.9) ^f	240
$[\text{Cu}_2(\text{tpydx})(\text{MeO})](\text{PF}_6)_2$ (not given)	m C2/c 4	13.481(2) 14.530(2) 22.393(3)	99.81(1)	CuN_3O_2	N μO μMeO	2.050(8, 45) 2.218(8) 1.964(5) 1.946(5)	3.121(3) not given 74.1(3)	N,N N,O	93.2(3, 1.7) ^f 98.2(3, 5.1) ^f 162.9(3, 5.9)	276
$[\text{Cu}_2(\text{H-apenol})(\text{apenol})\text{ClO}_4]$ (blue green)	m $\text{P}2_1/c$ 4	16.126(3) 13.403(3) 14.004(3)	115.69(3)	CuO_3N_2	N O μO	1.951(3, 36) 1.878(2) 2.383(3) 1.921(3, 40) 2.524(3)	3.121(9) 107.2(1) 88.9(1) 80.6(1, 78)	O,O O,N	91.7(1, 4.7) 88.7(1, 8.0) 111.0(1, 5.4) 166.0(1, 9.0) 81.9(1, 1.2) ^e 92.9(1) ^f 87.5(1, 6) ^e	277

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å] Cu-L-Cu [°] μ L-Cu- μ L [°]	L-Cu-L [°]	Ref.
[Cu ₂ (ump)Br ₂ ·4H ₂ O (green)	m C2/m 2	7.9196(13) 17.1380(4) 11.2232(14)	92.111(13)	CuO ₂ N ₂ Br	Br N μ O	3.124(2) 103.6(3) 76.43(20)	Br,O Br,N O,N 164.21(21) 97.0(3) ^f	273
[Cu ₂ (hem)(MeO)](BPh ₄) ₂ (green)	tr P-1 2	10.843(2) 15.045(3) 23.170(4)	90.14(2) 100.29(2) 96.27(2)	CuN ₃ O ₂	N μ O μ MeO	3.128(10) 105.69(1.7) 74.4(8.5)	O,N 104.9(10) 162.0(10,7.5) 96.2(11,3.0) ^f	278
[Cu ₂ (prahmf)(Cl) ₂ ·6H ₂ O (green)	m C2/m 2	7.720(1) 17.079(1) 11.171(1)	91.50(1)	CuO ₂ N ₂ Cl	Cl N μ O	3.133(1) 104.5(1) 75.5(1)	N,N N,N Cl,N Cl,O 99.1(1)	279
[Cu(F ₆ phobzim)] ₂ (not given)	tr P-1 1	9.066(1) 10.583(3) 10.710(6)	99.64(3) 114.33(3) 94.58(2)	CuO ₄ N	N O μ O	3.147(1) 93.74(5) 86.26(5)	O,O 174.70(5) 94.17(6,4.4) ^f 169.16(6)	240
[Cu(F ₆ clobzim)] ₂ (not given)	tr P-1 1	9.044(3) 9.300(3) 13.432(4)	95.46(2) 117.51(2) 108.14(2)	CuO ₄ N	N O μ O	3.143(1) 94.14(3) 85.86(3)	O,O 174.70(3) 92.6(4,6) ^f 106.03(4) 165.06(4)	240
[Cu(N-mhb)(F ₆ pdhb)] ₂ (green)	m C2/c 4	23.414(2) 7.727(1) 16.430(1)	91.33(1)	CuO ₄ N	O N μ O	3.181 93.2(1) 86.8(1)	O,O 89.6(1) ^f 89.4(1,3.5) 175.2(1) 94.0(2) ^f 96.1(2,5.4) 168.1(2)	280
[Cu ₂ (C ₁₀ H ₃₆ N ₃ O) (Cl-C ₄ H ₄ CO ₃)]·(ClO ₄) ₂ ·MeCN (not given)	m C2/c 8	23.149(6) 13.327(3) 32.935(5)	97.78(2)	CuN ₃ O ₂	N μ O μ O	3.197 109.1(4.8) 71.0(3.2)	O,N 94.9(4,5.0) 108.0(4,1.5) 156.9(4,6.6) 96.5(4,3.6) ^f	281

[Cu(oxibz(3-Mepy)(NO ₂)) ₂] (green)	tr P-1 2	10.651(3) 9.853(3) 8.658(4)	114.23(3) 87.36(3) 80.30(3)	Cu ₂ O ₄ N ₂	N O ₂ NO O μO μO	1.958(3,36) 2.636(3) 2.059(3) 1.919(3) 2.476(3)	3.208 not given	O,O N,O N,N	174.2(1) 90.0(1,7.2) 82.8(1) ^e 91.7(1) ^f 172.4(2)	282
[Cu(PhO) ₂ (en)] ₂ ·2PhOH (deep green)	m P ₂ /n 4	19.000(13) 10.930(9) 8.968(5)	89.20(2)	Cu ₂ O ₄ N ₂	enN O μPhO	2.029(5,4) 1.947(4) 1.926(3) 2.265(4)	3.215(3) 99.9(2) 80.1(3)	O,O O,N	100.1(3,1.3) 94.2(3,6.9) 157.2(4) 171.6(4)	283
[Cu(pyNO)Cl ₂] ₂ (green)	m P ₂ /b 4	5.844(5) 10.049(5) 13.643(5)	104.52(10)	Cu ₂ O ₂ Cl ₂	Cl μO	2.22(-,2) 2.05(3,6)	3.23 104 76	N,N not given	83.5(3) ^e not given	284
[Cu(4-phpyNO)Cl ₂] ₂ [Cu(4-pyNO)(H ₂ O)Cl ₂] ₂ (green)	tr P-1 2	10.069(8) 12.857(5) 10.143(5)	106.16(5) 99.75(5) 97.3(5)	Cu ₂ O ₃ Cl ₂	Cl H ₂ O μ-O	2.217(2,28) 2.356(7) 2.010(6,30)	3.285(1) 109.6(2) 70.4(2)	Cl,Cl Cl,O	99.3(1) 95.9(2,3.0) 162.8(7,3)	285
[Cu(pyNO)Br ₂] ₂ (dark brown)	m P ₂ /c 2	10.977(5) 10.007(5) 7.88(1)	110.30(10)	Cu ₂ O ₂ Br ₂	Br μO	2.333(2,1) 1.980(9,15)	3.244(2) 110.1(4) 69.9(3)	Br,Br O,Br	99.2(1,1.4) 89.4(3,7.1)	286
[Cu(pyNO)Cl ₂] ₂ (green)	m P ₂ /b 4	5.844(5) 10.049(5) 13.643(5)	104.52(10)	Cu ₂ O ₂ Cl ₂	Cl μO	2.212(5,6) 2.008(11,29)	3.245(4) 107.8(6) 72.2(10)	Cl,Cl Cl,O	99.4(3) 96.0(6,1.6)	287
[Cu(F ₃ sbmobzim)] ₂ (not given)	tr P-1 1	7.978(2) 10.031(1) 12.399(3)	117.89(2) 100.46(2) 92.65(2)	Cu ₂ O ₄ N	N μO	1.990(1) 1.958(1,13) 1.902(1) 2.437(1)	3.248(1) 96.14(4) 83.86(4)	O,O O,N	90.2(4,5.59) ^f 171.28(4) 93.2(1,1) ^f 109.21(4) 154.98(4)	240
[Cu(4-MepyNO)Br ₂] ₂ (dark brown)	m P ₂ /c 4	6.086(1) 15.064(3) 10.469(2)	106.14(1) 70.8(2)	Cu ₂ O ₂ Br ₂	Br μO	2.342(1,5) 1.995(3,12)	3.252(1) 109.2(2) 70.8(2)	Br,Br O,Br	98.4(1,11.7) 89.5(1,5.0) 165.4(1)	288

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-L-Cu [Å] Cu-L-Cu [°] μ L-Cu- μ L [°]	L-Cu-L [°]	Ref.
[Cu(C ₂₁ H ₂₃ N ₃ (OH)) ₂ (PF ₆) ₂ ·2H ₂ O (blue)	tr P-1 1	9.426(4) 11.415(2) 11.586(3)	74.78(2) 88.72(2) 74.14(2)	CuN ₃ O ₂	N μ HO 2.298(4)	3.271 101.0(2) 79.0(2)	N,N 168.0(2) 89.0(2,9) 103.7(2,2.8) 174.4(2)	289
[Cu(py)NO(H ₂ O)Cl] ₂ (green)	tr P-1 1	7.976(2) 9.469(3) 5.906(1)	81.02(2) 96.38(2) 98.77(3)	CuO ₃ Cl ₂	Cl H ₂ O μ O 2.005(2,10)	3.272(1) 109.4(1) 70.6(1)	O,Cl 96.4(1,3.1) Cl,Cl 97.33(3) O,O 93.8(1.6)	290
[Cu(py)NO(H ₂ O)Cl] ₂ (doped with Mn(II)) (not given)	tr P-1 1	5.912(2) 7.973(3) 9.462(3)	81.25(3) 81.06(3) 83.66(2)	CuO ₃ Cl ₂	Cl H ₂ O μ O 1.993(4,14)	3.272(1) 110.3(2) 69.7(2)	Cl,O 96.7(1,2.8) 161.2(1,1) 97.44(5) O,O 93.6(2,4)	291
[Cu(py)NO(H ₂ O)Cl] ₂ (green)	m P2 ₁ /c 2	9.899(2) 10.028(1) 10.006(2)	117.20(1)	CuO ₃ Cl ₂	Cl H ₂ O μ O 2.221(14,2) 2.267(8) 2.012(33,2)	3.288(15) 109.6(1.5) 70.4(1,2)	O,O 92.9(14,48) 95.1(20,19) 101.7(14) 160.1(19,5.4)	292
[Cu(salpa)Cl] ₂ (brown)	m P2 ₁ /c 2	8.56(1) 12.35(2) 10.31(2)	18.43(3)	CuO ₃ NCl	Cl N O μ O 2.22(1)	3.294(7) 110.3(6) 69.7(6)	Cl,O 104.4(4,5.8) 126.2(5) 92.5(5) 76.0(6) 99.6(6) ^f 123.4(7)	293a
[Cu(salphala)Cl] ₂ (brown)	m C2 12	22.053(6) 12.715(3) 16.476(3)	89.98(2)	CuO ₄ N	O N μ H ₂ O 1.96(2,3) 1.91(2,0) 1.97(2,1)	3.30(1) not given not given	O,N 84.9(9) ^f 94.4(9) 107.8(8) 158.2(8) 89.1(8,4.1) 177.3(9,9)	293b

$[\text{Cu}(\text{ae})(\text{ac})_2]$ (blue)	tr P-1 1	8.1362(8) 9.9886(8) 7.345(11)	92.42(1) 96.48(1) 69.76(1)	CuO_3N_2	aeN aeO μacO	1.975(2, 37) 1.925(1) 1.955(1) 2.490(1)	3.305 95.34(5) 84.66(5)	O,N	93.53(6, 10, 12) 172.70(5, 1.62) 94.58(6) ^f 87.59(6, 2.93) 85.67(6) ^e	294
$[\text{Cu}(\text{pyNO})_2\text{Cl}_2]$ (yellow)	m $\text{P}2_{1/2}$ 4	6.900(4) 15.065(7) 12.065(5)	97.00(4)	CuO_3Cl_2	Cl H_2O μO	2.187(1) 2.225(1, 1) 2.018(1, 21)	3.306(1) 110.0(1) 70.0(1)	O,Cl Cl,Cl O,O	94.1(1, 1) 97.0(1) 87.3(1)	295
$[\text{Cu}(\text{Hfpts})(\mu\text{-OSO}_2)_2]$ (blue green)	m C2/c 4	14.75(3) 9.138(2) 17.468(4)	104.9(2)	$\text{CuO}_2\text{N}_2\text{S}$	N S μO	1.989(2, 36) 2.279(1) 1.923(2) 2.305(2)	3.310(1) ^d 102.70(7) 77.30(8)	N,N S,N O,N	80.24(8) ^e 85.09(6) ^e 160.07(7) 93.73(11, 1.54) 101.43(8) 175.31(11)	296
$[\text{Cu}(\text{tgy})_2(\text{bpy})_2 \cdot 2\text{H}_2\text{O}]$ (blue)	tr P-1 1	15.799(2) 10.337(2) 9.574(2)	87.88(1) 102.01(1) 80.41(1)	CuO_3N_2	N O μO	1.997(3, 5) 1.933(2) 1.968(2) 2.350(3)	3.317(1) 100.0(1) 80.0(1)	O,S N,N N,O	101.77(10, 2.18) 80.9(1) ^e 96.7(1, 3.5) 172.7(1, 2.0)	297
$[\text{Cu}(\text{hip})_2(\text{H}_2\text{O})_2]$ (blue green)	m $\text{P}2_{1/2}$ 4	7.253(1) 40.169(3) 7.466(1)	102.81(1)	CuO_5	H_2O O μO	2.00(1, 0) 1.91(1) 1.93(1) 2.37(1)	3.33(1) 101.0(5) 79.0(5)	O,O O,O	92.7(5, 2.3) 176.4(5)	298
$\gamma\text{-}[\text{Cu}(\text{N-Mesala})_2]$ (brown)	or $\text{P}2_1\text{P}2_1\text{P}2_1$ 8	18.86(2) 10.25(2) 14.64(2)	99.86(2)	CuO_3N_2	O N μO	1.89(-, 1) 1.96(-, 4) 1.90(-, 1) 2.45(-, 1)	3.33 100.4(-, 6) 79.6(-, 5)	N,O	90.0(-, 3.2) ^f	299
$[\text{Cu}(\text{bpyo}_2\text{Cl}_2)]_2$ (yellow orange)	m $\text{P}2_{1/2}$ 2	7.912(2) 9.878(2) 15.086(3)	99.86(2)	CuO_3Cl_2	Cl O μO	2.220(1, 1) 2.173(4) 2.045(3, 17)	3.333(1) 109.2(1) 70.8(1)	Cl,Cl Cl,O	102.2(1) 97.3(1, 5.2) 158.6(1, 3.9)	300
$[\text{Cu}(\text{pyNO})_2\text{Br}_2]_2^e$ (not given)	tr P-1 2	10.510(2) 10.883(1) 11.818(5)	78.57(3) 89.88(3) 81.17(1)	CuO_3Br_2	O Br μO	1.944(4) 2.454(1, 53) 1.975(4) 2.162(4)	3.336(1) 107.4 72.60(16)	Br,Br Br,O O,O	118.60(4) 96.01(14, 1.42) 106.03(11) 134.61(11) 84.34(18) 156.33(19)	301

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å] Cu-L-Cu [°] μ L-Cu- μ L [°]	L-Cu-L [°]	Ref.
[Cu(pyNO)(Me ₂ SO)Cl ₂] ₂ (light green)	m P2 ₁ /c 4	7.17(1) 15.444(7) 11.183(4)	104.8(1)	CuO ₃ Br ₂	O Br μ O 2.40(4)	3.415(1) 108 71.99(15)	Br, Br Br, O O, O 162.48(17)	302
[Cu(dpyam)(salal)(ClO ₄) ₂] (dark green)	tr P-1 2	9.363(2) 9.964(3) 10.093(2)	75.39(2) 73.49(4) 83.34(3)	CuO ₃ Cl ₂	Me ₂ SO Cl μ O 2.050(7)	3.342(3) 109.2(3) 70.8(2)	O, O O, Cl O, O 160.6(2), 1.0)	303
[Cu(4-MepyNO) ₂ Cl ₂] ₂ (yellow)	m P2 ₁ /n 2	7.368(10) 19.857(5) 10.773(5)	111.25(10)	CuO ₂ N ₂	N O ₃ ClO O μ O 2.436(2)	3.343(1) ^d 99.2(1) 80.78(9)	Cl, Cl O, O O, N N, N 91.9(1) ^f	304
[Cu(dtbsq) ₂] ₂ (dark green)	tr P-1 2	10.262(3) 14.554(4) 9.418(2)	101.09(2) 92.31(2) 108.87(2)	CuO ₃ Cl ₂	O Cl μ O 2.153(6)	3.348(2) 109.0(2) 71.0(2)	Cl, Cl Cl, O O, O 109.0(2) 154.1(5)	305
[Cu(salal)(phen)(ClO ₄) ₂] (green)	tr P-1 2	9.139(4) 9.290(3) 11.679(5)	96.27(2) 111.07(2) 97.00(2)	CuO ₄ N ₂	O ₃ ClO N μ O 1.921(2), 2.1)	3.360(2) ^d 100.3(2) 79.7(2)	O, O O, O 119.7(2) 151.8(2) 177.1(2)	306a

[Cu(Mesprp)(ac) ₂] (not given)	tr P-1 1	8.247(3) 9.173(2) 10.239(3)	108.88(2) 111.20(3) 76.49(3)	CuO ₃ N ₂	N O acO μacO	2.005(4, 40) 1.918(3) 2.828(6) 1.978(3) 2.512(5)	3.379(2) not given not given	N,N O,N O,O	94.2(2) ^f 88.0(2, 5.5) 103.5(2) 171.1(2, 2.4) 51.1(2) ¹ 86.5(2, 1)	306b
[Cu(N-chsalim) ₂] (green)	m P2 ₁ /n 8	23.134(6) 9.525(3) 21.472(8)	99.42(1)	CuO ₃ N ₂	O N μO	1.90(1, 1) 2.03(1, 1) 1.91(1, 1)	3.383(3) 95.4(5, 9) 80.1(4, 4)	O,N O,O	91.5(6, 2.2) ^f 114.1(5, 3.5) 85.7(8, 1.2) 164.9(5, 1.7) 154.8(6, 2.7)	307
[Cu(mesalpr)(μ-ac) ₂] ₂ ·2H ₂ O (green)	m C2/c 4	17.755(3) 9.208(3) 20.393(3)	105.26(2)	CuO ₃ N ₂	O N μacO	1.895(8) 1.993(10, 30) 1.960(8) 2.498(8)	3.384(3) 98.1(3) 81.9(3)	O,N O,O N,N	84.(3, 1.8) ^f 100.0(3, 6.7) 88.1(3, 6) 93.6(3) ^f	308
[Cu(C ₁₂ H ₁₀ NO) ₂] ₂ ·2H ₂ O (brown)	m P2 ₁ /c 4	10.5250(6) 14.740(11) 12.605(19)	104.80(2)	CuO ₃ N ₂	N μO	1.971(5) 1.917(4) 2.600(4)	3.388(1) ^d 96.01(17) 84.0(2)	O,N O,O N,N	92.9(2, 3.2) ^f 97.2(2) 178.1(2) 171.2(2)	309
[Cu(C ₁₂ H ₁₀ NO) ₂] ₂ (brown)	m P2 ₁ /c 4	10.5250(6) 14.740(11) 12.605(19)	104.80(2)	CuO ₃ N	O N μO	1.917(4) 1.971(4) 2.600(4)	3.3878(9) 96.0(2) 84.0(1)	O,N O,O N,N	91.5(2, 4.7) ^f 97.2(2) 178.1(2) 171.2(2)	310
[Cu(F ₆ pd)(bzacac) ₂] (green)	m P2 ₁ /c 4	12.289 8.571 16.645	108.21	CuO ₅	F ₆ acacO bzacacO μbzacacO	1.948(3, 3) 1.887(3) 1.903(3) 2.56	3.39 not given 93.9(1)	O,O	92.5(1, 1.5) ^f	310
[Cu(mnsalpr)(ac) ₂] (green)	tr P-1 1	9.305(3) 9.209(3) 8.993(3)	94.94(2) 94.92(2) 92.78(2)	CuO ₄ N ₂	prO N acO μacO	1.933(2) 1.988(3, 41) 2.630(3) 1.976(2) 2.577(2)	3.409(1) 96.1 83.9(1)	O,O O,N	54.9(1) ^f 90.0(1, 2.0) 138.8(1) 85.1(1, 4.3) 96.0(1, 2.9) 92.9(2) ^f 110.6(1, 1.9) 165.9(1, 1.4) 98.3(2) ^f	311

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å] Cu-L-Cu [°] μ L-Cu- μ L [°]	L-Cu-L [°]	Ref.
[Cu(npsalim)] ₂ ·2dio (not given)	tr P-1 2	12.402(3) 10.187(2) 11.617(2)	101.10(1) 87.76(2) 106.97(1)	CuO ₃ N ₂	O N μ O 2.58	3.41 97.7 82.3(2)	O,N N,N O,O 176.4(3)	312
[Cu(thp)] ₂ ·(ClO ₄) ₂ (not given)	tr P-1 2	11.709(8) 12.750(12) 12.891(11)	62.98(7) 67.90(6) 71.75(7)	CuO ₆	O μ O 2.436(6)	3.417(3) 100.9(3) 79.1(3)	O,O O,O 175.3(3, 1.3)	313
[Cu(salphalal)(H ₂ O)] ₂ (not given)	trg P ₃ ,2 ₁ 3	12.724(3) 16.476(3)	102.74(3) 102.94(3)	CuO ₄ N	H ₂ O N μ O 2.541(15)	3.422(3) 98.0(6) not given	O,N O,O O,O 176.7(5)	314
[Cu(pyames)(H ₂ O)] ₂ ·Cl ₂ (green)	tr P-1 1	7.139(1) 8.586(2) 10.072(2)	107.07(3) 90.14(3) 102.94(3)	CuO ₃ N ₂	H ₂ O N μ O 2.353(5)	3.426(2) not given 75.4(2)	N,N N,O O,O 92.3(2, 1.5)	315a
[Cu(acachfaac)] ₂ (green)	tr P-1 2	6.6958(2) 12.061(8) 8.776(2)	89.35(4) 114.07(2) 80.01(4)	CuO ₅	O μ O 2.704	3.43 not given not given	O,O O,O 92.7(2, 1.9)	315b
[Cu ₂ (diam) ₂ (OH)(ClO ₄) ₃] (blue violet)	m P ₂ ₁ 2	11.896(7) 9.424(3) 11.468(7)	117.97(4)	CuO ₃ N ₃	O ₃ ClO N μ O μ O ₃ ClO 2.62(2, 10)	3.435(1) 128.1(4) not given	N,O N,O N,N 84.6(7, 2.9) ^c	316
β -[Cu(8-OHQw)] ₂ (brown)	m P ₂ ₁ /c 4	10.644(4) 8.593(3) 15.239(4)	102.18	CuO ₃ N ₂	N O μ O 2.830(9)	3.441 not given not given	O,N O,O N,N 173.3(6)	317
[Cu(pht)(bpy)] ₂ ·4H ₂ O (dark blue)	m P ₂ ₁ /n 4	15.685(11) 12.900(9) 8.825(3)	100.45(3)	CuO ₃ N ₂	bpyN O μ O 2.416(3)	3.442(2) not given 76.4(1)	N,N O,O O,N 81.3(2) ^c 94.8(1) 89.7(1) 105.0(1)	318

[Cu(C ₇ H ₇ N ₄ S)(μ-ac)] ₂ (black)	tr P-1 1	8.834(1) 8.989(1) 8.801(1)	117.48(1) 91.77(1) 110.94(1)	CuO ₂ N ₂ S	N S μacO 2.011(2, 65) 2.268(1) 1.946(2) 2.422(2)	3.442(3) not given 76.5(1)	O,S N,S N,O N,N O,O O,O O,N O,N O,N O,N O,S O,O O,N N,N O,O	99.2(1,3) 83.2(1) ^c 162.5(1) 94.3(1, 2.5) 174.5(1) 80.5(1) ^c 90.2(1, 2.8) 175.2(2, 1.7) 94.9(1, 4) ^f 83.1(1, 2) ^e 107.3(1) 169.6(1)	319
[Cu(mhsalim)(μ-ac)] ₂ ·H ₂ O· EtOH (green)	m P ₂ ,in 4	10.587(3) 16.972(8) 18.432(6)	97.37(2)	CuO ₄ N	N O μacO 1.937(2, 0) 2.002(1, 4) 2.615(2, 169) 1.929(1, 41)	3.445(1) 99.2(1, 3.5) 81.8(1)	O,O O,O O,N	320	
[Cu(2-bac)Br] ₂ (olive green)	or P ₂ ,P ₂ ,P ₂ 4	21.16(2) 15.15(2) 8.40(1)		CuO ₂ NBr	Br N μO 2.38 2.06 1.89(-, 8)	3.450(2) 105 75	Br,O N,O 86 ^c	98 86 ^c	321
[Cu(fts)(μ-ac)] ₂ (dark green)	tr P-1 1	8.827(3) 8.813(3) 8.997(3)	117.49(2) 110.96(3) 91.65(3)	CuO ₂ N ₂ S	N S μO 2.015(2, 45) 2.274(1) 1.951(2) 2.427(2)	3.450(1) ^d 103.5 76.53(8)	N,N S,N O,N O,N	80.60(8) ^f 83.20(7) ^c 162.60(7) 91.61(7) 174.50(9) 99.2(6, 3)	296
[Cu(bpy)(salal)(ClO ₄) ₂ (green)]	tr P-1 2	8.513(5) 9.453(8) 11.826(6)	77.93(5) 69.71(6) 83.10(4)	CuO ₄ N ₂	bpyN O ₃ ClO O μO 1.982(3, 1) 2.555(4) 1.948(3) 1.897(2)	3.454(2) ^d 96.08(1) 83.92(1)	O,S O,O O,N N,N	88.1(6, 6.5) ^f 94.1(1, 2.9) 173.4(1, 7) 81.8(1) ^c	322
[Cu(pyNO) ₂ (NO ₃) ₂ (green)]	m P ₂ ,in 4	11.820(5) 14.862(1) 8.005(5)	95.50(2)	CuO ₅	O ₂ NO pyNO μO 1.967(5, 1) 1.951(5) 1.968(5) 2.439(6)	3.458(5) 102.9 77.1	O,O O,O O,O	91.3(-, 6.1)	323a
[Cu(mal)(Meen)(H ₂ O)] ₂ (not given)	tr P-1 2	9.607(8) 9.016(6) 5.785(5)	102.86(6) 79.09(7) 79.46(7)	CuO ₃ N ₂	enN H ₂ O μmalO 2.019(7, 7) 2.513(7) 1.940(6) 2.681(6)	3.4647(7, 7) not given not given	N,N O,O N,O	85.2(3) ^c 95.4(2, 4.6) 89.6(6, 4.1)	323b
[Cu(bpy)(Ph ₃ mgly)] ₂ (blue)	tr P-1 1	10.098(1) 12.573(11) 16.979(3)	93.11(3) 102.70(1) 99.99(2)	CuO ₃ N ₂	bpyN O μO 2.031(4, 0) 1.922(3) 1.975(3) 2.423(3)	3.470(1) 103.7(1) 76.3(1)	N,N N,O O,O	79.9(2) ^c 98.7(2, 10.7) 172.2(2, 6) 90.3(2, 17)	324

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]			α [°] β [°] γ [°]			Chromophore	Cu-L [Å]	Cu-Cu [Å] Cu-L-Cu [°] μL-Cu-μL [°]		L-Cu-L [°]	Ref.
		a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]			Cu-Cu [Å]	Cu-L-Cu [°]		
[Cu(plampb)] ₂ ·H ₂ O (not given)	m C2/c 8	16.75(1) 9.46(1) 15.03(1)			92.0(1)			CuO ₄ N	N O μO 2.663(3)	1.962(2) 1.936(3,8) 1.894(3) 2.663(3)	3.488(2) not given 81.0(2)	N/O O/O 106.7(2)	325
[Cu(glvhgy)] ₂ ·1.2H ₂ O (blue violet)	tg P4 ₂ ,2 ₁ 8	14.41(1) 26.50(3)						Cu ₃ N ₃ O ₂	N μO	2.01(-,4) 2.27(-,27)	3.50 not given not given	not given	326
[Cu(sval)(bpy)] ₂ ^c (deep blue)	tr P-1 2	16.864(4) 16.075(4) 13.783(3)			75.6(1) 73.4(1) 85.5(1)			CuO ₃ N ₂	bpyN O μO	2.006(9,39) 1.899(7) 1.983(6) 2.452(8)	3.501 103.7 76.3	N,N N/O 106.3(4) 173.3(7,1.7)	327
[Cu(mbrsalpr)(ac)] ₂ (green)	m P2 ₁ /a 2	14.519(2) 10.859(2) 9.547(3)			93.35(2)			CuO ₃ N ₂	N O	2.023(9,7) 1.960(8,39) 2.410(11)	7.226(5) not given	O/O N,N N/O 172.5(5)	311
[Cu(α)(μ-ac)] ₂ ·0.6H ₂ O (blue green)	m P2 ₁ 4	9.380(3) 18.570(9) 9.725(8)			93.99(5)			CuO ₃ N ₂	mbrsalprO N ac μacO	1.918(4) 2.006(6,29) 2.604(6) 2.003(4) 2.665(4)	3.506(1) 96.3 83.7(2)	O/O O/O O,N 93.1(1) 128.3(2,11.0) 168.1(2,3.3) 98.3(2)	328
[Cu(C ₁₂ H ₁₄ NO ₂) ₂] ₂ (green)	m P2 ₁ 2	11.725(2) 17.404(1) 12.062(3)			109.03(2)			CuO ₃ N ₂	N O μO	1.945(11,5) 1.911(7) 1.868(-,6) 2.783(-,21)	3.509 ^d 95.6(-,1) 81.5(-,9)	O/O O,N N,N 169.5(5)	329

[Cu(4-MeOpyNO) ₂ (NO ₃) ₂] ₂ (not given)	tr P-1 1	11.466(8) 10.610(8) 7.683(9)	111.3(5) 78.3(5) 98.9(4)	CuO ₅	O ₂ NO MeOpyNO μO	1.980(7, 3) 1.930(6) 1.930(6, 0)	3.529(1) not given 78	O,O	95(-, 3) 86(-, 4)	330
[Cu(pypyp)(μ-ac)] ₂ ·1.46H ₂ O (dark blue)	m C2/c 4	17.36(2) 14.20(4) 13.418(3)	112.61(1)	CuN ₃ O ₂	N O μO	1.991(5, 33) 2.817(4) 1.987(4) 2.497(4)	3.542(2) not given 66.0(2)	O,N N,N	94.2(2, 5.3) 107.1(2) 175.1(2) 81.9(2) ^f 91.4(2) ^f 168.7(2)	331
[Cu(mal)(1, 3-pn)] ₂ (blue)	tr P-1 2	6.377(2) 8.706(3) 9.387(5)	98.36(5) 77.31(4) 117.89(3)	CuO ₃ N ₂	pnN O μmalO	1.998(8, 29) 1.994(7) 1.988(7)	3.546(2) 103.1(3) 76.9(3)	N,N N,O O,O	92.9(3) ^f 88.6(4, 3.5) 89.2(3) ^f 106.9(3, 4)	332
[Cu(fpts)(μ-F ₃ ac)] ₂ ·2F ₃ acH (green black)	tr P-1 1	9.6015(7) 10.837(1) 8.811(2)	100.71(1) 117.06(1) 80.877(7)	CuO ₂ N ₂ S	fptsN fptsS μF ₃ acO	1.995(3, 42) 2.273(1) 1.955(2) 2.519(4)	3.557(4) 104.8(1) 75.2(1)	N,N N,S N,O	80.2(1) ^e 84.3(1) ^e 163.9(1) 94.3(1, 2.4) 111.0(1) 172.9(1) 98.0(1, 4)	333
[Cu(HB(3, 5-i-Pr ₂ pz) ₃)] ₂ (μ-O ₂)]· 6CH ₂ Cl ₂ (purple)	m C2/c 4	26.36(2) 13.290(4) 29.29(2)	114.59(6)	CuN ₃ O ₂	N μO	1.997(14, 4) 2.258(8) 1.915(11, 12)	3.560(3) not given 43.3(4)	O,N N,N	111.1(4, 3.9) 149.6(4, 8) 89.5(4, 3.2) ^f	169
[Cu(4-pyx)(bpy)(ClO ₄)] ₂ (blue green)	m P2 ₁ /c 4	9.782(3) 14.440(4) 14.541(3)	103.58(2)	CuO ₃ N ₂	bpyN O ₃ ClO O μO	1.990(6, 5) 2.528(6) 1.910(3) 1.893(4) 2.964(5)	3.593(1) not given 87.2(2)	O,O O,N N,N	91.7(2, 3.7) ^f 90.7(2, 6.5) 174.4(2, 1.1) 81.6(2) ^f	334
[Cu(Cu ₁₁ H ₁₃ NO ₃)] ₂ (black)	m C2/c 8	20.700(9) 9.555(6) 21.64(1)	92.49(4)	CuO ₃ N	N O μO	1.979(8, 11) 1.922(7, 51) 1.922(8, 36)	3.6 104.3(3, 3) 75.7(3, 3)	O,O O,N	91.3(3) 166.8(3) 98.8(3) ^f 172.7(3)	272
[Cu(py) ₂ (NO ₃) ₂] ₂ ·py (not given)	m P2 ₁ /c 4	9.79(3) 10.89(3) 16.15(3)	98.0(2)	CuO ₃ N ₂	pyN ONO ₂	2.001(8, 6) 2.035(6) 2.618(8) 2.906(7)	3.693(3) ^d 106.8(1) 73.2(3)	O,O	52.7(2, 2.7) ⁱ 90.8(3, 4.2) 133.9(3, 10.7) 165.3(3, 2.7)	335

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å]			α [°]			Chromophore	$Cu-L$ [Å]	$Cu-Cu$ [Å]		$L-Cu-L$ [°]	Ref.
		b	c	β	γ	$Cu-Cu$	$\mu L-Cu-\mu L$						
[Cu(pyccaro)] ₂ ·8H ₂ O (violet)	tr	6.988(2)		63.06(2)				μO_2NO	2.042(6)			89.9(3,8,7)	336
	P-1	11.748(2)		81.17(1)			CuO_3N_2	O	1.918(1)	3.737(0)		175.7(3)	
	2	12.289(2)		73.02(2)			μO	N μO	1.907(2, 1) 1.913(1) 2.916(2)	not given 80.7(1)		87.0(1) ^c 96.0(1, 4.3) ^f 177.8(2, 1.3) 82.8(1, 2.5)	
C: Cu(μ-NL)₂Cu													
[Cu(Bu'py) ₂ (N ₃) ₂](ClO ₄) ₂ (dark blue)	m	12.819(3)		100.00(2)			CuN_4	N	2.001(1)	3.042(3)		93.5(9, 1.7)	337
	P2 ₁ /c 2	13.76(1)	13.65(1)				μN_3	μN	1.98(1, 1)	100.5(6) 79.5(5)		172(4, 1)	
Na[Cu(eggby)] ₂ ·H ₂ O (violet)	m	14.328(6)		92° 58' (1')			CuN_4O	O	1.933(7)	3.077(2)		76.0 ^c	338
	I2/c 8	10.556(6)	13.175(6)				μN	N μN	1.965(8, 74) 1.997(8) 2.568(8)	83.7 94.0		89.2(-, 6.8) 110.9 165.7	
(PPh ₃) ₂ Cu(N ₃) ₃] ₂ (brown)	tr	10.474(5)		101.26(3)			CuN_4	N	1.932(2, 9)	3.128		173.2	339
	P-1 1	11.311(7)	11.794(6)	109.31(3) 103.42(3)			μN	μN	2.003(2, 17) 77.3(1)	102.7(1) 77.3(1)		95.1(1, 4.9) 163.0(4, 8)	
[Cu(2-ampy)(N ₃) ₂ (H ₂ O)] ₂ (black)	tr	7.142(1)		96.52(1)			CuN_4O	N	1.982(3, 20)	3.150(1) ^d		94.0(1, 2.9)	340
	P-1	7.812(1)		92.52(1)			H_2O	N	2.371(2)	103.11(9)		165.7(1, 3.9)	
[Cu ₃ ([24]-aneN ₂ O ₆)(N ₃) ₄ ·H ₂ O] (green)	1	9.727(1)		113.47(1)			μN_3	μN_3	2.011(2, 7)	76.9(1)		94.5(1, 10.5)	341
	m	17.780(2)		109.32(5)			CuN_4O_2	N	2.031(2)	3.162(0)		76.4(1, 2)	
Na ₂ [Cu(hmtiam)(N ₃) ₃]·3H ₂ O (dark red)	P2 ₁ /n 4	9.719(1)	17.361(2)				CuN_5	O	2.609(3, 1)	103.6(9, 1.9)		94.6(1, 3.9)	342
	or Pnnm Pnn2 2	8.944(3)	14.534(6)	12.651(5)			μN_3	N μN_3	1.964(2) 2.017(2, 27)	76.4(8, 2)		171.7(1, 1.9) 73.1(1, 2.1) 91.2(1, 7.3) 106.7(1, 3.9) 146.5(1, 9)	

[Cu(Me ₂ en)(NCO) ₂] ₂ (dark blue)	m P2 ₁ /c 4	12.216(2) 10.662(1) 14.997(4)	96.09(3)	CuN ₅	Me ₂ enN N ₃ μN ₃ 2.037(5, 48) 1.956(5, 20) 2.005(5, 23) 2.406(15, 60)	2.037(5, 48) 1.956(5, 20) 2.005(5, 23) 2.406(15, 60)	3.2464(9) 94.3(2, 1.2) 84.3(2, 2.1)	N ₁ N N ₁ N	91.7(2, 10.5) ^e 167.7(2, 8.0)	343a
[Cu(μ-cpca)(ac)(phen) ₂] ₂ ·2H ₂ O (green)	tr P-1 1	8.171(5) 10.060(6) 13.377(7)	74.33(4) 84.79(5) 72.24(4)	CuN ₄ O	acO phenN cpcaN 1.948(5) 2.015(5, 1) 1.950(6) 2.454(6)	1.948(5) 2.015(5, 1) 1.950(6) 2.454(6)	3.247(5) 94.3(2) 85.7(2)	N ₁ N N ₁ O	81.2(2) ^e 91.3(2, 1.9) 172.8(2) 93.7(2, 1.3) 172.1(2)	343b
[Cu(2-bzpy)(N ₃) ₂] ₂ (black)	tr P-1 1	7.471(2) 10.477(3) 9.389(3)	100.77(2) 109.83(2) 82.21(2)	CuN ₄ O	2-bzpyN 2-bzpyO N ₃ μN ₃ 2.036(2) 1.999(3) 1.928(3) 1.984(3) 2.424(3)	2.036(2) 1.999(3) 1.928(3) 1.984(3) 2.424(3)	3.298(1) ^d 96.3(1) 83.64(12)	N ₁ N O ₁ N	94.2(1, 1.5) 105.6(1) 170.1(1) 79.2(1) ^e 91.7(1, 0) 161.4(1)	344
[Cu(terpy)(N ₃) ₂ (PF ₆) ₂] (green)	m P2 ₁ /m 4	10.149(2) 15.593(2) 11.694(4)	103.57(2)	CuN ₅	N μN ₃ 1.969(7, 36) 1.992(8, 38)	1.969(7, 36) 1.992(8, 38)	3.313(7, 3) 96.3(3) 83.7(2)	N ₁ N N ₁ N	81.3(3, 2.4) ^e 94.2(3, 2.6) 104.4(3) 166.2(3, 7.7)	345
[Cu(impyae)(N ₃) ₂ (ClO ₄) ₂] (not given)	m P2 ₁ /c 2	9.654(4) 11.158(3) 14.625(6)	106.49(2)	CuN ₅	N μN ₃ 2.010(4, 41) 1.975(4) 2.536(4)	2.010(4, 41) 1.975(4) 2.536(4)	3.391(2) 96.7(2) 83.3(3)	N ₁ N	87.5(3, 6.5) ^e 95.9(3, 7.2) ^f	346
[Cu(terpy)(NCO)(H ₂ O)] ₂ (PF ₆) ₂ (green)	tr P-1 2	9.129(1) 10.489(2) 11.106(3)	104.90(2) 86.61(1) 113.93(1)	CuN ₅ O	terpyN H ₂ O μOCN 2.000(6, 67) 2.210(4) 1.906(8)	2.000(6, 67) 2.210(4) 1.906(8)	3.678(1) 83.5(3) 96.5(2)	N ₁ N O ₁ N	79.9(2, 1) ^e 99.5(2, 2) 162.9(2, 3.3) 72.9(2, 3.1) 94.8(2, 4.2) 165.1(2)	347
[Cu(papfy)(μ-NCS) ₂] ₂ (green)	m P2 ₁ /a 4	15.778(3) 9.937(2) 9.795(3)	91.32(2)	CuN ₅ S	N NCS μN 2.009(14, 38) 2.699(5) 1.919(13) 3.054(13)	2.009(14, 38) 2.699(5) 1.919(13) 3.054(13)	3.730(3) 94.4(5) 85.6(5)	N ₁ N	78.5(6) ^e 83.2(4, 3.6) 99.8(6, 5) 162.2(6, 4.3) 95.4(4, 2.8) 176.7(3)	348
D: Cu(μ-Cl)₂Cu [Cu(epma)Cl] ₂ (not given)	lg I4 ₁ /a 8	25.416(33) 12.524(11)		Cu ₂ N ₂ Cl ₂	N μCl 2.113(6, 42) 2.327(2, 51)	2.113(6, 42) 2.327(2, 51)	3.011(2) 80.6(2) 99.4(2)	N ₁ Cl N ₁ N	118.9(2, 10.0) 81.2(2) ^e	349

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	<i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]	α [°] β [°] γ [°]	Chromophore	<i>Cu-L</i> [Å]	<i>Cu-Cu</i> [Å] <i>Cu-L-Cu</i> [°] $\mu L-Cu-\mu L$ [°]	<i>L-Cu-L</i> [°]	Ref.
(1,2-Me ₂ pyH)[Cu ₅ Cl ₄ (H ₂ O)] (orange green)	tr P-1 2	7.077(1) 8.308(1) 12.655(2)	87.63(1) 78.90(1) 71.37(1)	CuCl ₄ CuCl ₃ O	Cl μ Cl Cl H ₂ O μ Cl	2.236(1,40) 2.328(1,13) 2.245(1) 1.990(2) 2.278(1,8)	Cl,O Cl,Cl 168.0(1) 173.0(1,2,30)	350
[Cu(2-Mepy) ₂ Cl] ₂ (yellow (at 193K))	tr P-1 1	8.908(3) 9.038(4) 9.532(3)	95.06(3) 117.42(3) 109.06(3)	CuN ₂ Cl ₂	N μ Cl	3.150(2) 79.93(5) 100.07(5)	Cl,N N,N 107.6(1,6,2) 124.0(2)	351
[Cu(pri ₃ ph) ₂ Cl] ₂ (not given)	tr P-1 1	10.000(3) 12.493(3) 13.037(4)	66.49(3) 87.89(3) 74.53(2)	CuCl ₃ P ₂	P μ Cl	3.207(1) 84.69(5) 95.31(5)	P,P P,Cl 115.87(5) 110.92(5,3,10)	352
[Cu(tlma)(Ph ₃ P)Cl] ₂ (not given)	tr P-1 1	9.395(15) 13.587(6) 13.659(8)	116.07(4) 70.76(7) 106.46(8)	CuCl ₃ NP	N P μ Cl	2.242(2,4) 2.381(1,10) 1.993(4) 2.19(2) 2.349(3) 2.558(2)	Cl,N Cl,N 87.32(16) 112.32(15) 113.8(1,7)	353
[Cu(15-crown-5)(MeCN)Cl ₃] ₂ [Cu ₂ Cl ₆] (red)	m P2 ₁ /a 4	14.732(5) 11.357(4) 13.520(3)	112.25(2)	CuCl ₄	Cl μ Cl	3.295(2) ^d 90.9(7) 89(2)	Cl,Cl Cl,Cl 101.5(2,14) 136.5(2,6)	354
[Cu(15-crown-5)(MeCN)] ₂ [CuCl ₃] ₂ (orange)	m P2 ₁ /c 4	11.367(6) 13.521(7) 14.751(9)	112.40(4)	CuCl ₄	Cl μ Cl	3.296(2) 90.68(7) 89.32(8)	Cl,Cl Cl,Cl 100.51(8,2,18) 136.46(8,64)	355
[Na(bz-15-crown-5)] ₂ [CuCl ₃] ₂ (not given)	m P2 ₁ /c 2	9.805(3) 9.449(3) 21.382(7)	104.84(5)	CuCl ₄	Cl μ Cl	3.306(1) 92.2(1) 87.8(1)	Cl,Cl Cl,Cl 99.0(1,1) 141.9(1,4)	356
[Cu(Ph ₄ m) ₃][CuCl ₃] ₂ ·Me ₂ CO (not given)	m P2 ₁ /c 4	13.144(1) 19.701(3) 30.109(4)	90.88(1)	CuCl ₄	Cl μ Cl	3.333(1) 87.0(1,3) 87.0(1,3)	Cl,Cl Cl,Cl 90.4(1,3,2) 104.7(1,5,3) 129.2(1,8,9) 148.4(1)	357

