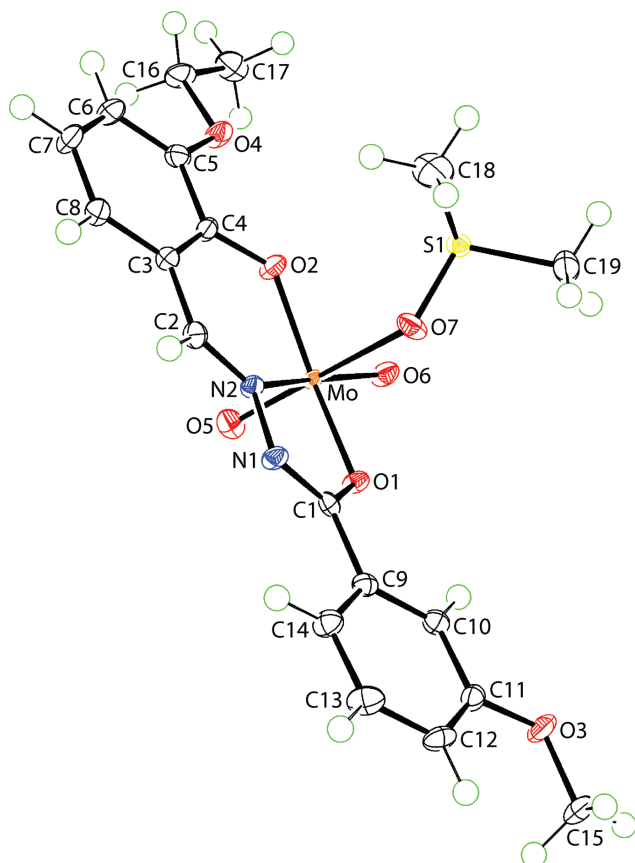


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Crystal structure of (*N,N*-dimethylsulphoxide)-[*N*-(3-ethoxy-2-(oxide)benzylidene)-3-methoxybenzenecarbohydrazonato- $\kappa^3 N,O,O'$]-dioxomolybdenum(VI), $C_{19}H_{22}MoN_2O_7S$



Abstract

$C_{19}H_{22}MoN_2O_7S$, triclinic, $P\bar{1}$ (no. 2), $a = 7.9719(2)$ Å, $b = 10.3854(2)$ Å, $c = 13.1042(3)$ Å, $\alpha = 81.451(2)^\circ$, $\beta = 72.444(2)^\circ$, $\gamma = 87.930(2)^\circ$, $V = 1022.85(4)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0181$, $wR_{ref}(F^2) = 0.0503$, $T = 100(2)$ 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.

Table 1: Data collection and handling.

Crystal:	Brown prism
Size:	0.20 × 0.14 × 0.11 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	6.60 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	24067, 3664, 0.023
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 3660
$N(param)_{refined}$:	275
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

