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Bis[μ-3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazonato]bis[pyridinecopper(II)] methanol disolvate

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Key indicators

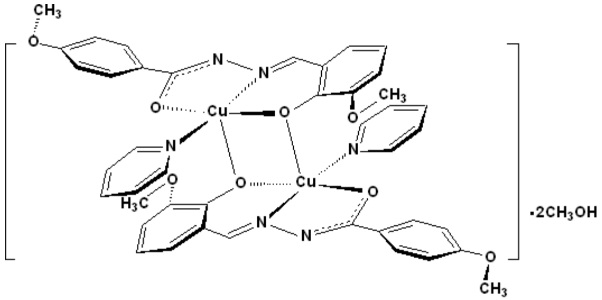
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.037
wR factor = 0.097
Data-to-parameter ratio = 17.3

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

The title complex crystallizes as a methanol solvate, $[Cu_2(C_{16}H_{14}O_4N_2)_2(C_5H_5N)_2]\cdot 2CH_4O$. The dinuclear complex is generated from the atoms of the asymmetric unit by inversion symmetry, resulting in a Cu$\cdots$Cu separation of 3.497 (3) Å. The copper(II) species has a square-pyramidal geometry, with the basal plane defined by two O atoms and one N atom from the hydrazone ligand and a pyridine N atom. The apical site is occupied by a phenolate O atom in the symmetry-generated hydrazone ligand, which also bonds to the second Cu atom. Intramolecular O—H$\cdots$N hydrogen bonds are formed between the methanol solvent molecules and the uncoordinated N atoms of the hydrazone ligand.

Comment

The study of transition metal–hydrazone complexes, in which the hydrazone ligands are formed by condensing hydrazine with β-diketones, salicylaldehyde and their derivatives, has attracted considerable attention because of the biological activity and chemical versatility of these complexes (Dutta *et al.*, 1995; Liu & Gao, 1998; Gao *et al.*, 1998). However, there is relatively little information about the structures of metal complexes containing the 3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazone ligand (H_2L), which is a potentially tridentate chelating agent, formed by condensing 3-methoxysalicylaldehyde with 4-methoxybenzoylhydrazine. We have recently reported the structures of one iron and two oxovanadium(V) complexes of this ligand, in which the ligand possesses different formal charges (−2 for the vanadium systems and −1 for the iron system; (Huo, Gao, Liu, Zhao & Ng, 2004; Huo, Gao, Liu, Li, Zhao & Zhao, 2004; Huo, Gao, Liu, Li & Ng, 2004). As part of our continuing investigation of the coordination behavior of this hydrazone ligand, we have synthesized the title complex, $[Cu(C_{16}H_{14}O_4N_2)(C_5H_5N)]_2\cdot 2(CH_4O)$, (I), in which the phenolato O atom acts as a μ^2 bridging species, thus forming a dinuclear structure.



(I)

As shown in Fig. 1, the crystal structure of (I) consists of an asymmetrically bridged dimer, [Cu(*L*)(pyridine)]$_2$, accom-

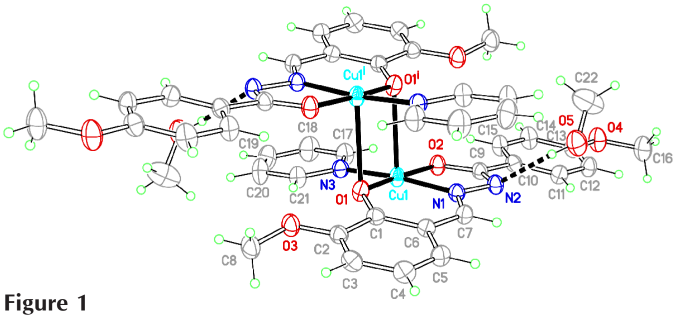


Figure 1

A view of the dimeric structure of (I), with displacement ellipsoids at the 30% probability level. The O—H···N hydrogen bonds are indicated by dashed lines. Symmetry code as in Table 1.

