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Review

Tetramers $Cu_4(\mu_4\text{-}O)(\eta\text{-}X)_6(L_4)$: Analysis of structural data

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ABSTRACT

This review summarizes structural parameters for forty five $Cu_4(\mu_4\text{-}O)(\eta\text{-}X)_6(L_4)$ tetramers. There are four types of structurally equal core units, $CuCl_3ON$, $CuCl_3OO$, $CuCl_3OCl$ and $CuBr_3ON$. There are also tetramers which contain structurally unequal core units: $CuCl_3ON$ (x2) and $CuCl_2BrON$ (x2); $CuCl_3ON$ (x1), $CuCl_2BrON$ (x2) and $CuCl_3OCl$ (x1). There is a tendency for an elongated Cu···Cu separation as well as Cu–L bond distances with increase of the covalent radius of the coordinating atom(s). Tetrahedral distortion around oxygen atom (OCu_4) increases in the order: 1.67° ($CuCl_3OCl$) < 2.10° ($CuCl_3ON$) < 2.11° ($CuCl_3OO'$) < 2.27° ($CuBr_3ON$). The mean Cu–Cl–Cu bridge angle of 80.5° is about 4.0° more open than that of a Cu–Br–Cu (76.5°). The cluster $Cu_{16}O_4Br_7Cl_{17}(4\text{-Mepy})_{16}$ (4-Mepy = 4-methylpyridine) contains four crystallographically independent tetramers: $Cu_4OBrCl_5(4\text{-Mepy})_4$ (1), $Cu_4OBrCl_5(4\text{-Mepy})_4$ (2) $Cu_4OBr_2Cl_4(4\text{-Mepy})_4$ (3) and $Cu_4OBr_3Cl_3(4\text{-Mepy})_4$ (4), which is a unique example of stereoisomerism. There are other examples which exist in two isomeric forms. Another contains two or even four crystallographically independent tetramers within the same crystal, differing mostly by degree of distortion and is an examples of distortion isomerism. Pairs of $Cu_4OCl_6(n\text{-Meim})_4$ (*n*-Meim = *n*-methylimidazole) (*n* = 1 or 2) are examples of ligand isomerism.

1. Introduction

The chemistry of copper complexes has been extensively investigated, and the relationship between structure and reactivity ranging from industrial catalysis to biomedical activity, is of major importance. The overwhelming majority and variability of the stereochemistry of all X-ray crystallographic studies of transition metal coordination complexes are of copper complexes.

Structural features of tetrameric copper(II) complexes can be divided into six major categories: (I) $Cu_4(\mu_4\text{-}O)$tetrahedron; (II) central Cu_4O_4 cubane type; (III) bifolded dimers; (IV) chain type; (V) step-like structures and (VI) Unique structures [1]. The first two

Abbreviations: 1,2-Me_2im, 1,2-dimethylimidazole; 1-Mebtz, 1-methylbenzotriazole; 1-Meim, N-methylimidazole; 2-Etpz, 2-ethylpyrazine; 2-Meim, 2-methyl-1H-imidazole; 2-Mepy, 3-methylpyridine; 3,5-Me_2pz, 3,5-dimethylpyrazole; 3,5-Me_2pz, 3,5-dimethylpyrazole; 3-quin, 3-quinuclidinone; 4-Bu-3-Meim, 4-buthyl-3-methylimidazole; 4-Mepy, 4-methylpyridine; ain, 7-azaindole; bim, benzimidazole; dhmt, 4,5-dihydro-2-methyl-1,3-thiazole; dmf, dimethylformamide; dnda, 5,5-dichloro-4,6-dioxo-3,7-diaza-1,9-nonanebis(dimethylanonium); Et_2na, N,N-diethylnicotinamide; Et_2NH_2, diethylammonium; Et_2SO, diethylsulfoxide; Et_3PO, triethylphosphine oxide; Ettz, ethyltetrazole; hmt, hexamethylenetetraamine; mor, morpholine; mpd, N-methyl-2-pyrrolidine; NMe_4, tetramethylammonium; Ph_3PO, triphenylphosphine oxide; pi, piperidine; pim, 5-phenyl-1H-imidazolium; py, pyridine; pyNo, pyridine-N-oxide; tbpt, N,N′,N″-tri-tert-butylphosphorictriamide; tbpt, tris(tert-butylamino)phosphineoxide; tmpp, 5-(2,4,6-trimethylphenyl)pyrazole.

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Table 1
Selected Structural Parameters for $Cu_{16}O_4Br_7Cl_{17}(4\text{-Mepy})_{16}$(four crystallographically independent tetramers)[a] [3].

