Crystal and Molecular Structure of Tetrachloro-di-μ_3-oxo-tetra-μ-propoxo-tetraoxodipropoxotetramolybdenum(2*Mo–Mo*)

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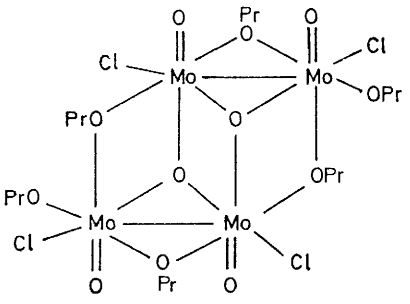
Crystals of the title compound are triclinic, space group $P\bar{1}$, a = 12·054(13), b = 7·695(8), c = 10·183(11) Å, α = 103·9(1), β = 105·8(1), γ = 96·5(1)°, Z = 1. The structure was determined from diffractometer *X*-ray data by Patterson and Fourier methods and refined by full-matrix least-squares techniques to R 0·063 for 1366 independent reflections. The compound has imposed $\bar{1}$ symmetry. The two molybdenum atoms in the asymmetric unit have different environments although both are formally seven-co-ordinate, being bonded to each other [2·669(2) Å], to one chlorine atom [2·395(5), 2·367(6) Å] and five oxygen atoms. The metal–metal bond has little effect on the geometries of the co-ordination polyhedra of the molybdenum atoms which are best described as distorted octahedra. These four octahedra in the tetramer are bridged through edges. Two oxide oxygens form terminal bonds [1·617(15) and 1·634(16) Å], the third bridging three molybdenum atoms [1·993(9), 1·962(12), and 2·237(13) Å]; one propoxide oxygen is terminal [2·134(13) Å], and the other two bridge pairs of molybdenum atoms [1·981(11), 1·985(14), 2·048(13), and 2·182(14) Å]. Variations in Mo–O bond lengths are explained in terms of differing bond types (and orders). The propoxide carbon atoms have high thermal motion and some are disordered.

THERE is considerable interest in the alkoxides and alkyls of molybdenum [1-3] and we have been investigating the stability of the molybdenum–carbon bond [4] in various methyl compounds, including $MeMoCl_2(OPr)_2$, [OPr = n-propoxide]. During this work, we attempted to grow crystals of this compound, suitable for an *X*-ray analysis. After several weeks, a few crystals appeared in the reaction vessel and these were used in an *X*-ray structure determination. However, this analysis showed that the crystals had formula $Mo_4Cl_4O_6(OPr)_6$. The structure of this tetramer, which we report here, is tetrachloro-di-μ_3-oxo-tetra-μ-propoxo-tetraoxodipropoxotetramolybdenum(2*Mo–Mo*) (I).



(I)

EXPERIMENTAL

Trichlorodipropoxomolybdenum, $MoCl_3(OPr)_2$, was prepared from molybdenum pentachloride and dry propanol at −80 °C. $MoCl_3(OPr)_2$ was then treated with a slight excess of zinc dimethyl in diethyl ether to give a light brown solid, $MeMoCl_2(OPr)_2$ (Found: Mo, 32·2; Cl, 23·8. Calc. for $C_7H_{17}Cl_2MoO_2$: Mo, 31·95; Cl, 23·65%). $MeMoCl_2(OPr)_2$ was then dissolved in pentane and red crystals grew after several weeks (in light) in a double ampoule. There were a few crystals only and no elemental analysis was carried out.†

Crystal Data.—$C_{18}H_{42}Cl_4Mo_4O_{12}$, M = 971·1, Triclinic, a = 12·054(13), b = 7·695(8), c = 10·183(11) Å, α = 103·9(1), β = 105·8(1), γ = 96·5(1)°, U = 865·9 Å^3, Z = 1, D_c = 1·87, $F(000)$ = 564. Mo-K_α radiation, λ = 0·7107, μ(Mo-K_α) = 17·4 cm^{-1}. Spacegroup $P\bar{1}$ was confirmed by the successful structure determination.