[Na(dbz-18-crown-6)] ₂ [CuCl ₃] ₂ (not given)	m P2 ₁ /n 2	12.754(5) 12.006(5) 14.996(6)	92.80(5)	CuCl ₄	Cl μCl	2.220(1,26) 2.29(1,4)	3.341(1) 93.6(1) 86.4(1)	Cl,Cl	97.1(1,2.8) 147.0(1,3.0)	355
(etaps) ₂ [CuCl ₃] ₂ (brown)	m P2 ₁ /n 4	13.364(2) 16.772(9) 7.493(2)	92.46(2)	CuCl ₄	Cl μCl	2.193(3,2) 2.299(3,6)	3.345(2) 93.4(1) 86.6(1)	Cl,Cl	94.3(1,77) 146.5(1)	358
[Cu(2,2,5,5-MeapvNO)Cl ₃] ₂ (dark brown)	m P2 ₁ /c 4	12.045(5) 13.642(5) 7.679(3)	98.46(2)	CuCl ₃ O	O Cl μCl	1.940(1) 2.155(1) 2.284(1)	3.347(1) ^d 92.8(1) 87.2(1)	Cl,Cl	155.0(1)	359
(PPh ₄) ₂ [CuCl ₃] ₂ (red yellow)	m P2 ₁ /n 4	13.601(2) 19.272(3) 9.216(2)	107.9(1)	CuCl ₄	Cl μCl	2.192(5,6) 2.310(5,18)	3.353(4) not given 86.9(2)	Cl,Cl	98.4(2,2.7) 143.2(2,4)	360
(PPh ₄) ₂ [CuCl ₃] ₂ (red brown)	m P2 ₁ /c 4	9.226(8) 19.301(15) 13.842(15)	111.26(6)	CuCl ₄	Cl μCl	2.190(3,11) 2.307(2,15)	3.355(1) 95.1(1,18) 86.7(1)	Cl,Cl	97.1(1,3.8) 143.5(1,1)	361
[Co(15-crown-5)(MeCN)] ₂ [Cu ₂ Cl ₆] (brown orange)	tr P-1 1	7.243(2) 9.383(3) 9.566(3)	82.32(2) 86.13(2) 83.12(2)	CuCl ₄	Cl μCl	2.193(3,12) 2.315(3,22)	3.369(3) ^d 93.4(1) 86.6(1)	Cl,Cl	99.6(1,2.6) 144.3(1)	362
(Ph ₄ As) ₂ [CuCl ₃] ₂ (not given)	m P2 ₁ /a 4	13.73(1) 19.64(1) 9.290(5)	111.55(2)	CuCl ₄	Cl μCl	2.207(3,9) 2.319(2,14)	3.382(1) 93.7(1) 86.3(1)	Cl,Cl	95.0(1,8.7) 144.9(1,3)	363
[Cu ₂ (bim) ₂ Cl ₃ Cl·2H ₂ O] (green)	or Pnma 4	19.506(3) 17.384(4) 11.940(2)		CuN ₃ Cl ₂	N μCl	1.980(4,0) 2.010(4) 2.488(2,64)	3.386(1) 85.5(1,3.7) 94.6(1,7)	N,N N,Cl	88.6(1) 175(2) 100.1(1,17.7) 147.0(1)	364
[Cu(mop)Cl ₃] ₂ (red violet)	tr P-1 2	7.414(2) 8.686(2) 14.766(4)	79.16(2) 82.20(2) 74.19(2)	CuCl ₄ O ₂	Cl O μCl	2.245(4,4) 2.627(1) 2.283(4,8)	3.389(2) ^d 95.8(1) 84.1(1)	Cl,O Cl,Cl	90.(3,2.9) 91.9(1,7) 175.8(1,2)	365
(Kbz-15-crown-5) ₂ [CuCl ₃] ₂ (green)	tr P1 1	11.224(2) 12.831(2) 13.663(2)	75.47(1) 67.44(1) 70.46(1)	CuCl ₄	Cl μCl	2.203(2,5) 2.291(2,1)	3.389(1) 95.4(1) 84.6(1)	Cl,Cl	95.3(1,6) 155.9(1)	366
[Cu(HB(pz) ₃)Cl] ₂ (green)	m P2 ₁ /n	13.144(15) 13.247(3)	96.073(14)	CuN ₃ Cl ₂	N	1.989(5,4) 2.200(5)	3.394(2) 94.51(7)	N,Cl	97.31(16,9.85) 167.23(17,4.56)	367

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	<i>a</i> [Å]			α [°]	β [°]	γ [°]	Chromophore	<i>Cu-L</i> [Å]	<i>Cu-Cu</i> [Å]		<i>L-Cu-L</i> [°]	Ref.
		<i>b</i> [Å]	<i>c</i> [Å]	<i>Cu-L</i> [Å]						<i>Cu-Cu</i> [Å] μ <i>L-Cu-μL</i> [°]			
(PhSB) ₂ [CuCl ₃] ₂ (not given)	2 m P2 ₁ /n	7.467(13) 13.412(4) 19.894(4)						CuCl ₄	μ Cl Cl μ Cl	85.49(7) 3.400(3) 94.6(1) 85.4(1)	N,N Cl,Cl 147.7(1.3)	368	
(1-MepyH)[Cu ₂ Cl ₅ (H ₂ O)] (red orange)	2 m P2 ₁ /n 4	9.501(2) 12.050(3) 7.493(2) 15.211(4)			109.6(3)		CuCl ₄	Cl μ Cl	2.267(2, 14) 3.407(2) 94.7(1, 1) 85.3(1, 6)	Cl,Cl Cl,Cl	91.9(1, 1.5) 172.9(1, 1.3)	369	
(4-ampyH)[Cu ₂ Cl ₅ (H ₂ O)]·H ₂ O (red orange)	m P2 ₁ /n 2	3.740(1) 11.948(3) 15.355(4)			93.76(2)		CuCl ₃ O	H ₂ O Cl μ Cl	1.992(3) 2.261(2) 2.303(2, 9)	Cl,O Cl,Cl	92.5(1) 175.7(1) 90.4(1, 1.9)	369	
[Cu(bpyo) ₂ Cl] ₂ (green)	tr P-1 1	8.664(2) 8.732(2) 9.099(3)					CuCl ₄	Cl μ Cl H ₂ O	2.231(4) 2.747(2) 2.313(2, 13) 1.976(10) 2.252(2) 2.313(2, 13)	Cl,Cl Cl,Cl Cl,Cl Cl,O	93.1(3, 7.3) 166.0(2)	300	
(4-bzpipH) ₂ [CuCl ₃] ₂ (red orange)	m C2/c 4	28.877(8) 8.440(2) 12.023(2)			95.62(2) 107.04(2) 114.05(2)		CuCl ₃ O ₂	O Cl μ Cl	1.989(3, 25) 2.626(1) 2.272(1, 7)	Cl,Cl Cl,O O,O	93.7(1, 1.5) 95.1(1, 12.8) 163.4(1, 9.3) 83.9(1) ^b	370	
[Cu(amoc)Cl] ₂ (dark green)	m P2 ₁ /c 2	6.150(1) 11.224(2) 15.057(3)			101.9(1)		CuCl ₄	Cl μ Cl	2.269(3, 8) 2.261(3, 53)	Cl,Cl not given 84.8(1)	87.1(1) 91.8(1, 2.3) 104.4(1, 4.0) 151.0(1) 177.5(1)	371	
					99.08(1)		CuN ₂ Cl ₂ O	O N μ Cl	1.926(2) 1.976(3, 11) 2.329(1) 2.808(1)	N,Cl not given 97.1(1)	86.8(1, 3.2) 112.4(1) 150.2(1) 89.4(1, 3.7) 89.6(1) ^c 92.9(1) ^d 169.1(1)		

$(\text{dbztsf})_2[\text{CuCl}_3]_2$ (dark reddish)	m C ₂ /m 2	9.216 24.958 7.300	108.23	CuCl_4	Cl μCl	2.220(4.0) 2.294(3.0)	3.419(4) ^d 83.64(1) 96.4(1)	Cl,Cl	90.1(1.6,5) 173.2(1)	372
$(\text{dbztsfH})_2[\text{CuCl}_3]_2$ (dark red)	m C ₂ /m 2	9.224(1) 24.976(3) 7.317(2)	108.28(1)	CuCl_4	Cl μCl	2.224(1) 2.297(1)	3.420(1) ^d 96.24(6) 83.76(6)	Cl,Cl	92.7(6.1,6)	373
$[\text{Cu}(\text{pan})\text{Cl}]_2$ (dark)	m P ₂ /a 4	15.817(3) 8.255(1) 10.404(3)	103.46(2)	$\text{CuN}_2\text{Cl}_2\text{O}$	N O μCl	1.978(2.14) 1.984(2) 2.263(1) 2.677(1)	3.421(1) ^d 87.79(3) 92.21(3)	N,N O,N Cl,N	78.53(9) ^f 81.50(9) ^f 159.34(10) 97.13(7.23) 170.06(7) 101.50(7)	374
$[\text{Cu}(\text{msimp})\text{Cl}_2]_2 \cdot \text{CCl}_4$ (green)	m P ₂ /n 4	11.027(3) 14.073(3) 15.602(3)	94.27(2)	CuCl_3N	N Cl μCl	1.985(2) 2.214(1) 2.300(1.10)	3.421(1) 96.1(1) 84.0(1)	Cl,Cl Cl,Cl N,Cl	87.5(1.3,5) 166.0(1) 93.8(1.1,6) 167.3(1)	375
$[\text{Cu}(\text{dzcyc})\text{Cl}_2]_2$ (blue)	m P ₂ /c 4	13.406(3) 11.454(2) 12.605(3)	115.01(2)	CuCl_3N_2	N Cl μCl	2.003(3.3) 2.245(1.8) 2.316(1.14) 2.648(1.6)	3.422(0) not given 92.9(0.2)	Cl,Cl Cl,N N,N	97.7(0.2,3) 94.4(1.4,8) 163.9(1.1,3) 77.2(1.3) ^e	376
$[\text{Cu}(3\text{-ampyH})\text{Cl}_3]_2$ (red)	m P ₂ /a 2	7.623(1) 14.700(2) 8.121(1)	93.09(1)	CuCl_4N	N Cl μCl	2.049(1) 2.279(1) 2.496(1) 2.235(1.5)	3.425(2) 94.9(1) 85.1(1)	Cl,Cl Cl,Cl Cl,N	93.0(1,6) 106.6(1.4,4) 146.6(1) 88.3(1.3,9) 175.7(1)	377
$[\text{Cu}(\text{pydiox})\text{Cl}_2]_2$ (blue)	m P ₂ /c 4	9.022(2) 12.503(3) 13.564(5)	108.50(3)	$\text{CuCl}_3\text{N}_2\text{O}$	N O Cl Cl μCl	2.040(1.16) 2.678(1) 2.269(1) 2.273(1) 2.844(1)	3.428(1) ^d 96.68(1) 83.32(1)	N,N N,Cl Cl,Cl Cl,Cl	85.04(5) ^f 90.72(4.1,53) 167.32(4.4,72) 99.94(2.4,23)	378
$(\text{tmsfs})_2[\text{CuCl}_3]_2$ (not given)	tr P-1 1	8.871(3) 10.652(3) 12.505(3)	109.70(2) 106.10(3) 102.63(3)	CuCl_4	Cl μCl	2.202(2.14) 2.306(2.14)	3.433(1) 96.3(1) 83.7(1)	Cl,Cl	92.1(1.8,4) 156(1.3)	379
$[\text{Cu}(\text{epthscarb})\text{Cl}]_2$ (green)	m P ₂ /n 4	11.785(1) 8.202(1) 11.057(1)	95.70(1)	CuCl_2ONS	O N S μCl	2.054(5) 1.975(6) 2.245(3) 2.236(2) 2.819(2)	3.439(2) ^d 95.11(6) 84.89(6)	O,N S,N S,O Cl,N Cl,O Cl,S	80.4(2) ^e 84.7(2) ^e 164(2) 171.0(2) 95.0(2) 99.0(1)	380

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å]			Chromophore	Cu-L [Å]			Cu-Cu [Å]		L-Cu-L [°]	Ref.
		b [Å]	c [Å]	α [°]		β [°]	γ [°]	Cu-L	Cu-Cu	Cu-L-Cu [°]		
(NH ₄) ₂ [CuCl ₃] ₂ (not given)	m	4.0344(7)			CuCl ₄	Cl	2.271(2, 10)	3.441(2) ^d	Cl, Cl	92.18(8, 67)	381	
	P2 ₁ /c	14.206(2)		96.43(2)		μ Cl	2.311(2, 3)	96.24(8)	174.17(10, 1.60)			
(dma) ₂ [CuCl ₃] ₂ (green)	m	12.09			CuCl ₄	Cl	2.275(7, 26)	3.444(6)	Cl, Cl	92.3(2, 4.7)	382	
	1 2/a	8.63		97.5		μ Cl	2.326(6, 21)	not given	106.7(2)			
	8	14.49				84.4(2)	84.4(2)	166.0(2, 10)				
[Cu(dmg)Cl] ₂ (green)	tr	7.6970(6)		108.135(9)	CuCl ₃ N ₂	N	1.986(11, 28)	3.445(3)	Cl, N	93.08(34, 3.71)	383	
	P-1	8.1743(12)		69.160(6)		Cl	2.249(4)	88.0(1)	166.31(34, 38)			
	2	8.1203(7)		78.692(8)		μ Cl	2.238(4)	92.0(1)	93.14(23, 1.07)			
[Cu(amzh)Cl] ₂ (dark green)	m	6.018(1)			CuN ₂ Cl ₂ O	O	1.918(2)	3.445(1)	Cl, O	91.4(1)	384	
	P2 ₁ /n	12.648(4)		101.39(2)		N	1.979(3, 20)	not given	90.9(1)			
[Cu(ophsalim)Cl] ₂ ·2dmf·H ₂ O (not given)	m	8.771(1)			CuO ₂ Cl ₂ N	N	1.932(2, 7)	3.448(1)	Cl, O	90.9(1, 6.8)	385	
	P2 ₁ /c	13.440(2)		97.113(4)		O	1.962(2, 84)	84.6(1, 4)	102.9(1, 8)			
	4	29.060(4)			μ Cl	2.260(1)	92.9(1, 5)	162.6(1, 1.9)				
[Cu(N ₃ bz) ₂ Cl] ₂ ·H ₂ O ^e (green)	tr	8.591(3)		110.62(5)	CuCl ₃ N ₂	N	1.985(8, 5)	3.448(3)	Cl, Cl	133.8(2, 4.8)	386	
	P-1	11.906(4)		91.95(5)		Cl	2.260(6)	87.5(1)	N, Cl	90.0(3, 1.7)		
	2	16.183(4)		92.04(6)	μ Cl	2.493(4, 52)	92.5(1)	176.5(6)				
					N	2.011(9, 9)	3.520(2)	116.4(1)				
					Cl	2.277(4)	89.3(1)	152.9(2)				
					μ Cl	2.694(4)	90.7(1)	89.6(3, 4.1)				
								173.4(2)				

[Cu ₂ (mapycarb)Cl ₄] (not given)	tr P-1 2	8.558(8) 10.824(8) 15.335(3)	89.77(5) 84.47(6) 72.72(7)	CuCl ₄	Cl μCl	2.195(1,2) 2.327(1,62)	3.454(1) not given	not given	387
[Cu(Me ₂ en)Cl ₂] (not given)	or Pbca 4	9.765(9) 8.518(6) 20.767(20)		CuCl ₃ N ₂	N Cl μCl	1.967(3) 1.982(4,69) 2.306(1) 2.634(1)	3.458(3) 86.13(8) 93.87(8)	84.1(2) ^f 91.2(2,3.9) 170.7(2,3.0)	388
[Cu(pri) ₂ Cl ₂] (green)	tr P-1 2	7.278(1) 8.862(2) 9.973(2)	108.69(2) 103.38(1) 90.72(2)	CuCl ₃ O ₂	O Cl μCl	1.971(3,8) 2.238(1) 2.320(1) 2.670(1)	3.460(1) 87.50(4) 92.50(4)	108.34(5) 159.07(5) 90.1(1,4.4) 176.5(1)	389
[Cu(S4pp)Cl ₂] (green)	or Pbca 4	15.383(6) 11.409(3) 17.423(4)		CuCl ₃ S ₂	Cl S μCl	2.234(3) 2.354(3,5) 2.321(3)	3.464(7) 86.87(10) 93.13(10)	98.59(12,2.30) 87.50(12,3.75) 171.25(12,1.21)	390
(tms) ₂ [CuCl ₃] (black)	tr P-1 1	8.591(3) 11.314(6) 11.868(6)	63.44(3) 88.18(3) 74.28(3)	CuCl ₄	Cl μCl	2.210(1,7) 2.294(1,1)	3.467(1) 98.2(1) 81.8(1)	88.28(12) ^f 90.1(1,8.4) 170.1(1,1)	379
[Cu(β-ala)Cl ₂] (green)	m P ₂ /c 4	7.960(1) 12.249(2) 6.875(1)	94.10(1)	CuCl ₄ O ₂	O Cl μCl	1.955(8,17) 2.280(3) 2.336(3) 2.679(3)	3.468(2) ^d 87.2(1) 93.5(1)	90.2(2,2.0) 173.8(1)	391
[Cu(ehmp)Cl ₂] (green)	m P ₂ /c 4	6.188(2) 11.404(2) 15.161(4)	109.60(2)	CuCl ₃ O ₂	O Cl μCl	1.984(1,8) 2.228(1) 2.271(1) 2.690(1)	3.474(1) not given 91.5(1)	93.6(1,2.1) 105.8(1,4.4) 91.0(1,4.4) 158.3(1) 173.0(1)	392a
[Cu(μ-Cl)(dtic)Cl] ₂ (green)	m P ₂ /c 4	9.059(1) 13.647(1) 9.538(1)	92.28(1)	CuCl ₃ ON	N O Cl μCl	1.951(2) 2.079(2) 2.248(2) 2.246(2) 2.740(2)	3.484(1) ^d 85.8 94.2(4)	84.7(1,3.3) 92.3(1) 173.3(1) 91.9(1,2) 107.1(5) 161.7(1) 89.9(1)	392b

TABLE II (Continued)

Compound (color)	<i>Cryst. cl.</i> <i>space G.</i> <i>Z</i>	<i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]	α [°] β [°] γ [°]	Chromophore	<i>Cu-L</i> [Å]	<i>Cu-Cu</i> [Å] <i>Cu-L-Cu</i> [°] μ <i>L-Cu-μL</i> [°]	<i>L-Cu-L</i> [°]	Ref.
[Cu(himmet)Cl] ₂ ·H ₂ O (not given)	m C2/c 8	21.838(3) 19.936(2) 12.997(2)	116.24(1)	CuO ₂ Cl ₂ N	O N μ Cl 2.788(1)	3.4995(3) 83.29(2.3) not given	Cl ₂ O Cl ₂ N O 172.6(1) 82.5(1) ^f 92.1(1) ^f	393
[Cu(saliqu)Cl] ₂ ·2MeOH (bright green)	tr P-1 1	11.951(3) 8.943(2) 8.111(2)	112.02(2) 107.45(2) 79.40(2)	CuN ₂ Cl ₂ O	O N μ Cl 2.856(2)	3.502(1) not given 95.0(2)	O ₂ Cl N ₂ Cl O ₂ N 174.0(1) 82.0(1) ^e	394
[CuCl ₂ (cycol) ₂ (cycol)(thf) (green)]	m not given	8.120(2) 34.90(2) 11.132(4)	105.71(2)	CuCl ₃ O ₂	O Cl μ Cl 2.680(2) 2.804(2)	3.511(1) 88.6(1.18) not given	Cl ₂ Cl 101.5(1.4) 91.0(2, 10.3) 167.5(2, 5) 80.1(2) ^e	395
{Cu(smp)Cl ₂ ·2H ₂ O (brown)}	m P2 ₁ /c 4	7.316(3) 15.944(4) 10.391(2)	117.50(2)	CuCl ₃ NS	N S Cl μ Cl 2.301(1) 2.737(1)	3.518(1) ^d 91.83(2) 88.17(2)	N ₂ Cl 169.12(10) S ₂ Cl 171.92(10) Cl ₂ Cl 95.66(10, 3.83)	396
[Cu(pyqux)Cl] ₂ (yellow)]	m P2 ₁ /n 2	8.385(6) 14.708(7) 10.44(6)	92.5(5)	CuCl ₃ N ₂	N Cl μ Cl 2.272(2) 2.274(2) 2.473(2)	3.522(1) 95.7(1) 84.3(1)	Cl ₂ Cl 144.2(1) Cl ₂ N 95.0(2, 8.9) 114.1(1) 169.7(2) 79.7(2) ^e	397
[Cu ₂ (thf) ₂ (cycol)Cl ₆] (brown)]	m C2/c 4	16.561(3) 13.217(2) 13.290(3)	134.05(1)	CuCl ₄ O ₂	O Cl μ Cl 2.293(2, 57) 2.726(3) 2.293(2, 57) 2.726(3)	3.525(2) 90.1(1.1) 79.8(1)	Cl ₂ Cl 179.9(1.1) Cl ₂ O 168.6(1) O ₂ O 81.9(2) ^e 180.0(2)	398

[Cu(4-Meth)2Cl3]2·2MeOH (dark blue)	m P2 ₁ /n 2	7.506(4) 15.987(6) 12.472(5)	96.24(4)	CuCl ₃ N ₂	N Cl μCl	2.002(3, 2) 2.303(1) 2.350(1) 2.645(1)	3.543(1) 90.15(3) 89.85(3)	Cl, Cl	89.85(3) 107.75(4) 162.39(4) 90.38(10, 3.12) 172.78(13)	399
[Cu(hemim)2Cl3]2 (green)	m P2 ₁ /c 4	7.075(3) 19.051(7) 14.161(7)	90.42(4)	CuCl ₃ N ₂	N Cl μCl	1.998(4, 5) 2.358(2, 61) 2.619(1, 0)	3.558(1) ^d 89.8 90.2	Cl, Cl Cl, N N, N	134.9(1, 8) 90.1(1, 2.2) 175.4(2)	400
[Cu(guan)Cl3]2·2H ₂ O (yellow brown)	m C2/c 8	16.952(1) 10.183(1) 13.185(1)	99.97(1)	CuCl ₄ N	N Cl μCl	1.977(5) 2.365(2) 2.288(2) 2.448(2)	3.566(1) ^d 97.68(7) 82.32(7)	Cl, N Cl, Cl Cl, Cl	87.8(2, 3.4) 168.9(2) 94.56(6) 109.2(1, 8.0) 132.9(1)	401
[Cu(guan)Cl3]2 (not given)	m C2/c not given	16.954(3) 10.175(3) 13.169(3)	99.87(1)	CuCl ₄ N	N Cl μCl	1.976 2.298(1, 29) 2.368(1, 80)	3.572(1) ^d 97.9 82.1	Cl, Cl	103.7(-, 10.6) 134.0	402
[Cu(pzc)Cl3]2 (not given)	m P2 ₁ /c 8	12.992(1) 9.614(1) 16.376(3)	130.08(1)	CuCl ₃ ON	O N Cl μCl	1.985(4, 25) 2.035(4, 25) 2.225(4, 5) 2.26(4) 2.80(4)	3.58(4) 87(4, 1) 92(4, 2)	Cl, Cl Cl, N O, Cl O, N	91.0(3) 108.0(3) 163.0(3) 167.5(3, 2.5) 165.0(3) 80(0.3, 1) ^f	403
[Cu(atha)Cl3]2 (blue)	m P2 ₁ /c 2	9.777(2) 11.922(3) 9.247(4)	101.98(3)	CuCl ₃ N ₂	N Cl μCl	2.018(13, 12) 2.278(5) 2.288(5) 2.767(5)	3.594(5) ^d 90.1(2) 90.0(2)	Cl, Cl Cl, N N, N	97.8(2, 4.2) 92.0(4, 3.2) 83.0(5) ^e	404
[Cu(eyehol)2Cl3]2 (green)	m P2 ₁ /n 4	15.318(8) 7.781(2) 15.682(8)	105.93(4)	CuCl ₃ O ₂	O Cl μCl	1.977(4, 15) 2.217(1) 2.245(1, 28)	3.610(1) 91.75(5) 88.43(5)	O, O O, Cl	78.3(1) ^e 92.9(1, 3.6) 161.6(1, 5)	405
[Cu(dmf)2Cl3]2 (not given)	m C2/c 8	13.296(4) 13.254(4) 14.702(6)	113.76(3)	CuCl ₃ O ₂	O Cl μCl	1.981(3, 8) 2.247(2) 2.284(1) 2.661(2)	3.613(2) 93.57(4) 86.43(4)	Cl, Cl Cl, O	103.49(5, 9.01) 91.73(10, 6.30) 148.92(89) 172.20(9)	406
(bpyH)[CuCl3]2 (brown)	tr P-1 1	10.37(2) 10.96(2) 3.99(1)	96.9(5) 96.7(5) 115.9(5)	CuCl ₄	Cl μCl	2.258(12, 3) 2.358(12, 4)	3.615(12,) 100.1(6) 79.9(1)	O, O Cl, Cl	86.75(11) 92.1(5, 4.2) 173.6(5, 1.9)	407

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	$Cu-L$ [Å]	$Cu-Cu$ [Å] $Cu-L-Cu$ [°] $\mu L-Cu-\mu L$ [°]	$L-Cu-L$ [°]	Ref.
$Cu_2(3,4-Me_2phpz)-(4,5-Me_2phpz)Cl_2$ (green)	tr P-1 1	9.071(1) 11.008(1) 11.358(1)	93.42(1) 97.50(1) 96.16(1)	$CuCl_3N_2$	N Cl μCl 2.004(3, 1) 2.297(1) 2.3047(9) 2.6420(9)	3.6164(7) 93.70(3) 86.30(3)	Cl, Cl Cl, N 155.32(8) 178.44(7)	408
$[Cu(dempz)Cl_2]_2$ (not given)	m P2 ₁ /b 4	9.445(3) 9.579(3) 22.253(5)	96.43(3)	$CuCl_3N_2$	N Cl μCl 2.00(-, 2) 2.293 2.331 2.597	3.620 ^d 94.4(2) 85.6(2)	N, N Cl, N 154.0(3) 176.2(3)	409
$[Cu(dpm)Cl_2]_2$ (dark green)	m P2 ₁ /c 2	8.744(2) 12.124(3) 11.648(2)	104.43(3)	$CuCl_3N_2$	N Cl μCl 2.034(2, 1) 2.261(1) 2.315(1) 2.629(1)	3.629(1) 93.8(1) 86.2(1)	N, N N, N N, Cl 150.7(1) 95.6(1, 7.1) Cl, C 100.2(1, 6.5)	410
$[Cu(dtd)Cl_2]_2$ (dark green) (at 140 K)	m P2 ₁ /c 2	9.592(2) 17.193(4) 7.813(2)	101.03(2)	$CuCl_3S_2$	S Cl μCl 2.335(1, 18) 2.274(1, 19) 2.663(1)	3.630(1) 93.8(1) 86.1(1)	Cl, Cl S, S Cl, S Cl, S 90.7; 139.7(1)	411
$[Cu(bzrh)Cl_2]_2$ (blue green)	tr P-1 2	8.795(7) 11.402(9) 6.830(6)	101.24(2) 96.31(3) 106.33(3)	$CuCl_3ON$	O N Cl 1.974(3) 2.122(4) 2.232(2) 2.258(2) 2.735(2)	3.631(3) 92.83(5) 87.17(5)	O, Cl 172.61(13) 96.54(12, 1.56) 151.23(12) 91.78(5, 4.61) 108.78(5)	412
$[Cu(dien)Cl_2]_2(ClO_4)_2$ (not given)	or Pbn2 ₁ 4	7.637(1) 13.549(3) 20.866(4)		CuN_3Cl_2	N μCl 2.010(20, 31) 2.313(5) 2.770(5)	3.643(2) not given 87.0(1)	N, Cl 176.3(3, 3.1) 85.4(5, 3) ^c	413

[Cu(pio)]Cl ₂ ₂ (green)	or Pbcn 8	20.710(2) 11.401(6) 17.469(4)	CuCl ₃ O ₂	O Cl μCl	1.967(5, 21) 2.230(1, 29) 2.225(2, 7) 2.664(2) 3.080(2)	3.647(1) 97.0(1, 11) 85.7(1, 5.0)	Cl, Cl Cl ₂ O	85.7(1, 5.0) 101.7(1, 6.5) 90.3(1, 5.3) 107.6(2, 3.5) 144.9(2) 167.1(1, 2.2) 77.4(2, 2) ^c	414
[Cu(dmf) ₂ Cl ₂] ₂ (green)	m P ₂ /a 2	11.720(5) 11.641(5) 9.012(4)	CuCl ₃ O ₂	O Cl μCl	1.992(2, 16) 2.153(2) 2.302(2)	3.673(2) ^d 89.4 90.6	O ₂ O O ₂ O Cl ₂ O	88(1) 91.8(1, 3) 145.5(1) 172.0(1) 92.8(1)	415
[Cu(2-amepy)Cl ₂] ₂ (blue green)	tr P-1 1	7.093(1) 9.412(1) 9.541(2)	CuCl ₃ N ₂	N Cl μCl	2.036(3) 2.253(1) 2.283(1) 2.862(1)	3.683(1) not given 89.30(3)	Cl, Cl Cl, N Cl, N	95.90(4, 3.47) 80.4(0) ^e 92.3(1, 3.7) 171.5(10, 9)	416
[Cu(pyep)Cl] ₂ ·2H ₂ O (dark blue)	m P ₂ /n 4	10.134(2) 14.141(4) 9.108(4)	CuN ₃ Cl ₂	N μCl	1.986(3, 28) 2.31(1) 2.831(1)	3.693(1) 91.1(1) 88.9(1)	Cl, N N ₃ N	94.6(1, 4.6) 173.0(1) 81.3(0) ^e 91.5(1) ^f 167.8(1)	417
[Cu(bzcarb)Cl ₂] ₂ ·2MeOH (green)	tr P-1 2	10.370(3) 11.074(4) 11.186(4)	CuCl ₃ N	Cl N μCl	2.323(1) 2.004(4, 4) 2.279(2)	3.702(1) 90.22(4) 89.78(4)	Cl, Cl Cl, N N, N	90.82(5) 178.85(2) 92.2(1, 4.1) 166.2(1)	418
[Cu(Et ₃ en)Cl ₂] ₂ (not given)	tr P-1 1	8.536(2) 9.194(5) 7.766(2)	CuCl ₃ N ₂	N Cl μCl	2.068(3, 53) 2.307(1) 2.284(1) 2.728(1)	3.703(1) 94.84(4) 85.16(4)	Cl, N Cl, N Cl, Cl N, N	94.25(10, 8.68) 145.69(9) 174.91(10) 102.84(4, 8.12) 84.29(11) ^e	419
[Cu(4-Meth)(dmf)Cl ₂] ₂ (not given)	m P ₂ /n 2	7.349(7) 20.306(7) 8.909(3)	CuCl ₃ ON	O N Cl μCl	1.990(4) 2.006(4) 2.238(2) 2.296(2) 2.724(1)	3.721(1) not given 84.71(7)	Cl, Cl Cl, Cl Cl, N Cl, O N, O	101.33(7, 7.31) 84.71(7) 92.0(1, 1.2) 155.0(1) 175.2(2) 93.4(1, 3.0) 85.5(1)	420
[CuCl ₂ (tms ₂) ₂] ₂ (not given)	m P ₂ /c	9.205(1) 14.614(9)	CuCl ₃ O ₂	O Cl	1.948(-, 3) 2.270	3.737(2) not given	Cl, O Cl, O	83(1) 92.2(1, 8)	421

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	<i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]			Chromophore			<i>Cu-L</i> [Å]	<i>Cu-Cu</i> [Å] <i>Cu-L-Cu</i> [°] <i>μL-Cu-μL</i> [°]		<i>L-Cu-L</i> [°]	Ref.	
		<i>α</i> [°] <i>β</i> [°] <i>γ</i> [°]	Chromophore		<i>α</i> [°] <i>β</i> [°] <i>γ</i> [°]	<i>Cu-Cu</i> [Å] <i>Cu-L-Cu</i> [°] <i>μL-Cu-μL</i> [°]	<i>L-Cu-L</i> [°]						
	4	9.660(4)						<i>μ</i> Cl	2.280 3.020	91.5(1)	Cl ₂ Cl O ₂ O Cl ₂ Cl Cl ₂ S 153.12(17) 177.29(17) 82.67(15) ^c	122.8(1) 145.7(1) 165.2(1)	
[Cu(S ₅ tpp)Cl ₂] ₂ (green)	m A2/a 4	12.616(1) 10.054(6) 29.180(2)	95.81(1)	CuCl ₃ S ₂	Cl S <i>μ</i> Cl 2.661(4)	2.265(4) 2.357(5.2) 2.277(4) 2.661(4)	3.749(2) 90.94(4) 89.06(14)	Cl ₂ Cl Cl ₂ S	96.31(17, 7.25) 93.01(16, 9.01)		390		
[Cu([12]-aneS ₂)Cl ₂] ₂ (not given)	tr P-1 1	9.646(3) 11.823(4) 7.934(2)	109.61(2) 79.23(2) 113.55(2)	CuCl ₃ S ₂	S Cl 2.242(2) <i>μ</i> Cl 2.266(2) 2.825(2)	2.339(2, 31) 2.242(2)	3.749(2) 94.22(5) 85.78(5)	Cl ₂ Cl Cl ₂ S	108.90(6, 10.84) 79.34(5)		422		
[Cu(Me ₆ en)Cl ₂] ₂ (blue)	tr P-1 1	7.713(7) 8.560(8) 9.249(8)	98.44(6) 94.39(7) 118.63(5)	CuCl ₃ N ₂	N Cl <i>μ</i> Cl 3.147(4)	2.068(4, 14) 2.259(2)	4.089(4) 96.8(1) not given	S,S N,N N,Cl Cl ₂ Cl	85.3(1) ^c 92.3(1, 4.1) 164.2(1, 6.7) 99.8(1, 6.2)		423		
E: Cu(<i>μ</i> -SL) ₂ Cu [Cu(C ₁₄ H ₁₆ N ₂ OS) ₂] (not given)	m P2 ₁ /c 4	9.408(3) 15.571(4) 11.996(3)	103.42(2)	CuS ₂ ON	O N <i>μ</i> S 2.348(3, 5)	1.893(8, 6) 1.931(8, 4)	2.656(2) 70.6(1, 3) 84.4(1, 2)	<i>μ</i> S,S <i>μ</i> S,N N,O	93.9(2, 6) 87.6(3, 3) 95.5(3, 4)		424		
[Cu(tbaa)(tbi)Br] ₂ (not given)	m P2 ₁ /n 2	9.120(2) 18.597(8) 10.062(6)	110.73(4)	Cu ₃ Br	Br S <i>μ</i> S 2.659(4)	2.491(3) 2.287(3) 2.272(3)	3.049(3) 75.9(1) 104.1(1)	Br ₂ S S S,S	113.6(1, 3.3) 96.8(1) 103.5(1) 120.9(1)		425		
[Cu(hesc) ₂] ₂ (brown)	tr P-1 2	11.946(3) 7.826(3) 9.789(4)	69.65(3) 83.06(3) 81.78(3)	CuS ₅	S <i>μ</i> S 2.318(5, 11) 2.335(4)	2.318(5, 11) 2.335(4)	3.451(2) not given not given	S,S	76.5(2, 0) ^j 101.3(2, 1.0)		426		
[Cu(desc) ₂] ₂ (green)	m P2 ₁ /c	9.907 10.627	113.52	CuS ₅	S	2.307(2, 10) 2.851	3.588(1) not given	S,S	77.19(9) ^j 101.59(9, 30)		427a		

[Cu(μ -dalthe) ₂] ₂ (black brown)	4 tr P-1 2	16.591 10.161(4) 9.294(4) 10.518(3)	77.46(3) 77.10(3) 89.02(3)	CuS ₅	μ S S μ S 2.888(2)	2.320(2, 19) 2.316(2, 8) 2.328(2) 2.888(2)	76.27(9) 3.742(2) not given not given	S,S	76.7(1, 1) ^c	427b
F ₂ Cu(μ -Br) ₂ Cu (NPr ₂) ₂ [CuBr ₃] ₂ (orange)	m C2/c 4	17.460(6) 14.625(4) 15.061(4)	103.82(2)	CuBr ₄	Br μ Br	2.338(3, 8) 2.429(3, 12)	3.518(3) ^d 92.8(1) 87.2(1)	Br, Br	96.5(1, 1.3) 148.(1, 7)	428
[Cu(ae)Br] ₂ ·0.3HBr (blue)	m P2 ₁ /n 2	6.1707(6) 13.045(2) 12.719(1)	102.237(6)	CuBr ₄ N ₂ O	N O μ Br	1.971(3, 20) 1.912(3) 2.469(1) 2.956(1)	3.5445(7) 81.04(2) 98.96(2)	N,N N,O Br,N	85.0(1) ^e 94.7(1) ^f 175.2(2) 83.0(1) 103.2(1)	429
(Pr ₂ NH ₄) ₂ [Cu Br ₃] ₂ (green)	tr P-1 1	9.612(2) 9.602(2) 12.006(3)	102.27(2) 104.30(2) 112.79(1)	CuBr ₄	Br μ Br	2.337(2, 4) 2.444(2, 4)	3.554(2) 93.3(1) 86.7(1)	Br,O Br, Br	92.4(1) 97.3(1, 1.8) 146.4(1, 1.2)	428
[Cu(Me ₂ em)Br ₂] ₂ (not given)	or Pbca 4	9.990(5) 8.795(3) 20.828(1)		CuBr ₃ N ₂	N Br μ Br	2.031(6, 39) 2.401(1) 2.463(2) 2.868(2)	3.570(3) 83.71(5) 96.29(5)	N,N N, Br Br, Br	84.6(2) ^e 91.5(2, 4.3) 169.6(2, 3.4) 94.4(4, 1.8)	388
[Cu(MeSbpy)Br ₂] ₂ (not given)	tr P-1 2	9.040(1) 13.100(2) 15.455(2)	120.26(1) 92.80(1) 111.31(1)	CuBr ₃ NS	Br S N μ Br	2.356(3) 2.353(5) 2.04(2) 2.412(3) 2.965(4)	3.591(4) 84.5(1, 1.5) 86.2(1, 1.4)	Br, Br Br, Br	93.3(1, 6) 103.4(1) 125.3(1) 90.2(2, 7.6) 142.1(2)	430
[Cu(bdd)Br ₂] ₂ (not given)	tr P-1 2	7.759(1) 8.594(1) 8.273(1)	71.56(1) 69.08(1) 101.20(1)	CuBr ₃ N ₂	Br N μ Br	2.372(1) 2.004(8, 10) 2.387(1) 2.883(1)	3.599(1) 85.94(4) 94.41(4)	S,N N,N Br, Br	85.2(5, 1) ^e 76.3(4) ^c 96.60(4, 25)	431
(dbztsH) ₂ [CuBr ₃] ₂ (dark red)	tr P-1 1	9.982(1) 12.122(1) 7.893(1)	83.70(1) 112.80(1) 104.97(1)	CuBr ₄	Br μ Br	2.425(1, 9) 2.363(1, 6)	3.603(1) ^d 95.98(3) 84.02(3)	Br, Br	93.37(3, 2.60) 174.02(4, 76)	432

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å] Cu-L-Cu [°] μ L-Cu- μ L [°]	L-Cu-L [°]	Ref.
[Cu(4-Meox)Br ₂] ₂ (green)	m P2 ₁ /n 2	8.546(4) 13.062(5) 11.049(6)	96.88(4)	CuBr ₃ N ₂	Br N μ Br	3.626(1) 87.00(3) 93.00(3)	109.85(3) 157.15(4) 90.(2,3,4) 172.7(3)	433
[Cu(terpy)Br ₂ (PF ₆) (blue)	m P2 ₁ /a 4	20.40(2) 13.35(2) 6.453(8)	97.74(9)	CuN ₃ Br ₂	N μ Br	3.64(4) 89(0) 91(0)	81(1,1) ^c 97(1,6) 174(1)	434
(bpyH)[CuBr ₂] ₂ (black)	tr P-1 1	4.1018(5) 10.275(1) 11.0355(9)	113.89(7) 94.975(8) 95.935(9)	CuBr ₄	Br μ Br	3.653(1) 96.28(2) 83.72(2)	91.99(3,2,45) 173.14(3,46)	435
[Cu(tmsio) ₂ Br ₂] ₂ (green)	m P2 ₁ /c 2	9.578(3) 14.896(6) 9.727(4)	94.51(3)	CuBr ₃ O ₂	Br O μ Br	3.714 85.5(1) 94.5(1)	94.5(1) 132.5(1,6,6) 89.8(2) 169.9(3)	436
[Cu(phed)Br ₂] ₂ (not given)	m P2 ₁ /c 2	7.830(2) 16.846(4) 12.311(3)	102.19(2)	CuBr ₃ N ₂	Br N μ Br	3.737(2) not given 101.9(0)	96.(0,1,1) 78.7(2,4,5) 92.9(1,3) 169.4(1,5) 76.8(2) ^c	437
[Cu(eyehol) ₂ Br ₂] ₂ (brown)	m P2 ₁ /n 4	15.215(2) 8.088(3) 15.885(2)	106.07(1)	CuBr ₃ O ₂	O Br μ Br	3.766(2) 90.17(4) 89.83(4)	78.5(2) ^c 93.1(1,3,0) 165.6(1,4,0) 96.3(1,6,5)	405
[Cu(dien)Br ₂ (ClO ₄) ₂] (blue)	m C2/c 8	23.054(8) 7.669(1) 14.061(9)	116.02(3)	CuN ₃ Br ₂	N μ Br	3.790(1) not given 89.37(2)	85.2(2,1,2) ^c 160.6(2) 95.0(1,9) 178.8(1)	438
[Cu(maepy)Br ₂] ₂ (green)	tr P-1 1	9.545(3) 7.015(2) 9.221(3)	76.13(2) 76.49(2) 102.12(3)	CuBr ₃ N ₂	Br N μ Br	3.803(4) 92.14(9) 87.86(9)	93.95(8) 122.21(9) 91.8(1,5,3) 141.6(1) 172.8(2) 83.9(2) ^c	439

