Crystal and Molecular Structure of Tri-μ-Chloro-bis[dicarbonylbis(trimethyl phosphite)molybdenum] Tetrachloro(dimethyl phosphito)oxomolybdate

By **Michael G. B. Drew,*** Department of Chemistry, The University, Whiteknights, Reading RG6 2AD
John D. Wilkins, Department of Chemistry, University College, London WC1H 0AJ

Crystals of the title compound are triclinic, space group $P\bar{1}$, with a = 11.714(13), b = 15.493(12), c = 15.038(13) Å, α = 117.06(10), β = 99.43(11), γ = 96.96(14)°, Z = 2. The structure was determined from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares techniques to R 0.077, for 3 066 observed reflections. While both cation and anion are in general positions, the cation has approximate C_{2v} (mm) symmetry. The two molybdenum atoms in the cation are both seven-co-ordinate each being bonded to three bridging chlorines [2.533(7), 2.551(4), 2.549(6); 2.551(6), 2.538(6), 2.564(6) Å], to two carbonyls [1.94(2), 1.91(2); 1.92(2), 1.92(2) Å] and to two phosphorus atoms of trimethyl phosphite ligands [2.402(8), 2.438(6); 2.428(5), 2.420(7) Å]. The geometry of the co-ordination sphere of both metal atoms is a (4 : 3) tetragonal base–trigonal base with the three chlorines in the trigonal base shared by both metal atoms. At least one of the twelve methoxy-groups is disordered. In the anion the metal atom is octahedral being bonded to a terminal oxygen [1.60(2) Å], four chlorine atoms [2.369(8), 2.375(8), 2.376(8), 2.350(8) Å], and an oxygen [2.18(2) Å] of an oxydimethoxyphosphine group. This ligand, apart from the oxygen atom bonded to the metal, is disordered between two possible sites, with occupancy ratio *ca.* 2 : 1.

THE majority of the seven-co-ordinate complexes whose structures have been determined by X-ray crystallography have geometries which are related to one of three ideal polyhedra: the pentagonal bipyramid, the capped trigonal prism, and the capped octahedron. A further type, the tetragonal base–trigonal base, while considered [1] to have energy comparable to that of the first three, is much less frequently found. Recent examples include monoclinic ZrO_2,[2] $[Fe(CO)_3C_4(Ph)_4]$,[3] and two cadmium compounds containing two small chelate rings.[4,5]

Most seven-co-ordinate complexes of the early transition metals are monomeric, although some examples of oxygen bridges are known [2] as are examples of bidentate ligands acting as a bridge {*e.g.* in $[\{M(CO)_2X_2(dpe)_{1.5}\}_2]$, M = Mo or W; X = Cl, Br, or I; dpe = bis(diphenylphosphino)ethane}.[6] There are no structural data on halogen bridges for such metals but some interesting examples with uranium have been observed recently {UBr_4,[7] $[(UO_2)_2F_9]^{5-}$,[8] and $[(UO_2)_2F_8]^{4-}$ (ref. 9)}.

A compound which exhibits both the tetragonal base–trigonal base geometry and contains bridging atoms therefore merits a full X-ray examination. This we have done inadvertently with a crystal structure determination of $[Mo_2Cl_3(CO)_4\{P(OMe)_3\}_4]^{n+}[MoOCl_4\{OP(OMe)_2\}]^{n-}$, (I), which we now report.

EXPERIMENTAL

We attempted to prepare $[Mo(CO)_2\{P(OMe)_3\}_3Cl_2]$ from the reaction between trimethyl phosphite and $[Mo(CO)_4Cl_2]$ following the (very brief) experimental details.[10] However, we obtained this dichloro-complex only when the stoicheiometric quantity of the ligand and short reaction times (*ca.* 10 min) were used. With longer reaction times more complicated reactions occur and the complex (I) can be isolated as follows. $[Mo(CO)_4Cl_2]$ Was prepared [11] from $Mo(CO)_6$ (2 g) and dissolved in dichloromethane (30 cm^3) and filtered. The solution was stirred and trimethyl phosphite (2.7 cm^3) was added by syringe over a period of 5 min. The solution was set aside for *ca.* 5 h at room temperature. Solvent was removed *in vacuo* leaving a sticky brown solid. This procedure was repeated 3 times. The brown solid was then washed with light petroleum and pumped dry. The solid was crystallised by slow evaporation from a mixture of dichloromethane–toluene (1 : 1) yielding yellow-green crystals of (I) which were used in this X-ray determination.† I.r. spectrum (cm^{-1}) ($CHCl_3$), ν(C–O): 1 987m, 1 919s; ν(Mo=O): 974ms. By contrast $[Mo(CO)_2\{P(OMe)_3\}_3Cl_2]$ shows ν(C–O) 1 972s and 1 893s.

Crystal Data.—$C_{18}H_{42}Cl_7Mo_3O_{20}P_5$, Triclinic, M = 1 269.4, a = 11.714(13), b = 15.493(12), c = 15.038(13) Å, α = 117.06(10)°, β = 99.43(13)°, γ = 96.96(14)°, U = 2 318.9 Å^3, D_m = 1.81(2), Z = 2, D_c = 1.82. Mo-K_α radiation, λ = 0.7107 Å; μ(Mo-K_α) = 13.8 cm^{-1}. Space group $P\bar{1}$ or $P1$, shown by successful refinement to be the former.

