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μ-Oxo-bis{[2,3-dimethyl-2,3-butanediolato(1−)][2,3-dimethyl-2,3-butanediolato(2−)]oxomolybdenum(VI)}

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Abstract. $Mo_2(C_6H_{12}O_2)_2(C_6H_{13}O_2)_2O_3$, $C_{24}H_{50}Mo_2O_{11}$, monoclinic, $C2/c$, $a = 16{\cdot}907\ (4)$, $b = 13{\cdot}450\ (2)$, $c = 13{\cdot}556\ (2)$ Å, $\beta = 92{\cdot}6\ (1)°$, $V = 3079{\cdot}6$ Å^3, $M_r = 690{\cdot}51$, $D_o = 1{\cdot}52\ (7)$, $D_c = 1{\cdot}52$ Mg m^{-3}, $Z = 4$, $\mu(\mathrm{Cu}\ K\alpha) = 7{\cdot}478$ mm^{-1}. The yellow complex is based on a O=Mo—O—Mo=O core in which each Mo atom is coordinated by two bidentate pinacol ligands, one of which is singly deprotonated and the other doubly deprotonated. Two intramolecular hydrogen bonds link ligands attached to different Mo atoms.

Introduction. Samples of the title compound were prepared (Knobler, Penfold, Robinson, Wilkins & Yong, 1979) as translucent yellow crystals. Crystals are stable in a dark, dry atmosphere but otherwise slowly turn dark blue. Laue symmetry, $2/m$, and the systematic absences observed in photographs, established the space group as either Cc or $C2/c$. The crystal used for intensity measurements was a hexagonal prism of length 0·2 mm and mean cross-section 0·1 mm. It was sealed in a 0·3 mm tapered capillary tube, and intensities were recorded with a Hilger & Watts four-circle diffractometer, Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) and the θ–2θ technique. 1007 independent reflections were collected in the range $0 < 2\theta < 110°$. Of these, 885 had $I > 3\sigma(I)$ and were used in the structure determination and refinement. The procedures for data collection and assignment of errors were as described by Countryman & Penfold (1972). Corrections for absorption and isotropic extinction were applied.

The structure was solved by the heavy-atom method with the unique Mo atom, located from the Patterson function, used for phasing. Consideration of vector peaks arising from symmetry-related atoms indicated the space group $C2/c$ rather than Cc and this was confirmed by the satisfactory refinement. Difference syntheses showed all O, C and several H atoms. Least-squares refinement was carried out, varying three positional parameters for all Mo, C and O atoms and the non-methyl H atom, the methyl H positions being constrained to ideal tetrahedral geometries. Mo atoms only were assigned anisotropic thermal parameters. The final R was 0·073 for all 885 reflections. In the full-matrix least-squares procedure, the function minimized was $w||F_o| - |F_c||^2$ and the weights, w, were $4|F_o|^2/(\sigma|F_o|^2)^2$. Scattering factors for Mo, C and O were from Cromer & Mann (1968), those of H from Stewart, Davidson & Simpson (1965); anomalous-dispersion corrections were from Cromer & Liberman (1970). Positional and thermal parameters are listed in Table 1,* selected bond distances and angles in Tables 2 and 3.

Discussion. The title compound results from the coordination to a *cis*-dioxomolybdenum(VI) core of two molecules of a vicinal diol in which the C atoms

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34616 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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bearing the hydroxyl groups carry two substituents. For such complexes, two alternative structures (I) and (II) have been proposed: (Snam Progetti SPA, 1971).

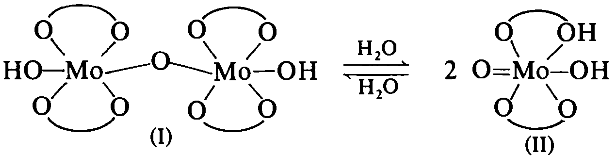

Table 1. *Atomic coordinates* (×10³) *and thermal parameters* (×10³)

U values are mean-square amplitudes of vibration. For H(1) to H(24), *U* (×10³) is fixed at 50·0 Å² and for H(25) at 60 Å². Anisotropic parameters (×10³) for Mo are U_{11} 35·7 (9), U_{22} 48·1 (2), U_{33} 29·4 (2), U_{23} −3·6 (8), U_{13} 3·7 (7), U_{12} 5·9 (6), where the expression for the anisotropic thermal ellipsoid is:

