O113—Zr1—Cl12	89.66 (9)	C114—O113—Zr1	129.1 (3)
O153—Zr1—Cl12	161.53 (8)	C112—O113—Zr1	116.6 (3)
Cl11—Zr1—Cl12	96.88 (4)	C152—C151—C15	109.7 (4)
O113—Zr1—Cl13	79.22 (8)	O153—C152—C151	108.9 (4)
O153—Zr1—Cl13	81.63 (8)	C154—O153—C152	108.6 (4)
Cl11—Zr1—Cl13	83.62 (4)	C154—O153—Zr1	124.2 (3)
Cl12—Zr1—Cl13	80.87 (5)	C152—O153—Zr1	121.8 (3)

H atoms were calculated and refined as riding atoms with $U_{\rm iso}$ = 1.2(or 1.5)$U_{\rm eq}$(host)

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *DIAMOND* (Brandenburg, 1996). 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: JZ1264). Services for accessing these data are described at the back of the journal.

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An Exact Quasi-Ferrodistortive Ordering in (*N*,*N*′-Di-*n*-butylthiourea-*S*)(*N*-salicylideneglycinato-*O*,*N*,*O*′)copper(II)

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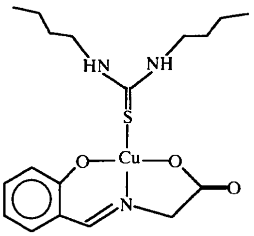
Abstract

The Cu^{II} atom in the title compound, [$Cu(C_9H_7NO_3)$-($C_9H_{20}N_2S$)], adopts distorted square-planar coordination, with a tridentate *N*-salicylideneglycinato Schiff base dianion and an *N*,*N*′-dibutylthiourea ligand bonded *via* its S atom. The molecules stack along [001] and are ordered quasi-ferrodistortively with two different magnetic orientations.

Comment

Owing to the diversity of the resulting structures, copper(II) complexes with tridentate Schiff base dianions of the *N*-salicylideneaminoacidato type (TSB^{2-}) represent suitable models for the elucidation of structural and spectroscopic correlations. We are interested in the behaviour of the EPR (electron paramagnetic resonance) signal of Jahn–Teller-distorted ions with respect to the local geometry and the dipolar interaction between differently oriented polyhedra or molecular axes. For an unambiguous interpretation of EPR results, X-ray structure determinations of a series of substances were undertaken, including that of the title compound, (I).



(I)

Recently, the monomeric structure of (pyrazine)(*N*-salicylidene-α-amino-2-methylpropanato)copper(II) was reported (Warda, 1997, and references therein), for which the quasi-ferrodistortive ordering and the coupled **g** tensor were discussed. The copper(II) layers are stacked parallel and the molecular axes are tilted with

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respect to each other at an angle of $2\xi = 60°$, so that the **g** tensors couple, reducing the orthorhombic splitting factor (2ξ describes the angle between differently oriented molecular axes). In this communication, a structure with $2\xi = 90°$ and its influence on the EPR signal are reported.

The copper(II) environment is approximately square planar with a distinct distortion from the planar configuration. The basal plane is occupied by the tridentate Schiff base *N*-salicylideneglycinato dianion (ONO^{2-} chelator) and the S atom of the neutral monodentate *N*,*N*′-di-*n*-butylthiourea, with a mean deviation of 0.27 (1) Å from the plane. The deviations of the two angles O1—Cu—O2 [162.1 (2)°] and N1—Cu—S [160.7 (1)°] from 180° indicate a significant shift of the planar geometry around copper towards tetrahedral coordination. Such distortions are known to minimize inter-ligand repulsion, which is pronounced because of the steric hindrance from the bulky substituents (Reinen & Atanasov, 1991).