A crystal *ca.* 0.1 × 0.2 × 0.65 mm was mounted with a^* perpendicular to the instrument axis of a General Electric XRD 5 diffractometer which was used to measure diffraction intensities and cell dimensions, the latter *via* least-squares refinement of the 2θ values of high-angle reflections. It was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered molybdenum X-radiation 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. The intensities of several standard reflections monitored throughout data collection showed no significant changes. Of 4 443 independent reflections measured by the

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† Before the structure determination, we thought that the stoicheiometry of the crystals was similar to that of the original compound as M for $[MoCl_2(CO)_2\{P(OMe)_3\}_3]$ is 595.1, and, with Z = 4, D_c is 1.70, close to the observed value.

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TABLE 1

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

Atom	x	y	z	$U(\times 10^3)$
Mo(1)	3 385(1)	3 839(1)	6 351(1)	*
Mo(2)	6 410(1)	3 881(1)	7 293(1)	*
Cl(1)	5 378(4)	4 992(4)	6 782(5)	*
Cl(2)	4 778(5)	2 694(4)	5 677(4)	*
Cl(3)	4 560(4)	3 900(4)	7 983(4)	*
P(1)	2 026(5)	2 219(4)	5 405(4)	*
P(2)	2 796(5)	5 406(4)	6 841(5)	*
P(3)	7 040(6)	2 339(5)	6 749(5)	*
P(4)	7 708(5)	5 497(5)	8 522(4)	*
C(1)	2 638(17)	3 748(15)	5 062(16)	62(5)
O(1)	2 267(14)	3 690(11)	4 246(12)	86(5)
C(2)	2 176(17)	3 918(14)	7 087(15)	59(5)
O(2)	1 504(12)	3 942(10)	7 573(10)	65(4)
C(3)	7 700(19)	4 023(15)	6 708(16)	69(6)
O(3)	8 485(15)	4 096(12)	6 305(12)	92(5)
C(4)	7 059(17)	3 825(14)	8 535(15)	60(5)
O(4)	7 322(13)	3 760(11)	9 278(12)	83(4)
O(11)	2 272(14)	1 435(12)	5 786(12)	90(5)
O(12)	2 151(12)	1 631(10)	4 276(11)	75(4)
O(13)	0 667(13)	2 121(11)	5 313(11)	82(4)
C(11)	2 139(22)	1 622(19)	6 803(20)	96(8)
C(12)	1 566(24)	0 550(20)	3 540(21)	102(8)
C(13)	−0 038(21)	2 589(18)	4 880(18)	86(7)
O(21)	1 458(13)	5 284(11)	6 452(11)	80(4)
O(22)	3 509(17)	6 193(14)	6 687(15)	121(6)
O(23)	2 999(18)	6 109(14)	8 141(15)	120(6)
C(21)	0 833(27)	6 124(23)	6 646(24)	121(10)
C(22)	3 588(26)	6 093(22)	5 738(24)	116(12)
C(23)	4 030(33)	6 650(26)	8 874(28)	143(12)
O(31)	7 159(14)	1 866(12)	5 597(11)	87(5)
O(32)	6 172(19)	1 429(15)	6 696(16)	131(7)
O(33a)	7 946(31)	2 086(28)	7 291(25)	90(10)
O(33b)	8 536(36)	2 715(28)	7 514(25)	80(10)
C(31)	6 788(31)	0 871(31)	4 827(32)	173(15)
C(32)	5 494(25)	1 389(21)	7 397(22)	109(8)
C(33a)	9 143(84)	2 574(73)	7 432(67)	146(31)
C(33b)	9 209(66)	1 950(59)	7 411(56)	132(25)
O(41)	8 085(13)	6 130(11)	7 989(11)	83(4)
O(42)	7 132(15)	6 230(12)	9 325(13)	96(5)
O(43)	8 875(20)	5 415(16)	9 095(16)	137(7)
C(41)	8 127(30)	7 131(26)	8 320(26)	141(9)
C(42)	6 784(25)	6 184(21)	10 176(22)	111(9)
C(43)	10 025(51)	5 928(40)	9 377(42)	234(22)
Mo(5)	7 924(1)	0 112(1)	1 718(1)	*
Cl(51)	9 601(6)	1 269(5)	1 923(5)	104(2)
Cl(52)	6 127(7)	−1 097(6)	1 119(6)	116(2)
Cl(53)	8 962(6)	−1 170(5)	1 199(5)	104(2)
Cl(54)	6 792(9)	1 328(8)	1 889(8)	160(3)
O(51)	8 210(17)	0 380(15)	2 907(15)	124(6)
O(52)	7 566(14)	−0 225(11)	0 112(12)	88(5)
P(5a) †	6 744(11)	−0 182(9)	−0 729(9)	101(3)
P(5b)	7 958(17)	−0 125(14)	−0 681(15)	85(9)
O(53)	7 359(25)	0 644(20)	−0 941(21)	171(9)
C(53a)	8 367(47)	1 182(37)	−0 576(38)	127(16)
O(54a)	6 632(54)	−0 982(44)	−1 758(45)	182(22)
C(54a)	5 943(75)	−1 232(63)	−2 570(68)	220(33)
O(54b)	7 184(56)	−1 168(46)	−1 820(46)	104(19)
C(53b) ‡	7 725	1 478	−0 244	140
C(54b)	6 221	−1 575(55)	−1 936(53)	73(20)

* Anisotropic thermal parameters, given in Table 2. † Population parameter for P(5a) refined as 0.64(2). Atoms in the a part of the anion were given this population parameter and those in the b molecule 0.36; O(53), common to both, was given 1.0. ‡ Parameters for this atom fixed.

stationary-crystal–stationary-counter method 3 066 with $I > \sigma(I)$, where the standard deviation $\sigma(I)$ of the reflections was taken to be $[I + 2E + 0.03I^2]^{\frac{1}{2}}$ and E is the estimated background of the reflection, were used in subsequent calculations. Neither an absorption nor an extinction correction was made.

