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A new Schiff base copper (II) complex: bis[*N*-(4-hydroxysalicylidene)-*N*′,*N*′-diethylethylenediamine-κ^2N,O]bis[(oxalato-κ^2O,O')copper(II)] dihydrate

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The synthesis and characterization of a copper(II) complex of salicylaldimine, $[Cu_2(C_2O_4)_2(C_{13}H_{20}N_2O_2)_2]\cdot 2H_2O$, is described. The reaction of 2,4-dihydroxybenzaldehyde and *N*,*N*-diethylethylenediamine with $K_2[Cu(C_2O_4)_2]$ produces a centrosymmetric binuclear Cu^{II} complex. Its structure reveals that the copper(II) ion is five-coordinate and situated in a distorted square-pyramidal environment.

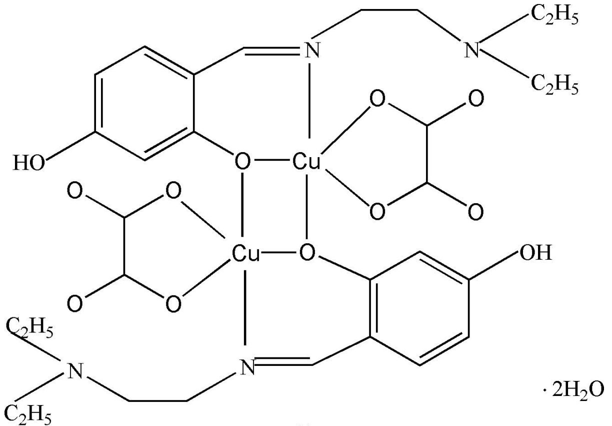
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.031
wR factor = 0.081
Data-to-parameter ratio = 15.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The environment around the metal center and its conformational flexibility are the key factors for a metalloprotein to carry out a specific physiological function, *e.g.* dioxygen binding, oxygen utilization *etc*. In order to emulate the biological activity of metalloproteins, particularly their active sites, various model metal complexes containing Schiff base ligands have been synthesized and studied for their dioxygen uptake (McLendon & Martell, 1976; Niederhoffer *et al.*, 1984; Smith & Pilbrow, 1981; Tovrog *et al.*, 1976; Martell & Sawyer, 1988; Busch & Alcock, 1994) and oxidative catalysis (Holm, 1987; Srinivasan *et al.*, 1986; Dixit & Srinivasan, 1988; Rihter *et al.*, 1993; SriHari & Masnovi, 1990). Recently, our group has studied the synthesis and the magnetic properties of Schiff base complexes (Bian, Gu *et al.*, 2003; Bian, Xu *et al.*, 2003*a*,*b*; Bian *et al.*, 2004). We report here a new five-coordinate copper(II) complex with a tridentate Schiff base ligand, which is condensed from *N*,*N*-diethylethylenediamine and 2,4-dihydroxybenzaldehyde.



(I)

The title complex, (I), is a dimer composed of two Cu^{II}–salen units [salen is *N*-(4-hydroxysalicylidene)-*N*′,*N*′-diethylethylenediamine], which are related by an imposed center of symmetry. The two Cu(salen) units are staggered, such that the two Cu^{II} centers are bridged by a pair of phenolate O

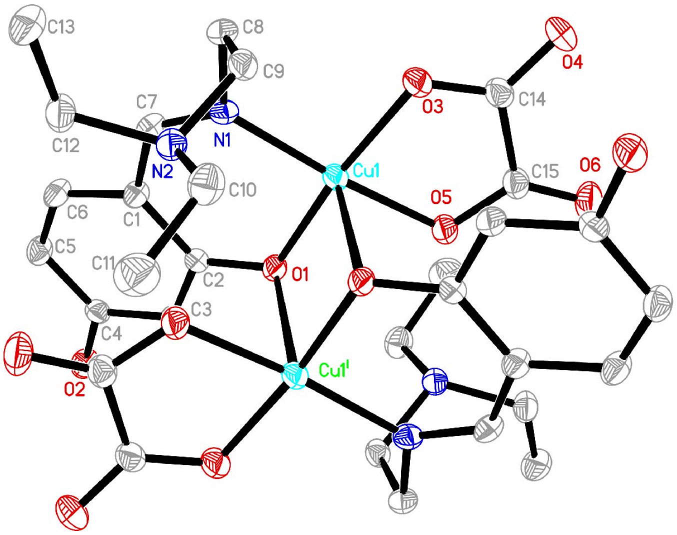


Figure 1
A view of the complex molecule of (I), with the atomic labeling scheme. Displacement ellipsoids are shown at the 30% probability level. H atoms and water molecules have been omitted for clarity. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

