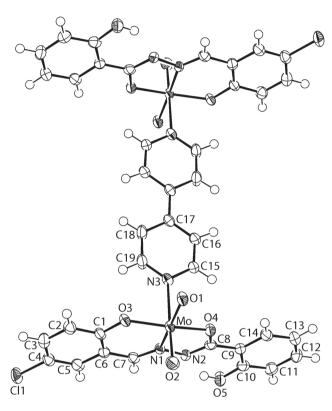
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Kong Mun Lo, See Mun Lee and Edward R.T. Tiekink*

Crystal structure of bis{(N-[(5-chloro-2-oxidophenyl)methylidene]-2hydroxybenzenecarbohydrazonato)-dioxo-molybdenum(VI)}(µ2-4,4'bipyridine), C₃₈H₂₆Cl₂Mo₂N₆O₁₀



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Abstract

 $C_{38}H_{26}Cl_2Mo_2N_6O_{10}$, triclinic, $P\bar{1}$ (no. 2), a = 7.7151(2) Å, b = 10.5336(2) Å,c = 12.5668(2) Å, $\alpha = 73.027(2)^{\circ}$ $V = 917.83(4) \text{ Å}^3, Z = 1,$ $\beta = 76.226(2)^{\circ}$ $\gamma = 72.269(2)^{\circ}$, $R_{\rm gt}(F) = 0.0234$, $wR_{\rm ref}(F^2) = 0.0612$, T = 100(2) K.

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Kong Mun Lo and See Mun Lee: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 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: $0.12\times0.08\times0.07~\text{mm}$ Wavelength: Cu Kα radiation (1.54178 Å) 7.54 mm^{-1} XtaLAB Synergy, ω Diffractometer, scan mode: θ_{max} , completeness: 67.1°, >99% N(hkl)_{measured}, N(hkl)_{unique}, R_{int}: 21955, 3275, 0.030 Criterion for I_{obs} , $N(hkl)_{gt}$: $I_{\rm obs} > 2 \ \sigma(I_{\rm obs}), 3250$ N(param)_{refined}: 263 CrysAlisPRO [1], SHELX [2, 3], Programs: WinGX/ORTEP [4]

Source of material

All chemicals and solvents were used as purchased without further purification. The melting point was determined on 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 range 4000 to 400 cm $^{-1}$. The ¹H NMR spectrum was recorded in DMSO-d₆ solution on a Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane.

The Schiff base molecule was synthesized from the reaction of 5-chlorosalicylaldehyde (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 Schiff base (0.29 g, 1 mmol) were dissolved in methanol (30 mL) and the mixture was refluxed for 2 h. Next, 4,4'-bipyridine (Sigma Aldrich, 0.08 g, 0.5 mmol) was added into the mixture. After filtration, the filtrate was evaporated slowly until light-brown crystals were formed. The crystals were filtered, washed with a minimum amount of methanol and air-dried in vacuo over P₄O₁₀. Yield: 0.24 g (49%). **M.pt:** 491–493 K. **IR** (cm⁻¹) 1610 (m) ν (C–N), 1601 (s) $\nu(C-N)$, 1542 (s) $\nu(C-O)$, 1343 $\nu(C-O)$, 1261 $\nu(C-O)$, 1092 (m) $\nu(C-O)$, 931(m) $\nu(Mo-O)$, 902 (m) $\nu(Mo-O)$. 1 H NMR (DMSO-d₆, ppm): δ 6.98–7.04 (m, 6H, Ph—H), 7.87 (d, 4H, J = 9.10 Hz, py—H), 7.59 (d, 4H, J = 8.81 Hz,

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\mathring{A}^2).

