All calculations were performed on the University of South Africa's Burroughs B6800 computer with *SHELX* (Sheldrick, 1978). I thank Dr G. Gafner of the CSIR, Pretoria, for the diffractometer data collection.

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Di-μ-methoxo-bis{[2,3-dimethylbutane-2,3-diolato(1−)]-*cis*-dioxomolybdenum(VI)}—Methanol (1/2)

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Abstract. $[Mo(CH_3O)(C_6H_{13}O_2)O_2]_2.2CH_3OH$, $C_{14}H_{32}Mo_2O_{10}.2CH_4O$, monoclinic, $P2_1/c$, $a = 7{\cdot}167\,(2)$, $b = 11{\cdot}499\,(4)$, $c = 15{\cdot}789\,(4)$ Å, $\beta = 101{\cdot}65\,(2)°$, $V = 1274{\cdot}42$ Å^3, $M_r = 552{\cdot}3$, $D_c = 1{\cdot}44$ Mg m^{-3}, $Z = 2$, μ(Mo $K\alpha$) = 0·916 mm^{-1}. $R = 0{\cdot}046$ for 838 reflections. In this colourless dimeric complex the Mo atoms are linked by a double methoxy bridge. The coordination about each Mo is completed by two O atoms from a bidentate singly deprotonated pinacol ligand and two terminal oxo ligands. Intermolecular hydrogen bonds link pinacol O atoms through methanol molecules.

Introduction. Crystals of the title compound were prepared (Knobler, Penfold, Robinson, Wilkins & Yong, 1980) as colourless parallelepipeds. Crystals are stable in their mother liquor but when dry they slowly become opaque dark blue. The space group $P2_1/c$ was established uniquely from systematic absences. The crystal used for intensity measurements was 1·2 mm long with a cross-section of 0·14 mm and was sealed in a capillary tube. Intensities were recorded on a Hilger & Watts four-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) and the θ–2θ scan technique. 1077 reflections were recorded (before decomposition) at room temperatures (298 K) in the range $0 < 2\theta < 42°$. Of these, 838 had $I > 3\sigma(I)$ and were used in the analysis. The detailed procedures for data collection and assignment of errors were as described by Countryman & Penfold (1972). Corrections for absorption were not applied.

Coordinates of the Mo atom were ascertained from the Patterson function and the remaining 14 non-hydrogen atoms were located from electron-density maps. Positions of all these atoms were refined by full-matrix least squares until R had fallen to 0·047 for a completely isotropic model. H atoms of methyl groups were then introduced as members of rigid groups constrained to C—H = 1·0 Å and H—C—H = 109·5°. From a difference map, one of the remaining H atoms was located (as the highest peak >1·5 Å from Mo) 1·0 Å from a diol O atom and 1·8 Å from the O atom of the methanol solvate. The hydroxy H atom of the methanol solvate was not located and was not included in the model. Refinement converged at R = 0·046, based on 84 parameters and 838 reflections. The function minimized was $\sum w||F_o| - |F_c||^2$ and the weights w were $2{\cdot}568/[\sigma^2(F) + 0{\cdot}000034\,F^2]$. Scattering factors for Mo, C, and O were from Cromer & Mann (1968), those of H from Stewart, Davidson & Simpson (1965); anomalous-dispersion corrections f' and f'' were from Cromer & Liberman (1970). Positional and thermal parameters are listed in Table 1,

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selected interatomic distances and angles in Tables 2 and 3.[*]

Table 1. *Atomic coordinates* ($\times 10^3$) *and thermal parameters* ($\times 10^3$)

U values are mean-square amplitudes of vibration. Positions of methyl H atoms [H(31) to H(83)] were fixed as members of rigid groups with C—H = 1·0 Å and H—C—H = 109·5°. One overall U was refined for these atoms.

	x	y	z	U (Å^2)
Mo	56·9 (2)	357·0 (1)	479·2 (1)	32·9 (4)
O(1)	217 (1)	274·3 (5)	572·6 (4)	38 (2)
O(2)	−123 (1)	321·1 (6)	583·4 (4)	36 (2)
O(3)	−137 (1)	481·9 (5)	444·5 (4)	37 (2)
O(4)	225 (1)	386·4 (5)	422·1 (4)	43 (2)
O(5)	−76 (1)	253·6 (6)	420·8 (5)	45 (2)
O(6)	552 (1)	199·8 (7)	524·0 (5)	60 (2)
C(1)	143 (2)	201·2 (8)	634·0 (6)	38 (3)
C(2)	−14 (2)	270·2 (8)	663·3 (6)	33 (2)
C(3)	316 (2)	177·7 (10)	709·6 (8)	59 (4)
C(4)	74 (2)	88·4 (9)	589·5 (7)	50 (3)
C(5)	58 (2)	373·3 (9)	722·1 (7)	51 (3)
C(6)	−143 (2)	194·4 (9)	705·4 (8)	50 (3)
C(7)	−338 (2)	457·2 (10)	410·2 (7)	53 (3)
C(8)	495 (2)	148·0 (11)	439·4 (8)	64 (4)
H(2)	−223 (19)	265 (9)	565 (7)	73 (36)
H(31)	280	135	759	93 (10)
H(32)	373	254	730	
H(33)	410	131	685	
H(41)	48	31	634	
H(42)	183	60	564	
H(43)	−42	97	543	
H(51)	126	344	780	
H(52)	−58	418	729	
H(53)	145	425	697	
H(61)	−67	148	754	
H(62)	−207	141	659	
H(63)	−243	240	727	
H(71)	−418	528	394	
H(72)	−400	406	448	
H(73)	−325	414	357	
H(81)	580	81	434	
H(82)	498	204	391	
H(83)	362	120	436	