A crystal with dimensions *ca.* 0·6 × 0·25 × 0·03 mm was mounted with the a^* axis parallel to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions. It was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered molybdenum *X*-radiation was used. The stationary-crystal–stationary-counter method was used with a 4° take-off angle and a counting time of 10 s. Individual backgrounds were taken for those reflections which were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of background as a function of 2θ. Several standard reflections were measured repeatedly during the course of the experiment, but no significant change in intensity was detected. 2367 independent reflections were measured with $2\theta < 45°$. No absorption or extinction corrections were applied. The standard deviation $\sigma(I)$ of the reflections was taken to be $[I + 2E + (0{\cdot}03I^2)]^{\frac{1}{2}}$, where E is the estimated background of the reflection. 1366 reflections with $I > 3\sigma(I)$ were used in subsequent calculations.

Structure Determination.—The positions of the molybdenum atoms were determined from a Patterson function and Fourier syntheses were then calculated to determine the positions of the remaining atoms. The structure was refined by full-matrix least squares. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of F_o and $\sin\theta/\lambda$, was $\sqrt{w} = 1$ for $F_o < 45$ and $\sqrt{w} = 45/F_o$ for $F_o > 45$. Calculations were made on an ATLAS computer (at S.R.C., Chilton, Berkshire) with the programs described in ref. 5, and with some of our own programs of an Elliott 4130 at this university.

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† Subsequently, after the crystal structure analysis had shown the crystals to be of $Mo_4Cl_4O_6(OPr)_6$, the preparation was successfully repeated. Investigations are continuing to discover the course of the reaction.

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Atomic scattering factors for molybdenum, chlorine, carbon, and oxygen were taken from ref. 6, together with corrections for the real and imaginary part of the anomalous dispersion for molybdenum and chlorine. The anisotropic thermal parameter is defined as exp $(-2\pi^2\sum_i\sum_j U_{ij}h_ih_j)$ $(i,j = 1$—$3)$, and the isotropic thermal parameter as exp $-8\pi^2U(\sin^2\theta/\lambda^2)$. In each of the three independent n-propoxide groups, the β and γ carbon atoms were difficult to locate. A difference-Fourier map based on all other atomic parameters showed broad peaks for these atoms spreading in some directions *ca.* 0·75 Å. In two groups, these carbon atoms were refined in single positions although these had high thermal parameters and gave unlikely dimensions. For the third group, two positions were chosen for each carbon atom at either end of the broad peak and these were refined with half-occupancy. We do not believe that there were two distinct positions for each carbon atom (as would be the case if the correct space group were $P1$),* but the method of refinement outlined was the most successful of the several ways in which we attempted to account for the electron density map. In a final difference-Fourier map, no peak was $>0{\cdot}33$ of the height of a carbon atom. The final R was 0·063 and in the final cycle of refinement, no shift was $>0{\cdot}040\sigma$. The 1001 reflections given zero weight in the refinement showed no large discrepancies. The final list of positional co-ordinates and thermal parameters, together with standard deviations, are given in Tables 1 and 2. Bond distances and angles are given in Table 3. Observed and calculated structure factors are listed in Supplementary Publication SUP 20680 (8 pp.).†

TABLE 1

Atomic co-ordinates ($\times 10^4$) and isotropic thermal parameters, with estimated standard deviations in parentheses

	x	y	z	$U(\times 10^2)$
Mo(1)	0235(1)	1360(2)	1646(1)	*a*
Mo(2)	−2036(1)	0568(2)	0128(1)	*a*
Cl(1)	1724(4)	4070(6)	2551(5)	*a*
Cl(2)	−3463(4)	2119(8)	−0917(6)	*a*
O(1)	−0817(9)	−0923(15)	0295(11)	6·1(3)
O(2)	−1552(10)	0112(16)	−1825(12)	7·1(3)
O(3)	−0887(10)	2901(17)	0992(13)	7·7(4)
O(4)	−3217(12)	−1921(20)	−1137(15)	9·3(4)
O(5)	0078(11)	1246(17)	3153(13)	8·3(4)
O(6)	−2532(11)	0439(18)	1451(14)	8·7(4)
C(20)	−1926(19)	0967(31)	−3052(27)	9·4(6)
C(21)	−2961(27)	−0415(42)	−4054(33)	14·3(10)
C(22)	−3294(28)	0407(45)	−5464(34)	15·4(12)
C(30)	−0942(17)	4885(27)	1239(21)	8·0(6)
C(31a)	−1424(84)	5157(137)	2883(112)	17·8(38)
C(31b)	−1474(45)	5673(76)	2232(58)	9·9(16)
C(32a)	−1514(46)	7251(78)	2996(57)	11·7(16)
C(32b)	−0904(59)	5619(93)	3514(70)	12·4(22)
C(40)	−4257(28)	−2796(43)	−0807(33)	13·7(10)
C(41)	−5081(43)	−4239(69)	−2109(60)	21·9(19)
C(42)	−5400(45)	−4239(67)	−3276(61)	24·0(22)

[a] Anisotropic thermal parameters in Table 2.