$$\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)].$$

	x	*y*	*z*	*U* (Å²)
Mo	83·3 (1)	190·8 (1)	163·3 (1)	
O(1)	−13·4 (7)	300·6 (9)	99 (1)	48 (4)
O(2)	37·0 (6)	134 (1)	49 (1)	43 (3)
O(3)	117·7 (6)	292·4 (9)	262 (1)	42 (3)
O(4)	155·4 (6)	270 (1)	96 (1)	54 (4)
O(5)	0·0	169 (1)	250·0	32 (4)
O(6)	140·7 (6)	96 (1)	201 (1)	54 (4)
C(1)	−38 (1)	276 (2)	−6 (2)	54 (5)
C(2)	−31·9 (8)	162 (2)	−13 (2)	37 (5)
C(3)	167·8 (9)	372 (2)	233 (2)	41 (4)
C(4)	213 (1)	329 (2)	150 (2)	48 (5)
C(5)	−124 (1)	315 (2)	−30 (2)	43 (5)
C(6)	20 (1)	335 (2)	−71 (2)	61 (6)
C(7)	−101 (1)	113 (2)	30 (2)	62 (8)
C(8)	−25 (1)	130 (2)	−117 (2)	60 (7)
C(9)	219 (1)	407 (2)	321 (2)	63 (6)
C(10)	118 (1)	459 (2)	200 (2)	59 (6)
C(11)	279 (2)	263 (3)	186 (3)	80 (9)
C(12)	243 (1)	408 (2)	77 (2)	79 (7)
H(1)	330	300	178	
H(2)	295	221	146	
H(3)	264	207	237	
H(4)	265	434	133	
H(5)	194	460	18	
H(6)	295	361	41	
H(7)	263	455	290	
H(8)	244	343	341	
H(9)	173	451	370	
H(10)	158	548	159	
H(11)	79	483	237	
H(12)	80	450	125	
H(13)	−137	301	−132	
H(14)	−119	390	−37	
H(15)	−173	271	5	
H(16)	7	320	−168	
H(17)	71	295	−49	
H(18)	28	384	−27	
H(19)	−167	111	4	
H(20)	−115	106	103	
H(21)	−88	57	23	
H(22)	−85	179	−163	
H(23)	−25	42	−129	
H(24)	18	124	−131	
H(25)	−69 (10)	303 (11)	152 (14)	

Sheldon (1973) has suggested that the binuclear structure (I) is more likely. Elemental analysis accords with (I) but the observed IR stretching frequency at 950 cm⁻¹ implies proton migration to give Mo=O linkages resulting in two non-equivalent ligands (Yong, 1975), a feature not observed elsewhere.

The molecular unit, shown in Fig. 1, established by the structure analysis, consists of two identical Mo*LL'* units linked by a single oxygen bridge lying on a diad axis, where *L* is a singly deprotonated and *L'* a doubly deprotonated diol. The complex is thus based on two distorted MoO_6 octahedra sharing a corner. It contains a central Mo_2O_3 core, the only authenticated example for Mo^{VI} compounds. Two intramolecular O—H···O hydrogen bonds link *L* and *L'* ligands attached to the two different Mo atoms.

The diol ligands form five-membered chelate rings in their coordination to the Mo atoms as in the dioxomolybdenum complexes formed by ethylene glycol (Schröder, Scherle & Hazell, 1975) and 2,3-butanediol

Table 2. *Bond lengths* (Å)

Mo—O(1)	2·34 (1)	C(1)—C(2)	1·54 (3)
Mo—O(2)	1·86 (1)	C(1)—C(5)	1·56 (2)
Mo—O(3)	1·98 (1)	C(1)—C(6)	1·57 (3)
Mo—O(4)	1·89 (1)	C(2)—C(7)	1·49 (2)
Mo—O(5)	1·90 (1)	C(2)—C(8)	1·48 (3)
Mo—O(6)	1·67 (1)	C(3)—C(4)	1·51 (2)
O(1)—C(1)	1·50 (2)	C(3)—C(9)	1·51 (3)
O(2)—C(2)	1·45 (2)	C(3)—C(10)	1·49 (3)
O(3)—C(3)	1·43 (2)	C(4)—C(11)	1·49 (3)
O(4)—C(4)	1·43 (2)	C(4)—C(12)	1·55 (3)
O(1)—H(25)	1·2 (2)	Mo···Mo'	3·76 (1)
O(3)—H(25)	1·5 (2)		

Table 3. *Bond angles* (°)

