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trans-μ-Oxamido-*N*,*N*′-diethanoato-bis[diaquacopper(II)] dihydrate

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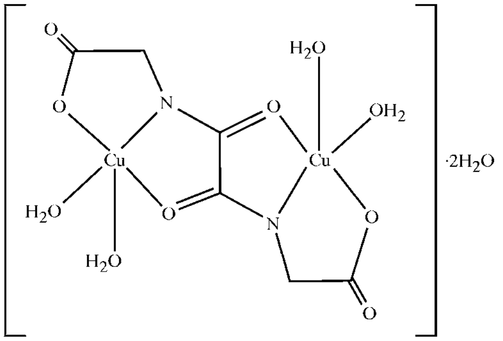
The title complex, *trans*-{μ-2,2′-[(1,2-dioxoethane-1,2-diyl)diimino]diethanoato(4−)}bis[diaquacopper(II)] dihydrate, $[Cu_2(C_6H_4N_2O_6)(H_2O)_4]\cdot 2H_2O$, with a three-dimensional framework, displays a square-pyramidal coordination geometry. The structure consists of a neutral centrosymmetric binuclear unit in which the oxamide ligand has a *trans* geometry, is fully deprotonated and acts in a bis-tridentate fashion.

Comment

Much research effort has been dedicated to studying oxamide-bridged transition metal complexes because of their expected magnetic properties and biological relevance (Santana *et al.*, 2004; Messori *et al.*, 2003; Kou *et al.*, 2003). One of the most outstanding characteristics of oxamide ligands is their versatile bonding mode with metal ions, which makes it practical to design tunable molecular materials with extended structures (Li *et al.*, 1998; Lloret, Julve *et al.*, 1992). Taking into account the above facts and in continuation of our work on polynuclear complexes with bridging oxamide groups (Li *et al.*, 2003), in this paper we describe the synthesis of a new binuclear copper(II) complex, *viz.* $[Cu_2(obe)(H_2O)_4]\cdot 2H_2O$, (I), using 2,2′-[(1,2-dioxoethane-1,2-diyl)diimino]diethanoate (obe) as bridging ligand. The crystal structure of (I) was determined in order to examine the effect of pH on the bonding mode of the obe ligand with copper(II).

The molecular structure of (I) is illustrated in Fig. 1. Single-crystal X-ray analysis reveals that the complex contains a neutral centrosymmetric binuclear molecule in which the oxamide ligand has a *trans* geometry, is fully deprotonated and acts in a bis-tridentate fashion. The Cu atom has a square-pyramidal coordination geometry, with three atoms (N1, O2 and O3) from the oxamide ligand and one water molecule (O5) in the basal plane, and with one water molecule (O4) in the apical position. The deviations of atoms N1, O2, O3 and O5 from the least-squares plane through these atoms are 0.0408 (10), 0.0365 (9), 0.0358 (8) and 0.0315 (7) Å, respectively, while the Cu atom is displaced 0.1322 (9) Å from this plane. The Cu—O distance of 2.314 (2) Å in the axial direction is longer than those in the basal plane by 0.315, 0.299 and 0.392 Å (Table 1). The Cu···Cu separation within each binuclear unit is 5.228 (4) Å.



(I)

As shown in Fig. 2, a two-dimensional network parallel to the (101) plane is formed *via* hydrogen bonding between the coordinated water molecule (O5) in the basal plane and atoms O1 and O2 from the carboxylate group (the hydrogen-bonding geometries are listed in Table 2). Moreover, through hydrogen bonds between the other coordinated water molecule (O4), in the apical position, and atom O3 of the oxamide group, the two-dimensional hydrogen-bonding network is assembled into a three-dimensional supramolecular structure (Fig. 3), in which the uncoordinated water molecules participate by hydrogen bonding to atom O1(x, y, $1 + z$).