Compound	Cu–Cu [Å]	Cu–μ_4O [Å]	Cu–μX [Å]	Cu–N [Å]	Cu–O–Cu[b] [°]	Cu–X–Cu [°]
1. $Cu_4OBrCl_5(4\text{-Mepy})_4$	3.115(–,39)	1.973(–,20)	Cl 2.474(–,98)	1.999 (–,23)	1.2	Cl 78.8
$CuCl_3ON$ (x2)		1.908(–,16)	Cl 2.449(–,51)	1.973(–,23)		Cl 78.8
$CuCl_2BrON$ (x2)			Br 2.542(–,21)			Br 76.7
2. $Cu_4OBrCl_5(4\text{-Mepy})_4$	3.121(–,26)	1.923(–,16)	Cl 2.474(–,114)	1.988(–,44)	1.6	Cl 79.0
$CuCl_3ON$ (x2)		1.900(–,10)	Cl 2.467(–,53)	2.002(–,6)		Cl 79.0
$CuCl_2BrON$ (x2)			Br 2.488(–,9)			Br 77.7
3. *cis*-$Cu_4OBr_2Cl_4(4\text{-Mepy})_4$	3.122(–,21)	1.930	Cl 2.448(–,75)	1.963	1.4	Cl 78.5
$CuCl_3ON$ (x1)		1.904(–,3)	Cl 2.483(–,49)	1.981(–,12)		Cl 78.5
$CuCl_2BrON$ (x2)			Br 2.498(–,8)			Br 77.6
		1.910	Cl 2.407	1.961		Cl 78.5
$CuBr_2ClOn$ (x1)			Br 2.510(–,14)			Br 77.6
4. *mer*-$Cu_4OBr_3Cl_3(4\text{-Mepy})_4$	3.121(–,21)	1.923(–,7)	Cl 2.436(–,48)	1.985(–,18)	3.1	Cl 79.6
$CuCl_2BrON$ (x2)			Br 2.469(–,42)			Br 78.6
		1.900(–,0)	Cl 2.415(–,12)	1.976(–,21)		Cl 79.6
$CuBr_2ClON$ (x2)			Br 2.476(–,35)			Br 78.6

[a] There are four crystallographically independent molecules. The mean values are tabulated. The first number in parenthesis is e.s.d., and the second is maximum deviation from the mean.
[b] The maximum deviation from the ideal tetrahedral angle of 109.5°.

types are the most common. Structurally, the tetrameric $Cu_4(\mu_4\text{-}O)(\mu\text{-}X)_6(L)_4$ (X = Cl, prevails by far; Br; L = N-, O-donor ligands or Cl), have stimulated extensive crystal chemistry studies, with over forty solved crystal and molecular structures.

We pay attention to the $Cu_4(\mu_4\text{-}O)(\mu\text{-}X)_6(NL)_4$ tetramers, especially to those with a mixed X-donor atoms (Cl plus Br). We had prepared complexes of the composition $Cu_4OBr_5Cl(4\text{-Mepy})_4$, $Cu_4OBrCl_5(4\text{-Mepy})_4$ and $Cu_4OBr_3Cl_3(4\text{-Mepy})_4$. Unfortunately, the complexes were obtained only in a microcrystalline form and were studied by EPR spectroscopy. In addition $Cu_{16}O_4Br_7Cl_{17}(4\text{-Mepy})_{16}$ was prepared and characterized by X-ray analysis [2]. The X-ray parameters of the complex show that there are four crystallographically independent tetramers. Preliminary data of the tetramers [2] show that introduction of bromine atoms into the molecules increases bio-activity which will be the subject of our next study. For this reason we have analyzed our data and compound with those found in familiar $Cu_4OX_6(L)_4$ complexes. This review correlates the crystallographic and structural data for such complexes found in the Cambridge Crystallographic Data Base up to 2009.

2. $Cu_4(\mu_4\text{-}O)$ tetrahedra

There are over forty examples of such tetrahedra in this review. There are six categories of the tetramers: $Cu_4(\mu_4\text{-}O)(\mu\text{-}X)_6(NL)_4$ (X = Cl or Br), $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6L_4$ (L = OL or Cl), $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(NL)_3Cl$ and $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}Br)_3(Ph_3PO)_4$.

2.1. $Cu_{16}(\mu_4\text{-}O)Br_7Cl_{17}(4\text{-Mepy})_{16}$

Selected structural parameters for $Cu_{16}(\mu_4\text{-}O)Br_7Cl_{17}(4\text{-Mepy})_{16}$ are given in Table 1. X-ray analysis of the clusters shows that there are four crystallographically independent tetramers, with the composition of $Cu_4OBrCl_5(4\text{-Mepy})_4$ (1,2), *cis*-$Cu_4OBr_2Cl_4(4\text{-Mepy})_4$ (3) and *mer*-$Cu_4OBr_3Cl_3(4\text{-Mepy})_4$ (4) (Fig. 1). The inner coordination sphere around copper(II) atoms are $CuCl_3ON$ (x2) and $CuCl_2BrON$ (x2) in the tetramers 1 and 2; $CuCl_3ON$ (x1), $CuCl_2BrON$ (x2) and $CuBr_2ClON$ (x1) in tetramer 3 and $CuCl_2BrON$ (x2) and $CuBr_2ClON$ (x2) in tetramer 4. The tetramers 1 and 2 differ by the degree of distortion (Table 1). The mean Cu–L bond distances (tetramer 1 vs tetramer 2) are elongated in the order 1.915 vs 1.91 Å (Cu–μ_4O) < 1.985 vs 1.995 Å (Cu–N) < 2.46 vs 2.47 Å (Cu–μCl) < 2.54 vs 2.49 Å (Cu–μBr). The deviations of the Cu–O–Cu tetrahedral angles from the ideal value of 109.5° are 1.2 and 1.6°, respectively. The tetramer 2 is somewhat more distorted than the tetramer 1. These *tetramers are classical examples of distortion isomerism [3].