Structure Determination.—The structure was solved from a Patterson function with some difficulty. We expected four molybdenum atoms; the Patterson map revealed six at sites consistent with space group $P\bar{1}$. Fourier syntheses revealed part of the structure as two entities, one of formula $[Mo_2Cl_3(CO)_4\{P(OMe)_3\}_3P(OMe)_2]$ and the other of formula $[MoO_2Cl_4]$. These were refined to R 0.14 and had reasonable dimensions and thermal parameters. In a difference-Fourier, there was a peak elongated over *ca.* 1 Å in the fourth tetrahedral position of the unique phosphorus atom in the first entity. This spread was surprising as one would expect such a position to be well defined. The peak for the methyl position was equally spread. We refined two possible positions each with ½ occupancy for both the oxygen and carbon atoms of this methoxy-group. Refinement of the parameters converged but with unsatisfactory dimensions and it is probable that our explanation of the disorder is insufficient.

The other entity $[MoO_2Cl_4]$ was octahedral and the remaining peaks found in the difference-Fourier map were in the vicinity of one of the oxygen atoms. We disentangled these peaks as belonging to two possible orientations of $P(OMe)_2$ thus making each entity $[MoOCl_4O\{P(OMe)_2\}_2]$. The individual occupancies of the two phosphorus atoms were allowed to refine dependently and gave R values of 0.64 and 0.36. The remaining atoms in each ligand (named a and b) were given the same occupancies as their respective phosphorus atoms. There is considerable overlap between atoms in these ligands (see Figure 2). In particular, one oxygen atom, O(53), is common to both orientations and this atom was given an occupancy factor of 1.0. All atoms converged successfully except C(53b) whose parameters were fixed. All these atoms were then refined by least squares, using 6 large blocks of equivalent size, to R 0.077 for 3 066 observed reflections. Molybdenum, chlorine, and phosphorus atoms were refined anisotropically, carbon and oxygen atoms isotropically. A difference-Fourier map showed no peaks of significant height in the region of the disorder (or elsewhere) which suggested that we had described the disorder † adequately.

TABLE 2

Anisotropic thermal parameters ($\times 10^3$) for (I)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	44.7(10)	51.5(11)	43.1(10)	15.3(8)	9.9(9)	26.2(9)
Mo(2)	43.5(10)	65.4(12)	46.5(11)	19.4(8)	11.8(8)	30.1(9)
Mo(5)	83.2(14)	65.4(13)	69.9(13)	18.0(11)	30.8(11)	35.6(11)
Cl(1)	46(3)	75(4)	111(5)	10(3)	12(3)	64(5)
Cl(2)	54(3)	75(4)	56(3)	24(3)	1(3)	8(3)
Cl(3)	53(3)	118(5)	50(3)	26(3)	12(3)	56(3)
P(1)	53(3)	62(4)	57(3)	10(3)	3(3)	30(3)
P(2)	61(4)	57(4)	90(4)	22(3)	22(3)	43(3)
P(3)	84(5)	106(5)	90(5)	58(4)	41(4)	59(4)
P(4)	57(4)	92(5)	52(4)	5(3)	9(3)	31(3)

The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of F_0 and $\sin\theta/\lambda$, was $\sqrt{w} = 1$ for $F_0 < 60$ and $\sqrt{w} = 60/F_0$ for $F_0 > 60$. Calculations were made on a CDC 7 600 computer at the University of London Computer Centre with the programs described in ref. 12 and on an ICL 1904S Computer at Reading University with our unpublished programs. Atomic scattering factors for

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† Attempted refinements in space group $P1$ were not successful.

‡ See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[12] '*X*-Ray' system of programs, ed. J. M. Stewart, University of Maryland Technical Report 67 58, version of July 1970.

molybdenum, chlorine, phosphorus, carbon, and oxygen were taken from ref. 13, as were the corrections for the real and imaginary part of the anomalous dispersion for molybdenum, phosphorus, and chlorine. The 1 377 unobserved reflections showed no serious discrepancies. In the final cycle of refinement, no shift was $>0.10\sigma$. Final positional co-ordinates and thermal parameters are given in Tables 1 and 2. Final observed and calculated structure factors are listed in a Supplementary Publication No. SUP 21409 (11 pp., 1 microfiche).‡ Bond lengths and angles in the ions are given in Table 3.

TABLE 3

Molecular dimensions for (I), distances (Å), angles (°), with estimated standard deviations in parentheses

