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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1139). Services for accessing these data are described at the back of the journal.

References

Bino, A. & Cotton, F. A. (1979). *Inorg. Chem.* **18**, 2710–2713.

Blake, A. J., Parsons, S., Downs, A. J. & Limberg, C. (1995). *Acta Cryst.* C**51**, 571–573.

Enraf-Nonius (1994). *CAD*-4 *EXPRESS*. Version 5.1/1.2. Enraf-Nonius, Delft, The Netherlands.

Garner, C. D., Hill, L. H., Mabbs, F. E., McFadden, D. L. & McPhail, A. T. (1977). *J. Chem. Soc. Dalton Trans.* pp. 853–858.

Gordon, J. C., Mattamana, S. P., Poli, R. & Fanwick, P. E. (1995). *Polyhedron*, **14**, 1339–1342.

Harms, K. (1997). *XCAD*-4. *Program for the Reduction of CAD*-4 *Diffractometer Data*. University of Marburg, Germany.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Schumaker, C., Weller, F. & Dehnicke, K. (1982). *Z. Anorg. Allg. Chem.* **495**, 135–147.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Siemens (1994). *SHELXTL*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1998). C**54**, 187–189

Aqua(2,3-dimethylpyridine-*N*)(*N*-salicylideneglycinato-*O*,*N*,*O*′)copper(II)

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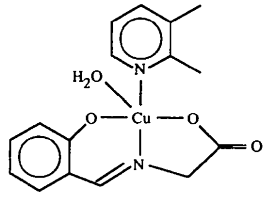
Abstract

In the title compound, $[Cu(C_9H_7NO_3)(C_7H_9N)(H_2O)]$, the Cu^{II} centre has a square-pyramidal environment with a tridentate *N*-salicylideneglycinato Schiff base dianion and a 2,3-dimethylpyridine ligand coordinated in the basal plane. The apex of the pyramid is occupied by the O atom of the coordinated water molecule at a distance of 2.384 (3) Å. The monomers are associated through hydrogen bonds, forming infinite chains. The copper(II) polyhedra are arranged in a single magnetic orientation.

Comment

Copper(II) complexes with tridentate Schiff base dianions of the *N*-salicylideneamino-carboxylato type (TSB^{2-}) represent relatively simple models for the study of cooperative bonding effects, which can be investigated by electron paramagnetic resonance (EPR) spectroscopy. In these complexes, which are of the general type $[Cu(TSB)(L)]_n$ (Warda, 1994), three donor atoms (O, N and O) of the Schiff base and a fourth donor atom from the neutral ligand *L* (N, O or S) normally define the base of a square pyramid. For isolated (monomeric) structures, the copper coordination geometry can be square planar or square pyramidal when a neutral donor ligand is located at the apical site (n = 1) (Ueki *et al.*, 1969). If a phenolic O atom from an adjacent molecule is apically coordinated, dimeric structures are formed (n = 2) (Warda, 1994). A tetrameric structure (n = 4) is found in the case of (4-ethylpyridine)(*N*-salicylideneglycinato)copper(II) (Warda, 1997*a*). Polymeric structures ($n = \infty$) are generally achieved when the apical position is occupied by a carboxylic O atom from an adjacent molecule, thus forming infinite zigzag chains (Ueki *et al.*, 1967), or when a bidentate ligand connects the apical sites to form one-dimensional chains (Warda, 1994). In this communication, a complex, (I), with n = 1, but with chain character arising from hydrogen bonding, is reported.



(I)

The Cu^{II} ion has square-pyramidal [4+1] coordination geometry, with the tridentate Schiff base *N*-salicylideneglycinato dianion and the monodentate 2,3-dimethylpyridine ligand in the basal plane. The apical position is occupied by a water O atom at a distance of 2.384 (3) Å. The pyridine ring is inclined with respect to the basal plane (through O1, O2, N1 and N2) at an angle of 70.0 (1)° and the Cu atom lies 0.155 (1) Å out of this plane, displaced towards the O4 atom (*PLATON*; Spek, 1997).

The monomers are associated through hydrogen bonding, forming chains *via* O4—H41···O3 interactions that are connected by O4—H42···O3 hydrogen bonds to a second, inverted chain. These chains run parallel to the crystallographic *x* axis (Fig. 2).

