

catena-Poly[aquacopper(II)- μ -[N-(1-oxido-2-naphthylmethylene)-glycinato-O,N,O':O']]

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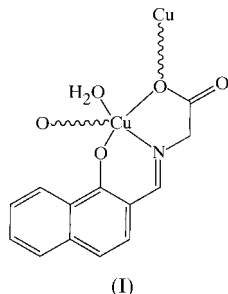
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In the title compound, $[\text{Cu}(\text{C}_{13}\text{H}_9\text{NO}_3)(\text{H}_2\text{O})]_n$, the Cu^{II} ion is in a slightly distorted square-pyramidal environment, with four short bonds in the basal plane formed by three donor atoms of the Schiff base and a water O atom. A symmetry-related neighbouring molecule provides an apical carboxylate O atom at a distance of 2.551 (3) Å; this contact leads to the formation of zigzag polymeric chains. In addition, the chain fragments are connected to each other by hydrogen bonding.

Comment

Metal complexes of amino-acid Schiff bases have attracted attention as models for vitamin B₆ and its analogues in catalyzed non-enzymatic transamination reactions in solution (Metzler *et al.*, 1954; Longenecker & Snell, 1957). The general model assumes transfer of charge density from the α -C region of the amino-acid residue toward the more electronegative pyridine N atom. The metal atom can act as a catalyst by promoting the formation of a Schiff base and maintaining the planarity of the conjugated system by means of the formation of a chelate. Moreover, the metal ion increases the withdrawal of electrons from the α -C region. Several X-ray structural studies of copper complexes of amino-acid Schiff bases have been published so far (Ueki *et al.*, 1967, 1968, 1969; Bkouche-Waksman *et al.*, 1988; Warda *et al.*, 1996; Warda, 1997). The present paper describes a new example, the title compound,



(I), which illustrates a different way of generating the polymeric chain (through the other carboxylic O atom) than that

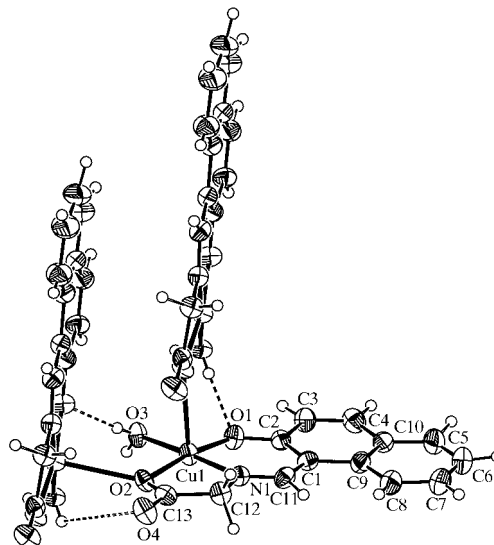
found in [aqua(*N*-salicylidene-glycinato)]copper(II) hemihydrate (Bkouche-Waksman *et al.*, 1988), (II).

The Cu^{II} ion in (I) is five-coordinated (Table 1 and Fig. 1) in the form of a slightly distorted square pyramid, with the basal atoms being O1, O2 and N1 of the Schiff base and O3 of the water molecule. The apical O2' atom [symmetry code: (i) $x, -y, \frac{1}{2} + z$] of a neighbouring molecule completes the coordination. The τ parameter of Addison *et al.* (1989) indicates a 7.5% trigonal-bipyramidal distortion. The basal atoms deviate by up to 0.039 (4) Å from their least-squares plane and the Cu^{II} ion is displaced by 0.099 (1) Å towards the apical donor.

The apical Cu—O2' bond [2.551 (3) Å] is long compared with the corresponding bond in (II) [2.308 (1) Å] and links the molecules to form polymeric chains propagated along the *c* axis (Fig. 2). In these chains, Cu··Cu distances of 3.916 (1) and 5.940 (1) Å are found between nearest-neighbour (*c*-glide related) and cell-translated Cu^{II} ions, respectively. The Cu—O1 and Cu—O2 bond lengths [1.909 (4) and 1.951 (3) Å, respectively] are consistent with there being more negative charge on the phenolic O1 atom than on the carboxylate O2 atom, as noted by Capasso *et al.* (1974) and others.

The bond distances at C12, the α -C implicated in the catalytic activity of such complexes (see, for example, Bkouche-Waksman *et al.*, 1988), *i.e.* C $_{\alpha}$ —C $_{\beta}$ and C $_{\alpha}$ —N, are 1.505 (7) and 1.460 (6) Å, respectively, in the present study, compared with 1.526 (1) and 1.455 (1) Å in (II). In the carboxylate group, only O2 coordinates to the Cu atom, while O4 participates in hydrogen-bond formation (see below and Table 2). The resulting difference in C—O distances of 0.044 (6) Å is considerably larger than in (II), α -glycine (Legros & Kvikic, 1980) or χ -glycine (Kvikic *et al.*, 1980), with values of 0.022 (1), 0.002 (1) and 0.008 (1) Å, respectively.

As expected, the Cu coordination renders the C12/N1/C11/C1/C2 conjugated system planar (within 2.5σ). The six-membered Cu1/O1/C2/C1/C11/N1 chelate ring is, however, only approximately planar (within 7σ). The naphthalene rings are planar within 2.5σ , with an angle of 1.4 (3)° between them.

