Crystal and Molecular Structure of Dicarbonylchlorobis-[*o*-phenylene(dimethylarsino)]molybdenum(II) Tri-iodide–Bischloroform

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Crystals of the title compound are orthorhombic, space group *Pnma*, with a = 11·75(1), b = 15·27(1), c = 24·15(2) Å, Z = 4. The structure was solved by the heavy-atom method from 1048 independent reflections, collected by counter methods, and refined by full-matrix least-squares techniques to R 0·080. The symmetry of the cation is very close to C_{2v} (*mm*) with one of the mirror planes imposed by the space group. Thus the molybdenum atom has a 1,4,2-capped trigonal prismatic environment with a chlorine atom in the unique capping position [2·575(11) Å], four arsenic atoms in the capped quadrilateral face [2·614(5), 2·617(5) Å], and two carbonyl groups making up the remaining edge [1·92(5), 1·87(5) Å]. The tri-iodide ion lies with the central atom on a crystallographic mirror plane [2·903(2) Å, 176·9(2)°].

THE energy differences between the three basic polyhedra (1,5,1-pentagonal bipyramidal, D_{5h}; 1,3,3-capped octahedral, C_{3v}; 1,4,2-capped trigonal prismatic, C_{2v}) are considered to be very low.[1] Thus the choice of polyhedron for a given complex is dictated by a variety of factors including symmetry, ligand–ligand repulsions, steric constraints of multidentate ligands, electronic structure of the metal, and crystal packing energies. We have determined the crystal structures of a number of seven-co-ordinate molecules [2] as part of a systematic attempt to understand the relative importance of these factors in determining the stability and geometry of such molecules. We report here the crystal structure of the complex dicarbonylchlorobis-[*o*-phenylenebis(dimethylarsino)molybdenum(II)] tri-iodide–bischloroform.

EXPERIMENTAL

$[Mo(diars)_2(CO)_2I]^+ I^-$ [diars = *o*-phenylenebis(dimethylarsine)] was prepared by the published method [3] and gave satisfactory analysis and i.r. spectra. This complex (0·5 g) was heated under reflux in dry ethanol-free chloroform (40 cm^3) giving a deep red solution which on cooling yielded a quantity of red crystals. Subsequent X-ray examination showed that two distinct types of crystals were present, one belonging to the orthorhombic and the other to the triclinic system. The structure analysis on the orthorhombic crystals, reported here, has established that they contain $[Mo(diars)_2(CO)_2Cl]^+I_3^-,2CHCl_3$, the formation

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

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

[3] H. L. Nigam, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 1960, 1807.

of the cation being probably attributable to the presence of traces of phosgene in the chloroform. We have been unable to repeat the crystallisation of this product with phosgene-free chloroform or indeed any other solvent. These orthorhombic crystals decomposed over a few days. The triclinic crystals have remained stable over several months.[*]

Crystal Data.—$C_{24}H_{32}As_4Cl_7I_3Mo$, Orthorhombic, $M = 1346{\cdot}7$, $a = 11{\cdot}75(1)$, $b = 15{\cdot}27(1)$, $c = 24{\cdot}15(2)$ Å, $U = 4330{\cdot}0$ Å^3, $D_c = 2{\cdot}06$,[†] $Z = 4$, $F(000) = 2520$. Space group *Pnma*, from systematic absences: $0kl$ $k + l = 2n + 1$; for $hk0$ $h = 2n + 1$; confirmed from the structure determination. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; $\mu(\text{Mo-}K_\alpha) = 60{\cdot}8$ cm^{-1}.

A crystal with dimensions $0{\cdot}2 \times 0{\cdot}4 \times 0{\cdot}5$ 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. It was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. A molybdenum tube was used with a zirconium filter at the receiving slit. 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 whose counts 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 (1 day) but no significant change in intensity was detected. This was particularly fortunate as the crystals decomposed a few days afterwards. 2050 Independent reflections were measured with $2\theta < 45°$. No absorption or extinction correction was 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. 1048 Reflections having $I > 2\sigma(I)$ were used in subsequent calculations.

