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(Methanol-κ*O*)[3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazonato(2−)-κ^3*O*,*O*′,*N*]-dioxomolybdenum(VI)

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In the title complex, $[Mo(L)O_2(CH_3OH)]$ [H_2L is 3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazone, $C_{16}H_{16}N_2O_4$], the Mo atom has a distorted octahedral O_5N configuration, defined by two O atoms from oxo groups, two O atoms and one N atom from the tridentate hydrazone ligand, and one O atom from the solvent methanol molecule. The intermolecular O—H···N hydrogen bonds form centrosymmetric dimers, which are held in the crystal structure by van der Waals forces.

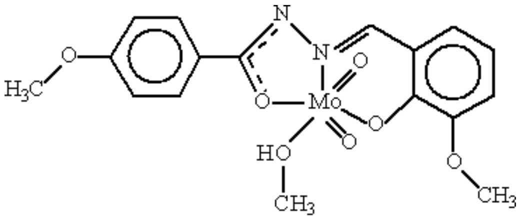
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.028
wR factor = 0.074
Data-to-parameter ratio = 16.4

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

Comment

The study of molybdenum–hydrazone complexes has attracted the interest of many researchers owing to the possible function of these complexes as nitrogenase models. A number of molybdenum(VI) complexes with hydrazone ligands have been structurally characterized to date; in these complexes, the hydrazone ligands are formed by condensing benzoylhydrazine with acetylacetones, salicylaldehydes and their derivatives (Rao *et al.*, 1999; Sur *et al.*, 1991). 3-Methoxysalicylaldehyde (4-methoxybenzoyl)hydrazone is a potential tridentate chelating agent formed by condensing 3-methoxysalicylaldehyde with 4-methoxybenzoylhydrazine. Recently, we have reported two VO^{3+} complexes, $[VOL(OCH_2CH_3)(CH_3CH_2OH)]$ (Huo, Gao, Liu, Zhao & Ng, 2004) and $[VOL(CH_3O)]$ (Huo, Gao, Liu, Li & Ng, 2004), and one Fe^{3+} complex, $[Fe(HL)Cl_2(CH_3OH)]\cdot CH_3OH$ (Huo, Gao, Liu, Li, Zhao & Zhao, 2004), based on the H_2L ligand [H_2L = 3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazone]; in the VO^{3+} complexes, the tridentate hydrazone ligand exhibits a formal charge of −2, whereas in the Fe^{3+} complex, the tridentate hydrazone ligand exhibits a formal charge of −1. We present here the new MoO_2^{2+} complex, $[MoO_2(L)(CH_3OH)]$, (I), obtained by the reaction of $MoO_2(acac)_2$ [$acac^-$ = acetylacetonate anion] and H_2L in methanol solution.



(I)

As shown in Fig. 1, the hydrazone ligand is fully deprotonated. The Mo(VI) ion has a distorted octahedral O_5N configuration (Table 1), defined by two O atoms from oxo

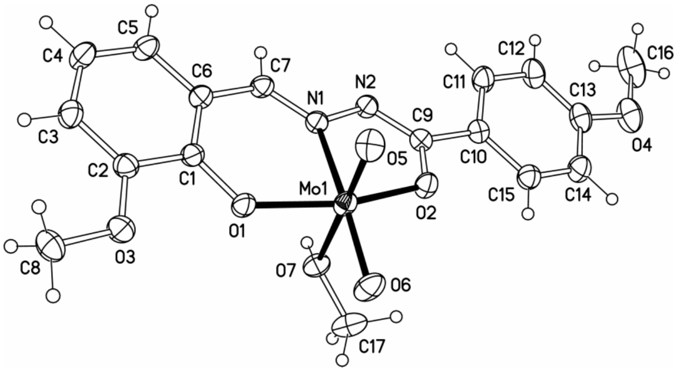


Figure 1
ORTEP plot of (I), with 30% probability displacement ellipsoids.

groups, two O atoms and one N atom from the tridentate hydrazone ligand, and one O atom from the solvent methanol molecule. The equatorial plane is defined by atoms O1, O2 and N1 of the fully deprotonated tridentate hydrazone ligand and atom O6 of the oxo group [r.m.s. deviation = 0.022 (3) Å]. The Mo^{VI} atom is displaced by 0.345 (3) Å from the equatorial plane towards the axial oxo atom O5. The axial sites are occupied by atoms O5 and O7, the O5—Mo—O7 angle being 171.71 (7)°. The bond distances in the equatorial plane follow the order oxo O < phenoxide O < enol O < imine N. The distances between the Mo atom and the two terminal oxo O atoms [1.7048 (17) and 1.6985 (15) Å] show that these bonds have partial double-bond character; the O5—Mo—O6 angle is 105.94 (8)°. The Mo—O7 distance [2.3970 (16) Å] is the longest of all the Mo—O bond lengths. The C7—N1 [1.286 (3) Å], N1—N2 [1.402 (2) Å], C9—N2 [1.306 (2) Å] and C9—O2 [1.315 (2) Å] distances are relatively short, indicating delocalization. The five-membered O2/C9/N1/N2/Mo1 chelate ring [r.m.s. deviation = 0.008 (3) Å] is approximately planar; the six-membered O1/C1/C6/C7/N1/Mo1 chelate ring is also basically planar, with an r.m.s. deviation of 0.140 (3) Å, and the dihedral angle between these planes is 8.92 (6)°. The planes of the two benzene rings in the hydrazone ligand make a dihedral angle of 0.52 (7)°. Intermolecular O—H···N hydrogen bonds (Table 2) involving the hydroxyl group of the methanol molecule and the adjacent deprotonated uncoordinated atom N2 of the tridentate hydrazone ligand form centrosymmetric dimers, which are held in the crystal structure by van der Waals forces (Fig. 2).

