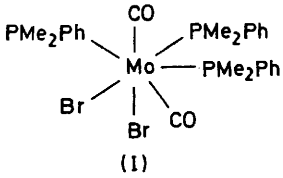
Geometrical Isomers of the Capped Octahedron in the Solid State. Crystal and Molecular Structure of Dibromodicarbonyltris(dimethylphenylphosphine)molybdenum(II)–Acetone (1/1)

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

Crystals of the title compound are monoclinic, space group $P2_1$ with a = 12.145(8), b = 11.789(10), c = 12.296(10) Å, β = 104.86(10)°, Z = 2. The intensities of 2 377 independent reflections above background were collected by counter methods and refined to R 0.062. The molecule is a seven-co-ordinate monomer in which the metal atom occupies a capped octahedral environment. A carbonyl group occupies the capping position [1.900(16) Å], three phosphorus atoms are in the capped face [2.586(5), 2.520(4), and 2.503(5) Å] and two bromine atoms [2.680(2) and 2.666(2) Å] and the remaining carbonyl group [2.026(25) Å] make up the uncapped face. The molecule is disordered with one site in the uncapped face, occupied by 87% carbonyl and 13% bromine. The arrangement of atoms in the co-ordination sphere is different from that found in the analogous dichloro-compound in which a carbonyl group occupies the capping position, two phosphorus atoms and carbonyl group the capped face, and two chlorines and a phosphorus atom the uncapped face.

GEOMETRICAL isomers in the solid state are most commonly found in polytopes where all sites are equivalent such as the octahedron and the square plane. For the five-co-ordinate polyhedra, such as the square pyramid and the trigonal bipyramid, examples are rare, and indeed for the seven-co-ordinate polyhedra, as shown in a recent review,[1] examples are unknown or at any rate not yet established by *X*-ray diffraction. This is not surprising, as each of the seven-co-ordinate polyhedra has two or three different sites which will be preferentially occupied by one ligand or another. For example an Ma_5b_2 molecule with unidentate ligands has potentially four geometric isomers (ignoring enantiomorphs) in a pentagonal bipyramid (PB), six in a capped octahedron (CO), and eight in a capped trigonal prism (CTP) and yet only one isomer is ever found. The same is true for other stoicheiometries. Indeed, the geometries of seven-co-ordinate complexes are nearly always predictable[1] particularly with chelate ligands.

We decided that the seven-co-ordinate complexes most likely to have isomers are those of general formula



(I)

$[MoX_2(CO)m(PR_3)_{5m}]$ with R = alkyl and/or aryl, m = 2 or 3, X = Cl or Br, and we are investigating some of these structures. Those of $[MoCl_2(CO)_2(PMe_2Ph)_3]$ [2] and $[MoCl_2(CO)_3(PEt_3)_2]$ [3] have been determined previously and we report here the structure of $[MoBr_2(CO)_2(PMe_2Ph)_3]$ (I).

EXPERIMENTAL

The complex (I) was prepared in a method similar to that of ref. 4 except that the intermediate $[MoBr_2(CO)_4]$ was prepared by the method of Colton and Tomkins.[5] The complex was recrystallised from an acetone solution by addition of light petroleum (b.p. 40—60 °C) and cooling. I.r. spectrum ($CHCl_3$) : ν(CO) 1 838 and 1 947 cm^{-1}.

Crystal Data.—$C_{29}H_{39}Br_2MoO_3P_3$, M = 695.32, Monoclinic, a = 12.145(8), b = 11.789(10), c = 12.296(10) Å, β = 104.86(10)°, U = 1 700.9 Å^3, Z = 2, D_c = 1.35. Mo-K_α radiation, λ = 0.7107 Å, μ(Mo-K_α) = 6.98 cm^{-1}. Space-group $P2_1$, from systematic absences: $0k0$, $k = 2n + 1$ and the successful structure determination. D_m could not be obtained as the crystals dissolved in every solvent we used.