Along the crystallographic [001] direction, there is a weak interaction between Cu and N1 of a symmetry-related molecule at a distance of 3.452 (4) Å ($1+y$, $1-x$, $\frac{1}{4}+z$), and between O1 and Cu at a distance of 3.538 (4) Å ($1+y$, $1-x$, $\frac{1}{4}+z$) (Fig. 2). Furthermore, the molecules are stabilized by hydrogen bonding: intermolecular through N3—H31···O3 (Table 2), to form infinite one-dimensional chains along [001], and intramolecular, forming a six-membered ring defined by atoms N2, H21, O1, Cu, S and C10 (Fig. 1).

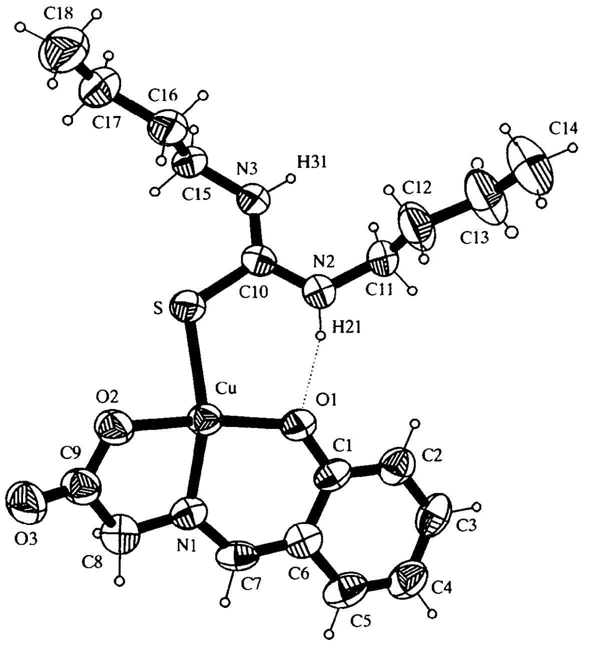

Fig. 1. The asymmetric unit of the title compound with the atomic numbering scheme. Ellipsoids are drawn at the 40% probability level.

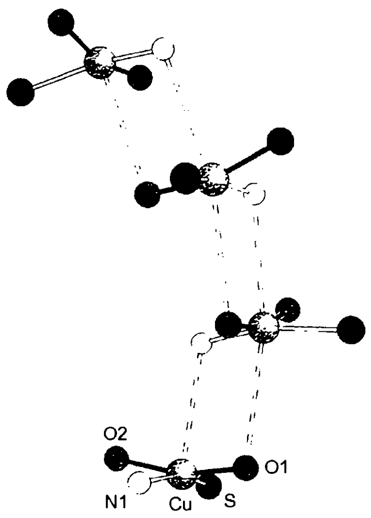

Fig. 2. The stacking of the copper coordination planes at z, $z+\frac{1}{4}$, $z+\frac{1}{2}$ and $z+\frac{3}{4}$. Only the copper(II) environment is shown; all other atoms have been omitted for clarity.

At a cursory inspection, the EPR patterns of compound (I) seem to display a molecular (non-coupled) **g** tensor indicating an exact ferrodistortive ($2\gamma = 0°$) ordering. However, the electronic difference between the molecular axes O1—Cu—O2 (x axis) and N1—Cu—S (y axis) should result in a significant orthorhombic splitting of the **g** tensor. This behaviour can be explained by taking into consideration the packing of the molecules. They are stacked parallel along the [001] direction but related by the 4_3 screw axis. Therefore, the molecular x and y axes are oriented perpendicular in the $\frac{1}{4}+z$ plane and parallel in the $\frac{1}{2}+z$ plane along [001] (Fig. 2), so that the **g** tensor related to x and to y is an averaged one and the orthorhombic splitting cannot be observed. The resulting **g** tensor is hence pseudo-molecular and the ordering mode can be referred to as quasi-ferrodistortive.

Experimental

The title compound was synthesised from aqua(*N*-salicylideneglycinato)copper(II) hemihydrate according to analogous procedures described by Ueki *et al.* (1967) and Warda (1994), with dibutylthiourea in DMF.

