H atoms were isotropically refined as riding atoms

Extinction correction: none

Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Ni7—B3	2.087 (4)	Ni7—P1	2.3343 (13)
Ni7—B2	2.092 (4)	S2—C2	1.680 (4)
Ni7—B8	2.168 (4)	S1—C1	1.664 (4)
Ni7—B11	2.203 (4)	B3—O2	1.463 (5)
Ni7—S1	2.2735 (11)	B2—O1	1.486 (4)
Ni7—S2	2.3118 (13)		
B3—Ni7—B2	49.8 (2)	B3—Ni7—S2	81.83 (12)
B3—Ni7—B8	49.8 (2)	B2—Ni7—S2	115.09 (12)
B2—Ni7—B8	86.8 (2)	B8—Ni7—S2	91.22 (13)
B3—Ni7—B11	86.3 (2)	S1—Ni7—S2	87.86 (5)
B2—Ni7—B11	48.5 (2)	B8—Ni7—P1	96.38 (13)
B8—Ni7—B11	89.9 (2)	B11—Ni7—P1	94.18 (12)
B3—Ni7—S1	119.15 (12)	S1—Ni7—P1	94.67 (4)
B2—Ni7—S1	83.49 (11)	S2—Ni7—P1	102.13 (4)
B11—Ni7—S1	87.82 (12)		

Considering both *R* and U_{eq}, the site-occupation factor of the hexane solvent molecule was estimated as 0.5.

Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *Manual*. Data reduction: *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai & Huttner, 1994). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1447). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A (4-Ethylpyridine)(*N*-salicylideneglycinato)copper(II) Tetramer

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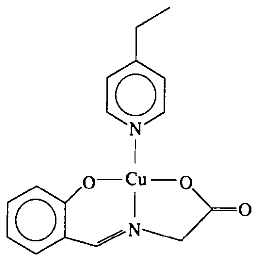
Abstract

The title compound, *cyclo*-tetrakis[(4-ethylpyridine-*N*)(*N*-salicylideneglycinato-*O*,*N*,*O*′:*O*″)copper(II)], [Cu($C_9H_7NO_3$)(C_7H_9N)]$_4$, adopts a square-pyramidal Cu^{II} coordination with the tridentate *N*-salicylideneglycinato Schiff base dianion (TSB^{2-}) and the 4-ethylpyridine ligand bound in the basal plane. The apex of the pyramid is occupied by a carboxylic O atom from the neighbouring chelate at an apical distance of 2.458 (2) Å. Four such molecules build a tetrameric unit, in which all copper positions are magnetically non-equivalent. The unit cell contains four tetramers.

Comment

Copper(II) complexes with the tridentate Schiff base dianion of the *N*-salicylideneaminoalkanoate 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; Warda, Friebel, Sivý, Plesch & Švajlenová, 1996). Polymeric structures ($n = \infty$) result when the apical position is occupied by a carboxylic O atom from an adjacent molecule to make infinite chains (Ueki, Ashida, Sasada & Kakudo, 1967). In this communication, we report for the first time a structure consisting of a tetrameric moiety (n = 4), (I).



(I)

The title molecule is characterized by an approximately square-pyramidal Cu^{II} coordination with the tridentate dianionic Schiff base TSB^{2-} and a monodentate ligand (4-ethylpyridine) in the basal plane. The apical Cu—O3A($\frac{5}{4} - y$, $\frac{1}{4} + x$, $-\frac{3}{4} - z$) distance of 2.458 (2) Å, originating from a carboxylic O atom of a neighbouring molecule, is elongated compared with the corresponding bonds in aqua(N-salicylideneglycinato)copper(II) hemihydrate (Ueki, Ashida, Sasada & Kakudo, 1967). Four such molecules make up a tetrameric unit. The Cu^{II} ions are magnetically non-equivalent since the square pyramids are differently oriented. They form the corners of a strongly flattened tetrahedron. In accordance with this, the EPR powder spectra display an isotropic signal resulting from exchange narrowing of the coupled molecular g tensors.

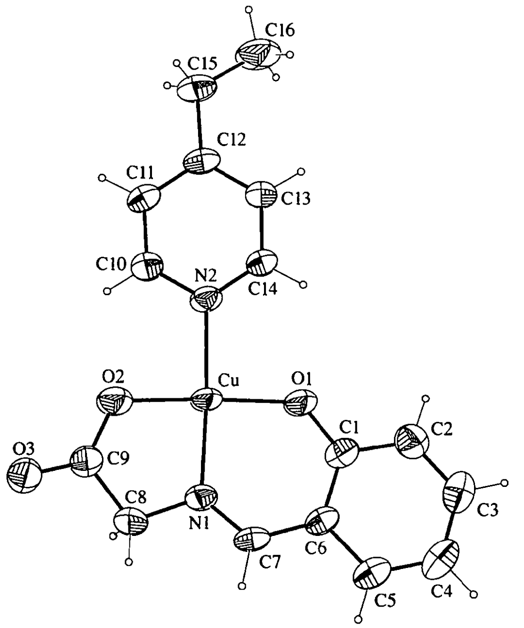


Fig. 1. Diagram of the title compound showing the asymmetric unit with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