A crystal with dimensions *ca.* 0.3 × 0.9 × 0.55 mm was mounted with the *b* axis parallel to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions, the latter *via* least-squares refinement 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 whose intensities 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 during the course of the experiment but no crystal decay was observed. 3 150 independent reflections with $2\theta < 50°$ were measured by the stationary-crystal–stationary-counter method. 2 377 reflections with $I > \sigma(I)$ were used in subsequent calculations. No absorption or extinction corrections were applied.

Structure Determination.—The structure was solved by Patterson and Fourier methods and the positions of all atoms in the $[MoBr_2(CO)_2(PMe_2Ph)_3]$ complex and the

---

[1] M. G. B. Drew, *Progr. Inorg. Chem.*, 1977, in the press.

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

[3] M. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1977, 194.

[4] J. R. Moss and B. L. Shaw, *J. Chem. Soc.*, 1970, 595.

[5] R. Colton and I. B. Tomkins, *Austral. J. Chem.*, 1966, **19**, 1143.

acetone solvent molecule were located and refined successfully (to R 0.086) except for one of the carbonyl groups. A difference-Fourier map based on all atoms except for this carbonyl group showed a triangle of three peaks of similar height in this area all *ca.* 1 Å apart. Two of these peaks formed a carbonyl group while the other at *ca.* 2.6 Å from the metal was obviously either a bromine or phosphorus atom. We attempted to refine the carbonyl group with a population parameter of x and the remaining atom as bromine and then phosphorus with a population parameter of $1-x$ but this did not converge. However, a difference-Fourier map did not indicate the presence of the -Me_2Ph appendages to phosphorus and indeed any such group would be too close to the solvent molecule. We therefore assumed the peak to be bromine, fixed the thermal parameters of the three atoms at reasonable values, and refined the population parameters, which converged independently to 0.13 (Br) and 0.87 (CO). An attempt to do the same thing with phosphorus was unsuccessful because the thermal parameter of the carbonyl atoms would have to be unreasonably low for the sum of the population parameters to be 1.0. It seems likely that the disorder is confined to the uncapped face, particularly as in solution all three sites are equivalent. Thus the other two sites would be occupied by a total of 1.87 bromine atoms and 0.13 carbonyl groups. We were not able to confirm this from a difference-Fourier map, but this was not unexpected as the scattering from the carbonyl group would be only *ca.* 1 e per atom. In the final refinement, therefore, both bromine atoms were given population parameters of 1.0, and for the disordered carbonyl group and adjacent bromine atom values of 0.87 and 0.13 were fixed. Molybdenum, bromine, and phosphorus atoms were refined anisotropically, the remaining atoms isotropically to R 0.062 in a full-matrix least-squares procedure (the alternative enantiomorph gave R 0.064). In the refinement, the weighting scheme, chosen such that $w\Delta^2$ was constant over ranges of F_o and $\sin\theta/\lambda$, was $\sqrt{w} = 1$ for $F_o < 22$ and $\sqrt{w} = 22/F_o$ for $F_o > 22$. In the final cycle of refinement, no shift was $>0.05\sigma$. A final difference-Fourier map showed no significant peaks and the zero-weighted reflections no serious discrepancies. Anisotropic thermal parameters are defined as $\exp(-2\pi^2 \sum_i \sum_j U_{ij}h_ih_jb_ib_j)$; $i,j = 1,2,3$ where b_i is the i^{th} reciprocal lattice dimension. The isotropic thermal parameters take the form $\exp(-8\pi^2U\sin^2\theta/\lambda^2)$. Calculations were carried out on a CDC 7600 computer at the University of London Computer Centre, using the programs of ref. 6. Scattering factors for molybdenum, bromine, phosphorus, carbon, and oxygen were taken from ref. 7 as were the real and imaginary parts of the anomalous dispersion for molybdenum, bromine, and phosphorus. Final positions are given in Table 1 together with isotropic thermal parameters. Anisotropic thermal parameters are given in Table 2 and molecular dimensions in Table 3. Observed and calculated structure factors are listed in a Supplementary Publication No. SUP 21904 (8 pp., 1 microfiche).*

TABLE 1

Atomic co-ordinates (× 10^4) and isotropic thermal parameters (× 10^3) for (I), with estimated standard deviations in parentheses

