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Bis(μ-salicylaldehyde semicarbazonato)-bis[formatocopper(II)]

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.003 Å
R factor = 0.033
wR factor = 0.090
Data-to-parameter ratio = 23.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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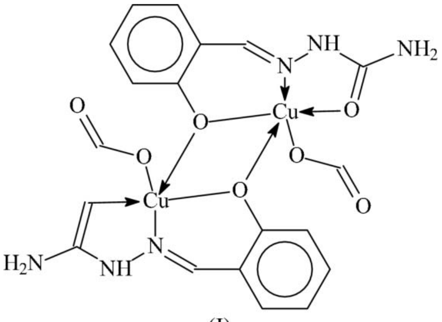
The salicylaldehyde semicarbazonate anion O,N,O-chelates to the Cu atom in the title compound, bis[μ-2-(semicarbazonomethyl)phenolato]-1κ^3O^3,N^1,O:2κO;1κO:2κ^3O^3,N^1,O-bis-[(formato-κO)copper(II)] [$Cu_2(C_8H_8N_3O_2)_2(CHO_2)_2$], the N and O atoms occupying three sites of the square-planar environment around it. The fourth site is occupied by the negatively charged O atom of the formate anion. Two molecules are bridged through the phenoxy O atom across a center of symmetry to give a dinuclear compound, so that the Cu atom exists in a square-pyramidal geometry [$Cu \leftarrow O_{phenoxy}$ = 2.546 (1) Å in the apical position]. Hydrogen bonds link the dinuclear molecules into a three-dimensional network architecture.

Comment

Only a very small number of metal complexes of the terdentate Schiff base that is formed by condensing salicylaldehyde with semicarbazide have been crystallographically authenticated; the complexes of salicylaldehyde semicarbazone, which is an approximately planar molecule (Valdes-Martinez *et al.*, 1990), are limited to the vanadium derivative, *cis*-dioxo(salicylaldehyde semicarbazonato)vanadium(V) (Noblia *et al.*, 2004) and the copper derivatives monomeric (chlorosalicylaldehyde semicarbazonato)copper dihydrate (Patole *et al.*, 2001; Samus' *et al.*, 1990) and diaqua(salicylaldehyde semicarbazonato)copper, aqua(salicylaldehyde semicarbazonato)(dimethylformamide)copper sulfate trihydrate (Chumakov *et al.*, 1996).


(I)

In the title compound, (I), the negatively charged formate O atom is linked to the O,N,O-chelated Cu atom, the N atom and three O atoms comprising a basal square plane around the Cu atom. Two molecules are bridged through the phenoxy O atom to form a dinuclear species across a center of inversion (Fig. 1). The symmetry-related phenoxy O atom occupies the apical position of the resulting square pyramid, and the bridging $Cu-O_{phenoxy}$ bond is significantly longer than both

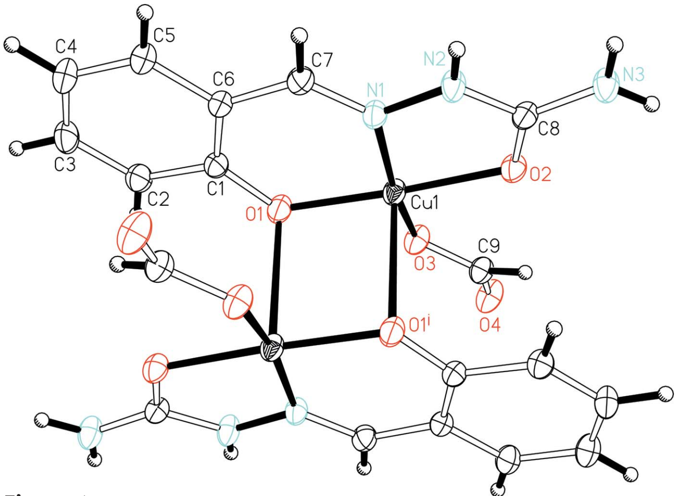


Figure 1
ORTEPII plot (Johnson, 1976) of (I). Displacement ellipsoids are drawn at the 70% probability level [symmetry code: (i) $1 - x, 1 - y, 1 - z$].

the covalent Cu—$O_{phenoxy}$ and Cu—$O_{carbonyl}$ bonds in the basal plane. Adjacent dinuclear units are linked by hydrogen bonds (Table 2) to form a three-dimensional network.