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Source of material

The ligand, 3-ethoxysalicylaldehyde 3-methoxybenzoic hydrazone was prepared from the 1:1 molar reaction of 3-ethoxysalicylaldehyde (Merck) and 3-methoxybenzoic hydrazide (Sigma-Aldrich). Next, $MoO_2(acetylacetonate)_2$ (Sigma-Aldrich; 0.33 g, 1 mmol) was added to the freshly prepared Schiff base ligand (1 mmol, 0.302 g) in methanol (40 mL). The resulting solution was refluxed for 3 h. The filtrate was evaporated until a beige precipitate was obtained. The precipitate was recrystallised from acetone-methanol by slow evaporation to yield brown crystals. The mixture was refluxed for 2 h. The title compound was isolated from the recrystallisation of the complex in DMSO. Yield: 0.32 g (63.5%). **M.pt** (Mel-temp II digital melting point apparatus): 457–459 K. **Calcd.** for $C_{19}H_{22}MoN_2O_7S$: C, 44.02; H, 4.52; N, 5.40; S, 6.18%; Found: C, 43.78; H, 4.21; N, 5.25; S, 6.37%.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
Mo	0.63757(2)	0.52131(2)	0.22781(2)	0.00681(6)
S1	0.35944(5)	0.60157(4)	0.08143(3)	0.00964(9)
O1	0.72761(15)	0.70120(11)	0.22000(9)	0.0095(2)
O2	0.44349(16)	0.39946(12)	0.26529(10)	0.0121(3)
O3	1.02885(17)	1.12676(12)	0.07792(10)	0.0158(3)
O4	0.30680(17)	0.16869(12)	0.28011(10)	0.0143(3)
O5	0.75568(17)	0.44367(12)	0.30673(10)	0.0139(3)
O6	0.75092(16)	0.49783(12)	0.09827(10)	0.0131(3)
O7	0.45077(17)	0.65056(12)	0.15598(10)	0.0138(3)
N1	0.50584(19)	0.73704(14)	0.37379(12)	0.0099(3)
N2	0.46125(19)	0.61073(14)	0.36605(11)	0.0087(3)
C1	0.6469(2)	0.77439(16)	0.29460(13)	0.0090(3)
C2	0.3272(2)	0.55767(17)	0.44178(14)	0.0103(3)
H2	0.269685	0.605569	0.498753	0.012*
C3	0.2600(2)	0.42909(17)	0.44443(14)	0.0107(3)
C4	0.3193(2)	0.35610(17)	0.35869(14)	0.0102(3)
C5	0.2427(2)	0.23274(17)	0.36720(14)	0.0119(3)
C6	0.1089(2)	0.18586(18)	0.46033(15)	0.0154(4)
H6	0.056701	0.103271	0.465960	0.018*
C7	0.0506(2)	0.25867(18)	0.54533(15)	0.0157(4)
H7	-0.040306	0.225286	0.608556	0.019*
C8	0.1242(2)	0.37857(18)	0.53802(14)	0.0127(4)
H8	0.083584	0.427837	0.596176	0.015*
C9	0.7209(2)	0.90563(16)	0.28371(14)	0.0096(3)
C10	0.8445(2)	0.95763(17)	0.18728(14)	0.0105(3)
H10	0.885136	0.907328	0.129816	0.013*
C11	0.9081(2)	1.08386(17)	0.17577(14)	0.0111(3)
C12	0.8502(2)	1.15780(17)	0.25960(15)	0.0129(4)
H12	0.893928	1.243801	0.251533	0.015*
C13	0.7271(2)	1.10421(18)	0.35587(15)	0.0150(4)
H13	0.686753	1.154527	0.413347	0.018*
C14	0.6630(2)	0.97915(17)	0.36879(15)	0.0128(3)
H14	0.580227	0.943322	0.434967	0.015*
C15	1.1074(3)	1.25225(18)	0.06526(16)	0.0172(4)
H15A	1.016291	1.319053	0.071545	0.026*
H15B	1.195254	1.269555	-0.006061	0.026*
H15C	1.164495	1.254022	0.121628	0.026*
C16	0.2625(2)	0.03221(17)	0.29531(16)	0.0156(4)
H16A	0.133539	0.020704	0.313662	0.019*
H16B	0.301976	-0.015489	0.355084	0.019*
C17	0.3536(3)	-0.01911(18)	0.19127(16)	0.0182(4)
H17A	0.305435	0.022881	0.134240	0.027*
H17B	0.334859	-0.113459	0.201222	0.027*
H17C	0.479985	-0.000186	0.170530	0.027*
C18	0.1309(3)	0.6058(2)	0.15159(17)	0.0254(5)
H18A	0.103717	0.541367	0.217195	0.038*
H18B	0.062940	0.585427	0.104825	0.038*
H18C	0.100001	0.692804	0.171420	0.038*
C19	0.3722(3)	0.73839(18)	-0.02091(15)	0.0185(4)
H19A	0.342784	0.817728	0.012768	0.028*
H19B	0.288895	0.726219	-0.060560	0.028*
H19C	0.491842	0.746293	-0.071098	0.028*