[Cu(3-ampy)Br ₃] ₂ ·H ₂ O (dark violet)	m C2/c 4	19.096(5) 6.729(1) 19.499(5)	126.89(1)	CuBr ₄ N	N Br μBr	2.070(8) 2.413(2, 1) 2.451(2) 2.791(2)	3.8205(1) 93.4(1) 86.6(1)	Br, Br	91.7(1, 5) 110.0(1, 8) 139.9(1) 89.5(3, 3, 0) 174.7(2)	377
[Cu(dpy)Br ₃] ₂ (dark green)	m P2 ₁ /n 2	8.988(8) 13.933(8) 9.795(6)	98.54(4)	CuBr ₃ N ₂	N Br μBr	2.022(5, 6) 2.391(1) 2.488(1) 2.804(1)	3.869(1) not given 86.2(2)	Br, Br Br, N	101.7(3, 7, 6) 92.5(1, 3, 8) 154.8(1) 176.5(1) 86.0(2) ^f	440
[Cu(4-Meth) ₂ Br ₂] ₂ (green)	tr P-1 1	8.669(4) 10.985(4) 7.495(3)	97.98(3) 104.65(3) 71.55(4)	CuBr ₃ N ₂	Br N μBr	2.420(1) 1.984(5, 6) 2.492(1) 3.033(1)	4.063(2) 94.16(3) 11.98(3)	Br, Br Br, N N, N	93.91(3, 8, 07) 91.6(2, 4, 8) 169.2(2)	441
[Cu(Me ₄ en)Br ₂] ₂ (not given)	m P2 ₁ /c 4	8.404(2) 11.363(2) 11.700(3)	102.34(2)	CuBr ₃ N ₂	Br N μBr	2.41(0) 2.09(2, 1) 2.42(0) 3.20(0)	4.20 not given 84.4(5)	N, N N, Br	85.4(7) ^s 92.6(4, 4) 165.8(5, 7, 5) 91.4(5, 1, 5) 104.4(5)	442
G: Cu(μ-I) ₂ Cu	m A2/a 8	25.620(6) 7.495(2) 20.314(4)	111.60(1)	CuN ₃ I ₂	N μI	2.07(2, 1) 2.686(4, 1)	3.364(5) 77.6(1) 102.4(1)	I, N N, N	108.1(6, 5, 3) 120.6(8)	443
H: Cu(μ-OL)(μ-NL) ₂ Cu	trg P4 ₂ /mnm 2	9.5(2) — 13.94(3)		CuN ₃ O	N μHO μN ₃	1.18(4, 1) 1.915 2.015	2.988(3) HO 102.5 N ₃ 95.7	not given		444a
[Cu ₂ (Me ₄ en) ₂ (N ₃ (OH))(ClO ₄) ₂] (dark blue)	or Fddd 8	14.979(8) 26.247(1) 18.905(1)		CuO ₂ N ₂ S	O ₃ ClO S N μO μN ₃	2.466(9) 2.330(3) 1.922(8) 2.005(6) 1.919(7)	3.036(1) O 98.4(4) N 104.6(5) 78.5(3)	O, S S, N	93.4(4, 2, 9) 91.8(2) ^f 162.8(1) 87.2(3) 97.2(4, 7) 174.2(3)	444b
Cu ₂ (bzsmph)(μ-N ₃)(NO ₃) ₂ (not given)	or Pbcn 4	12.605(6) 14.024(7) 17.003(9)		CuO ₂ N ₂ S	O ₂ NO S N	2.172(7) 2.325(2) 1.918(7)	3.131(3) O 106.4(4) N 100.7(5)	N, N S, O S, N	97.9(3) 98.4(2, 6, 5) ^f 90.7(2) ^f 146.3(1)	206

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	<i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]			α [°] β [°] γ [°]			Chromophore	Cu-L [Å]	Cu-Cu [Å] Cu-L-Cu [°] μ L-Cu- μ L [°]		L-Cu-L [°]	Ref.
		<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]	α [°]	β [°]	γ [°]			Cu-Cu [Å]	Cu-L-Cu [°]		
[Cu ₂ (C ₁₆ H ₁₈ N ₆ O)(NO)](PF ₆) ₂ CH ₂ Cl ₂ (not given)	m P2 ₁ /n 2	11.924(2) 11.352(3) 18.347(4)			108.45(2)			CuN ₄ O	μ O μ N ₃ N 2.019(10, 60) 2.189(8) 1.935(6) μ N 2.036(10)	76.7(3) 3.140(1) O 108.5(5) N 75.1(2)	O,O O,N N,N O,N O,N N,N 113.2(3) 151.3(2)	91.4(2) 101.5(2, 5.5) 171.2(2) 96.6(3) 95.9(3, 1.5) ^f 159.5(3) 94.2(4, 7.6) ^f 94.7(3, 1.3) ^f 160.3(4, 1.4) 94.3(4, 4.4) ^f 103.0(4, 3.8) 155.6(5, 1)	445
[Cu ₂ (pea)(N ₃)](PF ₆) ₂ (not given)	tr P-1 2	9.583(1) 10.123(2) 23.738(4)			87.19(1) 88.83(1) 84.85(1)			CuN ₄ O	N μ O μ N ₃ 2.023(10, 38) 2.173(10, 32) 1.970(8, 6) 2.026(12, 2)	3.185(3) O 107(3) N 103.6(5) 74.2(4, 2)	O,N O,N N,N	94.7(3, 1.3) ^f 160.3(4, 1.4) 94.3(4, 4.4) ^f 103.0(4, 3.8) 155.6(5, 1)	446
I:Cu(μ -OL)(μ -Cl)Cu [Cu(pntphpy)(OH)Cl ₃] (yellow green)	m P2 ₁ /m 2	7.6949(1) 16.434(2) 7.9231(1)			107.974(9)			CuN ₂ Cl ₂ O	Cl N μ O μ Cl 2.288(1) 2.524(2) 1.946(1) 2.555(1)	3.022(1) O 101.8(2) Cl 72.5(1)	Cl,N N,N Cl,Cl N,O Cl,O	94.1(1) 160.2(1) 79.4(1) 107.7(1) 89.2(1) 90.8(1)	447a
[Cu ₂ (pyimcres)Cl ₃] \cdot 2H ₂ O (green)	tr P-1 2	11.247(3) 9.300(3) 12.291(2)			90.19(2) 104.73(2) 103.17(2)			CuN ₂ Cl ₂ O	Cl N μ O μ Cl 2.323(2) 2.524(2) 1.97(5, 43) 1.983(4, 5) 2.309(2) 2.017(5)	3.167(2) Cl 86.87(6) O 105.8(2) 83.2(1)	Cl,O Cl,N Cl,N O,N N,N Cl,Cl	91.4(1, 8.2) 104.6(1) 95.5(1, 2.2) 159.3(2) 92.4(2) ^f 164.7(2) 82.8(2) ^f 101.95(8)	447b
[Cu ₂ (sbzph)Cl ₃] \cdot MeOH (not given)	or Pna2 ₁ 4	15.801(5) 23.15(1) 8.190(3)						CuCl ₂ ONS	Cl S N 2.350(-, 25) 2.424(-, 36) 1.978(-, 6)	3.2365 ^d O 113.3 Cl 86.1	N,N Cl,Cl	not given	448

[Cu ₂ (bzsmph)Cl] \cdot Cl ₂ (not given)	or Pna ₂₁ 4	15.801(5) 23.15(1) 8.190(3)	CuCl ₂ ONS	μ O 1.949(-, 4) μ Cl 2.385(-, 0) Cl 2.347(2, 25) S 2.424(3, 38) N 1.980(7, 8) μ O 2.384(2, 2) μ Cl 1.948(4, 7)	80.0(-, 1) 3.255(1) Cl 86.1(0) O 113.4(2) 79.95(1, 15)	Cl ₂ Cl Cl ₂ S Cl ₂ N Cl ₂ O S ₂ O S ₂ N O ₂ N O ₂ N	116.3(1, 7.5) 107.0(1, 4.2) 135.6(0, 3.3) 97.0(2, 5.6) 92.2(1, 6) 89.5(1, 7) ^f 88.0(2, 1.6) ^f 166.6(2, 9)	206
[Cu ₂ (hem)Cl](BPh ₄) ₂ Me ₂ CO (green)	tr P-1 2	10.986(3) 15.138(3) 23.292(3)	CuN ₃ OCl	N 2.019(9, 55) 2.155(11, 3) μ O 1.976(7, 11) μ Cl 2.316(3, 0)	3.265(10) O 111.4(3) Cl 89.6(1) 79.5(2, 2)	O ₂ N O ₂ N Cl ₂ N Cl ₂ N	92.8(4, 1.9) ^f 88.5(2, 4) 103.7(3, 1.1) 158.2(4, 2.2) 96(4, 4.0) ^f	278
[Cu ₂ (amsoph)Cl ₃] (black)	m P _{21/c} 4	11.657(3) 19.647(5) 8.845(2)	CuCl ₂ ONS	Cl 2.276(2, 26) N 1.992(6, 2) O 1.925(4) S 2.355(3, 3) μ Cl 2.323(2) 2.735(2)	3.311(1) O 102.6(2) Cl 81.3(1) 88.8(1)	Cl ₂ Cl O ₂ S O ₂ Cl N ₂ S N ₂ Cl N ₂ O Cl ₂ S	93.7(1, 8) 92.0(1, 2.0) ^f 94.3(1, 8.0) 84.7(2, 1.9) ^c 90(2, 5.8) 163.6(2) 95.7(2) 166.3(2) 132.5(1, 2.1) 179.4(1)	449
J-Cu(μ -OL)(μ -Br) ₂ Cu [Cu ₂ (pmp)Br] ₂ Br ₂ (brown)	tr P-1 2	7.601(7) 11.456(4) 13.266(8)	CuN ₂ Br ₂ O	Br 2.413(2) μ Br 2.426(2) 2.707(2) N 1.977(8, 40) μ O 1.970(6, 25)	3.151(2) Br 75.50(4) O 106.2(3) 83.(2, 3.3)	Br ₂ Br Br ₂ O Br ₂ N O ₂ N	96.5(5, 10) 90.8(2, 3.8) 107.9(2) 93.2(2, 6.4) 102.8(2, 1.3) 131.7(3, 2.5) 175.5(2) 90.0(3, 2) ^f 146.5(3) 163.0(3) 82.0(3, 6) ^f	203
[Cu ₂ (C ₁₇ H ₂₂ N ₄ O)Br] ₂ Br ₂ (dark olive)	or Pbca 8	11.836(2) 16.543(4) 23.021(5)	CuN ₃ Br ₂ O	Br 2.677(3) 2.889(3) N 2.014(14, 52)	3.245 ^d not given 75.6(3)	Br ₂ Br Br ₂ O Br ₂ N	96.06(9, 5.29) 94.1(3, 8.7) 96.1(4, 5.8)	192

TABLE II (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]			Chromophore	Cu-L [Å]	Cu-Cu [Å] Cu-L-Cu [°] μ L-Cu- μ L [°]			L-Cu-L [°]	Ref.
		α [°]	β [°]	γ [°]			Cu-Cu	Cu-L-Cu	μ L-Cu- μ L		
[Cu ₂ (hem)Br](PF ₆) ₂ ·0.5CH ₂ Cl ₂ (green)	m C2/c 4	15.740(4) 32.033(4) 13.033(4)	134.03(2)	CuN ₃ OBr	N μ hemO μ Br	2.417(3, 1) 1.972(10, 16)	3.347(92)	O 114.6(13) Br 84.8(3) 80.3(7)	N,N O,N O,N Br,N	116.4(1) 160.0(4, 7.9) 87.8(5, 1.0) ^f 169.8(5) 85.4(6) ^g	278

^a When more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean. ^b The chemical identity of the coordinated atom or ligand is specified in these columns. ^c Five-membered metallocyclic ring. ^d The Cu-Cu distance was calculated by us. ^e There are two crystallographically independent molecules. ^f Six-membered metallocyclic ring. ^g There are four crystallographically independent molecules. ^h Seven-membered metallocyclic ring. ⁱ Four-membered metallocyclic ring.

distance of 2.499(1) Å is again shorter than those found for the CuO₅ and CuO₄N chromophore type (Table IA,B). In the latter a square pyramidal arrangement about each Cu(II) atom is build up by four 3-ethyl-2-pyridonate anions and an apical position is occupied by dmf molecule. The copper–copper distance between two CuO₃N₂ chromophores type is 2.550(1) Å.

In another several species^{138–142} two Cu(II) atoms are held together by four bidentate N-donor; ligands in a syn–syn arrangement forming a plane about each Cu(II) atom with water,^{139,140} dimethylformamide¹³⁸ or chlorine atom^{141,142} in an apical position. The mean Cu–N_{eq} bond distance is 2.018 Å, Cu–O_{ap} 2.215 Å and Cu–Cl_{ap} 2.429(6) Å.

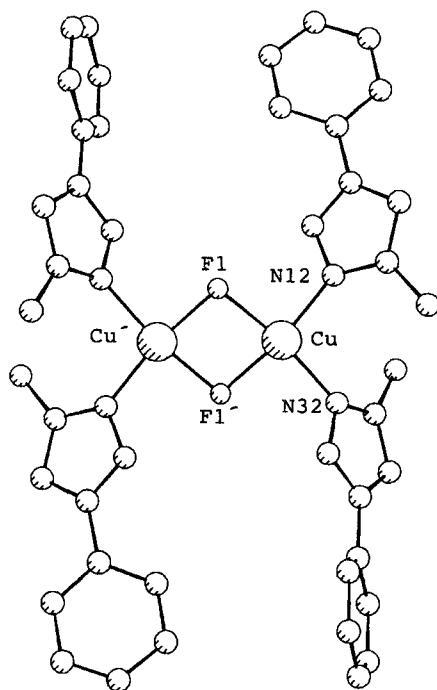
In blue–green Cu₂(fluf)₄(H₂O)(cof)¹⁴³ (Table IF) two Cu(II) atoms are held together by four flufenamate anions in syn–syn arrangements and form an identical equatorial plane about each Cu(II) atom. On the other hand, the apical positions differ; in one Cu(II) is occupied by water (Cu–OH₂ = 2.141(5) Å) and in another by coffeine (Cu–N = 2.239(5) Å). The deviations of the Cu(II) atom from the basal plane O₄ is also different by 0.189 Å toward the water and by 0.223 Å toward to the coffeine.

There are several species^{20,24,30,31,56,91,97,127} which contain two crystallographically independent molecules, differing mostly by degree of distortion. The coexistence of two or more species, within the same crystal, differing only by degree of distortion, is typical of the general class of distortion isomerism.¹⁴⁴

2.2 Doubly-Bridged Cu(II) Dimers

2.2.1 By Two Single Atom Bridges

Crystallographic and structural data for over three hundred and sixty doubly bridged Cu(II) dimers are gathered in Table II. The structures are tabulated in the order of increasing covalent radii of a bridging atoms and of increasing distance between the two Cu(II) atoms. Structure of blue [Cu(μ-F)(3-Mephpz)₂]₂(BF₄)₂¹⁴⁶ is shown in Figure 2 for example. Each Cu(II) atom is coordinated by two fluorine ions (bridging) and two Mephpz ligands. The mean Cu–F (bridge) bond distance is 1.923(3) Å and Cu–F–Cu bridge angle is 98.9(8)°. Each Cu(II) atom has a square-planar arrangement (CuF₂N₂). The dimeric system seems to be further stabilized by hydrogen bonding of the N–H groups to the fluorine ions. The BF₄[–] ions coordinate weakly to the Cu(II) atoms [Cu–F 2.531(5) and 2.693(2) Å]. This coordination may be designated as “semi-coordination”. There are six blue

FIGURE 2 Structure of $[\text{Cu}(\mu\text{-F})(3\text{-Mephpz})_2]_2^{2+}$ (see Ref. 146).TABLE IIK Summary of Cu- μL , Cu-L and Cu-Cu distances [\AA] for doubly bridged compounds^a

<i>L</i>	Cov. rad. of <i>L</i> [\AA]	Cu- μL	Cu-L	Cu-Cu
F	0.72	1.86–2.96(2.10)		2.893–3.444
OL	0.73	1.76–2.62(2.015)	1.90–2.99(2.26)	2.830–3.737
NL	0.75	1.92–2.54(2.06)	1.79–2.33(2.01)	3.042–3.730
Cl	0.99	2.23–3.20(2.45)	2.11–2.78(2.26)	3.011–4.089
SL	1.02	2.27–2.66(2.465)	2.29–2.70(2.49)	2.656–3.588
Br	1.14	2.35–3.20(2.62)	2.24–2.74(2.40)	3.518–4.20
I	1.33	2.68	2.55–3.03(2.77)	3.364

^aThe mean values are given in parenthesis.

examples^{145–149} in which the bridging involves two fluorine atoms. In each complex cation both Cu(II) atoms are identically coordinated. For example, in $[\text{Cu}(\mu\text{-F})(3\text{-Mephpz})_2]_2^{2+}$ (see Ref. 146) a distorted square planar environment containing two *cis*-pairs atoms, nitrogen and fluorine is shown. In another four examples^{145,147,148} a trigonal-bipyramidal environment containing two fluorine atoms with one nitrogen in a plane and two apical

positions are occupied by another two nitrogen donor ligands. In the remaining complex cation, $[\text{Cu}(\mu\text{-F})(\text{tmpa})]_2^+$ (see Ref. 149) a *pseudo*-octahedral coordination about each Cu(II) atom is built up by one tetradentate N-macrocyclic ligand and by two fluorines with the chromophore CuN_4F_2 . The Cu–Cu distance in this series range from 2.893(4) Å¹⁴⁵ to 3.444(1) Å.¹⁴⁹ There are relationships between the Cu–Cu distances, the Cu–F–Cu angles and the μF –Cu– μF angles. The first increases as the second opens and the third closes, for example: 2.893(4) Å, 91.1° and 88.9(3)°,¹⁴⁵ 2.9962(9) Å, 93.73(8)° and 86.27(8)°,¹⁴⁷ 3.014(8) Å, 94.59(7)° and 85.41(7)°,¹⁴⁷ 3.131(1) Å, 97.19(8)° and 82.81(8)°.¹⁴⁸

There are over two hundred and twenty derivatives in which two O-donor; ligands, serve as bridges between two Cu(II) atoms.^{150–336} Mostly are green and blue of color, but there are also violet, purple, yellow, brown and even black. By far prevail examples, in which both Cu(II) atoms are identically coordinated; four-coordinated,^{159,160,162,163,167,172,176,181,184,185,189–191,194,197,199,201,205,207–210,212,213,215,218,222,223,228–231,233,236–238,241–246,251,253,254,260,262,263,265,272–275,284,286–288,310,321} five-coordinated,^{150,151,154–158,161,164–166,168,169,171,173,179,180,183,186–188,193,195,198,200,204,206,211,214,216,217,219–221,224–227,232,235,239,240,247–249,252,255–259,261,264,266–270,273,276–281,283,289–302,304,305,307–310,312,314,315,317–320,323–333,336} six-coordinated^{152,153,170,174,175,250,282,303,306,311,313,316,322,334} and even seven-coordinated.³³⁵ There are examples, which contain two non-equivalent Cu(II) atoms; one four- and the other five-coordinated,^{163,172,178,182,192,196,265,185} one five- and the other six-coordinated,^{203,271} one four- and the other six-coordinated.^{222,234,244} There are examples^{212,265} which contain two different chromophores, CuO_2N_2 and CuO_2Cl_2 in the same dimer unit. Two crystallographically independent molecules within the same crystal have been found in several species^{154,195,222,234,301,327} and four such molecules are present in $[\text{Cu}_2(\mu\text{-hepra})\text{Cl}]_2$.¹⁶⁴ All these differ mostly by degree of distortion and are examples of distortion isomerism.¹⁴⁴

The Cu–Cu distance in the series of doubly O-bridged derivatives, range from 2.830(2) Å¹⁵⁰ to 3.737 Å.³³⁶ There is a cooperative effect between the Cu–Cu distance, the Cu–O–Cu and μO –Cu– μO angles. The Cu–Cu distance elongated with an opening of the Cu–O–Cu angle and at same time the μO –Cu– μO angle is closed (Table II).

There are eleven examples^{337–348} in which two N-donor; ligands serve as a bridge. In two four-coordinated Cu(II) atoms two azide groups are doubly bridged.^{337,339} In another six examples^{338,340,342–347} there are two penta-coordinated Cu(II) atoms and in the remaining three derivatives^{341,346,348} two hexacoordinated Cu(II) atoms are present. The Cu–Cu distance in this

series range from 3.042(3) Å³³³ to 3.730(3) Å.³⁴⁸ The Cu–N–Cu and μ N–Cu– μ N angles range from 83.5 to 103.7° and from 76 to 94°, respectively.

There are almost eighty examples (Table II) in which two tetra-coordinated,^{349–363,366,368–370,372,373,375,379,387,407,418} two pentacoordinated,^{300,317,364,367,371,374,376,377,380,383–386,388–390,392–397,399–406,408–417,419,423} or two hexacoordinated Cu(II) atoms are doubly bridged by two chlorine atoms. There are examples which contain two non-equivalent Cu(II) atoms, CuCl₄ with CuCl₃O^{350,369} and CuN₃Cl₂ with CuCl₃N₂.³⁶⁴ Green [Cu(N₃bz)₂Cl₂]₂·H₂O,³⁸⁶ contains two crystallographically independent molecules, differing mostly by degree of distortion. The Cu–Cu distance ranges from 3.011(2) Å³⁴⁹ to 4.089(4) Å.⁴²³ The Cu–Cu distances and Cu–Cl–Cu and μ Cl–Cu– μ Cl are independent.

There is an example, [Cu(C₁₄H₁₆N₂OS)]₂⁴²⁴ in which two tetra-coordinated Cu(II) atoms are doubly bridged by two sulfur donor ligands, and the remaining two positions are occupied by O and N donor atoms of the same macrocyclic ligands. The Cu–Cu distance of 2.656(2) Å is the shortest found in the series of doubly-bridged Cu(II) dimers. In another three derivatives^{425–427} two bridging sulfur donor ligands bring the Cu(II) atoms within 3.049(3) Å,⁴²⁵ 3.451(2) Å⁴²⁶ and 3.588(1) Å.⁴²⁷

When two bromine atoms serve as a bridge between two Cu(II) atoms,^{377,388,405,428–442} the Cu–Cu distance ranges from 3.518(3) to 4.20 Å which ruled out metal–metal bond.

Two iodine atoms which held together two tetrahedrally coordinated Cu(II) atoms in yellow [Cu(qu)₂I]₂⁴⁴³ bring the Cu(II) atoms within 3.364(5) Å with Cu–I–Cu angles of 77.6(1)°.

There are twelve derivatives in which pairs of pentacoordinated Cu(II) atoms are doubly bridged by two heteroligands, oxygen and nitrogen,^{206,444–446} oxygen and chlorine,^{206,278,447–449} and oxygen and bromine.^{192,203,271} The Cu–Cu separations ranging from 3.036(1) to 3.185(3) Å in the first series, from 3.167(2) to 3.311(1) Å, in the second series, and from 3.151(2) to 3.3473(92) Å in the third one. These separations ruled out metal–metal bond. The mean Cu–L–Cu bond angle opens with a decreasing covalent radius of the L (in the parenthesis) in the order: 75.2° (L = Br, 1.14 Å) < 86.0° (Cl, 0.99 Å) < 103.0° (N, 0.75 Å) < 108.0° (O, 0.73 Å).


Inspection of the data in Table II reveals that the ligands involved are mono- through heptadentate, the most common being the O- and N-donor ligands. The mean Cu–L bond distance in the series of monodentate ligands increases in the sequence: 2.01 Å (NL) < 2.26 Å (OL) < 2.265 Å (Cl) < 2.40 Å (Br) < 2.77 Å (I). The multidentate ligands include both

homo- and hetero-donor atoms, with O- and N-donors being by far the most common. The Cu–L bond distances for the homo-bidentate ligands increase in the order: 2.03 Å (NL) < 2.13 Å (OL) < 2.41 Å (SL). Noticeable, in the series of hetero-bidentate ligands (O plus N, O plus S, N plus S, and O plus Cl), O donor atoms “prefer” only bridge positions with the mean Cu–L bond distances which increase in order: 1.97 Å (μ -OL) < 2.015 Å (NL) < 2.34 Å (SL) < 2.98 Å (Cl). Tridentate ligands include those with two O plus one N, one O plus N, two N plus S; O plus N plus S, three O, and those with three N-donor; sites. The mean Cu–L bond distances homo- vs. hetero-tridentate ligands are: 1.95 vs. 1.97 Å (μ -OL), 1.91 vs. 2.02 Å (OL), 2.06 vs. 2.02 Å (NL), and 2.32 Å (SL). The tetradentate are either three O plus N, one O plus three N, two O plus two N, and those with four N-donor; sites, with the mean Cu–L bond distances of 2.02 Å (OL), 2.11 Å (μ -OL), 2.04 Å (N-heteroL) and 2.15 Å (N-homoL). Pentadentate ligands include one O plus four N, and one O plus two N plus two S-donor sites, with the mean Cu–L bond distance of 1.96 Å (μ -OL), 1.99 Å (NL) < 2.36 Å (SL). The hexadentate ligand contains four O plus two N-donor; sites. The heptadentates are either one O plus six N, and one O plus N plus four S-donor sites. The effects of both electronic and steric factors are observed in the values of the L–Cu–L bond angles of the metallocyclic rings. In four-membered rings the mean L–Cu–L intra-ligand angles range from 52.7 to 56.7° (mean 55.0°, O-donor;) and 76.5 and 77.2° (S-donor). For the five-membered rings the values are: from 77.4 to 84.0° (mean 81.5°, O-donor;), 76.0 to 90° (mean 83.2°, N-donor;), 82.2 to 89.0° (mean 87.3°, S-donor), 74.1 to 96.2° (mean 83.5°, O + N-donor;), 84.0 to 85.8° (mean 85.0°, O + S-donor), and 83.2 to 88.2° (mean 85.0°, N + S-donor). For six-membered rings, the values are from 77 to 95° (mean 90.5°, O-donor;), 84 to 100.3° (mean 94.5°, N-donor;), 84.5 to 100° (mean 93.5°, O + N-donor;), 89.5 to 98.5° (mean 93.8°, O + S-donor) and 88 to 93.2° (mean 91.5°, N + S-donor).

Noticeable, at the same Cu–Cu distance, the mean Cu–L–Cu bond angles are closed and μ L–Cu– μ L bond angles are open with an increased covalent radius of L. For example: 3.0141(8) Å, 94.59(7) and 85.41(7)° (L = F, 0.72 Å),¹⁴⁷ 3.011(3) Å, 91.1(6) and 88.9(6)° (O, 0.73 Å),²²² 3.011(2) Å, 80.6(2) and 99.6(2)° (Cl, 0.99 Å),³⁴⁹ 3.049(3) Å, 75.9(1) and 104.1(1)° (S, 1.02 Å);⁴²⁵ 3.557(4) Å, 104.8(1) and 75.2(1)° (O, 0.73 Å),³³³ 3.558(1) Å, 89.8 and 90.2° (N, 0.75 Å),⁴⁰⁰ 3.5445(7) Å, 81.04(2) and 98.96(2)° (Br, 1.14 Å).⁴²⁹

Summaries of the Cu– μ L, Cu–L and Cu–Cu distances for doubly-bridged Cu(II) dimers are presented in Table IIK.

TABLE III Crystallographic and structural data for unsymmetrically doubly bridged copper(II) dimers^a

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]			α [°] β [°] γ [°]			Chromophore	Cu-L [Å]	Cu-Cu [Å] Cu-L-Cu [°]		L-Cu-L [°]	Ref.
		a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]			Cu-Cu [Å]	Cu-L-Cu [°]		
A:  Cu	tr P-1 2	7.8064(11)	12.9137(14)	14.8564(14)	69.857(8)	80.074(10)	83.659(11)	CuO ₃ N ₂	1.999(7) 2.489(7) N 1.985(7, 8) μ HO 1.880(6)	3.156(2) 113.7(3)	O,N ^b 104.0(3) 165.7(3, 6.4) O,O 55.6(3) ^c N,N 89.6(3) ^d O,N 93.7(3, 8.2) 155.8(3) 176.9(3) O,O 54.3(3) ^c 85.7(3, 6.4) 117.0(3) 167.6(3) 89.2(3) ^d	450	
		[Cu ₂ (μ -OH)(μ -papfs)(NO ₃) ₂ · (H ₂ O)]NO ₃ (bluish green)	CuO ₄ N ₂	(NO ₃)O 2.056(6) 2.560(7) H ₂ O 2.565(9) N 1.955(7) 2.012(7) μ HO 1.889(6)									
[Cu ₂ (μ -sb)(μ -2-Opy)] (green)	m P2 ₁ /n 4	23.808(7)	8.353(2)	9.548(4)	92.57(3)			CuO ₂ N ₂	sbO 1.908(9) sbN 1.937(9) 2-OpyN 2.002(9) sb μ O 1.948(7)	3.249(2) 113.2(4)	O,O 168.1(4) N,O 86.2(3) ^c 91.1(4, 7) 93.8(4) ^d N,N 169.4(4)	451	
	CuO ₃ N	2-OpyO 1.939(7) sbO 1.908(8) sbN 1.935(9) sb μ O 1.944(7)									O,O 90.3(3, 2.9) 177.9(3) N,O 85.9(3) ^c 93.8(4) ^d 173.1(4)		

[Cu ₂ (μ-phtN ₆)(μ-OH)(H ₂ O) ₂] (ClO ₄) ₂ ·H ₂ O (brown)	m P2 ₁ /n 4	8.011(2) 24.100(5) 15.675(2)	100.24(2)	CuN ₃ O ₂	N 1.941(8, 44) 1.987(8, 48) H ₂ O 2.385(8, 68) μHO 1.925(6, 25)	3.296(2) 117.8(3)	O ₁ N 96.8(4, 8, 56) 166.1(3, 4) 79.3(3, 1, 9) ^f 157.8(3, 1, 1) O ₁ O 91.5(4, 3, 5)	452									
									[Cu ₂ (μ-L-Et)(μ-NO ₂)](ClO ₄) ₂ (green)	m P2 ₁ /n 4	14.229(3) 22.683(6) 15.913(4)	98.92(2)	CuN ₄ O	O ₂ N 1.96(1) N 2.07(1, 1) μO 1.87(1)	3.325(2) 127.1(5)	O ₁ N 83.6(4) ^f 86.2(5) 123.6(5, 2) 82.3(4, 1, 2) 105.1(5, 3, 0) 169.6(5)	453
[Cu ₂ (μ-sdap)(μ-pz)]·H ₂ O (purple)	or Pbcn 8	14.983(2) 8.276(5) 31.163(4)	3.359(4) 125.1(7)	N ₁ O 83.3(6, 3) ^f 95.0(6, 3) ^d 94.8(6, 1, 1) 174.5(7, 1, 9) N ₁ N 169.5(7, 5)	455												
						[Cu ₂ (μ-sdb)(μ-pz)] (purple)	m P2 ₁ /c 4	11.813(6) 18.049(6) 9.680(4)	105.67(4)	CuO ₂ N ₂	pzN 1.946 O 1.900 N 1.960 μO 1.914	3.360 121.8	O ₁ N 90.1(-, 3, 4) ^d O ₁ O 90.9(-, 2, 6) 173.1(-, 7) N ₁ N 169.8(8, 1, 8)	456			

TABLE III (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	$Cu-L$ [Å]	$Cu-L-Cu$ [Å] $Cu-L-Cu$ [°]	$L-Cu-L$ [°]	Ref.
$[Cu_2(\mu-dpp)(\mu-OH)(NO_3)Cl_2]$	tr	14.500(3)	84.8(1)	CuO_2N_2Cl	N 2.014(11,26)	3.361(4)	Cl,O 92.3(6,2.4)	457
$[Cu_2(\mu-dpp)(\mu-OH)(NO_3)Cl_2] \cdot 1.5H_2O$ (green)	P-1 2	13.049(3) 10.874(2)	110.1(1) 110.5(1)		Cl 2.211(4) O_2NO 2.72(4) μHO 1.893(1)	124.0(5)	Cl,N 100.2(3) 175.4(4) O,N 70.0(7) 89.5(8,5.8) 164.0(4)	
							O,O 94.5(8,1.3) N,N 77.6(4) ^e	
				CuO_2N_2Cl	N 1.984(10,11) Cl 2.230(4) H_2O 2.343(13) μHO 1.914(9)		Cl,O 99.7(3,4.1) Cl,N 98.3(3) 173.4(4) O,N 86.3(5,4.0) 162.0(4) O,O 97.6(4) N,N 78.8(4) ^e	
$[Cu_2(\mu-dpp)(\mu-OH)(H_2O)Cl_3]$ (greenish blue)	tr P-1 2	10.240(7) 11.245(9) 8.521(6)	90.0(1) 114.1(1) 102.3(1)	CuO_2N_2Cl	N 2.006(7,6) Cl 2.196(3) H_2O 2.359(8) μHO 1.887(7)	3.376 not given	O,Cl 94.9(2) 103.3(2) O,N 90.6(3,5.8) 163.6(3) N,N 78.8(3) ^e N,Cl 99.0(2) 167.0(2) O,O 88.8(3) O,Cl 94.5(2,1.2) O,N 85.4(3) 162.4(3) N,N 78.3(3) ^e N,Cl 88.8(2,1) 100.1(2) 162.3(2) Cl,Cl 109.0(1)	458

[Cu ₂ (μ-ppdme)(μ-OH)Cl ₂] [CuCl _{1.5} (H ₂ O)]·H ₂ O ^e (deep green)	m Am 2	7.4942(4) 20.418(1) 7.5091(5)	90.93(1)	CuN ₂ OCl	N Cl μHO	2.003(7) 2.229(2) 1.898(4) 2.006(6)	3.384(2) 126.0(5)	O,N N,N N,Cl Cl,O	85.6(3) 164.4(3) 78.8(3) ^e 103.1(2) 172.3(2) 92.4(2)	459
[Cu ₂ (μ-ibpd)(H ₂ O)](ClO ₄) ₂ (violet)	m P ₂ _{1/c} 4	11.909(4) 13.084(3) 15.909(2)	95.4(2)	CuCl _{1.5} O (monomer) CuN ₄ O	H ₂ O N H ₂ O μN	2.252(3) 1.963(13) 1.973(7.33) 2.721(8) 1.939(6.23)	3.390(7) not given	N,N O,N N,N	81.8(3) ^e 93.1(3, 2.4) ^d 91.1(2)	460
[Cu ₂ (μ-sdp ₃)(μ-pz)] (green)	m P ₂ _{1/a} 4	19.279(5) 9.021(2) 11.945(3)	98.83(2)	CuO ₂ N ₂	pzN O N μO	1.935(-, 12) 1.907(-, 4) 1.937(-, 3) 1.952(-, 10)	3.401 121.3	O,N O,O N,N	87.9(-, 2.9) ^e 93.0(-, 2.4) ^d 168.0(-, 1.2) 170.3(-, 5.4)	454
[Cu ₂ (μ-OMe)(μ-ONO)(NO ₂) ₂ · (bpy) ₂] (deep green)	m C ₂ _{1/c} 4	16.633(8) 8.320(6) 18.986(9)	114.6(1)	CuO ₃ N ₂	bpyN O ₂ NO μMeO μONO μO ₂ N	2.041(6.11) 2.634(8) 1.934(3) 2.074(6) 2.177(13)	3.403(1) 123.2(3)	O,O N,N O,N	49.5(2) ^e 90.8(2, 2.6) 80.2(2) ^e 96.3(3, 3.4) 91.4(3, 3.4) 130.2(3, 7.3) 168.7(2)	461
[Cu ₂ (μ-ppd)(μ-OH)(H ₂ O)Br ₃] 0.6H ₂ O (dark green)	tr P-1 2	7.7381(20) 10.1462(23) 11.151(4)	98.14(2) 93.93(3) 90.93(2)	CuO ₂ N ₂ Br	N Br H ₂ O μHO	2.003(8.1) 2.334(2) 2.861(2) 1.983(1)	3.413(2) 118.9(1)	O,N N,N N,Br	87.1(2, 5.2) 167.0(2) 77.7(3) ^e 97.4(2) 174.0(2)	462
				CuN ₂ Br ₂ O	N Br μHO	2.003(8.6) 2.361(2) 2.856(2) 1.981(1)		Br,O O,O O,N N,N N,Br	95.2(1, 4) 89.8(1) 88.8(2) 163.0(2) 77.1(3) ^e 92.6(2, 5.3) 166.0(2)	

TABLE III (Continued)

Compound (color)	Cryst. cl. space G. Z	<i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]	α [°] β [°] γ [°]	Chromophore	<i>Cu-L</i> [Å]	<i>Cu-L-Cu</i> [Å] <i>Cu-L-Cu</i> [°]	<i>L-Cu-L</i> [°]	Ref.
$[\text{Cu}_2(\mu\text{-mip})(\mu\text{-OH})(\text{H}_2\text{O})\text{Br}_3]\cdot\text{H}_2\text{O}$ (dark green)	m P2 ₁ /n 4	10.175(7) 21.478(5) 10.198(8)	97.41(2)	CuO ₂ N ₂ Br	N H ₂ O Br μHO 2.016(10,11) 2.276(2) 2.378(3) 1.936(7)	3.420(2) 124.9(4)	Br ₂ O Br ₂ O ₂ N 163.8(4) N ₂ N 78.6(5) ^e N ₂ Br 97.3(3) 160.0(3) O ₂ Br 99.6(3,3.1) O ₂ O 91.5(2) O ₂ N 85.5(4) 159.2(4) N ₂ N 78.3(5) ^e N ₂ Br 92.0(3,7.1) 173.1(3) Br ₂ O 97.7(3,7) Br ₂ Br 100.3(1)	462
$[\text{Cu}_2(\mu\text{-ppd})(\mu\text{-OH})(\text{H}_2\text{O})\text{Cl}_3]\cdot 0.8\text{H}_2\text{O}$ (green)	tr P-1 2	7.6810(6) 9.9823(6) 10.7380(9)	96.83(1) 93.28(1) 91.50(1)	CuO ₂ N ₂ Cl	N H ₂ O Cl μHO 2.008(3,15) 2.783(1) 2.208(1) 2.028(1)	3.454(2) 116.4(1)	O ₂ N 87.4(1,6.2) 167.5(1) N ₂ N 77.8(1) ^e N ₂ Cl 95.8(1) 171.5(1) Cl ₂ O 95.0(1,1.6) O ₂ O 90.2(1) O ₂ N 89.7(1) 165.1(3) N ₂ N 77.4(1) ^e N ₂ Cl 92.3(1,3.9) 166.3(1) Cl ₂ O 95.6(1,8) Cl ₂ Cl 102.6(1)	462

[Cu ₂ (μ-LS)(μ-pz)(MeO)] ^h (brown purple)	m P ₂₁ /c 8	15.887(5) 12.714(4) 29.178(6)	91.81(2)	CuN ₂ OS	pzN 1.90(1) O 1.93(1) N 1.95(1) μS 2.227(5)	3.474(3) 101.5(2)	S,O 168.4(1) S,N 91.7(4,2) O,N 81.1(5) ^g 95.5(5) N,N 176.5(5)	463									
									CuO ₂ N ₂ S	pzN 1.92(1) O 1.94(1) N 1.95(1) MeO 2.39(1) μS 2.258(5)	S,O 105.6(3) 160.3(4) S,N 89.7(4,1.6) O,N 81.9(5) ^g 93.1(5, 5.4)						
												CuN ₂ OS	pzN 1.94(1) O 1.92(1) N 1.95(1) μS 2.236(5)	S,O 165.6(4) S,N 91.9(4,8) O,N 80.5(5) ^g 96.8(5) N,N 176.0(6)			
															CuO ₂ N ₂ S	pzN 1.94(1) O 1.91(1) N 1.93(1) MeO 2.40(1) μS 2.251(5)	S,O 96.0(3) 157.8(4) S,N 90.6(4,8) O,N 81.5(5) ^g 93.2(6, 3.4)
												CuN ₂ Cl ₂ O	N 2.026(4, 23) Cl 2.247(1) 2.679(2) μHO 1.919(3)	O,Cl 98.6(1, 2.6) N,Cl 93.1(1, 6.8) 172.0(1) O,N 84.4(1) 157.6(1) N,N 78.4(1) ^g			
									CuO ₂ N ₂ Cl	N 2.021(4, 18) Cl 2.235(1) H ₂ O 2.286(4) μHO 1.921(3)	O,Cl 100.7(1, 3.5) N,Cl 97.5(1) 160.4(1) O,O 91.5(1) O,N 91.3(1, 6.5) 162.7(1) N,N 78.3(1) ^g						
												[Cu ₃ (μ-mip)(μ-OH)(H ₂ O)Cl ₃] H ₂ O (green)	m P ₂₁ /n 4	10.063(1) 20.967(1) 9.919(1)	96.48(1)	CuN ₂ Cl ₂ O	N 2.026(4, 23) Cl 2.247(1) 2.679(2) μHO 1.919(3)
									CuO ₂ N ₂ Cl	N 2.021(4, 18) Cl 2.235(1) H ₂ O 2.286(4) μHO 1.921(3)	O,Cl 100.7(1, 3.5) N,Cl 97.5(1) 160.4(1) O,O 91.5(1) O,N 91.3(1, 6.5) 162.7(1) N,N 78.3(1) ^g						

TABLE III (Continued)

Compound (color)	Cryst. cl. space G. 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 (μ -boacp)(μ -N ₃ (Me ₅ dien). (ClO ₄)ClO ₄ (dark green)	tr	16.880(8)	106.04(2)	CuN ₄ O	N 1.933(13.30)	3.449(3)	N,N 84.2(5,5.2) ^e	465
	P-1	11.488(4)	83.78(2)		O ₃ ClO 2.39(1)	112.4(5)	101.9(5,9.0)	
	2	8.769(2)	95.99(3)		N ₃ μ N 1.969(10)		166.5(5,1.8) 94.5(5,7.8)	
[Cu ₂ (μ -dpp)(μ -Cl)Cl ₃ (H ₂ O)] (green)	m	9.809(1)		CuN ₄ O	diendtN 2.045(13.7)		N,N 85.2(5,1.6) ^e	466
	P2 ₁ /c	9.212(1)	100.4(1)		boacpO 1.935(10)		101.1(5)	
	4	19.316(2)			N ₃ μ N 2.179(10)		148.1(5)	
							N,O 90.3(5,3.2)	
							165.0(4)	
[Cu ₂ (μ -dpp)(μ -Cl)Cl ₃ (H ₂ O)] \cdot H ₂ O (yellow green)	tr	11.685(6)	66.94(8)	CuCl ₃ N ₂	N 2.022(9,16)	3.51	Cl,Cl 97.1(1,6.7)	467
	P-1	10.003(6)	78.86(8)		Cl 2.228(3)	106.1(1)	Cl,N 96.4(3,3.5)	
	2	8.570(5)	83.07(8)		2.500(3)		161.1(3,5.2)	
					μ Cl 2.239(3)		78.8(3) ^e	
					N 1.991(9,15)		O,Cl 99.8(2,5.2)	
					Cl 2.195(4)		O,N 91.8(3,3)	
					H ₂ O 2.313(7)		Cl,N 93.3(3,2.6)	
					μ Cl 2.223(3)		165.4(3,3.0)	
							N,N 79.2(3) ^e	
							Cl,Cl 92.1(1)	
						Cl,Cl 97.8(2,8.9)		
						Cl,N 92.2(3,5.1)		
						165.6(3,1.1)		
						79.7(4) ^e		
						N,N 97.4(3,5.7)		
						O,Cl 94.0(3,3.4)		
						Cl,N 93.2(3,2.6)		
						166.8(3,6)		
						80.3(4) ^e		
						Cl,Cl 91.0(2)		


