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Key indicators

Single-crystal X-ray study  
T = 294 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$   
Disorder in solvent or counterion  
R factor = 0.045  
wR factor = 0.125  
Data-to-parameter ratio = 13.7

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

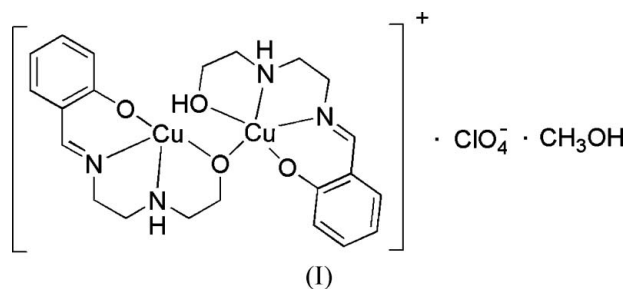
A new Schiff base–copper(II) complex:  $[\text{N}-(2\text{-hydroxyethyl})\text{-N}'-(2\text{-oxidobenzylidene})\text{ethylenediamine-}1\kappa^4\text{O,N,N',O}'][\mu\text{-N}-(2\text{-oxidobenzylidene})\text{-N}'-(2\text{-oxidoethyl})\text{ethylenediamine-}1\kappa\text{O:}2\kappa^4\text{O,N,N',O}']\text{-dicopper(II) perchlorate methanol solvate}$

The synthesis and characterization of the title  $\text{Cu}^{\text{II}}$  complex,  $[\text{Cu}_2(\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_2)(\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}_2)]\text{ClO}_4 \cdot \text{CH}_4\text{O}$ , is described. The reaction of salicylaldehyde and *N*-(2-hydroxyethyl)ethylenediamine with  $[\text{Cu}(\text{ClO}_4)_2] \cdot 6\text{H}_2\text{O}$  produced the binuclear  $\text{Cu}^{\text{II}}$  complex in which the adjacent  $\text{Cu}^{\text{II}}$  atoms are connected by a  $\mu\text{-O}$  bridge. One of the  $\text{Cu}^{\text{II}}$  atoms is in an elongated square-pyramidal geometry and the other has a distorted square-planar geometry.

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Comment

A series of binuclear transition-metal complexes, which display different physical properties, have been investigated intensively during the past two decades. This interest is partly due to the relevance of these compounds as active site structures of metal proteins and enzymes (Karlin & Tyeklar, 1993; Jun & True, 1990), and partly because of attempts to understand the relationship between the structure and the magnetic properties (Gatteschi *et al.*, 1984; Kahn, 1985, 1987; Doman *et al.*, 1990; Kawato *et al.*, 1992; Kavlakoglu *et al.*, 2000). 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 copper(II) complex with a tetradentate Schiff base ligand, which is condensed from salicylaldehyde and *N*-(2-hydroxyethyl)ethylenediamine.



ethane], a  $\text{ClO}_4^-$  anion and a methanol molecule, As observed in similar structures (Okawa *et al.*, 1973; Jgrzybowski *et al.*, 1973; Lorosch *et al.*, 1987; Shen *et al.*, 1999), atoms Cu1 and Cu2 in the  $[\text{Cu}_2(\text{L})(\text{LH})]^+$  cation are bridged by the O atom of the deprotonated hydroxyl group. Atom Cu1 is in an elongated square-pyramidal geometry (Table 1) with a  $\tau$  value of 0.22. The  $\tau$  parameter was introduced by Addison & Rao (1984) for five-coordinate copper complexes to measure the distortion of a square-pyramidal structure ( $\tau = 0$ ) toward trigonal bipyramidal ( $\tau = 1$ ). The basal plane of atom Cu1 contains two N and one O atoms from a tetradentate Schiff base ligand and one bridging O atom from a second ligand; the Cu—O bond distances are 1.920 (3) and 1.966 (3) Å, and the Cu—N distances 1.931 (3) and 2.017 (4) Å, respectively. The remaining O atom of the first ligand occupies the apical position of the pyramid with a Cu—O length of 2.384 (3) Å. Atom Cu2 has a distorted square-planar geometry with average Cu—O and Cu—N bond lengths of 1.923 (6) and 1.959 (7) Å, respectively.

## Experimental

A methanol solution (10 ml) of *N*-(2-hydroxyethyl)-ethylenediamine (1 mmol) was added to a methanol solution (10 ml) of salicylaldehyde (1 mmol) and refluxed for 1 h. The ligands were not isolated from the methanol solution and the solution was added first to a methanol solution (5 ml) of  $[\text{Cu}(\text{ClO}_4)_2] \cdot 6\text{H}_2\text{O}$  (1 mmol) and then to a methanol solution (5 ml) of  $\text{Et}_3\text{N}$  (1 mmol), and refluxed for 2 h. Crystals of suitable quality for X-ray analysis were obtained by slow evaporation of the resulting solution (yield 75%).