Atom	x	y	z	U/Å^2
Mo	3 002(1)	0 000 [a]	2 049(1)	[b]
Br(1)	3 900(2)	1 807(2)	3 285(2)	[b]
Br(2)	1 280(2)	1 422(2)	1 232(2)	[b]
Br(3) [c]	1 743(14)	−0 262(15)	3 502(13)	63(4)
P(1)	3 868(4)	1 122(4)	0 663(4)	[b]
P(2)	4 618(4)	−0 888(4)	3 508(3)	[b]
P(3)	1 459(4)	−1 315(4)	1 034(4)	[b]
C(1)	3 686(12)	−1 113(13)	1 316(12)	36(3)
O(1)	4 137(11)	−1 773(13)	0 857(10)	63(3)
C(2) [d]	2 345(20)	−0 597(20)	3 294(18)	58(5)
O(2) [d]	1 950(15)	−0 908(17)	3 952(15)	80(5)
C(11)	5 418(18)	1 080(20)	0 991(18)	70(5)
C(12)	3 560(18)	2 645(19)	0 506(18)	67(5)
C(13)	3 463(16)	0 670(16)	−0 804(15)	53(4)
C(14)	2 412(16)	1 006(18)	−1 451(16)	62(5)
C(15)	2 086(24)	0 681(24)	−2 628(23)	92(7)
C(16)	2 837(26)	−0 072(40)	−2 990(25)	116(9)
C(17)	3 827(27)	−0 365(28)	−2 389(26)	112(9)
C(18)	4 177(18)	0 018(27)	−1 260(18)	81(5)
C(21)	4 600(18)	−2 422(20)	3 563(18)	67(5)
C(22)	4 718(19)	−0 555(21)	4 991(20)	76(6)
C(23)	6 061(15)	−0 522(16)	3 366(15)	52(4)
C(24)	6 601(19)	−1 254(20)	2 727(18)	72(6)
C(25)	7 662(24)	−0 961(27)	2 680(23)	98(8)
C(26)	8 264(25)	−0 044(35)	3 217(25)	119(9)
C(27)	7 705(26)	0 650(27)	3 858(25)	107(9)
C(28)	6 566(20)	0 421(21)	3 900(19)	79(6)
C(31)	0 027(19)	−1 123(21)	1 259(18)	74(6)
C(32)	1 132(17)	−1 248(19)	−0 492(17)	67(5)
C(33)	1 744(15)	−2 826(16)	1 389(15)	53(4)
C(34)	2 139(17)	−3 497(20)	0 719(17)	69(5)
C(35)	2 470(24)	−4 674(28)	1 063(23)	106(9)
C(36)	2 174(23)	−5 057(32)	1 956(23)	105(8)
C(37)	1 715(26)	−4 422(28)	2 627(25)	107(9)
C(38)	1 437(20)	−3 229(24)	2 330(20)	86(7)
C(3)	0 432(24)	2 495(26)	4 619(24)	90(21)
O(3)	0 027(22)	2 135(23)	5 369(21)	143(9)
C(4)	−0 091(59)	3 359(68)	3 901(56)	273(32)
C(5)	1 541(37)	2 358(41)	4 541(34)	160(16)

[a] Parameter fixed. [b] Anisotropic thermal parameters given in Table 2. [c] Population parameter 0.13. [d] Population parameter 0.87.

TABLE 2

Anisotropic thermal parameters (× 10^3)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	32.6(6)	34.8(6)	32.2(6)	0.1(7)	12.1(4)	−2.9(7)
Br(1)	74.9(13)	46.1(11)	50.6(10)	−2.8(10)	5.1(9)	−16.5(9)
Br(2)	58.6(13)	59.0(14)	91.8(17)	14.9(11)	13.4(11)	4.5(12)
P(1)	52.2(26)	45.0(25)	47.5(24)	1.5(21)	16.0(20)	3.8(20)
P(2)	56.4(27)	56.8(28)	32.3(20)	11.9(22)	6.5(19)	−0.4(19)
P(3)	42.9(25)	49.7(26)	50.2(25)	−7.0(21)	12.8(20)	−5.8(22)

DISCUSSION

The molecule is shown in Figure 1, together with the atom numbering scheme. The geometry is a relatively undistorted capped octahedron in which one carbonyl

---

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

[6] ' *X*-Ray' system of programs, July 1970, version, ed. J. M. Stewart, University of Maryland Technical Report TR 192.