Atom	х	у	Z	U _{iso} */U _{eq}
Мо	0.55579(2)	0.32783(2)	0.31241(2)	0.01358(8)
Cl1	-0.09949(8)	0.14896(6)	0.83536(5)	0.02601(14)
01	0.6590(2)	0.25368(16)	0.20158(14)	0.0185(3)
02	0.7201(2)	0.28583(18)	0.39486(14)	0.0218(4)
03	0.3947(2)	0.21441(16)	0.40121(13)	0.0174(3)
04	0.5864(2)	0.51599(16)	0.23371(13)	0.0168(3)
05	0.3506(2)	0.86723(18)	0.37065(15)	0.0238(4)
H50	0.3318	0.7888	0.3985	0.036*
N1	0.3595(3)	0.47508(19)	0.41200(16)	0.0138(4)
N2	0.3761(3)	0.6092(2)	0.37409(16)	0.0160(4)
N3	0.2983(3)	0.4181(2)	0.20163(16)	0.0165(4)
C1	0.2799(3)	0.2048(3)	0.50102(19)	0.0175(5)
C2	0.2291(3)	0.0809(2)	0.5502(2)	0.0204(5)
H2	0.2750	0.0077	0.5130	0.024*
C3	0.1131(3)	0.0648(3)	0.6520(2)	0.0223(5)
H3	0.0799	-0.0195	0.6858	0.027*
C4	0.0444(3)	0.1733(3)	0.7055(2)	0.0208(5)
C5	0.0874(3)	0.2970(3)	0.6575(2)	0.0201(5)
H5	0.0369	0.3701	0.6946	0.024*
C6	0.2070(3)	0.3156(2)	0.5530(2)	0.0174(5)
C7	0.2454(3)	0.4479(2)	0.50422(19)	0.0167(5)
H7	0.1833	0.5195	0.5419	0.020*
C8	0.4978(3)	0.6212(2)	0.2808(2)	0.0169(5)
C9	0.5398(3)	0.7530(2)	0.2240(2)	0.0171(5)
C10	0.4658(3)	0.8681(3)	0.2709(2)	0.0190(5)
C11	0.5138(4)	0.9908(3)	0.2135(2)	0.0224(5)
H11	0.4661	1.0685	0.2454	0.027*
C12	0.6297(4)	1.0003(3)	0.1111(2)	0.0238(5)
H12	0.6612	1.0845	0.0731	0.029*
C13	0.7013(4)	0.8882(3)	0.0626(2)	0.0233(5)
H13	0.7798	0.8959	-0.0086	0.028*
C14	0.6568(3)	0.7651(3)	0.1192(2)	0.0190(5)
H14	0.7059	0.6880	0.0866	0.023*
C15	0.3036(4)	0.5211(3)	0.1091(2)	0.0214(5)
H15	0.3916	0.5724	0.0973	0.026*
C16	0.1891(4)	0.5573(3)	0.0300(2)	0.0227(5)
H16	0.1984	0.6325	-0.0331	0.027*
C17	0.0604(3)	0.4839(2)	0.04265(19)	0.0164(5)
C18	0.0524(3)	0.3773(3)	0.1394(2)	0.0240(5)
H18	-0.0342	0.3244	0.1531	0.029*
C19	0.1703(3)	0.3488(3)	0.2151(2)	0.0230(5)
H19	0.1610	0.2763	0.2804	0.028*

py = H), 7.60-7.83 (m, 8H, Ph-H), 8.73 (s, 2H, NCH), 11.33 (s, 2H, OH).

Experimental details

The C-bound H atoms were geometrically placed (C— $\rm H=0.95~\mathring{A})$ and refined as riding with $U_{\rm iso}(\rm H)=1.2 U_{\rm eq}(\rm C)$. The O-bound H-atom was also geometrically placed (O— $\rm H=0.84~\mathring{A})$ and refined as riding with $U_{\rm iso}(\rm H)=1.5 U_{\rm eq}(\rm O)$. The maximum and minimum residual electron density peaks of 1.14 and 0.55 e \mathring{A}^{-3} , respectively, were located 0.63 and 0.72 \mathring{A} from the H11 and Mo atom, respectively, i.e. in chemically non-sensible positions.

Comment

Di-basic, tridentate Schiff base ligands containing two terminal hydroxy/phenol sites are known to form complexes with many metal ions. Without exception, the reaction of dioxomolybdenum cations with these Schiff base ligands results in the formation of six-coordinate complexes with the sixth coordination site occupied by a solvent molecule, as found in the structure related to the title structure [5], or, through dimerisation, via bridging through a donor atom of the complexing ligand. The presence of a labile site in these mononuclear dioxomolybdenum(VI) complexes also allows the binding and displacement of different substrate molecules [6, 7]. Further, these complexes have attracted research interest over the decades for their possible antitumour [8], anti-fungal [9] and anti-viral [10] properties. In this work and in continuation of structural studies in this area [11], the synthesis and X-ray crystal structure of the title binuclear molybdenum(VI) complex, MoO₂(L)(4,4'bipyridine) $MoO_2(L)$, (I), where H_2L is 4-chloro-2-[(1E)-[(Z)-2-[2hydroxy-2-(2-hydroxyphenyl) ethylidene]hydrazin-1-ylidene] methyl]phenol, are described.