(*a*) In the cation

Mo(1)–Cl(1)	2.551(6)	Mo(2)–Cl(1)	2.533(6)
Mo(1)–Cl(2)	2.538(6)	Mo(2)–Cl(2)	2.551(4)
Mo(1)–Cl(3)	2.564(6)	Mo(2)–Cl(3)	2.549(6)
Mo(1)–P(1)	2.428(5)	Mo(2)–P(3)	2.402(8)
Mo(1)–P(2)	2.420(7)	Mo(2)–P(4)	2.438(6)
Mo(1)–C(1)	1.925(24)	Mo(2)–C(3)	1.942(25)
Mo(1)–C(2)	1.918(23)	Mo(2)–C(4)	1.908(26)
Cl(1)–Mo(1)–Cl(2)	74.8(2)	Cl(1)–Mo(2)–Cl(2)	74.9(2)
Cl(1)–Mo(1)–Cl(3)	76.4(2)	Cl(1)–Mo(2)–Cl(3)	76.9(2)
Cl(2)–Mo(1)–Cl(3)	77.0(2)	Cl(2)–Mo(2)–Cl(3)	77.1(2)
Cl(1)–Mo(1)–P(1)	151.8(2)	Cl(1)–Mo(2)–P(3)	147.7(2)
Cl(1)–Mo(1)–P(2)	79.3(2)	Cl(1)–Mo(2)–P(4)	79.9(2)
Cl(1)–Mo(1)–C(1)	100.2(7)	Cl(1)–Mo(2)–C(3)	93.2(8)
Cl(1)–Mo(1)–C(2)	132.5(5)	Cl(1)–Mo(2)–C(4)	138.8(6)
Cl(2)–Mo(1)–P(1)	78.2(2)	Cl(2)–Mo(2)–P(3)	77.8(2)
Cl(2)–Mo(1)–P(2)	151.6(2)	Cl(2)–Mo(2)–P(4)	154.0(3)
Cl(2)–Mo(1)–C(1)	97.4(6)	Cl(2)–Mo(2)–C(3)	101.1(6)
Cl(2)–Mo(1)–C(2)	137.0(8)	Cl(2)–Mo(2)–C(4)	132.2(6)
Cl(3)–Mo(1)–P(1)	105.5(3)	Cl(3)–Mo(2)–P(3)	113.3(3)
Cl(3)–Mo(1)–P(2)	108.1(2)	Cl(3)–Mo(2)–P(4)	103.6(2)
Cl(3)–Mo(1)–C(1)	174.0(7)	Cl(3)–Mo(2)–C(3)	170.1(9)
Cl(3)–Mo(1)–C(2)	79.3(7)	Cl(3)–Mo(2)–C(4)	80.6(6)
P(1)–Mo(1)–P(2)	124.6(2)	P(3)–Mo(2)–P(4)	123.5(2)
P(1)–Mo(1)–C(1)	75.1(7)	P(3)–Mo(2)–C(3)	75.3(8)
P(1)–Mo(1)–C(2)	74.2(5)	P(3)–Mo(2)–C(4)	73.3(6)
P(2)–Mo(1)–C(1)	75.7(6)	P(4)–Mo(2)–C(3)	73.7(6)
P(2)–Mo(1)–C(2)	70.5(7)	P(4)–Mo(2)–C(4)	72.6(6)
C(1)–Mo(1)–C(2)	106.4(9)	C(4)–Mo(2)–C(3)	107.1(10)
Mo(1)–Cl(1)–Mo(2)	89.4(2)		
Mo(1)–Cl(2)–Mo(2)	89.3(2)		
Mo(1)–Cl(3)–Mo(2)	88.7(2)		
C(1)–O(1)	1.19(3)	C(3)–O(3)	1.20(3)
C(2)–O(2)	1.15(3)	C(4)–O(4)	1.16(3)
Mo(1)–C(1)–O(1)	174.4(19)	Mo(2)–C(3)–O(3)	177.6(17)
Mo(1)–C(2)–O(2)	174.8(18)	Mo(2)–C(4)–O(4)	172.6(18)
P(1)–O(11)	1.597(23)	P(3)–O(31)	1.584(19)
P(1)–O(12)	1.562(15)	P(3)–O(32)	1.598(26)
P(1)–O(13)	1.558(16)	P(3)–O(33a)	1.433(43)
P(2)–O(21)	1.537(16)	P(3)–O(33b)	1.793(38)
P(2)–O(22)	1.521(26)	P(4)–O(41)	1.589(22)
P(2)–O(23)	1.706(20)	P(4)–O(42)	1.551(18)
		P(4)–O(43)	1.543(26)
Mo(1)–P(1)–O(11)	116.2(5)	Mo(2)–P(3)–O(31)	112.4(9)
Mo(1)–P(1)–O(12)	111.7(6)	Mo(2)–P(3)–O(32)	117.6(9)
Mo(1)–P(1)–O(13)	120.8(6)	Mo(2)–P(3)–O(33a)	129.3(13)
		Mo(2)–P(3)–O(33b)	103.1(13)
O(11)–P(1)–O(12)	99.3(9)	O(31)–P(3)–O(32)	100.5(10)
O(11)–P(1)–O(13)	100.7(10)	O(31)–P(3)–O(33a)	106.1(16)
O(12)–P(1)–O(13)	105.4(8)	O(31)–P(3)–O(33b)	104.6(14)
		O(32)–P(3)–O(33a)	85.0(19)
		O(32)–P(3)–O(33b)	117.0(31)
Mo(2)–P(2)–O(21)	113.3(6)	Mo(2)–P(4)–O(41)	112.5(5)
Mo(2)–P(2)–O(22)	119.1(9)	Mo(2)–P(4)–O(42)	115.3(6)
Mo(2)–P(2)–O(23)	113.0(9)	Mo(2)–P(4)–O(43)	112.8(9)
O(21)–P(2)–O(22)	110.7(12)	O(41)–P(4)–O(42)	100.1(11)
O(21)–P(2)–O(23)	101.6(10)	O(41)–P(4)–O(43)	106.1(13)
O(22)–P(2)–O(23)	96.7(11)	O(42)–P(4)–O(43)	108.9(11)
P(1)–O(11)–C(11)	119.8(16)	P(3)–O(31)–C(31)	128.0(27)
P(1)–O(12)–C(12)	124.6(18)	P(3)–O(32)–C(32)	131.0(16)
P(1)–O(13)–C(13)	123.5(18)	P(3)–O(33a)–C(33a)	114.7(60)
P(2)–O(21)–C(21)	125.3(14)	P(3)–O(33b)–C(33b)	114.8(30)
P(2)–O(22)–C(22)	124.6(16)	P(4)–O(41)–C(41)	128.3(20)
P(2)–O(23)–C(23)	128.6(23)	P(4)–O(42)–C(42)	128.6(20)
		P(4)–O(43)–C(43)	132.4(38)

Bond lengths for O(*nm*)–C(*nm*), $m = 1$—3 are for $n = 1$, 1.46(4), 1.51(3), and 1.43(4); for $n = 2$, 1.51(4), 1.39(4), and 1.36(4); for $n = 3$, 1.40(4), 1.44(4), 1.44(10), and 1.44(10); for $n = 4$, 1.39(4), 1.43(4), and 1.37(6) Å.