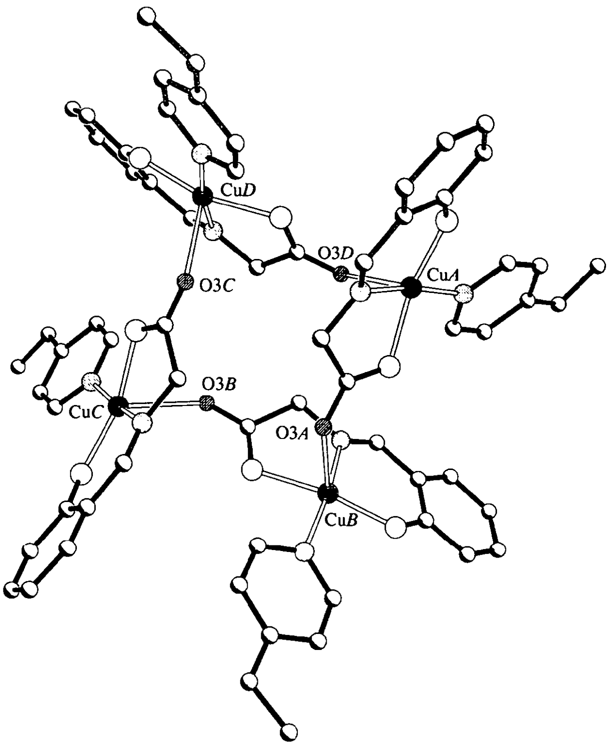


Fig. 2. Tetrameric association of the title compound.

Experimental

The title compound was synthesized from aqua(N-salicylideneglycinato)copper(II) hemihydrate (Ueki, Ashida, Sasada & Kakudo, 1967) and 4-ethylpyridine as solvent, and was obtained after evaporation of the solvent at room temperature. An amorphous olive green substance was precipitated. This product was recrystallized from ethanol several times at 268 K.

Crystal data

$[Cu(C_9H_7NO_3)(C_7H_9N)]_4$
M_r = 5962.2
Tetragonal
$I4_1/a$
a = 28.6630 (7) Å
c = 7.25719 (10) Å
V = 5962.3 (2) Å^3
Z = 4
D_x = 1.550 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 25 reflections
θ = 28.74–46.27°
μ = 2.194 mm^{-1}
T = 293 (2) K
Prism
0.205 × 0.125 × 0.120 mm
Dark green

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scans (*XPREP* in *SHELXTL*; Siemens, 1996*a*)
T_{min} = 0.364, T_{max} = 0.769
2315 measured reflections
2205 independent reflections

2015 reflections with $I > 2\sigma(I)$
R_{int} = 0.0336
θ_{max} = 59.88°
$h = -32 \rightarrow 0$
$k = 0 \rightarrow 32$
$l = -8 \rightarrow 0$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0435$
$wR(F^2) = 0.1254$
$S = 1.124$
2205 reflections
200 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0768P)^2 + 10.629P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.613$ e Å^{-3}
$\Delta\rho_{\min} = -0.465$ e Å^{-3}
Extinction correction: *SHELXL*96 (Sheldrick, 1996)
Extinction coefficient: 0.00044 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu—O1	1.912 (2)	Cu—O2	1.999 (2)
Cu—N1	1.927 (3)	Cu—O3$^{\text{i}}$	2.458 (2)
Cu—N2	1.992 (2)		
O1—Cu—N1	92.42 (10)	N2—Cu—O2	91.21 (10)
O1—Cu—N2	91.98 (10)	O1—Cu—O3$^{\text{i}}$	115.78 (11)
N1—Cu—N2	172.24 (11)	N1—Cu—O3$^{\text{i}}$	96.75 (10)
O1—Cu—O2	160.98 (11)	N2—Cu—O3$^{\text{i}}$	87.08 (9)
N1—Cu—O2	82.59 (10)	O2—Cu—O3$^{\text{i}}$	83.11 (10)

Symmetry code: (i) $\frac{5}{4} - y, \frac{1}{4} + x, -\frac{3}{4} - z$.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *XCAD*-4 (Harms, 1996). Program(s) used to solve structure: *SHELXS*96 (Sheldrick, 1996). Program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996). Molecular graphics: *SHELXTL* (Siemens, 1996*a*) and *XP* (Siemens, 1996*b*). Software used to prepare material for publication: *SHELXL*96.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: JZ1191). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cyclopentadienylcaesium by High-Resolution X-ray Powder Diffraction

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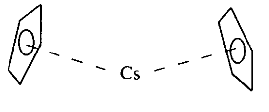
Abstract

The structure of solid (η^5-cyclopentadienyl)caesium, $[Cs(C_5H_5)]$, has been refined by high-resolution powder X-ray diffraction. Atomic parameters based on the isostructural Rb analogue were used in the starting model. The compound crystallizes in space group *Pnma*, with $Z = 4$ and unit cell parameters $a = 11.3664(2)$, $b = 8.8648(2)$ and $c = 5.7200(1)$ Å. $[Cs(C_5H_5)]$ shows a polymeric zigzag chain, a so-called multidecker structure, with an average Cs—Cp$_{\text{centroid}}$ distance of 3.140 (5) Å. $[Cs(C_5H_5)]$ contains a single chain along the *a* axis. The chains are bent with a Cp$_{\text{centroid}}$—Cs—Cp$_{\text{centroid}}$ angle of 129.7 (1)°.

Comment

The cyclopentadienyl anion, $C_5H_5^-$ (Cp), is one of the most important ligands in organometallic chemistry and can form compounds with virtually any metallic element (Wilkinson, Stone & Abel, 1982). The structure refinement of cyclopentadienylcaesium (CsCp), (I), has been carried out as part of a general study of solid base-free cyclopentadiene–alkali metal compounds.



(I)

Preparation of single crystals of (I) has proved to be impossible due to its poor solubility in non-coordinating solvents. Powder diffraction studies have been performed on $[Rb(C_5H_5)]$ (RbCp) (Dinnebier, Olbrich, van Smaalen & Stephens, 1996), which led to the structure solution of two polymorphic phases (in *Pnma* and *Pbca*). Visual inspection of the powder pattern of CsCp showed it to be isostructural with one of the Rb-containing phases. The crystal structure of CsCp has, therefore, been refined in space group *Pnma*