$[\text{Cu}_2(\mu\text{-pz})(\mu\text{-Br})(\text{dien})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}^e$ (violet blue)	tr P-1 4	23.294(10) 14.084(5) 7.750(2)	92.50(2) 92.07(2) 90.98(2)	$\text{Cu}_2\text{N}_4\text{Br}$	N pzN μBr	2.028(13,14) 1.960(10,6) 2.723(2,33)	3.752(2) 87.1(1)	Br,N N,N	88.3(3,8) 100.0(3,2,7) 83.8(5,2,4) ^e 94.9(5,2,0) 154.4(4,1,7) 173.4(4,1,2) 93.6(4,3,1) 102.5(5,5,1) 83.3(6,5) ^e 95.0(5,1,5) 152.7(6,1,9) 171.9(6,3)	468
	m P2 ₁ /n 4	7.981(10) 18.352(8) 19.247(8)	97.98(7)	CuO_2N_2	μHO propO phenN	1.918(3,1) 1.938(4,2) 2.016(4,5)	3.015(2) 103.6(2)	O,O N,N O,N	95.5(1,1) 81.5(1,1) ^e 91.1(2,2,3) 168.8(2,5,6)	469
$[\text{Cu}_2(\mu\text{-HO})(\mu\text{-ac})(\text{phen})_2] \cdot (\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (deep blue)	m P2 ₁ /n 4	8.107(10) 18.554(9) 18.616(7)	99.14(6)	CuO_2N_2	μHO acO phenN	1.923(3,1) 1.934(3,1) 2.028(4,11)	3.017(2) 103.4(2)	O,O N,N O,N	95.6(1,6) 81.5(2,1) ^e 91.0(1,2,6) 166.0(1,7,9)	469
$[\text{Cu}_2(\mu\text{-ac})(\mu\text{-dpepd})]$ (green blue)	tr P-1 2	13.398(8) 16.024(5) 11.691(3)	111.92(2) 116.50(2) 64.09(3)	CuO_3N	acO O N μO	1.933(6,2) 1.915(9,24) 1.908(6,8) 1.921(7,18)	3.129(2) 109.1(3)	O,N O,N O,N O,O	85.1(3,3) ^e 91.2(3,8) ^d 170.5(4,4,8) 90.1(3,4) 172.4(3,4,0)	470
$[\text{Cu}_2(\mu\text{-bz})(\mu\text{-deamp})]\text{PF}_6$ (green)	m P2 ₁ /c 4	14.504(7) 13.667(6) 21.563(7)	90.23(2)	CuO_3N_2	bzO N μO	1.972(9,23) 2.123(10,16) 2.045(14,43) 1.989(10,13)	3.297(3) 112.0(3)		not given	471

TABLE III (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-L-Cu [Å] Cu-L-Cu [°]	L-Cu-L [°]	Ref.
[Cu ₂ (μ -ac)(μ -tp)(H ₂ O)]·0.5dmf (blue) (at 173 K)	tr P-1 2	8.662(1) 10.010(1) 12.833(2)	83.27(1) 73.61(1) 79.35(1)	CuO ₃ N ₂	acO H ₂ O N μ O 1.907(4)	3.416 129.2(2)	not given	472
[Cu ₂ (μ -ac)(μ -L-Et)(ClO ₄) ₂] (green)	m P2 ₁ /n 4	14.190(3) 22.707(4) 15.883(4)	97.20(2)	CuO ₂ N ₂ CuN ₃ O ₂	acO N μ O 1.923(4) 1.946(5.47) 1.874(3)	3.459(2) 130.6(5)	not given 84.2(4, 0) ^e 99.1(4, 3.1) 123.0(4, 5.4) 178.1(4, 1.7) 81.1(4, 6) ^e 108.4(4, 5.1) 95.5(4, 3)	473
[Cu ₂ (μ -2,6-Me ₂ PhtCO ₂)(μ -sb)] (not given)	or Pbca 8	16.427(3) 13.920(2) 20.333(3)		CuO ₃ N	phCO ₂ O O N μ O 1.938(6, 13) 1.898(7, 2) 1.915(8, 2) 1.908(6, 1)	3.469(3) 130.8(3)	86.6(3, 1) 93.6(2, 1) 178.7(4, 6) 85.9(3, 5) ^e 94.2(3, 2) ^d 172.1(3, 1.0)	474
[Cu ₂ (μ -PhtCO ₂)(μ -sb)] (not given)	m P2 ₁ /a 4	20.778(7) 7.486(2) 14.137(4)	109.60(3)	CuO ₃ N	PhCO ₂ O O N μ O 1.933(5, 3) 1.901(4, 1) 1.912(7, 4) 1.904(4, 8)	3.482(1) 132.2(3)	90.5(2, 3.3) 93.5(2, 1) 172.6(2) 84.9(2, 6) ^e 95.4(2, 1) ^d 170.9(3, 3.8)	474

[Cu ₂ (μ-PhCO ₂)(μ-dpba)]H ₂ O (green blue)	m P2 ₁ /c 4	18.234(2) 11.478(2) 10.327(1)	100.09(1)	CuO ₂ N	PhCO ₂ O O N μO	1.945(6, 9) 1.904(6, 21) 1.920(7, 5) 1.901(6, 17)	3.482(2) 132.7(3)	O,N	84.5(3, 8) ^e 94.4(3, 6) ^d 172.9(3, 1, 3) 89.2(2, 5, 2) 178.4(3, 3)	470
[Cu ₂ (μ-ac)(μ-dpba)]MeOH (green blue)	or Pbca 8	18.196(5) 22.636(5) 9.731(1)		CuO ₃ N	acO N O μO	1.935(9, 16) 1.938(10, 8) 1.860(10, 8) 1.895(9, 18)	3.495(3) 134.5(4)	O,N	86.1(4, 5) ^e 92.2(4) ^d 173.8(5, 2, 0) 89.9(4, 4, 1) 175.0(4, 5)	470
[Cu ₂ (μ-Ph ₂ MeSiCO ₂ (μ-ac))] (not given)	or Pbca 8	16.444(2) 27.558(3) 12.485(2)		CuO ₂ N	Ph ₂ SiCO ₂ O O N μO	1.945(3, 30) 1.907(3, 6) 1.923(3, 11) 1.905(3, 2)	3.502(1) 133.6(2)	O,O	86.2(1, 2) 94.5(1, 1) 176.2(1, 3) 85.4(1, 8) ^e 94.7(1, 2) ^d 175.4(1, 2)	474
[Cu ₂ (μ-ac)(μ-sb)]·H ₂ O (dark blue)	m P2 ₁ /n —	17.716(3) 13.147(3) 7.716(1)	92.91(1)	CuO ₃ N	acO O N μO	1.938(6, 8) 1.898(6, 5) 1.961(7, 25) 1.908(6, 6)	3.502(2) 133.3(3)	O,N	85.5(3, 7) ^e 94.5(3) ^d 171.9(3, 2, 4) 85.6(3, 1) 94.7(3, 5) 178.8(3, 5)	475
[Cu ₂ (μ-2,6-MePhCO ₂ (μ-sb))· 0.5MeOH (not given)]	m P2 ₁ /n 4	26.431(1) 7.574(1) 11.356(2)	94.39(2)	CuO ₃ N	PhCO ₂ O O N μO	1.927(9, 18) 1.912(9, 7) 1.914(10, 3) 1.903(9, 13)	3.514(4) 134.8(4)	O,O	86.7(4, 1, 1) 93.3(4, 3) 178.4(4, 9) 84.9(4, 1, 5) ^e 94.0(4, 1) ^d 172.6(4, 2, 1)	474
[Cu ₂ (μ-2,6-Cl ₂ PhCO ₂ (μ-sb))· 0.7dmf (not given)]	tr P-1 2	11.205(2) 13.285(2) 9.722(2)	108.66(1) 95.40(1) 94.59(2)	CuO ₃ N	PhCO ₂ O O N μO	1.947(11, 7) 1.869(11, 7) 1.925(8, 3) 1.904(11, 20)	3.517(3) 135.0(5)	O,O	85.4(5, 1) 93.6(5, 5) 174.6(4, 1, 7) 85.7(5, 7) ^e 95.8(5, 7) ^d 176.4(5, 2, 1)	474

TABLE III (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å] Cu-L-Cu [°]	L-Cu-L [°]	Ref.
$[\text{Cu}_2(\mu\text{-ac})(\mu\text{-bpmp})](\text{PF}_6)_2$ (not given)	m P2 ₁ /a 4	17.843(4) 21.226(5) 11.206(3)	105.47(2)	CuN ₃ O ₂	acO N μO 2.193(7) 2.178(6)	3.549(2) 119.3(4)	N,N 83.1(4, 1.1) ^e 98.9(4) 157.0(4) 93.5(3, 1.5) 94.4(3, 2) ^d 90.0(3, 5.9) 115.4(3, 5) 168.6(3, 6.7)	232
$[\text{Cu}_2(\mu\text{-ac})(\mu\text{-pramcres})](\text{ClO}_4)_2$ Me ₂ CO (green)	or P2 ₁ /2 ₁ 4	13.999(5) 23.046(9) 12.523(5)		CuN ₃ O ₂	acO N μO 1.1943(14.3) 2.022(24.48) 2.155(16.35) 1.941(12.36)	3.562(3) 133.2(7)	O,N 84.8(3, 3) ^f 90.0(3, 4) 103.8(6, 1) 145.9(6, 5.6) 173.6(7, 7) 94.3(7, 2.3) ^d 104.9(6) 115.6(7)	476
$[\text{Cu}_2(\mu\text{-N}_3)(\mu\text{-L-Eu})(\text{BF}_4)_2$ (green)	m C2/m 4	19.082(3) 23.896(3) 13.230(2)	116.21(1)	CuN ₄ O	N ₃ N N μO 2.04(1) 2.05(1, 6) 1.944(8)	3.615(3) 136.9(6)	O,N 85.9(5) ^e 92.3(5) 114.2(4) 143.8(4) 83.0(5, 4) ^f 98.2(5, 1.1) 177.8(5)	473 477
$[\text{Cu}_2(\mu\text{-N}_3)(\mu\text{-pramcres})](\text{ClO}_4)_2$ thf (dark green)	or P2 ₁ /2 ₁ 4	12.977(2) 13.188(3) 22.033(6)		CuN ₄ O	N ₃ N N μO 2.007(9, 5) 2.036(9, 61) 2.131(8, 12) 2.015(6, 2)	3.765 138.2(3)	O,N 84.8(3, 2) ^f 90.1(3, 3) 111.1(3, 5.0) 136.0(3, 2.3) 91.4(4, 5.1) ^d 113.0(3, 2.8) 174.8(4, 0)	476

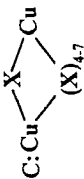
																																											
<p>[Cu₂(μ-tcc)(μ-pN₆O)](PF₆)₂ (orange)</p>	or Pbca 8	18.374(3) 18.346(3) 26.502(4)	CuN ₃ O	tccO N μO	1.995(9, 1) 2.068(12.73) 2.227(12.24) 1.943(8, 1)	3.248(2) 113.3(4)	O ₂ O ₂ N	84.8(4, 1.1) 91.0(4, 1.6) ^d 105.1(4, 2.8) 167.6(4, 9.6)	478																																		
																<p>[Cu₂(μ-OH)(μ-botb)](BF₄)₃ (dark green)</p>	m P2 ₁ /m 2	14.471(4) 17.201(5) 8.835(3)	CuO ₂ S ₂ N	N S O μO	2.06(5) 2.37(2, 2) 2.37(4) 1.85(2)	3.384(9) 132.2(4)	O ₂ N O ₂ S O ₂ O S ₂	94.8(9) 167.2(9) 95.5(8, 1) 98.1(9)	479																		
																														<p>[Cu₂(μ-dacpd)(H₂O)(ClO₄)₂· (MeCN)](ClO₄) (blue)</p>	tr P-1 2	13.040(2) 12.230(2) 12.720(3)	CuN ₄ O ₂	N MeCN μO O ₃ ClO	1.950(10.25) 2.003(9) 2.276(7) 1.971(9) 3.012(2)	3.638(8) 135.0(4)	N ₂ O N ₂ N	82.1(4) ^e 117.6(4) 158.9(4, 6) 79.6(4, 6) ^e	480				
<p>[Cu₂(μ-sbN₆O)(H₂O)(MeCN)] (ClO₄)₃ (blue)</p>																																											
			CuN ₃ O ₂	N H ₂ O μO	1.900(8) 2.050(8, 50) 2.388(18) 1.958(7)	77.9(4, 6) ^e 155.8(4) 82.0(4) ^e 94.0(5, 5.3) 121.8(4) 158.2(5) 91.2(4)	N ₂ N N ₂ O N ₂ O O ₂ O																																				

TABLE III (Continued)

Compound (color)	Cryst. cl. space G. 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 (μ -OH)(μ -tpe)(dpy)]· (ClO ₄) ₂ ·2H ₂ O (blue)	tr P-1 2	11.685(3) 14.569(2) 15.509(4)	87.97(2) 73.34(2) 74.15(1)	Cu ₄ O	dpyN tpeN μ HO	3.663(3) 137.9(4)	N,O N,N	83.3(4, 2.7) 94.0(3, 1.0) 174.8(5, 2) 88.0(4, 1) ^d 91.4(4, 1.2) 102.8(5, 1.4) 165.6(5, 5)	482
[Cu ₂ (μ -hdN ₆ O)(H ₂ O) ₂] (green brown)	m P2 ₁ /c 4	12.143(4) 21.356(5) 21.328(3)	107.95(2)	Cu ₃ O ₂	H ₂ O N μ O	3.875 128.4(6)	N,N N,O	81.5(7, 2.4) ^e 96.4(7) 165.3(8) 92.8(7, 6.8) ^d 115.3(7) 166.0(7, 3.0) 95.2(6, 5.4)	483

^a Where more than one chemically equivalent distance of angle 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 Four – membered metallocyclic ring. ^d Six membered – metallocyclic ring. ^e Five membered metallocyclic ring. ^f There are dimer and tetramer units. ^h There are two crystallographically independent molecules.

2.2.2 By One Single Atom Plus Two-atom Bridges

Crystallographic and structural data for Cu(II) dimers in which Cu(II) atoms are bridged by a single atom plus two-atoms of ligand moiety are gathered in Table IIIA, and they are listed in order of increasing Cu–Cu separation. There are over forty such derivatives, mostly green (23), but there some violet, purple (6), blue (5) and even brown (1); for others the color is not given.

The structure of bluish green $[\text{Cu}_2(\mu\text{-OH})(\mu\text{-papfs})(\text{NO}_3)_2(\text{H}_2\text{O})]\text{NO}_3$ ⁴⁵⁰ is shown in Figure 3 as an example of this class. In this dimer, the Cu–Cu separation of 3.156(2) Å is the shortest found. There are two non-equivalent Cu(II) atoms, while the stereochemistry at Cu(1) is distorted square pyramidal with the copper lying 0.105 Å above the mean plane of the four donors N(1)–N(3)–O(1)–O(5), the stereochemistry at Cu(2) is a tetragonally distorted *pseudo*-octahedron.

There are five derivatives^{451,454–456,459} in which each Cu(II) atom is in a square-planar environment with different degrees of distortion. In most derivatives^{452,453,457,458,461,462,464,465–467} the arrangement about Cu(II) atoms is distorted square-pyramidal. There are two examples,^{460,463} which contain non-equivalent Cu(II) atoms, one is square planar and the other is a distorted square-pyramid.

The Cu–Cu separation in this class of compounds range from 3.156 to 3.769 Å. From the single bridged ligands, by far the most prominent are

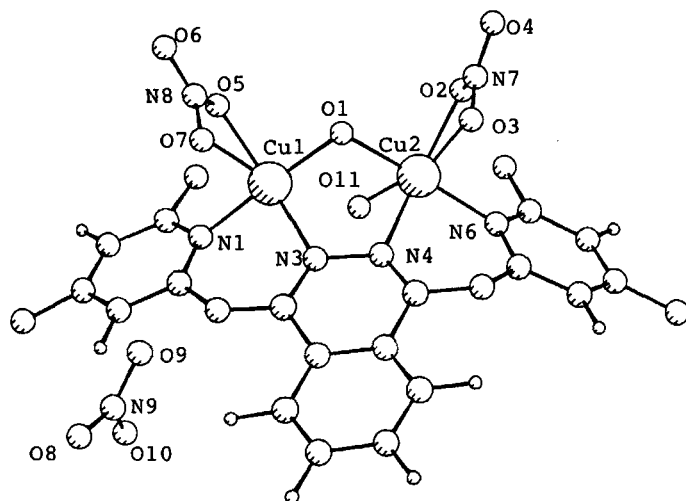


FIGURE 3 Structure of $[\text{Cu}_2(\mu\text{-OH})(\mu\text{-papfs})(\text{NO}_3)_2(\text{H}_2\text{O})]\text{NO}_3$ (see Ref. 450).

O-donor ligands, and nitrogen donor ligands are most common as pair bridges. The Cu–L–Cu bridge angles range from 89.0° (L=Br) to 127.1° (OL). The mean Cu–L–Cu bridge angle closes with an increase of covalent radius of L; simultaneously the mean Cu–Cu separation increases: 121.5° and 3.35 Å (L–O), 112.0° and 3.42 Å (N), 107.8° and 3.51 Å (Cl), and 88° and 3.76 Å (Br).

2.2.3 *By One Single Atom Plus Three-atom Bridges*

In Table IIIB are summarized data for blue (7) and green (6) dimeric Cu(II) derivatives, in which a μ -oxygen ligand and one RCOO[−] ligand in a syn–syn arrangement^{232,469–467} or a μ -oxygen ligand and one 1,3-bridging azide serve as bridges.^{473,476,477} The Cu–Cu separations range from 3.015 to 3.765 Å. There is a relationship between the Cu–Cu separation and the Cu–O–Cu bridge angle, with increases in Cu–Cu separation as the Cu–O–Cu bridge angle opens. For example, 3.015 Å and 103.6 Å,⁴⁶⁹ 3.297 Å and 112.0°,⁴⁷¹ 3.416 Å and 129.2°,⁴⁷² 3.514 Å and 134.8°,⁴⁷⁴ 3.615 Å and 136.9°,^{473,477} and 3.765 Å and 138.2°.⁴⁶⁷ Cu(II) atoms are four- (a distorted square planar),^{469,470,474,475} five- (a distorted square pyramid) coordinated^{232,471,473,476,477} and in⁴⁷² two compounds the Cu(II) atoms are non-equivalent with one four- and the other five-coordinated.

2.2.4 *By One Single Atom Plus Four-, Five-, Seven- or Eight-atom Bridges*

In the remaining six dimeric Cu(II) derivatives (Table IIIC), two compounds are distorted square-pyramidal moieties held together by a μ -oxygen ligand and by a four-atom bridge,⁴⁷⁸ one compound by a μ -oxygen ligand and by a five-atom bridge,^{480–482} one compound by a μ -oxygen ligand and by a seven-atom bridge,⁴⁸³ and one compound by a μ -oxygen ligand with an eight-atom bridge.⁴⁷⁹ The Cu–Cu separations range from 3.248 to 3.875 Å. When the Cu–Cu distance increases the Cu–O–Cu bridge angle opens. For example, 3.248 Å and 113.3°,⁴⁷⁸ 3.384 Å and 132.2°,⁴⁷⁹ 3.638 Å and 135.0°⁴⁸⁰ and 3.663 Å and 137.9°.⁴⁸² Inspection of the data in Table III reveals that there are two derivatives^{463,468} which contain two crystallographically independent molecules within the same crystal, differing mostly by the degree of distortion.

There are mono- through octadentate ligands. The mean Cu–L(bridge) distance increases with a covalent radius (in parentheses) of donor atom in the order: 1.93 Å (O, 0.73 Å) < 2.07 Å (N, 0.75 Å) < 2.19 Å (Cl, 0.99 Å) < 2.705 Å (Br, 1.14 Å). The mean Cu–L(terminal) distance for unidentate

ligands increases in the sequence: 2.27 Å (N) < 2.34 Å (Cl) < 2.485 Å (O) < 2.525 Å (Br). In the series of multidentate N donor ligands, the mean Cu–N distance increases in the order: 1.97 Å (bi-) ~ 1.97 Å (hexa-) < 2.02 Å (tetra-) < 2.035 Å (tri-) < 2.27 Å (unidentate). The hetero-multidentate ligands, include one O plus one N atom, two O plus a N atoms, one O plus three N atoms, three O plus two N atoms, one O plus four N atoms, two O plus two N plus one S atoms, one O plus six N atoms, and two O plus two N plus four S donor sites. Noticeable, the mean Cu–L bond distance increases with coordination number and the mean value of metallocyclic ring angle closes. For example, the mean Cu–O distance for monodentate ligands are: 2.44 Å (five-coordinated) < 2.67 Å (six-coordinated); for bidentate ligands are: 1.94 Å (four-coordinated) < 2.04 Å (five-coordinated) < 2.31 Å (six-coordinated). The mean values for five-membered metallocyclic ring angles are: 80.0° (five-coordinated) < 80.5° (four-coordinated) (N + N); for six-membered rings: 92.5° (five-coordinated) < 93.2° (four-coordinated) (O + N); and 91.0° (five-coordinated) < 94.5° (four-coordinated) (N + N).

2.2.5 By Two-atom or Three-atom Bridges

Crystallographic and structural data for Cu(II) compounds doubly bridged by two atoms or by three-atom bridges are gathered in Table IV. The structures are listed in order of increasing Cu–Cu separation. There are twenty-five derivatives in which two pairs of atoms serve as bridges between two Cu(II) atoms (Table IVA). The structure of black purple $[\text{Cu}_2(\mu\text{-dmgH})_2(\text{H}_2\text{dmg})(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ ⁴⁸⁴ is shown in Figure 4 as an example of this type complex. The $\text{Cu}(\text{dmgH})_2$ fragment coordinates to the $\text{Cu}(\text{H}_2\text{dmg})_2^{2+}$ unit through the oximate oxygens to afford a dimer skeleton doubly-bridged by oximate groups in a *cis* arrangement. The configuration about the Cu(II) atoms is a distorted square pyramid; in both complexes the apical position is occupied by a water molecule. The Cu–Cu separation of 3.526(4) Å is too long for a “real” bond.

There are only three types of bridging ligands, when both pairs of atoms are nitrogens,^{187,491–494,496,498–502} with an oxygen plus nitrogen atom (mostly in *trans* arrangement)^{484–490,495,497,504} and only one example where both pairs of atoms are oxygens.⁵⁰³

The Cu–Cu separations range from 3.396(1) to 7.678(2) Å. Cu(II) atoms are four-coordinate, in a distorted square-planar configuration,⁴⁹⁸ five-coordinate in a square-pyramidal arrangement^{187,484,485,487–489,493,494,496,497,504} or in a trigonal-bipyramidal arrangement,^{495,497} and six-coordinate.^{486,490–492,499–502}

TABLE IV Crystallographic and structural data for doubly bridged copper(II) dimers by pairs and by three atoms^a


Compound	Cryst. cl. space Gr.	Z	a [Å]			α [°]			Chromophore	Cu-L [Å]	Cu-Cu [Å]	L-Cu-L [°]	Ref.
			b [Å]	c [Å]	β [°]	γ [°]	γ [°]						
 A: Cu-Cu	m	P2 ₁ /c	19.680(8)			112.5(1)			CuN ₄ O	3.396(1)	N,N ^b	187	
			10.660(13)										
			15.558(9)										
[Cu ₂ (μ-dmgH) ₂ (H ₂ dmg)· (H ₂ O) ₂](ClO ₄) ₂ ·H ₂ O (dark purple)	m	P2 ₁ /n	15.991(3)			90.82(5)			CuO ₃ N ₂	3.526(4)	N,N N,O	484	
			11.682(1)										
			14.363(4)										
[Cu(μ-2,6-Mepydo)(H ₂ O)] ₂ · (BF ₄) ₂ (blue)	tr	P-1	8.251(4)			86.62(3)			CuN ₃ O ₂	3.545(1)	N,N N,O	485	
			12.268(3)			83.74(3)							
			13.411(3)			81.11(3)							
[Cu(μ-heiob)(H ₂ O)(ClO ₄) ₂] (dark green)	m	P2 ₁ /c	7.868(2)			112.73(4)			CuO ₄ N ₂	3.581(3)	N,O	486a	
			14.040(7)										
			11.401(5)										
[Cu(μ-dapo) ₂ (ClO ₄) ₂] [Cu ₂ (μ-dapo) ₂ (MeOH) ₂](ClO ₄) ₂ (black)	tr	P-1	10.021(4)			91.13(2)			CuN ₃ O ₂	3.684(1)	O,O	486b	
			10.090(5)			109.36(3)							
			21.249(8)			117.04(3)							

TABLE IV (Continued)

Compound	Cryst. cl. space Gr. Z	<i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å]	L-Cu-L [°]	Ref.
[Cu(μ -dpph)(H ₂ O)(ClO ₄) ₂ ·(ClO ₄) ₂] (pale yellow)	tr P-1 1	8.073(22) 10.088(19) 10.238(24)	97.357(18) 99.960(22) 106.677(18)	CuN ₄ O ₂	N 1.990(8, 29) H ₂ O 2.351(7) O ₃ ClO 2.615(12)	3.728(1) ^e	N,N 81.6(3, 4) ^c 98.3(3, 9, 1) 169.6(3, 3) O,N 90.0(4, 12, 0) O,O 165.8(3)	491
[Cu(μ -pzdad)(H ₂ O)(ClO ₄) ₂] (orange red)	m P2 ₁ /n 2	12.031(6) 9.517(4) 9.973(5)	100.16(4)	CuN ₄ O ₂	N 1.976(7, 2) 2.021(6, 7) H ₂ O 2.310(6) O ₃ ClO 2.554(6)	3.760(2)	N,N 80.5(4, 5) ^e 99.3(5, 6, 2) 126.8(7) O,N 90.2(4, 7, 9) 124.7(9)	492
[Cu(μ -enaoH)] ₂ (ClO ₄) ₂ (red)	m P2 ₁ /c 2	11.441(2) 12.992(2) 12.640(2)	110.20(1)	CuN ₄ O ₂	N 1.968(4, 44) O 2.185(4) 2.698(4)	3.815(2) ^e	N,N 84.3(2, 3, 5) ^e 97.5(2) 96.8(2, 2, 4) 107.2(2, 5)	493a
[Cu(μ -mpzdad)Cl] ₂ ·2H ₂ O (dark green)	tr P-1 1	8.520(15) 8.607(18) 8.671(14)	75.27(15) 69.96(17) 76.66(15)	CuN ₃ OCl	N 1.948(2, 15) 2.015(2) O 1.924(2) Cl 2.558(1)	3.815(1)	N,N 78.7(1) ^e 100.0(2) N,O 89.0(1, 1, 7) Cl,N 97.8(1, 3, 2) Cl,O 96.6(1, 7)	493b
[Cu(μ -mpzdad)Cl] ₂ ·2H ₂ O (brown) (at 288 K)	m P2 ₁ /a 2	11.490(5) 16.287(14) 6.253(4)	97.78(4)	CuN ₃ OCl	N 1.948(2, 19) 2.018(3) O 1.917(2) Cl 2.605(1)		N,N 78.6(2) ^e 99.8(2) N,O 89.3(2, 1, 7) Cl,N 98.7(2, 2, 4) Cl,O 96.4(1, 5)	493b
[Cu(μ -C ₁₇ H ₃₀ N ₆)] ₂ (BPh ₄) ₂ (pale blue)	tr P-1 1	13.437(4) 15.192(5) 12.364(4)	116.38(3) 113.71(3) 60.48(2)	CuN ₅	N 1.954(4, 48) 2.108(4) 2.496(5)	3.903(2)	N,N 81.0(2, 1, 2) ^e 96.1(2, 1, 6) 101.7(2, 1, 7) ^f	494

[Cu(μ -C ₁₂ H ₂₁ N ₄ O ₂) ₂](ClO ₄) ₂ (dark)	m P ₂ /n 4	6.490(2) 21.727(5) 12.398(4)	96.58(3)	CuN ₄ O	N O	1.978(5, 21) 2.264(3)	3.91(1)	N ₁ N	80.5(2, 3) ^c 102.6(2) ^f 93.9(2) 150.2(2) 173.0(2) 94.8(2, 1.5) 113.1(1)	495
[Cu(μ -4Br-3-CO ₂ mepz)- (4-Brdmpz) ₂] ₂ (purple)	m C ₂ /c 4	13.470(1) 16.005(2) 20.174(1)	98.142(6)	CuN ₄ O	O N Br-pzN	1.982(4) 2.083(5) 2.226(5) 1.980(5, 31)	3.923(1) ^e	O ₁ N O ₁ N	81.5(2) ^f 86.5(2, 3.4) 178.0(2) 95.3(2, 4.9) 110.9(2, 1.8) 135.8(2)	496
[Cu(μ -4-Br-3-CO ₂ mepz)- (4-BrdmpzH) ₂] ₂ (green)	tr P-1 1	10.152(3) 13.068(3) 10.033(3)	112.38(2) 116.46(2) 70.29(2)	CuN ₄ O	O N Br-pzN	1.992(5) 2.027(6) 2.273(7) 1.973(6, 26)	3.924(1) ^e	O ₁ N	81.6(2) ^f 85.9(2, 1.2) 179.0(3) 95.7(3, 3.5) 110.4(3, 6.0) 136.5(3)	496
[Cu(μ -C ₁₄ H ₂₉ N ₄ O ₂)Br] ₂ (dark green)	m C ₂ /c; Cc 8	21.798(8) 11.662(4) 15.670(7)	74.00(4)	CuN ₄ O	N O	1.97(1) 2.07(1, 1) 2.28(9)	3.949(4)	N ₁ N	84.4(4) ^f 92.9(5, 1.7) ^d 133.4(4) 174.2(4) 84.7(4) 96.4(4, 4.2) 125.4(4)	497
(NBu ₄) ₂ [Cu(μ -dep)] ₂ (blue)	tr P-1 1	10.899(4) 12.286(5) 9.899(3)	109.51(3) 101.88(3) 102.69(3)	CuO ₂ N ₂	O N	1.958(3, 3) 1.909(4, 2)	3.978(10)	N ₁ N N ₁ O	92.4(2) 81.7(2) ^e 104.1(1)	498
[Cu(μ -aamt)Br(H ₂ O)] ₂ ·Br ₂ · 2H ₂ O·MeOH (dark blue)	tr P-1 1	9.918(5) 7.000(2) 10.895(3)	114.42(2) 94.97(3) 102.20(3)	CuN ₄ OBr	N H ₂ O Br	1.944(3, 7) 2.038(3, 6) 2.647(3) 2.897(6)	4.0694(7)	N ₁ N N ₁ O N ₁ Br O ₁ Br	80.9(1, 1) ^e 98.9(1, 6.8) 171.6(1, 3) 87.6(1, 1.8) 92.54(9, 3.79) 174.22(7)	499

TABLE IV (Continued)

Compound	Cryst. cl. space Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å]	L-Cu-L [°]	Ref.
[Cu(μ -bpt)(CF ₃ SO ₃ (H ₂ O)) ₂] (dark blue)	tr	8.841(3)	112.58(3)	CuN ₄ O ₂	N 2.087(3, 5)	4.085(1)	N,N 79.1(1, 5) ^c	500
	P-1	14.131(6)	92.23(3)		H ₂ O 2.323(4)		90.2(1, 1)	
	2	14.392(6)	102.45(3)		CF ₃ SO ₃ O 2.802(4)		111.2(1, 1)	
[Cu(μ -aamt)(H ₂ O) ₂] ₂ (SO ₄) ₂ ·4H ₂ O (dark blue)	m	19.009(8)		CuN ₄ O ₂	N 1.96(1, 1)	4.088(3)	N,N 81.9(4, 4) ^c	501a
	C2/c	11.273(4)	103.50(4)		N 2.05(1, 1)		98.0(4, 6, 1)	
	4	13.144(7)			H ₂ O 2.62(1, 1)		143.7(4, 6)	
[Cu(μ -acm)(NH ₂) ₂ (H ₂ O)] ₂ ·2H ₂ O (blue)	tr	7.548(4)	93.59(6)	CuN ₅ O	acmN 2.024(4)	4.363(1) ^c	83.3(2, 2, 7)	501b
	P-1	8.205(17)	108.68(3)		2.546(4)		93.8(2, 2, 3)	
	1	10.797(3)	98.50(9)		H ₂ O 2.011(4)		168.0(2)	
[Cu ₃ (μ -qpy) ₂ (ac)](PF ₆) ₃ ·H ₂ O (brown)	tr	11.829(8)	103.0(1)	CuN ₆	1.991(14, 27)	4.503(2)	N,N 77.5(6, 2, 1) ^c	502
	P1	12.575(11)	82.9(1)		2.161(3, 0)		84.1(5, 4)	
	2	20.917(22)	114.4(1)		2.349(15, 30)		96.6(6, 1, 5)	
[Cu(μ -2-Obza) ₂ (H ₂ O)] ₂ ·H ₂ O (not given)	m	25.726(7)		CuN ₄ O ₂	O 2.023(21, 56)		N,N 78.6(6, 7) ^c	503
	C2	9.196(2)	102.97(2)		2.212(15)	5.138(2) ^c	109.5(6, 8, 4)	
	8	12.826(2)			2.038(11)		165.4(7)	
					2.683(16)		N,O 88.1(5, 2, 0)	
							158.6(6)	
							O,O 94.4(1, 1)	
							107.5(1, 2)	
							158.3(1, 3)	
							172.1(1, 7)	

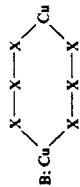
[Cu(μ -C ₈ H ₁₆ N ₃ O ₂) ₂](ClO ₄) ₂ (black)	m P2 ₁ /c 2	7.678(2) 10.647(5) 16.568(10)	91.28(4)	CuN ₃ O ₂	N O	1.966(5, 23) 2.044(6) 1.904(4) 2.367(6)	7.678(2) ^f	O,N N,N	87.5(1, 4.8) ^d 92.6(1, 3) 81.5(2, 1.1) ^e 102.3(2) 163.0(2, 3) 79.8(2) ^e 101.1(2) 91.2(2)	504
										
[Cu ₂ (μ -ac) ₂ (H ₂ O)(bpy) ₂](PF ₆) ₂ (not given)	m P2 ₁ /n 4	16.120(2) 12.482(4) 17.467(2)	113.98(1)	CuO ₃ N ₂	N H ₂ O acO	1.968(10, 25) 2.253(9) 1.948(8, 9)	2.965(3)	O,O N,O	91.7(4, 3.3) 94.7(4, 2.0) 170.2(4, 2.5) 81.6(4) ^e	505
[Cu(μ -ac)(phi)(H ₂ O)] ₂ (green)	m C2/c 4	23.441(5) 9.810(1) 13.752(3)	119.60(2)	CuO ₂ N ₂	N acO	1.986(9, 5) 1.924(7, 10)		O,O N,N	94.3(4, 9) 174.8(4, 1.5) 90.3(4) 81.2(4) ^e	506
[Cu(μ -phpp)(H ₂ O)(phen)] ₂ : (NO ₃) ₂ ·2H ₂ O (not given)	m C2/c 8	22.876(3) 12.284(2) 16.320(2)	111.03(2)	CuO ₃ N ₂	phiN acO H ₂ O	1.985(8, 31) 1.961(7, 2) 2.233(6)	3.014(2)	N,N N,O O,O	81.3(3) ^e 95.3(3, 50) 170.6(3, 5.2) 91.3(3, 2.0)	507
[Cu(μ -fm)(H ₂ O)(phen)] ₂ (NO ₃) ₂ ·4H ₂ O (deep blue)	not given	not given	not given	CuO ₃ N ₂	fmO H ₂ O phenN	1.954(3, 2) 2.009(4, 5) 2.201(3)	3.054(1)	N,N N,O O,O	82.74(15) ^e 92.86(15, 1.29) 101.53(15) 169.48(15, 4.62) 91.68(15, 1.36)	508

TABLE IV (Continued)

Compound	Cryst. cl. space Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å]	L-Cu-L [°]	Ref.
[Cu ₂ (μ -chh) ₂ (H ₂ O)](ClO ₄) ₂ 3.5H ₂ O ^b (blue)	m	22.97(2)	100.1(1)	CuO ₃ N ₂	H ₂ O 2.02(1)	3.570(3)	O,O 104.6(4,4)	509a
	P2 ₁	15.89(1)			N 1.98(1,1)		O,O 150.8(4)	
	4	10.00(1)			O 2.06(1)		N,O 89.7(6,2.4) ^d	
					N 2.21(1)		N,N 178.1(5)	
				CuN ₄	N 2.00(1,1)		N,N 94.6(5,3.9)	509b
					N 1.95(1)		O,O 135.3(6)	
							N,N 155.4(5)	
							O,O 105.5(4,2.6)	
				CuO ₃ N ₂	H ₂ O 2.07(1)		O,O 148.5(5)	509b
					N 1.96(1,1)		N,O 90.2(5,4.4) ^d	
					O 2.01(1)		N,N 176.8(5)	
					N 1.98(1,3)		N,N 95.0(5,4.6)	
				CuN ₄	N 1.97(1,1)		O,O 145.5(5,3.3)	509b
							O,N 82.35(7) ^d	
							O,N 94.50(9,2.48)	
							N,N 159.30(7)	
				CuO ₄ N	N 1.940(2)	3.923(2) ^e	O,O 91.54(9,2.12)	509b
					O 1.913(2,5)		O,O 102.80(6)	
					N 1.989(2)		O,O 174.37(7)	
							N,N 86.6(1) ^c	
				CuO ₃ N ₂	N 1.943(3,3)	4.525(1) ^c	O,N 94.4(1,2) ^d	510a
					O 1.920(3,4)		O,O 84.6(1)	
					N 2.006(5)		O,O 54.1(2) ^g	
					O 1.944(6,3)		O,O 84.6(2,1.1) ^c	
				CuO ₅ N	N 2.023(4)	4.566(1)	O,N 158.1(3,8.1)	510b
					O 2.665(5)		O,N 89.5(2,6.0)	
					H ₂ O 2.123(6)		O,N 114.2(3)	
							O,N 149.4(2)	

$[\text{Cu}(\mu\text{-NCNH})(\text{Me}_3\text{tac})]_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (green)	m P ₂ /n 4	16.458(4) 11.914(3) 16.646(4)	92.90(3)	CuN ₅	N HNCN	2.074(5.8) 2.221(6) 1.968(6.9) 2.017(6)	not given	N,N N,N	84.8(3) ^c 91.3(3, 1.7) 170(1)	511
$[\text{Cu}(\mu\text{-NCNH})(\text{Me}_3\text{tac})]_2$ (black)	m C ₂ /c 8	29.64(1) 14.756(5) 15.700(4)	117.42(2)	CuN ₅	N tacN	1.981(4, 8) 2.066(4, 22) 2.233(4, 3)	4.803(2)	N,N	84.0(2, 1.50) ^c 95.0(2, 4.2) 175.4(4, 2.0)	512
$[\text{Cu}(\mu\text{-etaH})(\mu\text{-eta})]_2(\text{NO}_3)_2$ (blue)	tr P-1 2	9.990(2) 11.454(1) 9.977(2)	111.10(1) 90.02(1) 119.92(1)	CuO ₂ N ₂	N O	1.990(5, 5) 1.958(5, 3)	4.940(5)	O,N N,N O,O	85.0(2, 1) ^c 98.6(2) 91.4(2)	513
$[\text{Cu}(\mu\text{-mepH})(\mu\text{-mep})(\text{H}_2\text{O})]_2 \cdot (\text{NO}_3)_2$ (violet)	m, P ₂ /c 2	6.232(1) 14.036(4) 17.097(4)	105.79(2)	CuO ₃ N ₂	N O H ₂ O	1.988(5, 1) 1.957(4, 9) 2.313	4.942(5)	O,N N,N O,O	84.8(2, 1) ^c 99.4(2) 91.1(2)	513
$[\text{Cu}(\mu\text{-tris})_2\text{H}(\text{H}_2\text{O})]_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (blue)	tr P-1 4	19.785 11.798(6) 6.489(3)	90.13(5) 96.39(5) 91.84(5)	CuO ₃ N ₂	N O H ₂ O	1.999(6, 1) 1.967(5, 27) 2.752(5) 2.361(5)	4.979	O,N O,N	84.0(2, 2) ^c 86.2(2, 3)	514
$[\text{Cu}_2(\text{mepH})_4(\text{H}_2\text{O})(\text{SO}_4)] \cdot \text{MeOH}$ (blue)	tr P-1 2	10.808(4) 10.958(4) 12.738(5)	78.27(3) 86.61(3) 77.07(3)	CuO ₃ N ₂	N O H ₂ O	1.999(4, 14) 1.945(3, 1) 2.271(4)	4.979(1)	O,N	84.6(1, 7) ^c 93.0(2, 5.4) 170.5(1, 1.5) 95.1(1, 8.1) 96.7(1)	515
$[\text{Cu}(\mu\text{-diimH})]_2$ (green)	tr P-1 2	9.554(3) 13.025(4) 11.662(3)	131.29(1) 98.02(3) 94.31(1)	CuO ₂ N ₂	N O O ₃ SO	2.012(4, 6) 1.945(3, 20) 2.366(3)	4.99(1)	O,N O,O N,N	84.1(1, 2) ^c 89.6(1, 1.7) 171.7(1, 2.1) 95.2(1, 6.2)	516
$[\text{Cu}(\mu\text{-N}_3)(\text{Me}_6\text{en})(\text{N}_3)]_2$ (dark green)	m P ₂ /c 2	9.581(5) 13.746(4) 8.869(1)	101.000(5)	CuN ₅	N N ₃ N	2.021(7, 78) 1.961(5, 18) 2.456(6)	5.004(2)	N,N	87.7(4, 2.1) ^c 93.8(6, 5.3) 169.0(9, 6.2)	517

TABLE IV (Continued)

Compound	Cryst. cl. space Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å]	L-Cu-L [°]	Ref.
[Cu(μ -pca) ₂ (phen)] ₂ (red)	m P2 ₁ /c 2	9.625(3) 20.945(5) 9.956(3)	97.10(2)	CuN ₅	bpyN pcaN 2.355(6)	5.009(6)	N,N N,N 166.2(2, 3, 6)	343b
[Cu(μ -H ₂ atp)(phen)] ₂ ·7H ₂ O (blue green)	m P2 ₁ 2	11.807(3) 24.824(5) 10.693(2)	94.98(3)	CuO ₄ N ₂	phenN atpO 2.284(8) 2.878(9)	5.028(3) ^f	N,O N,O O,O 91.7(4, 5.1) ^d	518
[Cu(μ -[datH](imH)] ₂ ·2H ₂ O (blue)	tr P-1 1	8.087(1) 9.334(1) 9.817(1)	77.80(1) 77.01(2) 82.88(1)	CuO ₃ N ₃	imN idaN O 1.939(1) 2.424(1) 2.873(2)	5.0295(3)	O,O 157.76(4) N,O 88.4(1, 5.0) 108.45(5) 175.17(6) 93.5(6, 5) 172.77(6)	519
[Cu(trisH)(tris)] ₂ Br ₂ (green)	m P2 ₁ /c 2	11.394(2) 10.049(2) 12.149(2)	95.89(2)	CuO ₂ N ₂	N O 1.994(13, 1) 1.981(11, 38)	5.044	O,O O,N N,N 83.8(5, 1.5) ^e 96.4(6)	520
[Cu(μ -3'-gmp)(H ₂ O)(phen)] ₂ · 7H ₂ O (blue green)	tr P1 1	6.857(1) 13.888(3) 14.815(2)	108.30(2) 88.96(2) 95.48(2)	CuO ₃ N ₂	gmpO phenN H ₂ O 2.472(6)	5.075(1) ^f	not given	521
[Cu(μ -ammpH)(H ₂ O)Cl] ₂ (blue green)	tr P-1 1	8.975(2) 8.658(2) 6.326(2)	90.32(1) 117.34(1) 94.37(1)	CuO ₃ Cl ₂	O H ₂ O Cl 1.938(7, 7) 2.014(6) 2.268(3) 2.637(2)	5.081(2)	Cl,Cl Cl,O O,O 172.9(3)	522a
[Cu(μ -cmp)(dpa)(H ₂ O)] ₂ ·5H ₂ O (green)	m P2 ₁ 2	7.724(3) 18.221(6) 18.563(6)	99.00(2)	CuO ₃ N ₂	dpaN H ₂ O cmpO 1.95(-, 2)	5.101(2) ^f	not given	522b

