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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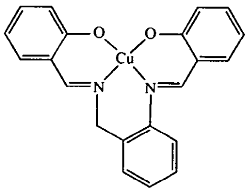
Abstract

In the title compound, $[\mathrm{Cu(C_{21}H_{16}N_2O_2)}]$ 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 $\mathrm{CuN_2}$ 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 $\mathrm{H_2}$(salabza). The $\mathrm{Mn^{III}}$ complex [Mn(salabza)Cl] shows high activity for dioxygen activation in the presence of cyclohexanecarboxaldehyde (Suzuki *et al.*, 1997). The corresponding $\mathrm{Cu^{II}}$ 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

N—Cu—O chelate angles (*ca* 187°). 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)°. These results can be compared with the coordination geometry around the Cu^{II} atom in [Cu(sal)] [sal is *N*,*N'*-ethylenebis(salicylideneiminato)], which is square planar, with an O–N–N–O coordination torsion angle less than 5° (Baker *et al.*, 1970*a*,*b*; Milburn *et al.*, 1974), or a little skewed, having tetrahedral distortion with an O–N–N–O coordination torsion angle of 19° (Ferrari *et al.*, 1976). The six-membered diamine chelate ring moiety of [Cu(salpn)] [salpn is *N*,*N'*-trimethylenebis(salicylideneiminato)] takes a flattened skew-chair form, with Cu—N—C—C torsion angles of 1 (1) and 44 (1)°, and an O–N–N–O coordination torsion angle of 11 (1)° (Drew *et al.*, 1985). The chelate ring in [Cu(sal-2-OH-pn)] [sal-2-OH-pn is *N*,*N'*-(2-hydroxytrimethylene)bis(salicylideneiminato)] takes a skew-boat form, with Cu—N—C—C torsion angles of 54 (1) and 67 (1)°, leading to a remarkable tetrahedral distortion with an O–N–N–O coordination torsion angle of 34 (1)° (Kitajima *et al.*, 1986).

In contrast to the low activity of [Cu(salabza)], the mononuclear copper(II) complex $[Cu(bdpg)Cl]^+$ [bdpg is *N*,*N*-bis(2-pyridylmethyl)-β-alanine-amide], with a tripodal ligand containing an amide group, exhibits high activity for the oxygenation reaction of cyclohexane in the presence of hydrogen peroxide, suggesting the formation of a square-pyramidal peroxo complex, $[Cu(bdpg)(OOH)]^+$, having an intramolecular Cu—O—O—H···O hydrogen bond (Okuno *et al.*, 1997).

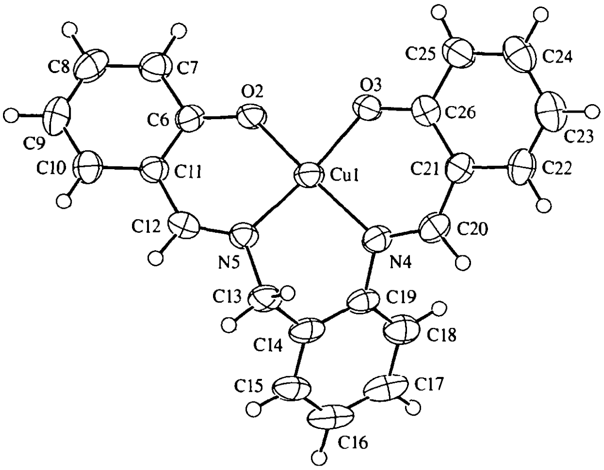


Fig. 1. The molecular structure of (I) with displacement ellipsoids at the 50% probability level. H atoms are represented by circles of radii 0.1 Å.

Experimental

The Schiff base H_2(salabza) was prepared from salicylaldehyde and 2-amino-1-benzylamine. Copper(II) acetate monohydrate was added to a methanol solution of H_2(salabza) and the resulting precipitate was filtered off and recrystallized from an ethanol solution.

Crystal data

$[Cu(C_{21}H_{16}N_2O_2)]$
$M_r = 391.92$
Monoclinic
$P2_1/a$
$a = 16.546 (3)$ Å
$b = 8.970 (2)$ Å
$c = 11.507 (2)$ Å
$\beta = 98.90 (2)°$
$V = 1687.3 (5)$ Å^3
$Z = 4$
$D_x = 1.543$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–15°$
$\mu = 1.312$ mm^{-1}
$T = 298$ K
Prism
0.55 × 0.20 × 0.10 mm
Black

Data collection

Rigaku AFC-5 diffractometer
$\theta–2\theta$ scans
Absorption correction: by integration (Coppens *et al.*, 1965)
$T_{min} = 0.610$, $T_{max} = 0.788$
4057 measured reflections
3870 independent reflections

2071 reflections with $|F_o| > 3\sigma(|F_o|)$
$R_{int} = 0.021$
$\theta_{max} = 27.5°$
$h = -21 \rightarrow 21$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 14$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.042$
$wR = 0.038$
$S = 1.21$
2071 reflections
235 parameters
H atoms riding with U_{iso} = 0.08 Å^2

