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

Ni—O1	1.8369 (15)	O2—C5	1.426 (3)
Ni—N1	1.853 (2)	N1—C3	1.300 (3)
Ni—N3	1.864 (2)	N1—N2	1.398 (2)
Ni—P	2.1829 (6)	N2—C1	1.316 (3)
S—C1	1.767 (2)	N3—C1	1.345 (3)
S—C2	1.783 (3)	N3—C4	1.451 (3)
P—C25	1.815 (2)	C3—C12	1.430 (3)
P—C19	1.816 (2)	C4—C18	1.510 (3)
P—C13	1.821 (2)	C5—C6	1.493 (4)
O1—C7	1.320 (3)	C7—C12	1.404 (3)
O2—C4	1.417 (3)		
O1—Ni—N1	95.52 (7)	N2—N1—Ni	117.03 (13)
O1—Ni—N3	176.60 (8)	C1—N2—N1	107.3 (2)
N1—Ni—N3	82.55 (8)	C1—N3—C4	120.6 (2)
O1—Ni—P	88.68 (6)	C1—N3—Ni	111.08 (13)
N1—Ni—P	173.05 (5)	C4—N3—Ni	127.87 (14)
N3—Ni—P	93.52 (6)	N2—C1—N3	122.0 (2)
C1—S—C2	101.69 (12)	N2—C1—S	117.0 (2)
C25—P—C19	105.07 (10)	N3—C1—S	121.0 (2)
C25—P—C13	106.81 (10)	N1—C3—C12	123.8 (2)
C19—P—C13	104.18 (9)	O2—C4—N3	113.2 (2)
C25—P—Ni	117.57 (8)	O2—C4—C18	104.9 (2)
C19—P—Ni	113.07 (7)	N3—C4—C18	113.1 (2)
C13—P—Ni	109.15 (7)	O2—C5—C6	108.4 (2)
C7—O1—Ni	126.49 (15)	O1—C7—C12	124.6 (2)
C4—O2—C5	114.2 (2)	O1—C7—C8	117.6 (2)
C3—N1—N2	115.9 (2)	C7—C12—C3	122.4 (2)
C3—N1—Ni	127.1 (2)	C18—C13—P	118.7 (2)
N3—Ni—P—C13	−31.11 (8)	Ni—P—C13—C18	39.4 (2)
P—Ni—N3—C4	−12.7 (2)	P—C13—C18—C4	3.3 (3)
Ni—N3—C4—C18	59.0 (2)	N3—C4—C18—C13	−55.1 (3)

The data collection nominally covered over a full hemisphere of reciprocal space by a combination of six sets of exposures with the area detector held at two 2θ swing angles (25 and 53°). The reciprocal space was scanned by 0.1° ω steps at a different φ for each set of exposures. The detector was placed at a distance of 5.02 cm from the crystal. Crystal decay was monitored by repeating the initial 70 frames at the end of data collection and analysing the duplicate reflections (*SADABS*; Sheldrick, 1996). No decay was observed. The structure was solved by Patterson and difference Fourier methods and refined by full-matrix least-squares methods. All H atoms were found in the difference Fourier map, but they were placed at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the parent atom.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SDP* (Frenz, 1982). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEX*3 (McArdle, 1994). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1226). Services for accessing these data are described at the back of the journal.

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Aqua(2,4-dimethylpyridine-*N*)(*N*-salicylideneglycinato-*O*,*N*,*O*′)copper(II)

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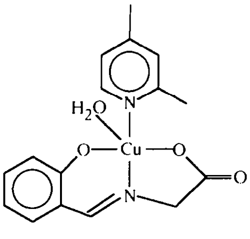
Abstract

The Cu^{II} atom of the title complex, [$Cu(C_9H_7NO_3)(C_7H_9N)(H_2O)$], has a square-pyramidal coordination sphere with a tridentate *N*-salicylideneglycinato Schiff base dianion and a 2,4-dimethylpyridine ligand bound in the basal plane. The apex of the pyramid is occupied by an O atom from the coordinated water molecule at an apical distance of 2.416 (2) Å. The monomeric moieties in the crystal are stabilized through hydro-

gen bonding, building a two-dimensional network. The copper(II) polyhedra are arranged in two magnetically inequivalent orientations, leading to a slightly distorted ferrodistortive coupled *g* tensor.

Comment

Copper(II) complexes with tridentate Schiff base dianions of the *N*-salicylideneaminoacidato type (TSB^{2-}) represent a relatively simple model for studies 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 can be square planar, or square pyramidal when a neutral donor ligand is located in the apical site ($n = 1$; Ueki *et al.*, 1969; Warda *et al.*, 1996). 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, resulting in infinite zigzag chains (Ueki *et al.*, 1967; Warda *et al.*, 1997). If a phenolic O atom from a neighbouring molecule is apically coordinated, dimeric structures are formed ($n = 2$; Warda, 1994). In this communication, we report a case of $n = 1$ with chain character, namely the title complex, (I).



(I)

The molecule is characterized by square-pyramidal Cu^{II} coordination with the tridentate Schiff base *N*-salicylideneglycinato dianion and a monodentate ligand in the basal plane (2,4-dimethylpyridine). The involvement of the water O atom at the apical site, with a Cu—O4 distance of 2.416 (2) Å, leads to a monomeric structure (Fig. 1). This distance is longer than the corresponding bond of 2.352 (7) Å found in aqua(*N*-salicylideneglycinato)copper(II) tetrahydrate (Ueki *et al.*, 1969). In the case of the polymeric structure of (3,5-dimethylpyridine)(*N*-salicylidenegylcinato)copper(II), the apical distance is 2.386 (2) Å, involving a carboxylic O atom from an adjacent complex molecule (Warda, 1997*b*).

