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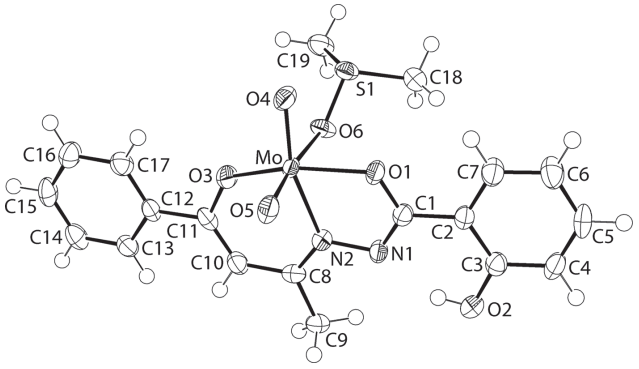
Crystal structure of (dimethyl sulfoxide)-dioxido-[2-hydroxy-*N′*-(4-oxo-4-phenylbutan-2-ylidene)benzohydrazidato κ^3*N*,*O*,*O′*]molybdenum(VI), $C_{19}H_{20}MoN_2O_6S$



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Abstract

$C_{19}H_{20}MoN_2O_6S$, orthorhombic, *Pbca* (no. 61), $a = 13.4060(1)$ Å, $b = 16.5112(1)$ Å, $c = 17.6357(1)$ Å, $V = 3903.65(4)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0217$, $wR_{ref}(F^2) = 0.0602$, $T = 100(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All chemicals and solvents were used as purchased without further purification. The melting point was determined using a Mel-temp II digital melting point apparatus and was uncorrected. The IR spectrum was obtained on a Bruker Vertex 70v FTIR Spectrometer in the scan range 4000–400 cm^{-1}. The ^{1}H NMR spectrum was recorded at room temperature in $CDCl_3$

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Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.12 × 0.09 × 0.08 mm
Wavelength:	Cu *Kα* radiation (1.54184 Å)
μ:	6.86 mm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	87956, 3477, 0.037
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3445
$N(param)_{refined}$:	268
Programs:	Bruker [1], SHELX [2, 3], WinGX/ORTEP [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Mo	0.70272(2)	0.64889(2)	0.40616(2)	0.01495(7)
S1	0.49306(4)	0.75913(3)	0.37860(3)	0.01992(12)
O1	0.67746(11)	0.64719(8)	0.29435(8)	0.0207(3)
O2	0.59180(12)	0.43933(9)	0.17240(8)	0.0257(3)
H2O	0.595(2)	0.4485(17)	0.2200(6)	0.039*
O3	0.66410(11)	0.61787(8)	0.50864(8)	0.0232(3)
O4	0.71491(11)	0.75179(9)	0.41181(8)	0.0224(3)
O5	0.82090(12)	0.61232(10)	0.40666(7)	0.0238(3)
O6	0.53144(11)	0.67586(9)	0.40306(8)	0.0216(3)
N1	0.61907(12)	0.51610(10)	0.30067(9)	0.0187(3)
N2	0.63576(12)	0.52886(10)	0.37796(9)	0.0186(3)
C1	0.64235(14)	0.58034(12)	0.26234(11)	0.0177(4)
C2	0.62973(14)	0.58199(12)	0.17992(11)	0.0180(4)
C3	0.60663(14)	0.51170(12)	0.13812(11)	0.0197(4)
C4	0.60024(15)	0.51606(13)	0.05935(12)	0.0245(4)
H4	0.5869	0.4685	0.0308	0.029*
C5	0.61325(16)	0.58913(15)	0.02273(12)	0.0281(5)
H5	0.6089	0.5913	−0.0310	0.034*
C6	0.63257(18)	0.65948(14)	0.06317(13)	0.0300(5)
H6	0.6395	0.7099	0.0377	0.036*
C7	0.64158(17)	0.65506(13)	0.14116(12)	0.0253(5)
H7	0.6562	0.7029	0.1690	0.030*
C8	0.61799(15)	0.46797(12)	0.42312(12)	0.0191(4)
C9	0.58919(16)	0.38593(12)	0.39468(12)	0.0219(4)
H9A	0.5511	0.3916	0.3476	0.033*
H9B	0.5482	0.3585	0.4328	0.033*
H9C	0.6495	0.3540	0.3850	0.033*
C10	0.62743(15)	0.47795(12)	0.50377(11)	0.0216(4)
H10	0.6185	0.4305	0.5335	0.026*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C11	0.64755(14)	0.54709(12)	0.54262(11)	0.0189(4)
C12	0.64907(14)	0.55244(12)	0.62672(11)	0.0183(4)
C13	0.62411(15)	0.48592(12)	0.67207(12)	0.0224(4)
H13	0.6060	0.4360	0.6492	0.027*
C14	0.62576(16)	0.49289(13)	0.75058(12)	0.0256(4)
H14	0.6096	0.4473	0.7811	0.031*
C15	0.65078(16)	0.56556(14)	0.78473(11)	0.0256(5)
H15	0.6520	0.5697	0.8385	0.031*
C16	0.67404(17)	0.63220(14)	0.74047(12)	0.0252(4)
H16	0.6905	0.6824	0.7636	0.030*
C17	0.67317(16)	0.62514(13)	0.66205(12)	0.0227(4)
H17	0.6894	0.6709	0.6319	0.027*
C18	0.42329(19)	0.74120(14)	0.29391(12)	0.0318(5)
H18A	0.4684	0.7230	0.2536	0.048*
H18B	0.3902	0.7914	0.2782	0.048*
H18C	0.3730	0.6994	0.3035	0.048*
C19	0.39214(16)	0.77829(13)	0.44150(12)	0.0260(4)
H19A	0.3472	0.7315	0.4420	0.039*
H19B	0.3556	0.8264	0.4245	0.039*
H19C	0.4180	0.7876	0.4927	0.039*