$[\text{Cu}(\mu\text{-5-ump})(\text{dpa})(\text{H}_2\text{O})]_2 \cdot 5\text{H}_2\text{O}$ (green)	m P2 ₁ /n 2	7.739(3) 18.248(6) 17.473(7)	90.04(2)	CuO_3N_2	umpO H ₂ O dpaN	1.94(1, 2) 2.32(1, 3) 1.99(1, 4)	5.122(3) ^e	N ₁ N N ₁ O	89.3(6, 4) ^d 91.4(6, 4.0) 103.6(5, 2.7) 168.1(6, 6.8) 91.1(5, 4.1)	523a
$[\text{Cu}(\mu\text{-poapH})(\text{H}_2\text{O})]_2$ (not given)	m P2 ₁ /n 4	9.977(7) 7.801(8) 14.615(11)	108.55(5)	CuO_4N	H ₂ O poapN O	1.939(5) 2.064(5) 1.963(4, 24)	5.142(4) ^f	N ₁ O	87.5(2, 3) ^e 96.3(2) 165.7(2) 93.7(3, 4.9) 173.8(2)	523b
$[\text{Cu}(\mu\text{-5'-imp})(\text{dpa})]_2 \cdot 3.62\text{H}_2\text{O}$ (not given)	m P2 ₁ 2	7.828(2) 18.552(3) 17.378(3)	91.16(3)	CuO_3N_2	N O	2.024(1, 3) 1.906(1, 4)	5.157(1) ^e	N ₁ N O ₁ N	89.87(2) ^d 88.4(2, 3.0) 168.07(4, 4.4) 91.25(2)	523c
$\beta\text{-}[\text{Cu}(\mu\text{-5'-imp})(\text{dpa})(\text{H}_2\text{O})]_2 \cdot 4\text{H}_2\text{O}$ (dark green)	m P2 ₁ 2	7.828(2) 18.552(3) 17.378(3)	91.16(2)	CuO_3N_2 ??	N O	2.015(1, 1) 1.942(1, 4)		N ₁ N O ₁ N	87.86(2) ^d 93.3(2, 6.7) 100.43(3) 169.3(3, 8) 90.4(2, 1)	523d
$[\text{Cu}(\mu\text{-N}_3)(\text{Me}_3\text{dien})]_2(\text{BF}_4)_2$ (not given)	m P2 ₁ /n 2	12.798(2) 19.538(3) 13.072(2)	93.64(1)	CuN_5	H ₂ O N ₃ N	2.27(2) 2.42(2) 2.02(2, 3) 1.92(2, 2)	5.157(3) ^e	O ₁ O O ₁ N	91(1, 1) 90(1, 2) 102(1, 4) 169(1, 5) 89(1, 1) ^d	524a
$\beta\text{-}[\text{Cu}(\mu\text{-NCS})(\text{NCS})(\text{dmpH})]_2$ (dark brown)	m P2 ₁ /n 4	10.928(3) 14.709(3) 12.804(3)	95.31(2)	CuN_4S	N SCN μNCS μSCN	2.027(2, 32) 1.937(2) 2.413(1) 2.205(2)	5.369(2) ^e	N ₁ N	92.6(1, 4.1) 102.0(1) 170.3(1) 87.5(1, 1.8) 100.5(1) 157.3(1)	524b

TABLE IV (Continued)

Compound	Cryst. cl. space Gr. Z	<i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]	α [°] β [°] γ [°]	Chromophore	<i>Cu-L</i> [Å]	<i>Cu-Cu</i> [Å]	<i>L-Cu-L</i> [°]	Ref.	
[Cu(μ -NCS)(den)(ClO ₄) ₂] (blue)	tr	11.81(2)	70.9(3)	CuN ₄ O ₈	N	2.02(1, 1)	N,N	84.3(5, 3) ^f	
	P-1	7.48(2)	89.7(3)		O ₃ ClO	2.90(1)	5.51	N,N	95.1(4, 1.0)
	2	7.48(2)	105.4(3)		μ -SCN μ -NCS	1.95(1) 2.76(1)		S,N	94.8(4, 5.7)
[Cu(μ -NCS)(dpr)(ClO ₄) ₂] (blue)	or	13.94(2)		CuN ₄ O ₈	dprN	2.02(1, 5)	N,N	85.7(4, 7)	
	Pbca	12.39(2)			SCN	2.00(1)	5.53	N,N	93.5(4, 2.2) ^d
	8	15.85(2)			NCS	2.79(1)		N,S	95.2(4, 4.8)
					O ₃ ClO	2.97(1)			
[Cu(μ -NCS)(NCS)(dmtp) ₂] (green)	m	19.088(7)		CuN ₄ S	N	2.010(8, 10)	N,N	90.0(4, 1.9)	
	C2/c	11.516(8)	104.51(4)		SCN	1.954(9, 1)	5.552	N,S	92.4(3, 7.9)
	28	20.118(7)			NCS	2.886(4)			
Na ₄ [Cu(μ -NCS)(sal- β -ala)] ₂ (NCS) ₂ ·4H ₂ O (dark green)	tr	6.989(3)	84.88(5)	CuO ₂ N ₂ S	O	1.924(3, 20)	O,O	170.8(1)	
	P-1	10.445(5)	70.13(4)		N	1.950(4)	5.768(1)	N,S	92.5(1, 2.3)
	2	12.692(6)	86.72(6)		SCN	1.978(4)		O,S	93.0(1, 4.7)
				NCS	2.933(2)		O,N	86.5(1, 4)	
								93.3(1, 7) ^d	
							N,N	174.8(2)	
[Cu(tren)(CN)] ₂ (BPh ₄) ₂ (blue)	m	13.792(7)		CuN ₄ C	N	2.12(-, 4)	N,N	82.9(2, 3) ^e	
	P2 ₁ /c	10.338(6)	94.27		NC	1.97	6.090(1)	N,N	118.5(2, 6.0)
	4	20.316(14)						N,C	97.1(2, 2.2)
								177.9(2)	
[Cu(μ -5'-amp)(bp)(H ₂ O)] ₂ · (NO ₃) ₂ ·6H ₂ O (blue)	tr	10.195(2)	88.92(1)	CuO ₃ N ₂	bpvN	1.993(-, 28)		not given	
	P-1	12.305(4)	108.99(1)		H ₂ O	2.375(-, 15)	not given		
	1	11.805(1)	104.41(1)		ampO	1.929(-, 14)			

[Cu(μ -NCS)(tren)] ₂ (BPh ₄) ₂ (green)	m P2 ₁ /c 2	14.977(5)	CuN ₅	N	2.068(6, 21)	N,N	83.9(2, 3) ^c	529			
		9.764(2)							μ SCN	6.136(1)	96.1(3, 7)
		21.226(6)								118.8(2, 6.5)	179.0(2)
[Cu(μ -NCO)] ₂ (tren)] ₂ (BPh ₄) ₂ (blue)	m P2 ₁ /c 2	14.003(6)	CuN ₅	N	2.08(1, 2)	N,N	83.8(5, 1.0) ^c	529			
		10.339(5)							OCN	6.540(2)	96.3(5, 3.3)
		20.436(9)								118.9(5, 7.3)	176.7(6)

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

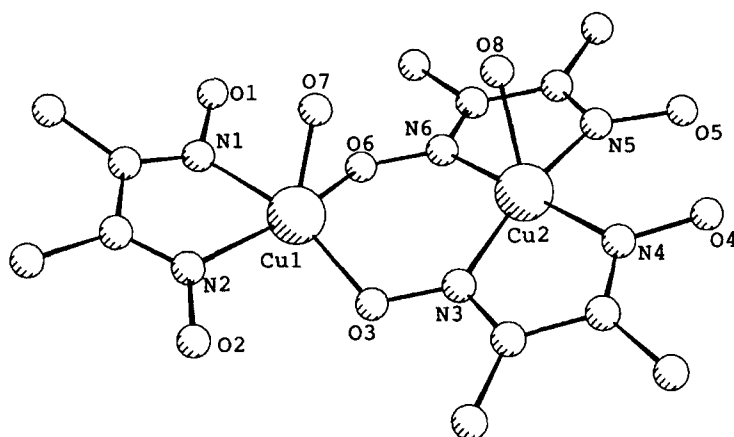


FIGURE 4 Structure of $[\text{Cu}_2(\mu\text{-dmgH})_2(\text{dmgh}_2)(\text{H}_2\text{O})]$ (see Ref. 484).

The structure of $[\text{Cu}(\mu\text{-C}_{15}\text{H}_{20}\text{N}_3\text{O}_2)(\text{ClO}_4)_2]_2[\text{Cu}(\mu\text{-C}_{15}\text{H}_{20}\text{N}_3\text{O}_2)(\text{MeOH})_2](\text{ClO}_4)_2$ ⁴⁸⁸ consists of a relatively isolated complex cation $[\text{Cu}_2\text{L}_2(\text{MeOH})_2]^{2+}$, a neutral $\text{Cu}_2\text{L}_2(\text{ClO}_4)_2$ molecule and unattached ClO_4^- anions. The Cu–Cu separations are almost identical, 3.684 and 3.686 Å, respectively.

The compound $\text{Cu}(\mu\text{-4Br-3CO}_2\text{mepa})(4\text{-Brdmpz})_2$ ⁴⁹⁶ exists in two isomeric forms, monoclinic and triclinic, differing mostly by the degree of distortion, with Cu–Cu separations of 3.923(1) and 3.924(1) Å, respectively.

There are thirty-six derivatives (Table IIIB) in which two Cu(II) atoms are doubly bridged by three atoms. The structure of $[\text{Cu}_2(\mu\text{-ac})_2(\text{H}_2\text{O})(\text{bpy})_2]^{2+}$ is shown in Figure 5⁵⁰⁵ as an example of this class. The structure consists of a dicopper(II) unit held by two acetate ions in a syn–syn bridging arrangement. The chelating 2,2'-bipyridine ligands occupy the equatorial sites and are in syn positions stabilized by stacking interactions. The coordination geometries of the two Cu(II) centers are square planar and square pyramidal. The Cu–Cu separation of 2.965(3) Å is the shortest in this class. In another four derivatives^{506–508,510} two carboxylate groups bridge two Cu(II) atoms in a similar way.⁵⁰⁵

In blue $[\text{Cu}_2(\mu\text{-chh})_2(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot 3.5\text{H}_2\text{O}$ ⁵⁰⁹ each of the two cyclo-L-histidyl-L-histidylato ligands (chh) used three atoms (OCN) for bridging two Cu(II) atoms.

There are six compounds^{513–516,520} where the dimers are held together by two cooperative O–H–O hydrogen bonds (oxygen–oxygen distances range from 2.31 to 2.52 Å). Two azide groups serve as a bridge^{517,524} while several others^{518,519,521–523} contain two OPO moieties in a syn–syn arrangement as

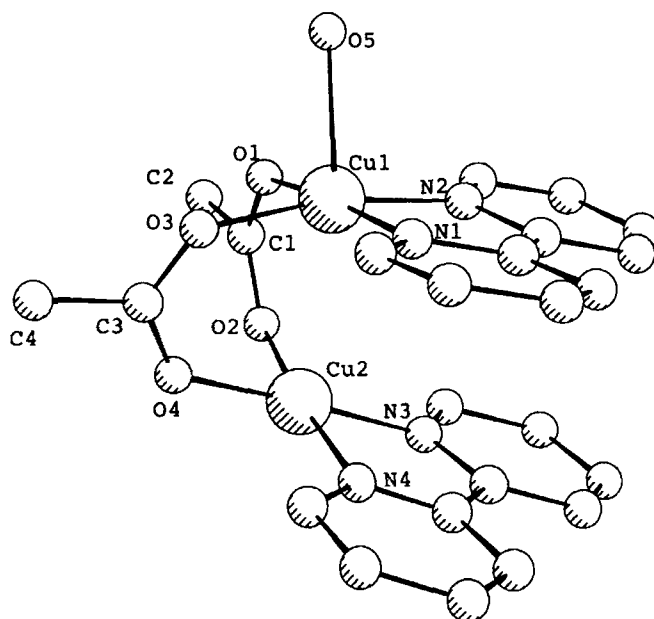


FIGURE 5 Structure of $[\text{Cu}_2(\mu\text{-ac})_2(\text{H}_2\text{O})(\text{bpy})_2]^{2+}$ (see Ref. 505).

bridges. Two thiocyanate groups acting as bridges between two Cu(II) atoms in five derivatives^{525–529} and in the remaining example⁵²⁹ two NCO groups serve as bridges.

The Cu–Cu separation in this class Table IVB ranges from 2.965(3) to 6.540(2) Å which is somewhat narrower than those found for derivatives given in Table IVA (3.396(1) to 7.678(2) Å).

The Cu(II) atoms are surrounded mostly by O and N donor atoms of the respective ligands in a square-planar,^{513,516,520} square-pyramidal,^{343,506–508,514,515,517,521–523,526,527} trigonal-bipyramidal,^{512,528,529} intermediate square-pyramidal ↔ trigonal-bipyramidal,⁵²⁴ and in a *pseudo*-octahedral arrangement.^{518,519,525} There are two examples, which contain two non-equivalent Cu(II) atoms, one⁵⁰⁵ has a square-pyramidal (CuO_3N_2) and a square-planar configuration (CuO_2N_2), and the other complex⁵⁰⁹ has an intermediate square planar ↔ trigonal bipyramidal (CuO_3N_2) and a tetrahedral configuration (CuN_4).

Inspection of the data in Table IV reveals that in the series of over fifty examples most are blue and green, but there are quite a few black, red, purple, brown and yellow compounds.

The mean Cu–L bond distance in the series of monodentate ligands increases with coordination number, five-coordinated *vs.* six-coordinate, the values are 1.96 *vs.* 1.98 Å for N donors and 2.32 *vs.* 2.52 Å for O donors. In the series of bidentate O donor ligands, the mean Cu–O bond distance increases in the order: 1.92 Å (four-) < 1.95 Å (five-) < 2.36 Å (six-coordinated).

On the other hand, in the series of bidentate N donor ligands, the mean Cu–N bond distance increases in the sequence: 1.98 Å (four-) < 2.015 Å (six-) < 2.07 Å (five-coordinate). In the series of multidentate ligands the mean Cu–L bond distance for six coordinate increases in the order: for O donors 2.36 Å (bi-) < 2.365 Å (tetra-) < 2.5 Å (monodentate) and for N donors in the order: 1.98 Å (mono-) < 2.01 Å (tetra-) < 2.015 Å (bi-) < 2.17 Å (pentadentate). For five-coordinate compounds the mean Cu–N bond distance increases in the order: 1.98 Å (mono-) < 2.05 Å (tri-) < 2.07 Å (bi-) ~ 2.07 Å (tetra-) < 2.08 Å (hexadentate).

The multidentate ligands include both homo- and hetero- donor atoms, with O- and N-donors being by far the most common. In the series of hetero-bidentate ligands O plus N and N plus S(NCS)-donor sites are found. Tridentate ligands include those with two O plus one N, and one O plus two N-donor sites. Tetradentate ligands, include three O plus one N, two O plus two N, one O plus three N donor sites. Pentadentate ligands, include four O plus one N, two O plus three N donor sites.

The steric effect can be seen in variations of the L–Cu–L bond angles. When there is an intra-ligand metallocyclic ring, the internal L–Cu–L angle closes with increasing coordination number. For example, for five-membered rings, the mean O–Cu–N bond angles are: 83.5°(four-) > 83.0°(five-) > 79.5°(six-coordinate); and for six-membered metallocyclic rings with N–Cu–N bond angles the values are: 95.4°(four-) > 92.8°(five-) > 89.5°(six-coordinate). The intra-ligand metallocyclic bite angle opens with an increasing number of atoms, as expected. For example, the mean O–Cu–O bond angles are: 54.0°(four-) < 84.5°(five-) < 91.5°(six-membered).

2.2.6 By Carbonate Group Bridges

Crystallographic and structural data for μ -carbonate Cu(II) dimers are given in Table V. The structures are in order of increasing Cu–Cu separation. There are five derivatives (green(3), blue(2)) in which the μ -carbonate bidentate group is bound to both Cu(II) centers symmetrically.

The structure of $[\text{Cu}_2(\mu\text{-CO}_3)(\text{tmtacd})_2]^{2+}$ (see Ref. 531) is shown in Figure 6 as an example of this group. In all five derivatives^{530–533} each Cu(II) atom is five coordinate (square-pyramidal^{530–532} and trigonal-bipyramidal.⁵³³ The Cu–Cu separations range from 4.044(2) to 4.601(2) Å and

TABLE V Crystallographic and structural data for μ -carbonate copper(II) dimers^a

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	Chromophore	α [°] β [°] γ [°]	$Cu-L$ [Å]	$Cu-Cu$ [Å] $Cu-O-Cu$ [°]	$L-Cu-L$ [°]	Ref.
$[Cu_2(\mu-CO_3)\{HB-(3,5-i-Pr_2pz)_2\}_2] \cdot 2MeCN$ (green)	or Pbca 8	24.058(7) 25.664(5) 22.844(6)	CuN_3O_2	N^b CO_3O μO	1.970(5,8) 2.000(5,1) 2.024(4,5)	4.044(2) 175.7(2)	O,O^b O,N 160.4(2,4,9) 91.2(2,2,3) ^c	530
$[Cu_2(\mu-CO_3)(tmtacd)_2](ClO_4)_2 \cdot dmf$ (green)	or Iba2 4	16.19(1) 16.67(1) 15.43(1)	CuN_3O_2	N CO_3O μO	1.970(8,9) 2.195(7) 2.028(5) 2.041(1)	4.080(1) ^e 176.6(2)	N,N N,N N,O 93.6(3,3) ^d 104.5(3) 97.6(4,1,2) 109.0(2) 144.2(3) 160.7(3) 65.3(3) ^e	531
$[Cu_2(\mu-CO_3)(Me_4pn)_2Cl_2]$ (dark green)	m P2 ₁ /n 4	16.922(4) 7.942(2) 17.343(4)	CuO_2N_2Cl	N Cl CO_3O μO	2.054(8,28) 2.360(3,1) 1.975(7,3) 2.076(6,7)	4.143(2) 172.7(4)	O,O Cl,O 119.2(2,1,2) 63.7(3) ^e Cl,N O,N 94.4(3,3,5) 136.1(4,2) 155.1(3,2) 97.8(3,1) ^e	532
$[Cu_2(\mu-CO_3)(Et_5dien)_2](ClO_4)_2$ (dark blue)	m P2 ₁ 2	12.037(1) 13.145(3) 12.519(2)	CuN_3O_2	N CO_3O μO	2.043(4,53) 2.264(3,10) 1.977(3,2)	4.495(1) ^f 165.8(1)	N,N O,O O,N 62.3(1,4) ^e 102.6(2,7,2) 164.7(2,3) 87.0(2,3) ^e 143.9(2,1)	533

TABLE V (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å]			α [°]			Chromophore	Cu-L [Å]	Cu-Cu [Å]		L-Cu-L [°]	Ref.
		b [Å]	c [Å]	β [°]	γ [°]	Cu-O	Cu						
[Cu ₂ (μ -CO ₃)(Et ₃ dien) ₂](ClO ₄) ₂ (dark blue)	or Cm2 ₁ 4	18.610(3)						CuN ₃ O	N	4.601(2) ^e	O,O	61.4(2.3) ^c	533
		15.449(3)							CO ₃ O	163.0(3)	O,N	103.6(4, 5.4)	
		14.499(7)							μ O			167.4(4, 9)	
											N,N	85.9(2.2) ^f	
												145.5(4, 1.8)	

^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 Four-membered metallocyclic ring. ^d Six-membered metallocyclic ring. ^e Calculated by us. ^f Five-membered metallocyclic ring.

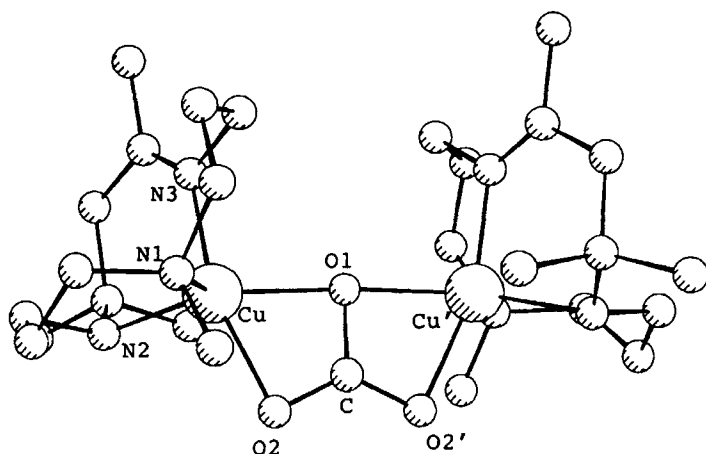


FIGURE 6 Structure of $[\text{Cu}_2(\mu\text{-CO}_3)(\text{tmtacd})_2]^{2+}$ (see Ref. 531).

Cu–O–Cu bridge angle from $176.6(2)$ to $163.0(3)^\circ$. There is a relationship between these two values, when the Cu–Cu separation elongates, the Cu–O–Cu bridge angle closes. For example: $4.086(1) \text{ \AA}$ and $176.6(2)^\circ$,⁵³¹ $4.143(2) \text{ \AA}$ and $172.7(4)^\circ$,⁵³² $4.495(1) \text{ \AA}$ and $165.8(1)^\circ$,⁵³³ and $4.601(2) \text{ \AA}$ and $163.0(3)^\circ$.⁵³³

The dark blue, $[\text{Cu}_2(\mu\text{-CO}_3)_2(\text{Et}_2\text{dien})_2](\text{ClO}_4)_2$ ⁵³³ exists in two isomeric forms, monoclinic and orthorhombic, differing mostly by degree of distortion provide another example of isomerism.¹⁴⁴

The mean Cu–O and Cu–O_(bridge) bond distances are 2.118 and 2.014 \AA , respectively. The mean Cu–N bond distances for bidentate ligands of 2.05 \AA is somewhat longer than those of tridentate ligands (2.025 \AA).

2.2.7 Oxalate Type

Crystallographic and structural data for the Cu(II) oxalate type dimers are summarized in Table VI. The structures are tabulated in order of the increasing Cu–Cu separation. There are almost thirty derivatives and most are blue, with some green and violet. The structure of the blue compound $[(\text{phen})(\text{NO}_3)\text{Cu}(\text{ox})\text{Cu}(\text{NO}_3)(\text{phen})]^{537}$ is shown as a representative example (Figure 7). The two $(\text{phen})\text{Cu}(\text{NO}_3)$ moieties are bridged by an oxalato group with each Cu(II) atom being bound to two oxygens from the two different carboxylic groups. Each Cu(II) is in a square-pyramidal environment with $\text{N}_{(1)}$, $\text{N}_{(2)}$, $\text{O}_{(1)}$, and $\text{O}_{(2)}$ in the basal plane and $\text{O}_{(3)}$ from a nitrate group coordinated in the apical position. The Cu–Cu separation is $5.158(1) \text{ \AA}$.

TABLE VI Crystallographic and structural data for copper(II) oxalate type dimers^a

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å]	L-Cu-L [°]	Ref.	
[Cu ₂ (μ-ox)(H ₂ O) ₂ (Me ₆ en) ₂] (ClO ₄) ₂ ·1.25H ₂ O ^c (blue)	tr	18.995(3) 10.019(3) 7.658(3)	98.30(3) 98.37(3) 88.19(2)	CuO ₃ N ₂	μoxO ^b N H ₂ O	5.147(2)	O,O ^b O,N N,N	84.0(2) ^d 89.3(2, 1.8) 96.3(2, 5.3) 171.3(2, 4.1)	534
	2			CuO ₃ N ₂	μoxO N H ₂ O	5.167(2)	O,O O,N N,N	84.0(2) ^d 91.8(2, 1) 96.1(2, 6.1) 169.4(2, 3.4) 87.6(2) ^d	
				CuO ₃ N ₂	μoxO N H ₂ O	5.149(1)	O,O O,N N,N	83.4(3) ^d 95.3(3, 7) 96.4(2, 2.1) 174.2(2, 1.5) 81.7(3) ^d	535
				CuO ₄ N ₂	N O ₂ NO H ₂ O μoxO	5.268(1)	O,O O,O N,N	87.7(3, 6.4) 93.9(3, 5.4) 103.5(2) 169.8(3) 172.3(3, 2) 81.0(2) ^d	
[Cu ₂ (μ-ox)(NO ₃) ₂ (mep) ₂] [Cu ₂ (μ-ox)(NO ₃) ₂ (mep) ₂ (H ₂ O)] ₂ (green blue)	m	20.073(4) 13.842(4) 20.070(4)	119.09(3)	CuO ₄ N ₂	N O ₂ NO H ₂ O μoxO		O,O O,O N,N	52.6(4) ^e 84.0(3, 6) ^d 90.1(3, 4.0) 117.5(3) 168.1(2) 94.5(3, 7.1) 105.9(3) 139.6(3) 171.1(3) 77.5(3) ^d	
	P2 ₁ /n			CuO ₄ N ₂	N O ₂ NO H ₂ O μoxO		O,O O,O N,N		
	4			CuO ₄ N ₂	N O ₂ NO H ₂ O μoxO		O,O O,O N,N		

[Cu ₂ (μ-ox)(H ₂ O) ₂ (bpy) ₂] [Cu(ox)(bpy)](NO ₃) ₂ (blue)	m C2/c —	21.739(2) 10.458(1) 16.023(2)	95.69(1)	CuO ₃ N ₂	bpyN H ₂ O μoxO 1.948(2,3) 2.246(2) 1.979(2,4)	5.154(1)	not given	536
[Cu ₂ (μ-ox)(NO ₃) ₂ (phen)] ₂ (blue)	tr P-1 2	9.977(6) 9.658(6) 7.036(3)	108.03(4) 95.40(4) 90.22(4)	CuO ₂ N ₂ (monomer) CuO ₃ N ₂	oxO bpyN phenN O ₂ NO μoxO 1.912(2) 1.956(2) 1.999(2,8) 2.216(2) 1.984(2,3)	5.158(3)	not given 82.5(1) ^d 96.1(1,4,6) 164.3(1,2,4) 84.6(1) ^d 97.8(1,5,5) 119.8(3,1)	537
[Cu ₂ (μ-ox)(H ₂ O) ₂ (bpy) ₂] [Cu(ox)(bpy)]SO ₄ (blue violet)	m C2/c 4	22.706(5) 10.485(3) 16.172(4)	92.63(3)	CuO ₃ N ₂	bpyN H ₂ O μoxO 2.044(12,21) 2.301(13) 2.012(13,22)	5.162	O,O 86.0(8) ^d 93.0(8,4,0) 97.1(8,2,8) 169.3(8,6,0) 78.8(7) ^d	538
[Cu ₂ (μ-ox)(H ₂ O) ₂ (mep) ₂](PF ₆) ₂ (mep).3H ₂ O (green blue)	or Pnma 8	21.864(3) 20.881(5) 11.451(3)		CuO ₂ N ₂ (monomer) CuO ₃ N ₂	oxO bpyN N H ₂ O μoxO 1.911(10) 2.041(22) 1.99(1,1) 2.24(1) 1.972(9,8)	5.175	O,O 84.7(4) ^d N,N 87.7(6) ^d O,N 94.0(6) O,N 97.3(4,4,9) 102.1(4) 166.0(4,4,0) 82.1(4) ^d 83.9(3) ^d 94.2(3,5,3)	535
[Cu ₂ (μ-bedao)(Me ₂ CO) ₂](BPh ₄) ₂ (violet)	m P2 ₁ /n 2	16.639(7) 18.305(9) 11.089(9)	103.2(2)	CuN ₃ O ₂	N O Me ₂ CO 1.899(6) 2.001(7,7) 1.988(5) 2.609(8)	5.189(2)	N,N 85.3(3,2,7) ^d 170.0(3) 84.9(2) ^d 93.8(3,10,2) 166.2(3) 97.1(2)	539
[Cu ₂ (μ-ox-d)(ClO ₄) ₂ (bpy) ₂] ₂ 2dmf (blue)	tr P-1 2	10.079(2) 10.457(2) 8.566(2)	96.99(2) 91.94(2) 100.69(1)	CuN ₃ O ₂	bpyN O ₃ ClO μoxO μoxdN 1.994(11) 2.433(9) 1.959(12) 1.944(9)	5.192(2)	O,O 97.1(2) N,O 86.1(4) ^d 94.3(4,4,6) N,N 83.6(4) ^d 90.2(4) O,O 96.2(4)	540

TABLE VI (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å]	L-Cu-L [°]	Ref.
$[\text{Cu}_2(\mu\text{-oxd})(\text{H}_2\text{O})_2(\text{Me}_4\text{en})_2]$ (PF_6) ₂ (blue)	m C2/c —	25.099(4) 12.419(2) 20.432(4)	106.62(1)	CuN_3O_2 Me ₄ en H ₂ O μoxd μoxdN	2.025(6,8) 2.636(5,35) 1.959(5,4) 1.944(5,14)	5.194(1)	O,O O,N 174.7(2,1,2) N,N 87.4(2,1) ^d 93.9(2,5) 173.9(2,2,0)	541
$[\text{Cu}_2(\mu\text{-oxpn})(\text{bpy})(\text{ClO}_4)_2]$ (not given)	m P2 ₁ /c 4	12.548(2) 19.314(4) 10.549(1)	96.72(1)	CuN_4O bpyN μoxpnN O ₃ ClO	1.993(3,4) 1.982(2,1) 2.887(5)	5.195(1)	O,N O,N N,N 92.4(1,4,2) 176.9(1,3)	542
$[\text{Cu}_2(\mu\text{-ox})(\text{fbo})_2(\text{Me}_4\text{en})_2] \cdot \text{C}_6\text{H}_6$ (blue)	m C2/m 2	14.581(5) 12.484(4) 13.239(5)	123.05(2)	CuO_3N_2 enN fboO μoxO	1.967(2,8) 1.930(2,2) 2.482(2)	5.215(3) ^f	O,O O,N N,N 82.15(9) ^d O,N 95.3(2,3,2) 160.3(2) 86.4(3) ^d 92.1(1) 82.8(1) ^d 102.7(1)	543a
$[\text{Cu}_2(\mu\text{-ox})(\text{H}_2\text{O})_2(\text{NO}_3)_2(\text{mep})_2]$ $\cdot 2\text{H}_2\text{O}$ (green)	m P2 ₁ 2	7.559(4) 14.659(3) 16.246(3)	98.6(2)	CuO_4N_2 mepN H ₂ O O ₂ NO μoxO	2.010(7,53) 2.276(7,33) 2.606(8,30) 1.994(7,17)	5.218(8) ^f	O,O O,O O,N O,N N,N 83.4(2,1,1) ^d 87.6(3,6,0) 173.2(2,2,3) 93.5(3,8,0) 172.8(3,2,9) 81.4(3,5) ^d	543b

$[\text{Cu}_2(\mu\text{-ox})(\text{ox})(\text{C}_7\text{H}_{18}\text{N}_2)_2]\cdot\text{H}_2\text{O}$ (blue)	m P2 ₁ /c 4	8.551(8) 11.876(9) 26.353(9)	99.37(7)	CuO_3N_2	oxO N	1.974(5, 11) 2.273(4) 2.018(5, 21)	5.226(3)	N ₁ N N ₁ O	85.5(2) ^d 94.9(2, 6) 106.9(2) 149.8(2) 179.2(2)	544
$[\text{Cu}_2(\mu\text{-ox})(\text{Me}_4\text{en})_2(\text{H}_2\text{O})_2]\cdot$ (PF ₆) ₂ ·2H ₂ O (bright blue)	tr P-1 1	7.932(5) 8.117(7) 12.089(15)	96.89(9) 97.03(8) 102.44(6)	CuO_3N_2	Me ₄ en H ₂ O μoxO	2.024(8, 13) 2.241(7) 2.012(6, 20)	5.232(4)	O ₁ O O ₁ N	83.4(2) ^d 91.9(2, 3, 7) 97.1(3, 5, 4) 168.1(3, 5, 8)	545
$[\text{Cu}_2(\mu\text{-oxpn})(\text{Me}_3\text{dien})(\text{ClO}_4)_2]$ (not given)	m P2 ₁ /c 4	12.973(4) 15.500(6) 17.241(6)	108.00(3)	CuN_3O_2	dienN μoxpnO	2.047(7, 23) 2.316(5) 1.973(5, 34)	5.237(3) ^f	N ₁ N O ₁ O O ₁ N	87.2(3) ^d 83.3(2) ^d 94.7(3, 6, 1) 154.3(2) 174.1(3) 85.9(3, 1, 6) ^d 114.3(3)	542
$[\text{Cu}_2(\mu\text{-dmaeoxd})(\text{H}_2\text{O})_2(\text{NCO})_2]$ (dark blue)	m P2 ₁ /a 2	11.589(3) 12.456(1) 6.771(2)	102.39(2)	CuN_fO_2	H ₂ O OCN μoxdO N	2.288(3) 1.920(3) 2.046(2) 1.928(2) 2.079(3)	5.306(1) ^f	O ₁ O O ₁ N	85.0(1) 82.5(1) ^d 97.1(1, 2, 9) 164.01(9) 82.2(1) ^d 97.5(1) 165.0(1)	546

TABLE VI (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å]	L-Cu-L [°]	Ref.
[AsPh ₄] ₂ [Cu ₂ (μ -C ₂ S ₄)(odt) ₂] (blue)	tr	12.880(3)	97.65(2)	CuS ₄	2.228(2, 1)	5.317(3) ^f	S,S	547
	P-1	11.904(2) 11.333(2)	111.16(2) 112.69(2)	μ C ₂ S ₄ S	2.234(2, 11)			91.5(1, 1.1) 159.5(1, 6)
[Cu ₂ (μ -ox)(Et ₄ dien) ₂](BPh ₄) ₂ (green)	m	9.776(5)	91.83(2)	CuN ₃ O ₂	2.049(6, 36) 2.196(6)	5.410(1)	O,O O,N	80.2(2) ^d 96.2(2, 3.4)
	P2 ₁ /n 2	25.004(12) 14.551(6)		μ oxO	1.972(4) 2.174(4)			131.1(2) 177.5(2) N,N 86.2(3, 1) ^d 131.4(2)
[Cu ₂ (μ -ox)(Me ₄ en) ₂ (2-Me-im) ₂] (PF ₆) ₂ (violet blue)	tr	8.224(2)	94.63(2)	CuN ₃ O ₂	2.041(2, 16)	5.434(2)	O,O	79.64(7) ^d
	P-1 2	10.414(3) 11.7549(3)	108.57(2) 103.1(2)	enN imN μ oxO	1.991(2) 1.997(2) 2.208(2)			O,N 103.40(8, 2.52) 174.57(8) N,N 86.6(1) ^d 96.1(1) 152.56(9)
[Cu ₂ (μ -ox)(bpca) ₂] (blue violet)	tr	7.6793(6)	83.80(1)	CuN ₃ O ₂	1.976(5, 55)	5.442(1)	N,N	82.6(2, 4) ^d
	P-1 2	9.238(2) 10.007(2)	68.37(1) 69.44(1)	bpcaN μ oxO	1.957(3) 2.264(4)			163.5(2) O,N 96.3(2, 1.9) 110.4(2) 170.1(2) 72.3(1) ^d

$[\text{Cu}_2(\mu\text{-ox})(\text{Et}_3\text{dien})_2](\text{PF}_6)_2$ (dark blue)	m I2/c 4	13.436(9) 22.29(2) 19.59(1)	103.68(7)	CuN_3O_2	dienN μoxO	2.078(5, 61) 1.971(4) 2.229(4)	5.457(3)	O,O O,N N,N N,N	79.5(1) ^d 98.4(2, 5, 6) 178.1(2) 86.9(2, 3) ^d 153.4(2)	545
$[\text{Cu}_2(\mu\text{-ox})(\text{terpy})_2]$ $[\text{Cu}_2(\mu\text{-ox})(\text{H}_2\text{O})_2(\text{terpy})_2]$ $(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (blue green)	m P2 ₁ /c 2	13.443(2) 23.183(4) 12.394(1)	116.29(1)	CuN_3O_2	terpyN μoxO	1.990(5, 66) 1.932(4) 2.297(6(5))	5.469(2)	O,O O,N N,N	79.2(2) ^d 96.8(2, 4, 4) 175.6(2) 80.7(5, 5) ^d 160.4(2)	550
$[\text{Cu}_2(\mu\text{-ox})(\text{ClO}_4)_2(\text{daea})_2]$ (not given)	or Pbc2 ₁ 4	7.02(1) 13.25(3) 25.27(4)		CuO_3N_3	terpyN H ₂ O μoxO	2.005(5, 66) 2.387(6) 1.952(4) 2.327(5)	5.528(2)	O,O O,N N,N	78.1(2) ^d 86.5(2) 163.9 90.0(2, 1, 5) 100.4(2, 3, 5) 177.8(2) 79.8(2, 2) ^d 159.0(2)	551
$[\text{Cu}_2(\mu\text{-bilm})(\text{Me}_3\text{dien})_2](\text{BPh}_4)_2$ (purple)	tr P-1 1	11.265(4) 10.234(4) 15.999(5)	101.78(3) 104.04(3) 107.06(3)	CuN_5	daeaN O ₃ ClO μoxO dienN μbilmN	2.02(1, 5) 1.88(1) 2.78(-) 2.96(-) 2.00(1, 3) 2.26(1, 3) 2.061(3, 37) 1.993(3) 2.324(3)	5.488(6) ^f 5.489(1)	N,N N,O O,O N,N	83.9(8, 6) ^d 162.5(7) 94.3(7, 3, 7) 103.0(7) 178.3(7) 77.9(6) ^d 84.4(1, 1, 7) ^d 93.6(1, 1, 3) 102.3(1, 2, 4) 155.70(13) 174.10(12)	552

TABLE VI (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]			α [°] β [°] γ [°]	Chromophore	$Cu-L$ [Å]	$Cu-Cu$ [Å]	$L-Cu-L$ [°]	Ref.
		a [Å]	b [Å]	c [Å]						
[Cu ₂ (μ -ox)(ox) ₂ (bpy) ₂ ·2H ₂ O] (blue)	tr	9.673(3)	105.718(3)	bpyN	2.007(4, 5)	5.566(2) ^f	N,N	80.9(2) ^d	553	
	P-1	8.940(3)	110.347(3)	μ oxO	1.988(4, 4)		O,N	94.4(2, 5)		
	2	9.103(3)	97.539(3)	oxO	2.320(4, 1)		O,O	101.0(2, 2.1) 174.7(1, 1.0) 88.8(2, 2.8) 77.7(2, 3) ^d 159.5(1)		
[Cu ₂ (μ -dt(metome) ₂)]Br ₂] (not given)	m	12.907(12)	111.06(2)	N	1.950(7)	5.666(3)	N,Br	166.1(2)	554	
	P2 ₁ /c	6.701(4)		S	2.265(3)		N,S	86.3(2) ^d		
	2	14.878(10)		O	2.405(3)		N,O	91.5(3)		
[Cu ₂ (μ -ia)(MeOH) ₂ (ClO ₄) ₂ · (dark green)	m	15.00(1)	103.07(5)	MeHO	2.406(6)	7.587(2)	O,O	83.2(2) ^d	555	
	P2 ₁ /n	10.121(6)		O ₃ ClO	2.911(10)			84.1(3, 5.3)		
	4	24.19(3)		μ iaO	1.953(5, 2)		O,N	168.0(3)		
				enN	2.009(7, 1)		O,N	93.5(3, 3.9) 172.1(3, 1)		
				MeHO	2.395(6)	7.592(2)	O,O	88.3(3) ^d		
				O ₃ ClO	2.961(9)			83.0(2) ^d		
			μ iaO	1.959(5, 5)		O,N	86.7(2, 7.9)			
			enN	2.015(6, 1)		O,N	165.7(2)			
						N,N	94.6(2, 3.9) 171.3(2, 6) 88.6(3) ^d			

[Cu ₂ (μ-ca)(terpy) ₂](PF ₆) ₂ (not given)	m P ₂ ₁ /n 2	9.217(5)	CuN ₃ O ₂	terpyN μcaO	1.993(3, 61)	7.843(1)	O,O	77.9(1) ^d	556
		12.852(2)			1.943(2)		O,N	95.3(2, 3, 1)	
		16.642(9)			2.268(2)			104.9(1, 6, 6)	
[Cu ₂ (μ-ox)(terpy) ₂](PF ₆) ₂ ·2H ₂ O (green)	m P ₂ ₁ /n 2	9.002(1)	CuN ₃ O ₂	not given			N,N	80.0(2, 2) ^d	556
		12.597(2)						170.6(1)	
		16.538(3)						158.5(1)	

^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 There are two crystallographically independent molecules. ^d Five-membered metallocyclic ring. ^e Four-membered metallocyclic ring. ^f Calculated by us.

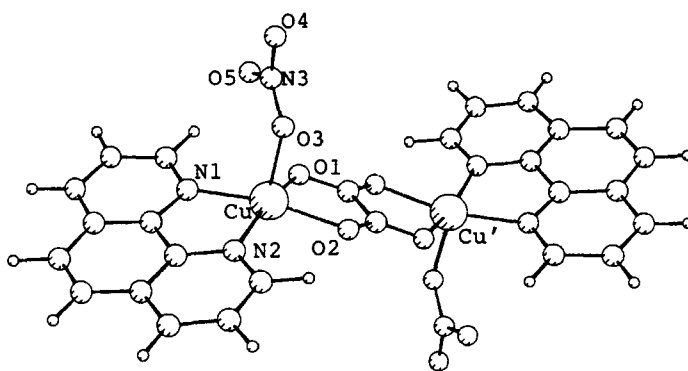


FIGURE 7 Structure of $[\text{Cu}_2(\mu\text{-ox})(\text{NO}_3)_2(\text{pheem})_2]^{537}$.

There are examples, in which μ -oxamidate,^{539–541} μ -oxamide,^{542,546} μ -tetrathiooxalate,⁵⁴⁷ μ -biimidazole,⁵⁵² μ -N,N'(1,2-dithioethane-1,2-diyl)bis-(methylmethionate),⁵⁵⁴ μ -iodanilate⁵⁵⁵ or μ -chloranilate⁵⁵⁶ serve as a bridge in the oxalate manner. In all remaining compounds a μ -oxalate serves as a bridge. In most derivatives^{524,534–537,539–542,545,546,549,552} each Cu(II) atom is in a square-pyramidal environment with different degrees of distortion. In two examples^{534,556} arrangement about Cu(II) atoms is intermediate between square pyramidal and trigonal bipyramidal. Another two derivatives^{548,554} are in a trigonal-bipyramidal environment. In one example each Cu(II) atom is coordinated by four S atoms in a square-planar configuration.⁵⁴⁷ Three examples^{551,553,555} contain *pseudo*-octahedrally coordinated Cu(II) atoms. Two non-equivalent Cu(II) atoms are present in two complexes;^{538,544} one has a square-pyramid and a square-planar environment; and the other one has a penta- and hexa-coordinate Cu(II).⁵³⁵ The Cu–Cu separations range from 5.147(2) to 7.843(1) Å, which exclude a metal–metal bond.

Inspection of the data in Table VI reveals that there are two examples^{534,555} which contain within the same crystal two crystallographically independent molecules, differing mostly by degree of distortion. Another two examples $[\text{Cu}_2(\mu\text{-ox})(\text{NO}_3)_2(\text{mep})_2][\text{Cu}_2(\mu\text{-ox})(\text{NO}_3)_2(\text{mep})_2(\text{H}_2\text{O})_2]^{535}$ and $[\text{Cu}_2(\mu\text{-ox})(\text{terpy})_2][\text{Cu}_2(\mu\text{-ox})(\text{H}_2\text{O})_2(\text{terpy})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}^{550}$ contain two crystallographically independent dimers. The Cu–Cu separations are 5.149(1) and 5.268(1) Å⁵³⁵ and 5.469(2) and 5.528(2) Å,⁵⁵⁰ respectively. Dimer and monomer within the same crystal were also found.^{536,538}

The environments about Cu(II) are built up mostly by O and N donors. The ligands involved are mono- through tetra-, hexa- and even octadentate.

