

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Mo	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)
O1	0.6590(2)	0.25368(16)	0.20158(14)	0.0185(3)
O2	0.7201(2)	0.28583(18)	0.39486(14)	0.0218(4)
O3	0.3947(2)	0.21441(16)	0.40121(13)	0.0174(3)
O4	0.5864(2)	0.51599(16)	0.23371(13)	0.0168(3)
O5	0.3506(2)	0.86723(18)	0.37065(15)	0.0238(4)
H5O	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–H = 0.95 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The O-bound H-atom was also geometrically placed (O–H = 0.84 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The maximum and minimum residual electron density peaks of 1.14 and 0.55 eÅ^{−3}, respectively, were located 0.63 and 0.72 Å 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 anti-tumour [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)MoO₂(L), (I), where H₂L is 4-chloro-2-[(1E)-[(Z)-2-[2-hydroxy-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 L^{2−} anion occupy mer positions. An intramolecular hydroxy-O–H...N(imine) hydrogen bond [O5–H5o...N2: H5o...N2 = 1.92 Å, O5...N2 = 2.653(3) Å with angle at H5o = 145°] 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)°] 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 five-membered 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 five-membered 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...O(oxide) [O5—H5O...O2ⁱⁱ: H5O...O2ⁱⁱ = 2.45 Å, O5...O2ⁱⁱ = 2.929(2) Å with angle at H5O = 117° for (ii) 1 - x, 1 - y, 1 - z], chlorophenyl-C—H...O(hydroxy), [C2—H2...O5ⁱⁱⁱ: H2...O5ⁱⁱⁱ = 2.50 Å, C2...O5ⁱⁱⁱ = 3.422(3) Å with angle at H2 = 163° for (iii) x, -1 + y, z], pyridyl-C—H...O(oxide) [C16—H16...O1^{iv}: H16...O1^{iv} = 2.31 Å, C16...O1^{iv} = 3.197(3) Å with angle at H16 = 155° and C18—H18...O1^v: H18...O1^v = 2.58 Å, C18...O1^v = 3.493(3) Å with angle at H18 = 162° for (iv) 1 - x, 1 - y, -z and (v) -1 + x, y, z] along with π ... π 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)°] 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 O...H/H...O [30.6%] contacts, accounting for over 80% of all surface contacts. Significant contributions are also made by C...H/H...C [6.6%], C...C [6.2%], O...O [3.6%] and O...C C...O [1.5%] contacts.

Acknowledgements: Sunway University Sdn Bhd is thanked for financial support of this work through Grant no. STR-RCTR-RCCM-0012019.

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