[7] ' International Tables for *X*-Ray Crystallography,' vol. IV, 1975, Kynoch Press, Birmingham.

TABLE 3

Molecular dimensions in (I); distances (Å), angles (°)

(*a*) Co-ordination sphere

Mo–Br(1)	2.680(2)	Mo–P(3)	2.503(5)
Mo–Br(2)	2.666(2)	Mo–C(1)	1.900(16)
Mo–P(1)	2.586(5)	Mo–C(2)	2.026(25)
Mo–P(2)	2.520(4)	Mo–Br(3)	2.652(19)
C(1)–Mo–P(1)	74.9(5)	P(2)–Mo–Br(1)	78.3(1)
C(1)–Mo–P(2)	72.3(4)	P(2)–Mo–Br(2)	157.0(1)
C(1)–Mo–P(3)	72.4(4)	P(2)–Mo–Br(3)	87.1(4)
C(1)–Mo–Br(1)	130.9(4)	P(2)–Mo–C(2)	72.8(6)
C(1)–Mo–Br(2)	130.7(4)	P(3)–Mo–Br(1)	156.6(1)
C(1)–Mo–Br(3)	129.6(6)	P(3)–Mo–Br(2)	77.8(1)
C(1)–Mo–C(2)	115.1(8)	P(3)–Mo–Br(3)	77.1(4)
P(1)–Mo–P(2)	107.9(2)	P(3)–Mo–C(2)	76.8(6)
P(1)–Mo–P(3)	111.6(2)	Br(1)–Mo–Br(2)	83.1(1)
P(1)–Mo–Br(1)	78.0(1)	Br(1)–Mo–Br(3)	86.0(4)
P(1)–Mo–Br(2)	81.0(1)	Br(1)–Mo–C(2)	91.7(6)
P(1)–Mo–Br(3)	155.1(4)	Br(2)–Mo–Br(3)	78.2(4)
P(1)–Mo–C(2)	169.1(7)	Br(2)–Mo–C(2)	94.6(6)
P(2)–Mo–P(3)	116.3(2)	Br(3)–Mo–C(2)	16.8(8)
C(1)–O(1)	1.176(22)	Mo–C(1)–O(1)	177.6(14)
C(2)–O(2)	1.104(33)	Mo–C(2)–O(2)	177.5(19)

(*b*) Phosphine groups

	$n = 1$	$n = 2$	$n = 3$
P(*n*)–C(*n*1)	1.821(22)	1.811(24)	1.844(25)
P(*n*)–C(*n*2)	1.833(23)	1.838(25)	1.818(21)
P(*n*)–C(*n*3)	1.822(19)	1.856(20)	1.846(19)
Mo–P(*n*)–C(*n*1)	114.4(8)	115.3(6)	117.6(8)
Mo–P(*n*)–C(*n*2)	117.6(8)	117.3(7)	115.1(7)
Mo–P(*n*)–C(*n*3)	116.8(7)	114.7(6)	114.2(6)
C(*n*1)–P(*n*)–C(*n*2)	102.8(10)	100.1(11)	100.7(10)
C(*n*1)–P(*n*)–C(*n*3)	102.2(10)	104.8(10)	102.1(10)
C(*n*2)–P(*n*)–C(*n*3)	100.7(9)	102.7(9)	105.3(9)
C(*n*3)–C(*n*4)	1.38(2)	1.43(3)	1.32(3)
C(*n*4)–C(*n*5)	1.45(3)	1.35(4)	1.47(4)
C(*n*5)–C(*n*6)	1.42(3)	1.38(4)	1.32(4)
C(*n*6)–C(*n*7)	1.29(3)	1.42(5)	1.34(5)
C(*n*7)–C(*n*8)	1.42(4)	1.42(4)	1.47(4)
C(*n*8)–C(*n*3)	1.38(3)	1.36(3)	1.39(3)
P(*n*)–C(*n*3)–C(*n*4)	117(2)	119(1)	120(1)
P(*n*)–C(*n*3)–C(*n*8)	122(1)	118(2)	117(2)
C(*n*4)–C(*n*3)–C(*n*8)	121(1)	123(2)	122(2)
C(*n*3)–C(*n*4)–C(*n*5)	118(2)	116(2)	120(2)
C(*n*4)–C(*n*5)–C(*n*6)	116(2)	125(3)	117(3)
C(*n*5)–C(*n*6)–C(*n*7)	124(3)	117(3)	125(3)
C(*n*6)–C(*n*7)–C(*n*8)	118(3)	121(3)	119(3)
C(*n*7)–C(*n*8)–C(*n*3)	121(2)	117(3)	116(2)