Experimental

The ligand 3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazone was synthesized by condensing 3-methoxysalicylaldehyde with equimolar 4-methoxybenzoylhydrazine in ethanol. A methanol solution (15 ml) of $MoO_2(acac)_2$ (2 mmol) was added dropwise to a methanol solution (15 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. Red prismatic crystals were obtained from the solution after several days. Analysis calculated for $C_{17}H_{18}MoN_2O_7$: C 44.56, H 3.96, N 6.11%; found: C 44.62, H 4.03, N 6.15%.

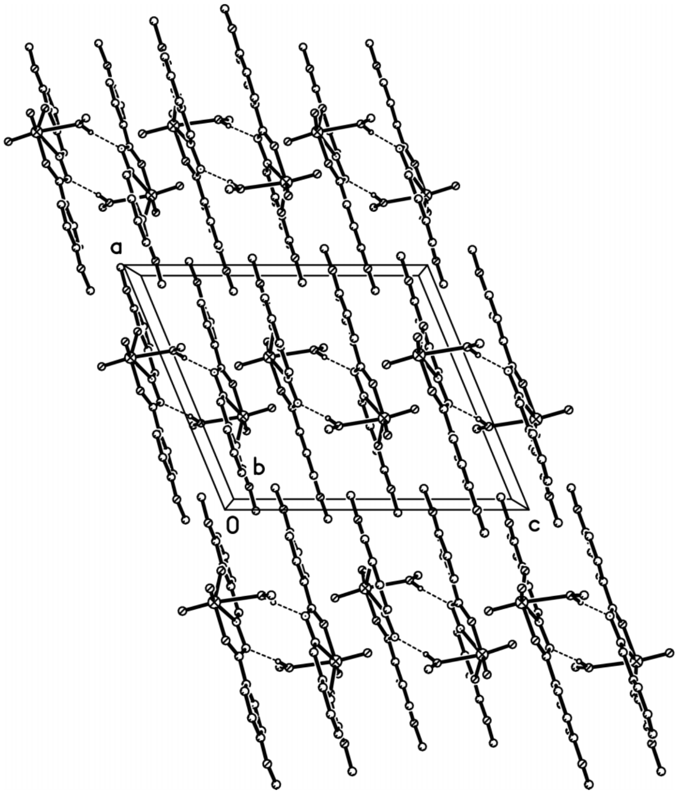


Figure 2
The packing of (I), with the O—H···O hydrogen bonds denoted by dashed lines. H atoms not involved in hydrogen bonding have been omitted.

Crystal data

$[Mo(C_{16}H_{14}N_2O_4)O_2(CH_4O)]$
$M_r = 458.27$
Monoclinic, $P2_1/c$
$a = 13.131$ (3) Å
$b = 9.942$ (2) Å
$c = 15.031$ (3) Å
$\beta = 112.47$ (3)°
$V = 1813.2$ (8) Å^3
$Z = 4$

$D_x = 1.679$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10 166 reflections
$\theta = 4.0$–28.0°
$\mu = 0.77$ mm^{-1}
$T = 293$ (2) K
Prism, red
0.39 × 0.26 × 0.21 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.754$, $T_{max} = 0.856$
16 671 measured reflections

4109 independent reflections
3774 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 27.5°$
$h = -17 \rightarrow 17$
$k = -12 \rightarrow 12$
$l = -19 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.074$
$S = 1.05$
4109 reflections
250 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 0.8397P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Mo1—N1	2.2405 (15)	N1—N2	1.402 (2)
Mo1—O1	1.9201 (14)	N1—C7	1.286 (3)
Mo1—O2	2.0164 (14)	N2—C9	1.306 (2)
Mo1—O5	1.7048 (17)	O1—C1	1.348 (2)
Mo1—O6	1.6985 (15)	O2—C9	1.315 (2)
Mo1—O7	2.3970 (16)		
N1—Mo1—O7	76.69 (6)	O5—Mo1—O1	100.56 (8)
O1—Mo1—N1	81.00 (6)	O5—Mo1—O2	96.78 (8)
O1—Mo1—O2	148.67 (6)	O6—Mo1—N1	156.95 (7)
O1—Mo1—O7	81.76 (6)	O6—Mo1—O1	102.21 (7)
O2—Mo1—N1	71.42 (6)	O6—Mo1—O2	97.79 (7)
O2—Mo1—O7	77.75 (6)	O6—Mo1—O5	105.94 (8)
O5—Mo1—O7	171.71 (7)	O6—Mo1—O7	81.17 (7)
O5—Mo1—N1	95.73 (7)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H18···N2^{i}	0.83 (3)	1.99 (3)	2.817 (2)	169 (3)

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

H atoms on C atoms were placed in calculated positions, with C—H = 0.93 Å (aromatic) and 0.96 Å (methyl), and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C_{methyl})$, in the riding-model approximation. The H atom on the hydroxy O atom was located in a difference Fourier synthesis maps and refined with an O—H distance restraint of 0.85 (1) Å and $U_{iso}(H) = 1.5U_{eq}(O)$.

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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