### Crystal data

$[\text{Cu}_2(\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_2)(\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}_2)] \cdot \text{ClO}_4 \cdot \text{CH}_4\text{O}$	$D_x = 1.621 \text{ Mg m}^{-3}$
$M_r = 672.06$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 1002 reflections
$a = 12.479 (3) \text{ \AA}$	$\theta = 3.1\text{--}25.8^\circ$
$b = 15.731 (4) \text{ \AA}$	$\mu = 1.70 \text{ mm}^{-1}$
$c = 14.274 (4) \text{ \AA}$	$T = 294 (2) \text{ K}$
$\beta = 100.590 (4)^\circ$	Block, blue
$V = 2754.5 (13) \text{ \AA}^3$	$0.24 \times 0.20 \times 0.16 \text{ mm}$
$Z = 4$	

### Data collection

Bruker SMART CCD area-detector diffractometer	5622 independent reflections
$\varphi$ and $\omega$ scans	3994 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.036$
$T_{\text{min}} = 0.568$ , $T_{\text{max}} = 0.762$	$\theta_{\text{max}} = 26.4^\circ$
15671 measured reflections	$h = -15 \rightarrow 15$
	$k = -19 \rightarrow 19$
	$l = -17 \rightarrow 15$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0651P)^2 + 0.0776P]$
$R[F^2 > 2\sigma(F^2)] = 0.046$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.126$	$(\Delta/\sigma)_{\text{max}} = 0.003$
$S = 1.10$	$\Delta\rho_{\text{max}} = 0.79 \text{ e \AA}^{-3}$
5622 reflections	$\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$
410 parameters	
H-atom parameters constrained	

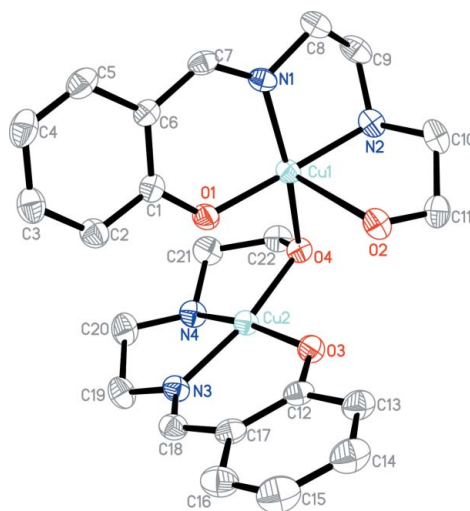


Figure 1

A view of the complex cation of (I), with the atomic labelling scheme. Displacement ellipsoids are shown at the 30% probability level. H atoms, perchlorate ions and methanol molecules have been omitted for clarity.

Table 1

Selected geometric parameters (Å, °).

Cu1—O1	1.920 (3)	Cu2—O3	1.907 (3)
Cu1—N1	1.931 (3)	Cu2—N3	1.928 (4)
Cu1—O4	1.966 (3)	Cu2—O4	1.939 (3)
Cu1—N2	2.017 (4)	Cu2—N4	1.991 (3)
Cu1—O2	2.384 (3)		
O1—Cu1—N1	93.42 (13)	O4—Cu1—O2	87.10 (11)
O1—Cu1—O4	87.13 (11)	N2—Cu1—O2	80.49 (12)
N1—Cu1—O4	164.18 (12)	O3—Cu2—N3	94.26 (13)
O1—Cu1—N2	177.47 (13)	O3—Cu2—O4	95.56 (11)
N1—Cu1—N2	84.46 (15)	N3—Cu2—O4	169.18 (13)
O4—Cu1—N2	95.29 (13)	O3—Cu2—N4	167.53 (14)
O1—Cu1—O2	98.92 (12)	N3—Cu2—N4	84.87 (14)
N1—Cu1—O2	108.38 (12)	O4—Cu2—N4	86.50 (13)

Three perchlorate O atoms show positional disorder, and they were refined as three groups sharing the same Cl and fourth O atom. The site occupancies of these three groups were refined to 0.352 (4), 0.524 (14) and 0.124 (14). The Cl—O and O...O distances in the disordered components were restrained to 1.44 (1) and 2.35 (1) Å, respectively. The  $U^{ij}$  components of atoms O6B, O7B and O8B were restrained to isotropic behaviour. Atoms H2A, H2B and H4A were located in a difference Fourier map and allowed to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$  (O—H = 0.95 Å and N—H = 0.93–0.95 Å). All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with O—H = 0.85 Å, C—H = 0.93–0.97 Å and  $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{carrier})$ .

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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