(*c*) Solvent molecule

C(3)–O(3)	1.23(4)	O(3)–C(3)–C(4)	122(4)
C(3)–C(4)	1.39(8)	O(3)–C(3)–C(5)	127(3)
C(3)–C(5)	1.38(6)	C(4)–C(3)–C(5)	110(4)

(*d*) Intermolecular distances in (I) < 3.70 Å

C(27) $\cdots$ O(3^{I})	3.43	C(12) $\cdots$ C(35^{II})	3.56
O(3) $\cdots$ C(15^{III})	3.48	C(22) $\cdots$ C(17^{III})	3.66
Br(1) $\cdots$ C(5)	3.65	Br(3) $\cdots$ C(5)	3.38
O(1) $\cdots$ C(11^{IV})	3.53	O(1) $\cdots$ C(12^{IV})	3.68
O(3) $\cdots$ O(2^{V})	3.58		

* Roman numerals as superscripts refer to the following equivalent positions with respect to the reference molecule at x,y,z:

I $1 + x, y, z$
II $x, 1 + y, z$
III $x, y, 1 + z$
IV $1 - x, -\frac{1}{2} + y, -z$
V $-x, \frac{1}{2} + y, 1 - z$

group occupies the capping position [1.900(16) Å], three phosphorus atoms are in the capped face [2.586(5), 2.520(4), and 2.503(5) Å], and two bromine atoms [2.680(2), 2.666(2) Å] and the remaining carbonyl group [2.026(25) Å] make up the uncapped face. There is disorder in that the site in the uncapped face predominantly occupied by a carbonyl group is occupied by a bromine atom in 13% of the unit cells. It is probable that one or both of the bromine atoms in the uncapped face are concomitantly replaced by carbonyl in the 13% unit cells but this has not been proved by the refinement. This arrangement of (I) in the 1 : 3 : 3 capped octahedra, abbreviated as C : PPP : BrCBr, is surprising particularly as in $[\mathrm{MoCl_2(CO)_2(PMe_2Ph)_3}]$ the arrangement is C : CPP : ClPCl and in the compounds of formula $[\mathrm{MoX_2(CO)_2(dpam)_2}]$ with X = Br (ref. 8) † or Cl (ref. 9) it is C : CAsAs : XAsX.

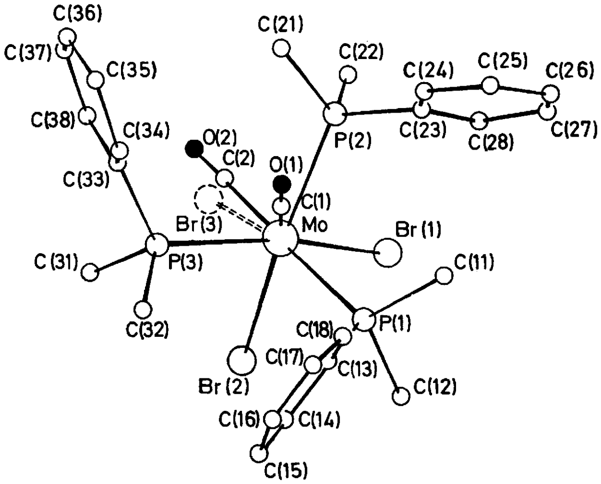


FIGURE 1 $[\mathrm{MoBr_2(CO)_2(PMe_2Ph)_3}]$: the carbonyl group C(2), O(2) and Br(3) (shown dotted) are alternative positions (see text)