The binuclear molecule in (I) is disposed about a crystallographic centre of inversion and is shown in the figure (70% probability displacement ellipsoids; unlabelled atoms are related by the symmetry operation (i) -x, 1-y, -z). The Mo(VI) centre is complexed by the oxo-O1 and O2 atoms, the phenoxide-O3, oxide-O4 and imine-N1 atoms, derived from the tridentate Schiff base di-anion, and the pyridyl-N3 atom of the μ_2 -bridging 4,4'-bipyridine molecule. The resulting N₂O₄ donor set describes an octahedral geometry where the oxo groups are cis, and where the three donor atoms of L²⁻ anion occupy mer positions. An intramolecular hydroxy-O-H···N(imine) hydrogen bond [O5-H50···N2: $H50 \cdots N2 = 1.92 \text{ Å}, \quad O5 \cdots N2 = 2.653(3) \text{ Å}$ with angle at $H50 = 145^{\circ}$] closes an S(6) loop. The tridentate mode of coordination of the Schiff base di-anion results in the formation of five- and six-membered chelate rings. The acute angles subtended by these rings [O3-Mo-N1=80.87(7)° and $O4-Mo-N1=72.13(6)^{\circ}$ are primarily responsible for the deviation of the O3-Mo-O4 angle [148.10(7)°] from linearity. To a first approximation, the five-membered ring is planar with the r.m.s. deviation of the fitted atoms being 0.0355 Å with maximum deviations above and below the best plane being 0.0361(7) and 0.0448(11) Å for the Mo and O4 atoms, respectively. An alternate description of the fivemembered chelate ring would be one based on an envelope configuration where the Mo flap atom lies 0.174(4) Å out of the plane defined by the four remaining atoms (r.m.s. deviation = 0.0013 Å). Such a description is certainly apt for the six-membered ring whereby the Mo atom lies 0.426(3) Å out of the least-squares plane defined by the five remaining atoms of the chelate ring (r.m.s. deviation = 0.0171 Å). The dihedral angle formed between the best plane through each chelate ring is 6.15(13)°. The dihedral angles between the fivemembered chelate ring and pendent hydroxyphenyl ring is 8.23(11)°, between the six-membered chelate ring and fused chlorophenyl ring is 6.92(10)° and between the peripheral rings is 2.90(12)°, all suggesting that to a first approximation, the Schiff base di-anion is planar. The attached pyridyl ring is inclined with respect to the five- and six-membered rings as seen in the respective dihedral angles of 67.03(6) and 63.06(6)°.

In the molecular packing of (I), weak hydroxy- $O-H\cdots O(oxide)$ $[O5-H50\cdots O2^{ii}: H50\cdots O2^{ii}=2.45 \text{ Å},$ $05 \cdot \cdot \cdot \cdot 02^{ii} = 2.929(2) \text{ Å}$ with angle at $H50 = 117^{\circ}$ for (ii) 1-x, 1-y, 1-z, chlorophenyl-C-H···O(hydroxy), $[C2-H2\cdots O5^{iii}: H2\cdots O5^{iii}=2.50 \text{ Å}, C2\cdots O5^{iii}=3.422(3) \text{ Å}]$ with angle at $H2 = 163^{\circ}$ for (iii) x, -1 + y, z], pyridyl- $C-H\cdots O(oxide)$ [C16-H16···O1^{iv}: H16···O1^{iv} = 2.31 Å, $C16 \cdot \cdot \cdot \cdot O1^{iv} = 3.197(3) \text{ Å with angle at H}16 = 155^{\circ} \text{ and C}18 - 155^{\circ}$ $H18 \cdots O1^{v}$: $H18 \cdots O1^{v} = 2.58 \text{ Å}$, $C18 \cdots O1^{v} = 3.493(3) \text{ Å with}$ angle at H18 = 162° for (iv) 1 - x, 1 - y, -z and (v) -1 + x, y, z] along with $\pi \cdots \pi$ stacking between chlorophenyl and hydroxyphenyl rings [inter-centroid Cg(C1-C6)···Cg(C9- $C14)^{ii}$ distance = 3.6605(15) Å with angle of inclination = $2.90(13)^{\circ}$] sustain a three-dimensional architecture.

An additional analysis was conducted to probe the molecular packing further. Thus, Crystal Explorer 17 [12] was employed to calculate the percentage contributions to the Hirshfeld surfaces as well as the full and delineated fingerprint plots for the entire binuclear molecule, following literature protocols [13]. This analysis showed the importance of several different contacts to the surface but, with the most prominent due to just two types of contact, namely H···H [51.6%] and $0 \cdots H/H \cdots O$ [30.6%] contacts, accounting for over 80% of all surface contacts. Significant contributions are also made by $C \cdots H/H \cdots C$ [6.6%], $C \cdots C$ [6.2%], $O \cdots O$ [3.6%] and $O \cdot \cdot \cdot C C \cdot \cdot \cdot O$ [1.5%] contacts.

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