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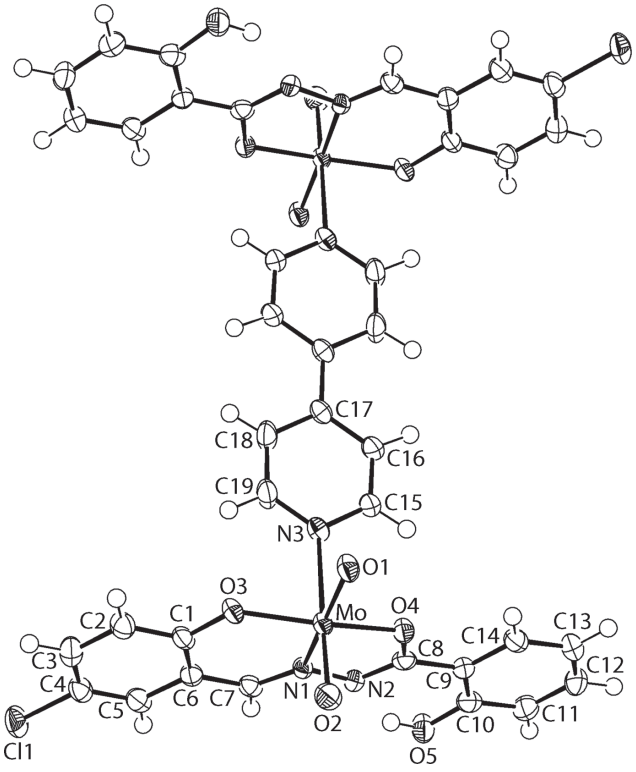
Crystal structure of bis{(*N*-[(5-chloro-2-oxidophenyl)methylidene]-2-hydroxybenzenecarbohydrazonato)-dioxo-molybdenum(VI)}(μ_2-4,4′-bipyridine), $C_{38}H_{26}Cl_2Mo_2N_6O_{10}$



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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, $\alpha = 73.027(2)°$, $\beta = 76.226(2)°$, $\gamma = 72.269(2)°$, $V = 917.83(4)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0234$, $wR_{ref}(F^2) = 0.0612$, $T = 100(2)$ 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:	0.12 × 0.08 × 0.07 mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ:	7.54 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	21955, 3275, 0.030
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3250
$N(param)_{refined}$:	263
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], 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 ^{1}H NMR spectrum was recorded in DMSO-d$_6$ 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 P_4O_{10}. Yield: 0.24 g (49%). **M.pt:** 491–493 K. **IR** (cm^{-1}) 1610 (m) ν(C—N), 1601 (s) ν(C—N), 1542 (s) ν(C—O), 1343 ν(C—O), 1261 ν(C—O), 1092 (m) ν(C—O), 931(m) ν(Mo—O), 902 (m) ν(Mo—O). **^{1}H NMR** (DMSO-d$_6$, 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,

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{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 $U_{iso}(H) = 1.2U_{eq}(C)$. The O-bound H-atom was also geometrically placed (O—H = 0.84 Å) and refined as riding with $U_{iso}(H) = 1.5U_{eq}(O)$. 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, MoO_2(L)(4,4′-bipyridine)MoO_2(L), (I), where H_2L is 4-chloro-2-[(1*E*)-[(*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 N_2O_4 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···O2^{ii}: H5O···O2^{ii} = 2.45 Å, O5···O2^{ii} = 2.929(2) Å with angle at H5O = 117° for (ii) $1-x$, $1-y$, $1-z$], chlorophenyl-C—H···O(hydroxy), [C2—H2···O5^{iii}: H2···O5^{iii} = 2.50 Å, C2···O5^{iii} = 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.

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References

1. Agilent Technologies: CrysAlis^{PRO}. Agilent Technologies, Santa Clara, CA, USA (2017).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. **C71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. **45** (2012) 849–854.
5. Ngan, N. K.; Wong, R. C. S.; Lo, K. M.; Ng, S. W.: [*N*′-(5-Chloro-2-oxido-benzyl-κ*O*)-2,4-dihydroxybenzohydrazidato-κ2*N*′,*O*](methanol-κ*O*)dioxidomolybdenum(VI)–4,4′-bipyridine (1/1). Acta Crystallogr. **E67** (2011) m747.
6. Ngan, N. K.; Lo, K. M.; Wong, R. C. S.: Synthesis, structure studies and electrochemistry of molybdenum(VI) Schiff base complexes in the presence of different donor solvent molecules. Polyhedron **30** (2011) 2922–2932.
7. Ngan, N. K.; Lo, K. M.; Wong, R. C. S.: Dinuclear and polynuclear dioxomolybdenum(VI) Schiff base complexes: synthesis, structural elucidation, spectroscopic characterization, electrochemistry and catalytic property. Polyhedron **33** (2012) 235–251.
8. Booth, B.; Donnelly, T.; Lettner, A.: Metabolic effects of zinc in intact cells-comparative studies of zinc chloride and the zinc chelate of kethoxal bis(thiosemicarbazone). Biochem. Pharmacol. **20** (1971) 3109–3118.
9. Kogan, V. A.; Popov, L. D.; Lukov, V. V.; Lokshin, V. A.: Copper(II) and nickel(II) complexes with mono- and bis-hydrazones of 2,6-diformylphenol. Zh. Neorg. Khim. **37** (1992) 2215–2222.
10. Carini, C.; Pelizzi, G.; Torasconi, P.; Pelizzi, C.; Molloy, K. C.; Watertield, P. C.: Synthesis, infrared, and tin-119 Mössbauer spectroscopic characterization of seven-co-ordinate diorganotin(IV) adducts with 2,6-diacetylpyridine acylhydrazones, including the X-ray crystal structure of $SnEt_2$(dapt) [H2dapt = 2,6-diacetylpyridine bis(2-thenoylhydrazone)]. J. Chem. Soc., Dalton Trans. (1989) 289–293.
11. Lo, K. M.; Lee, S. M.; Tiekink, E. R. T.: Crystal structure of (dimethyl sulfoxide)-dioxido-[2-hydroxy-*N*′-(4-oxo-4-phenylbutan-2-ylidene)benzohydrazidato κ^3*N*,*O*,*O*′] molybdenum(VI), $C_{19}H_{20}MoN_2O_6S$. Z. Kristallogr. NCS **235** (2019) 203–205.
12. Turner, M. J.; Mckinnon, J. J.; Wolff, S. K.; Grimwood, D. J.; Spackman, P. R.; Jayatilaka, D.; Spackman, M. A.: Crystal Explorer v17. The University of Western Australia, Australia (2017).
13. Tan, S. L.; Jotani, M. M.; Tiekink, E. R. T.: Utilizing Hirshfeld surface calculations, non-covalent interaction (NCI) plots and the calculation of interaction energies in the analysis of molecular packing. Acta Crystallogr. **E75** (2019) 308–318.