The salicylaldehyde–glycine dianion, which possesses bonding features similar to those of the salicylaldehyde semicarbazone monoanion, has been shown to bind to copper(II) as a terdentate chelate; the dimeric nature of the urea adduct also arises from bridging by the phenoxy O atom in that square-pyramidal compound (Valenta *et al.*, 2002).

Experimental

Salicylaldehyde semicarbazone (1.07 g, 6 mmol) was dissolved in hot ethanol (100 ml) and copper sulfate pentahydrate (1.50 g, 6 mmol) in water (10 ml). The aqueous solution was added to the ethanol solution and the mixture kept at 313–323 K for 30 min. The pale-green precipitate of bis[aqua(salicylaldehyde semicarbazonato)copper] sulfate dihydrate, (II), was collected and washed with ethanol (yield: 90%). (II) (0.34 g, 0.5 mmol) was dissolved in water (50 ml) and to this solution was added a large excess (10 ml) of formic acid. Dark-green crystals of (I) separated from the mixture within an hour in about 80% yield. Elemental analysis calculated for $C_{18}H_{18}Cu_2N_6O_8$: C 37.70, H 3.14, N 14.66%; found: C 37.53, H 3.02, N 14.60%.

Crystal data

$[Cu_2(C_8H_8N_3O_2)_2(CHO_2)_2]$
$M_r = 573.46$
Monoclinic, $P2_1/n$
$a = 7.7562$ (5) Å
$b = 14.1641$ (8) Å
$c = 9.6837$ (6) Å
$\beta = 102.743$ (1)°
$V = 1037.6$ (1) Å^3
$Z = 2$

$D_x = 1.835$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1754 reflections
$\theta = 2.6$–32.0°
$\mu = 2.11$ mm^{-1}
$T = 173$ (2) K
Prism, green
0.33 × 0.11 × 0.07 mm

Data collection

Bruker SMART 1000 area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.675$, $T_{max} = 0.866$
13226 measured reflections

3551 independent reflections
2997 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 32.0°$
$h = -11 \rightarrow 11$
$k = -21 \rightarrow 20$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.090$
$S = 1.04$
3551 reflections
154 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0459P)^2 + 0.5822P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.59$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.918 (1)	Cu1—O3	1.922 (1)
Cu1—O1^i	2.546 (1)	Cu1—N1	1.923 (1)
Cu1—O2	1.976 (1)		
O1—Cu1—O1^i	86.90 (5)	O1^i—Cu1—O3	96.57 (5)
O1—Cu1—O2	174.84 (5)	O1^i—Cu1—N1	96.11 (5)
O1—Cu1—O3	89.97 (5)	O2—Cu1—O3	95.16 (5)
O1—Cu1—N1	93.19 (6)	O2—Cu1—N1	81.67 (5)
O1^i—Cu1—O2	93.10 (5)	O3—Cu1—N1	167.07 (6)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$n\cdots$O4^{ii}	0.88	2.05	2.804 (2)	143
N3—H3n1$\cdots$O4^{iii}	0.88	2.09	2.931 (2)	159

Symmetry codes: (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 1, -y + 1, -z$.

H atoms were placed at calculated positions [C—H = 0.95 Å, N—H = 0.88 Å and $U_{iso}(H) = 1.2U_{eq}(C,N)$] and were included in the refinement in the riding-model approximation.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976).

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Acta Cryst. (2005). E**61**, m1816–m1817 Gerasimenko *et al.* • $[Cu_2(C_8H_8N_3O_2)_2(CHO_2)_2]$ **m1817**