In tetramer 3 the mean values of Cu–μ_4O and Cu–N bond distances are 1.93 and 1.96 Å for $CuCl_3ON$, 1.90 and 1.98 Å for $CuCl_2BrON$; and 1.91 and 1.96 Å for $CuBr_2ClON$. The mean Cu–μCl bond distances are 2.45, 2.48 and 2.41 Å, respectively, and the mean Cu–μBr bond distances are 2.50 for $CuCl_2BrON$ and 2.51 Å for $CuBr_2ClON$, The mean Cu···Cu separation is 3.122 Å. In tetramer 4, the Cu–Cu separation is 3.121 Å. There are two pairs of copper(II) atoms with the chromophores $CuCl_2BrON$ (x2) and $CuBr_2ClON$ (x2). The mean Cu–μ_4O, Cu–μCl, Cu–μBr and Cu–N bond distances are 1.92, 2.44, 2.47 and 1.985 Å in the former, and 1.90, 2.415, 2.48 and 1.975 Å in the latter. The deviation of the mean Cu–O–Cu bond angle from the ideal value of 109.5°, increases in the order: 1.2° (tetramer 1) < 1.4° (tetramer 3) < 1.6° (tetramer 2) < 3.1° (tetramer 4). Thus distortion of the central tetrahedron increases in the given order.

Noticeably, the sum of all twenty Cu–L {Cu–O} (x4), Cu–X (X = Cl or Br) (x12), Cu–N (x4) bond distances increases in the order 44.96 Å (tetramer 4) < 45.19 Å (tetramer 3) < 45.30 Å (tetramer 1) < 45.32 Å (tetramer 2) and in the same order, the number of Cu–μBr bonds decreases: 6 (tetramer 4) < 4 (tetramer 3) < 2 (tetramers 1 and 2), respectively. The presence of four crystallographically independent tetramers within the same crystal is a unique example of stereoisomerism in copper(II) chemistry. The $Cu_{16}O_4Br_7Cl_{17}(4\text{-Mepy})_{16}$ contains a pair of distortion isomers ($Cu_4OBrCl_5(4\text{-Mepy})_4$), geometrical *cis*-$Cu_4OBr_2Cl_4(4\text{-Mepy})_4$ and geometrical *mer*-$Cu_4OBr_3Cl_3(4\text{-Mepy})_4$ isomers. To our knowledge this is only example of such mixed variety of isomers within the same crystal.

There are forty five complexes which contain a μ_4-oxo group tetrahedrally coordinated to four copper(II) centers. Each pair of copper(II) centers is bridged by a single chlorine or bromine atom. There are several types of complexes with the composition of $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(NL)_4$ (x24), $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(OL)_4$ (x11) $Cu_4(\mu_4\text{-}O)(\mu\text{-}Br)_6(NL)_4$ (x4), $\{Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(NL)_3Cl\}^-$ (x1) and $\{Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6Cl_4\}^{4-}$ (x5).

2.2. $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(NL)_4$ with the $CuCl_3ON$ chromophore

Selected structural parameters for $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(NL)_4$ are summarized in Table 2. The coordination sphere about each copper(II) is trigonal bipyramidal with three chlorine atoms in the