solution on a Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane.

The Schiff base ligand was synthesised from the reaction of benzoylacetone (Sigma Aldrich) and 2-hydroxybenzhydrazide (Fluka) in a 1:1 molar ratio. Bis(acetylacetonato)dioxomolybdenum(VI) (Sigma Aldrich, 0.33 g, 1 mmol) and the prepared Schiff base were dissolved in methanol (30 mL) and the mixture was refluxed for 2 h. After filtration, the filtrate was evaporated slowly until yellow crystals were formed. The crystals were filtered, washed with a minimum amount of methanol and air-dried *in vacuo* over P_4O_{10}. **Yield:** 0.20 g (40%). **M.pt:** 469–471 K. **IR** (cm^{-1}) 1612 (m) ν(C—N), 1599 (s) ν(C—N), 1548 (s) ν(C—O), 1368 (m) ν(C—O), 1260 (m) ν(C—O), 1085 (m) ν(C—O), 1034 (m) ν(S—O), 931 (m) ν(Mo—O), 900 (m) ν(Mo—O). **^{1}H NMR** ($CDCl_3$, ppm): δ 2.46 (s, 3H, CH_3), 2.67 (s, 6H, CH_3), 6.12 (s, 1H, CH), 6.88 (d, 1H, J = 7.10 Hz, Ph—H), 6.91 (d, 1H, J = 8.10 Hz, Ph—H), 7.35–7.44 (m, 5H, Ph—H), 7.83 (d, 1H, J = 7.85 Hz, Ph—H), 7.84 (d, 1H, J = 7.90 Hz, Ph—H), 11.48 (s, 1H, OH).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.98 Å) and refined as riding with U_{iso}(H) = 1.2–1.5U_{eq}(C). The O-bound H-atom was also geometrically placed (O—H = 0.84 Å) and refined as riding with U_{iso}(H) = 1.5U_{eq}(O).

Comment

The study of di-oxido-molybdenum complexes with di-anionic tridentate ligands is particularly significant as the coordination environment of the $[MoO_2]^{2+}$ core is known to be crucial as an open active site for catalytic oxidation processes [5, 6]. In this work, the synthesis and crystal structure analysis of the title complex, $Mo(=O)_2(L)(O=SMe_2)$, (I), where H_2L is 2-hydroxy-*N*-[(2*Z*)-4-hydroxy-4-phenylbut-2-en-2-yl] benzenecarbohydrazonic acid, with a slight modification of the Schiff base ligand employed in earlier reported work [7], is described in continuation of on-going studies in this area [7–9].