DISCUSSION

The molecule of $Mo_4Cl_4O_6(OPr)_6$, (I), is shown in Figure 1, together with the atomic numbering scheme. The molecule has crystallographically imposed $\bar{1}$ symmetry. Only one of the two refined positions for C(31) and C(32) are shown.

TABLE 2

Anisotropic thermal parameters ($\times 10^3$) for molybdenum and chlorine atoms

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	48(1)	51(1)	42(1)	11(1)	10(1)	13(1)
Mo(2)	48(1)	60(1)	53(1)	15(1)	15(1)	16(1)
Cl(1)	79(4)	62(3)	88(4)	11(3)	13(3)	08(3)
Cl(2)	71(3)	98(4)	95(4)	41(3)	13(3)	22(3)

TABLE 3

Bond distances (Å) and angles (°) for (I) with estimated standard deviations in parentheses [a]

(*a*) Distances

Mo(1)–Mo(2)	2·669(2)		
Mo(1)–Cl(1)	2·397(5)	Mo(2)–Cl(2)	2·367(6)
Mo(1)–O(1$^{\mathrm{I}}$)	2·237(13)	Mo(2)–O(2)	2·182(14)
Mo(1)–O(2$^{\mathrm{I}}$)	2·048(13)	Mo(2)–O(4)	2·134(13)
Mo(1)–O(1)	1·993(9)	Mo(2)–O(1)	1·962(12)
Mo(1)–O(3)	1·985(14)	Mo(2)–O(3)	1·981(11)
Mo(1)–O(5)	1·617(15)	Mo(2)–O(6)	1·634(16)
O(2)–C(20)	1·535(29)	O(3)–C(30)	1·498(25)
C(20)–C(21)	1·49(4)	C(30)–C(31a)	1·89(12)
C(21)–C(22)	1·67(6)	C(31a)–C(32a)	1·61(12)
O(4)–C(40)	1·51(4)	C(30)–C(31b)	1·40(7)
C(40)–C(41)	1·52(5)	C(31b)–C(32b)	1·31(9)
C(41)–C(42)	1·15(9)		