$w = 1/[\sigma^2(F) + 0.000225F^2]$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Cu1—O2	1.889 (3)	O3—C26	1.303 (5)
Cu1—O3	1.902 (3)	N4—C19	1.434 (5)
Cu1—N4	1.965 (3)	N4—C20	1.295 (6)
Cu1—N5	1.943 (3)	N5—C12	1.288 (5)
O2—C6	1.304 (5)	N5—C13	1.492 (5)
O2—Cu1—O3	87.7 (2)	Cu1—N4—C19	117.8 (3)
O2—Cu1—N4	157.8 (2)	Cu1—N4—C20	123.5 (3)
O2—Cu1—N5	93.5 (2)	C19—N4—C20	118.5 (4)
O3—Cu1—N4	92.8 (2)	Cu1—N5—C12	125.1 (3)
O3—Cu1—N5	160.3 (2)	Cu1—N5—C13	116.7 (3)
N4—Cu1—N5	93.5 (2)	C12—N5—C13	118.1 (4)
Cu1—O2—C6	128.0 (3)	N5—C13—C14	109.4 (3)
Cu1—O3—C26	127.8 (3)	N4—C19—C14	118.4 (4)

The positions of all the H atoms were calculated geometrically and a riding model was used in their refinement (C—H 0.96 Å).

Data collection: *AFC/MSC Diffractometer Control System* (Rigaku Corporation, 1993). Cell refinement: *AFC/MSC Diffractometer Control System*. Data reduction: local programs. Program(s) used to solve structure: *CRYSTAN-GM* (Edwards *et al.*, 1996). Program(s) used to refine structure: *CRYSTAN-GM*. Molecular graphics: *CRYSTAN-GM*. Software used to prepare material for publication: *CRYSTAN-GM*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1184). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 193–195

A Dimeric Copper(II) 4-Chlorophenoxyisobutyrate Adduct with Methanol and a Monomeric Copper(II) 4-Chlorophenoxyisobutyrate Adduct with Pyridine

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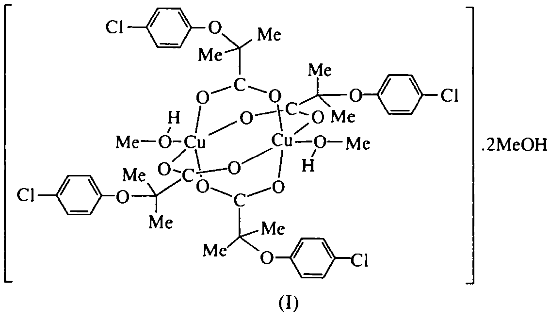
Abstract

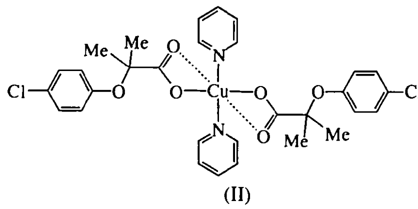
In the crystal structure of tetrakis(μ-4-chlorophenoxyisobutyrato-*O*,*O*′)di(methanol-*O*)dicopper(II) dimethanol solvate, $[Cu(pciba)_2(CH_3OH)]_2.2CH_3OH$ (pcibaH is 4-chlorophenoxyisobutyric acid, $C_{10}H_{11}ClO_3$), there is a dinuclear Cu^{II} complex which has a typical cage structure with a Cu···Cu distance of 2.6437 (4) Å. The magnetic $-2J$ value is 360 cm^{-1} ($H = -2JS_1.S_2$). In the crystal structure of *trans*-bis(4-chlorophenoxyisobutyrato-*O*,*O*′)dipyridinecopper(II), $[Cu(pciba)_2(C_5H_5N)_2]$, the monomeric Cu^{II} complex has a distorted octahedral coordination.

Comment

The dimeric title compound, (I), has a center of symmetry. The Cu1—O4 bond length is 1.991 (2) Å, which is *ca* 0.02 Å longer than the other Cu1—O(carboxyl) bonds as a result of the hydrogen bond between the O4 atom and crystal methanol (O11). The dimeric copper(II) complexes related by translation along **c** are connected by two hydrogen-bond bridges, Cu1—O4···H11—O11···H10^{i}—O10^{i}—Cu^{i} and Cu1—O10—H10···O11^{i}—H11^{i}···O4^{i}—Cu^{i} [symmetry code: (i) $1-x$, $-y$, $-1-z$]. Several kinds of dimeric copper(II) phenoxyalkanoates have been prepared and their crystal structures published (Reck & Jaehnig, 1979; Smith *et al.*, 1985; Mak *et al.*, 1987). However, their magnetic data were not reported. In this study, the magnetic susceptibility of (I) was measured using the Faraday method over a temperature range of 80–300 K, and the $-2J$ and g values were determined to be 360 cm^{-1} and 2.22, respectively, with the mole fraction of the monomeric Cu^{II} impurity being 1.3%. It was assumed that crystal methanol molecules were lost from the crystals under reduced pressure. The $-2J$ value is comparable with those of $[Cu(Ph_2MeCCOO)_2(EtOH)]_2.EtOH$ ($-2J$ = 347 cm^{-1}; Steward *et al.*, 1996) and $[Cu(PhMe_2CCOO)_2(H_2O)]_2$ ($-2J$ = 348 cm^{-1}; Fujita *et al.*, 1993). This indicates that there is a negligible influence on the antiferromagnetic interaction when a phenyl group is replaced by a phenoxy group bonded at the α-carbon of the bridging carboxylate ions.



(I)



(II)