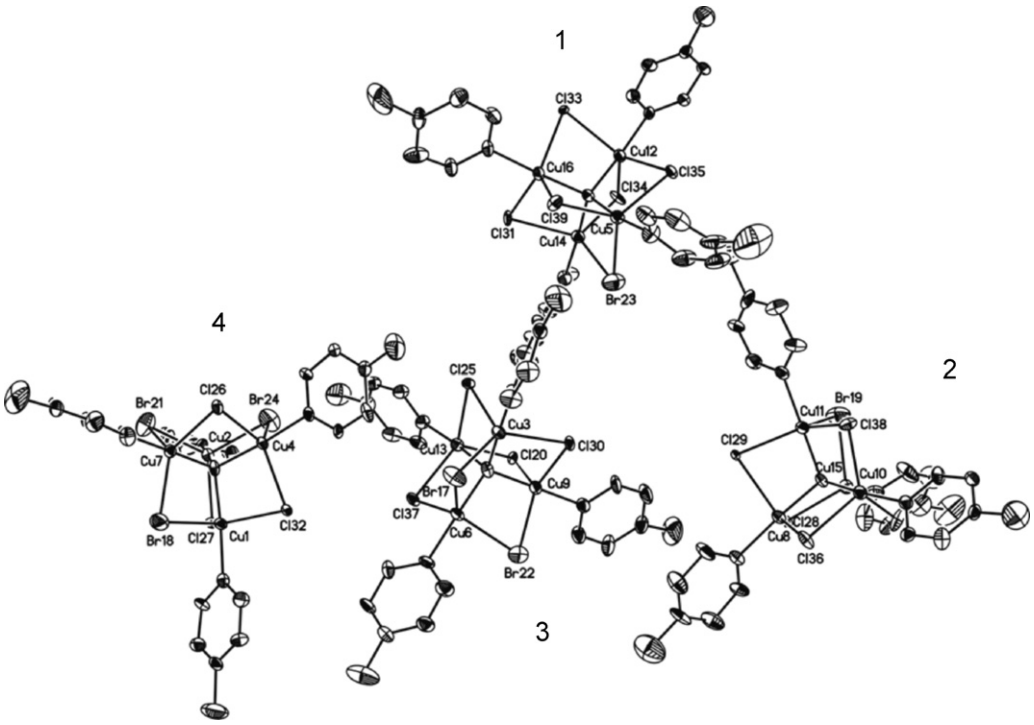

Fig. 1. Structure of $Cu_{16}O_4Br_7Cl_{17}(4\text{-Mepy})_{16}$. Four crystallographically independent molecules with the chromophores: (1) $Cu_4OBrCl_5N_4$, (2) $Cu_4OBrCl_5N_4$, (3) $Cu_4OBr_2Cl_4N_4$, (4) $Cu_4OBr_3Cl_3N_4$.

equatorial plane. The apical positions are occupied by the oxygen atom and the nitrogen atom of the respective ligand ($CuCl_3ON$). The equatorial plane is much less crowded than the apical sides, with the mean Cu–Cl_{eq} bond distance of 2.41 (range 2.325–2.46) Å and the mean Cu–O_{ap} and Cu–N_{ap} bond distances of 1.905 (range 1.89–1.92) Å and 1.97 (range 1.930–2.025) Å. The mean Cu···Cu separation of 3.110 Å (range from 3.090 to 3.133 Å), excludes a direct metal–metal bond. The deviation of the mean tetrahedral

Table 2
Selected structural parameters for $Cu_4(\mu_4\text{-O})(\mu\text{-Cl})_6(NL)_4$ with $CuCl_3ON$ chromophore[a].

$(NL)_4$	Cu–Cu [Å]	Cu–μ_4O [Å]	Cu–μCl [Å]	Cu–N [Å]	Cu–μ_4O–Cu[b] [°]	Cu–Cl–Cu [°]	Ref.
$(py)_4$	3.10(–,1)	1.90(2,2)	2.408(9,78)	1.96(2,2)	1.5	80.2(–,1.4)	[4]
$(2\text{-Mepy})_4$	3.097(6,109)	1.90(2,4)	2.374(8,84) 2.639(8,46)	1.99(2,3)	6.4	78.6(3,1.9)	[5]
$(4\text{-Mepy})_4$[c]	3.090(–,23)	1.897(–,13)	2.398(–,37)	1.975(–,32)	1.4	80.4(–,8)	[6]
	3.102(–,22)	1.900(–,5)	2.404(–,54)	1.976(–,28)	1.1	80.3(–,9)	
	3.094(–,36)	1.895(–,22)	2.407(–,98)	1.959(–,27)	2.6	80.1(–,1.0)	
	3.106(–,26)	1.902(–,17)	2.397(–,17)	1.962(–,19)	2.3	80.8(–,5)	
$(MeCN)_4$	3.102(1,20)	1.897(2,1)	2.325(1,59)	1.943(4,11)	1.1	80.8(1,1.0)	[7]
$(1\text{-Meim})_4$	3.104(2,13)	1.902(5,9)	2.415(3,41)	1.934(7,6)	1.2	79.7(10,3.0)	[8]
	3.107(2,36)	1.903(5,13)	2.419(3,59)	1.930(7,18)	1.7	79.7(10,3.0)	
$(1\text{-Meim})_4$	3.110(3,36) 3.117(3,7)	1.905(7,19)	2.418(4,75)	1.939(9,28)	1.1	80.1(1,7)	[9]
$(2\text{-Meim})_4$	3.123(–,29)	1.914(–,7)	2.399(–,78)	1.946(–,12)	1.3	80.3(–,9)	[10]
$(1,2\text{-Me}_2\text{im})_4$	3.122(3,30)	1.909(9,14)	2.416(5,50)	1.945(4,6)	1.8	80.4(2,1.4)	[11]
$(2\text{-Etpz})_4$	3.103(–,21)	1.900(–,7)	2.406(–,50)	1.982(–,4)	0.7	80.3(–,7)	[12]
$(3,5\text{-Me}_2\text{pz})_4$	3.108(1,65)	1.909(4,4)	2.412(3,87)	1.962(7,2)	3.4	80.8(1,2.0)	[13]
$(3,5\text{-Me}_2\text{pz})_4$	3.112(–,86)	1.906(–,9)	2.412(–,79)	1.954(–,3)	4.8	80.4(–,0)	[14]
$(bim)_4$	3.120(–,62)	1.911(–,11)	2.406(–,90)	1.965(–,16)	2.5	80.8(–,6)	[15]
$(bim)_4$	3.124(–,16)	1.913(–,10)	2.423(–,86)	1.952(–,6)	0.7	80.9(–,9)	[16]
$(2\text{-Ettz})_4$	3.097(–,14)	1.897(–,0)	2.406(–,28)	1.972(–,0)	0.8	80.1(–,2)	[17]
$(tmpp)_4$	3.093(–,76)	1.894(–,5)	2.422(–,85)	1.941(–,5)	3.6	80.1(–,2)	[18]
$(Et_2na)_4$	3.093	1.903(–,28)	2.411(4,93)	1.953(12,23)	0.3	80.3(1,1.7)	[19]
$(hmt)_4$	3.117(2,29)	1.909(5,3)	2.412(3,45)	2.001(8,3)	1.8	80.5(1,9)	[20]
$(pi)_4$	3.119(3,26)	1.91(1,5)	2.416(6,43)	1.99(2,4)	3.0	80.4(2,1.0)	[21]
$(iqht)_4$	3.117(–,20)	1.909(–,8)	2.406(–,49)	1.9759–,9)	0.9	80.5(–,9)	[22]
$(1\text{-Mebtz})_4$	3.120(–,32)	1.911(–,3)	2.399(–,50)	1.977(–,8)	1.3	81.1(–,1.4)	[23]
$(dhmt)_4$	3.132(–,48)	1.918(–, 2)	2.402(–,43)	1.980(–,48)	3.1	81.3(–,2.4)	[24]
$(ain)_4$	3.132(–,72)	1.919(5,0)	2.401(2,90) 2.619(2)	1.966(7,20)	3.7	81.2(1,1.4)	[25]
$(3\text{-quin})_4$	3.133(1,2.2)	1.919(5,6)	2.41393,22)	2.025(7,7)	2.8	81.0(1,5)	[26]

