*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.

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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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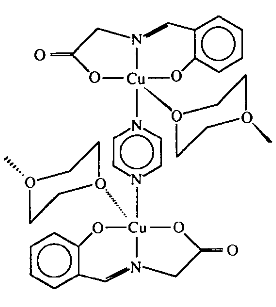
Abstract

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

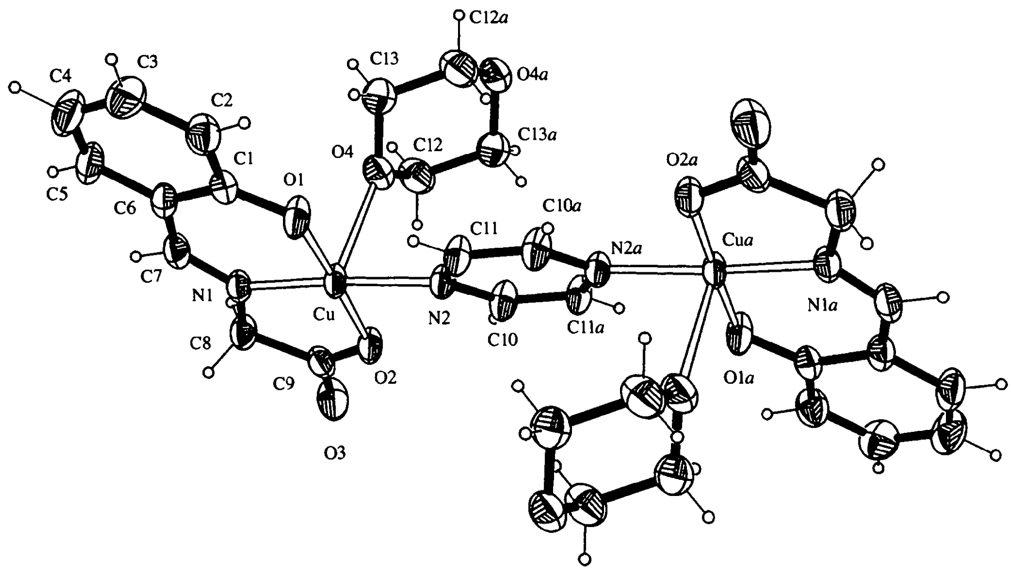


Fig. 1. The dicuprate unit of the title compound, with the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level; H atoms are represented by circles of arbitrary size. Atom labels appended by *a* are related by the symmetry operation $2-x$, $1-y$, z. Further coordination of the dioxane O4*a* atom and its symmetry equivalents is not shown.

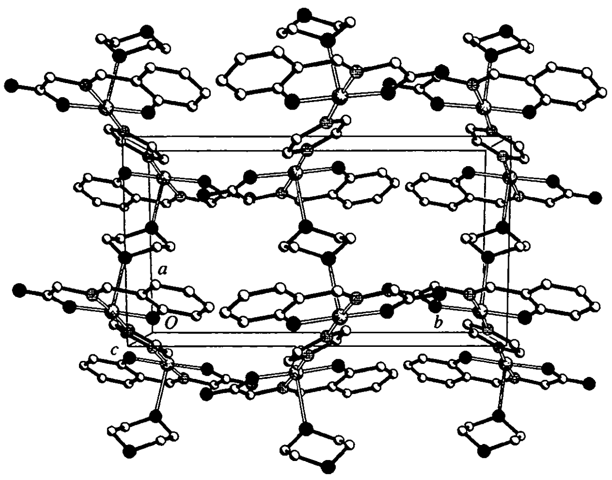


Fig. 2. Packing diagram of the title compound displaying the chains propagating along the crystallographic *x* axis.

respect to one another and should therefore be carefully distinguished from the cell parameter with the same label). The orthorhombic symmetry component of the g tensor is remarkably high.

In the case of monomeric (pyrazine)(*N*-salicylidene-α-amino-2-methylpropanoato)copper(II) reported recently (Warda, 1997) and synthesized in the same way as (I), the pyrazine ligand is monofunctional and the copper(II) coordination geometry is square planar.

Experimental

The title compound was synthesized from aqua(*N*-salicylideneglycinato)copper(II) hemihydrate (Ueki *et al.*, 1967; Warda, 1994) and pyrazine in dioxane–water (1:2).

