pentacoordinate resulting in coordination spheres with distorted square-pyramid geometries with non-bridging Cl atoms at the apex of the pyramid. The distortion is a result of the constraints imposed by the formation of a five-membered ring on one side due to the coordination of the metal ion by two N atoms. The axial bond distances of 2·523 (2) Å for Cu—Cl(1) and 2·524 (2) Å for Cu(2)—Cl(2) are significantly longer than the range of 2·27 to 2·35 Å found for non-axial Cu—Cl distances (Klein, Trefonas, O'Connor & Majeste, 1981; Swank, Needham & Willett, 1979; Roundhill, Roundhill, Bloomquist, Landee, Willett, Dooley & Gray, 1979) but significantly shorter than the Cu—Cl bridging bonds of 2·70 to 3·19 Å found in Cu—Cl—Cu bridging systems (Willett & Rundle, 1964; Hodgson, Hale & Hatfield, 1971).

The non-bridging Cl atoms are coordinated on opposite sides of the molecule. Each Cu^{II} ion is displaced from the plane in the direction of the non-bridging Cl atom which is coordinated to it [Cu(1) −0·411 (5) Å out of plane and Cu(2) +0·332 (5) Å out of plane], as can be seen from the packing diagram in Fig. 2. The ligand is near planar except for slight rotations of the pyridine ring planes [N(1)C(1)C(2)-C(3)C(4)C(5) and N(4)C(16)C(17)C(18)C(19)C(20)] about the C(5)—C(6) bond and the C(15)—C(16) bond. The resulting dihedral angles between pyridine ring planes and the rest of the ligand are 173·5 (7) and 166·3 (7)° respectively.

An intermolecular hydrogen-bond network results from the two water molecules of hydration found in the unit cell. Both are hydrogen-bonded to Cl(2) and also to a Cl(1) translated by one unit cell along the *a* axis. The hydrogen bonds linking two adjacent binuclear complexes result in an infinite linear chain of binuclear molecules. The water O—Cl distances are somewhat longer [Cl(1)—O(2) 3·265 (6), Cl(1)—O(3) 3·293 (8) Å and Cl(2)—O(2) 3·266 (6), Cl(2)—O(3) 3·199 (6) Å] than the Cl—O hydrogen-bond distances reported in the literature [2·99–3·05 (6) Å] (*International Tables for X-ray Crystallography*, 1968).

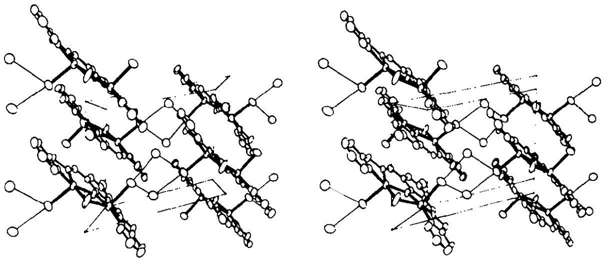

Fig. 2. Stereoview of the molecular-packing diagram showing the intermolecular hydrogen-bond network.

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1,3-Diethoxy-1,2;1,4;2,3,4:2,3;3,4;1,2,4-bis-μ_4-{[2-hydroxymethyl-2-methyl-1,3-propanediolato(3−)]-μ-*O*,μ-*O*′,μ-*O*″}-tetrakis[*cis*-dioxomolybdenum(VI)], $C_{14}H_{28}Mo_4O_{16}$

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Abstract. $M_r = 836·1$, triclinic, $P\bar{1}$, $a = 8·500$ (1), $b = 9·581$ (1), $c = 7·903$ (1) Å, $\alpha = 103·16$ (1), $\beta = 103·07$ (1), $\gamma = 100·41$ (2)°, $V = 591·90$ Å^3, $D_o = 2·34$, $D_x = 2·35$ Mg m^{-3}, $Z = 1$, $\lambda(\text{Cu } K\alpha) = 1·5418$ Å, $\mu(\text{Cu } K\alpha) = 18·548$ mm^{-1}, $R = 0·031$ for 1438 observed reflections. In this complex the four Mo coordination centres are of two kinds within one crystallographically centrosymmetric molecule. They are linked by a system of double and triple bridges formed by the O atoms of the triply deprotonated 2-hydroxymethyl-2-methyl-1,3-propanediol ligands. For one pair of Mo atoms this bridging itself provides six-coordination, but each Mo atom of the other pair carries an ethoxy group to complete the coordination.