(*b*) Angles

Cl(1)–Mo(1)–O(1$^{\mathrm{I}}$)	84·7(3)	Cl(2)–Mo(2)–O(2)	87·0(4)
Cl(1)–Mo(1)–O(2$^{\mathrm{I}}$)	87·9(3)	Cl(2)–Mo(2)–O(4)	87·5(5)
Cl(1)–Mo(1)–O(3)	87·0(4)	Cl(2)–Mo(2)–O(3)	89·9(4)
Cl(1)–Mo(1)–O(5)	97·4(4)	Cl(2)–Mo(2)–O(6)	96·2(6)
Cl(1)–Mo(1)–O(1)	159·7(4)	Cl(2)–Mo(2)–O(1)	159·2(4)
O(1$^{\mathrm{I}}$)–Mo(1)–O(2$^{\mathrm{I}}$)	69·8(5)	O(2)–Mo(2)–O(4)	79·0(6)
O(1$^{\mathrm{I}}$)–Mo(1)–O(3)	93·5(5)	O(2)–Mo(2)–O(3)	91·2(5)
O(1$^{\mathrm{I}}$)–Mo(1)–O(5)	162·4(6)	O(2)–Mo(2)–O(6)	167·5(6)
O(1$^{\mathrm{I}}$)–Mo(1)–O(1)	75·1(4)	O(2)–Mo(2)–O(1)	72·5(5)
O(2$^{\mathrm{I}}$)–Mo(1)–O(3)	162·9(6)	O(4)–Mo(2)–O(3)	170·0(6)
O(2$^{\mathrm{I}}$)–Mo(1)–O(5)	92·8(6)	O(4)–Mo(2)–O(6)	89·0(6)
O(2$^{\mathrm{I}}$)–Mo(1)–O(1)	86·6(5)	O(4)–Mo(2)–O(1)	85·5(5)
O(3)–Mo(1)–O(5)	104·1(7)	O(3)–Mo(2)–O(6)	100·8(6)
O(3)–Mo(1)–O(1)	92·5(5)	O(3)–Mo(2)–O(1)	93·6(5)
O(5)–Mo(1)–O(1)	102·4(6)	O(6)–Mo(2)–O(1)	103·2(7)
Mo(1)–O(3)–Mo(2)	84·6(5)	Mo(1)–O(2$^{\mathrm{I}}$)–Mo(2$^{\mathrm{I}}$)	108·3(6)
Mo(1)–O(3)–C(30)	138·6(9)	Mo(1)–O(2$^{\mathrm{I}}$)–C(20$^{\mathrm{I}}$)	122·2(13)
Mo(2)–O(3)–C(30)	135·9(11)	Mo(2)–O(2)–C(20)	128·7(12)
Mo(1)–O(1$^{\mathrm{I}}$)–Mo(2$^{\mathrm{I}}$)	109·4(5)	O(3)–C(30)–C(31a)	97(4)
Mo(1)–O(1$^{\mathrm{I}}$)–Mo(1$^{\mathrm{I}}$)	104·9(5)	O(3)–C(30)–C(31b)	118(4)
Mo(1)–O(1)–Mo(2)	84·9(4)	C(30)–C(31a)–C(32a)	92(6)
O(2)–C(20)–C(21)	102(2)	C(30)–C(31b)–C(32b)	111(5)
O(4)–C(40)–C(41)	111(3)	C(20)–C(21)–C(22)	102(3)
		C(40)–C(41)–C(42)	130(4)

[a] Roman numeral I as superscript refers to an atom with co-ordinates $-x$, $-y$, $-z$ relative to the reference x, y, z co-ordinates in Table 1.

The two molybdenum atoms in the asymmetric unit have different environments although both are formally seven-co-ordinate, being bonded to one other molybdenum atom, one chlorine atom, and five oxygen atoms. The metal–metal bond has little effect on the geometries of the co-ordination polyhedra of the molybdenum

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* We did not attempt a refinement in space group $P1$ for this reason and others, which included that (*a*) the refinement in space group $P\bar{1}$ was successful and (*b*) as a very high proportion of the scattering was compatible with the centric space group, refinement in $P1$ would have involved high correlation between parameters.

† For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. supplied as full-size copies.)

atoms which are most conveniently described as distorted octahedra. These four octahedra in the molecule are bridged together through edges in a manner equivalent to that found in the molecule of $Ti_4(OEt)_{16}$.[7] An idealised view of (I) is shown in Figure 2. An alternative (and more symmetric) way of bridging octahedra through edges is demonstrated in $[W(OH)(CO)_3H]_4$ in which the W_4O_4 unit forms an irregular cube; each hydroxo-group bridging three tungsten atoms.[8]