[a] The mean values of tabulated. The first number in parenthesis is e.s.d., and the second is the maximum deviation from the mean.
[b] The deviation of the Cu–O–Cu tetrahedral angles from the ideal value of 109.5°.
[c] There are four crystallographically independent tetramers.
[d] There are two crystallographically independent tetramers.

Table 3
Selected structural parameters for $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(OL)_4$ with $CuCl_3OO'$ chromophore[a].

$(OL)_4$	Cu–Cu [Å]	Cu–μ_4O [Å]	Cu–μCl [Å]	Cu–O [Å]	Cu–μ_4O–Cu[b] [°]	Cu–Cl–Cu [°]	Ref.
$(pyNO)_4\cdot H_2O$	3.093(–,74)	1.896(–,29)	2.417(–,205)	1.916(–,20)	4.0	79.5(–,1.3)	[10]
	3.102(–,23)	1.900(–,47)	2.405(–,149)	1.915(–,26)	2.6	80.2(–,1.8)	
$(Et_2SO)_4$	3.094(2,26)	1.895(7,16)	2.408(3,43)	1.922(8,13)	1.6	80.0(1,1.3	[27]
$(Me_2SO)_4\cdot Me_2SO$	3.094(–,2.4)	1.896(–,7)	2.411(–,41)	1.921(–,10)	0.9	79.8(–,1.3)	[28]
	3.095(3,23)	1.896(9,21)	2.412(5,52)	1.928(11,15)	2.1	79.8(1,1.4)	[29]
$(mpd)_3(H_2O)$	3.095(1,42)	1.895(4,7)	2.405(2,95)	1.927(5,24)	1.3	80.1(7,9)	[30]
$(Ph_3PO)_4\cdot MeNO_2$	3.098(2,0)	1.897(1,0)	2.381(1,0)	1.929(3,0)	Not given	Not given	[31]
$(Ph_3PO)_4$	3.102(2,0)	1.900(3,0)	2.387(5,0)	1.88(3,0)	Not given	81.0(2,0)	[32]
$(Ph_3PO)_4\cdot CH_2Cl_2$	3.107(1,0)	1.902(2,0)	2.398(2,0)	1.95(1,0)	Not given	80.0(1,0)	[32]
$(Ph_3PO)_4\cdot(Ph_4PO)_2$	3.110(3,0)	1.905(3,0)	2.38(1,0)	1.89(2,0)	Not given	Not given	[33]
$(dmf)_4$ (at 100 K)	3.103(3,16)	1.923(9,28)	2.398(5,39)	1.933(1,22)	Not given	Not given	[34]
$(dmf)_4$ (at 260 K)	3.104(3,21)	1.901(8,28)	2.398(5,40)	1.951(11,27)	Not given	Not given	[34]
$(tbpt)_4$	3.104(–,72)	1.901(–,13)	2.422(–,91)	1.911(–,8)	3.2	79.7(–,8)	[35]
$(Et_3PO)_4$	3.123(2,7)	1.913(4,17)	2.422(2,53)	1.934(6,2)	1.2	80.3(1,7)	[36]

[a] The mean values are tabulated. The first number in parenthesis is e.s.d., and the second is the maximum deviation from the mean.
[b] The maximum deviation from the ideal bond angle of 109.5°.

Cu–μO–Cu bond angle from the ideal value of 109.5° is 2.1° (range 0.3–6.4°). The Cu–μCl–Cu bond angle ranges from 76.7 to 82.7° (mean 80.4°) (Table 2).

