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Bis[μ-3-(hydroxyimino)butan-2-one benzoylhydrazonato]bis[pyridinecopper(II)] methanol solvate

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In the title complex, $[Cu_2(C_{11}H_{11}N_3O_2)_2(C_5H_5N)_2]\cdot CH_4O$, the two Cu^{II} atoms are bridged by two oxime O atoms of diacetyl monoxime benzoylhydrazone ligands, with a Cu···Cu distance of 3.644 (2) Å. The center of the dimer corresponds to a crystallographic center of symmetry. Each Cu^{II} atom shows a square-pyramidal geometry defined by two N and two O atoms of hydrazone ligands and one pyridine N atom. The methanol solvent molecules lie on special positions with twofold rotation symmetry and form intramolecular O—H···O hydrogen bonds.

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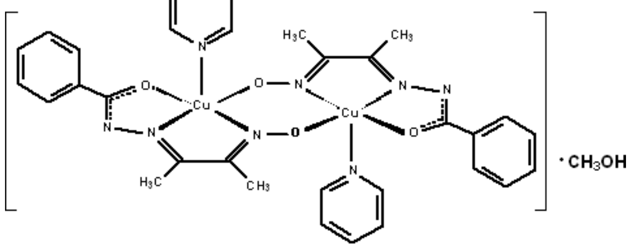
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
Disorder in solvent or counterion
R factor = 0.051
wR factor = 0.122
Data-to-parameter ratio = 16.8

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

Comment

Transition metal–hydrazone complexes, in which the hydrazone ligands are formed by condensing hydrazine with a β-diketone, salicylaldehyde and their derivatives, have been extensively studied in recent decades (Gao *et al.*, 1998; Liu & Gao, 1998). However, only one structure of a copper complex containing the 3-(hydroxyimino)butan-2-one benzoylhydrazone ligand has been reported to date (Chumakov *et al.*, 1979). As a contribution to this field, we have recently reported two mononuclear zinc complexes, *viz.* $[Zn(HL)(C_9H_7N)(OOCCH_3)]\cdot 0.5C_9H_7N$ and $[Zn(HL)(C_2H_3O_2)(C_3H_4N_2)]$ (H_2L is diacetyl monooxime benzoylhydrazone), in which the Zn atoms are in a geometry that is intermediate between square pyramidal and trigonal bipyramidal, and HL^- acts as a tridentate ligand (Gao *et al.*, 2004; Huo *et al.*, 2004). In order to gain more insight into the metal-binding modes of this ligand, we synthesized the title compound, $[Cu(L)(C_5H_5N)]_2\cdot 2CH_3OH$, (I), in which the hydrazone ligand acts as a tetradentate ligand and bridges two Cu^{II} atoms into a dimeric structure through the oxamate O atoms. The crystal structure of (I) is reported here.



(I)

As shown in Fig. 1, the crystal structure of (I) consists of a neutral dimeric complex $[Cu(L)(C_5H_5N)]_2$ and two disordered methanol solvent molecules on special positions with twofold rotation symmetry. The methanol molecules form intramolecular hydrogen bonds with the O atoms of the hydrazone ligand, with an O···O distance and an O—H···O angle of 2.950 (8) Å and 178°, respectively. The center of the dimer corresponds to a crystallographic center of symmetry. The dimer is bridged by two oxamate O atoms and two N atoms of the hydrazone ligands [Cu—O = 1.905 (2) Å], forming a six-membered ring, the Cu···Cu separation being 3.644 (2) Å. Each Cu^{II} atom has a distorted square-pyramidal geometry. The basal plane is defined by the atoms O1, O1^{i}, N1 and N2 [r.m.s. = 0.0554 (2) Å; Table 1], and the Cu—N and Cu—O bond lengths lie in the ranges 1.922 (3)–2.050 (3) and 1.905 (2)–2.028 (2) Å, respectively. The apical position is occupied by the pyridine N atom, with a longer Cu—N distance [2.246 (3) Å]. The Cu^{II} atoms deviate from the apical plane by 0.255 (3) Å towards the axial N atom. Bond lengths (Table 1) suggest some degree of electron delocalization in the hydrazone ligand. The two five-membered chelate rings O2/C5/N3/N2/Cu1 and N2/C3/C2/N1/Cu1 are both approximately planar with maximum deviations of 0.0026 (2) and 0.0397 (2) Å, respectively; the dihedral angle between them is 5.64 (4)°. The overall hydrazone ligand is also almost planar with a maximum deviation of 0.0756 (3) Å from the least-squares plane..