In the case of the polymeric structure of (3,5-dimethylpyridine)(*N*-salicylidenegylcinato)copper(II) reported recently (Warda, 1997*b*), the apical distance is 2.386 (2) Å to a carboxylic O atom of an adjacent molecule. In that structure, the copper(II) polyhedra are tilted with an angle 2γ of 85° (2γ is the angle describing the orientation of the main axes of the polyhedra with respect to one another and should therefore

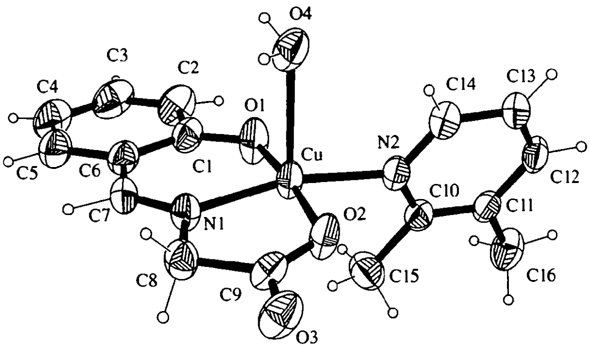


Fig. 1. The asymmetric unit of the title compound with the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level.

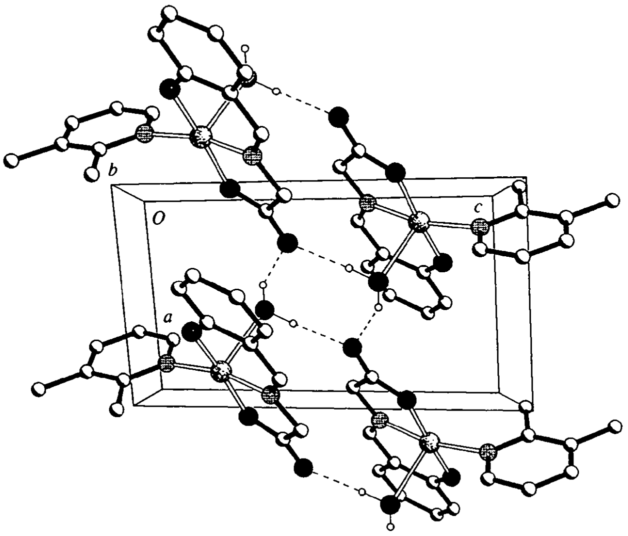


Fig. 2. Projection of the title compound onto the *xy* plane showing the hydrogen bonding; other H atoms have been omitted for clarity.

be carefully distinguished from the cell parameter with the same label). In the title compound, all the copper(II) polyhedra are oriented parallel ($2\gamma = 0°$) so that the **g** tensor is not coupled.

Experimental

The title compound was synthesised from aqua(*N*-salicylideneglycinato)copper(II) hemihydrate with 2,3-dimethylpyridine (Ueki *et al.*, 1967; Warda, 1994).

Crystal data

$[Cu(C_9H_7NO_3)(C_7H_9N)(H_2O)]$
$M_r = 365.86$
Triclinic
$P\bar{1}$
$a = 6.9449\ (7)$ Å
$b = 10.3618\ (13)$ Å
$c = 11.9715\ (14)$ Å
$\alpha = 75.392\ (11)°$
$\beta = 88.293\ (10)°$
$\gamma = 70.621\ (9)°$
$V = 785.04\ (15)$ Å^3
$Z = 2$
$D_x = 1.548$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 22.76–45.28°$
$\mu = 2.161$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.30 × 0.11 × 0.04 mm
Dark green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (Siemens, 1996*a*)
$T_{min} = 0.563$, $T_{max} = 0.926$
3185 measured reflections
2926 independent reflections
2442 reflections with $I > 2\sigma(I)$

$R_{int} = 0.052$
$\theta_{max} = 68.95°$
$h = -8 \rightarrow 0$
$k = -12 \rightarrow 11$
$l = -14 \rightarrow 14$
2 standard reflections frequency: 120 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.140$
$S = 1.039$
2926 reflections
216 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0957P)^2 + 0.1629P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.551$ e Å^{-3}
$\Delta\rho_{min} = -0.833$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu—O1	1.912 (2)	Cu—N2	2.004 (3)
Cu—N1	1.948 (3)	Cu—O4	2.384 (3)
Cu—O2	1.956 (2)		
O1—Cu—N1	93.21 (11)	O2—Cu—N2	91.20 (10)
O1—Cu—O2	173.17 (11)	O1—Cu—O4	94.13 (11)
N1—Cu—O2	83.09 (10)	N1—Cu—O4	97.04 (10)
O1—Cu—N2	91.23 (10)	O2—Cu—O4	92.03 (10)
N1—Cu—N2	166.99 (11)	N2—Cu—O4	94.83 (10)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H41···O3^i	0.89 (1)	1.96 (1)	2.825 (4)	162 (1)
O4—H42···O3^{ii}	0.89 (1)	1.90 (1)	2.773 (4)	164 (1)

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

The H atoms of the two methyl groups and of the C8 atom were included at calculated positions and refined using a riding model. All other H atoms were found from the difference-Fourier syntheses. Water H atoms were refined using O—H distance restraints. For CH, CH_2 and OH_2 groups, $U_{iso}(H) = 1.2U_{eq}$(carrier atom); for methyl groups, $U_{iso}(H) = 1.5U_{eq}$(carrier atom). The residual electron density of 0.551 e Å^{-3} and the deepest hole of −0.833 e Å^{-3} are close to the Cu atom, at distances of 1.11 and 0.92 Å, respectively.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *XCAD*-4 (Harms, 1997). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure:

*SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL* (Siemens, 1996*b*). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1244). Services for accessing these data are described at the back of the journal.