TABLE 3 (*Continued*)

(*b*) In the anion

Mo(5)–O(51)	1.604(23)	O(52)–Mo(5)–Cl(51)	83.9(5)
Mo(5)–O(52)	2.179(18)	O(52)–Mo(5)–Cl(52)	82.9(5)
Mo(5)–Cl(51)	2.369(8)	O(52)–Mo(5)–Cl(53)	85.0(5)
Mo(5)–Cl(52)	2.375(8)	O(52)–Mo(5)–Cl(54)	83.5(6)
Mo(5)–Cl(53)	2.350(8)	Cl(51)–Mo(5)–Cl(52)	166.6(3)
Mo(5)–Cl(54)	2.376(8)	Cl(52)–Mo(5)–Cl(53)	91.0(3)
O(51)–Mo(5)–O(52)	178.7(9)	Cl(51)–Mo(5)–Cl(54)	87.9(4)
O(51)–Mo(5)–Cl(51)	94.9(8)	Cl(52)–Mo(5)–Cl(53)	89.3(3)
O(51)–Mo(5)–Cl(52)	98.4(8)	Cl(52)–Mo(5)–Cl(54)	89.0(3)
O(51)–Mo(5)–Cl(53)	95.2(8)	Cl(53)–Mo(5)–Cl(54)	168.5(4)
O(51)–Mo(5)–Cl(54)	96.3(9)		

	Part (a)	Part (b)
O(52)–P(5)	1.49(2)	1.41(3)
Mo(5)–O(52)–P(5)	145.3(12)	148.9(11)
P(5)–O(53)	1.57(4)	1.61(4)
P(5)–O(54)	1.45(5)	1.73(5)
O(53)–C(53)	1.23(6)	1.20(10) *
O(54)–C(54)	1.21(10)	1.17(10)
O(52)–P(5)–O(53)	109.5(14)	111.7(19)
O(52)–P(5)–O(54)	115.2(31)	106.1(30)
O(53)–P(5)–O(54)	94.0(31)	95.0(30)
P(5)–O(53)–C(53)	131.3(40)	110.7(60) *
P(5)–O(54)–C(54)	131.3(70)	122.6(58)

* Guessed standard deviation.

DISCUSSION

The two entities are presumably ionic of the form $[Mo_2Cl_3(CO)_4\{P(OMe)_3\}_4]^{n+}$ and $[MoOCl_4\{OP(OMe)_2\}]^{n-}$. Possible values of n and of the oxidation states of the molybdenum atoms are discussed later. The cation is shown in Figure 1, together with the atomic numbering scheme, and the anion in Figure 2. The atoms in the anion are numbered with 5 as the first digit. Ignoring the methoxy-groups, the cation has approximately C_{2v} symmetry, the two-fold axis running through Cl(3) and the midpoint of the Mo(1) $\cdots$ Mo(2) vector. Of the two

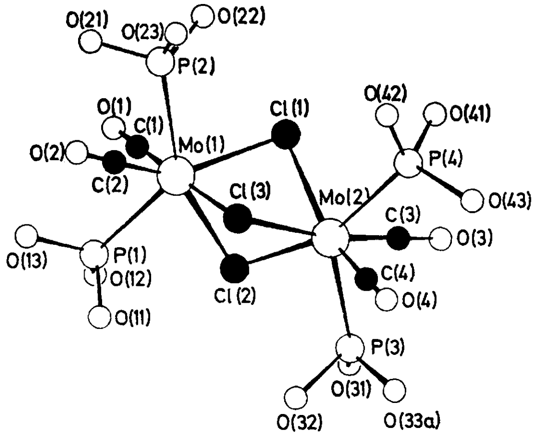

FIGURE 1 The cation $[Mo_2Cl_3(CO)_4\{P(OMe)_3\}_4]^{n+}$, methyl groups omitted for clarity

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[13] ' International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

mirror planes, the first contains Cl(1), Cl(2), and Cl(3), and the second both molybdenum atoms, the four carbonyl groups, and Cl(3). The maximum deviation of an atom from this second plane is 0.14 Å. Details of these least-squares planes (and others) are given in Table 4. Thus the co-ordination sphere of each molybdenum atom has C_s symmetry. This is shown in Figure 3 which is a projection of the co-ordination spheres of Mo(1) and Mo(2) on the trichloro-bridge, thus illustrating the 4 : 3 geometry. Both quadrilateral faces are planar and approximately parallel to the triangular face (angle of intersections 2.3 and 1.1°, Table 4). Muetterties and Wright [14] suggest two possible conformations of this 4 : 3 geometry, both with C_s geometry, the only difference being a trivial shift of the trigonal plane with respect to the tetragonal plane. In (I) we have the second conformation of ref. 14, in which an atom of the trigonal base and one of the tetragonal base overlap in this projection. It is not surprising that a chlorine atom overlaps a carbonyl group rather than one of the more bulky phosphorus ligands. In this conformation the P · · · Cl distances are greater than would be the case in the other 4 : 3 conformation.