IR (Bruker Vertex 70v FTIR Spectrophotometer; cm⁻¹): 1617 (m) ν(C–N), 1596 (s) ν(C–N), 1522 (s) ν(C–O), 1286 (s) ν(C–O), 1081 (m) ν(C–O), 922 (m) ν(Mo–O), 890 (s) ν(Mo–O). **¹H NMR** (Bruker Ascend 400 MHz NMR spectrometer, chemical shifts relative to Me₄Si, DMSO solution, p.p.m.): δ 1.38 (s, 3H, CH₃), 2.50 (s, 6H, SCH₃), 3.85 (s, 2H, OCH₂), 4.09 (s, 3H, OCH₃), 7.01–7.50 (m, 7H, Phenyl-H), 8.93 (s, 1H, NCH). **¹³C{¹H} NMR** (as for ¹H NMR): δ 15.2 (CH₃), 39.9 (SCH₃), 55.7 (OCH₂), 64.8 (OCH₃), 112.9, 118.6, 119.1, 120.9, 122.0, 126.0, 130.5, 131.8, 148.1, 149.9, 156.7, 159.8 (Aryl–C), 169.0 (CN).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5U_{eq}(C)$.

Comment

It is now well established that the sixth coordination site in mononuclear dioxidomolybdenum(VI) complexes of ONO-donor Schiff base dianions is labile [5–8], with exchange between different molecules, e.g. solvent, often observed. Further interest in these molecules arises as a result of investigations of putative anti-cancer potential [6, 8]. In continuation of structural studies of Mo complexes of Schiff bases [6, 9, 10], the title complex, (I), with a coordinated DMSO molecule, was investigated crystallographically with a further analysis of the molecular packing performed through the calculated Hirshfeld surfaces. The molecular structure of (I) is shown in the figure (70% displacement ellipsoids).

The Mo atom is coordinated within a NO₅ donor set defined by cis-oxo atoms [Mo–O5, O6 = 1.7003(12), 1.7145(12) Å] a DMSO-O [Mo–O7 = 2.2872(12) Å], and enolic-O [Mo–O1 = 2.0029(12) Å], phenolate-O [Mo–O2 = 1.9325(12) Å] and imine-N [Mo–N2 = 2.2337(14) Å] atoms of the di-negative, tridentate Schiff base ligand. The longer Mo–O6(oxo) bond has the O6 atom approximately trans [160.75(6)°] to the imine-N2 atom, and the more strongly bound oxo-O5 atom trans to the weakly-bound DMSO-O7 atom. The other trans angle in the six-coordinate geometry which approximates an octahedron is 150.01(5)°, for the O1–Mo–O2 angle. In this description, the Mo atom lies 0.3037(7) Å out of the basal plane defined by the O1, O2, O6 and N2 [r.m.s. deviation = 0.0091 Å] in the direction of the O5 atom.

The mode of coordination of the Schiff base di-anion leads to the formation of five- and six-membered chelate rings. The five-membered ring is planar, exhibiting a r.m.s. deviation of 0.0057 Å for the fitted atoms with the maximum deviation being 0.0083(8) Å for the O1 atom.

By contrast, the six-membered ring is non-planar and is best described as being based on an envelope with the Mo atom, the flap, lying 0.486(2) Å above the plane of the five remaining atoms [r.m.s. deviation = 0.0379 Å] with a maximum deviation = 0.0550(12) Å for atom C2. The dihedral angle between the five-membered chelate ring and the planar region of the six-membered ring is 11.25(9)°. The dihedral angle between the outer aromatic rings is 5.61(9)°.

The most closely related structure in the literature is of the analogue where the ethoxy substituent of (I) is methoxy [8]. As would be anticipated, the same trends in geometric parameters are evident.

Non-covalent C—H...O intermolecular interactions provide specific points of contact between molecules in the crystal of (I). The acceptor atoms are oxo-O5 and -O6 exclusively with the former forming three contacts and the later, two. The donor atoms are imine-C—H, phenyl-C—H, methoxy-C—H and DMSO-methyl-C—H [range of H...C = 2.42 to 2.58 Å and range of angles at H = 118 to 133°].

A further analysis of the molecular packing was performed by calculating the Hirshfeld surface as well as the full- and delineated two-dimensional fingerprint plots, following standard protocols [11] and the program Crystal Explorer 17 [12]. The analysis confirms the importance of C—H...O interactions in contributing to the stability of the crystal, contributing 30.8% of all surface contacts, and second only to H...H contacts, i.e. 43.0%. The other major contribution to surface contacts, at 16.8%, comes from C...H/H...C contacts. The only other contacts making over 1% contributions to the Hirshfeld surface are H...H/H...N [2.7%], N...C/C...N [1.8%] and C...C [1.6%].

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