Table 2. *Bond lengths* (Å)

Primed atoms are in symmetry positions $-x$, $1-y$, $1-z$. The starred atoms are in positions $x-1$, y, z.

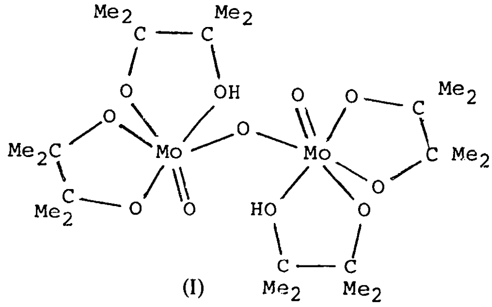
Mo···Mo′	3·484 (2)	O(6)—C(8)	1·44 (2)
Mo—O(1)	1·93 (1)	C(1)—C(2)	1·53 (2)
Mo—O(2)	2·32 (1)	C(1)—C(3)	1·56 (2)
Mo—O(3)	2·22 (1)	C(1)—C(4)	1·51 (2)
Mo—O(4)	1·68 (1)	C(2)—C(5)	1·53 (2)
Mo—O(5)	1·68 (1)	C(2)—C(6)	1·52 (3)
Mo—O(3′)	2·00 (1)	O(1′)···O(6′)	2·80 (2)
O(1)—C(1)	1·46 (2)	O(2)—H(2)	1·0 (2)
O(2)—C(2)	1·47 (2)	O(2)···O(6*)	2·72 (2)
O(3)—C(7)	1·46 (2)	O(6*)···H(2)	1·8 (2)

Table 3. *Bond angles* (°)

The double-starred atom is in position $x+1$, y, z.

O(1)—Mo—O(2)	72·6 (4)	O(1)—C(1)—C(2)	107 (1)
O(1)—Mo—O(3)	147·0 (4)	O(1)—C(1)—C(3)	106 (2)
O(1)—Mo—O(4)	97·5 (5)	O(1)—C(1)—C(4)	108 (1)
O(1)—Mo—O(5)	104·8 (5)	C(2)—C(1)—C(3)	112 (1)
O(1)—Mo—O(3′)	87·0 (5)	C(2)—C(1)—C(4)	113 (2)
O(2)—Mo—O(3)	82·3 (4)	C(3)—C(1)—C(4)	110 (1)
O(2)—Mo—O(4)	167·9 (5)	O(2)—C(2)—C(1)	104 (1)
O(2)—Mo—O(5)	85·9 (5)	O(2)—C(2)—C(5)	106 (1)
O(2)—Mo—O(3′)	83·4 (5)	O(2)—C(2)—C(6)	110 (2)
O(3)—Mo—O(4)	104·1 (5)	C(1)—C(2)—C(5)	114 (2)
O(3)—Mo—O(5)	94·1 (5)	C(1)—C(2)—C(6)	113 (1)
O(3)—Mo—O(3′)	68·9 (5)	C(5)—C(2)—C(6)	110 (2)
O(4)—Mo—O(5)	103·7 (6)	Mo—O(1)···O(6)	111 (1)
O(4)—Mo—O(3′)	89·3 (5)	Mo—O(2)···O(6*)	114 (1)
O(5)—Mo—O(3′)	160·9 (5)	C(2)—O(2)···O(6*)	111 (1)
Mo—O(1)—C(1)	124 (1)	C(1)—O(1)···O(6)	117 (1)
Mo—O(2)—C(2)	114 (1)	O(2)—H(2)···O(6*)	165
Mo—O(2)—H(2)	113 (11)	C(8)—O(6)···O(1)	107 (1)
Mo—O(3)—Mo′	111 (1)	C(8)—O(6)···O(2**)	126 (1)
Mo—O(3)—C(7)	122·8 (9)	O(1)···O(6)···O(2**)	118 (1)
C(2)—O(2)—H(2)	103 (9)		

Discussion. The title compound is a monopinacolate produced when the dipinacolate complex $[Mo(C_6H_{12}O_2)(C_6H_{13}O_2)O]_2O$, (I), containing a single oxygen bridge (Matheson & Penfold, 1979), is dissolved in methanol with restricted access of moisture. From the IR stretching frequency at 690 cm^{-1}, bridging by ligand oxygen was indicated but the elemental analysis did not allow an unambiguous structural assignment.