Compared with the previously reported complex $\{[Cu(H_2obe)(H_2O)_3]\cdot 4H_2O\}_n$ (Lloret, Sletten *et al.*, 1992), which was obtained from aqueous solutions of copper(II) nitrate trihydrate and H_4(obe) in a 1:1 molar ratio at a pH of ~3 by slow evaporation, the present complex has two important differences with respect to the obe ligand. The previously reported complex consists of one-dimensional $[Cu(H_2obe)]_n$ chains in which the ligand is deprotonated only at the terminal carboxylate groups and is bis-monodentate, and the N1—C3 and O3—C3 bond distances in the oxamide

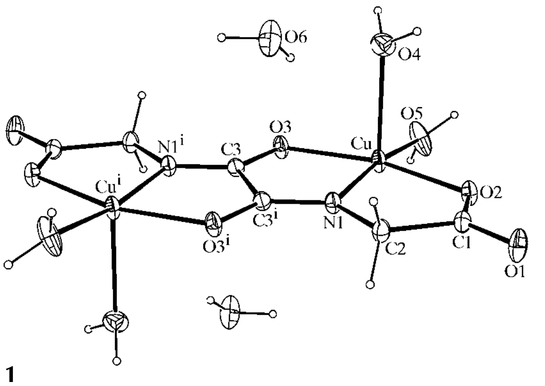


Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids. [Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$.]

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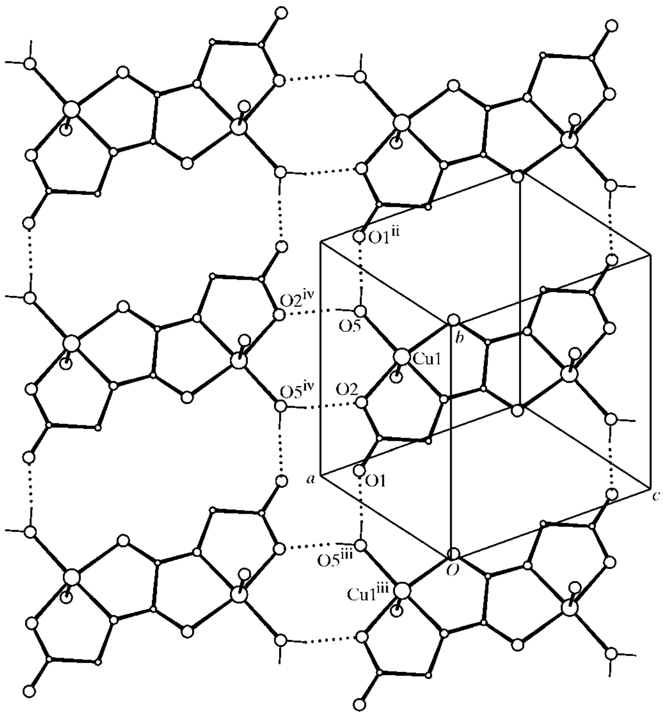

Figure 2
The two-dimensional hydrogen-bonding network parallel to the (101) plane. Dotted lines indicate hydrogen bonds. [Symmetry codes: (ii) $x, 1 + y, z$; (iii) $x, -1 + y, z$; (iv) $2 - x, 1 - y, -z$.]

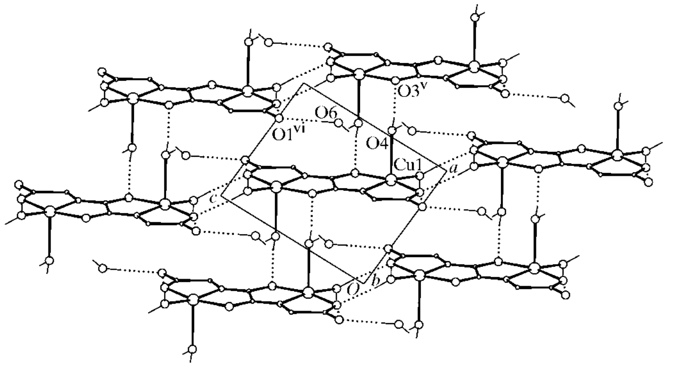

Figure 3
A view of the three-dimensional supramolecular structure. Dotted lines indicate hydrogen bonds. [Symmetry codes: (v) $x + 1, y, z$; (vi) $x, y, 1 + z$.]

group are 1.326 (1) and 1.228 (1) Å. In the present complex, the ligand is fully deprotonated, not only at the carboxylate groups but also at the oxamide group. The deprotonation at atom N1 and copper coordination at atoms N1 and O3 lead to highly significant changes in the N1—C3 [1.289 (3) Å] and O3—C3 [1.277 (3) Å] bond distances, which indicate a more effective π delocalization in the NCO fragment.