In the series of homo-dentate ligands, the mean Cu–L bond distance for four-coordinated derivatives increases in the order: 1.94 Å (tetra O-donor;s) < 1.99 Å (bi-N-) < 2.23 Å (bi-S- and tetra-S-); for five-coordinated the order is: 1.95 Å (mono-N-) < 2.025 Å (bi-N-) < 2.04 Å (tri-N-) < 2.06 Å (tetra-O-) < 2.16 Å (tetra-N-) < 2.33 Å (Br) < 2.38 Å (mono-O-), and for hexa-coordinate the order is: 1.95 Å (tri-N-) < 2.03 Å (bi-N-) < 2.045 Å (tetra-O-) < 2.29 Å (bi-O-) < 2.36 Å (mono-O-donor;).

The heterobidentate ligands involved an O plus N atom; hexadentate ligands involved two O plus four N atoms; and octadentate ligands involved two O plus six N atoms and two O plus two N plus four S-donor sites.

The values of the L–Cu–L bond angles of the metallocyclic rings reflect the effects of both electronic and steric factors as well as coordination number. In five-membered rings the mean L–Cu–L intra-ligand angles, for four-coordinate derivatives, increase in the order: 84.0° (O-donor;) < 86.0° (N-donor;) < 92.0° (S-donor;); for five-coordinate derivatives, the order is 81.0° (O+N-donor;) < 82.5° (O-donor;) < 83.5° (N-donor;), and for six-coordinate the values are: 81.5° (O-donor;) < 83.8° (N-donor;) < 86.0° (N+S-donor).

2.2.8 Multi-atom Bridges

Crystallographic and structural data for complexes in which two Cu(II) atoms are doubly bridged by multidentate ligands forming two four- (or more) atom bridges are gathered in Table VII. Structures are listed in the order of increasing Cu–Cu separation. The structure of the violet compound $[\text{Cu}_2(\mu\text{-tae})(\text{ClO}_4)_4]^{566}$ is shown in Figure 8 as an example. Each Cu(II) atom is coordinated by two ring nitrogens and two pendant amino nitrogens; the two CuN_4 coordination sets face each other. Their coordination geometry is nearly square planar. The Cu(II) atom is displaced from the plane by 0.178 Å towards the center of the complex cation. The separation between the two Cu(II) atoms is 5.048(2) Å.

There are a variety of coordination geometries observed: square planar,^{557,559,560,565,566,584,585,594,595} an intermediate between square planar and tetrahedral,⁵⁶⁴ square pyramidal,^{562,563,567,569,571–575,577,579,583,586,588,590–592,596,597,599–601} trigonal bipyramidal,⁵⁷⁰ an intermediate between square pyramidal and trigonal bipyramidal,⁵⁷⁸ and *pseudo*-octahedral.^{561,568,576,581,582,589,593,598}

There is an example⁵⁵⁸ which contains two nonequivalent Cu(II) atoms, CuN_4O (trigonal bipyramidal) and CuN_4 (tetrahedral). The Cu–Cu separations range from 2.987(1) to 8.892 Å. The ligands cover the range from

TABLE VII Crystallographic and structural data for doubly bridged copper(II) dimers by multidentate ligands forming two four- or more atom bridges^a

Compound (color)	Cryst. cl. space Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å]	L-Cu-L [°]	Ref.
$\text{Na}_4[\text{Cu}(\mu\text{-tart})]_2 \cdot 10\text{H}_2\text{O}$ (blue)	m $\text{P2}_1/\text{n}$ 4	9.290(4) 10.894(5) 11.556(5)	94.85(6)	CuO_4	O^b 1.947(3, 14) 1.903(3, 13)	2.987(1)	O, O^b 85.5(1, 3) ^c 94.4(1, 1.8) 112.9(2, 4.9) 176.0(1, 4)	557
$[\text{Cu}_2(\mu\text{-bpdem})_2(\text{H}_2\text{O})]_2 \cdot 4.6\text{H}_2\text{O}$ (green black)	tr P-1 2	9.038(6) 11.535(6) 14.834(10)	90.74(4) 105.25(3) 98.84(4)	CuN_4O	N 2.044(4, 4) 1.975(4, 3) H_2O 2.250(3)	3.250(1)	N, N 80.6(2, 2) ^c 151.2(2) 172.5(2) 86.4(1, 1.0) 103.8(2, 2.7)	558
$[\text{Cu}(\mu\text{-enbpa})]_2$ (not given)	or Fddd 16	23.561(3) 16.723(2) 19.818(3)		CuN_4	N 2.017(4, 1) 1.943(4, 1)		N, N 82.0(2, 1) ^c 102.7(2, 2) 156.8(2, 3.5)	559
$[\text{Cu}(\mu\text{-qp-7})]_2$ (not given)	m $\text{P2}_1/\text{c}$ 2	15.36(1) 9.34(1) 31.05(2)		CuN_4	N 1.925 1.976	3.29	N, N 84.4 ^e 99.7 158.1(-, -2)	560
$[\text{Cu}(\mu\text{-ppdm})(\text{SO}_4)]_2 \cdot 13\text{H}_2\text{O}$ (deep blue)	or C222_1 8	15.42(1) 24.92(2) 25.73(2)	111.22(2)	CuO_4N_2	O_3SO 2.3	3.9	not given	561
$[\text{Cu}(\mu\text{-pfp})(\text{H}_2\text{O})]_2 \cdot 2\text{H}_2\text{O}$ (green)	tr P-1 2	9.756(6) 9.866(5) 10.115(6)	112.44(4) 111.36(7) 89.08(9)	CuO_4N	O 1.942(1, 47) N 1.939(1) H_2O 2.227(1)	3.923(1) ^f	O, O 91.55(1, 2.24) 101.95(1) 174.37(1) 82.35(1) ^d 94.50(1, 2.48) 160.08(1)	562

[Cu(μ -dppm)Cl] ₂ SO ₄ ·8H ₂ O (blue)	m P2 ₁ /c 4	14.679(2) 13.070(2) 23.958(6)	111.56(2)	CuO ₂ N ₂ Cl	O N Cl	1.980(6, 10) 1.968(6, 7) 2.498(6, 2)	3.948(1)	N, O	82.2(1, 1) ^c 95.2(1, 1.0)	563
[Cu(μ -pbsalim)] ₂ (dark brown)	m C2/c 8	17.09(5) 14.49(4) 17.96(4)	111.5(1)	CuO ₂ N ₂	O N	1.90(1, 1) 1.97(1, 1)	4.203(5) ^e	O, O O, N	89.8(5) 92.8(5, 1.0) ^d 149.9(7, 1.4)	564
[Cu(μ -bbi)] ₂ ·0.5CH ₂ Cl ₂ ·H ₂ O (green)	m C2/m 2	26.802(5) 9.887(2) 9.021(2)	90.48(1)	CuO ₂ N ₂	N/O	1.905(3, 1)	4.321(1)	O, N	90.1(2, 7) 177.7(1)	565a
[Cu(xba)] ₂ (olive green)	m P2 ₁ /c 2	12.002(5) 7.434(2) 19.431(9)	99.47(3)	CuO ₄	O	1.893(8, 8)	4.917(2) ^e	O, O	90.00(2, 2.05) 178.69(3, 0.57)	565b
[Cu ₂ (μ -taep)](ClO ₄) ₄ (violet)	hx P-6c2 6	16.022(9)		CuN ₄	N	2.026(17, 39)	5.048(2)	N, N	85.9(6, 3.0) ^e 93.2(6, 1.1)	566
[Cu ₂ (μ -[24]-N ₆ O ₂)(H ₂ O) ₂ Br ₂] Br ₂ ·4H ₂ O (blue)	m P2 ₁ /c 2	24.400(11) 12.702(3) 7.885(1) 17.316(2)	112.00(1)	CuN ₃ OBr	N H ₂ O Br	2.049(5, 33) 2.342 2.384(2)	5.16	N, N N, Br O, N	166.5 172.6(2) 92.4(-, 3.7)	567
[Cu ₂ (μ -O ₂ NO)(NO ₃) ₂ (μ -nmedtb)] NO ₃ ·4H ₂ O (blue)	m C2/c 4	19.159(4) 15.907(2) 16.816(3)	109.57(2)	CuO ₂ N ₃	N O ₂ NO μ ONO ₂	1.936(6, 5) 2.118(5) 2.000(4) 2.626(5) 2.41(4)	5.171(2)	N, N O, O O, N	82.3(2) ^c 158.9(2) 53.5(2) ^f 83.0(2) 134.0(10) 92.0(2, 3.9)	568
[Cu(μ -suqnp)(H ₂ O) ₂] (not given)	tr P-1 2	7.865(3) 9.140(2) 7.646(2)	108.10(2) 90.60(3) 96.76(3)	CuO ₄ N	H ₂ O N O	1.98(3, 5) 1.99(4) 1.99(4) 2.37(4)	5.379(20) ^e	O, N O, O	89(2, 2) 164(2) 92(2, 7) 176(2) 104(2)	569

TABLE VII (Continued)

Compound (color)	C_{75} yst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	$Cu-L$ [Å]	$Cu-Cu$ [Å]	$L-Cu-L$ [°]	Ref.
$[Cu_2(\mu-bi-dptmd)(N_3)_2]$ (dark blue)	m $P2_1/n$ 4	18.508(5) 12.311(3) 20.185(6)	112.65	CuN_5	N 1.957(5, 43) 2.082(5, 69) N_3N 2.119(7, 16)	5.393(2)	N,N 79.6(2, 2) ^c 88.4(2, 2.9) 96.6(3, 3.7) 131.6(3, 7.7) 168.5(2, 4)	570
$[Cu_2(\mu-[24]-aneN_6)Br_4]$ (green)	m $P2_1/c$ 4	9.6220(17) 14.0543(23) 20.5581(29)	91.700(13)	CuN_3Br_2	N 2.041(12, 3) 2.201(13) Br 2.536(3, 44)	5.432(3)	Br, Br 164.1(1, 1.5) Br, N 86.5(3, 3) 92.1(4, 2.5) 103.5(4, 3.8) 95.2(5, 8) ^d 167.7(5, 1.4)	571
$[Cu(\mu-C_{37}H_{36}N_2O_7)]_2$ (green)	tg $I4_1/a$ 16	14.740(2) 47.512(8)		CuO_3N_2	N 1.967(5, 7) O 1.923(4, 19) 2.697(5)	5.457(2)	O, O 84.7(2) O, N 91.7(3, 2) 167.8(3, 1.0) N, N 94.1(4) ^d	572
$[Cu(\mu-C_{19}H_{23}N_3O_2)(H_2O)]_2 \cdot 2(CIO_4)_4$ (pale green)	tr P-1 4	15.536(8) 19.587(9) 9.841(6)	105.97(4) 106.32(5) 104.60(4)	CuO_4N	O 1.975(4, 8) 2.003(5, 14) 2.231(6, 23) N 1.896(5, 5) H_2O 1.917(5, 6)	5.46	O, O 95.5(2, 5.1) 161.5(2, 8) O, N 81.2(2, 4) ^c 99.6(2, 5.9) 167.2(2, 3.6)	573
$[Cu_2(\mu-taac)(ClO_4)_2](ClO_4)_2$ (violet)	or $Pnmm$ 2	11.709(1) 14.948(3) 9.938(2)		CuN_4O	N 2.033(6, 33) O_3ClO 2.562(7)	5.479(1)	N, N 84.4(2, 1.0) ^c 93.6(2, 1.0) 107.0(1)	574
$[Cu_2(\mu-taac)(NCS)_2](ClO_4)_2 \cdot H_2O$ (blue)	or $Pnmm$ 2	10.926(3) 16.005(3) 9.923(2)		CuN_5	N 2.034(5) 2.098(4) SCN 2.191(7)	5.565(1)	N, N 84.1(2) ^c 92.2(2, 1.4) 108.1(2) 170.1(6)	575

[Cu(μ -hepk)(H ₂ O) ₂ (ClO ₄) ₂ · (ClO ₄) ₂ (blue)]	m C2/c 4	15.132(11) 9.235(8) 23.030(17)	102.32(5)	CuO ₄ N ₂	N O H ₂ O O ₃ ClO 2.526(16)	1.964(18, 12) 2.282(14) 1.989(16, 16)	5.6	N,N N,O O,O	82.2(7) ^c 93.9(6, 6.1) 171.6(7, 2.6) 86.9(6, 4.7) 169.7(6)	576
[Cu ₂ (μ -C ₂₄ H ₄₈ N ₄ O ₂ S ₂)(ClO ₄) ₄ · H ₂ O (blue)]	m P2 ₁ /n 4	15.736(4) 27.491(7) 9.493(3)	100.50(2)	CuN ₂ S ₂ O	N O S 2.319(1, 19)	2.037(6, 21) 2.287(5, 4)	5.6211(1)	N,O N,N N,S	80.3(1, 4) ^c 126.5(2, 1) 153.0(2, 5) 88.5(1, 4) ^c 87.8(1, 5) 92.1(1, 4) 103.6(1, 2) 163.2(-, 8)	577
[Cu ₂ (μ -tpmta)Br ₂](ClO ₄) ₂ (green)]	m P2 ₁ /c 2	9.029(1) 21.120(5) 11.376(2)	111.47(1)	CuN ₄ Br	N Br 2.028(4, 32) 2.140(4, 8) 2.412(1)	5.74(1)	5.74(1)	N,N Br,N	80.8(2, 5) ^c 87.7(2, 2.1) 116.3(2) 158.1(2) 94.9(1) 109.5(1, 2.6) 131.5(1)	578
[Cu(μ -bsd _a) ₂ ·2Me ₂ CO (green)]	m P2 ₁ /c 2	12.86(1) 16.74(2) 9.86(1)	105.1(1)	CuN ₃ O ₂	O N 1.956(3, 20) 1.973(3, 11) 2.405(3)	5.809(5) ^c	5.809(5) ^c	O,O O,N N,N	143.7(1) 90.6(1, 2.0) 124.8(1) 77.1(1) ^c 100.0(1) 176.2(1)	579
[Cu(μ -pd _{cno})(MeOH)(py) ₂ (blue)]	tr P-1 1	8.033(5) 9.056(5) 11.013(5)	96.76(3) 103.65(3) 111.52(3)	CuO ₄ N	O MeOH py,N 2.002(9)	1.943(7, 20) 2.298(9)	5.832(3) ^c	O,O N,O	88.5(3, 1.5) ^d 90.9(3, 2)	580
[Cu ₂ (μ -bpmab)(H ₂ O)(μ -ClO ₄)· (ClO ₄) ₂](ClO ₄) ₄ ·4H ₂ O (green)]	or Pmn2 ₁ 2	23.554(3) 8.998(2) 9.863(2)	111.52(3)	CuO ₃ N ₃	O ₃ ClO H ₂ O N 1.969(5, 3) 2.089(5) μ O ₂ ClO ₂ 2.393(5)	2.393(5) 1.985(5) 1.969(5, 3) 2.089(5) 2.393(5)	5.873(1)	N,N N,O O,O	84.0(2, 1) ^c 167.9(2, 3.4) 78.0(2) 90.3(2, 8.0) 107.8(2) 86.7(2, 3.3) 171.7(2)	581

TABLE VII (Continued)

Compound (color)	Cryst. cl. space G. Z	<i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å]	L-Cu-L [°]	Ref.
[Cu(μ -gly)(H ₂ O) ₂] ₂ 2{P(Ph ₂ O ₂)O ₂ }·2H ₂ O (blue)	or Pca2 ₁ 4	16.994(4) 5.953(2) 41.537(8)		CuO ₅ N	H ₂ O 2.247(4) O 1.976(3,26) 2.800(4,64) N 2.008(4,8)	6.139(1) ^e	O,O 89.3(2,7.3) 99.3(2,4.1) 137.9(1) 163.4(2,94) 84.1(2,70) ^e 113.5(2) 125.9(1)	582
[Cu(μ -poh)(NO ₃) ₂ ·6H ₂ O (dark green)]	tr P-1 1	8.727(1) 10.308(1) 12.845(2)	110.00(1) 78.94(1) 114.35(1)	CuO ₃ N ₂	O 1.925(2,32) N 1.977(2,30) O ₂ NO 2.643(2)	6.217(1) ^e	O,O 88.8(1,1.5) 105.2(1) O,N 88.8(1,2.8) ^d 169.8(1,4.0) N,N 93.6(1) ^d	583
[Cu(μ -hxa)] ₂ (blue)	m P2 ₁ /c 2	14.538(2) 10.454(2) 11.177(2)	95.03(1)	CuO ₄	O 1.885(2,4)	6.256(1)	O,O 84.24(8,22) ^f 95.76(8,12) 178.16(8,1.74)	584
[Cu ₂ (μ -por)] ₂ ·2H ₂ O (not given) (at 83 K)	m P2 ₁ /c 2	11.878(6) 13.304(7) 23.725(13)	114.60(2)	CuN ₄	N 1.987(5,8)	6.332(4)	N,N 90.0(2,2.5) ^d 179.5(2,2)	585
[Cu(μ -pennas)(H ₂ O)] ₂ ·7H ₂ O (blue)	m C ₂ 4	12.266(5) 19.769(5) 15.698(5)	92.14(5)	CuO ₃ N ₂	O 1.96(2,2) N 2.00(2,5) H ₂ O 2.43(3,5)	6.399(5)	N,O 84.2(9,1.2) ^f 95.8(9,3.3) N,N 171(1) O,O 89.0(8,1.3) 175.6(9,6)	586
[Cu ₃ (μ -iabm)(NO ₃) ₄]·6H ₂ O (purple)	m P2 ₁ /a; P2 ₁ /c 4	12.656(3) 15.411(6) 16.426(5)	100.05(2)	CuN ₄ O ₂	N 2.02(1,5) O ₂ NO 2.51(1,5)	6.4	N,N 85.6(5,8) ^f 94.4(6,1.4) 178.0(6,1.4) 84.2(5,9.6) O,O 175.0(5,6)	587

$[\text{Cu}_2(\mu\text{-tcoa})(\text{tos})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (blue violet)	tr P-1 1	11.811(3) 12.448(1) 9.994(2)	106.23(1) 113.45(1) 76.98(1)	CuN_4O	tooaN tosO	2.028(10, 11) 2.140(4) 2.153(6)	6.876(3)	O,N	96.7(3, 3) 109.2(3)	588
$\text{Na}_4[\text{Cu}(\text{pdta})_2] \cdot 18\text{H}_2\text{O}$ (dark green)	tr P-1 1	9.977(1) 10.533(1) 12.453(1)	80.37(1) 73.41(2) 88.13(1)	CuO_4N_2	O N	1.948(7, 21) 2.293(7) 2.075(8) 2.509(8)	6.931(8)	O,O O,N	92.9(3, 5.1) 75.2(3, 2.4) ^c 87.2(3, 3.0) 158.2(3, 4.0) 120.4(3)	589
$[\text{Cu}_2(\mu\text{-}[24]\text{-aneN}_2\text{S}_2)\text{Cl}_4] \cdot 2\text{H}_2\text{O}$ (dark green)	m P2 ₁ /c 4	7.943(2) 22.481(6) 17.538(5)	100.97(2)	$\text{CuCl}_2\text{S}_2\text{N}$	N Cl μS	2.024(5, 9) 2.250(1, 10) 2.476(1, 23) 2.293(1, 57) 2.421(1, 24)	7.228(1)	N,Cl	92.5(1, 6) 166.5(2, 3.6) 85.5(2, 1.6) ^c 101.0(1, 2.9) 92.6(1, 3.2) 102.4(1, 5.3) 157.3(1, 4)	590
$[\text{Cu}_2(\mu\text{-}[28]\text{-mN}_8)(\text{HNCS})_2] \cdot (\text{BPh}_4)_2 \cdot 1.5\text{MeCN}$ (green)	tr P-1 2	14.695(11) 14.051(11) 20.721(11)	111.5(1) 98.8(1) 100.3(1)	CuN_5	N μN SCN	1.990(23, 82) 2.047(19, 54) 2.322(20, 8)	7.25 ^c	N,N	78.5(10, 9) ^c 89.5(8, 4.3) 97.8(8, 1.8) 104.5(7, 2.2) 158.5(8, 3.4) 171.2(6)	591
$[\text{Cu}_2(\mu\text{-}[30]\text{-aneN}_{10})\text{HCl}]_2 \cdot (\text{ClO}_4)_3 \cdot 4\text{H}_2\text{O}$ (blue)	m P2 ₁ /n 2	21.491(5) 7.696(4) 12.210(4)	103.04(5)	CuN_4Cl	N Cl	2.04(2, 2) 2.43(1)	7.26(1)	Cl,N N,N	99.5(6, 8.7) 85.3(6, 6) ^{c,d} 97.8(6)	592
$[\text{Cu}(\mu\text{-arg}(\text{ac}))_2] \cdot 6\text{H}_2\text{O}^{\text{e}}$ (blue)	m P2 ₁ 4	15.948(2) 16.878(2) 10.378(2)	108.47(1)	CuO_4N_2	acO O N	2.570(15) 1.937(12, 1) 2.884(14) 1.991(13)	7.312(2) ^f	N,O O,O	84.6(6, 1.6) ^c 96.2(5, 2.4) 86.2(6, 2.5) 93.8(6, 2.8) 177.2(5, 5) 173.3(4)	593
				CuO_4N_2	acO O N	2.563(16) 1.943(15, 2) 2.944(16) 1.991(14, 5)	7.312(2) ^f	N,O O,O	85.6(7, 3.8) ^f 92.6(7, 3.3) 85.4(7, 4) 94.7(7, 3.1) 176.0(6, 1.3) 178.4(5)	

TABLE VII (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å]	L-Cu-L [°]	Ref.
[Cu(μ -nba)] ₂ ·2CHCl ₃ (not given)	m C2/c 4	19.942(5) 10.371(2) 26.656(9)	116.85(2)	CuO ₄	not given	7.349(1)	not given	594
[Cu ₃ (μ -C ₁₇ H ₂₀ F ₁₂ N ₂ O ₂) ₂] (deep blue)	m P2 ₁ /c 4	20.008(2) 9.009(1) 29.296(3)	118.86(1)	CuO ₂ N ₂	O N 2.014(9, 17)	7.356(3) ^e	O,O N,N O,N 167.0(4, 6.0) 160.7(4, 4.1) 91.2(4, 5.0) ^d	595
[Cu(μ -btim)(NCS)] ₂ (NCS) ₂ (blue)	m P2 ₁ /n 2	14.381(4) 10.834(3) 15.824(4)	108.988(20)	CuN ₅	N SCN 2.190(10)	7.472(10)	N,N N,N 165.1(4, 1.7)	596
[Cu(μ -bpmb)(H ₂ O)] ₂ (ClO ₄) ₄ · 2H ₂ O (green)	tr P-1 1	11.871(4) 12.313(7) 10.441(14)	108.45(9) 102.98(8) 91.23(4)	CuN ₅ O	N N 2.018(13, 53) 2.513(13) H ₂ O 2.706(15)	7.520(2)	N,N N,N N,O 77.4(5, 6) ^e 90.0(6, 7.4) 105.4(5, 2.5) 174.6(6, 1.6) 88.7(5, 8, 5) 169.2(4)	581
[Cu(μ -denc) ₂ Cl ₂] ₂ (blue)	tr P-1 2	10.563(1) 13.123(1) 9.829(2)	98.77(1) 116.05(1) 100.34(1)	CuN ₂ Cl ₂ O	N N 2.007(4) 2.012(3) 2.475(3)	7.701(1) ^e	Cl,Cl Cl,N N,N 149.4(1) 105.3(1, 5) 171.7(1)	597
[Cu(μ -glu)(Et ₄ en)] ₂ (blue)	m P2 ₁ /n 2	9.365(4) 15.211(15) 12.738(11)	105.33(5)	CuO ₄ N ₂	Et ₄ en glu 2.066(9, 7) 1.955(7, 18) 2.780(10, 66)	7.758(6) ^e	N,N O,N O,O 86.4(3) ^c 95.3(3, 6.3) 123.3(3, 2) 52.6(3, 1.6) ^f 87.6(3, 3.3) 122.2(2)	598
[Cu(μ -pmaH)(ClO ₄) ₂ ·2H ₂ O] (deep blue)	m P2 ₁ /c 4	10.956(4) 8.907(4) 23.252(9)	93.95(3)	CuN ₄ O	N O ₂ ClO 2.51(1)	7.824	N,O N,N N,N 90.4(6, 8.8) 82.9(4, 1.3) ^c 97.2(4, 1.8) 169.2(5, 3.5)	599

[Cu ₂ (μ-dpce)Cl ₄] (yellow green)	tr	12.918(5)	102.08(3)	CuN ₂ Cl ₂ O	N	1.946(10)	8.892 ^c	not given	600
	P-1	12.816(5)	99.12(3)		O	2.123(9)			
	2	18.576(7)	118.14(2)		Cl	2.319(7)			
[Cu(μ-dfpp)] ₂ ^d (not given)	m	16.076(5)	91.34(5)	CuO ₂ N ₂	O	1.87(6, 1)	not given	O, O	158(2)
	P2 ₁ /c	33.709(4)			N	1.96(7, 5)		N, N	156(3)
	4	20.094(5)		CuO ₂ N ₂ S	O	1.96(5, 2)		O, O	156(2)
					N	1.91(8, 4)		N, N	174(3)
					S	3.00(3)			
				CuO ₂ N ₂	O	1.89(4, 2)	not given	O, O	154(2)
					N	2.02(6, 1)		N, N	152(2)
				CuO ₂ N ₂ S	O	1.96(5, 1)		O, O	154(2)
					N	1.95(6, 0)		N, N	178(2)
					S	2.90(3)			
[Cu(μ-car)(H ₂ O)] ₂ ·2H ₂ O (blue)	trg	8.641(9)		CuN ₃ O ₂	N	1.97(-, 4)	not given	not given	601b
	P3 ₁ 2				O	1.93			
	6	30.576(15)			H ₂ O	2.48			

^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 Calculated by us. ^f Four-membered metallocyclic ring. ^g There are two crystallographically independent molecules.

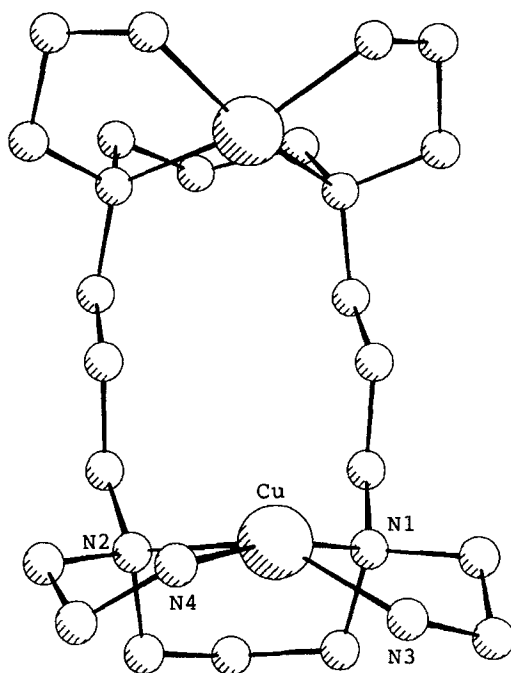


FIGURE 8 Structure of $[\text{Cu}_2(\mu\text{-taeo})]^{4+}$ (see Ref. 566).

mono- to octadentate. The mean Cu–L bond distances formed for monodentate ligands in the series of five-coordinated derivatives increases in the order: 2.14 Å (N) < 2.38 Å (Cl) < 2.44 Å (Br). In the series of multidentate O-donor; ligands the mean Cu–O bond distance increases in the order: 1.885 Å (octa-) < 1.94 Å (tri-) < 2.15 Å (tetra-) < 2.32 Å (mono-) < 2.40 Å (bidentate); and Cu–N bond distance in the order: 1.98 Å (tetra-) < 2.06 Å (hexa-) < 2.07 Å (bi-) < 2.14 Å (mono-) < 2.17 Å (octa-) < 2.265 Å (pentadentate).

The hetero-donor ligands are: bidentate with O plus N atom donors; tridentate with two O plus one N atom donors, and one O plus two N atom donors; tetradentate with three O plus one N atom donors, two O plus two N atom donors, and one O plus three N atom donors; pentadentate with three O plus two N atom donors, hexadentate with four O plus two N atom donors, and two O plus four N-donor; sites.

Both steric and electronic factors associated with the donor atom appear to influence the L–Cu–L bond angles of the various metallocyclic rings. The mean values for the angles are: five-membered rings, 82.2° (O+N-donor); < 83.0° (N-donor); < 85.0° (O-donor); < 87.0° (N+S-donor); six-membered rings, 88.0° (O+N-donor); < 88.5° (O-donor); < 92.0° (N-donor);

Two independent molecules differing by degree of distortion and coexisting in the same crystal have been found in blue $[\text{Cu}_2(\mu\text{-arg})_2(\text{ac})_2]\cdot 6\text{H}_2\text{O}$.⁵⁹³ The compounds given in Table VII are blue and green, but there are some violet/purple, red and even brown compounds.

2.3 Triply Bridged

Crystallographic and structural data for triply bridged Cu(II) dimers are summarized in Table VIII. The structures are tabulated in order of increasing Cu–Cu separation. Triply-bridged derivatives can be divided into several groups.

There is only one example,¹⁶² in which two $\text{Cu}(\text{dpym})^{2+}$ moieties are triply bridged by single oxygen atoms of monodentate ligands, two $\mu\text{-OH}$ groups and one $\mu\text{-OH}_2$ molecule. The Cu–Cu distance of 2.799(1) Å is the shortest in this series. Each Cu(II) atom is in a square-pyramidal environment with a CuO_3N_2 chromophore. In another three examples^{203,604} two Cu(II) atoms are bridged by one single atom of monodentate ligands ($\mu\text{-OH}$,²⁰³ $\mu\text{-N}_3$ or $\mu\text{-NCO}$),⁶⁰⁴ by the oxygen atom of a pentadentate ligand (pmp, N_4O ;²⁰³ $\text{C}_{17}\text{H}_{27}\text{N}_4\text{O}$, N_4O ⁶⁰⁴) and by one bidentate ligand (ClO_4 ;²⁰³ acetate⁶⁰⁴) in syn–syn arrangement. The Cu–Cu distances are 2.947, 2.978(2) and 2.995(1) Å. Each Cu(II) atom is in a square-pyramidal environment (CuO_3N_2 ²⁰³ and CuN_3O_2 ⁶⁰⁴).

In several examples^{602,605,607,609} two Cu(II) atoms are held together by two monodentate ligands ($\mu\text{-OH}$ and $\mu\text{-Cl}$,⁶⁰² $\mu\text{-OH}$ and $\mu\text{-OH}_2$,^{605,607} $\mu\text{-1}$, $1\text{-N}_3(\times 2)$ ⁶⁰⁹) and by bidentate ligands ($\mu\text{-RCOO}^-$,^{602,605,607} $\mu\text{-O}_2\text{NO}$ ⁶⁰⁹) in syn–syn arrangement. While in other examples^{602,605,607} each Cu(II) atom is five-coordinate (square pyramidal) or six-coordinate.⁶⁰⁹ Each five-coordinate Cu(II) atom deviates slightly from the basal plane, the mean values are 0.245 Å,⁶⁰² 0.15 and 0.14 Å⁶⁰⁵ and 0.126 Å.⁶⁰⁷

In several other derivatives, a pair of distorted square-pyramidal^{603,610,611,613,617,621} or distorted trigonal bipyramidal⁶⁰⁶ units are held together by two monodentate ligands and by two nitrogen atoms of a tetradentate ligand (N_4) (Table VIII). The Cu(II) atom deviates from a basal plane toward an apical ligand. The mean values of the deviations are: 0.3 Å,⁶⁰³ 0.142 and 0.162 Å,⁶¹⁰ 0.52 Å,⁶¹³ 0.139 and 0.293 Å⁶¹⁷ and 0.185 Å.⁶²¹

In green $[\text{Cu}_2(\mu\text{-hphen})_2(\mu\text{-ac})]\text{PF}_6$ ⁶⁰⁸ as can be seen in Figure 9 a pair of distorted square-pyramidal units are triply bridged by the phenolic oxygen atoms of two tridentate 2-(2-hydroxyphenyl)-1,10-phenanthroline anions (ON_2) and by an acetate group in syn–syn arrangement with a Cu–Cu separation of 3.073(2) Å and mean Cu–O–Cu bridge angles of 89.2°.

TABLE VIII Crystallographic and structural data for triply bridged copper(II) dimers^a

Compound (color)	Cryst. cl. Space G. Z	<i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]	α [°] β [°] γ [°]	Chromophore	<i>Cu</i> - <i>L</i> [Å]	<i>Cu</i> - <i>Cu</i> [Å] <i>Cu</i> - <i>L</i> - <i>Cu</i> [°]	<i>L</i> - <i>Cu</i> - <i>L</i> [°]	Ref.
[Cu ₂ (μ-OH) ₂ (μ-H ₂ O)(dpyam)]· Cl ₂ ·2H ₂ O (orange red)	or Cmc2 ₁ 4	15.675(3) 8.563(1) 18.115(3)		CuO ₃ N ₂	N ^b μH ₂ O μHO	2.799(1) 91.6(3,2) 70.7(2)	O,O N,N O,N 173.9(2,1.0)	162
	m P2 ₁ /n 4	21.167(4) 8.836(4) 13.834(3)	109.22(2)	CuO ₃ N ₂	μO ₃ ClO pmpN μpmpO μHO	2.947 99.8(7,6) 78.8(6,1)	O,O O,N 171.5(7,4.2) 84.6(6) ^c	203
	m P2 ₁ /n 2	8.434(1) 16.074(2) 9.430(1)	98.09(1)	CuO ₂ N ₂ Cl	N μCl μHO μacO	2.957(1) 70.6(1) 100.7(2)	O,O Cl,N Cl,O 105.0(1) 80.6(2) ^c 92.3(2,2.6) 151.4(1) 175.4(2) 94.2(2)	602
[Cu ₂ (μ-OH)(μ-Cl)(μ-ac)(bpy) ₂] (ClO ₄) ₂ ·H ₂ O (violet blue)	m P2 ₁ /c 8	12.950(1) 14.262(1) 22.773(2)	96.07(1)	CuN ₂ Cl ₂ O	N Cl μHO μCl	2.972(1) ^f 100.1(2) not given Cl	O,O O,Cl Cl,N N,N N,O 82.9(2,5)	603
	Ir P1 2	13.973(2) 11.289(1) 9.224(2)	74.97(2) 74.22(2) 77.88(2)	CuN ₂ Cl ₂ O	N μN ₃ N acO μO	3.001(1) ^f 101.8(2) not given HO Cl	O,Cl Cl,N Cl,N N,N N,O 91.8(1,6) 94.4(1,7) 85.3(2,1.7) ^d 83.7(2,2)	604
	(not given)					2.978(2) not given	not given	

[Cu ₂ (μ-NCO)(μ-ac)(μ-C ₁₇ H ₂₇ N ₄ O)]·PF ₆ (not given)	m P2 ₁ /c 8	10.352(9) 26.44(1) 10.459(1)	1.09.28(3)	Cu ₂ N ₃ O ₂	μOCN μacO μO 1.954(4,3)	2.024(5) 2.266(5) 1.982(5) 2.182(6)	2.995(1) not given	not given	604
[Cu ₂ (μ-OH)(μ-OH ₂)(μ-pr)(phen) ₂](NO ₃) ₂ (deep blue)	m P2 ₁ /n 4	7.981(10) 18.352(8) 19.247(8)	97.98(7)	Cu ₂ O ₃ N ₂	phenN μHO μH ₂ O μprO 1.938(4,2)	2.017(4,5) 1.918(3,1) 2.348(4,15) 1.938(4,2)	3.015(2) 103.6(2) 95.5(1,1)	O,N 168.8(2,6,0) N,N 81.5(2,1) ^c	605
[Cu ₂ (μ-OH)(μ-OH ₂)(μ-ac)(phen) ₂](NO ₃) ₂ (deep blue)	m P2 ₁ /n 4	8.107(10) 18.554(9) 18.616(7)	99.14(6)	Cu ₂ O ₃ N ₂	phenN μHO μH ₂ O μacO 1.934(3,1)	2.024(4,7) 1.933(3,1) 2.349(4,7) 1.934(3,1)	3.017(2) 103.4(2) 95.6(1,6)	O,N 168.8(1,6,7) N,N 81.5(2,10) ^c	605
[Cu ₂ (μ-OH)(μ-Cl)(μ-Etbitp)(Cl ₂)]·dmf (green)	tr P-1 2	8.9198(5) 13.5738(8) 13.7178(7)	105.318(5) 105.255(5) 99.461(5)	Cu ₂ N ₂ Cl ₂ O	N μHO μCl Cl 2.260(1,2)	2.551(1,19) 2.144(3,14) 1.906(3,5) 2.551(1,13)	3.017(1) 104.7(1) 72.50(3)	N,N O,N N,Cl O,Cl 86.6(1,2) ^d 83.8(1,4) 169.1(1,7) 94.1(1,1,4) 135.4(1,1,7) 91.0(1,9,1)	606
[Cu ₂ (μ-OH)(μ-OH ₂)(μ-ac)(bpy) ₂](ClO ₄) ₂ (deep blue)	tr P-1 2	11.286(2) 16.414(4) 8.047(2)	97.31(1) 103.78(1) 72.59(1)	Cu ₂ O ₃ N ₂	bpyN μHO μH ₂ O μacO 1.938(4,7)	2.008(5,2) 1.929(4,1) 2.392(4,13)	3.035(2) 103.8(2) 78.7(1)	O,O O,N O,N N,N 96.6(2,2,4) 94.9(2,5,6) 169.9(2,8,3) 81.1(2,1) ^c	607
[Cu ₂ (μ-hphen) ₂ (μ-ac)]PF ₆ (green)	m C2/c 4	18.180(5) 13.570(3) 15.818(4)	119.65(2)	Cu ₂ O ₃ N ₂	μacO N μphenO 2.449	1.942(2) 1.990(3,11)	3.073(2) ^f 89.2	O,N O,O O,O N,N 91.7(1,1,6) 171.2(1,2,9) 92.3(1) 83.4(1) ^c	608
[Cu ₂ (μ-1,1N ₃) ₂ (μ-NO ₃)(NO ₃)·(3-Mepp) ₄ (H ₂ O)] (black)	m P2 ₁ /c 4	8.330(5) 20.506(9) 18.818(8)	98.04(3)	Cu ₂ N ₄ O ₂	μN ₃ pyN μO ₂ NO O ₂ NO μN ₃ pyN μO ₂ NO H ₂ O 2.338(8)	1.992(9,6) 1.983(10,3) 2.691(8) 2.465(12) 2.003(9,9) 1.998(9,10) 2.670(8)	3.087(3) 101.7(4)	N,N N,N O,O N,O N,N N,N O,O N,O 94.0(4,2,0) 168.5(4,4,5) 172.6(4) 90.0(4,13,7) 78.8(4,3) 93.6(4,1,8) 170.2(4,8) 168.6(3) 89.8(4,9,4)	609

TABLE VIII (Continued)

Compound (color)	Cryst. cl. Space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	$\text{Cu}-L$ [Å]	$\text{Cu}-\text{Cu}$ [Å] $\text{Cu}-L-\text{Cu}$ [°]	$L-\text{Cu}-L$ [°]	Ref.
$[\text{Cu}_2(\mu\text{-OH})(\mu\text{-ONO}_2)_2(\mu\text{-pap6me})(\text{NO}_3)_2] \cdot 0.5\text{H}_2\text{O}^f$ (green)	m $P2_1/a$ 8	14.136(5) 19.865(14) 18.259(11)	96.319(4)	CuO_3N_2	N O_2NO μHO $\mu\text{O}_2\text{NO}$	3.134(2) 112.6(5) HO HO	O,O 53.8(4, 7) ^f 75.5(4, 2.1) 93.6(4, 5.6) 117.7(3, 8.9) 167.6(3, 5.1) 78.9(3) 90.3(4, 6.8) 104.9(4, 5.8) 158.7(4, 5.7) 173.2(5, 3.5) 89.0(4, 1.1) ^d	610
$[\text{Cu}_2(\mu\text{-OH})(\mu\text{-Cl})(\mu\text{-pa})\text{Cl}_2] \cdot 3\text{H}_2\text{O}$ (green)	m $C2/c$ 8	21.139(6) 12.797(1) 20.312(7)	111.37(2)	CuO_3N	N O_2NO μHO $\mu\text{O}_2\text{NO}$	3.134(3) 114.1(5) HO Cl	O,O 53.4(4, 1.9) ^f 75.3(4, 4.7) 91.0(5, 3.9) 122.6(3, 3.4) 168.8(2) 92.2(5, 7.9) 155.0(5, 1) 173.6(5, 5.5) 90.0(4, 7) ^d	611
$[\text{Cu}_2(\mu\text{-OH})(\mu\text{-O}_2\text{NO})_2(\mu\text{-pap4me})(\text{NO}_3)(\text{H}_2\text{O})_2]\text{NO}_3$ (deep blue)	m $P2_1/a$ 4	27.078(1) 13.4451(4) 7.3744(6)	105.575(4)	CuO_4N_2	μHO μCl N H_2O O_2NO $\mu\text{O}_2\text{NO}$ μHO N	3.137(2) ^f 112.2(4) not given HO Cl HO	O,O 51.3(1) ^f 79.8(1, 1) 95.3(1, 4.4) 129.8(1) 168.9(1) 88.5(1, 8.6) 114.8(2, 3.1) 172.0(1, 3.2) 89.1(1, 1) ^d	612

[Cu ₂ (μ-N ₃)(μ-Br)(μ-dpdt)Br ₂] MeCN (brown)	m P2 ₁ /n 4	8.437(5) 25.146(8) 11.858(4)	92.68(3)	CuN ₃ Br ₂	Br N μBr μN ₃	2.374(4, 11) 1.97(2.2) 2.15(2, 17) 2.596(4, 25) 1.98(2)	Br N ₃	3.138(3) 74.7(1) 105.0(8)	Br,N N,N	142.2(4, 3.5) 175.6(7, 3.9)	613
[Cu ₂ (μ-OH)(μ-ac)(μ-him)] (ClO ₄) ₂ ·1.5H ₂ O·MeOH (blue)	m P2 ₁ /m 2	8.529(4) 27.883(4) 11.133(5)	102.81(2)	CuO ₂ N ₂	N μHO μacO	1.976(8, 3) 1.934(5) 1.937(7)	HO	3.156(3) 109.3(4)	O,N N,N	90.3(4, 2.4) 89.1(3)	614
[Cu ₂ (μ-OH)(μ-O ₂ IO)(μ-pap) (IO ₃) ₂ ·4H ₂ O (turquoise-blue)	m P2 ₁ /c 4	7.266(1) 15.269(1) 25.870(1)	96.40(1)	CuO ₃ N ₂	not given	not given	HO	3.165(1) 113.8(2)		not given	615
[Cu ₂ (μ-OH)(μ-fm) ₂ (bpy) ₂]BF ₄ (blue green)	m C2/c 8	33.260(8) 10.614(14) 13.776(10)	95.32(4)	CuO ₃ N ₂	bpyN μHO μHCO ₂	2.014(5, 13) 1.928(4, 1) 1.998(5, 31) 2.165(5, 25)	HO	3.171(1) 110.7(2)	O,N	147.2(2) 167.9(2, 5.1)	616
[C ₂ (μ-Cl) ₂ (μ-bpip)(Cl) ₂]·EtOH (red)	m C2/c 8	33.9022(8) 9.1626(5) 15.4885(5)	114.853(2)	CuCl ₃ N ₂	N Cl μCl	2.039(7, 37) 2.227(9, 1) 2.269(1, 1) 2.652(1, 47)	Cl	3.198(1) 80.7(1, 1.00)	Cl,N	90.94(8, 7.6) 154.08(8) 173.30(8) 89.13(8, 2.59) 121.45(4) 86.8(1) ^d	617
[Cu ₂ (μ-OH)(μ-ac)(μ-pdmm) (pdmm)(bpy) ₂] ^c (not given)	or Pna2 ₁ 8	9.738(10) 32.142(5) 23.673(5)		CuO ₄ N ₂	O bpyN acO μHO μacO	2.68(1) 2.03(2, 1) 2.28(1) 1.93(1) 1.96(1)	HO	3.231(2) 113.5(6)	N,N O,O N,N	80.4(6) ^e 90.7(5, 4.2) 108.6(5) 85.1(6, 5.9) 96.9(6, 8)	618
				CuO ₃ N ₂	bpyN acO μHO μacO	2.00(1) 2.23(1) 1.93(1) 1.97(1)			N,N O,O O,N	82.3(6) ^e 97.1(6, 1.0) 103.3(5) 90.0(6, 4.6)	
				CuO ₄ N ₂	O bpyN acO μHO μacO	2.87(2) 2.03(2, 1) 2.41(2) 1.96(1) 1.91(1)	HO	3.240(4) 114.1(7)	N,N O,O O,N	79.8(8) ^f 83.4(5, 4.2) 93.4(6, 1.4) 113.0(6) 84.2(7, 5.3) 99.0(7, 2.8)	

