

A linear cyclic oximate-bridged tetracopper(II) complex¹

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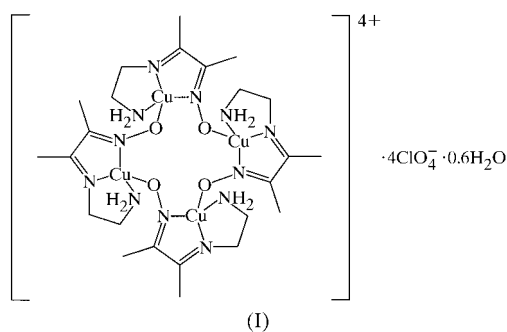
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The crystal structure of the title complex, tetrakis[μ -6-amino-3-methyl-4-azahex-3-en-2-one oximato(1-)- $\kappa^4 N, N', N'' : O$]-tetracopper(II) tetraperchlorate 0.6-hydrate, $[\text{Cu}_4(\text{C}_6\text{H}_{12}\text{N}_3\text{O})_4](\text{ClO}_4)_4 \cdot 0.6\text{H}_2\text{O}$, shows the cation to be an oximate-bridged tetramer composed of four 6-amino-3-methyl-4-azahex-3-en-2-one oxime ligands and four copper(II) ions and to have crystallographically imposed $\bar{4}$ symmetry. Each Cu^{II} atom is four-coordinated by the three N atoms of one oxime ligand and by the O atom of another oxime ligand in a distorted square-planar geometry.

Comment

Studies on multinuclear copper(II) complexes have focused on the magneto-structural relationships and characterization of the active site in multicopper proteins (Alagi *et al.*, 1997). Linear, di- and trinuclear copper(II) complexes with oximate groups ($\text{C}=\text{N}-\text{O}^-$) have been widely studied (Cervera *et al.*, 1997; Dominguezvera *et al.*, 1997; Luneau *et al.*, 1989), but tetranuclear copper(II) complexes occur less frequently. In the present study, the isolation and X-ray structure of the tetranuclear copper(II) complex tetrakis[μ -6-amino-3-methyl-4-azahex-3-en-2-one oximato(1-)- $\kappa^4 N, N', N'' : O$]tetracopper(II) tetraperchlorate 0.6-hydrate, (I), is reported.



Each Cu ion in the structure is coordinated by three N atoms from one 6-amino-3-methyl-4-aza-hex-3-en-2-one

¹ Contribution No. N216.

oximate ligand (L^-) and by the oxime O atom from a second L^- ligand in a distorted square-planar arrangement. The O1, N1, N2 and N3 donor atoms are planar within 0.124 (2) Å, and the Cu atom deviates by 0.129 (2) Å from this plane. Four of these $\text{Cu}L$ subunits are linked into a discrete tetrameric cation which has $\bar{4}$ crystallographic symmetry (Fig. 1) and which contains a 12-membered heterocyclic ring of composition $(\text{Cu}, \text{O1}, \text{N3})_4$. The unit cell contains two of these tetramers.

Unlike the structures of square tetranuclear metal complexes in which the four metal ions lie in a plane (Chaudhuri *et al.*, 1993; Maekawa *et al.*, 1999), the central tetranuclear copper(II) core of the title complex has an 'open-butterfly' configuration with the four copper(II) ions located at the corners of a flattened tetrahedron and is much different from rhombic structures (Raper, 1997; Castro *et al.*, 1995; Gomez-Garcia *et al.*, 1992; Sletten *et al.*, 1990; Tandon *et al.*, 1991). The degree of distortion of the tetrahedron is indicated by the two $\text{Cu} \cdots \text{Cu}$ distances of 4.244 (1) Å perpendicular to the c axis and the other four $\text{Cu} \cdots \text{Cu}$ distances of 3.469 (1) Å within the tetramer. The oxime group adopts an out-of-plane coordination mode as a diatomic (μ -1,2)-bridging ligand between copper(II) ions (Ruiz *et al.*, 1998). The orientations of the oxime ligands in the tetramer are alternately up and down.

The $\text{Cu}/\text{N1}/\text{N2}/\text{C1}/\text{C2}$ and $\text{Cu}/\text{N1}/\text{N2}/\text{C1}/\text{C2}$ five-membered rings are in the skew form and are planar within 0.158 (5) and 0.051 (3) Å, respectively. The $\text{Cu}-\text{N}$ bond lengths, ranging from 1.939 (4) to 2.004 (4) Å, are considered normal coordination bonds. The order of the $\text{Cu}-\text{N}$ distances, *i.e.* amine [2.004 (4) Å] > oxime [1.989 (3) Å] > imine [1.941 (3) Å], is the same as that observed for other oximate-bridged Cu^{II} complexes (Nasakkala *et al.*, 1981; Butcher *et al.*, 1979). The $\text{Cu}-\text{O}$ (bridging oxime) distance [1.941 (3) Å] is slightly longer than that found in these other oximate-bridged Cu^{II} complexes because of the steric effect of the bulky folded conformation (Nasakkala *et al.*, 1981; Butcher *et al.*, 1979). Owing to the weak metal-ligand interactions in the title complex, the $\text{N}-\text{O}$ distance [1.339 (4) Å] is longer than that