There are two pairs, $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(3,5\text{-}Me_2py)_4$ [13,14] and $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(bim)_4$ [15,16], which exist in two isomeric forms, which differ not only by degree of distortion, but also by crystal classes, monoclinic [13,15] and triclinic [14,16]. There is an example $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(4\text{-}Mepy)_4$ [6] which contains four crystallographically independent tetramers within the same crystal and in another two derivatives, $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(1\text{-}Meim)_4$ [8,9] and $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(aim)_4$ [25], two such tetramers are present. These all are examples of distortion isomers [3] (Table 2).

The complexes, $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(n\text{-}Mepy)_4$ (n = 2 [5] and 4 [6]), $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(n\text{-}Meim)_4$ (n = 1 [8,9] and 2 [10]), are examples of ligand isomerism. The mean Cu–N (n-Mepy) bond distances reflect the position of the n-Mepy group and decrease in the order: 1.99 Å (2-Mepy) > 1.97 Å (4-Mepy). The mean Cu–N (n-Meim) bond distance also reflects the position of the n-Meim group, increasing in the order: 1.93 Å (1-Meim) < 1.95 Å (2-Meim).

2.3. $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(OL)_4$ with the $CuCl_3OO'$ chromophore

Selected structural parameters for $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(OL)_4$ tetramers with the $CuCl_3OO'$ chromophore are summarized in Table 3. The coordination sphere about each copper(II) atom is trigonal bipyramid. A trigonal plane is created by the chlorine atoms and apical positions are occupied by oxygen atoms. The Cu–Cl (bridge) bond distances range from 2.380 to 2.422 Å with the mean value of 2.403 Å. The mean Cu–μ_4O and Cu–OL bond distances are 1.90 Å (range 1.895–1.923 Å) and 1.92 Å (range 1.88–1.95 Å). The Cu···Cu separation range from 3.093 to 3.123 Å (mean 3.100 Å) excluded a direct bond. The deviation of the mean tetrahedral Cu–μO–Cu bond angle from the ideal value of 109.5° is 2.1° (range 0.9–4.0°). The mean Cu–μCl–Cu bond angle is 80.0° range from 78.2° to 82.0°.

The derivative $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(pyNO)_4\cdot H_2O$ [10], contains two crystallographically independent tetramers within the same crystal and is another example of distortion isomerism [3].

The $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(dmf)_4$ [34] was studied at 100 K (green) and 260 K (yellow). Note that the colour of the complex depends on temperature. As can be seen (Table 3) while the mean values of Cu···Cu separations and Cu–μCl bond distances are "insensitive" to the respective temperatures, the mean Cu–μ_4O bond distance are elongated with lowering of temperature (1.90 Å at 260 K and 1.92 Å at 100 K) while the mean Cu–O bond distance decreases (1.95 vs 1.91 Å).

Noticeably, while the mean values of selected Cu–L bond distances as well as Cu···Cu separation for $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(R_2SO)_4$ (R = Et [27], or Me [28,29]) are identical, the mean values for $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(R_3PO)_4$ (R = Ph [31–33] or Et [36]) are sensitive to R. All mean values are somewhat shorter when R is phenyl than those when R is the ethyl group. The values (phenyl vs ethyl) are: 3.104 vs 3.123 Å (Cu···Cu), 1.901 vs 1.913 Å (Cu–μ_4O), 2.39 vs 2.42 Å (Cu–μCl) and 1.91 vs 1.93 Å (Cu–O).

2.4. $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6Cl_4$ with the $CuCl_3OCl$ chromophore

There are five derivatives with the $CuCl_3OCl$ chromophore and their selected structural parameters are gathered in Table 4A. These derivatives also contain a μ_4-oxo group tetrahedrally coordinated to four copper(II) centers. Each pair of copper(II) centers is bridged by a single chlorine atom. The coordination sphere about each copper(II) is trigonal bipyramidal with three chlorine atoms in the trigonal plane with the mean Cu–μCl bond distance of 2.42 Å (range 2.398–2.461 Å). The apical positions are occupied by oxygen and chlorine atoms. The mean Cu–μ_4O and Cu–Cl bond distances are 1.93 Å (range 1.913–1.958 Å) and 2.23 Å (range 2.170–2.268 Å). The mean Cu···Cu separation of 3.150 Å (range 3.121–3.198 Å) ruled out direct bond. The deviation of the mean tetrahedral Cu–μO–Cu bond angle from the ideal tetrahedral value of 109.5° is 1.7° (range 0.9–4.0°). The mean Cu–μCl–Cu bond angle is 81.4° range from 78.2 to 82.0°.

Red cubic $(NMe_4)[Cu_4(\mu_4\text{-}O)(\mu\text{-})Cl_4]$ was studied by two scientific groups [40,41]. This complex contains two crystallographically independent tetramers within the same crystal, differing mostly by degree of distortion (Table 4A) and is another example of distortion isomerism.