panied by solvated methanol molecules. The dimer is generated by inversion symmetry from the unique atoms, resulting in a Cu···Cu^{i} (see Table 1 for symmetry code) distance of 3.497 (3) Å. Phenolate atom O1 of the hydrazone ligand acts as the bridging species, resulting in one short [1.910 (2) Å] and one very long [2.725 (3) Å] Cu—O bond length (Table 1). Each Cu^{II} atom exists in a square-pyramidal geometry. The basal plane is defined by atoms O1, O2 and N1 from the hydrazone ligand and pyridine atom N3, with an r.m.s. deviation from the mean plane of 0.066 Å. The apical site is occupied by O1^{i} of the symmetry-generated hydrazone ligand. The Cu^{II} atom deviates from the basal plane by 0.0649 (8) Å towards the apical atom O1^{i}. Bond lengths (Table 1) indicate electron delocalization in the hydrazone ligand, which results in atom N2 being easily deprotonated. Both the six-membered chelate ring N1/C7/C6/C1/O1/Cu1 (r.m.s. deviation = 0.063 Å) and the five-membered chelating ring O2/C9/N1/N2/Cu1 (r.m.s. deviation = 0.021 Å) are close to planar, and the dihedral angle between them is 5.64 (4)°. The methanol molecules form intramolecular hydrogen bonds with the uncoordinated N atoms of the hydrazone ligand (Table 2).

Experimental

The 3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazone ligand was synthesized by condensing 3-methoxysalicylaldehyde with equimolar 4-methoxybenzoylhydrazine in ethanol. Copper(II) acetate monohydrate (2 mmol) was added to a methanol solution (30 ml) containing 3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazone (2 mmol). The resulting mixture was refluxed with stirring for 1.5 h, and then cooled slowly to room temperature and filtered. Blue prism-shaped crystals were obtained from the solution after several days. Analysis calculated for $C_{44}H_{46}Cu_2N_6O_{10}$: C 55.87, H 4.90, N 8.88%; found: C 55.99, H 4.85, N 8.82%.

Crystal data

$[Cu_2(C_{16}H_{14}N_2O_4)_2(C_5H_5N)_2]\cdot 2CH_4O$
$M_r = 945.97$
Triclinic, $P\overline{1}$
$a = 7.8618\ (16)$ Å
$b = 11.709\ (2)$ Å
$c = 13.231\ (3)$ Å
$\alpha = 105.25\ (3)^\circ$
$\beta = 102.68\ (3)^\circ$
$\gamma = 104.42\ (3)^\circ$
$V = 1083.8\ (5)$ Å^3

$Z = 1$
$D_x = 1.449$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10 363 reflections
$\theta = 3.2\text{–}27.5^\circ$
$\mu = 1.05$ mm^{-1}
$T = 293\ (2)$ K
Prism, blue
0.38 × 0.25 × 0.17 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.692$, $T_{\max} = 0.842$
10 513 measured reflections

4904 independent reflections
4285 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\max} = 27.5^\circ$
$h = -8 \rightarrow 10$
$k = -15 \rightarrow 15$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.097$
$S = 1.06$
4904 reflections
284 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0599P)^2 + 0.1918P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Cu1—O1	1.910 (2)	O2—C9	1.283 (2)
Cu1—N1	1.920 (2)	N2—C9	1.324 (2)
Cu1—O2	1.947 (2)	N1—N2	1.398 (2)
Cu1—N3	2.006 (2)	N1—C7	1.290 (2)
Cu1—O1^{i}	2.725 (3)		
O1—Cu1—N1	92.90 (7	N1—Cu1—O2	80.97 (7)
O1—Cu1—O2	173.85 (5)	O1^{i}—Cu1—O1	83.61 (5)
O1—Cu1—N3	93.09 (7)	O1^{i}—Cu1—O2	96.42 (5)
O2—Cu1—N3	93.05 (7)	O1^{i}—Cu1—N1	95.63 (6)
N1—Cu1—N3	170.26 (6)	O1^{i}—Cu1—N3	92.71 (5)

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

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H23···N2	0.82	2.01	2.830 (2)	175

The H atoms on C and hydroxy O atoms were placed in calculated positions, with C—H = 0.93 (aromatic) and 0.96 Å (methyl), O—H = 0.82 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) or 1.5$U_{\rm eq}$(O,C$_{\rm methyl}$) in the riding-model approximation.

Data collection: *RAPID-AUTO* (Rigaku Corporation, 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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