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Introduction. 2-Hydroxymethyl-2-methyl-1,3-propanediol, $CH_3C(CH_2OH)_3$, or trimethylolethane (trianion tme), forms an Mo^{VI} complex of composition $MoO_2(Htme)$ (Knobler, Penfold, Robinson, Wilkins & Yong, 1980). Prolonged extraction of this compound with dry ethanol (Hider & Wilkins, 1983) causes elimination of one-half of the ligand to give a crystalline ethoxy derivative of empirical composition $(MoO_2)_2(tme)(C_2H_5O)$ which is stable in air. The infrared spectrum indicated bridging by ligand O, and the presence of MoO_2 cores in more than one environment. The crystal structure shows the molecule to be centrosymmetric, with a doubled formula $[(MoO_2)_4(tme)_2(C_2H_5O)_2]$.

Experimental. Crystal 0·86 × 0·106 × 0·083 mm, density measured by flotation in $CCl_4 + CHBr_3$; X-ray photographs consistent with the triclinic crystal system and the analysis confirmed the space group $P\bar{1}$; Hilger & Watts four-circle diffractometer, Ni-filtered Cu $K\alpha$ radiation, 12 reflections used to determine lattice parameters, θ–2θ scan technique, $2\theta_{\max} = 114°$ (h, $0 \rightarrow 9$; k, $10 \rightarrow -10$; l, $8 \rightarrow -8$), 1616 reflections recorded, 1568 unique, 1438 with $I > 3\sigma(I)$ used in the structure refinement, 143 unobserved; absorption corrections applied, maximum and minimum values for the correction factors being 6·10 and 3·38; no intensity variation for three standard reflections.

Coordinates of the Mo atoms, obtained from the Patterson function, showed there to be a group of four within the cell. The remaining 15 crystallographically independent non-hydrogen atoms were located from electron density maps. H atoms were not located, but were introduced as members of rigid methyl and methylene groups constrained so that C—H = 1·0 Å. Following usual procedures (Countryman & Penfold, 1972) refinement of 88 parameters converged at $R(F) = 0·031$, $R_w = 0·033$ $\{w = 1/[\sigma^2(F) + 0·000112F^2]\}$; $F(000) = 408$. Anisotropic thermal parameters assigned only to the Mo atoms, methyl and methylene H-atom temperature factors grouped separately for refinement purposes. There was evidence for secondary extinction amongst some low-angle reflections and so an isotropic extinction parameter (0·00943) was refined. Final difference Fourier maps showed no regions of abnormally high electron density (max. N 0·5 e $Å^{-3}$; min. N −0·5 e $Å^{-3}$); ratio of maximum least-squares shift to error ~ 0·1 for non-H atoms; intensity data processed using programs *HILGOUT* (based on *DRED* by J. F. Blount and *PICKOUT* by R. J. Doedens) and *ABSORB* (a major revision by L. K. Templeton and D. Templeton of the program *AGNOST*, installed locally by A. Zalkin); structure solution and refinement and geometry calculations made using programs *SHELX* (Sheldrick, 1976) and *GEOM* (S. Motherwell); diagrams produced using *ORTEP* II (Johnson, 1976).

Discussion. Positional and thermal parameters are listed in Table 1,* and selected interatomic distances and bond angles in Table 2.

The four coplanar Mo atoms in the molecule are linked entirely by a close-knit network of ligand-O, O_l, bridges, as shown by the darkened lines in Fig. 1. The atoms O(1), O(2) [likewise O(1′), O(2′) from the second tme ligand] each form a bridge between two Mo