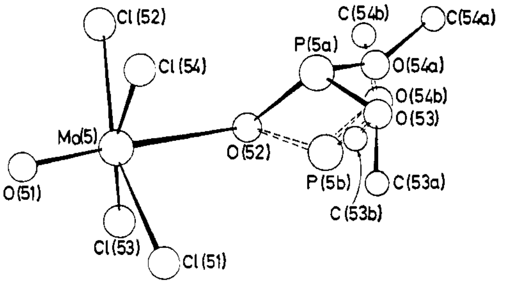

FIGURE 2 The anion $[\mathrm{MoOCl_4\{OP(OMe)_2\}}]^{n-}$. Continuous bonds are drawn between atoms in part a, dotted bonds between atoms in part b

TABLE 4

Equations of least-squares planes for (I) in the form $Ax + By + Cz = D$, where x, y, z are the crystallographic non-orthogonalised fractional co-ordinates. Distances (Å) of relevant atoms from each plane are given in square brackets

	A	*B*	*C*	*D*
Plane (1): Cl(1)—(3)	10.84	−4.44	3.35	5.88
[Mo(1) −1.78, Mo(2) 1.78, P(1) −2.85, P(2) −2.95, P(3) 2.95, P(4) 2.87, C(1) −2.98, C(2) −2.88, C(3) 2.90, C(4) 2.91]				
Plane (2): Mo(1), Mo(2), Cl(3), C(1)—(4)	−0.22	13.54	−0.06	5.10
[Mo(1) −0.01, Mo(2) −0.03, Cl(3) 0.03, C(1) −0.11, C(2) 0.12, C(3) 0.14, C(4) −0.13]				
Plane (3): P(1), P(2), C(1), C(2)	10.98	−3.93	2.83	2.87
[P(1) 0.01, P(2) 0.01, C(1) −0.01, C(2) −0.01]				
Plane (4): P(3), P(4), C(3), C(4)	10.83	−4.17	3.35	8.90
[P(3) 0.00, P(4) 0.00, C(3) −0.00, C(4) −0.00]				

Angles (°) between planes: (1)–(3) 2.3, (1)–(4) 1.1, (3)–(4) 2.0, (1)–(2) 89.4, (2)–(3) 89.3, (2)–(4) 88.2.

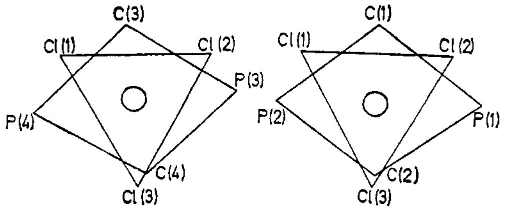

FIGURE 3 The co-ordination spheres of Mo(1) and Mo(2) in diagrammatic form comparable to that in ref. 16; projection on the Cl(1), Cl(2), Cl(3) plane

Although the structure of a monomeric complex containing three chlorine, two phosphorus, and two carbon atoms in the co-ordination sphere has not been determined, its geometry can be predicted as being a capped octahedron with a carbonyl in the unique position, one carbonyl and two phosphorus in the capped face, and three chlorine atoms in the uncapped face.* The difference between such capped octahedra and the present dimer is that the Cl–Mo–Cl angles are *ca.* 76 and not 90°. Thus there is more space available for the remaining four ligands and the 4 : 3 geometry is possible. The distances between phosphorus and carbon atoms in the 4 face range between 2.54 and 2.69 Å, distances which are not unreasonably small. Thus the trichloro-bridge and the 4 : 3 geometry are particularly well suited.

The Cl–Mo–Cl (*ca.* 76°) and Mo–Cl–Mo angles (89°) ensure that there is no metal–metal bonding in (I), the Mo · · · Mo contact being 3.575 Å. This contrasts with $Cs_3Mo_2Cl_9$,[15] also a trichloro-bridged dimer in which Cl–Mo–Cl are 94.2°, Mo–Cl–Mo 64.5°, and Mo · · · Mo 2.655 Å. Bond lengths involving the molybdenum atoms are discussed later. Ten of the twelve P–O bond lengths are as expected, mean 1.56 Å, with two exceptions. First P(2)–O(23) is 1.706(20) Å, a high value which has no reasonable explanation particularly as the other distances are well within the expected range. A difference-Fourier map shows no residual peak in this area. Secondly dimensions involving O(33a) and O(33b) are unrealistic (see Experimental section). One reason for this could be that the true space group is *P*1 and that each refined position in the present structure is an average of two independent positions. This would account for the occasional odd dimension though not for the 2 : 1 disorder in the anion. As stated in the Experimental section, refinement in *P*1 was not successful, presumably because of the high correlation between parameters, a very large percentage of the scattering being compatible with space group *P*1.

The Mo–P–O angles (mean 115°) are as usual much larger than the O–P–O angles (mean 103°).[16] The orientations of the three oxygen atoms around each phosphorus atom are characterised by their dihedral

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* This geometry can be written C:C,P,P:Cl,Cl,Cl. It is predictable from such structures as $[\mathrm{MoCl_2(CO)_2(PMe_2Ph)_3}]$ [21] which is C:C,P,P:P,Cl,Cl and $[\mathrm{MoCl_4(PMe_2Ph)_3}]$ which is Cl:P,P,P:Cl,Cl,Cl [L. M. Muir, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 59].

[14] E. L. Muetterties and C. M. Wright, *Quart. Rev.*, 1967, **21**, 109.

[15] R. Saillant, R. B. Jackson, W. E. Streib, K. Folting, and R. A. D. Wentworth, *Inorg. Chem.*, 1971, **10**, 1453.

[16] M. G. B. Drew, *J.C.S. Dalton*, 1972, 1329.

angles (Table 5). As expected the angles L–Mo–P(*n*)–O(*nm*), where L = Cl or C, *n* = 1—4, and *m* = 1—3, are large, the minimum being 28.3° (ignoring −26.7° for an angle in the disordered grouping), when the L–Mo–P(*n*) angle is ⩽90° thus ensuring that L ··· O(*nm*) contacts are not too short.