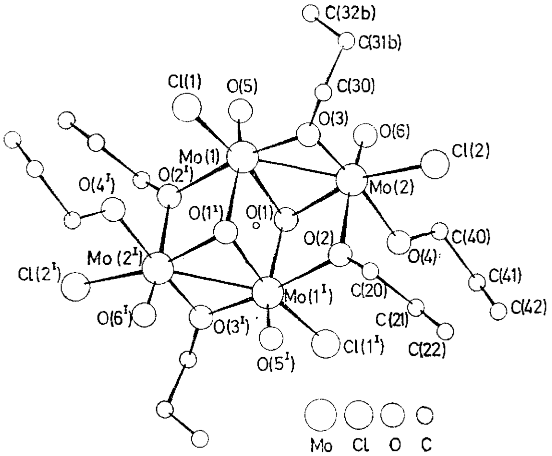

FIGURE 1 The molecule of $Mo_4Cl_4O_6(OPr)_6$

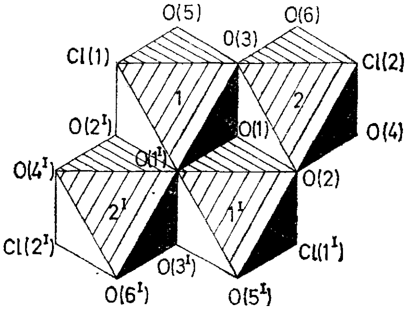

FIGURE 2 The four bridging octahedra in (I) in idealised form

In (I), one oxide oxygen * O(1) bridges three molybdenum atoms, two oxide oxygens, O(5) and O(6), form terminal Mo–O bonds; one of the three propoxide oxygen atoms, O(4) is terminal, while the others O(2) and O(3) bridge two molybdenum atoms. Mo(1) shares edges (Figure 2) with all three molybdenum atoms, while Mo(2) shares edges with only two of them, namely Mo(1) and Mo(1^{I}).

The major distortion from the idealised model of Figure 2 is caused by the formation of a metal–metal bond between the two molybdenum atoms in the asymmetric unit, Mo(1) and Mo(2). The Mo–Mo bond length [2·669(2) Å] is slightly longer than has been suggested for a Mo–Mo two-electron covalent bond; 2·541 Å in $Ba[Mo_2O_4(C_2O_4)_2(H_2O)_2]$.[9] A similar value (2·563 Å) is obtained in di-μ-oxo-bis[oxo-(ethyl L-cysteinato-*N,S*)molybdenum(V)].[10] It is not surprising that the bond length in (I) is longer than these values as two *d* electrons are not available for such a bond. The formula of (I) would indicate that two molybdenum atoms have oxidation state V and the other two VI, but it is more probable that the two *d* electrons are shared unequally between the four atoms.

It is also possible that the Mo–Mo bond in (I) is lengthened in order to increase ligand–ligand contacts, particularly O(5) $\cdots$ O(6). The Mo_2O_2 group [Mo(1), Mo(2), O(1), O(3)] is a folding bridge with the two MoO_2 sections intersecting at 156·8° (*cf.* 143·7° in ref. 10). Each molybdenum atom is bonded to a terminal oxide oxygen atom, at 1·617(15) and 1·634(16) Å. These oxygens are in eclipsed positions [see Figures, dihedral angle O(5)–Mo(1)–Mo(2)–O(6) is 2·4°] in the two octahedra and the fold in the bridge decreases the O(5) $\cdots$ O(6) contact (as in ref. 10). In (I) the O(5)–Mo(1)–Mo(2) and Mo(1)–Mo(2)–O(6) angles are 95·7 and 97·8° and O(5) $\cdots$ O(6) is 3·06 Å. In the folding bridge, the Mo–O distances are 1·985(14), 1·993(9), 1·981(11), and 1·962(12); the Mo–O–Mo angles are 84·6 and 84·9°, and the O–Mo–O angles are 92·5 and 93·6°. Thus the bridge is remarkably symmetrical despite the fact that O(1) is an oxide and O(3) a propoxide oxygen. All these dimensions are greater than those obtained for the similar folding bridge in ref. 10 (mean values 1·94 Å, and 83·0 and 91·5°), which allied to the longer Mo–Mo bond, indicate a slightly weaker bridge. A consequence of the Mo–O(3)–Mo angle being so small is that the Mo–O(3)–C(30) angles are 136 and 139°, C(30) being 0·09 Å from the plane of the Mo(1), Mo(2), and O(3) atoms. The Mo–O terminal bonds (mean 1·625 Å) are among the shortest such bonds known {*cf.* 1·63 in $MoOCl_3$,[11] 1·64 in $[(EtOCS_2)MoO]_2O$,[12] and 1·69 Å in $K_2[MoO_2(C_2O_4)(H_2O)]_2O$ [13]}.

Mo(1) also shares edges (pairs of oxygen atoms) with both Mo(2^{I}) and Mo(1^{I}). The two oxygens in the bridge to Mo(2^{I}) are similar in type to those oxygens which bridge between Mo(1) and Mo(2), namely one oxide oxygen O(1^{I}) and one propoxide oxygen O(2^{I}). However, there is no metal–metal bonding [Mo(1) $\cdots$ Mo(2^{I}) being 3·43 Å] and the bridge is almost planar; the maximum deviation of an atom from the Mo(1), O(1^{I}), Mo(2^{I}), O(2^{I}) plane being 0·02 Å. In this bridge, the Mo(1)–O(1^{I}) and Mo(2^{I})–O(2^{I}) bonds are respectively

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* An i.r. spectrum confirmed that (I) contained no hydroxo-group.