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

	x	y	z	U(Å²)*
Mo(1)	−70·2 (1)	35·0 (1)	207·5 (1)	†
Mo(2)	322·0 (1)	210·4 (1)	192·3 (1)	†
O(1)	274‡	−1‡	−4‡	30 (1)
O(2)	170	49	296	27 (1)
O(3)	−49	−145	−26	24 (1)
O(4)	276	355	360	37 (1)
O(5)	−138	−93	307	39 (1)
O(6)	−90	198	328	39 (1)
O(7)	375	303	48	45 (2)
O(8)	500	182	310	45 (2)
C(1)	321	−128	48	36 (2)
C(2)	224	−83	327	33 (2)
C(3)	27	−259	29	31 (2)
C(4)	210	−196	148	31 (2)
C(5)	272	−326	196	44 (2)
C(6)	316	377	556	43 (2)
C(7)	216	477	633	59 (3)

* Methylene H atoms were refined to a common U value 118 (18), and methyl H to 115 (17).

† Anisotropic parameters for Mo(1) and Mo(2) respectively were: U_{11}, 28 (1), 25 (1); U_{22}, 29 (1), 29 (1); U_{33}, 21 (1), 31 (1); U_{23}, 6 (1), 5 (1); U_{13}, 11 (1), 8 (1); U_{12}, 7 (1), 2 (1).

‡ E.s.d.'s are 1 × 10^{-3} for all O and C atoms.

Table 2. *Bond lengths* (Å) *and selected angles* (°)

Mo(1)—O(1′)	2·001 (4)	Mo(2)—O(8)	1·688 (5)
Mo(1)—O(2)	1·972 (4)	C(1)—C(4)	1·517 (10)
Mo(1)—O(3)	2·287 (4)	C(1)—O(1)	1·463 (9)
Mo(1)—O(5)	1·683 (5)	C(2)—C(4)	1·538 (10)
Mo(1)—O(6)	1·689 (5)	C(2)—O(2)	1·465 (8)
Mo(2)—O(1)	2·157 (4)	C(3)—C(4)	1·553 (10)
Mo(2)—O(2)	2·256 (4)	C(3)—O(3)	1·462 (8)
Mo(2)—O(3′)	2·282 (4)	C(4)—C(5)	1·527 (10)
Mo(2)—O(4)	1·855 (5)	C(6)—C(7)	1·505 (12)
Mo(2)—O(7)	1·688 (5)	C(6)—O(4)	1·464 (9)

O(1)—Mo(2)—O(2)	75·1 (2)	O(3)—Mo(1)—O(3′)	71·4 (2)
O(1)—Mo(2)—O(3′)	71·2 (2)	O(3)—Mo(1)—O(5)	91·0 (2)
O(1)—Mo(2)—O(4)	156·4 (2)	O(3)—Mo(1)—O(6)	161·3 (2)
O(1)—Mo(2)—O(7)	92·2 (2)	O(5)—Mo(1)—O(6)	106·0 (2)
O(1)—Mo(2)—O(8)	90·4 (2)	Mo(1′)—O(1)—Mo(2)	111·6 (2)
O(2)—Mo(2)—O(3′)	69·6 (2)	Mo(1)—O(2)—Mo(2)	111·2 (2)
O(2)—Mo(2)—O(4)	85·4 (2)	Mo(1)—O(3′)—Mo(2)	100·2 (2)
O(2)—Mo(2)—O(7)	158·9 (2)	Mo(1)—O(3)—Mo(1′)	108·6 (2)
O(3′)—Mo(2)—O(8)	155·7 (2)	Mo(1′)—O(1)—C(1)	119·0 (4)
O(7)—Mo(2)—O(8)	106·3 (3)	Mo(1′)—O(3)—C(3)	114·6 (4)
O(2)—Mo(1)—O(1′)	150·5 (2)	Mo(1)—O(2)—C(2)	119·2 (4)
O(2)—Mo(1)—O(3′)	74·9 (2)	Mo(2)—O(2)—C(2)	120·7 (4)
O(2)—Mo(1)—O(5)	97·3 (2)	Mo(2)—O(4)—C(6)	126·6 (4)
O(2)—Mo(1)—O(6)	102·7 (2)	C(4)—C(1)—O(1)	113·2 (4)