In contrast three of the O(nm_1)–P(*n*)–O(nm_2)–C(nm_2) angles ($n = 1$—4, $m_1,m_2 = 1$—3) are very small (Table 5), presumably because the size of the O–P–O angle is sufficiently large to increase O ··· C distances to reasonable values (2.79, 2.77, and 2.79 Å) without requiring large dihedral angles.

TABLE 5

(*a*) Dihedral angles (°) of the type L–Mo–P(*n*)–O(*nm*), where L–Mo–P(*n*) is <90°

	m		
	1	2	3
Cl(2)–Mo(1)–P(1)–O(1*m*)	60.0	−52.9	−177.7
C(1)–Mo(1)–P(1)–O(1*m*)	161.1	48.2	−76.6
C(2)–Mo(1)–P(1)–O(1*m*)	−86.6	160.4	35.7
Cl(1)–Mo(1)–P(2)–O(2*m*)	161.1	28.3	−84.0
C(1)–Mo(1)–P(2)–O(2*m*)	57.5	−75.2	172.4
C(2)–Mo(1)–P(2)–O(2*m*)	−56.0	171.2	58.8
Cl(2)–Mo(2)–P(3)–O(3*m*)	55.2	−60.8	−168.2,* 167.3
C(3)–Mo(2)–P(3)–O(3*m*)	−49.8	−165.8	86.7,* 62.2
C(4)–Mo(2)–P(3)–O(3*m*)	−163.2	80.8	−26.7,* −51.1
Cl(1)–Mo(2)–P(4)–O(4*m*)	−48.7	65.4	−168.7
C(3)–Mo(2)–P(4)–O(4*m*)	47.7	161.7	−72.3
C(4)–Mo(2)–P(4)–O(4*m*)	162.2	−83.8	42.2

(*b*) Dihedral angles (°) of the type Mo–P(*n*)–O(*nm*)–C(*nm*) and O(nm_1)–P(*n*)–O(nm_2)–C(nm_2) less than 40°

O(32)–P(3)–O(31)–C(31)	−10.9
O(42)–P(4)–O(41)–C(41)	13.0
O(41)–P(4)–O(43)–C(43)	15.9

* Values for O(33a) and for O(33b).

The anion is shown in Figure 2. The environment of the molybdenum atom is a distorted octahedron with the two oxygen atoms mutually *trans*. The distortions are due to the *trans*-effect of the terminal oxygen. All four O(51)–Mo(5)–Cl angles are much larger than 90°, mean 96.2°. The Mo(5)–O(52) bond [2.179(18) Å] is *trans*-weakened by the terminal bond. The O(52)–Mo(5)–Cl angles are much less than 90°, mean 83.8°. As is often found for such distorted octahedra, the eight O ··· Cl distances are comparable. The exact stoicheiometry of the disordered part of the anion was difficult to disentangle. However, having assumed that the P(5a) and P(5b) atoms are not part of the same molecule, the present interpretation seems the most reasonable. The Mo(5)–O(52)–P(5) angles are similar (and quite large) at 145.3(12) and 148.9(11)°. Not much can be said about the remaining dimensions. We were particularly interested to see whether the ligand could be O=P$(OMe)_3$ and calculated the fourth tetrahedral position around P(5a) and P(5b), but there was no electron density in these positions.

The room-temperature magnetic moment of the complex is 1.4 B.M. per three molybdenum atoms, a value which is not particularly helpful in elucidating the oxidation states of the metal atoms. Indeed from a comparison of the magnetic moments of molybdenum complexes listed in refs. 17 and 18, several possible oxidation states cannot be ruled out. The most likely values for *n* are 1, 2, and 3. This would be concomitant with oxidation states in the cation of +2, +2.5, +3 and in the anion of +6, +5, +4 respectively. The bond lengths in the ions also give information as to the oxidation states of the molybdenum atoms though wide variations in distances are found in various compounds for seemingly equivalent bonds {see *e.g.* [$MoOCl_2(PMe_2Ph)_3$], and [$MoOCl_2(PEt_2Ph)_3$]}.[19,20]

In the cation the Mo–P bonds [mean 2.42 Å] are equivalent but shorter than Mo^{II}–P bonds in a number of seven-co-ordinate complexes {*e.g.* 2.500(4) in [$MoBr_2(PPh_2{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)(CO)_3$],[16] and 2.500(14) Å in [$Mo(CO)_2(PMe_2Ph)_3Cl_2$] (ref. 21)} but this could be due to more favourable orbital overlap in the present 4 : 3 geometry. The Mo–CO bond lengths [mean 1.92 Å in (I)] do not alter much with oxidation state and no conclusions can be drawn from them. The Mo–Cl-(bridge) bonds [mean 2.548(6) Å] are compatible with values found in monomeric seven-co-ordinate molybdenum(II) complexes, *e.g.* 2.486(16) and 2.561(14) (ref. 21) and 2.575(11) Å in [$MoCl(CO)_2(diars)_2$]$^+$ where diars = *o*-phenylenebis(dimethylarsine).[22] The Cl ··· Cl contacts are 3.09—3.16 Å.

