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(1*H*-Benzimidazole-κN^3)[3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazonato-$\kappa^3 O,N,O'$]copper(II) methanol solvate

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In the title complex, $[Cu(C_{16}H_{14}N_2O_2)(C_7H_6N_2)]\cdot CH_4O$, $[Cu(L)(1H\text{-benzimidazole})]\cdot CH_3OH$, [$H_2L$ = 3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazone, $C_{16}H_{16}N_2O_4$], the Cu^{II} atom is coordinated by two O atoms and one N atom of the fully deprotonated tridentate hydrazone ligand and one N atom from the 1*H*-benzimidazole molecule, thus defining a square planar coordination geometry. Adjacent molecules are linked by hydrogen bonds into a chain structure.

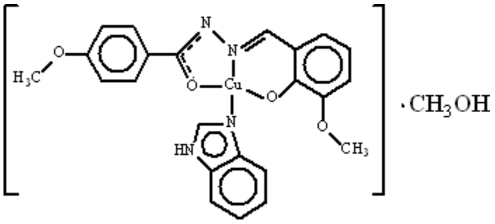
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.039
wR factor = 0.089
Data-to-parameter ratio = 15.5

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

Comment

The study of metal–hydrazone complexes is currently a subject of extensive research owing to their increasingly recognized biochemical activities. Most of the hydrazone ligands are formed by condensing benzoylhydrazine with acetylacetones, salicylaldehydes and their derivatives (Iskander *et al.*, 2000; Rao *et al.*, 1999). 3-Methoxysalicylaldehyde (4-methoxybenzoyl)hydrazone is a potential tridentate chelating agent formed by condensing 3-methoxysalicylaldehyde with 4-methoxybenzoylhydrazine. Recently, we have reported some complexes, *viz*. $[VOL(OCH_2CH_3)(CH_3CH_2OH)]$ and $[Fe(HL)Cl_2(CH_3OH)]\cdot CH_3OH$ (Huo, Gao, Liu, Zhao & Ng, 2004; Huo, Gao, Liu, Li *et al.*, 2004), in which the metal ions display distorted octahedral geometry, and $[VOL(CH_3O)]$ (Huo, Gao, Liu, Li & Ng, 2004), in which the V atom displays a distorted square-pyramidal configuration. As a result of our continuing study in the field, we report here the crystal structure of a new copper(II) complex, (1*H*-benzimidazole-κN^3)[3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazonato-$\kappa^3 O,N,O'$]copper(II) methanol solvate, $[Cu(L)(1H\text{-benzimidazole})]\cdot CH_3OH$ [H_2L = 3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazone], (I), acquired from the reaction of copper diacetate monohydrate, 1*H*-benzimidazole and H_2L in methanol solution.



(I)

As shown in Fig. 1, the asymmetric unit of the crystal structure of (I) consists of the mononuclear $[Cu(L)(1H\text{-benzimidazole})]$ complex and one methanol molecule. The coordination geometry of the Cu^{II} atom is square planar, in which the four coordination sites are occupied by two O atoms

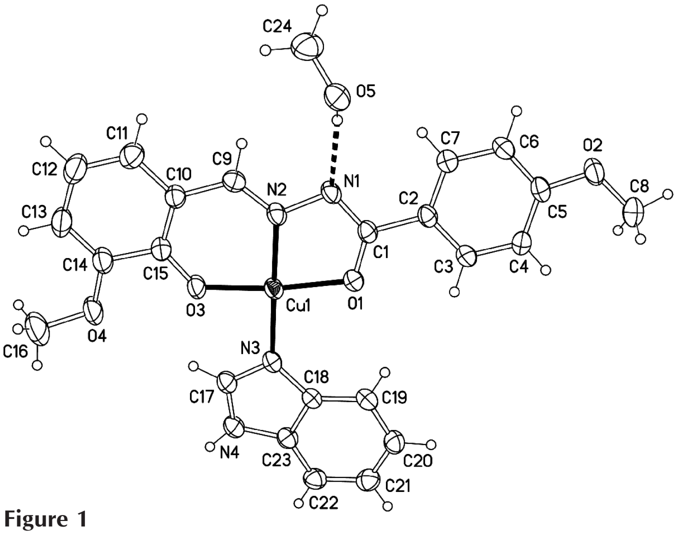


Figure 1
*ORTEP*II (Johnson, 1976) plot of (I), shown with 30% probability ellipsoids

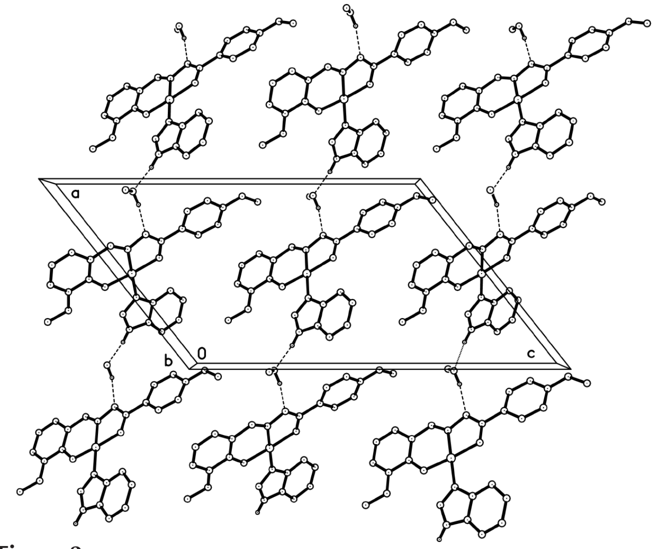


Figure 2
Detail of (I) showing part of the hydrogen-bonded chain structure. Hydrogen bonds are indicated by dashed lines. H atoms not involved in hydrogen bonding have been omitted.