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2·237(13) and 2·182(14) Å. Both bonds are considerably longer than any others in (I) because they are *trans* to the multiple Mo–O terminal bonds. The Mo(1)–O(2^{I}) distance [2·048(13) Å] is longer than Mo–O bonds in the folding bridge (mean 1·98 Å). The fourth bond in the bridge is Mo(2^{I})–O(1^{I}) 1·962(12) Å, a bond shared with the folding bridge, *vide supra*. Despite these four different Mo–O bonds, the bridge is remarkably symmetric; the angles subtended at Mo(1) and Mo(2^{I}) being 69·8 and 72·5°, while those subtended at O(1^{I}) and O(2^{I}) are 109·4 and 108·3°. The Mo(2^{I})–O(2^{I})–C(20^{I}) angle is larger than the Mo(1^{I})–O(2^{I})–C(20^{I}) angle (128·7 and 122·2°), in which it differs from the two Mo–O(3)–C(30) angles in the folding bridge, which are equivalent. The effect of this disparity around O(2^{I}) is to increase the contacts between the propoxide group and O(5) and decrease them between the group and Cl(2^{I}).

The other four-membered ring in (I) contains atoms Mo(1), O(1), O(1^{I}), and Mo(1^{I}) and is therefore planar. The bond distances have already been described. Of the two independent angles, that at Mo(1) is 75·1 and at O(1) 104·9°. Thus the two molybdenum atoms Mo(1) and Mo(1^{I}) are closer together in this ring than in the other planar ring, but the Mo $\cdots$ Mo distance of 3·36 Å cannot be considered as a bond. Thus O(1) bridges three molybdenum atoms, the Mo–O(1)–Mo angles being 109·4, 104·9, and 84·9°. This latter angle is the odd one out, being in the folding bridge. A more symmetric arrangement is found in a structure containing no metal–metal bonds, such as $[\mathrm{W(OH)(CO)_3H}]_4$,[8] in which the oxygen atoms bridge three tungsten atoms, the six independent W–O–W angles range between 102 and 105°. In (I), O(1) is 0·95 Å out of the plane of the three molybdenum atoms Mo(1), Mo(2), and Mo(1^{I}) to which it is bonded. There is one other molybdenum–oxygen bond, Mo(2)–O(4) 2·134(15) Å, where O(4) is a terminal propoxide oxygen.

Thus the ten independent Mo–O bond lengths cover a large range (1·62—2·24 Å) but the differences are understandable in terms of different types and orders of the bonds. All bonds of similar type in the molecule have equivalent bond lengths. The order is Mo–O$_{t}$ [*] 1·62 $<$ Mo–OPr$_{fb}$, Mo–O$_{fb}$ 1·98 $<$ Mo–OPr$_{b}$ 2·05 $<$ Mo–OPr$_{t}$ 2·14 $<$ Mo–OPr$_{b}$ (*trans* to Mo–O$_{t}$) 2·19 $<$ Mo–O$_{tb}$ (*trans* to Mo–O$_{t}$) 2·24 Å.

In addition to the oxygen bonds described, each molybdenum atom is bonded to a terminal chlorine atom. The two distances are possibly different [Mo(1)–Cl(1) 2·397(5) and Mo(2)–Cl(2) 2·367(6) Å]. It is not obvious why these distances should be different, although the two molybdenum atoms have different electronic environments which will affect the atomic radii. Both these distances are considerably longer than the terminal Mo–Cl bonds in $\mathrm{MoOCl_3}$ (2·26),[11] $\mathrm{Mo_2Cl_{10}}$ (2·24),[14] and $\mathrm{MoNCl_3}$ (2·24) Å.[15] This Mo–Cl bond lengthening could be due to the *trans*-influence of the Mo(2)–O(1) and Mo(1)–O(1) bonds. Such an effect has been noted for Mo–S bonds [10] [*i.e.* Mo–S(*trans* to Mo–O$_{fb}$) being 2·49, 2·53 Å as against 2·385 Å with no *trans* atom]. In those examples (a full list is given in ref. 10), the Mo–O$_{fb}$ bond lengths were *ca.* 1·95 Å. Although the bond lengths in (I) are 1·99 and 1·96 Å, these still represent bond orders $>$1·0 (*ca.* 1·3) and therefore some *trans* weakening effect on the Mo–Cl bonds would be likely.