TABLE 6

Intermolecular distances <3.70 Å

C(33a) ··· O(2^{I})	3.19	C(22) ··· C(3^{VII})	3.65
C(33b) ··· O(2^{I})	3.61	C(41) ··· O(1^{VII})	3.40
O(3) ··· O(21^{I})	3.66	C(22) ··· O(3^{VII})	3.46
C(33b) ··· O(13^{I})	3.65	O(41) ··· O(1^{VII})	3.46
O(3) ··· C(13^{I})	3.27	O(22) ··· Cl(54^{VII})	3.54
O(3) ··· C(21^{I})	3.70	C(31) ··· O(11^{VIII})	3.62
C(33b) ··· C(11^{I})	3.64	C(32) ··· Cl(52^{VIII})	3.30
O(51) ··· C(13^{I})	3.43	O(51) ··· C(11^{VIII})	3.31
C(41) ··· O($54a^{\mathrm{II}}$)	3.62	C(33b) ··· C(12^{VIII})	3.46
C(41) ··· O($54b^{\mathrm{II}}$)	3.06	C(54a) ··· O(12^{IX})	3.57
C(41) ··· C($54b^{\mathrm{II}}$)	3.26	O(54b) ··· O(12^{IX})	3.66
C(43) ··· O(4^{III})	3.26	C(54a) ··· Cl(54^{IX})	3.52
Cl(51) ··· C(41^{IV})	3.59	O(54b) ··· C(12^{IX})	3.59
Cl(53) ··· C($33b^{\mathrm{V}}$)	3.65	C(54b) ··· Cl(54^{IX})	3.60
C(42) ··· Cl(3^{VI})	3.44	C(53a) ··· Cl(53^{X})	3.41
O(4) ··· C(23^{VI})	3.66	C(31) ··· O(51)	3.40

Roman numeral superscripts represent the following atom transformations relative to the reference molecule at *x*, *y*, *z*:

I	$1 + x, y, z$	VI	$1 - x, 1 - y, 2 - z$
II	$x, 1 + y, 1 + z$	VII	$1 - x, 1 - y, 1 - z$
III	$2 - x, 1 - y, 2 - z$	VIII	$1 - x, -y, 1 - z$
IV	$2 - x, 1 - y, 1 - z$	IX	$1 - x, -y, -z$
V	$2 - x, -y, 1 - z$	X	$2 - x, -y, -z$

The evidence from the Mo–Cl bond lengths in the anion

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[18] M. J. Bennett, J. V. Brencic, and F. A. Cotton, *Inorg. Chem.*, 1969, **8**, 1060.

[19] L. M. Muir, *J. Chem. Soc.* (*A*), 1971, 2796.

[20] L. M. Muir and K. W. Muir, *J.C.S. Dalton*, 1972, 686.

[21] A. Mawby and G. E. Pringle, *J. Inorg. Nuclear Chem.*, 1972, **34**, 517.

[22] M. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1973, 2664.

is more informative, particularly as there are many octahedral molybdenum (and tungsten, whose atomic radius is similar) structures for comparison which contain mutually *trans*-Mo–Cl bonds. Values of 2.24 in Mo_2Cl_{10},[23] 2.26 in $MoOCl_3$,[24] 2.29 and 2.27 in two tungsten(VI) complexes,[25,26] but larger values of 2.34 Å are found for W–Cl in $[WSeCl_4(OCH_2{\cdot}CH_2{\cdot}OMe)_2]$.[27] Values in the present compound (2.37 Å) are thus significantly longer than comparable bonds in molybdenum-(V) and -(VI) complexes. For Mo^{IV}–Cl and W^{IV}–Cl bonds, values of 2.339 Å are found in $[WCl_4(PMe_2Ph)_2]$,[28] but values in the range 2.424—2.551 Å are reported in refs. 19 and 20. These comparisons are not conclusive and we cannot exclude any of the possible oxidation states for the molybdenum atoms.

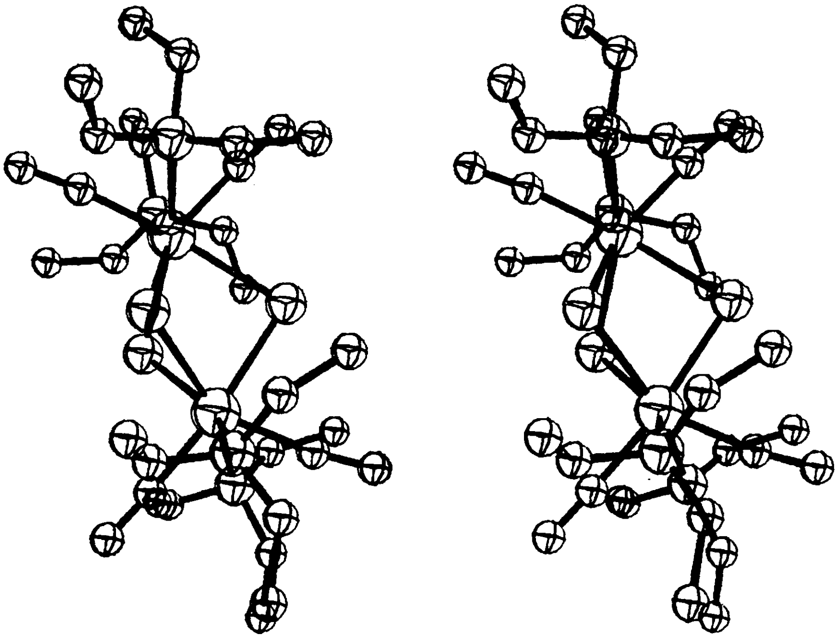

FIGURE 4 A stereodiagram of the cation

The reaction mechanism for formation of (I) is not known as we have not investigated the organic products. However, of the reactions which have occurred there are precedents for the formation of Mo=O from the reaction of molybdenum (and tungsten) chloro-compounds with oxygen-containing ligands,[17] and for the cleavage of ether linkages.[27]

The intermolecular dimensions show some very close contacts. While the majority of these include one or two atoms which are disordered, there are a number of C···O contacts of *ca.* 3.25 Å which are short (but not impossibly so) for van der Waals contacts. All values <3.70 Å are given in Table 6. The stereopair for the cation is given in Figure 4.

We thank A. W. Johans for assistance with the crystallographic investigations.

[5/029 *Received, 7th January,* 1975]

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