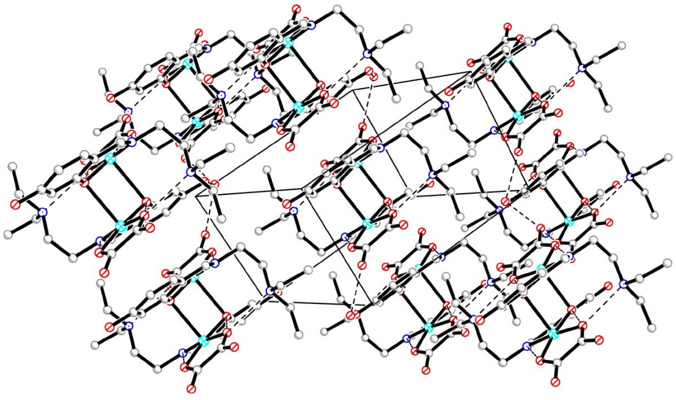


Figure 2
A packing view, showing the O—H$\cdots$O hydrogen-bond network between the complex molecules and the water molecules. Hydrogen bonds are shown as dashed lines.

atoms from two ligands [Cu1^i—O1 = 2.650 (2) Å; symmetry code: (i) $1 - x, 1 - y, 1 - z$]. Similar to other dimers of Cu(salen)-type compounds (Vaidyanathan *et al.*, 1998; Luo *et al.*, 1999; Mohan & Srinivas, 1993), complex (I) is best described as having elongated square-pyramidal geometry (Table 1) because of its τ value of 0.05. The τ parameter was introduced by Addison & Rao (1984) for five-coordinate copper complexes to measure the distortion of a square-pyramidal structure toward trigonal bipyramidal. The basal plane of each Cu^{II} atom contains one N and one O donor atom from the tridentate Schiff base ligand and two O donor atoms from the oxalate ligand. The Cu^{II} atom is displaced by 0.0848 (3) Å towards the bridging O atom, from the mean plane of the donor atoms.

In addition to an N—H$\cdots$O hydrogen bond within the complex, there are O—H$\cdots$O hydrogen bonds involving the hydroxy groups and water molecules, resulting in an intricate network (Table 2 and Fig. 2).

Experimental

A methanol solution (10 ml) of *N*,*N*-diethylethylenediamine (3 mmol) was added to a methanol solution (10 ml) of 2,4-dihydroxybenzaldehyde (3 mmol) and the resulting mixture was refluxed for 1 h. The ligands were not isolated from the methanol solution and the solution mixture was added to a dimethyl sulfoxide solution of $K_2[Cu(C_2O_4)_2]$ (3 mmol) and refluxed for 2 h. Crystals of suitable quality for X-ray analysis were obtained by slow evaporation.

Crystal data

$[Cu_2(C_2O_4)_2(C_{13}H_{20}N_2O_2)_2]\cdot 2H_2O$
$M_r = 811.79$
Triclinic, $P\overline{1}$
$a = 8.372$ (3) Å
$b = 10.449$ (3) Å
$c = 10.781$ (3) Å
$\alpha = 96.099$ (5)°
$\beta = 110.379$ (5)°
$\gamma = 99.826$ (5)°
$V = 857.0$ (5) Å^3

$Z = 1$
$D_x = 1.573$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 843 reflections
$\theta = 3.0$–26.3°
$\mu = 1.32$ mm^{-1}
$T = 293$ (2) K
Block, green
0.24 × 0.20 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.737$, $T_{max} = 0.810$
4966 measured reflections

3482 independent reflections
2871 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 26.4$°
$h = -10 \rightarrow 10$
$k = -9 \rightarrow 13$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.081$
$S = 1.05$
3482 reflections
229 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 0.0467P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9121 (16)	Cu1—O3	1.9523 (16)
Cu1—O5	1.9462 (16)	Cu1—N1	1.9579 (19)
O1—Cu1—O5	87.76 (6)	O1—Cu1—N1	94.05 (7)
O1—Cu1—O3	170.92 (7)	O5—Cu1—N1	173.84 (7)
O5—Cu1—O3	83.98 (7)	O3—Cu1—N1	93.78 (7)

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

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
N2—H2*A*$\cdots$O5^i	0.91	1.98	2.861 (3)	164
O2—H2$\cdots$O7^{ii}	0.82	1.84	2.648 (2)	166
O7—H7*A*$\cdots$O4^{iii}	0.85	1.99	2.815 (3)	163
O7—H7*B*$\cdots$O4^{iv}	0.85	2.04	2.869 (3)	166

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

All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry, with C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$, but each group was allowed to

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rotate freely about its C—C bond. H atoms attached to water molecules were treated as riding (O—H = 0.85 Å and H···H = 1.39 Å), with $U_{iso}(H) = 1.5U_{eq}(O)$. All other H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 and 0.97 Å, O—H = 0.82 Å, and $U_{iso}(H) = 1.2U_{eq}(C)$ and $1.5U_{eq}(O)$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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