TABLE VIII (Continued)

Compound (color)	Cryst. cl. Space G. Z	<i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]	α [°] β [°] γ [°]	Chromophore	<i>Cu-L</i> [Å]	<i>Cu-Cu</i> [Å] <i>Cu-L-Cu</i> [°]	<i>L-Cu-L</i> [°]	Ref.
$[\text{Cu}_2(\mu\text{-Cl})_2(\mu\text{-pap}46\text{Me})(\text{Cl})_2]$ (green)	m C2/c 4	15.795(3) 10.661(3) 16.155(4)	113.82(3)	CuO_3N_2 CuCl_3N_2	bpyN acO μHO μacO N Cl μCl 2.019(2.3) 2.267(1) 2.277(1) 2.589(1)	3.251(1) 83.57(4) Cl	N,N O,O O,N Cl,N 154.08(8) 173.30(8) 89.13(8, 2.59) 121.45(4) 86.8(1) ^c not given	617
$[\text{Cu}_2(\mu\text{-ac})_2(\mu\text{-bmpcl})\text{ClO}_4]$ $3\text{H}_2\text{O}$ (dark green)	m P2 ₁ /n 4	20.127(7) 14.480(4) 11.263(2)	92.88(3)	CuO_3N_2	N μO μacO 2.035(8.11) 1.949(8.7) 1.929(7.6) 2.169(7.0)	3.263(2) 113.7(3) O	N,N not given	619
$[\text{Cu}_2(\mu\text{-Cl})(\mu\text{-bptp})_2](\text{ClO}_4)_3$ MeCN (green)	or Pmcn 8	10.325(3) 17.917(5) 22.458(4)		CuN_4Cl	N μCl 1.998(6.4) 2.018(6) 2.439(5.9)	3.269(2) 84.2(1) Cl	N,N N,N 163.3(2.1) 98.0(2.3.2)	620
$[\text{Cu}_2(\mu\text{-N}_3)(\mu\text{-O}_2\text{ClO}_2)(\mu\text{-baaep})]$ $(\text{bpy})_2(\text{ClO}_4)_2$ ^c (dark green)	tr P-1 4	20.86(3) 15.028(16) 9.466(9)	105.35(9) 93.86(11) 94.98(8)	CuN_4O_2	N O_3ClO O N $\mu\text{N}_3\text{N}$ 1.979(16) 1.981(16) 1.895(14) $\mu\text{N}_3\text{N}$ 1.981(16) O_3ClO 2.380(17)	3.295(4) 112.6(8) N ₃	N,N N,N 85.0(7.27) ^d 169.3(7.2.6) ^e 85.0(7.6.4) 94.9(8.4.6) 167.6(6) N,N 83.7(7) ^f 96.9(6) ^d 161.7(7) N,O 93.2(7.6.3) 172.1(7) 90.8(6)	465
CuN_4O_2				CuN_4O_2	N O_3ClO O N 2.002(19.15) 2.60(2) 2.664(16) 1.956(17)	3.367(4) 117.9(9) N ₃	O,O N,N 78.3(8) ^f 95.8(7) ^d 93.4(7.6.5) 166.6(8.3.2)	

TABLE VIII (Continued)

Compound (color)	Cryst. cl. Space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	$Cu-L$ [Å]	$Cu-L-Cu$ [Å] $Cu-L-Cu$ [°]	$L-Cu-L$ [°]	Ref.
$[Cu_2(\mu-OH)(\mu-tpmc)](ClO_4)_3 \cdot 2H_2O$ (green)	m Cm 2	11.048(1) 22.318(3) 9.459(1)	111.95(1)	CuN_4O	N μHO	3.712(1) 134.5(2) HO	O,N 107.8(2, 1.8) 96.1(2) 127.2(2) 82.2(2, 1.7) ^c 92.8(2) 123.2(2) 157.9(1)	625
$[Cu_3(\mu-OH)(\mu-bistren)]Br_3$ $6H_2O$ (not given)	m C2/c 4	15.793(3) 11.100(5) 24.506(6)	90.92(2)	CuN_4O	N μOH	3.767(1) 155.5(4) HO	O,N 94.1(2, 6) 100.7(2) 175.6(2) 84.2(2, 6) ^c 107.8(2, 3.5) 141.4(2)	626
$[Cu_2(\mu-mepH)(\mu-H_2O)] \cdot 2Clbz$ 2-PrOH (blue)	tr P-1 2	11.919(7) 15.063(4) 15.648(9)	117.82(3) 98.95(4) 97.48(4)	CuO_3N_2	N μO μH_2O	3.893(2)	O,N 84.0(3, 1.5) ^c 100.9(2, 3.4) 91.8(3, 2.5) N,N 97.7(3, 5)	515
$[Cu_2(\mu-F)(tpmc)](ClO_4)_3 \cdot 2MeCN$ (not given)	m P2 ₁ /a 4	21.543(4) 18.020(4) 11.987(2)	91.13(2)	CuN_4F	N μF	3.993(2) 148.6(4) F	F,N 91.3(4, 2.9) 111.0(4, 8.6) 83.2(5, 2.6) ^c 103.6(5, 3) 156.4(5, 10.5)	627
$[Cu_2(\mu-taac)(\mu-N_3)](ClO_4)_3$ (blue)	or Pnn2 ₁ 2	8.875(4) 8.076(1) 21.756(9)		CuN_5	N μN_3N	4.312(1)	N,N 85.3(2, 1.3) ^c 95.3(2, 3.2) 108.8(2, 1.2)	575
$[Cu_3(\mu-taac)(\mu-NCO)](ClO_4)_3$ (blue)	or Pnn2 ₁ 2	8.885(2) 8.047(1) 21.847(4)		CuN_5	N μNCO	4.340(2)	N,N 85.2(3, 2.2) ^c 95.5(3, 3.4) 108.9(2, 1)	575

[Cu ₂ (μ-Cl)(μ-tpmc)](ClO ₄) ₃ · H ₂ O (blue)	m P2 ₁ /n 4	15.054(2) 22.452(2) 12.895(1)	92.48(1)	Cu ₂ N ₄ Cl	N μCl	2.042(8, 35) 2.528(2, 26)	Cl	4.470(2) 124.3(1)	N,N	83.7(3, 2.2) ^c 104.5(3, 4)	627
[Cu ₂ (μ-O ₂ NO)(μ-tpmc)](PF ₆) ₃ (blue)	m P2 ₁ /n 4	18.685(4) 25.563(5) 9.393(1)	92.59(2)	Cu ₂ N ₄ O	N μO ₂ NO	2.006(14, 43) 2.059(14, 34) 2.231(15) 2.007(12) 2.456(11)		4.651	O,N	84.4(5) 95.5(5, 5.6) 123.0(5) 85.5(6, 8.3) ^c 105.0(6, 2.1)	625
[Cu ₂ (μ-Br)(μ-taec)](ClO ₄) ₃ (blue)	or Pca2 ₁ 4	15.590(1) 14.460(1) 14.602(1)		Cu ₂ N ₄ Br	N μBr	2.050(20, 62) 2.688(4) 2.730(3)	Br	4.656(3) 118.5(1)	N,N	85.3(11, 1.4) ^c 90.3(10, 5.3) 147.3(8, 2) 163.4(10, 1.8) 91.3(9, 9) 104.6(5, 9) 122.1(6, 5)	574
[Cu ₂ (μ-N ₃)(μ-tach)](ClO ₄) ₃ (deep blue)	m P2 ₁ /a 4	25.909(2) 14.093(1) 9.418(2)	94.28(2)	CuN ₅	N N ₃ N	2.052(5, 52) 2.104(4, 1) 2.212(4, 17)		5.541(1)	N,N	83.9(2, 3) ^c 90.3(2, 4.9) 107.8(2, 5.3) 120.3(1)	566
[Cu ₂ (μ-im)(μ-[24]-smeN ₆ O ₂)- (imH) ₂](ClO ₄) ₃ (blue)	m C2/c;Cc 4	15.008(3) 10.186(2) 26.062(3)	100.48(1)	CuN ₅	N imN μimN	2.08(4, 5) 2.25(1) 2.133(1) 1.946(1)		5.866(2) ^g	N,N	83.1(4, 1) ^c 91.3(4, 7.4) 130.5(4, 2.6) 171.5(4)	628 629
[Cu ₂ (μ-im)(μ-sbm)](CF ₃ SO ₃) ₃ · H ₂ O·3thf (green)	tr P-1 2	18.016(6) 18.287(6) 9.704(4)	99.99(2) 92.74(2) 73.79(2)	Cu ₂ N ₄ O	N O imN	2.025(4, 97) 2.248(2) 2.442(3) 1.953(4, 8)		5.918(1)	N,N	78.5(1, 3) ^c 101.3(1, 1.1) 156.2(2, 5) 171.4(1, 6.4) 97.2(1, 1.3)	630

TABLE VIII (Continued)

Compound (color)	Cryst. cl. Space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å] Cu-L-Cu [°]	L-Cu-L [°]	Ref.
$[\text{Cu}_2(\mu\text{-N}_3)](\mu\text{-}[30\text{-m}]\text{N}_6\text{O}_4)$ $(\text{N}_3)_2\text{ClO}_4$ (not given)	m P2 ₁ /n 4	17.89(7) 10.939(11) 20.361(13)	106.10(8)	CuN ₅	N 2.04(3, 12) 1.93(3) $\mu\text{N}_3\text{N}$ 2.23(3, 2)	6.02	not given	631
$[\text{Cu}_2(\mu\text{-im})]([24\text{-ane}]\text{N}_6\text{O}_2)$ $(\text{Meim})_2(\text{ClO}_4)_3$ (blue)	or Pnma 3	16.670(4) 28.112(18) 9.195(9)		CuN ₅	N 2.03(3) 2.11(4, 2) imN 2.08(3) μimN 1.95(2)	6.579(7) ^e	N ₃ N 84.8(15, 6.3) ^c 96.2(13, 2.6) 107.0(11) 126.1(15, 5.9) 165.1(12)	629
$[\text{Cu}_2(\mu\text{-nba})_2(\mu\text{-dabco})]$ $2\text{CH}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (not given)	or Pnma 4	22.771(6) 22.326(5) 11.621(3)		CuO ₄ N	not given	7.403(4)	not given	594

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

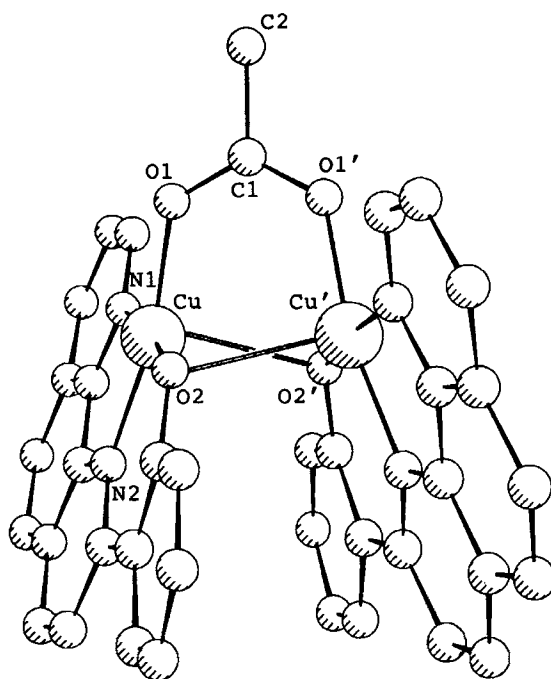


FIGURE 9 Structure of $[\text{Cu}_2(\mu\text{-hphen})_2(\mu\text{-ac})]^{2+}$ (see Ref. 608).

There are three blue examples^{612,614,615} in which a pair of tetragonal-bipyramidal,⁶¹² a square-pyramidal⁶¹⁴ and an intermediate between square-pyramidal and trigonal bipyramidal⁶¹⁵ units are triply bridged by an oxygen atom of $\mu\text{-OH}$ group, by bidentate anions ($\mu\text{-O}_2\text{NO}$,⁶¹² $\mu\text{-O}_2\text{IO}$ ⁶¹⁵) in *syn-syn* arrangements and by the two nitrogen atoms of a tetradentate (N_4) ligand with Cu–Cu separations of 3.138(1), 3.156(3) and 3.165(1) Å.

Two Cu(II) atoms in several other derivatives^{465,607,616,618,622,623} are triply bridged by one single atom ligand and by two bidentate ligands. In blue green $[\text{Cu}_2(\mu\text{-OH})(\mu\text{-HCOO})_2(\text{bpy})_2]\text{BF}_4$,⁶¹⁶ two nonequivalent Cu(II) atoms (one a distorted square-pyramid and the other a distorted trigonal bipyramid) are held together by a $\mu\text{-OH}$ group and by two $\mu\text{-HCOO}$ groups in *syn-syn* arrangements with a Cu–Cu separation of 3.171(1) Å.

Two non-equivalent Cu(II) atoms (five- and six-coordinate) are triply bridged by a $\mu\text{-OH}$ group and by two bidentate ligands ($\mu\text{-acetate}$ and $\mu\text{-pdm}$) in *syn-syn* arrangements.⁶¹⁸ There are two crystallographically independent molecules with Cu–Cu separations of 3.231(2) and 3.240(1) Å, respectively.

In dark green $[\text{Cu}_2(\mu\text{-N}_3)(\mu\text{-O}_2\text{Cl})_2(\mu\text{-baaep})(\text{bpy})_2(\text{ClO}_4)]^{465}$ two crystallographically independent dimers are found, in both of which the five- and six-coordinated Cu(II) atoms are held together by a μ -1,1-azide, $\mu\text{-O}_2\text{ClO}_2$ (syn–syn arrangement) and by $\mu\text{-baaep}$, with Cu–Cu separations of 3.295(4) and 3.367(4) Å, respectively.

The two square-pyramidal units in one example⁶²² are bridged by a single chlorine atom and by two bidentate pyrazole molecules, which brings the Cu(II) atoms to within 3.387(6) Å. The mean value of the displacement of Cu(II) atoms from the basal plane towards the apical ligand is 0.15 Å.

In blue $[\text{Cu}_2(\mu\text{-ac})_3(\text{bpy})_2]\text{ClO}_4$ ⁶⁰⁷ two types of acetate group are present, one bridging only through one O atom and the remaining two as bidentate in a syn–syn arrangement. The Cu(II) atoms are different from the stereochemical point of view, one square-pyramidal and the other an intermediate between square-pyramidal and trigonal-bipyramidal configurations with a Cu–Cu separation of 3.392(1) Å.

Two square pyramidal units in a deep green derivative⁶²³ are triply bridged by a single O atom of water and by two bidentate trichloroacetate groups in syn–syn arrangements. The mean value of the displacement of Cu(II) atoms from the basal plane is 0.435 Å and Cu–Cu separation is 3.529 Å.

In dark green $[\text{Cu}_2(\mu\text{-ac})_2(\mu\text{-bmpc})]\text{ClO}_4 \cdot 3\text{H}_2\text{O}$ ⁶¹⁹ two square pyramidal (CuO_3N_2) units are bridged by the phenolic oxygen of a pentadentate bmpc ligand (ON_4) and by two acetate groups in syn–syn arrangements, which bring the Cu(II) atoms to within 3.263(2) Å.

Green $[\text{Cu}_2(\mu\text{-Cl})(\mu\text{-ptp})_2(\text{ClO}_4)_3 \cdot \text{MeCN}]$ ⁶²⁰ involving a triple-bonding arrangement between the two square-pyramidal Cu(II) centers (a chlorine bridge and two pair of nitrogen atom bridges of two tetradentate ptp molecules (N_4)). Each Cu(II) atom is raised above the mean plane of the four equatorial nitrogen donors (0.282 and 0.286 Å) with a Cu–Cu separation of 3.269(2) Å. In blue $[\text{Cu}_2(\text{mepH})_4(\text{H}_2\text{O})](2\text{-cebez}) \cdot 2\text{PrOH}$,⁵¹⁵ the dimeric complex cation comprises two very simple building blocks, each of which has copper in square-pyramidal coordination with a mepH–Hmep ligand pair defining the basal plane. The basal planes of the building blocks are joined by two hydrogen bonds (oxygen–oxygen distances of 2.446(7) and 2.494(8) Å) the building blocks share a water ligand at the apices of their square pyramids. The Cu–Cu separation is 3.893(2) Å. The mean value of displacement of copper from the basal plane toward the water molecule is 0.204 Å.

There are several derivatives^{566,574,57,594,625–631} in which two Cu(II) atoms are “sitting” in the cavity of macrocyclic hexa- or octadentate N donor

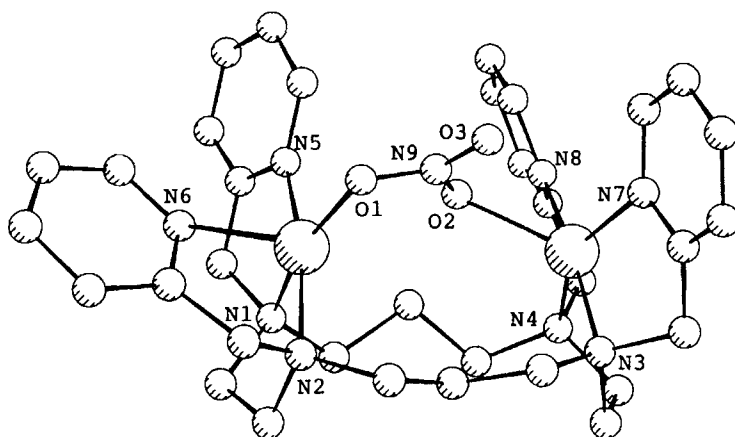


FIGURE 10 Structure of $[\text{Cu}_2(\mu\text{-O}_2\text{NO})(\mu\text{-tpmc})]^{3+}$ (see Ref. 625).

ligands, serving as a double bridge and an additional bridge is created or by a single $\mu\text{-1,1-N}_3$,⁵⁷⁵ $\mu\text{-OH}$,⁶²⁴⁻⁶²⁶ $\mu\text{-F}$,⁶²⁷ $\mu\text{-Br}$,⁵⁷⁴ atom; or by a bidentate ligand; $\mu\text{-1,3-N}_3$,^{566,631} $\mu\text{-O}_2\text{NO}$,⁶²⁵ $\mu\text{-imidazole}$.^{94,628-630} The structure of the green complex $[\text{Cu}_2(\mu\text{-O}_2\text{NO})(\mu\text{-tpmc})]\text{PF}_6)_3$ ⁶²⁵ is shown in Figure 10 as an example. The two Cu(II) atoms "sitting" in the cavity of macrocyclic tpmc ligand are additionally bridged by the nitrate group in syn-syn arrangements. Each Cu(II) atom has a distorted square-pyramidal environment. The Cu1 and Cu2 atoms are pushed from the basal planes toward the apices by 0.07 and 0.24 Å, respectively. The Cu-Cu separation for this series ranges from 3.57 to 7.403(4) Å. There is one derivative⁶²⁴ in which one Cu(II) atom is six- and the other one is five-coordinate. Two derivatives^{625,626} contain Cu(II) atoms in distorted trigonal bipyramidal arrangement and in all remaining examples^{66,574,575,594,625,627-631} each Cu(II) atom has a distorted square-pyramidal geometry. The mean values of the displaced Cu(II) atoms from the basal planes toward the apical ligands increases in the order: 0.14 Å⁵⁹⁴ < 0.16 Å⁶⁰⁵ < 0.26 Å⁶²⁹ < 0.28 Å⁶³¹ < 0.31 Å^{628,629} < 0.339 Å⁵⁶⁶ < 0.34 Å⁶²⁷ < 0.38 Å⁶²⁷ < 0.43 Å⁵⁷⁴ < 0.45 Å.⁵⁷⁵

Inspection of the data in Table VIII reveals that these derivatives are predominantly green and blue with some examples of red, brown and black. The ligands involved are mono- through hexa- and octadentate with N and O donors being by far the most common. The mean Cu-L_(terminal) bond distances are shorter than those of Cu-L_(bridge) when L are N, Cl or Br, with the values 1.97 vs. 2.05 Å (N), 2.33 vs. 2.535 Å (Cl) and 2.38 vs. 2.64 Å (Br), but the opposite pattern is observed when L is an O donor, 2.435 vs.

2.00 Å. One reason is the “small” size of the μ -OH group which mostly serves as a bridge.

The mean Cu–N bond distance increases in the order: 1.97 Å (mono-) < 2.015 Å (tetra-) < 2.020 Å (bi-) < 2.08 Å (octa-) < 2.165 Å (hexadentate). There are three types of hetero-donor ligands: tridentate including those with one O plus two N-donor; sites; pentadentate containing one O plus four N-donor; sites, and octadentate with two O plus six N-donor; sites.

The mean L–Cu–L bond angles of the metallocyclic rings open with decreasing coordination number. For example, in four-membered rings the mean O–Cu–O intra-ligand angles are 51.3°(six-) and 53.5°(five-coordinate); in five-membered rings (N–Cu–N) are 80.5°(six-) and 83.0°(five-coordinate).

There are four derivatives^{465,603,610,618} which contain two crystallographically independent dimers, differing mostly by degree of distortion and are further examples of distortion isomerism.¹⁴⁴

2.4 Quadruply Bridged

Crystallographic and structural data for the quadruply-bridged Cu(II) dimers are given in Table IX. There are several types of bridging, the distorted double edge-shared bi-octahedral structure with two types of bridge involving a pair of monodentate O-donor; ligands and of bidentate perchlorate groups. The structures are tabulated in the order of increasing Cu–Cu distance.

A crystal structure of $\text{Cu}_2(\mu\text{-Cl})_2(\mu\text{-npthd})_2\text{Cl}_2$ ⁶³² is shown in Figure 11. The molecular structure includes two types of bridge between the Cu(II) atoms: two asymmetric bridges involving chlorine atoms and two symmetric bridges involving npthd molecules and terminal chlorine atoms completed a square-pyramidal arrangement about each Cu(II) atom. There are two crystallographically independent molecules differing by degree of distortion with Cu–Cu distances of 2.659(4) and 2.664(5) Å, respectively.

There are several examples^{271,633,635–638} in which two Cu(II) atoms are bridged by two μ -OL groups and two intramolecular bidentate perchlorate groups. The geometry at each copper atom is distorted octahedral.

Another three examples^{633,636} involve bridges formed by μ -OL, μ -N₃ in an end-end fashion and by two perchlorate groups. Each copper is six-coordinate.

In dark brown $\text{Cu}_2(\mu\text{-OMe})(\mu\text{-ac})(\mu\text{-ttc6})$,⁶³⁹ two Cu(II) atoms are coordinated to two bidentate aminotropone iminate portions of the macrocycle (tetradentate N₄) and additionally bridged by both a methoxide (μ -OMe)

TABLE IX Crystallographic and structural data for quadriply bridged copper(II) dimers^a

Compound (color)	Cryst. cl. Space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-L-Cu [Å] Cu-L-Cu [°]	L-Cu-L [°]	Ref.
[Cu(μ -Cl)(μ -mthy)Cl] ₂ ^c (not given)	m C2/c 8	9.171(5) 14.931(5) 25.324(5)	90.2(1)	CuCl ₃ N ₂	N ^b Cl μ Cl 2.007(22) 2.275(14) 2.299(14) 2.667(14)	Cl ^b 2.659(4) 115.7(5)	Cl ^b 98.3(5) 146.0(6) 171.1(10) 89.9(1.2, 4.7)	632
[Cu ₂ (μ -OH)(μ -fdmen) (μ -O ₂ ClO ₂)] (dark green)	m P2 ₁ /c 4	9.124(2) 30.930(8) 9.174(5)	99.01(3)	CuCl ₃ N ₂ CuO ₄ N ₂	N Cl μ Cl 2.043(21.3) 2.253(16) 2.322(18) 2.667(20)	Cl HO O 2.664(5) 115.9(6) 2.924(1) 97.4(2) 99.3(2)	Cl, Cl N, N N, N Cl, N 89.7(6) 145.2(7) 171.3(8) 89.7(9, 7.8)	633
[Cu ₂ (μ -OCN)(μ -fdmen) (μ -O ₂ ClO ₂)] (dark green)	m P2 ₁ /c 4	8.814(2) 31.645(6) 9.233(5)	81.19(4)	CuO ₄ N ₂	μ HO N μ O 1.919(5.4) 1.974(9, 44) 1.942(7, 3) 2.483(9) 2.655(9) 2.710(10) 3.080(10) 1.925(10.5)	O NCO 2.933(2) 98.1(3) 99.3(4)	N, N N, O O, O 86.0(4, 2) ^d 91.0(3, 3) ^e 102.0(4, 1) 81.2(4, 2)	633
α -[Cu(μ -OH)(μ -O ₂ ClO ₂) (dmacp)] ₂ (blue)	tr P-1 1	9.164(5) 10.049(5) 8.953(5)	82.30(2) 56.72(2) 68.52(2)	CuO ₄ N ₂	μ NCO N μ HO μ O ₂ ClO ₂ 2.749(3, 33)	HO 2.938(1) 98.35(9)	O, O O, N N, N 85.2(1, 4, 6) 167.05(7) 93.4(1, 5, 4) 95.0(1) ^e	634
[Cu ₂ (μ -OH)(μ -O ₂ ClO ₂) ₂ (μ -amazpb)] (black purple)	tr P-1 2	13.366(13) 9.430(9) 11.760(9)	95.04(2) 109.51(3) 111.245(8)	CuO ₄ N ₂	μ O ₂ ClO ₂ N μ O 2.679(11, 94) 2.940(9) 1.975(9, 28) μ O 1.940(6, 12) 1.955(6, 1)	HO O 2.957(2) 99.3(3) 98.3(3)	O, O O, N N, N 84.5(3, 5, 5) 165.9(3, 5, 7) 91.2(3, 2, 0) ^e 102.9(3, 1, 2) 170.2(3, 9) 98.2(3, 1, 7) ^e	635

TABLE IX (Continued)

Compound (color)	Cryst. cl. Space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-L-Cu [°]	Cu-Cu [Å] Cu-L-Cu [°]	L-Cu-L [°]	Ref.
$[\text{Cu}_2(\mu\text{-N}_3)(\mu\text{-fdmen})\cdot(\mu\text{-O}_2\text{ClO}_2)]$ (green)	m P2 ₁ /c 4	8.797(3) 31.84(2) 9.253(5)	98.97(3)	CuO_3N_3	N μO $\mu\text{O}_2\text{ClO}_2$		2.972(2) 98.7(2) 100.0(4)	N,O 90.8(3.1) ^e 86.2(3.1) ^d 102.7(3.1) 80.5(3.1)	633
$[\text{Cu}_2(\mu\text{-EtOH})(\mu\text{-O}_2\text{ClO}_2)_2\cdot(\mu\text{-mmfp})\cdot\text{H}_2\text{O}]$ (dark green)	m P2 ₁ /c 4	9.346(2) 32.517(4) 8.866(6)	97.04(3)	CuO_4NS	$\mu\text{N}_3\text{N}$ μEtHO μO S N $\mu\text{O}_2\text{ClO}_2$		2.985(2) 100.4(3) 103.1(3)	S,O 100.6(2.1) 92.0(3.3) ^e 89.2(3.1) ^d 77.9(3.1.2)	636
$[\text{Cu}_2(\mu\text{-C}_3\text{H}_7\text{H}_3\text{N}_4\text{N}_4\text{O}_2)\cdot(\mu\text{-O}_2\text{ClO}_2)]$ (deep blue)	or Fddd 8	16.985(2) 17.180(3) 20.558(4)		CuO_4N_2	N μO $\mu\text{O}_2\text{ClO}_2$		2.993(2) 102.8(2)	O,O 76.1(1.1.2) 89.9(1) 160.7(1) 95.5(2.1.9) 166.9(2) 96.9(2) ^e	637
$[\text{Cu}_2(\mu\text{-N}_3)(\mu\text{-O}_2\text{ClO}_2)_2\cdot(\mu\text{-mmfp})\cdot\text{H}_2\text{O}]$ (not given)	m P2 ₁ /c 4	9.669(2) 30.860(4) 8.717(3)	98.08(2)	$\text{CuO}_3\text{N}_2\text{S}$	$\mu\text{O}_2\text{ClO}_2$ μN_3 N S μO		3.007(2) 100.4(3) 102.8(4)	S,N 94.5(3.5.0) ^e O,N 92.4(3.3) ^e O,O 78.1(3.9)	636
$[\text{Cu}_2(\mu\text{-OCN})(\mu\text{-O}_2\text{ClO}_2)_2\cdot(\mu\text{-mmfp})\cdot\text{H}_2\text{O}]$ (dark green)	m Cc 4	12.773(5) 32.167(5) 8.980(4)	130.35(5)	CuO_4N_2	$\mu\text{O}_2\text{ClO}_2$ μNCO N μO		3.017(2) 98.5(3) 101.7(4)	N,N 95.0(4.1.2) ^e O,N 93.0(4.3.1) ^e O,O 79.8(3.9)	636

[Cu(μ -pvaal)(μ -O ₂ ClO ₂) ₂ ·2H ₂ O (dark green)]	tr P-1 1	10.522(6) 9.132(5) 8.346(5)	102.38(12) 121.86(14) 93.75(10)	CuO ₄ N	μ -O ₂ ClO ₂ N μ O	1.871(4) 1.961(4) 1.945(3, 9)	3.022(2) 102.0(2)	O,N O,O	95.5(2, 5.8) ^f 78.0(2) 84.7(2, 3.1) 96.8(2, 3.7)	638
[Cu ₂ (μ -ubm)(μ -O ₂ ClO ₂) ₂] (dark khaki)]	m P2 ₁ /c 8	8.6653(3) 16.717(1) 9.9714(6)	97.273(4)	CuO ₄ N ₂	μ -O ₂ ClO ₂ N μ O	2.522(3) 2.790(3) 1.957(3, 22) 1.956(2, 13)	3.0354(7) 101.8(1)	O,O	78.2(1) 84.0(1, 8.2) 162.55(9) 100.36(1) ^f 91.8(1, 2.2) ^f 97.4(1, 4.7) 168.1(1, 8)	271
[Cu ₂ (μ -N ₃)(μ -O ₂ ClO ₂)(mmfp)] (dark green)]	m Cc 4	12.723(9) 32.125(7) 8.987(7)	130.39(5)	CuO ₃ N ₃	μ -O ₂ ClO ₂ μ N ₃ N μ O	2.671(1, 12) 1.90(1, 2) 1.97(1, 1) 1.99(1, 2)	3.035(2) 99.4(5) 106.1(6)	N,N O,N O,O	96.2(5, 2) ^f 91.0(5, 2) ^e 77.3(5)	636
[Cu ₂ (μ -MeO)(μ -ac)(μ -tfc6)] (dark brown)]	or Cmc21 4	18.352(3) 15.841(3) 9.912(2)		CuO ₂ N ₂	N μ acO μ MeO	1.92(1, 0) 1.975(8) 1.945(8)	3.100(3) 105.6(5)	N,N N,O	82.7(5) ^d 97.5(5, 3.4) 159.1(5, 3.5) 89.4(5)	639
[Cu ₂ (μ -OH)(μ -H ₂ O). (μ -[20-m]N ₆)(μ -O ₂ ClO ₂) ₂]. ClO ₄ ·H ₂ O (blue)]	tg P4 ₂ /n 4	15.20(1) 14.50(1)		CuO ₃ N ₃	N μ -O ₂ ClO ₂ μ HO μ H ₂ O	2.014(13, 98) 2.480(13) 1.916(9) 2.519(12)	3.145(4) 77.3(4) 110.3(7)	O,O H ₂ O HO	92.6(5, 6.4) 174.9(3) 88.9(5, 2.6) 100.9(4, 1.0) 170.8(5) 79.4(5, 1.0) ^d 158.2(5)	640
[Cu ₂ (μ -OH)(μ -O ₂ ClO ₂)(μ -hadit)] (ClO ₄) ₂ ·CHCl ₃ (not given)]	m P2 ₁ /c 4	14.487(2) 15.282(2) 15.573(2)	91.79(1)	CuN ₃ O ₂	N μ -O ₂ ClO ₂ μ HO	2.033(5, 40) 2.554(8, 14) 1.917(4, 5)	3.642 143.6(2)	O,N HO	83.8(3, 3.5) 96.1(2, 6) 108.9(3, 6) 171.3(2, 7) 91.2(3, 6) 85.2(2, 6) ^d 159.4(2, 1.1)	641

TABLE IX (Continued)

Compound (color)	Cryst. cl. Space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	$Cu-L$ [Å]	$Cu-Cu$ [Å] $Cu-L-Cu$ [°]	$L-Cu-L$ [°]	Ref.
$[Cu_2(\mu-N_3)_2(\mu-[24]-aneN_2S_4)(N_3)_2]$ (dark yellow)	m C2/m 2	10.126(2) 13.246(3) 11.156(2)	93.47(1)	CuN_4S_2	N S N ₃ N μN_3N	5.145(1)	N,N N,N N,S 85.33(8) 97.5(1, 3, 4) 156.58(4)	590
$[Cu_4(\mu-N_3)_2(\mu-[24]-aneN_2O_2)(N_3)_2]$ (not given)	m C2/m 2	9.533(1) 12.305(1) 11.913(1)	107.25(4)	CuN_5	N	5.973(1)	N,N 107.8(1) 142.0(1) 175.0(1, 9)	341

^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 There are two crystallographically independent molecules. ^d Five-membered metallocyclic ring. ^e Six-membered metallocyclic ring. ^f Seven-membered metallocyclic ring.

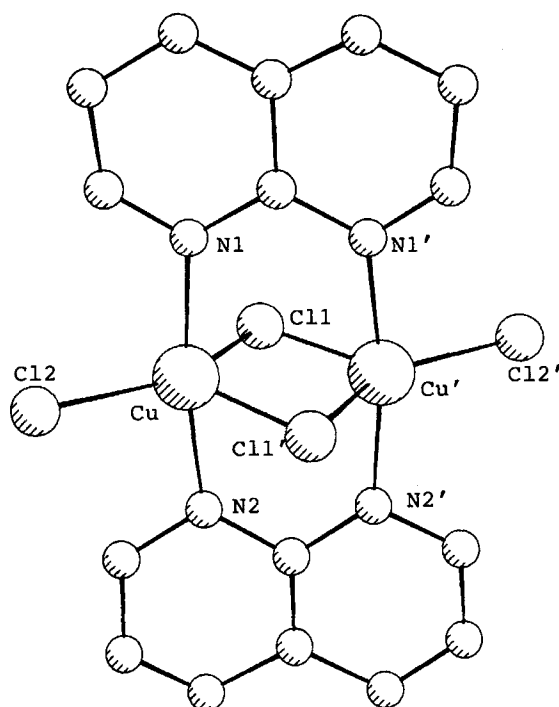


FIGURE 11 Structure of $[\text{Cu}(\mu\text{-Cl})(\mu\text{-npthd})\text{Cl}_2]^{2+}$ (see Ref. 632).

and a bidentate acetate ligand in a syn-syn arrangement. In the center are two tetrahedrally distorted Cu(II) atoms separated by 3.100(3) Å.

Each Cu(II) atom in the blue derivative⁶⁴⁰ is bonded to the three nitrogen atoms of a hexadentate macrocycle and additionally bridged by a OH group and a water molecule. The sixth position about each Cu(II) atom is occupied by a perchlorate group.

A square pyramidal arrangement about each Cu(II) atom⁶⁴¹ is built up by a hexadentate N_6 macrocycle (to three N atoms about each copper), an oxygen atom of bridged OH-group and by a bidentate perchlorate group which also serves as a bridge between two Cu(II) atoms.

Finally, there are two other examples^{341,590} where two Cu(II) atoms are located in the cavity of a macrocycle and additionally bridged by two azide groups in an end-to-end fashion. The Cu-Cu separations of 5.145(1)⁵⁹⁰ and 5.973(1) Å³⁴¹ are much longer than found in all other quadruply bridged derivatives (Cu-Cu separations range from 2.659(4) to 3.642 Å) (Table IX).

Eighteen derivatives which are summarized in Table IX are mostly green and blue, but there are examples of purple, brown and yellow, one of each.

The mean Cu–L_(bridge) bond distance increases in the order: 1.92 Å (N₃) < 1.93 Å (OH) < 2.49 Å (Cl). In the series of multidentate ligands, the mean Cu–L bond distance increases in the sequence: 1.975 Å (tetra-N-) < 2.02 Å (bi-N-) < 2.03 Å (hexa-N-) < 2.67 Å (bi-O-donor;). There are some multidentate ligands including hetero-donor atoms; tridentate ligands with two O-plus one N atom; pentadentate ligands with one O plus four N atoms or one O plus two N and plus two S atoms, and hexadentate ligands with two O plus four N-donor; sites. The mean N–Cu–N bond angles of the macrocyclic rings, increases with ring size as expected in the order: 85.0°(five-) < 96.0° (six-) < 100.3°(seven-membered ring).

2.5 By Single Atom Bridges

Structural data for twenty (blue and green) Cu(II) dimers bridged by a single atom are summarized in Table X. The structures are tabulated by increasing Cu–Cu distance. The most common bridging ligands are O-donor; ^{232,239,619,642–647,649} In four derivatives^{648,650,651,653} a chlorine atom, in another two⁶⁵² a sulfur atom of a ligand and in one⁶⁵⁴ a bromine atom serve as a bridge. The stereochemistry about Cu(II) atoms is four-, ^{644,646,653} five-, ^{232,239,619,643,647,650,652,654} and six-coordinate. ^{619,642,645} Two non-equivalent Cu(II) atoms are found; four- and five^{619,648} and five- and six-coordinate. ^{649,651} The Cu–Cu distances range from 2.657(3) to 5.604(2) Å and Cu–L–Cu bridge angle from 107.5 to 180.0°.

The mean Cu–L_(bridge) bond distance increases in the order: 1.92 Å (OH) < 1.96 Å (OL) < 2.47 Å (SL) < 2.48 Å (Cl) < 2.80 Å (Br). The multidentate ligands include both homo- and hetero-donor atoms, with N- and O-donor;s being by far the most common. The mean Cu–N bond distances increase in the order: 2.005 Å (tetra-) < 2.015 Å (tri-) < 2.04 Å (mono-) < 2.12 Å (bidentate). Hetero donor ligands are tridentate (include two O plus one N), tetradentate (O+3N), (2N+2S), pentadentate (3O+2N; O+4N), hexadentate (4O+2S) and heptadentate (O+6N). Notice only O-atoms are used for bridges.

There are two examples^{643,644} which contain two crystallographically independent molecules differing mostly by degree of distortion.

2.6 By Single Multi-Atom Bridges

Crystallographic and structural data are summarized in Table XI. The structures of sixty derivatives are tabulated. The bridge systems are complex and therefore it is difficult to classify them. For example, in dark green

$\text{Cu}_2(\text{pmk})\text{Cl}_4$ ⁶⁵⁵ a bridge connecting the two Cu(II) centers consists of an azine linkage. There is a rotation about the N–N bond, which results in a Cu–N–N–Cu torsion angle of 70.8°. The Cu–Cu separation of 3.67 Å excludes a metal–metal bond, but is the shortest in this group.

In a dark red derivative⁶⁵⁶ each Cu(II) is approximately square planar, a coordinated to three nitrogen atoms of the tridentate bmpi ligand and to one oxygen atom of the bridging carbonate group.

In a purple complex⁶⁵⁷ a *trans* μ -1,2- O_2^{2-} group bridges the two CuN_4 moieties and completes a distorted trigonal bipyramidal configuration about each Cu(II) atom. The Cu–Cu separation is 4.359(1) and the O–O bond length is 1.482(6) Å.

In a cofacial dimer,⁶⁵⁸ two Cu centers are separated by 4.625(1) Å and each Cu(II) atom is in a square planar environment, CuN_4 .

Two structurally distinct types of Cu(II) atoms (CuN_3O and $\text{CuN}_2\text{Cl}_2\text{O}$) are held together by a -N–N- bridge in a further example.⁶⁵⁹

The structure of $[\text{Cu}_2(\text{im})(\text{dtma})_2]^+$ (see Ref. 671) is shown in Figure 12. Two pentacoordinate Cu(II) atoms are bridged by a deprotonated imidazole. Each Cu(II) atom has a distorted square-pyramidal configuration. The mean value of displacement for Cu(II) atoms from the plane toward the apical ligand is 0.235 Å and Cu–Cu separation is 5.984 Å.

The structure of blue $\text{Cu}_2(\mu\text{-bdta})(\text{im})_2(\text{H}_2\text{O})_2$ ⁶⁶⁶ is shown in Figure 13. In this centrosymmetric complex, the 1,4-butanediaminetetraacetate anion bridges two Cu(II) atoms with separation of 7.942(2) Å. Each Cu(II) atom has a distorted square pyramidal environment.

In a dark green compound $[\text{Cu}_2(\mu\text{-F}_2\text{SiF}_4)(\text{spca})_2]\cdot 4\text{H}_2\text{O}$,⁶⁹⁷ two distorted square-pyramidal Cu(II) atoms are linked by a single hexafluorosilicato bridge (Cu–F–Si–F–Cu). The Cu(II) atoms are located 0.0075(1) Å above the O_2N_2 plane with Cu–Cu separation of 7.950(7) Å.

There are two examples, $[\text{Cu}_2(\mu\text{-1,3-pn})(1,3\text{-pn})_4]\text{X}_4$ ($\text{X} = \text{BF}_4$,⁶⁹⁸ ClO_4 ⁷⁰⁰) in which two distorted square-pyramidal moieties are bridged by 1,3-propanediamine (Cu–N–C–C–N–Cu) with Cu–Cu separations of 8.07(7) and 8.104 Å, respectively.