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* Lists of structure factors and hydrogen-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38127 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

atoms (described as 'double bridging') while O(3) and O(3′) each span three Mo atoms ('triple bridging'). These bridges provide octahedral coordination for one pair of Mo atoms, but for the second pair six-coordination is completed by non-bridging ethoxy groups which also give overall charge balance. Thus Mo(1) is coordinated with the two double-bridging atoms O(1′) and O(2), the two triple-bridging atoms O(3) and O(3′), and the terminal atoms O(5) and O(6) of the *cis*-dioxo core. Mo(2) is linked to the double-bridging atoms O(1) and O(2), the triple-bridging O(3′), the ethoxy O(4), and O(7) and O(8) of the core. Upon coordination, the ligand develops three six-membered chelating rings, each in a chair configuration providing bonding through the O pairs towards different Mo centres. The rings formed by the lower ligand in Fig. 1 are thus: Mo(2)–O(1)–C(1)–C(4)–C(2)–O(2), Mo(1′)–O(1)–C(1)–C(4)–C(3)–O(3) and Mo(1)–O(2)–C(2)–C(4)–C(3)–O(3). In addition, a bond from the triple-bridging O(3) extends to the fourth Mo atom, Mo(2′).

The Mo–O_l bond lengths to the coordinated tme fall into three groups (Table 3), which show the usual correlation with the nature of the *trans* groups (Schröder, 1975). The long bonds to triple-bridging O(3) and O(3′) lie opposite terminal O atoms. The double bridges are unsymmetrical; thus, for the Mo(1)–O(2)–Mo(2) bridge the longer arm, Mo(2)–O(2) = 2·256 (4) Å, is again *trans* to terminal O, but the shorter link, Mo(1)–O(2) = 1·972 (4) Å, is *trans* to the bond Mo(1)–O(1′) of its own type. With the Mo(1′)–O(1)–Mo(2) bridge the longer arm, Mo(2)–O(1) = 2·157 (4) Å, is opposite the ethoxy O(4). The intermediate *trans*-lengthening influence of the ethoxy group affords evidence of an intermediate π-electron density in its bond to Mo. The ethoxy bond length itself, Mo(2)–O(4) = 1·855 (5) Å, is close to that of a non-bridging isopropoxy group, 1·865 Å in $Mo_6O_{10}(OPr^i)_6$ (Chisholm, Folting, Huffman & Kirkpatrick, 1982).

Table 3. Mo–O *bond lengths* (Å) *in relation to the trans group*

		trans group
Mo(1)–O(1′), Mo(1)–O(2)	1·97–2·00	Bridging O
Mo(2)–O(1)	2·16	Non-bridging ethoxy
Mo(1)–O(3), Mo(2)–O(2), Mo(2)–O(3′)	2·26–2·28	Terminal O

The coordination behaviour of the ligand may be compared with that of the simpler 2,2′-dimethyl-1,3-propanediol (neopentylglycol, dianion npg). In the npg complex $[\{MoO_2(npg)OH_2\}_2]$ only one of the O atoms of the chelating group engages in ligand bridging (Chew & Penfold, 1975), whereas in the present compound the ligand configuration is such that each of the three O atoms participates in the bridging to form a more highly condensed structure. The Mo(1)···Mo(2) and Mo(1′)···Mo(2) distances, 3·493 (1) and 3·440 (1) Å respectively, are close to Mo···Mo in the binuclear npg complex, *viz* 3·45 Å, but Mo(1)···Mo(1′) at 3·700 (1) Å is longer since the latter pair are linked only through the longer bonds to the triple-bridging O(3) and O(3′).

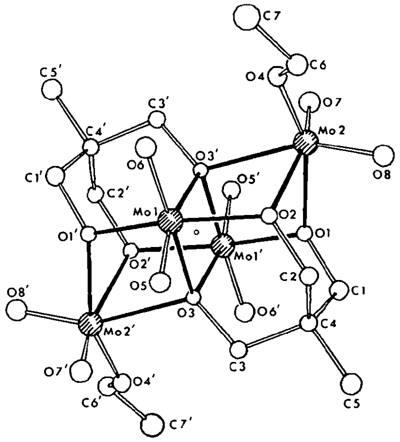

Fig. 1. A perspective view of one molecule of $[(MoO_2)_4(tme)_2(C_2H_5O)_2]$. Primed atoms are related to the corresponding unprimed ones by the crystallographic centre of symmetry.

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