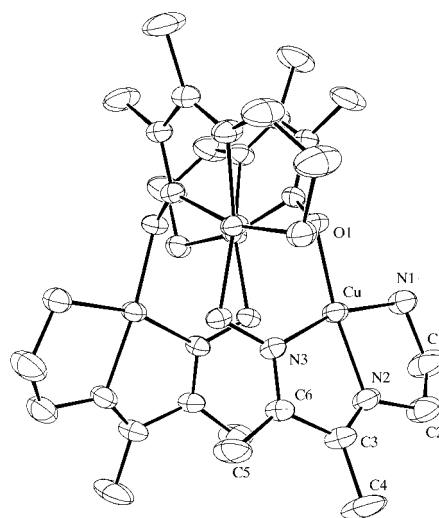


Figure 1

The structure of the title compound showing 30% probability displacement ellipsoids. Only the asymmetric part of the tetramer is labelled. The water molecule and the perchlorate ions have been omitted for clarity.

found in complexes with strongly coordinated bridging-oxime groups [1.311 (3) Å; Raston *et al.*, 1978; Butcher *et al.*, 1979]. The bond angles of the oxime and imine N atoms are approximately 120°, in keeping with the expected sp^2 -hybridization stabilized by π -bonding. The N3ⁱ—O1—Cu [112.7 (2)°; symmetry code: (i) $\frac{3}{2} - y, x, \frac{1}{2} - z$] angle indicates a variation from sp^2 hybridization for the oxime O atom, resulting from coordination to another Cu atom. The N—O distance does show some decrease in going from the free ligand (1.375 Å) to complexes with weak interactions [1.339 (4) Å, this study] to complexes with strong interactions [1.311 (3) Å; Raston *et al.*, 1978; Butcher *et al.*, 1979].

There appears to be a water molecule on a partially occupied site [occupancy = 0.30 (3)] on a twofold axis. This is external to the tetramer and is loosely held by hydrogen bonding to the perchlorate ion (Table 2). There are two equivalent sites on the axis that are 2.80 (3) Å apart. Other hydrogen bonds are detailed in Table 2.

Experimental

The ligand 6-amino-3-methyl-4-azahex-3-en-2-one oxime was prepared according to the method of Singh *et al.* (1977). Equimolar quantities of copper perchlorate hexahydrate and the ligand were mixed in methanol and the solution heated under reflux for 2 h. The resulting solution was cooled to room temperature and evaporated to dryness by rotatory evaporation. The crude product was washed with acetonitrile and recrystallized from methanol by slow evaporation.

Crystal data

[Cu ₄ (C ₆ H ₁₂ N ₃ O) ₄](ClO ₄) ₄ ·0.6H ₂ O	Mo K α radiation
$M_r = 1232.32$	Cell parameters from 25 reflections
Tetragonal, $P4_2/n$	$\theta = 5.4\text{--}17.3^\circ$
$a = 12.440$ (3) Å	$\mu = 2.15$ mm ⁻¹
$c = 14.851$ (7) Å	$T = 293$ (2) K
$V = 2298.2$ (12) Å ³	Square bipyramidal, black
$Z = 2$	$0.47 \times 0.34 \times 0.29$ mm
$D_x = 1.790$ Mg m ⁻³	

Data collection

Nonius CAD-4 diffractometer	$\theta_{\max} = 30.0^\circ$
ω -2 θ scans	$h = 0 \rightarrow 17$
Absorption correction: empirical (North <i>et al.</i> , 1968)	$k = 0 \rightarrow 17$
$T_{\min} = 0.37$, $T_{\max} = 0.54$	$l = 0 \rightarrow 20$
3349 measured reflections	3 standard reflections
3349 independent reflections	frequency: 60 min
1710 reflections with $I > 2\sigma(I)$	intensity decay: 3%

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.066$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
$wR(F^2) = 0.183$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{\max} = 0.031$
3349 reflections	$\Delta\rho_{\max} = 1.31$ e Å ⁻³
153 parameters	$\Delta\rho_{\min} = -0.74$ e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

Cu—N2	1.939 (4)	Cu—N3	1.989 (3)
Cu—O1	1.941 (3)	Cu—N1	2.004 (4)
N2—Cu—O1	165.50 (16)	N2—Cu—N1	84.26 (16)
N2—Cu—N3	79.54 (15)	O1—Cu—N1	99.28 (16)
O1—Cu—N3	96.66 (15)	N3—Cu—N1	163.78 (15)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A ⁱ ···O2 ⁱ	0.90	2.31	3.181 (6)	164
N1—H1B ⁱⁱ ···O3 ⁱⁱ	0.90	2.34	3.158 (8)	151
OW—(H)···O4 ⁱⁱⁱ			3.305 (10)	

Symmetry codes: (i) $\frac{1}{2} - y, x, \frac{1}{2} - z$; (ii) $x, 1 + y, z$; (iii) $1 - y, \frac{1}{2} + x, \frac{1}{2} + z$.

H atoms were placed geometrically and refined as riding (N—H = 0.90 Å and C—H = 0.96 or 0.97 Å), with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C, N or O})$. The water H atoms were not located. The largest peak in the difference map is near the Cu atom.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990) and *NRCVAX*; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *NRCVAX*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1319). Services for accessing these data are described at the back of the journal.

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