O(2)—Mo—O(1)	72·2 (5)	C(5)—C(1)—O(1)	109 (2)
O(2)—Mo—O(3)	160·5 (5)	C(6)—C(1)—O(1)	105 (2)
O(2)—Mo—O(4)	95·0 (5)	C(5)—C(1)—C(2)	113 (2)
O(3)—Mo—O(1)	89·6 (4)	C(6)—C(1)—C(2)	115 (2)
O(4)—Mo—O(1)	85·4 (4)	C(5)—C(1)—C(6)	108 (2)
O(4)—Mo—O(3)	76·2 (5)	C(1)—C(2)—O(2)	106 (1)
O(5)—Mo—O(1)	78·6 (4)	C(7)—C(2)—O(2)	106 (2)
O(5)—Mo—O(2)	99·1 (4)	C(8)—C(2)—O(2)	112 (1)
O(5)—Mo—O(3)	83·6 (4)	C(7)—C(2)—C(1)	111 (1)
O(5)—Mo—O(4)	154·3 (6)	C(8)—C(2)—C(1)	111 (2)
O(6)—Mo—O(1)	169·2 (5)	C(8)—C(2)—C(7)	110 (2)
O(6)—Mo—O(2)	98·7 (5)	C(4)—C(3)—O(3)	104 (1)
O(6)—Mo—O(3)	100·1 (5)	C(9)—C(3)—O(3)	110 (2)
O(6)—Mo—O(4)	101·5 (5)	C(10)—C(3)—O(3)	110 (1)
O(6)—Mo—O(5)	97·5 (5)	C(9)—C(3)—C(4)	115 (1)
C(1)—O(1)—Mo	112 (1)	C(10)—C(3)—C(9)	106 (2)
H(25)—O(1)—C(1)	112 (6)	C(11)—C(4)—O(4)	108 (2)
H(25)—O(1)—Mo	110 (5)	C(12)—C(4)—O(4)	107 (2)
C(2)—O(2)—Mo	132 (1)	C(3)—C(4)—O(4)	104 (1)
C(3)—O(3)—Mo	119 (1)	C(11)—C(4)—C(3)	112 (2)
H(25)—O(3)—Mo	117 (6)	C(12)—C(4)—C(3)	114 (2)
H(25)—O(3)—C(3)	120 (5)	C(11)—C(4)—C(12)	110 (2)
C(4)—O(4)—Mo	120 (1)	Mo—O(5)—Mo'	162·2 (9)
C(2)—C(1)—O(1)	105 (1)	O(1)—H(25)—O(3)	162 (5)

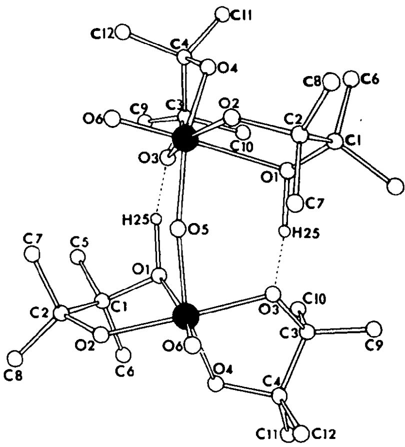

Fig. 1. One molecule of the binuclear complex showing the intramolecular hydrogen bonds. Mo atoms are shown as filled circles.

(Butcher, Penfold & Sinn, 1979). In the latter two compounds, in the absence of oxo bridging there is a simple distinction between long Mo—O_l (O_l = ligand oxygen) bonds *trans* to terminal O atoms (O_t) and short Mo—O_l *cis* to O_t, a feature now well established in oxomolybdenum complexes. However, in the present structure, only in the *L* ligand is there a bond Mo—O(1) *trans* to O_t and this is indeed 0·48 (2) Å longer than Mo—O(2) in the same ligand. In the *L′* ligand the bond Mo—O(4) *trans* to O_b, the bridging O(5) atom, is significantly (six e.s.d.'s) shorter than Mo—O(3). However, O(3), unlike O(4), is involved in hydrogen bonding and this effect is a likely contributor to relative bond lengthening of Mo—O(3).

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Di-μ-acetato-bis[(trimethylphosphine)(trimethylsilylmethyl)molybdenum(II)](*Mo—Mo*)

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Abstract. $[Mo_2(C_2H_3O_2)_2(C_3H_9P)_2(C_4H_{11}Si)_2]$, $C_{18}H_{46}Mo_2O_4P_2Si_2$, $M_r = 636{\cdot}6$, triclinic, $P\bar{1}$, $a = 8{\cdot}501$ (2), $b = 9{\cdot}844$ (3), $c = 10{\cdot}294$ (3) Å, $\alpha = 99{\cdot}54$ (3), $\beta = 111{\cdot}72$ (4), $\gamma = 98{\cdot}69$ (4)°, $U = 767{\cdot}7$ Å^3, $Z = 1$, $D_c = 1{\cdot}377$ Mg m^{-3}, $F(000) = 328$, μ(Mo $K\alpha$) = 0·92 mm^{-1}, λ(Mo $K\alpha$) = 0·71069 Å. The structure has been refined to $R = 0{\cdot}0273$ for 3810 diffractometer data. The dimeric molecules lie on crystallographic inversion centres. The short Mo—Mo distance [2·0984 (5) Å] is consistent with the presence of a quadruple bond.

Introduction. The title compound was obtained as orange-red prisms by reacting $Mo_2(O_2CMe)_4$ with $Mg(CH_2SiMe_3)_2$ in the presence of trimethylphosphine (Anderson, Jones, Wilkinson, Hursthouse & Malik, 1977; Anderson, Jones & Wilkinson, 1978). We undertook an X-ray study of this material both for complete structural characterization and as part of a general investigation of the structures of molecules containing bulky alkyl ligands. Since the compound is air-sensitive, suitable crystals were sealed under nitrogen in Lindemann capillaries. The cell parameters were initially determined from oscillation and Weissenberg photographs and later refined on a Nonius CAD-4 diffractometer from the setting angles for fifteen high-angle [16 < θ(Mo $K\alpha$) < 17°] reflections. Intensities of

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