2.5. $Cu_4(\mu_4\text{-}O)(\mu\text{-}Br)_6NL_4$ with the $CuBr_3OCl$ chromophore

There are three derivatives, $Cu_4(\mu_4\text{-}O)(\mu\text{-}Br)_6(NL)_4$ (NL = ettz [42], py [43,44] and mor [45]) with selected structural parameters given in Table 4B. Each pair of copper(II) centers is bridged by a single bromine atom, which created a trigonal plane with the mean Cu–μBr bond distance of 2.53 Å (range 2.522–2.539 Å). The oxygen atom, which is tetrahedrally coordinated to four copper(II) centers, occupies one of the apical positions with the mean Cu–μ_4O bond distance of 1.925 Å (range 1.920–1.932 Å). The second apical position is occupied by the N atom of the respective ligand, with the mean Cu–N bond distance of 2.00 Å (range 1.95–2.07 Å). The mean Cu–Cu separation of 3.145 Å (range 3.136–3.155 Å) excludes a direct bond. The deviation of the mean tetrahedral Cu–μO–Cu

Table 4
Selected Structural Parameters for $[Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6Cl_4]^{4-}$ with $CuCl_3OCl$ chromophore (A) $Cu_4(\mu_4\text{-}O)(\mu\text{-}Br)_6(NL)_4$ with $CuBr_3ON$ chromophore (B) and $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(pim)_3Cl$ with unequal chromophores (C).[a].

A: $(X)_4^+$	Cu–Cu [Å]	Cu–μ_4O [Å]	Cu–μCl [Å]	Cu–Cl [Å]	Cu–μ_4O–Cu[b] [°]	Cu–Cl–Cu [°]	Ref.
$Cl_4\cdot(Et_2(NH_2)_4$	3.121(1,53)	1.913(5,10)	2.461(2,126)	2.243(3,7)	3.3	80.4(1,9)	[37]
$Cl_4\cdot(dnda)_4$	3.130(–,14)	1.917(–,0)	2.411(–,57)	2.248(–,10)	0.8	81.1(–,2.0)	[38]
$Cl_4\cdot(1\text{-}Bu\text{-}3\text{-}Meim)_4$	3.138(–,40)	1.922(–,14)	2.418(–,92)	2.235(–,13)	2.2	82.5(–,8.4)	[39]
$Cl_4\cdot(NMe_4)_4$	3.137(3,1)	1.921(2,0)	2.398(4,33)	2.268(4,0)	Not given	Not given	[40]
	3.198(3,0)	1.958(2,0)	2.420(5,0)	2.203(4,0)	Not given	Not given	
$Cl_4\cdot(NMe_4)_4$	3.14(1,0)	1.92(1,0)	2.41(2,0)	2.25(2,0)	0,4	81.3(1,1)	[41]
	3.18(1,0)	1.93(1,0)	2.43(3,0)	2.1792,0)	0	81.5	

B: $(NL)_4$	Cu–Cu [Å]	Cu–μ_4O [Å]	Cu–μBr [Å]	Cu–N [Å]	Cu–μ_4O–Cu[b] [°]	Cu–Br–Cu [°]	Ref.
$(ettz)_4$	3.136(–,49)	1.922(–,86)	2.522(–,84)	1.972(–,23)	4.8	76.8(–,1.9)	[42]
$(py)_4$	3.142(6,19)	1.92(1,1)	2.534(4,76)	2.02(2,5)	1.1	76.7(2,1.0)	[43]
$(py)_4$	3.152(–,84)	1.930(–,8)	2.539(–,75)	1.985(–,14)	1.5	76.7(–,1.2)	[44]
$(mor)_4$	3.155(2,12)	1.932(8,23)	2.535(3,48)	2.02(2,0)	1.7	76.9(1,7)	[45]

C: $(pim)_3Cl$	Cu–Cu [Å]	Cu–μ_4O [Å]	Cu–μCl [Å]	Cu–N [Å]	Cu–μ_4O–Cu[b] [°]	Cu–Cl–Cu [°]	Ref.
$CuCl_3ON$(x3)	3.107(–,49)	1.908(–,13)	2.409(–,90)	N 1.923(–,6)	2.8	80.6(–,2.1)	[46]
$CuCl_3OCl$(x1)		1.912	2.411(–,80)	Cl 2.237			

bond angle from the ideal value is 2.0° (range 1.1–4.8°). The mean Cu–μBr–Cu bond angle is 76.8° (range 75.0–78.7°).

2.6. $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(pim)_3Cl$ with unequal chromophores

X-ray analysis of triclinic $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(pim)_3Cl$ showed [46] that there are two types of copper(II) center, three with the $CuCl_3ON$ chromophore and the remaining one with the $CuCl_3OCl$ chromophore (Table 4C). A trigonal plane about each copper(II) center is built up of three chlorine atoms with the mean Cu–μCl bond distances of 2.409 Å in $CuCl_3ON$ and 2.418 Å in $CuCl_3OCl$. In both "chromophores" one apical position is occupied by an oxygen atom with the mean values of 1.908 and 1.912 Å, respectively. The second apical side is occupied by a nitrogen atom with the mean Cu–N bond distance of 1.92 Å in the former, and by a chlorine atom with the Cu–Cl bond distance of 2.24 Å in the latter. The mean Cu···Cu separation is 3.107 Å and the deviation of the mean Cu–O–Cu bond angle from the ideal tetrahedral angle is 2.8°. The mean Cu–Cl–Cu bond angle is 80.6°.

