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Aqua(2-methylpyridine-*N*)(*N*-salicylidene-glycinato-*O,N,O'*)copper(II)

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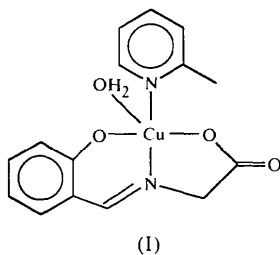
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Abstract

In the title compound, [Cu(C₉H₇NO₃)(C₆H₇N)(H₂O)], the copper(II) centre has a square-pyramidal environment with a tridentate *N*-salicylidene-glycinato Schiff base dianion and a 2-methylpyridine ligand coordinated in the basal plane. The apex of the pyramid is occupied by the O atom from the coordinated water molecule at a distance of 2.425 (3) Å. The monomeric units are associated through hydrogen bonds, forming infinite chains. There are two magnetically different copper(II) polyhedra.

Comment

Recently, we reported the monomeric structure of aqua(2-ethylpyridine)(*N*-salicylidene-glycinato)copper(II), (Warda, 1998). In this paper, we present the structure of the closely related compound aqua(2-methylpyridine)(*N*-salicylidene-glycinato)copper(II), (I), for which the averaged *g* tensor is significantly lowered compared with the 2-ethylpyridine compound.



The Cu^{II} ion has a square-pyramidal [4 + 1] coordination geometry, with the tridentate Schiff base *N*-salicylidene-glycinato dianion and the monodentate 2-methylpyridine ligand in the basal plane (Fig. 1). The apical position is occupied by a water O atom at an apical distance of 2.425 (3) Å. It is noteworthy that the coordination of water to Cu^{II} is invariably at an apical site of the tetragonally elongated square pyramids if a second neutral ligand is present. This seems to be a general result for five-coordinated Cu^{II} complexes (Warda, 1998, and references therein).

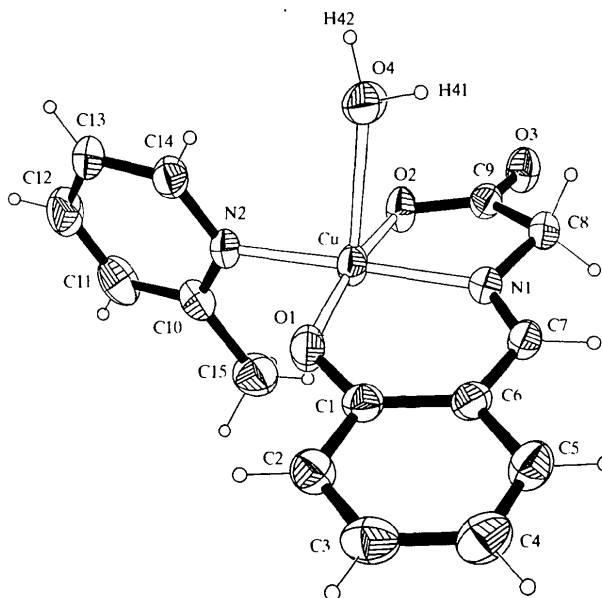


Fig. 1. The asymmetric unit of the title compound with the atomic numbering scheme. Ellipsoids are drawn at the 50% probability level.

The pyridine ring is inclined with respect to the basal plane (through O1, O2, N1 and N2) at an angle of 79.4 (2)° and the Cu atom lies 0.134 (1) Å out of this plane, displaced towards the O4 atom (PLATON; Spek, 1994). The Cu—N and Cu—O bond distances in the equatorial plane [Cu—N 1.933 (3) and 1.998 (3) Å; Cu—O 1.913 (3) and 1.981 (3) Å] do not differ significantly when compared to the 2-ethylpyridine compound.

The monomers are associated through hydrogen bonding, forming chains *via* O4—H41···O3 interactions that are connected by O4—H42···O2 hydrogen bonds to a second, inverted chain. These chains run parallel to [100]. The former hydrogen bond is much shorter [O4···O3 2.776 (4) and O4···O2 2.928 (4) Å]. These features are also found in the 2-ethylpyridine compound (Warda, 1998).

From electron paramagnetic resonance single-crystal and powder spectra, the ordering is ferrodistorptive and there is no evidence for a tilting angle. The *g* tensor is significantly lowered in comparison with that of the 2-ethylpyridine compound. This detected weakening of the apical ligand on going from a 2-ethyl- to a 2-methylpyridine equatorial ligand is in accord with the apical distances [2.388 (3) Å for the 2-ethyl- and 2.425 (3) Å for the 2-methylpyridine compound].

The copper(II) polyhedra are arranged in two magnetically inequivalent orientations ($x, \frac{1}{2} - y, -\frac{1}{2} + z$) with a Cu···Cu distance of 6.8957 (9) Å and 2γ of 14.4 (2)° so that the *g* tensor is slightly affected by this value, indicating a distorted ferrodistorptive ordering ($0 < 2\gamma <$

45°). Furthermore, the molecular axes are not exactly parallel to each other; an angle 2ξ of 4.0(1)° is subtended between two O1—Cu—O2 axes. (2γ is the angle describing the orientation of the main axes of the polyhedra with respect to one another and should therefore be carefully distinguished from the cell parameter with the same symbol.) It should be noted that the g tensor appears to be molecular if there is a small 2γ and/or 2ξ angle between differently oriented paramagnetic centres within the coupling range.