The metal–metal bond Mo(1)–Mo(2) has only a slight effect on the co-ordination sphere of each individual atom, the O(1) $\cdots$ O(3) shared edge being slightly lengthened (O–Mo–O angles 92·5, 93·6°). The co-ordination spheres are therefore most conveniently considered as distorted octahedra. The environments of Mo(1) and Mo(2) are very similar; they can be compared by taking pairs of atoms positioned either side of an approximate mirror plane running through atoms O(1) and O(3) and which is perpendicular to the Mo(1)–Mo(2) bond. Thus, atoms Cl(1), O(5), O(1^{I}), and O(2^{I}) around Mo(1) are compared with Cl(2), O(6), O(2), and O(4) around Mo(2). Atoms O(1) and O(3) are common. The angles from the two co-ordination spheres are compared in Table 3; only three of the fifteen angles differ from the equivalent angles in the other co-ordination sphere by more than 4°. The determining factors in the geometry are the *trans*-effect of the terminal oxide oxygens and the sharing of edges with other octahedra.

Considering Mo(1), the *trans*-influence [†] of O(5) is such that the O(5)–Mo–X$_{eq}$ angles are all greater than 90°, being 97·4, 92·8, 104·1, and 102·4° for X$_{eq}$ = Cl, O(2^{I}), O(3), and O(1). The angles are largest for the two folding bridge atoms, presumably so that the O(5) $\cdots$ O(6) distance is increased. A similar result is found for the *trans*-influence of O(6) on the Mo(2) co-ordination sphere. The angles subtended by pairs of X$_{eq}$ atoms at the molybdenum atoms are close to 90° in both co-ordination spheres (maximum deviation 4·5°, mean deviation 1·2°). The remaining angles to be considered are those subtended by atoms *trans* to O(5) and O(6), with the atoms in the equatorial plane X$_{eq}$. These would be expected to be less than 90° but considerable variations occur due to the formation of the four-membered rings. Thus, although the angles O(1^{I})–Mo(1)–O(1) and O(1)–Mo(2)–O(2) are similar (75·1 and 72·5°), all atoms being bridging oxygens, the angle O(1^{I})–Mo(1)–O(2^{I}) is 69·8° while O(2)–Mo(2)–O(4) is 79·0°, the difference arising as O(4) is a terminal oxygen, unlike O(2^{I}). In general, these angles are much smaller than those subtended with the other equatorial atoms

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[*] t = Terminal, b = bridge, fb = folding bridge, and tb = tertiary bridge.

[†] The term '*trans*-influence' is commonly used to describe the weakening of a M–L$_1$ bond *trans* to a M–L$_2$ multiple bond in an octahedral molecule. However, one of the consequences of this *trans*-weakening is that the four equatorial ligands X$_{eq}$ are displaced, away from L$_2$ towards L$_1$, such that X $\cdots$ L$_1$ and X $\cdots$ L$_2$ ligand–ligand repulsions are equated. Thus we feel justified in stating that the increase in O(5)–Mo(1)–X$_{eq}$ angles in (I) is due to the '*trans*-influence' of O(5).

[14] D. E. Sands and A. Zalkin, *Acta Cryst.*, 1959, **12**, 723.

[15] J. Straehle, *Angew. Chem. Internat. Edn.*, 1969, **8**, 925*A*.

Cl(1), Cl(2), and O(3). Indeed, both angles subtended at Mo with O(3) by O(1^{I}) and O(2) are greater than 90°.

In the propoxide groups, the O–α-C bond lengths are reasonable (mean 1·51 Å). However, unlike the α-C atoms, the β and γ carbon atomic positions are not well defined; they also had high thermal parameters and were probably disordered to some extent. For that reason, intermolecular distances are hard to assess with much accuracy and these are not listed. However, it would appear that the molecules of (I) are packed together with the normal van der Waals' forces, as several contacts are *ca.* 3·4 Å.

We thank A. W. Johans for assistance with the crystallographic investigations, Professor G. W. A. Fowles for his interest in this work, and Mrs. C. Y. Hurst for assistance with the computing at S.R.C. Chilton.

[2/2589 *Received*, 15*th November*, 1972]