The arrangement in (I) is therefore unique and unexpected in that the two carbonyl groups are not mutually *cis*. There are precedents for three phosphorus groups occurring in the capped face e.g. $[\mathrm{MoX_4(PMe_2Ph)_3}]$ X = Cl (ref. 10) or Br (ref. 11). Maybe the structure is stabilised in the crystal by the disorder as is also observed in $[\mathrm{MeTaCl_2(prcd)_2}]$ (prcd = *NN'*-di-isopropylacetamide).[12] It is thus possible that the two geometrical isomers C : CPP : XPX and C : PPP : XCX could be isolated in the solid state for both $[\mathrm{MoCl_2(CO)_2(PMe_2Ph)_3}]$ and $[\mathrm{MoBr_2(CO)_2(PMe_2Ph)_3}]$. Presumably in solution a pseudorotation pathway exists between the two.

The disorder found in (I) is fully accounted for by a

---

† In a recent study of seven-co-ordinate geometries (J. K. Kouba and S. S. Wreford, *Inorg. Chem.*, 1976, **15**, 1465), it is suggested, on the basis of δ′ angles 47.3, 5.2, and 6.3°, that this molecule has a marginally distorted C_{2v} structure and not a capped octahedral structure. Unfortunately these authors have mis-calculated the δ′ angles which are in fact 25.1, 21.6, and 9.3° before normalisation and 25.0, 21.8, and 1.7° after normalisation; consistent with a description [8] of its geometry as a capped octahedron distorted towards a capped trigonal prism.

[8] M. G. B. Drew, *J.C.S. Dalton*, 1972, 626.

[9] M. G. B. Drew, A. P. Wolters, and I. B. Tomkins, *J.C.S. Dalton*, in the press.

[10] L. Manojlovic-Muir, *J.C.S. Dalton*, 1976, 192.

[11] M. G. B. Drew, J. D. Wilkins, and A. P. Wolters, *J.C.S. Chem. Comm.*, 1972, 1278.

[12] M. G. B. Drew and J. D. Wilkins, *Acta Cryst.*, 1975, **B31**, 2642.

rotation of the whole molecule by 120° about the pseudo-C_3 axis. The bond lengths in the molecule are as expected from consideration of similar structures.[1] The Mo–P(1) bond is longer than the other two because it is *trans to the* carbonyl group in the uncapped face C(2)-O(2). The Mo–Br(3) and Mo–C(2) bonds are by no means co-axial, the Br(3)–Mo–C(2) angle being 16.8(8)°. The angles subtended at the metal atom (Table 3) show that the position of Br(3) is equivalent to those of Br(1) and Br(2) with respect to the capping atom and the atoms in the capped face. Thus the C(1)–Mo–Br(3) angle is 129.6(6)°, identical to the other C(1)–Mo–Br angles but much greater than C(1)–Mo–C(2) [115.1(8)°]. Other differences in angles between those involving C(2) and Br(3) are shown by the pairs P(2)–Mo–C(2) 72.8(6) and P(2)–Mo–Br(3) 87.1(4)°, and Br(2)–Mo–C(2) 94.6(6) and Br(2)–Mo–Br(3) 78.2(4)°. The first pair are easily explicable; the enlargement being due to the possible close contacts between bromine and the methyl groups and phenyl rings on P(2); the second pair are not, Br(2)–Mo–Br(3) being too small. It may be that when C(2) is replaced by Br(3), then Br(2) is replaced by a carbonyl group. It would certainly appear from the thermal parameters that Br(2) has a lower population parameter than Br(1).

It would appear from these angles that as far as C_{3v} geometry is concerned the bromine atom is more symmetrically placed than the carbonyl group. This interpretation has been confirmed by calculations of the root-mean-square deviations[1,13] from ideal C_{3v} geometry of the metal co-ordination sphere. After normalisation of bond lengths to 1.0 Å to allow valid comparison of the two geometries, we obtain values of 0.042 and 0.067 Å for the bromine and carbonyl containing structures respectively. δ' angles[14] (again on normalised bond lengths) are 21.4, 18.0, and 12.3°, and 21.4, 18.0, and 1.3°,* values which lead to the same conclusion.