The mononuclear title complex in (I) is shown in the figure (70% probability displacement ellipsoids). The Mo(VI) centre is complexed by O1, O3 and imine-N2 atoms, derived from the tridentate Schiff base di-anion, the oxido-O4 and O5 atoms as well as the O6 atom of the dimethylsulphoxide ligand [10]. This results in a N_2O_4 donor set that defines an approximate octahedral geometry in which the oxido groups are *cis* to each other, and where the three donor atoms of the L^{2-} anion occupy meridional positions. The O1—Mo—O3 angle [149.93(6)°] deviates significantly from linearity, which is due mainly to the acute angles subtended by the five-[O1—Mo—N2 = 72.54(6)°] and six-membered [O3—Mo—N2 = 82.32(6)°] chelate rings owing to the tridentate mode of coordination of the Schiff base di-anion. Each of the five- and six-membered chleate rings adopts an envelope configuration with the Mo atoms being the flap atom. In the smaller chelate ring, the Mo flap atom lies 0.106(3) Å out of the plane defined by the four remaining atoms (r.m.s. deviation = 0.0014 Å). In the larger chelate ring, the envelope configuration is significantly more pronounced with the Mo atom lying 0.446(3) Å out of the least-squares plane defined by the five remaining atoms of the chelate ring (r.m.s. deviation = 0.0158 Å). The dihedral angle formed between the least-squares planes through the chelate rings is 9.37(5)°. The dihedral angles between the five-membered chelate ring and the pendent hydroxyphenyl ring is 10.94(6)°, between the six-membered ring and adjacent phenyl ring is 2.45(6)°, and between the hydroxyphenyl and phenyl rings is 7.58(6)°. Thus, to a first approximation, the Schiff base ligand is planar. An intramolecular loop – S(6) graph set – is evident owing to the formation of a hydroxy-O—H···N(imine) hydrogen bond [O2—H2O···N1: H2O···N1 = 1.837(19) Å, O2···N1 = 2.619(2) Å with angle at H2O = 151(3)°].

In the crystal of (I), C—H···O interactions connect complexes into a three-dimensional architecture. Thus, hydroxyphenyl, phenyl- and imine-methyl-C—H···O(oxo) [C6—H6···O4^{i}: H6···O4^{i} = 2.52 Å, C6···O4^{i} = 3.239(3) Å with angle at H6 = 132°; C14—H14···O5^{ii}: H14···O5^{ii} = 2.60 Å, C14···O5^{ii} = 3.333(3) Å with angle at H14 = 135° and C9—H9c···O4^{iii}: H9c···O4^{iii} = 2.53 Å, C9···O4^{iii} = 3.449(3) Å with angle at H9c = 157° for symmetry operations (i) x, 3/2 − y, −1/2 + z, (ii) 3/2 − x, 1 − y, 1/2 + z and (iii)

$3/2 - x$, $-1/2 + y$, z] interactions lead to the formation of a supramolecular layer in the *bc*-plane. The coordinated dimethylsulphoxide groups protrude to either side of the layer and inter-digitate with neighbouring layers with the connections between them being of the type dimethylsulphoxide-C—H···O(oxide) [C18—H18b···$O1^{iv}$: H18b···$O1^{iv}$ = 2.60 Å, C18···$O1^{iv}$ = 3.331(3) Å with angle at H18b = 131° for (iv) $1 - x$, $1/2 + z$, $1/2 - z$].

Further analysis of the molecular packing was conducted with Crystal Explorer 17 [11] to calculate the Hirshfeld surfaces of (I) along with the full and delineated two-dimensional fingerprint plots following literature precedents [12]. This analysis showed, reflecting the formation of many C—H···O contacts in the crystal, that O···H/H···O contacts amounted to 30.7% of all contacts on the calculated Hirshfeld surface, approaching the 41.3% contributed by H···H contacts. The C···H/H···C contacts to the surface, at 15.7%, were also prominent with smaller but, notable C···C [4.8%], N···H/H···N [2.1%], O···C/C···O [1.6%] and N···C/N···C [1.4%] contacts. However, these occur at separations greater than the sum of the respective van der Waals radii.

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