**Figure 1**

The structure of (I) with the atom-numbering scheme, with displacement ellipsoids drawn at the 50% probability level.

The chelate ring and the condensed naphthalene ring make an angle of $4.9 (2)^\circ$. The bonds and angles within the naphthalene moiety are in the ranges $1.348 (8)$ – $1.452 (7) \text{ \AA}$ and $117.5 (5)$ – $123.1 (5)^\circ$, respectively.

The formation of chains and the packing of the molecules results in close intermolecular $O4 \cdots C13^{ii}$ and $C5 \cdots C11^{iii}$ contacts [$3.029 (6)$ and $3.295 (8) \text{ \AA}$, respectively; symmetry codes: (ii) $x, -y, z - \frac{1}{2}$; (iii) $x, y, 1 + z$]. Both H atoms of the water molecule participate in hydrogen-bond formation (Table 2). The bond to O1 occurs within the polymeric chains (Fig. 1), but that to O4 occurs between chains, linking them into sheets parallel to $[010]$.

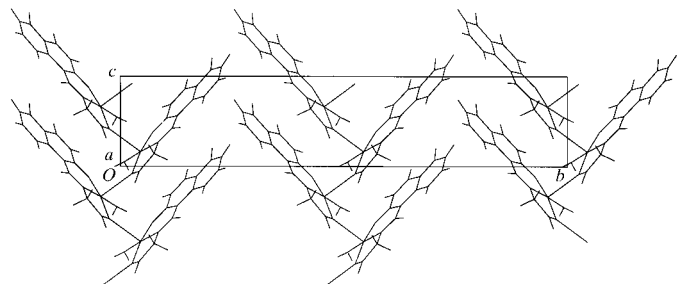


Figure 2
The polymeric association of (I).

Experimental

An ethanol solution (50 ml) of glycine (1 mmol, 0.07 g) and 2-hydroxy-1-naphthaldehyde (1 mmol, 0.17 g) was kept at 343 K in a reflux condenser for 30 min. An ethanol solution (50 ml) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1 mmol, 0.17 g) was then added, and the temperature readjusted to 343 K and kept constant for 30 min. The resulting dark-green solution was filtered and allowed to evaporate slowly.

Crystal data

$[\text{Cu}(\text{C}_{13}\text{H}_9\text{NO}_3)(\text{H}_2\text{O})]$
 $M_r = 308.78$
 Monoclinic, Cc
 $a = 7.043 (1) \text{ \AA}$
 $b = 28.741 (6) \text{ \AA}$
 $c = 5.940 (1) \text{ \AA}$
 $\beta = 103.06 (3)^\circ$
 $V = 1171.3 (4) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.751 \text{ Mg m}^{-3}$
 $D_m = 1.70 (2) \text{ Mg m}^{-3}$

D_m measured by measured by
 flotation in $\text{CH}_2\text{I}_2/\text{CCl}_4$
 Mo $K\alpha$ radiation
 Cell parameters from 15
 reflections
 $\theta = 10$ – 20°
 $\mu = 1.87 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Needle, dark green
 $0.4 \times 0.1 \times 0.1 \text{ mm}$

Data collection

Siemens P3 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.723$, $T_{\max} = 0.856$
 3771 measured reflections
 1735 independent reflections (plus
 150 Friedel-related reflections)
 1740 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$
 $\theta_{\text{max}} = 30.1^\circ$
 $h = -9 \rightarrow 9$
 $k = -40 \rightarrow 40$
 $l = -8 \rightarrow 8$
 2 standard reflections
 every 100 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.099$
 $S = 1.06$
 1885 reflections
 172 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 1.9P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.45 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.13 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983)
 Flack parameter = $-0.01 (2)$

Table 1
Selected geometric parameters (Å , $^\circ$).

Cu1—O1	1.909 (4)	Cu1—N1	1.905 (4)
Cu1—O2	1.951 (3)	Cu1—O2 ⁱ	2.551 (3)
Cu1—O3	1.944 (3)		
O1—Cu1—O2	171.62 (15)	O3—Cu1—N1	176.23 (16)
O1—Cu1—O3	86.99 (14)	O2 ⁱ —Cu1—O3	86.71 (13)
O1—Cu1—N1	91.77 (16)	O2 ⁱ —Cu1—N1	96.94 (14)
O1—Cu1—O2 ⁱ	94.53 (13)	Cu1—O1—C2	128.7 (3)
O2—Cu1—O3	94.80 (14)	Cu1—O2—C13	113.4 (3)
O2—Cu1—N1	85.92 (15)	Cu1—O2—Cu1 ⁱⁱ	120.24 (14)
O2—Cu1—O2 ⁱ	93.74 (12)	Cu1 ⁱⁱ —O2—C13	123.3 (3)

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

Table 2
Hydrogen-bonding geometry (Å , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O3-H2A \cdots O4^{iv}$	0.96	1.73	2.653 (5)	159
$O3-H2B \cdots O1^{ii}$	0.96	1.75	2.654 (5)	154
$O3-H2B \cdots O3^{ii}$	0.96	2.35	3.006 (5)	125

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

All H atoms were included at calculated positions and refined using a riding model [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}, \text{O})$; $\text{C}-\text{H} = 0.93$ – 0.97 \AA].

Data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: XDISK in SHELXTL/PC (Sheldrick, 1990); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1148). Services for accessing these data are described at the back of the journal.

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