Experimental

All chemicals were of reagent grade and were used without further purification. The ligand oxamidodiethanoic acid, H_4(obe), was synthesized according to the reported method of Yu *et al.* (1991). A solution of copper(II) chloride dihydrate (68.2 mg, 0.4 mmol) dissolved in methanol (5 ml) was added dropwise to a water/methanol (20 ml, 1:5 *v*/*v*) mixture containing the ligand (0.2 mmol). An appropriate amount of piperidine was then added to adjust the pH to 7. The mixture was heated under reflux with stirring for 12 h. The precipitate was filtered off, washed with cold water, methanol and diethyl ether in turn, and then redissolved in water. Green crystals (yield 49.6 mg, 57%) were obtained from the solution after 5 d by slow evaporation at room temperature. Analysis calculated: C 16.55, H 3.70, N 6.44%; found: C 16.48, H 3.62, N 6.37%. IR (KBr pellet, cm^{-1}): ν(O—H) 3157 (*s*, *br*), ν_a(COO$^-$) 1661 (*vs*), ν(N—C=O) 1585 (*vs*), ν_{as}(COO$^-$) 1384 (*s*).

Crystal data

$[Cu_2(C_6H_4N_2O_6)(H_2O)_4]\cdot 2H_2O$
$M_r = 435.31$
Triclinic, $P\overline{1}$
$a = 6.870$ (6) Å
$b = 7.283$ (7) Å
$c = 7.929$ (7) Å
$\alpha = 73.693$ (14)°
$\beta = 87.795$ (14)°
$\gamma = 67.342$ (14)°
$V = 350.3$ (6) Å^3
$Z = 1$
$D_x = 2.064$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1696 reflections
$\theta = 2.7$–27.6°
$\mu = 3.10$ mm^{-1}
$T = 293$ (2) K
Block, green
0.19 × 0.15 × 0.12 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.578$, $T_{max} = 0.689$
2108 measured reflections
1541 independent reflections
1431 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 27.0°$
$h = -5 \rightarrow 8$
$k = -7 \rightarrow 9$
$l = -9 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.071$
$S = 1.06$
1541 reflections
100 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0378P)^2 + 0.2235P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.67$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—N1	1.903 (2)	Cu—O5	1.922 (2)
Cu—O2	1.999 (2)	N1—C3	1.289 (3)
Cu—O3^i	2.015 (2)	O3—C3	1.277 (3)
Cu—O4	2.314 (2)		
N1—Cu—O2	82.22 (8)	O2—Cu—O4	93.80 (8)
N1—Cu—O3^i	83.85 (8)	O3^i—Cu—O4	91.50 (9)
N1—Cu—O4	94.39 (10)	O5—Cu—O2	96.84 (10)
N1—Cu—O5	169.86 (9)	O5—Cu—O3^i	96.13 (9)
O2—Cu—O3^i	165.42 (7)	O5—Cu—O4	95.75 (11)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*A*···O3^v	0.85	1.94	2.773 (3)	166
O5—H5*A*···O1^{ii}	0.90	1.82	2.713 (4)	172
O5—H5*B*···O2^{iv}	0.86	1.87	2.721 (3)	170
O6—H6*B*···O1^{vi}	0.85	1.92	2.770 (3)	171

Symmetry codes: (ii) $x, 1 + y, z$; (iv) $2 - x, 1 - y, -z$; (v) $x + 1, y, z$; (vi) $x, y, 1 + z$.

H atoms attached to C atoms were positioned geometrically and treated as riding on their parent C atoms, with C—H distances of 0.97 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$. Water H atoms were located in a difference Fourier map and were included in the structure-factor calculations with fixed positional and isotropic displacement parameters [O—H = 0.83–0.90 Å and $U_{iso}(H) = 0.08$ Å^2].

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1246). Services for accessing these data are described at the back of the journal.

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