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(Imidazole-N^3)(N-salicylidene-α-amino-isobutyrato-O,N,O')copper(II) Dimer†

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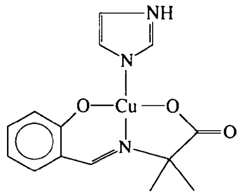
Abstract

The title compound, $[Cu(C_{11}H_{11}NO_3)(C_3H_4N_2)]$, adopts a square-pyramidal Cu^{II} coordination with the tridentate N-salicylidene-α-aminoisobutyrato Schiff base dianion and the imidazole ligand bound in the basal plane. The apex of the pyramid is occupied by a phenolic O atom from the neighbouring chelate at an apical distance of 2.623 (2) Å, building a dimeric structural unit in which the copper(II) ions are magnetically equivalent. The dimeric moieties in the crystal packing are tilted with respect to each other leading to a distorted antiferrodistortive ordering.

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 at the apical site (n = 1; Ueki, Ashida, Sasada & Kakudo, 1969; Warda, Friebel, Sivý, Plesch & Švajlenová, 1996); n = 4 is found in the case of (4-ethylpyridine)(N-salicylideneglycinato)copper(II) (Warda, 1997). Polymeric structures ($n = \infty$) are generally achieved when the apical position is occupied by a carboxylic O atom from an adjacent molecule to make infinite zigzag chains (Warda, Friebel, Sivý, Plesch & Bláhová, 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 on such a case.



(I)

The molecule is characterized by a square-pyramidal Cu^{II} coordination with the tridentate Schiff base N-salicylidene-α-aminoisobutyrato dianion and a monodentate ligand in the basal plane (imidazole). The involvement of the phenolic O atom of a neighbouring molecule at the apical site, with a Cu—O1^i distance of 2.623 (2) Å, leads to a dimeric structure [symmetry code: (i) $2-x$, $1-y$, $-z$]. This distance is comparable with the corresponding bond [2.591 (3) Å] in (imidazole)[N-salicylidene-(R,S)-alaninato]copper(II) (Warda, 1994).

The dimers of the title compound are linked by N3—H31···O3 hydrogen bonds to form a ribbon structure parallel to the x axis (Fig. 2).

It has been found (Warda, 1994) that EPR patterns display a coupled g tensor (non-molecular), indicating a distorted antiferrodistortive ($90 > 2\gamma > 45°$) ordering, with a tilting angle of $2\gamma = 66°$ (EPR result), when the distance between the differently oriented paramagnetic centres is shorter than the critical distance of 8.3 Å; these features are found in the title compound, with a

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† Alternative name: bis-μ-[2-(2-hydroxybenzylideneamino)-2-methylpropionato-O,N,O':O]-bis[(imidazole-N^3)copper(II)].

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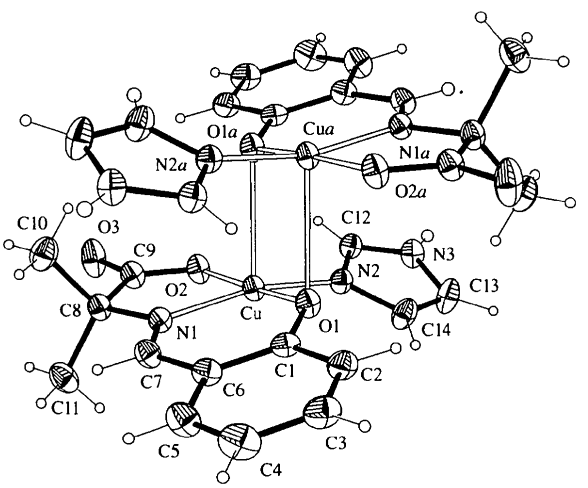

Fig. 1. The title compound in the crystal showing the dimeric unit with the atom-numbering scheme. Ellipsoids are drawn at the 40% probability level. Symmetry code: (*a*) $2-x$, $1-y$, $-z$.

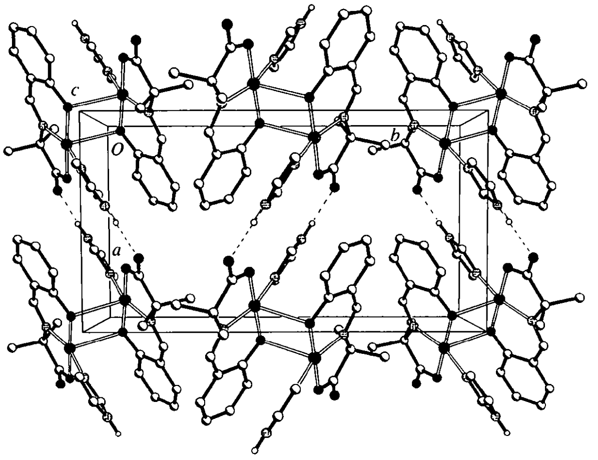

Fig. 2. Projection of the title compound showing the tilting angle (see text) and hydrogen bonding between the dimeric units. Radii are arbitrary; H atoms (except imidazole H) have been omitted for clarity.

tilting angle of 66.7 (2) Å and a Cu···Cu($1-x$, $1-y$, $-z$) spacing of 7.4460 (6) Å.

In conclusion, there are two magnetic orientations to be observed, which are consistent with the space group, $P2_1/c$, and the presence of 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*-salicylidene-α-aminoisobutyrato)copper(II) and imidazole according to Fujimaki, Oonishi, Muto & Nakahara (1971) and Warda (1994).