Crystal data

$[Cu(C_9H_7NO_3)(C_9H_{20}N_2S)]$
$M_r = 429.03$
Tetragonal
$P4_3$
$a = 12.1747 (16)$ Å
$c = 13.791 (2)$ Å
$V = 2044.2 (5)$ Å^3
$Z = 4$
$D_x = 1.394$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 5000 reflections
$\theta = 2.23–25.97°$
$\mu = 1.192$ mm^{-1}
$T = 293 (2)$ K
Needle
0.87 × 0.15 × 0.12 mm
Violet

Data collection

Stoe IPDS diffractometer
Image plate, Stoe IPDS scans
Absorption correction: integration (*XPREP*; Siemens, 1996*a*)
$T_{\min} = 0.425$, $T_{\max} = 0.875$
16 171 measured reflections
3788 independent reflections
2729 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.058$
$\theta_{\max} = 25.97°$
$h = -14 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.080$
$S = 1.018$
3788 reflections
241 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0362P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.279$ e Å^{-3}
$\Delta\rho_{\min} = -0.276$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.000 (13); 1799 Friedel pairs

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

Cu—O1	1.882 (2)	Cu—O2	1.940 (3)
Cu—N1	1.924 (3)	Cu—S	2.2791 (11)
O1—Cu—N1	93.34 (12)	O1—Cu—S	101.49 (8)
O1—Cu—O2	162.05 (15)	N1—Cu—S	160.74 (11)
N1—Cu—O2	83.92 (12)	O2—Cu—S	85.57 (8)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H21···O1	0.90	1.85	2.722 (4)	160
N3—H31···O3$^{\rm i}$	0.90	1.99	2.865 (4)	165

Symmetry code: (i) $1 - y, x, z - \frac{1}{4}$.

An analytical absorption correction was based on face-indexing and was carried out with the following faces and distances (mm): $\bar{1}00$ 0.0578; 100 0.0578; 001 0.4312; $00\bar{1}$ 0.4351; $\bar{1}10$ 0.0770; $1\bar{1}0$ 0.0770. The contributions of the H atoms of the two butyl groups were included at calculated positions using *SHELXL*97 (Sheldrick, 1997) and refined using a riding model. All other H atoms were found from difference Fourier syntheses. $U_{\rm iso}$ values for H atoms of CH, NH and CH_2 or the methyl groups were taken as $1.2U_{\rm eq}$ or $1.5U_{\rm eq}$ of the parent atoms, respectively. The positions of the H21 and H31 atoms were refined using N—H distance restraints. Atoms C14 and C18 display slight disorder. Nonetheless, no disorder model was employed because of the insignificance of the positions of these atoms with respect to the overall structure.

Data collection: *EXPOSE* (Stoe, 1997*b*). Cell refinement: *CELL* (Stoe, 1997*a*). Data reduction: *INTEGRATE* (Stoe, 1997*c*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97. 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: JZ1262). Services for accessing these data are described at the back of the journal.

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2-[(2,5-Dimethoxyphenyl)(ferrocenyl)methyl]-3,6-dimethoxybenzonitrile†

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Abstract

The cyano group of ferrocenylacetonitrile migrates to the phenyl ring of an aryne during a tandem addition–rearrangement reaction that yields the title compound, [$Fe(C_5H_5)(C_{23}H_{22}NO_4)$]. The two cyclopentadienyl rings of the ferrocenyl moiety are in a staggered conformation.

Comment

We have found that the reaction of ferrocenylacetonitrile with 2-bromo-1,4-dimethoxybenzene, (1), in the presence of lithium diisopropylamide (LDA) in tetrahydrofuran (THF) gives a significant amount (63%) of a solid material, which was identified as the title compound,

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† Alternative name: [1-(2-cyano-3,6,2′,5′-tetramethoxybenzhydryl)-η^5-cyclopentadienyl](η^5-cyclopentadienyl)iron(II).

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