(I)

Among the bridged compounds of the Mo^{VI} complexes surveyed by Knobler, Penfold, Robinson, Wilkins & Yong (1980), it is found that the Mo—O$_{lb}$ (ligand bridge) lengths are in the range 2·00 to 2·22 Å compared with 1·88 to 1·90 Å for the Mo—O$_b$ (oxygen bridge) lengths. Correspondingly the Mo—O$_{lb}$—Mo IR bands lie at lower wave numbers than the Mo—O$_b$—Mo bands.

The molecular unit, Fig. 1, consists of two identical MoO$_2$$L$ units (L = singly deprotonated diol) linked by two methoxy bridges around a crystallographic centre of inversion. Bridging by ligands not involved in chelation with the Mo atom has not previously been

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[*] A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35818 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

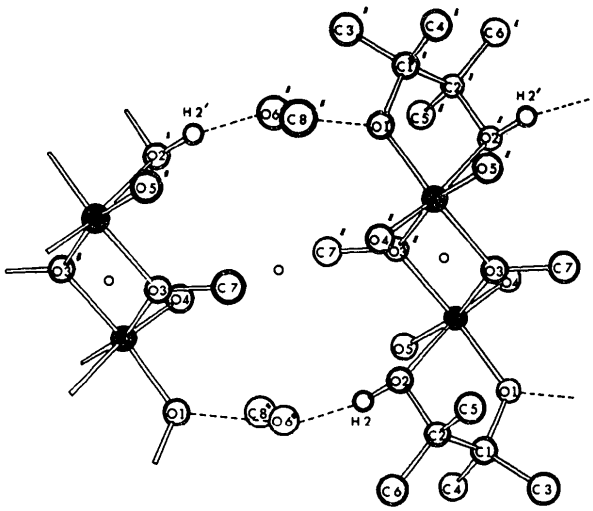

Fig. 1. Two members of the infinite connected array of dimers hydrogen bonded through methanol solvate molecules. Mo atoms are shown as black spheres.

observed in oxo-molybdenum complexes and makes this structure distinctive. Each methanol solvate forms two hydrogen bonds, with O$_l$ atoms (O$_l$ = pinacolate ligand oxygen) of two different molecules so that endless chains are formed approximately parallel to **a**.

Details of the geometry of the complex are most usefully considered in comparison with the parent compound (I) which has a single oxygen bridge and two diol ligands coordinated to each Mo. We shall refer to this compound as SB and to the title double-bridged compound as DB. In oxo-molybdenum(VI) complexes, the bonds *trans* to Mo—O$_t$ (O$_t$ = terminal oxygen) are invariably lengthened. In DB, where there are two Mo—O$_t$ bonds, this *trans* effect is more far-reaching than in SB (where there is only one such bond) and indeed can be seen as the controlling factor in the coordination geometry. Thus, of the two Mo—O$_{lb}$ bonds, that *trans* to Mo—O$_t$ [bond Mo—O(3)] is longer by 0·22 (2) Å and, of the two Mo—O$_l$ bonds, that *trans* to Mo—O$_t$ [bond Mo—O(2)] is longer by 0·39 (2) Å. The Mo—O$_{lb}$ bonds are confirmed to be significantly longer [0·10 (2) and 0·32 (2) Å] than the Mo—O$_b$ bond in SB and almost identical in length to the Mo—O$_{lb}$ bonds in the double oxygen-bridged Mo^{VI} complex with 2,2-dimethylpropane-1,3-diol (Chew & Penfold, 1975). Direct comparison may be made of the dimensions of the chelate ring in DB and that formed by the singly deprotonated diol in SB. The angles subtended at the Mo agree within one σ (72·6, 72·1°). The corresponding bond lengths agree within one σ with the single exception of the shorter of the two Mo—O$_l$ bonds. This bond in DB, 1·93 (1) Å, is 0·07 (2) Å longer than that in SB, but in DB this bond is *trans* to Mo—O$_{lb}$ (rather than to Mo—O$_l$) and it has been noted (Butcher, Penfold & Sinn, 1979) that Mo—O (bridge) bonds do have a *trans* lengthening effect. In both compounds the O$_l$ atom *trans* to O$_t$ is the protonated oxygen which, in SB, is involved in an intramolecular hydrogen bond to another ligand, but which, in DB, is hydrogen bonded to a methanol solvate molecule.

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