and one N atom of the fully deprotonated tridentate hydrazone ligand, and one N atom from the benzimidazole molecule [r.m.s. deviation = 0.02 (3) Å and deviation of the Cu atom from the mean plane = 0.019 (3) Å]. The Cu—O1 distance [1.938 (2) Å] is longer than that of Cu—O3 [1.875 (2) Å], and the Cu—N3 distance of 1.960 (3) Å is the longest among all the coordination bond lengths. It should be noted that the O1—C1, O3—C15, N1—C1 and N2—C9 bond lengths of 1.274 (4), 1.302 (4), 1.323 (4) and 1.283 (5) Å, respectively, are relatively short, suggesting delocalization in the hydrazone ligand. The fully deprotonated tridentate hydrazone ligand is essentially planar, with an overall r.m.s. deviation of 0.10 (3) Å. The five-membered O1/C1/N1/N2/Cu1 chelate ring [r.m.s. deviation = 0.02 (3) Å] and the six-membered O3/C9/C10/C15/N2/Cu1 chelate ring [r.m.s. deviation = 0.03 (3) Å] are approximately coplanar, the dihedral angle being 2.4 (3)°.

The crystal structure is stabilized through intermolecular hydrogen bonds between the hydroxyl H atom of methanol and the uncoordinated hydrazidic N atom of an adjacent molecule, and the hydroxyl O atom of methanol also acts as a hydrogen-bond acceptor, forming a hydrogen bond with the NH group of benzimidazole. Adjacent molecules are linked by these hydrogen-bond interactions into a chain structure (Table 2 and Fig. 2).

Experimental

The ligand 3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazone was synthesized by condensing 3-methoxysalicylaldehyde with equimolar 4-methoxybenzoylhydrazine in ethanol (Gao *et al.*, 1998). Copper diacetate monohydrate (1 mmol) and 1*H*-benzimidazole (1 mmol) were added to a 30 ml methanol solution containing 3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazone (1 mmol). The resulting mixture was refluxed with stirring for 45 min and then cooled slowly to room temperature and filtered. Blue prism-shaped crystals were obtained from the solution over a period of several days. Analysis calculated for $C_{24}H_{24}CuN_4O_5$: C 56.30, H 4.72, N 10.94%; found: C 56.35, H 4.67, N 10.99%.

Crystal data

$[Cu(C_{16}H_{14}N_2O_4)(C_7H_6N_2)]\cdot CH_4O$
$M_r = 512.02$
Monoclinic, *Pc*
$a = 13.534$ (3) Å
$b = 5.0710$ (10) Å
$c = 21.294$ (6) Å
$\beta = 128.31$ (2)°
$V = 1146.7$ (6) Å^3
$Z = 2$

$D_x = 1.483$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9816 reflections
$\theta = 3.0$–27.5°
$\mu = 1.00$ mm^{-1}
$T = 293$ (2) K
Prism, blue
0.38 × 0.25 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.703$, $T_{max} = 0.841$
10 067 measured reflections

4912 independent reflections
4199 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 27.5°$
$h = -17 \rightarrow 17$
$k = -6 \rightarrow 6$
$l = -27 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.089$
$S = 1.02$
4912 reflections
316 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Absolute structure: Flack (1983), 2320 Friedel pairs
Flack parameter = 0.015 (11)

Table 1
Selected geometric parameters (Å, °).

Cu1—N2	1.920 (3)	N1—N2	1.394 (3)
Cu1—N3	1.960 (3)	N2—C9	1.283 (5)
Cu1—O1	1.938 (2)	O1—C1	1.274 (4)
Cu1—O3	1.875 (2)	O3—C15	1.302 (4)
N1—C1	1.323 (4)		
N2—Cu1—N3	179.2 (1)	O3—Cu1—N2	92.5 (1)
N2—Cu1—O1	80.8 (1)	O3—Cu1—N3	88.2 (1)
O1—Cu1—N3	98.5 (1)	O3—Cu1—O1	172.9 (1)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N4—H25$\cdots$O5^{i}	0.91 (2)	1.86 (2)	2.756 (4)	171 (4)
O5—H26$\cdots$N1	0.85 (5)	1.99 (5)	2.800 (4)	158 (5)

Symmetry code: (i) $x-1, 1-y, z-\frac{1}{2}$.

H atoms on carbon were placed in calculated positions, with C—H = 0.93 (aromatic) and 0.96 Å (methyl), and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) or $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(methyl C) in the riding-model approximation. H atoms on oxygen and nitrogen were located in difference Fourier synthesis maps and refined with O—H and N—H distance restraints of 0.85 (1) and 0.90 (1) Å, respectively, and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(N,O).

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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