Inspection of the data in Table XI reveals that there are four-, five- and six-coordinate Cu(II) atoms. In several examples^{655,656,658,666,672} each Cu(II) atom has a square-planar environment with a different degree of distortion and in one case⁶⁸⁰ are tetrahedrally coordinated. The most common coordination number is five, distorted square-pyramidal environments are present in many complexes^{346,661–663,667–671,675,678,680–685,687–690,693–698,700,701} and trigonal bipyramidal in some.^{657,664,665,684,703,704} An intermediate between a square pyramide and trigonal bipyramide are present in a few

TABLE X Crystallographic and structural data for copper(II) dimers bridged by a single atom (Cu–X–Cu)^a

Compound (color)	Cryst. cl. space G. 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(topcb)(H ₂ O)(ClO ₄) ₂ · 3EtOH (blue)]	tr P-1 2	10.160(1) 13.014(1) 15.934(2)	74.18(1) 84.83(1) 71.54(1)	CuO ₄ N ₂	O ^b not given	2.657(3) ^f not given	O, O ^b not given	642
[Cu ₂ (μ-OH)(tacc) ₂ · 2NaClO ₄ ·2H ₂ O ^c (not given)]	m P2 ₁ /c 4	8.423(7) 22.737(3) 17.926(3)	92.90(3)	CuN ₃ O ₂	N O μHO 1.937(6)	3.17 not given	N, N 83.1(3, 1.1) ^d 165.6(3) 105.3(3, 4.9) 167.4(3)	643
[Cu ₂ (μ-bmpe)(NO ₂) ₂ (H ₂ O) ₂ · ClO ₄ ·H ₂ O (green black)]	or Pbca 8	20.654(1) 20.087(2) 13.873(3)		CuO ₄ N ₂	N O μHO 1.931(6)	3.17 not given	N, N 82.5(4, 3) ^d 171.0(3) 111.0(3, 5.2) 156.8(3)	619
[Cu ₂ (μ-bmpe)(N ₃) ₂ · [Cu ₂ (μ-bmpe)(N ₃) ₂ ClO ₄ ·2H ₂ O (green black)]	tr P-1 2	19.250(4) 13.405(3) 12.873(3)	121.77(1) 98.88(1) 95.86(1)	CuN ₃ O	N N ₃ N μO 1.98(1)	3.605(2) 132.3(5)	not given not given	619
[Cu ₂ (μ-C ₃₆ H ₃₆ N ₆ O) ^c (not given)]	m P2 ₁ /n 8	13.861(4) 31.482(8) 16.956(5)	98.20(2)	CuN ₃ O	N N ₃ N μO 1.98(1)	3.619 128.0(4)	O, N 91.8(4, 1.1) ^e 115.0(4, 5.5) 102.0(4, 1.6) 123.0(5, 68)	644

[Cu ₂ (μ-OH)(H ₂ O)(terp)] ₂ : (ClO ₄) ₃ (blue)	tr	8.825(5)	88.24(2)	CuN ₃ O	N	1.936(10,18) 2.077(11)	3.715	O ₁ N	94.7(4,2.1) ^f 105.4(4,2.7)	645
	P-1	10.391(10)	99.27(3)		H ₂ O	2.187(11,9)	O		140.8(4)	
	2	19.258(8)	96.63(4)		O ₃ ClO	2.050(9,76)			98.4(4,2.7) ^f 104.1(4,2.7)	
					μHO	1.902(4)			142.5(5)	
					N	2.005(5,82) 2.424(7)	HO			
[Cu ₂ (μ-dpma)(MeO) ₂] (not given)	m	28.45(1)	110.96(4)	CuO ₃ N ₃	N	2.008(6,85) 2.541(8)			169.3(2)	646
	P2 ₁ /a	6.952(4)			O ₃ ClO	2.821(7)			79.4(2,7) ^d 159.5(2)	
	4	10.128(8)			μHO	1.909(4)			83.8(2,1.3) 94.8(2,7.4)	
									173.6(2) 92.1(2,1.0) 174.8(2)	
					MeO	1.915(9,1) 1.927(10,4)		3.644(2)		
[Cu ₂ (μ-OH)(bpy) ₂](ClO ₄) ₃ (blue)	m	14.839(8)	92.87(3)	CuN ₄ O	N	1.909(10,12) 1.954(9,10)			173.7(5,5) 90.1(5,6) 176.2(4,3)	647
	P2 ₁ /n	18.197(9)							92.5(2.9) 103.2(2)	
	4	16.491(8)			μHO	2.024(7,55) 2.186(16,61) 1.930(5,0)	HO		120.3(2,2.7) 132.9(2) 162.4(2,8.2)	
									78.7(2,2.1) ^d 93.5(2,5.4)	
									100.9(2,3.2) 100.0(11,8.7)	
[Cu ₂ (μ-Cl)(mnttc)(Cl) ₃] (dark green)	or	18.045(6)		CuN ₄ Cl	N	2.014(4,8)			174.7(2,1.1)	648
	Pham	9.551(5)			μCl	2.507(2)	Cl		85.59(15,1.04) ^d 95.32(12)	
	4	11.142(3)							159.33(14)	

TABLE X (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å]			α [°]			Chromophore	Cu-L [Å]	Cu-Cu [Å] Cu-L-Cu [°]	L-Cu-L [°]	Ref.	
		b [Å]	c [Å]	β [°]	γ [°]								
[Cu ₂ (μ -bimp)(MeOH)](ClO ₄) ₂ (green)	m P2 ₁ /n 4	17.855(3)			105.78(2)			CuCl ₄	Cl μ Cl	4.09(2) O 142.9(2)	Cl,Cl N,N O,O O,N	98.66(4, 19) 134.28(8, 2.22) 83.0(2, 6) ^d 152.2(2, 2.4) 92.3(2, 6.6) 98.3(2, 7.0) 172.6(2, 6.4)	239
		18.054(4)							μ O MeHO				
		12.065(4)			102.85(3)				CuN ₃ OCl	N N	4.128(3) O 140.2(5)	N,N N,N	82.8(7, 1.1) ^e 160.0(7, 1.4) 95.6(7, 6.8) 95.6(5, 6) 169.9(5, 1.7) 96.5(6)
[Cu ₂ (μ -bpmp)Cl ₂](ClO ₄) ₂ (not given)	m Pn 2	12.592(5)			102.85(3)				μ O Cl				
		12.006(4)											
		13.103(6)			90.8(2)				CuO ₄ N ₂	O N	4.176(2) ^f not given O	O,N O,O	77.9(1, 4.4) ^d 103.2(4, 2.1) 92.5(1, 9.1) 155.4(1, 4.2) 176.6(1)
[Cu ₂ (μ -pydca)(bpy)] ₂ ·4H ₂ O (blue)	m P2 ₁ /c 4	17.815(7)			90.8(2)								
		15.302(7)											
		13.103(6)			90.8(2)				CuN ₄ O	bpy,N μ O	4.200(4) ^f 1.74.2 Cl	N,N N,N N,N N,O	80.4(4, 6) ^d 98.2(4, 6) 108.7(4) 93.1(4) 138.9(4)
[Cu ₂ (μ -Cl)(tertb)](ClO ₄) ₂ (blue)	m C2/c 4	28.03(8)			116.9(1)								
		9.334(9)											
		20.96(5)											
[Cu ₂ (μ -Cl)(aert) ₂ Cl](ClO ₄) ₂ (not given)	m P2 ₁ /c 8	12.323(2)			101.53(2)								
		10.426(3)											
		27.689(6)											

[Cu ₂ (μ-4-mpb)(fbb) ₂](ClO ₄) (not given)	tr P-1 2	94.45(5) 15.447(6) 11.018(7)	CuN ₂ S ₂ Cl	S N μCl	2.431(6) 2.565(6) 1.980(16.4) 2.304(6)	Cl ₁ N N ₁ S	90.2(5, 1.4) 85.3(5, 7) ^d 94.9(5, 2.3) 120.1(2) 85.6(2) ^d	652
[Cu ₂ (μ-4-Clpb)(hbo) ₂](PF ₆) (dark green)	tr P-1 2	12.329(6) 15.447(6) 92.22(5) 96.13(4)	CuN ₄ S	N μS	1.968(18,41) 2.471(7, 35)	S ₁ N	95.0(6, 1.8) 106.8(8, 5.6) 80.8(7, 2.6) ^d 92.8(7, 4.0) 152.0(7, 10.8)	652
[Cu ₂ (μ-tacac)] ₂ (ClO ₄) ₂ (not given)	tr P-1 2	11.230(3) 14.079(3) 12.540(3)	CuN ₄ S	N μS	1.964(7, 18) 2.472(3, 13)	S ₁ N	95.4(2, 2.4) 105.4(2, 2.1) 80.1(3, 1) ^d 96.1(3, 2.9) 159.2(3, 2.9)	643
[Cu ₂ (μ-tacac)] ₂ (ClO ₄) ₂ (not given)	or P2 ₁ ² ₁ ² ₁ 4	7.802(2) 7.921(2) 21.187(3)	CuN ₃ O ₂	N O μO	2.045(10,18) 2.195(7) 1.952(7) 1.982(7)	O ₁ N	110.1(4, 3.5) 164.0(3, 5.9) 83.1(4, 3) ^d	653
[Cu ₂ (μ-Cl)(pea) ₂](PF ₆) ₃ (not given)	m C2/m 2	16.428(4) 12.721(3) 12.526(6)	CuN ₃ Cl	N μCl	2.034(8, 5) 2.530(1)	N ₁ N	89.5(3, 4) ^e 168.4(3, 2.7)	654
[Cu ₂ (μ-Br)(bpic) ₄](ClO ₄) ₃ (blue)	m C2/c 4	22.336(2) 9.370(1) 25.842(3)	CuN ₄ Br	N μBr	2.049(84,8) 2.802(1)	Br ₁ N	87.5(2, 3) 100.1(2, 6) 84.8(3, 4) ^d 96.2(3, 3) 167.5(3, 7, 6)	654

^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 There are two crystallographically independent molecules. ^d Five-membered metallocyclic ring. ^e Six-membered metallocyclic ring. ^f Calculated by us.

TABLE XI Crystallographic and structural data for copper(II) dimers bridged by a single ligand (Cu-(X)_n-Cu)^a

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]			α [°] β [°] γ [°]			Chromophore	Cu-L [Å]	Cu-Cu [Å]	L-Cu-L [°]	Ref.
		a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]					
[Cu ₂ (μ-pmk)Cl ₄] (dark green)	m P2 ₁ /n 4	9.058(2) 14.115(3) 14.892(3)	106.26(2)				CuN ₂ Cl ₂	N ^b Cl	2.016(4.8) 2.052(4.6) 2.254(1.4)	3.67	94.3(6.6) 93.8(1.1,2) 168.7(1.1,2) 77.3(2.3) ^c	655
[Cu ₂ (μ-O ₂ CO)(bmp) ₂] (dark red)	tr P-1 2	11.420(1) 16.479(1) 10.954(1)	90.98(1) 113.83(1) 101.71(1)				Cu ₂ O	N μO ₂ CO	1.885(6.4) 2.020(6.8) 1.921(4.9)	4.293(1) ^g	O,N O,N N,N 160.8(4.1,7)	656
[Cu ₂ (μ-O ₂ (tpma) ₂](PF ₆) ₂ ·5Et ₂ O (purple) (at 178 K)	tr P-1 1	11.062(3) 12.758(4) 13.280(5)	96.72(3) 110.57(3) 103.73(3)				Cu ₂ N ₄ O	N μO ₂	2.078(7.54) 1.852(5)	4.395(1)	O,N 103.7(3,1.1) 173.7(3) 80.3(3,1.1) ^c 117.2(3,8.1)	657
[Cu ₂ (μ-C ₇₄ H ₈₈ N ₈)]·CH ₂ Cl ₂ · MeOH (not given)	m P2 ₁ /n 4	19.208(7) 14.672(5) 24.170(7)	111.5(3)				CuN ₄	N	1.998(8.4)	4.625(1) ^g	N,N 90.0(1,1.0) ^d 178.1(1.4,4)	658
[Cu ₂ (μ-pkph)Cl ₂]·H ₂ O (green)	m P2 ₁ /n 4	9.644(1) 16.345(5) 14.438(3)	90.52(1)				CuN ₂ O	O N	1.959(4) 1.877(4) 1.970(4,19)	4.659(1)	O,N 106.5(2) 161.1(2) 80.9(2) ^c 91.9(2) 87.2(2)	659
[Cu ₂ (μ-dapsc)(H ₂ O)Cl ₂]·Cl ₂ ·H ₂ O (green)	m P2 ₁ /c 4	6.9706(6) 41.927(5) 7.1097(7)	101.959(7)				CuN ₂ Cl ₂ O	O N Cl	2.068(4) 1.954(4) 2.025(4) 2.230(2) 2.443(2)	4.716(1) ^g	O,N N,N 155.9(2) 98.5(1,2,3) 156.4(1) 94.3(1,2,9) 107.4(1)	660

	CuO ₃ NCI			O N Cl H ₂ O	1.947(6, 1) 1.945(8) 2.241(3) 2.393(8)			not given	
	Cu ₃ N ₃ Cl ₂	118.33(1)	9.265(2) 9.865(1) 12.145(3)	N 2.045(1, 13) 2.474(1) Cl 2.252(1, 5)	5.206(1) ^g			81.3(1, 2, 3) ^c 91.6(1, 7) 123.4(1) 162.7(1, 8, 6) 96.6(1)	661
	Cu ₃ N ₃ OS	107.414(9)	27.876(19) 12.338(9) 13.414(9)	N O S	1.95(3, 6) 1.95(2, 0) 3.22(1, 6)	5.21 ^g		73.0(1, 6) ^e 98.0(1, 1) 110.0(1, 1) 81.0(1) ^e 101.0(1) 173.0(1, 2) 85.0(1, 1) ^e 94.0(1, 1)	662
	Cu ₃ N ₄ O	108.08(2) 92.01(2) 101.49(2)	13.174(3) 13.994(4) 13.978(4)	N N μO ₂ CO	2.074(9, 51) 2.218(10) 1.920(7)	5.375(1)		98.0(3, 8) 178.8(3) 81.8(4, 1, 2) ^e 100.9(3, 4, 7) 150.6(4)	663
	Cu ₃ N ₄ (CN)	98.51(2)	24.040(8) 15.062(5) 12.525(4)	N μCN	2.05(-, 3) 2.12	5.4		83.8(2, 7) ^e 93.5(2, 8) 112.7(2, 1, 0) 134.6(1) 174.0(1)	664
	Cu ₃ N ₅	100.585(7)	16.880(2) 26.011(1) 14.686(1)	tmbmaN bztzN	2.073(5, 32) 1.929(5)	5.536(2)		80.4(2, 1) ^e 93.9(2) 101.4(2) 124.3(2, 2, 4) 174.1(2)	665
	Cu ₃ N ₄		14.226(2) 16.214(3) 7.970(2)	N μimN	2.010(8, 46) 1.923(7)	5.6619(7)		86.9(2) ^e 96.1(2) 160.3(3, 3, 8)	666

TABLE XI (Continued)

Compound (color)	Cryst. cl. space G. Z	<i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å]	L-Cu-L [°]	Ref.
[Cu ₂ (μ-tic)(5-Me-imH ₂) ₂ ·2H ₂ O (not given)]	m C2/c 4	22.503(5) 7.491(2) 17.367(2)	110.76(1)	CuO ₂ N ₂ S	imN ticO N S	5.707(1)	O,S 88.44(9) 101.6(1) 165.0(1) O,O N,S 91.4(1,6,5) 84.9(1,4) ^c N,O 94.9(1,1,4) N,N 177.0(1)	667
[Cu ₂ (μ-megtb)Cl ₂ Cl ₂ ·6H ₂ O (green)]	tr P-1 2	14.066(3) 15.204(6) 15.756(3)	105.97(3) 110.89(2) 96.72(3)	CuN ₃ OCl	N O Cl	5.760(4)	Cl,O 106.9(5, 1.2) Cl,N 97.9(6, 1.4) 173.5(6, 1.4) O,N 79.6(7, 3) ^c 83.8(6) 102.9(6, 3, 7) N,N 81.6(8, 6) ^c	668
[Cu ₂ (μ-megtb)F ₂ (BF ₄) ₂ ·2H ₂ O· H ₂ OBF ₃ (green blue)]	or Pccn 4	12.159(2) 16.909(2) 25.654(5)		CuN ₃ FO	N O F	5.834(2)	F,O 106.9(4, 8) O,N 80.2(4, 8) ^c 94.7(5, 7, 7) N,N 81.7(4, 1) ^c 159.3(4)	668 669
[Cu ₂ (μ-edta)(H ₂ O) ₄] (grey)]	m B2/b, Bb 4	16.26(3) 18.45(3) 6.72(2)	120(0.5)	CuO ₄ N	O N H ₂ O	5.89(7) ^f	O,N 80.9 ^c 93.9 O,O 92.5(-4, 8) 174.1	670
[Cu ₂ (μ-bim)(Me ₃ dien) ₂ (ClO ₄) ₂ · ClO ₄ ·H ₂ O (brown)]	or Iba2 8	17.443(5) 37.510(17) 12.468(5)		CuN ₄ CuN ₄ O	N μimN N O ₃ ClO μimN	5.930(4) ^g	N,N 86.6(9) ^c 95.2(9, 1.9) 164.6(9, 2.1) N,N 85.6(7, 9) ^c 93.0(8) 169.8(7, 5, 8) N,O 94.6(7, 4, 7)	666

[Cu ₂ (μ-im)(dtma) ₂](ClO ₄) ₂ ·2.5H ₂ O (blue)	m P2 ₁ /a 4	13.133(2) 14.224(3) 15.788(3)	114.22(2)	CuN ₄ O	N O μimN	2.049(7.38) 2.184(6.4) 1.966(5.4)	5.984 [#]	N,N	84.3(2,3) ^f	671
									94.9(2,1.2)	
									155.6(3,2.5) 175.3(3,2.6) 81.2(2,1) ^e 95.6(3,4) 103.7(3,3.1)	
[Cu ₂ (μ-sata)] ^f (brown)	tr P-1 4	16.691(1) 17.106(1) 15.641(1)	117.25(1) 117.95(1) 88.83(1)	CuO ₂ N ₂	O N	1.883(12.4) 1.929(11.8) 1.927(13.6)	6.118(3) [#]	O,O O,N N,N	87.6(6,6)	672
									94.4(6,6) ^d	
									84.6(5,3) ^e 88.2(7,5) 94.4(6,1.3) ^d 84.1(6,1) ^e	
[Cu ₂ (μ-NO ₂)(bpy) ₄](PF ₆) ₃ (dark blue)	tr P-1(P1) 2	11.918(6) 14.250(4) 15.013(5)	85.51(2) 68.81(2) 76.67(2)	CuN ₄ O ₂	bpyN μO ₂ NO	2.030(6,89) 2.120(5) 2.788(6)	6.123 [#]	O,O O,N	49.0(2) ^e	673
									88.2(2,2.5)	
									104.1(2) 143.6(2,4.8) 81.1(3,9) ^e 101.1(3,4.5) 120.0(2) 174.2(3)	
[Cu ₂ (μ-bpim)(NO ₃) ₂ (ClO ₄) ₂ · (H ₂ O)]·H ₂ O (dark blue)	tr P-1 2	12.673(2) 13.919(2) 8.086(2)	102.64(1) 96.22(1) 94.25(1)	CuO ₃ N ₃	NO ₃ O H ₂ O N	2.012(6) 2.566(7) 2.356(8) 2.015(7) 1.964(7,3)	6.137(2)	N,N N,O	86.8(3,5.3) ^d	674
									173.6(3)	
									87.8(3,1.5) 93.6(3,3.0) 106.9(3,5.2) 166.0(3) 54.7(3) ^e 91.9(3) 146.1(3)	

TABLE XI (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]			α [°] β [°] γ [°]			Chromophore	Cu-L [Å]	Cu-Cu [Å]	L-Cu-L [°]	Ref.	
		α [°]	β [°]	γ [°]									
[Cu ₅ (μ -fumo)(C ₁₄ H ₃₃ N ₃) ₂](ClO ₄) ₂ (blue violet)	m P2 ₁ /n 2	CuO ₃ N ₃			NO ₂ O	2.011(6)	2.408(7)	2.610(12)	2.052(7.44)	6.313(2)	N,N	87.6(3, 6.1) ^d 174.1(3) 92.5(4, 2.5) 106.8(3) 161.0(3, 2.5) 57.5(3) ^e 101.0(4)	675
		8.6808(9)	14.892(2)	16.679(3)		90.52(1)	1.969(5)	2.424(6)	169.5(2)	86.4(3) ^e 150.0(3)	O,N	96.2(2, 1.5) 169.5(2)	
[Cu ₅ (μ -trien)Me ₆ (F ₆ pd) ₂] (green)	m P2 ₁ /a 2	CuO ₄ N ₂			O	1.990(23.9)	2.287(22.68)	2.065(25.15)	1.990(23.9)	6.424(6) ^e	O,O	85.1(9, 2.9) ^d 164.1(8) 94.5(10, 5.0) 176.9(10, 1.7)	676
		10.268(3)	25.255(8)	10.392(3)		119.29(2)	2.065(25.15)	1.935(4, 6)	2.408(4)	150.0(3)	O,N	85.1(9, 2.9) ^d 164.1(8) 94.5(10, 5.0) 176.9(10, 1.7)	
[Cu ₅ (μ -ebdta)(H ₂ O) ₂ ·2H ₂ O (blue)]	m C2/c 4	CuO ₄ N			H ₂ O	1.941(4)	2.005(1)	1.935(4, 6)	1.941(4)	6.549(2) ^e	O,O	94.5(2, 2.4) 103.8(2) 163.0(2)	677
		20.988(6)	7.537(2)	13.560(4)		90.86(2)	2.005(1)	1.935(4, 6)	2.408(4)	150.0(3)	O,N	94.5(2, 2.4) 103.8(2) 163.0(2)	
[Cu ₅ (μ -tped)(NO ₃) ₂ (H ₂ O) ₂] (NO ₃) ₂ ·2MeOH (blue green)	m P2 ₁ /n 4	CuN ₃ O ₂			O ₂ NO H ₂ O tpedN	2.063(3)	1.947(3)	2.003(4, 10)	2.063(3)	6.563(1)	N,O	90.0(1, 2.4) 106.6(1) 157.6(1) 173.1(1)	678
		12.683(4)	10.374(2)	19.229(4)		111.92	1.947(3)	2.003(4, 10)	2.303(3)	176.8(2)	O,N	90.0(1, 2.4) 106.6(1) 157.6(1) 173.1(1)	
[Cu ₅ (μ -C ₁₃ H ₃₂ N ₄ S ₄)](S ₂ O ₈) ₂ (dark blue)	tr P-1 2	CuO ₂ N ₂ S ₂			N S H ₂ O	2.010(3, 5)	2.314(1, 8)	2.428(2)	2.010(3, 5)	6.591	S,S	93.4 ^d 95.2(1) 85.8(1, 3) ^e 175.6(1, 3, 3) 88.6(1, 3, 7) 95.1(1, 2)	679
		8.227(2)	13.103(3)	16.423(4)		68.68(2) 86.68(2) 75.50(2)	2.428(2)	2.587(2)	2.587(2)	85.5(1)	O,O	93.4 ^d 95.2(1) 85.8(1, 3) ^e 175.6(1, 3, 3) 88.6(1, 3, 7) 95.1(1, 2)	

TABLE XI (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	$Cu-L$ [Å]	$Cu-Cu$ [Å]	$L-Cu-L$ [°]	Ref.
$[Cu_5(\mu-ddd)(H_2O)_2] \cdot 8H_2O$ (purple)	tr P-1 1	7.669(2) 8.757(3) 10.596(2)	79.57(3) 83.36(2) 89.17(3)	Cu_4O	N H_2O 2.460(3)	6.9	N,N N,N O,N 102.6(1, 2.3)	683
$[Cu_5(\mu-bmpmp)Cl_2](ClO_4)_2 \cdot 2MeOH$ (green)	or Pcab 4	14.895(2) 19.559(3) 13.263(2)		Cu_4Cl	Cl N 2.169(5)	6.917(2)*	N,N N,N Cl,N 177.9(2)	684
$[Cu_5(\mu-taet)(H_2O)_2] \cdot 8H_2O$ (purple)	tr P-1 1	8.775(5) 10.621(8) 7.684(5)	96.67(6) 90.81(5) 79.66(5)	Cu_4O	N H_2O 2.477(3)	6.927	O,N N,N N,N 84.5(2, 7) 169.3(2, 8)	685
$[Cu_5(\mu-dba)(H_2O)_2] \cdot 4H_2O$ (blue)	m C2/c 4	28.547(5) 7.630(2) 14.580(4)	134.08(2)	CuO_5N	H_2O N O 2.369(3) 2.870(4)	6.977(2)*	O,N O,N O,O 83.9(2, 2.2) ^c 95.0(1) 175.1(2) 80.8(1) ^c 93.0(2, 5.0) 103.4(1) 167.9(2, 6.5)	686
$[Cu_5(\mu-C_2H_4N_8)(H_2O)_2] \cdot (ClO_4)_4 \cdot 2H_2O$ (not given)	tr P-1 2	14.894(2) 15.144(2) 10.734(1)	91.04(1) 108.80(1) 87.22(1)	Cu_4O Cu_4O	N H_2O N 2.010(7) 2.255(8)	6.985(2) 7.08(2)	N,N N,N N,N 80.0(4, 3) ^c 99.1(3, 1) ^d 80.0(3, 3) ^c 99.3(3, 1, 2) ^d	687
$[Cu_5(\mu-dabco)(F_6pd)_4]$ (green)	m I2/c 8	22.854(6) 25.548(4) 12.601(2)	92.26(2)	CuO_4N	O N 2.254(11, 21)	7.097(3)*	O,N O,O 97.5(2, 5.5) ^d 89.1(-, 4.3) ^d 165.0(-, 9.1)	688

$[\text{Cu}_2(\mu\text{-egta})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (blue)	m C2/c 4	20.962(5) 7.513(2) 13.545(2)	90.85(2)	CuO_4N	H_2O N O	1.938(2) 1.992(2) 1.934(2, 6) 2.408(2)	7.513(2) ^g	N,O	85.6(1,4) ^c 177.2(2) 94.4(1,5,1) 163.1(1)	689
$[\text{Cu}_2(\mu\text{-C}_4\text{O}_4)(\text{H}_2\text{O})_4(\text{bpy})_2] \cdot (\text{C}_6\text{O}_4\text{H}_2) \cdot 4\text{H}_2\text{O}$ (green)	tr P-1 2	9.021(2) 9.017(2) 12.581(4)	98.58(2) 106.81(2) 106.03(2)	CuO_3N_2	H_2O bpyN $\text{O}_3\text{C}_4\text{O}$	1.964(4) 2.186(4) 2.005(4, 4) 1.965(4)	7.536(3) ^f	O,N	92.7(2, 4,3) 167.2(2, 1,2) 95.5(2,8) 80.9(2) ^c	690
$[\text{Cu}_2(\mu\text{-C}_4\text{O}_4)(\text{H}_2\text{O})_2(\text{bpy})_2 \cdot \text{Br}_2]$ (dark green)	m P2 ₁ /n 4	10.480(4) 8.503(1) 14.590(2)	99.75(2)	$\text{CuO}_2\text{N}_2\text{Br}$	H_2O bpyN Br $\text{O}_3\text{C}_4\text{O}$	2.004(7) 1.997(7, 6) 2.632(2) 1.963(6)	7.607(2) ^f	O,N	91.3(3, 2,4) 108.0(2) 161.5(3, 6,9) 95.7(3, 8) 80.7(3) ^c	690
$[\text{Cu}_2(\mu\text{-ttha})(\text{H}_2\text{O})_2]$ (pale blue)	m P2 ₁ /c 2	7.165 13.137 17.079	112.6	CuO_4N_2	H_2O O N	1.988(8) 1.953(9, 6) 2.512(9) 2.065(8) 2.262(9)	7.655(2)	N,O	163.6(4, 8,6) 177.3(4)	691
$[\text{Cu}(\mu\text{-rib})(\text{H}_2\text{O})_2] \cdot 8\text{H}_2\text{O}$ (dark orange)	tr P1 1	7.701(2) 11.230(3) 17.336(4)	101.85(2) 96.41(2) 89.90(2)	CuO_6	O H_2O	1.97(2) 2.40(2, 10) 1.96(2, 1)	7.701(2) ^g	O	not given	692
$[\text{Cu}_2(\mu\text{-tcb})(\text{tetac})_2]$ (turquoise blue)	or Pbca 4	14.400(4) 16.963(5) 15.879(7)		CuO_4N_2	H_2O N	2.002(0) 2.22(2, 22) 2.00(2, 0)	not given	not given	not given	693
$[\text{Cu}_2(\mu\text{-C}_4\text{O}_4)(\text{H}_2\text{O})_2(\text{bpca})]$ (green)	tr P-1 1	7.222(2) 10.272(1) 10.362(2)	82.85(1) 70.89(2) 69.94(2)	CuN_3O_2	N tcbO N H_2O $\text{O}_3\text{C}_4\text{O}$	2.035(4) 2.188(4) 1.946(3, 3) 1.978(2, 56) 2.178(3) 1.923(2)	7.833(1)	N,N	82.0(1, 2) ^c 158.8(1) 97.0(1, 1,6) 166.7(1)	694
$[\text{Cu}_2(\mu\text{-bpmp})\text{Cl}_2](\text{ClO}_4)_2$ (blue)	tr P-1 1	10.004(1) 12.212(2) 7.791(1)	100.99(1) 86.26(1) 112.76(1)	CuN_4Cl	Cl N	2.233(1) 2.03(2, 31) 2.257(3)	7.838(1) ^g	O,O	96.3(1)	684
								Cl,N	81.2(1, 2,5) ^c 101.6(2, 7,5) 149.2(1) 96.6(1, 1,0) 105.7(1) 175.4(1)	

TABLE XI (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å]	L-Cu-L [°]	Ref.
$[\text{Cu}_2(\mu\text{-ca})(\text{Me}_2\text{dien})_2](\text{BPh}_4)_2$ (not given)	m P2 ₁ /a 2	23.432(5) 9.933(2) 15.039(3)	98.00(2)	CuN ₃ O ₂	N caO 2.023(6, 35) 1.956(4) 2.196(4)	7.858(2)	O,O O,N 78.9(2) ^c 92.8(2, 5) 103.9(2, 2.1) 177.3(2) 86.6(2, 2) ^c 151.8(2)	695
$[\text{Cu}_2(\mu\text{-dd})(\text{ClO}_4)_2](\text{ClO}_4)_2$ (purple)	trg P3 ₂ /21 3	13.671(2) 13.929(2)		CuN ₄ O	N μ N O ₃ ClO 2.007(5, 9) 2.006(4, 2) 2.543(7)	7.9 ^g	N,N N,N 86.2(2) ^c 93.8(2, 2.7) ^d 172.6(2, 4.8)	683
$[\text{Cu}_2(\mu\text{-bdta})(\text{tm})_2(\text{H}_2\text{O})_2]$ (blue)	m P2 ₁ /c 4	7.071(1) 15.486(4) 12.290(3)	110.15(2)	CuO ₃ N ₂	O N imN H ₂ O 1.951(6, 6) 1.995(4) 1.947(6) 2.379(6)	7.942(2) ^g	O,O N,N O,N 88.6(3, 1.4) 168.2(3) 84.5(3, 1.1) ^c 95.9(3, 3.8)	696
$[\text{Cu}_2(\mu\text{-F}_2\text{SiF}_2)(\text{speca})_2] \cdot 4\text{H}_2\text{O}$ (dark green)	m P2 ₁ /n 2	10.000(2) 8.8510(2) 18.1899(2)	92.0583(1)	CuO ₂ N ₂ F	O N μ F ₂ SiF ₂ 1.940(2, 11) 1.883(2) 2.001(2) 2.528(1)	7.9507(6)	N,N O,O N,O 81.12(8) ^d 99.41(7) 80.19(7) ^c 98.96(8) 167.7(1, 6.5)	697
$[\text{Cu}_2(\mu\text{-1,3-pn})(1,3\text{-pn})_4](\text{BF}_4)_4$ (dark blue)	or Pbca 8	14.573(11) 15.761(13) 30.669(13)		CuN ₅	N 2.03(2, 3) 2.24(2, 1)	8.07(7)	O,F N,F 96.8(1, 5.0)	698
$[\text{Cu}_2(\mu\text{-dhnq})(\text{dien})_2](\text{BPh}_4)_2$ (blue)	m P2 ₁ /n 2	15.505(4) 17.700(4) 10.533(3)	92.56(2)	CuN ₃ O ₂	dienN dhnqO 2.018(7, 11) 2.233(8) 1.912(5, 16)	8.075(3) ^g	O,O O,N N,N 91.7(2) ^d 94.4(2, 4.7) 149.2(3) 177.2(2) 83.6(3, 1.2) ^c 114.1(3)	699

$[\text{Cu}_2(\mu-1,3\text{-pn})(1,3\text{-pn})_2](\text{ClO}_4)_4$ (blue)	or Pbca 8	30.882(9) 14.664(6) 15.737(6)	CuN ₅	N 2.04(1,2) 2.26(1,1)	8.104	N,N	88.9(6, 1.5) ^d 93.0(6, 6.9) 109.0(6, 3.1) 161.6(7, 11.3)	700
$[\text{Cu}_2(\mu\text{-pdtb})(\text{H}_2\text{O})_4](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (bluish green)	m C2/c 4	17.581(12) 11.604(10) 25.90(2)	CuN ₅ O ₂	N 1.954(7, 1) 2.102(7) H ₂ O 1.990(7) 2.236(9)	8.956 ^f	O,O	84.3(3, 2.8) 167.7 79.7(-, 2.2) 95.0(3, 3.6) 105.0(3, 5.0) 162.8(3) 81.4(3, 5) ^e 161.5(3)	701
$[\text{Cu}_2(\mu\text{-tpt})(\text{Et}_3\text{dien})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (blue violet)	or Pbca 8	28.48(1) 26.363(2) 12.591(5)	CuN ₅ O ₂	N 2.033(9, 61) 1.972(6, 1) tptO 2.363(6, 16)	10.710(2)	N,N	86.7(4, 5) ^e 147.2(4, 5.0) 97.0(3, 1.2) 104.6(3, 4.6) 166.7(3, 2.1) 59.4(4, 6) ^e	702
$[\text{Cu}_2(\mu\text{-tpt})(\text{H}_2\text{O})_2](\text{Me}_3\text{dien})_2 \cdot (\text{ClO}_4)_2$ (blue violet)	m P2 ₁ /c 4	8.42(5) 14.40(4) 15.99(5)	CuN ₅ O ₂	N 2.049(4, 20) H ₂ O 2.225(4) tptO 1.931(3)	11.129(1)	N,O	94.0(2, 5.1) 103.0(2, 3.0) 167.1(2) 85.8(2) ^e 154.7(2)	702
$[\text{Cu}_2(\mu\text{-tpt})(\text{H}_2\text{O})_2 \cdot (\text{Me}_3\text{dien})_2] \cdot (\text{Me}[9]\text{-aneN}_4)_2(\text{ClO}_4)_2$ (not given)	m P2 ₁ /c 4	8.619(4) 14.059(3) 15.156(9)	Cu ₃ N ₅	N 2.034(5) 2.217(5) H ₂ O 2.009(4) tptO 1.972(4) O ₃ ClO 2.992(6)	11.252(4)	not given	not given	693
$[\text{Cu}_2(\mu\text{-C}_{10}\text{H}_{16}\text{N}_3\text{Cl}_4) \cdot 2\text{H}_2\text{O}$ (green)	m P2 ₁ /c —	8.752(4) 15.149(9) 14.468(5)	CuN ₃ Cl ₂	N 2.008(6, 4) 2.214(5) Cl 2.394(2, 52)	11.71	Cl,Cl Cl,N	118.9(1) 102.9(1) 138.0(1) 89.8(2, 4.1) ^d 178.1(2)	703
$[\text{Cu}_2(\mu\text{-bzd})(\text{tren})_2](\text{NO}_3)_4 \cdot \text{f}$ (dark green)	m P2 ₁ /c 8	29.799(4) 13.960(2) 18.732(3)	CuN ₅	trenN 2.044(11, 21) 2.125(11, 92) bzdN 2.038(8, 5)	12.273(2)	N,N	84.4(4, 1.6) ^e 94.9(4, 2.4) 108.9(4, 7.5) 135.6(4, 6) 176.0(4, 9)	704

TABLE XI (Continued)

Compound (color)	Cryst. cl. space G. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Cu-L [Å]	Cu-Cu [Å]	L-Cu-L [°]	Ref.
[Cu ₂ (μ -pprz)(NO ₂) ₂ (H ₂ O) ₄] (green)	m	8.554(1)	96.14(1)	CuN ₅	treN	12.083(2)	N,N	84.4(4, 1.5) ^c
	P2 ₁ /n 2	15.768(4) 8.916(1)			bsdN	2.043(11, 17) 2.155(10, 22) 2.034(8, 2)	not given	93.6(4, 1.2) 107.2(4, 6.7) 136.6(4, 4.6) 175.4(4, 1)
					O ₂ NO H ₂ O pprzN	1.990(3) 1.958(3) 2.182(3) 2.017(3, 5)		

^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. ^f There are two crystallographically independent molecules. ^g Calculated by us.

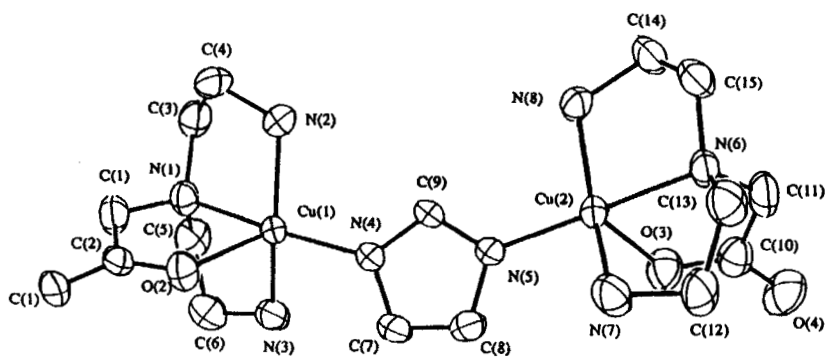


FIGURE 12 Structure of $[\text{Cu}_2(\mu\text{-im})(\text{dtma})_2]$ (see Ref. 671).

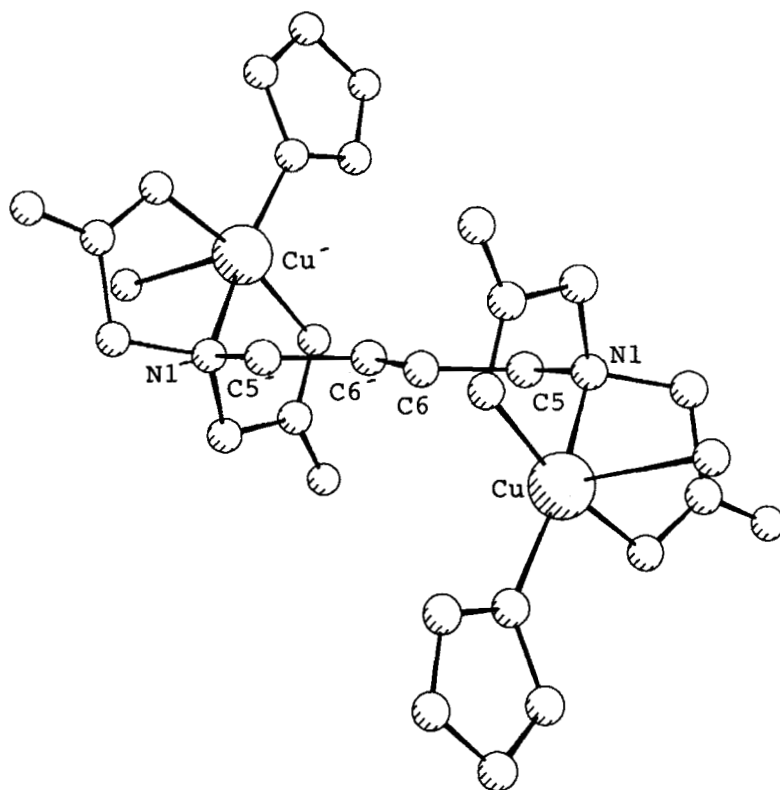


FIGURE 13 Structure of $\text{Cu}_2(\mu\text{-bdta})(\text{im})_2(\text{H}_2\text{O})$ (see Ref. 696).

cases.^{673, 695,699,702} A *pseudo*-octahedral coordination about each Cu(II) atom was found.^{674,676,686,691,693} There are also four derivatives, which contain non-equivalent Cu(II) atoms, four- and five-coordinate,^{659,666} or five- and six-coordinate.^{673,679} In the series of a square pyramidal configurations the displacement of Cu(II) from the basal plane toward an apical ligand range from 0.016 to 0.35 Å.

In three cases two crystallographically independent molecules, differing by degree of distortion, have been found to be present in one crystal.^{672,687,704}

The Cu–Cu separation in this series ranges from 3.67 to 12.273(2) Å. The mean Cu–L bond distance, in the series of monodentate ligands, increases in the order: 1.86(F) < 1.95 Å (NL) < 2.23 Å (OL) < 2.29 Å (Cl) < 2.505 Å (Br). The multidentate ligands include both homo- and heterodonor atoms, with N- and O-donor;s being by far the most common. The mean Cu–O bond distance increases in the order 1.85 Å (O₂, bidentate) < 2.06 Å (OL,bi-) < 2.12 Å (OL,tetra-) < 2.47 Å (OL,tridentate) and Cu–N bond distances: 2.05 Å (bi-, tri-, octa-) < 2.10 Å (tetra-) < 2.11 Å (hexadentate).

3. CONCLUSIONS

This review has classified nine hundred Cu(II) dimers for which crystallographic and structural data are available. Copper(II) compounds are for the most part green and blue. There are several types of bridges, of which a double bridge of the Cu–(X)₂–Cu type is the most common.³⁶⁰ The most common mono- and multidentate ligands are O- and N-donors. From a stereochemical point of view, a square planar arrangement, with different degrees of distortion about the Cu(II) atom, is the most common. The Cu–Cu distances range from 2.44 to 12.27 Å.

Several relationships were found, between the Cu–Cu distance, the Cu–L–Cu bridge angle and the type of bridging, and between the intraligand L–Cu–L ring angles and coordination number. These have been discussed separately in each section. Some Cu(II) compounds occur in two isomeric forms which differ mostly by degree of distortion in both the Cu–L distances and L–Cu–L angles. Two independent molecules differing by degree of distortion have been found in several cases. The coexistence of two or more species differing only by degree of distortion is typical of the general class of distortion isomerism.¹⁴⁴

A summary of the copper-ligand(atom) bond lengths for Cu(II) dimers with different geometries is given in Table XII. In general, the Cu–L bond

TABLE XII Summary of the mean Cu(II)-L [\AA] bond distances^a

Coord. atom ^a	Cov. rad. [\AA]	4-coordination	5-coordination	6-coordination
LO	0.73	1.915	2.27	2.46
L ² O		1.93	2.03	2.37
L ³ O			1.99	2.47
L ⁴ O		1.93	2.09	2.26
LN	0.75	1.97	2.06	2.08
L ² N		1.98	2.04	2.07
L ³ N			2.05	1.95
L ⁴ N		1.99	2.06	1.98
L ⁵ N				2.21
L ⁶ N		1.975	2.08	2.015
L ⁸ N		2.05	2.15	
Cl	0.99	2.23	2.37	2.31
L ² S	1.02	2.23	2.41	
Br	1.14		2.50	
I	1.33		2.77	

^a L^x = X-dentate.

distances increase with increasing coordination number and covalent radius of the respective donor atoms. The mean Cu-L bridge distance for five-coordination increases with covalent radius (in parenthesis) in the order: 2.02 \AA (O, 0.73 \AA) < 2.07 \AA (N, 0.75 \AA) < 2.32 \AA (Cl, 0.99 \AA) < 2.465 \AA (S, 1.02 \AA) < 2.66 \AA (Br, 1.14 \AA) < 2.69 \AA (I, 1.133 \AA).

This review, together with its precursor for monomeric Cu(II) compounds,^{14,15} represents the first overview of structural data for Cu(II). A related review of the structural chemistry of trimeric to polymeric Cu(II) complexes is currently in progress. During the collection and organization of the data it became clear that, despite the increasing availability of data retrieval systems, the tracing of relevant material is not always 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 it is necessary to make a systematic overall review, and that such reviews serve the useful purpose of delineating areas of both interest and weakness.

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