Experimental

The title compound was synthesized from aqua(*N*-salicylidene-glycinato)copper(II) hemihydrate according to the methods of Ueki *et al.* (1967) and Warda (1994) with 2-methylpyridine in a 1:3 ethanol–water mixture at 333 K. Dark-green prismatic crystals grew within a few days.

Crystal data

| | |
|--|---|
| [Cu(C ₉ H ₇ NO ₃)(C ₆ H ₇ N)- (H ₂ O)] | Cu K α radiation |
| $M_r = 351.84$ | $\lambda = 1.54178 \text{ \AA}$ |
| Monoclinic | Cell parameters from 25 reflections |
| $P2_1/c$ | $\theta = 20.5\text{--}45.8^\circ$ |
| $a = 13.6203(8) \text{ \AA}$ | $\mu = 2.279 \text{ mm}^{-1}$ |
| $b = 10.8747(4) \text{ \AA}$ | $T = 293(2) \text{ K}$ |
| $c = 9.9647(3) \text{ \AA}$ | Prism |
| $\beta = 93.774(4)^\circ$ | $0.24 \times 0.20 \times 0.10 \text{ mm}$ |
| $V = 1472.74(11) \text{ \AA}^3$ | Dark green |
| $Z = 4$ | |
| $D_x = 1.587 \text{ Mg m}^{-3}$ | |
| D_m not measured | |

Data collection

| | |
|--|---|
| Enraf–Nonius CAD-4 diffractometer | 1879 reflections with $I > 2\sigma(I)$ |
| ω – 2θ scans | $R_{\text{int}} = 0.027$ |
| Absorption correction: empirical with ψ scans (<i>XPREP</i> in <i>SHELXTL</i> ; Siemens, 1996b) | $\theta_{\text{max}} = 68.92^\circ$ $h = -16 \rightarrow 16$ $k = 0 \rightarrow 13$ $l = 0 \rightarrow 12$ |
| $T_{\text{min}} = 0.611$, $T_{\text{max}} = 0.804$ | 2 standard reflections |
| 2896 measured reflections | frequency: 120 min |
| 2724 independent reflections | intensity decay: none |

Refinement

| | |
|--|---|
| Refinement on F^2 | $\Delta\rho_{\text{max}} = 0.310 \text{ e \AA}^{-3}$ |
| $R[F^2 > 2\sigma(F^2)] = 0.047$ | $\Delta\rho_{\text{min}} = -0.334 \text{ e \AA}^{-3}$ |
| $wR(F^2) = 0.112$ | Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997a) |
| $S = 1.017$ | Extinction coefficient: 0.00123(17) |
| 2724 reflections | Scattering factors from <i>International Tables for</i> <i>Crystallography</i> (Vol. C) |
| 207 parameters | |
| H atoms: see below | |
| $w = 1/[\sigma^2(F_o^2) + (0.0470P)^2$ $+ 0.5773P]$ | |
| where $P = (F_o^2 + 2F_c^2)/3$ | |
| $(\Delta/\sigma)_{\text{max}} < 0.001$ | |

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

| | | | |
|----------|------------|----------|------------|
| Cu—O1 | 1.913(3) | Cu—N2 | 1.998(3) |
| Cu—N1 | 1.933(3) | Cu—O4 | 2.425(3) |
| Cu—O2 | 1.981(3) | | |
| O1—Cu—N1 | 93.28(12) | O2—Cu—N2 | 90.21(12) |
| O1—Cu—O2 | 169.11(12) | O1—Cu—O4 | 101.58(12) |
| N1—Cu—O2 | 83.58(12) | N1—Cu—O4 | 88.07(11) |
| O1—Cu—N2 | 91.97(12) | O2—Cu—O4 | 88.76(12) |
| N1—Cu—N2 | 172.24(13) | N2—Cu—O4 | 96.47(12) |

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

| D—H...A | D—H | H...A | D...A | D—H...A |
|---------------------------|---------|---------|----------|---------|
| O4—H41...O3 ⁱ | 0.89(4) | 1.88(4) | 2.776(4) | 175(4) |
| O4—H42...O2 ⁱⁱ | 0.89(4) | 2.04(4) | 2.928(4) | 175(4) |

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

All H atoms except the water H atoms were included at calculated positions using *SHELXL97* (Sheldrick, 1997a) and refined using a riding model. The U_{iso} values for H atoms of CH and CH₂/CH₃ groups were taken as 1.2 U_{eq} or 1.5 U_{eq} of the carrier atoms, respectively. The methyl group of the pyridine ligand was refined as a rigid group. The H41 and H42 atoms were found from difference Fourier syntheses and refined with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the water O atom. O—H distances were restrained to be equal.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *XCAD4* (Harms, 1997). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997b). Program(s) used to refine structure: *SHELXL97*. Molecular graphics: *XP* in *SHELXTL* (Siemens, 1996a). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1310). Services for accessing these data are described at the back of the journal.

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