The torsion angles around the Mo–P bonds are listed in Table 4. As found in other capped octahedra, there is no difficulty in staggering the three carbon atoms bonded to phosphorus with the three nearest-neighbours bonded to molybdenum. Indeed the minimum torsion angle is 36.8°. The C(1)–Mo–P(*n*)–C(*n*3) torsion angles are very similar (those for $n = 1$ and 3 being identical), thus the three ligands are arranged in a C_3 fashion around the Mo–C(1) bond (Figure 1). There are only a few intermolecular distances <3.70 Å, many of which involve the acetone of crystallisation. The dimensions of this molecule are as expected. The packing diagram for the complex in the *b* projection is given in Figure 2.

TABLE 4

Torsion angles (°) in (I), of the type L–Mo–P–C where the L–Mo–P angle is less than 100°

C(1)–Mo–P(1)–C(11)	−65.9	Br(1)–Mo–P(2)–C(23)	−70.1
C(1)–Mo–P(1)–C(12)	173.4	C(2)–Mo–P(2)–C(21)	72.6
C(1)–Mo–P(1)–C(13)	53.4	C(2)–Mo–P(2)–C(22)	−44.9
Br(1)–Mo–P(1)–C(11)	72.7	C(2)–Mo–P(2)–C(23)	−165.6
Br(1)–Mo–P(1)–C(12)	−48.0	C(1)–Mo–P(3)–C(31)	173.8
Br(1)–Mo–P(1)–C(13)	−167.9	C(1)–Mo–P(3)–C(32)	−67.8
Br(2)–Mo–P(1)–C(11)	157.5	C(1)–Mo–P(3)–C(33)	54.1
Br(2)–Mo–P(1)–C(12)	36.8	Br(2)–Mo–P(3)–C(31)	−46.0
Br(2)–Mo–P(1)–C(13)	−83.2	Br(2)–Mo–P(3)–C(32)	72.4
C(1)–Mo–P(2)–C(21)	−51.8	Br(2)–Mo–P(3)–C(33)	−165.6
C(1)–Mo–P(2)–C(22)	−169.3	C(2)–Mo–P(3)–C(31)	51.7
C(1)–Mo–P(2)–C(23)	70.0	C(2)–Mo–P(3)–C(32)	170.1
Br(1)–Mo–P(2)–C(21)	168.0	C(2)–Mo–P(3)–C(33)	−67.9
Br(1)–Mo–P(2)–C(22)	50.6		

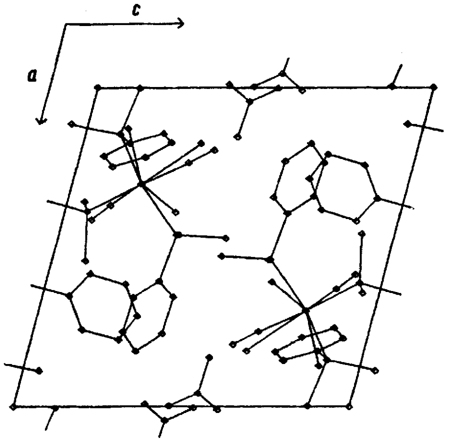


FIGURE 2 The unit cell in the *b* projection

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

[6/1434 *Received, 21st July,* 1976]

---

* There has been some controversy over the best method for describing deviations from ideal geometry. We have argued elsewhere[1,13] that root-mean-square deviations are the best guide while others[14] favour δ' angles; common practice is to study angles subtended at the metal. It is however, often the case that, as for the present molecule, all three methods lead to equivalent conclusions.

[13] M. G. B. Drew and C. J. Rix, *J. Organometallic Chem.*, 1975, **102**, 467.

[14] E. L. Muetterties and L. J. Guggenberger, *J. Amer. Chem. Soc.*, 1974, **96**, 1748.