Crystal data

$[\mathrm{Cu}(\mathrm{C}_{11}\mathrm{H}_{11}\mathrm{NO}_3)(\mathrm{C}_3\mathrm{H}_4\mathrm{N}_2)]$
$M_r = 336.83$
Monoclinic
$P2_1/c$
$a = 9.1844\,(4)$ Å
$b = 16.9279\,(7)$ Å
$c = 9.3097\,(4)$ Å
$\beta = 94.489\,(6)^\circ$
$V = 1442.96\,(11)$ Å^3
$Z = 4$
$D_x = 1.550$ Mg m^{-3}
D_m not measured

Cu *Kα* radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 40.48–46.68^\circ$
$\mu = 2.265$ mm^{-1}
$T = 293\,(2)$ K
Needle
0.33 × 0.09 × 0.06 mm
Violet

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: empirical, ψ scans (*XPREP*; Siemens, 1996*a*)
$T_{\min} = 0.476$, $T_{\max} = 0.846$
2286 measured reflections
2140 independent reflections

2064 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.039$
$\theta_{\max} = 59.95^\circ$
$h = -10 \rightarrow 0$
$k = 0 \rightarrow 19$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.093$
$S = 1.087$
2140 reflections
191 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 1.3387P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.361$ e Å^{-3}
$\Delta\rho_{\min} = -0.359$ e Å^{-3}
Extinction correction: *SHELXL*96
Extinction coefficient: 0.0025 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu—O1	1.9127 (18)	Cu—N2	1.962 (2)
Cu—N1	1.933 (2)	Cu—O1$^{\mathrm{i}}$	2.623 (2)
Cu—O2	1.9434 (18)		
O1—Cu—N1	93.69 (8)	O2—Cu—N2	92.48 (8)
O1—Cu—O2	175.40 (8)	O1—Cu—O1$^{\mathrm{i}}$	86.89 (7)
N1—Cu—O2	83.83 (8)	N1—Cu—O1$^{\mathrm{i}}$	101.31 (8)
O1—Cu—N2	90.90 (8)	O2—Cu—O1$^{\mathrm{i}}$	89.78 (7)
N1—Cu—N2	164.74 (9)	N2—Cu—O1$^{\mathrm{i}}$	93.46 (8)

Symmetry code: (i) $2-x$, $1-y$, $-z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H31···O3$^{\mathrm{i}}$	0.86	1.85	2.707 (3)	178

Symmetry code: (i) $1+x$, $1+y$, z.

Data collection: *CAD*-4 *Express* (Enraf–Nonius, 1992). Cell refinement: *CAD*-4 *Express*. Data reduction: *XCAD*-4 (Harms, 1997). Program(s) used to solve structure: *SHELXS*96 (Sheldrick, 1996*a*). Program(s) used to refine structure:

*SHELXL*96 (Sheldrick, 1996*b*). Molecular graphics: *XP* (Siemens, 1996*b*). Software used to prepare material for publication: *SHELXL*96.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1216). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1590–1593

The Chain Polymers (Imidazole)(*N*-salicylideneglycinato)copper(II) and (2-Ethylimidazole)(*N*-salicylideneglycinato)copper(II)

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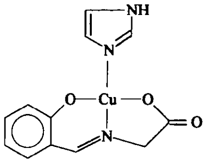
Abstract

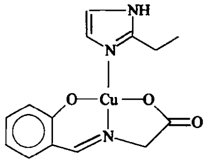
The title compounds, (imidazole-N^3)(N-salicylideneglycinato-O,N,O')copper(II), $[Cu(C_9H_7NO_3)(C_3H_4N_2)]$, (I), and (2-ethylimidazole-N^3)(N-salicylideneglycinato-O,N,O')copper(II), $[Cu(C_9H_7NO_3)(C_5H_8N_2)]$, (II), adopt square-pyramidal Cu^{II} coordination with the tridentate *N*-salicylideneglycinato Schiff base dianion and the imidazole ligand bound in the basal plane. In both structures, the apex of the distorted pyramid is occupied by a carboxylic O atom from the neighbouring chelate at an apical distance of 2.563 (2) and 2.683 (2) Å in (I) and (II), respectively, thus building infinite zigzag chains. According to the electron paramagnetic resonance patterns, in compound (I), the Cu^{II} complexes are arranged in two and in compound (II), in four, magnetically inequivalent orientations.

Comment

Copper(II) complexes with tridentate Schiff base dianions of the *N*-salicylideneaminoalkanoato 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 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 at the apical site (n = 1; Ueki, Ashida, Sasada & Kakudo, 1969; Warda, 1994; Warda, Friebel, Sivý, Plesch & Švajlenová, 1996). Polymeric structures ($n = \infty$) are achieved when the apical position is occupied by a carboxylic O atom from an adjacent molecule to form infinite chains (Ueki, Ashida, Sasada & Kakudo, 1967; Warda, Friebel, Sivý, Plesch & Bláhová, 1997). In this paper, we report on chain formation in the two different cases of compounds (I) and (II).



(I)



(II)

In both structures, the molecules are characterized by a square-pyramidal Cu^{II} coordination with the tridentate Schiff base *N*-salicylideneglycinato dianion and a monodentate ligand in the basal plane, *i.e.* imidazole in (I) and 2-ethylimidazole in (II). The apical Cu—O3^i distances 2.563 (2) [symmetry code: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$ in (I)] and 2.683 (2) Å [symmetry code: (i) $\frac{3}{2}-x, \frac{1}{2}+y, z$ in (II)], involving a carboxylic O atom of a neighbouring molecule, are elongated in comparison with the corresponding bond [2.334 (6) Å] in aqua(*N*-salicylideneglycinato)copper(II) hemihydrate (Ueki, Ashida, Sasada & Kakudo, 1967). In structure (I), the molecules are connected *via* Cu···O3 bonds leading to an infinite one-

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