In the title compound, H atoms of the apically coordinated water molecule build a two-dimensional network by participating in hydrogen bonds: O4—H42···O3(x, $\frac{1}{2} - y$, $\frac{1}{2} + z$) and O4—H41···O2($-x$, $-y$, $-z$).

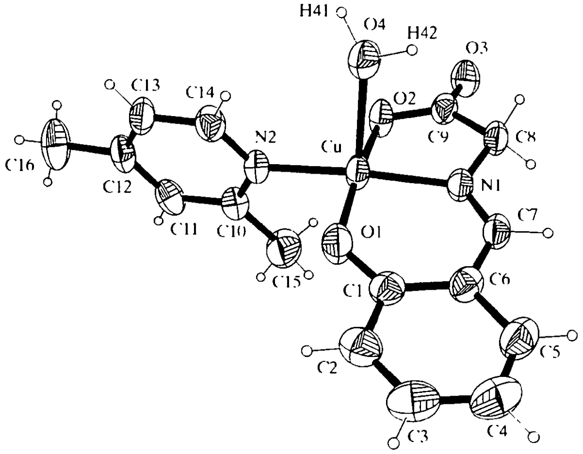


Fig. 1. The asymmetric unit of the title compound with the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level.

It has been found (Warda, 1994, and unpublished results) that EPR patterns display a weak coupled *g* tensor (non-molecular), indicating a distorted ferrodistortive ($45° > 2\gamma > 0°$) ordering with a small tilting angle of $2\gamma = 11°$, when the distance between the differently oriented paramagnetic centres is shorter than the critical distance of 8.3 Å (EPR results); these features are found in the title compound, with a tilting angle of 10.0 (1)° and a shortest Cu···Cu spacing between two magnetically inequivalent Cu^{II} orientations of 6.9667 (7) Å (symmetry relationship: x, $\frac{1}{2} - y$, $\frac{1}{2} + z$).

In conclusion, there are two magnetic orientations to be observed, which is consistent with the space group, $P2_1/c$, and a single molecule in the asymmetric unit. The EPR results are in good agreement with the structural results. At this stage in the documentation of EPR data for a systematic study of the *g* tensor and for cooperative ordering investigations, the X-ray crystal structure determinations are indispensable for the verification of spectroscopic results.

Experimental

The title compound was synthesized from aqua(*N*-salicylideneglycinato)copper(II) hemihydrate with 2,4-dimethylpyridine in analogy to procedures described by Ueki *et al.* (1967) and Warda (1994).

Crystal data

$[Cu(C_9H_7NO_3)(C_7H_9N)(H_2O)]$
$M_r = 365.86$
Monoclinic
$P2_1/c$

Mo *K*α radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 18.999–22.076°$

$a = 13.0786\,(8)$ Å
$b = 12.1740\,(7)$ Å
$c = 9.9027\,(9)$ Å
$\beta = 94.354\,(8)°$
$V = 1572.1\,(2)$ Å^3
$Z = 4$
$D_x = 1.546$ Mg m^{-3}
D_m not measured

$\mu = 1.411$ mm^{-1}
$T = 293\,(2)$ K
Plate
0.540 × 0.132 × 0.036 mm
Dark green

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scans (Siemens, 1996*b*)
$T_{min} = 0.516$, $T_{max} = 0.951$
3736 measured reflections
3428 independent reflections
2787 reflections with $I > 2\sigma(I)$

$R_{int} = 0.021$
$\theta_{max} = 27°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 15$
$l = -12 \rightarrow 12$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.101$
$S = 1.075$
3428 reflections
210 parameters
H-atom parameters constrained (see below)

$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 0.6515P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.419$ e Å^{-3}
$\Delta\rho_{min} = -0.805$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu—O1	1.9189 (19)	Cu—O2	1.9942 (18)
Cu—N1	1.9229 (19)	Cu—O4	2.416 (2)
Cu—N2	1.992 (2)		
O1—Cu—N1	93.66 (8)	N2—Cu—O2	90.73 (7)
O1—Cu—N2	90.53 (8)	O1—Cu—O4	98.99 (8)
N1—Cu—N2	169.31 (9)	N1—Cu—O4	90.66 (8)
O1—Cu—O2	170.16 (8)	N2—Cu—O4	98.40 (7)
N1—Cu—O2	83.50 (8)	O2—Cu—O4	90.47 (8)

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H41···O2^{i}	0.83	2.12	2.936 (3)	167
O4—H42···O3^{ii}	0.88	2.01	2.856 (3)	159

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

The methyl group H atoms were included at calculated positions and refined as rigid groups. All other H atoms were found from difference Fourier syntheses and refined using a riding model.

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*a*). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1096). Services for accessing these data are described at the back of the journal.

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Bis(guanidinium) (Hydrogen triethylenetetraminehexaacetato)bismuthate(III) Tetrahydrate†

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Abstract

The Bi atom in the title compound, $(CH_6N_3)_2[Bi(C_{18}H_{25}N_4O_{12})].4H_2O$, is nine-coordinated through four N and five O atoms of the ttha ligand, where ttha denotes triethylenetetraminehexaacetate. The non-coordinated COOH group is involved in a strong hydrogen bond with an O atom of a neighbouring complex, thereby forming dimeric units.

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† Alternative name: bis(guanidinium) [hydrogen 3,6,9,12-tetrakis(carboxylatomethyl-κO)-3,6,9,12-tetraaza-$\kappa^4 N$-tetradecanedioate-κO^1]bismuth(III) tetrahydrate.