2.7. $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}Br)_3(Ph_3PO)_4$ with the $CuCl_{1.5}Br_{1.5}OO'$ chromophore

X-ray analysis of $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}Br)_3(Ph_3PO)_4$ shows [47] that in each set the Cu–L bond distances are equal with the values of Cu···Cu 3.080 Å, Cu–μ_4O 1.888(2) Å, μCl/Br 2.461(2) and Cu–O($OPPh_3$) 1.88(1) Å. Interestingly the Cu–μCl and Cu–μBr bond distances are equal (2.461(2) Å) as well as Cu–X–Cu (X = Cl or Br) bridge angles (77.5(1)°). The Cu–μX (X = Cl or Br) bond distances in [47] lie in the middle between the mean Cu–μCl (2.41 Å) and Cu–μBr (2.53 Å) bond distances. The Cu–X–Cu (X = Cl or Br) in [47] also lies between the values of Cu–Cl–Cu (80.5°) and Cu–Br–Cu (76.6°) bridge angles.

3. Conclusions

This review summarizes structural data for forty five tetrameric copper(II) complexes which contain a μ_4-oxo group tetrahedrally coordinated to four copper(II) centers. Each pair of copper(II) centers is bridged by a single chlorine, bromine or mixed chlorine plus bromine atoms. The coordination sphere about each copper(II) is trigonal-bipyramidal, with three chlorine or bromine atoms in the trigonal plane. One apical position about each copper(II) is occupied by an oxygen atom, which is tetrahedrally coordinated to four copper(II) atoms. The second axial position is occupied by ligands with oxygen, nitrogen donor sites or by a chlorine atom. There are four types of structurally equal units: $CuCl_3ON$ (x4) (Table 2), $CuCl_3OO'$ (x4) (Table 3), $CuCl_3OCl$ (x4) (Table 4A) and $CuBr_3ON$ (x4) (Table 4B). In two derivatives [3,46] structurally unequal core units are present: $CuCl_3ON$ (x2) and $CuCl_2BrON$ (x2) [3]; $CuCl_3ON$ (x1), $CuCl_2BrON$ (x2) and $CuBr_2ClON$ (x1) [3]; $CuCl_2BrON$ (x2) and $CuBr_2ClON$ (x2) [3] (Table 1); $CuCl_3ON$ (x3) and $CuCl_3OCl$ (x1) [46] (Table 4C).

There is a tendency for an elongated Cu···Cu separation, and Cu–L bond distances with increase of the covalent radius of coordinated atoms in the order:

Cu···Cu: 3.10 Å ($CuCl_3OO'$, 4.43 Å) < 3.112 Å ($CuCl_3ON$, 4.47 Å) < 3.15 Å ($CuCl_3OCl$, 4.69 Å; $CuBr_3ON$, 4.82 Å)
Cu–μ_4O: 1.90 Å ($CuCl_3ON$) < 1.91 Å ($CuCl_3ON$) < 1.92 Å ($CuCl_3OCl$, $CuBr_3ON$)
Cu–μCl: 2.40 Å ($CuCl_3OO'$) < 2.41 Å ($CuCl_3ON$) < 2.42 Å ($CuCl_3OCl$)
Cu–μBr: 2.53 Å ($CuBr_3ON$)

The mean Cu–L (terminal) bond distances also increased with the covalent radius of the coordinated atoms in the order: 1.92 Å (O, 0.73 Å) < 1.97 Å (N, 0.75 Å) < 2.23 Å (Cl, 0.99 Å), as expected. Tetrahedral distortion around the oxygen atom (OCu_4) increases in the order: 1.67° ($CuCl_3OCl$) < 2.10° ($CuCl_3ON$) < 2.11° ($CuCl_3OO'$) < 2.27° ($CuBr_3ON$). The mean Cu–Cl–Cu bridge angle of 80.5° is about 4.0° more open than that of a Cu–Br–Cu bridge (76.5°).

The $Cu_{16}(\mu_4\text{-}O)(\mu\text{-}Br)_7(\mu\text{-}Cl)_{17}(4\text{-}Mepy)_{16}$ cluster [3] is a unique example of stereoisomerism. There are four crystallographically independent tetramers.(1) $Cu_4OBrCl_5(4\text{-}Mepy)_4$, (2) $Cu_4OBrCl_5(4\text{-}Mepy)_4$, (3) *cis*-$Cu_4OBr_2Cl_4(4\text{-}Mepy)_4$, and (4) *mer*-$Cu_4OBr_3Cl_3(4\text{-}Mepy)_4$. The first two (1 and 2) tetramers are typical examples of distortion isomerism. These tetramers are unique example of stereoisomerism.

There is $Cu_4OCl_6(4\text{-}Mepy)_4$ [6] which contains four crystallographically independent tetramers within the same crystal and in several derivatives [5,8,25,10,28,29,40,41] two such tetramers are present, differing by the degree of distortion. Three other derivatives $(NMe)_4[Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6Cl_4]$ [40,41], $Cu_4OCl_6(3,5\text{-}Mepz)_4$ [13,14] and $Cu_4OCl_6(bim)_4$ [15,16] exist in two isomeric forms, differing mostly by the degree of distortion.

Finally, there are $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(n\text{-}Mepy)_4$ (n = 2 [5] and 4 [6]), $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6(n\text{-}Meim)_4$ (n = 1 [8,9] and 2 [10]), which are examples of ligand isomerism.

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