Crystal data

$[Cu_2(C_9H_7NO_3)_2(C_4H_4N_2)(C_4H_8O_2)]$
$M_r = 649.58$
Monoclinic
$P2_1/c$
$a = 8.5214\ (7)$ Å
$b = 15.3737\ (18)$ Å
$c = 9.9845\ (5)$ Å
$\beta = 100.905\ (5)°$
$V = 1284.4\ (2)$ Å^3
$Z = 2$
$D_x = 1.680$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 17.54–21.41°$
$\mu = 1.715$ mm^{-1}
$T = 293\ (2)$ K
Prism
$0.36 \times 0.12 \times 0.05$ mm
Dark green

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scans (Siemens, 1996*a*)
$T_{min} = 0.577$, $T_{max} = 0.922$
2368 measured reflections
2234 independent reflections
1907 reflections with $I > 2\sigma(I)$

$R_{int} = 0.010$
$\theta_{max} = 24.97°$
$h = -10 \rightarrow 9$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.090$
$S = 1.080$
2234 reflections
181 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0564P)^2 + 0.4624P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.605$ e Å^{-3}
$\Delta\rho_{\min} = -0.439$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu—O1	1.8918 (18)	Cu—N2	2.032 (2)
Cu—N1	1.920 (2)	Cu—O4	2.510 (2)
Cu—O2	1.9357 (18)		
O1—Cu—N1	94.24 (9)	O2—Cu—N2	91.52 (8)
O1—Cu—O2	177.73 (9)	O1—Cu—O4	94.71 (8)
N1—Cu—O2	84.83 (8)	N1—Cu—O4	93.24 (8)
O1—Cu—N2	89.35 (9)	O2—Cu—O4	87.42 (8)
N1—Cu—N2	176.13 (9)	N2—Cu—O4	87.88 (8)

All H atoms were found from difference-Fourier syntheses and refined using a riding model with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(carrier atom). The residual electron density and the deepest hole of 0.605 and −0.439 e Å^{-3}, respectively, are close to the Cu atom at distances of 1.12 and 0.84 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: JZ1247). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 191–193

{2-[2-(Salicylideneaminomethyl)phenyliminomethyl]phenolato(2–)-*N*,*N*′,*O*,*O*′}copper(II)

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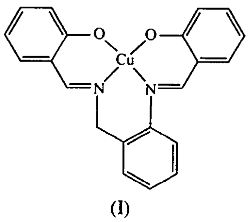
Abstract

In the title compound, $[{\rm Cu(C_{21}H_{16}N_2O_2)}]$ or [Cu(salabza)], the six-membered diamine chelate ring moiety takes a skew-boat form with Cu—N—C—C torsion angles of −47.2 (4) and −59.6 (3)°. The geometry around the Cu atom is tetrahedrally distorted from square planar. The dihedral angle between the two CuNO planes is 29 (1)°, and those between the $\rm CuN_2$ and CuNO planes are 19 (1) and 21 (1)°.

Comment

The tetradentate Schiff base ligand derived from salicylaldehyde and 2-amino-1-benzylamine is abbreviated as $\rm H_2$(salabza). The $\rm Mn^{III}$ complex [Mn(salabza)Cl] shows high activity for dioxygen activation in the presence of cyclohexanecarboxaldehyde (Suzuki *et al.*, 1997). The corresponding $\rm Cu^{II}$ complex, [Cu(salabza)], (I), was prepared, but it has low activity as a catalyst. This may indicate little formation of an octahedral acylperoxo complex, [Cu(salabza){OC(*R*)OO}]$^-$, from [Cu(salabza)], dioxygen and aldehyde [OC(*R*)OO$^-$ is a bidentate peroxo ligand with an alkyl group *R*].



(I)

The present crystal structure analysis of [Cu(salabza)] shows that there is a tetrahedral distortion of the coordination plane around the Cu1 atom which can be quantified by the O2–N5–N4–O3 coordination torsion angle of 26.8 (2)° as well as by the *trans*-N—Cu—O bond angles of 157.8 (2) and 160.3 (2)°, which are much less than the sum of the N—Cu—N and one of the