Experimental

The hydrazone ligand was synthesized by condensing benzoylhydrazine with an equimolar amount of diacetyl monooxime in ethanol. A methanol solution containing copper(II) acetate monohydrate (1 mmol) and pyridine (1 ml) was added dropwise to a methanol solution (15 ml) of the hydrazone ligand (1 mmol). The resulting mixture was refluxed with stirring for 0.5 h, cooled slowly to room temperature and filtered. Green crystals were isolated from the solution after 7 d. Analysis calculated for $C_{33}H_{36}Cu_2N_8O_5$: C 52.72, H 4.83, N 14.90%; found: C 52.57, H 4.89, N 14.93%.

Crystal data

$C_{32}H_{32}Cu_2N_8O_4{\cdot}CH_4O$
$M_r = 751.78$
Monoclinic, $C2/c$
$a = 17.617\ (4)$ Å
$b = 8.363\ (3)$ Å
$c = 23.099\ (4)$ Å
$\beta = 96.695\ (11)^\circ$
$V = 3380.0\ (16)$ Å^3
$Z = 4$

$D_x = 1.477$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7270 reflections
$\theta = 3.2$–27.5°
$\mu = 1.31$ mm^{-1}
$T = 293\ (2)$ K
Prism, dark blue
0.28 × 0.22 × 0.12 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.710$, $T_{max} = 0.859$
16098 measured reflections

3865 independent reflections
2569 reflections with $I > 2\sigma(I)$
$R_{int} = 0.068$
$\theta_{max} = 27.5^\circ$
$h = -20 \rightarrow 22$
$k = -10 \rightarrow 10$
$l = -29 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.122$
$S = 1.01$
3865 reflections
230 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0629P)^2 + 1.2139P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

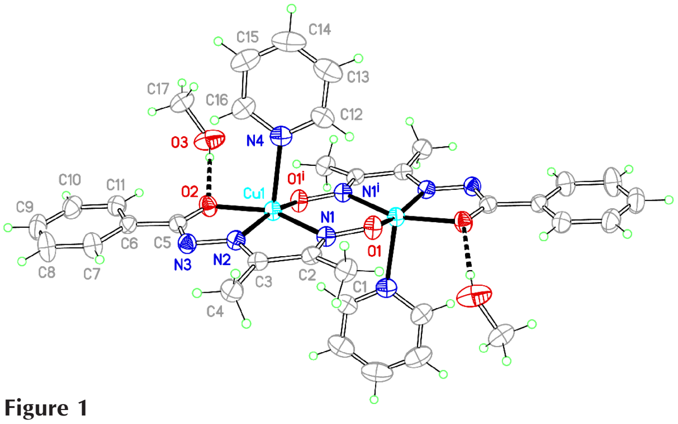


Figure 1
The molecular structure of (I) shown with 30% probability ellipsoids. Hydrogen bonds are indicated by dashed lines. Symmetry code as in Table 1

Table 1
Selected geometric parameters (Å, °).

Cu1—O1^{i}	1.905 (2)	N3—C5	1.328 (4)
Cu1—O2	2.028 (2)	N2—N3	1.373 (4)
Cu1—N1	2.050 (3)	N2—C3	1.287 (4)
Cu1—N2	1.922 (3)	C2—C3	1.472 (5)
Cu1—N4	2.246 (3)	C2—N1	1.303 (4)
O2—C5	1.285 (4)	O1—N1	1.343 (3)
O1^{i}—Cu1—N2	159.9 (1)	N2—Cu1—O2	78.3 (1)
O1^{i}—Cu1—O2	92.35 (9)	N2—Cu1—N1	79.2 (1)
O1^{i}—Cu1—N1	106.5 (1)	N2—Cu1—N4	102.6 (1)
O1^{i}—Cu1—N4	96.4 (1)	N1—Cu1—N4	93.7 (1)
O2—Cu1—N1	156.2 (1)	O1—N1—Cu1	127.6 (2)
O2—Cu1—N4	98.6 (1)	N1—O1—Cu1^{i}	119.3 (2)

Symmetry code: (i) $2 - x, -y, 1 - z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H18···O2	0.82	2.13	2.950 (8)	178

The H atoms on carbon and of the hydroxy group were placed in calculated positions, with C—H = 0.93 (aromatic), 0.96 (methyl) and 0.82 Å (hydroxy), and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(O, C-methyl) in the riding-model approximation. The methanol solvent molecule is disordered over the twofold axis. It was refined with a C—O distance restraint of 1.50 (1)Å. The torsion angle of the methyl group was refined, and the hydroxy group was allowed to rotate.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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m1612 Li-Hua Huo *et al.* • $C_{32}H_{32}Cu_2N_8O_4{\cdot}CH_4O$ *Acta Cryst.* (2004). E**60**, m1611–m1613

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Acta Cryst. (2004). E**60**, m1611–m1613 Li-Hua Huo *et al.* • $C_{32}H_{32}Cu_2N_8O_4{\cdot}CH_4O$ **m1613**