References

Enraf–Nonius (1994). *CAD-4 EXPRESS*. Version 5.1. Enraf–Nonius, Delft, The Netherlands.
Harms, K. (1997). *XCAD-4. Program for the Reduction of CAD-4 Diffractometer Data*. University of Marburg, Germany.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. Release 97-1. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1996*a*). *XPREP* in *SHELXTL*. *Program for Data Preparation and Reciprocal Space Exploration*. Version 5.05. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996*b*). *XP* in *SHELXTL*. *Molecular Graphics Program*. Version 5.06. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (1997). *PLATON. Molecular Geometry Program*. University of Utrecht, The Netherlands.
Ueki, T., Ashida, T., Sasada, Y. & Kakudo, M. (1967). *Acta Cryst.* **22**, 870–878.
Ueki, T., Ashida, T., Sasada, Y. & Kakudo, M. (1969). *Acta Cryst.* B**25**, 328–336.
Warda, S. A. (1994). *Bioanorganische Kupfer(II) Komplexe mit dreizähnigen O,N,O Chelat-Dianionen und additiven einzähnigen Donorliganden*. Aachen: Verlag Shaker.
Warda, S. A. (1997*a*). *Acta Cryst.* C**53**, 697–699.
Warda, S. A. (1997*b*). *Acta Cryst.* C**53**, 1010–1011.

Acta Cryst. (1998). C**54**, 189–191

catena-Poly[[(*N*-salicylideneglycinato-*N*,*O*,*O'*)copper(II)-μ-pyrazine-*N*:*N'*-(*N*-salicylideneglycinato-*N*,*O*,*O'*)copper(II)]-μ-1,4-dioxane-*O*:*O'*]

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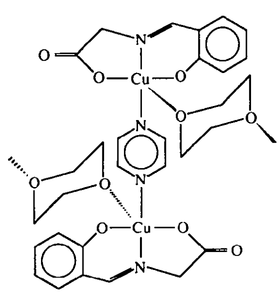
Abstract

In the title compound, $[Cu_2(C_9H_7NO_3)_2(C_4H_4N_2)(C_4H_8O_2)]$, each Cu^{II} ion has a square-pyramidal coordination environment with a tridentate *N*-salicylideneglycinato Schiff base dianion and a pyrazine ligand bound in the basal plane. The pyrazine ligand acts as a bifunctional ligand, joining two Schiff base complexes to form a binuclear unit. The apex of the pyramid is occupied by a dioxane O atom at an apical distance of 2.510 (2) Å. The binuclear units are associated into chains parallel to the *x* axis through dioxane bridges.

Comment

Recently, a series of copper(II) complexes with tridentate Schiff base (TSB^{2-}) and monodentate neutral ligands were reported (Warda, 1997); these complexes are suitable for studying the electron paramagnetic resonance (EPR) signal behaviour with respect to the local geometry and cooperative bonding effects. In this communication, a further structure, (I), with dioxane bridges between Cu–TSB moieties, is reported.



(I)

In compound (I), the Cu^{II} atom has square-pyramidal geometry; the basal sites are occupied by the *O*,*N*,*O'* donor set of the *N*-salicylideneglycinato dianion and an N atom of the pyrazine ligand. The pyrazine lies on an inversion centre and acts as a bifunctional ligand, connecting two Cu–TSB molecules to form a binuclear copper(II) unit. The dioxane rings lie on inversion centres and are apically coordinated *via* both donor sites at a distance (Cu—O4) of 2.510 (2) Å; thus, a chain structure is formed parallel to the crystallographic *x* axis (Fig. 2). The Cu^{II} atoms are slightly shifted [by 0.029 (1) Å] from the base of the pyramid (mean plane of N1, O1, N2 and O2); the pyrazine ligand forms an interplanar angle of 16.6 (3)° with the basal plane. Between the chains, the copper(II) polyhedra are tilted with respect to each other by an angle of 25.6 (2)°; the $Cu\cdots Cu(1-x,\ 1-y,\ -z)$ distance between two differently oriented polyhedra is 7.475 (1) Å (*PLATON*; Spek, 1994).

EPR patterns of the title compound display a coupled g tensor, indicating a distorted ferrodistortive ordering ($45° > 2\gamma > 0$); the tilting angle calculated from the EPR powder spectrum is 25° (2γ is the angle describing the orientation of the main axes of the polyhedra with

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