Structure Determination.—The structure was determined in the usual way from a Patterson function. This took a considerable time as we were looking for Mo $\cdots$ I vectors of *ca.* 2·9 Å, but eventually a $MoAs_4$ unit was located. Successive Fourier syntheses were then used to locate the positions of the remaining atoms. The cation, the anion, and the two solvent molecules all have crystallographically imposed *m* symmetry with some atoms (Mo, Cl, 2CO in the cation, IO in the anion, C, H, Cl in the solvent molecules) in special positions 4*c*. The remaining atoms are in general positions 8*d*. 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 $F_o < 125$ and $\sqrt{w} = F_o/125$ for $F_o > 125$. Calculations were made on a 1906 A computer at S.R.C. Chilton, Berkshire, with the programs described in ref. 4. Atomic scattering factors for molybdenum, iodine, arsenic, chlorine, carbon, and oxygen were taken from ref. 5, together with the corrections for the real and imaginary part of the anomalous dispersion for molybdenum, iodine, chlorine, and arsenic. The anisotropic temperature factor is defined as $\exp - 0{\cdot}25 \sum_i \sum_j h_i h_j U_{ij}$ $(i, j = 1\text{—}3)$, the isotropic thermal parameters as $\exp(-8\pi^2 U \sin^2\theta/\lambda^2)$. The structure was refined (molybdenum, iodine, arsenic, and chlorine anisotropically; carbon and oxygen isotropically) to R 0·080. 12 Reflections which had been obviously mismeasured were given zero weight. We were unable to remeasure these reflections as by this time the original batch of crystals had decomposed and we were unable to repeat the preparation. Difference-Fourier syntheses showed no significant peaks and in the final cycle of refinement, all shifts were $< 0{\cdot}040\ \sigma$. Final co-ordinates and thermal parameters, together with their standard deviations are listed in Tables 1 and 2. Bond distances and angles are given in Table 3. Final observed and calculated structure factors are listed in Supplementary Publication SUP 20820 (10 pp., 1 microfiche).[‡]

TABLE 1

Final positional ($\times 10^4$) and thermal parameters ($\times 10^3$), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	*U*
IO(1)	3372(4)	2500	−1052(2)	[a]
IO(2)	3346(4)	0599(3)	−1023(2)	[a]
Mo(1)	1205(4)	2500	1443(2)	[a]
As(1)	2198(4)	3827(3)	0959(2)	[a]
As(2)	0763(3)	3833(3)	2089(2)	[a]
Cl(1)	3084(8)	2500	1991(4)	25(3)
C(1)	−0422(47)	2500	1495(21)	66(15)
O(1)	−1417(35)	2500	1556(15)	83(11)
C(2)	0507(50)	2500	0747(25)	81(18)
O(2)	0198(38)	2500	0260(20)	113(15)
C(3)	3679(35)	3654(26)	0611(16)	85(12)
C(4)	1269(46)	4446(33)	0358(22)	125(17)
C(5)	−0697(37)	4392(29)	2031(18)	93(13)
C(6)	0954(31)	3617(24)	2890(15)	74(12)
C(11)	2458(30)	4757(22)	1499(14)	60(10)
C(12)	1808(31)	4744(23)	1954(15)	65(11)
C(13)	1929(32)	5503(26)	2338(15)	72(11)
C(14)	2770(39)	6151(33)	2203(19)	101(14)
C(15)	3374(35)	6086(30)	1738(17)	86(12)
C(16)	3293(31)	5442(25)	1368(15)	67(11)
C(7) [b]	0000	2500	8580	185
Cl(2)	0045(26)	2500	7907(12)	189(11)
Cl(3)	−0366(18)	3421(13)	8918(8)	188(8)
C(8)	2346(67)	2500	4996(32)	124(25)
Cl(4)	1156(30)	2500	5395(13)	205(12)
Cl(5)	2135(20)	3439(16)	4566(10)	220(7)

[a] Anisotropic thermal parameters for this atom given in Table 2. [b] Atomic parameters not refined.

TABLE 2

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

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
IO(1)	98(4)	156(5)	56(3)	00	00	01(2)
IO(2)	215(4)	144(4)	90(3)	−38(3)	−13(3)	37(3)
Mo(1)	52(3)	37(3)	21(2)	00	00	−06(2)
As(1)	88(3)	59(3)	43(2)	08(2)	−07(3)	09(2)
As(2)	69(2)	51(2)	41(2)	−06(2)	04(2)	04(2)

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[*] An *X*-ray analysis (M. G. B. Drew, G. M. Eggington, and J. D. Wilkins, to be published) has established their structure as $[MoCl_4(diars)_2]^+I_3^-$.

[†] D_m was found to be 2·33, which is obviously wrong. However, as this value is equivalent to D_c for the triclinic crystals, it is probable that the similarity of the two types of crystals led us to err

[‡] See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[4] '*X*-Ray '67' system of programs, J. M. Stewart, University of Maryland Technical Report, TR 67 58, 1967, revised July 1970.

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

TABLE 3

Molecular dimensions

(*a*) Bond distances (Å)

IO(1)–IO(2)	2·903(2)	As(2)–C(6)	1·98(4)
Mo(1)–As(1)	2·614(5)	As(2)–C(12)	1·88(4)
Mo(1)–As(2)	2·617(5)	C(11)–C(12)	1·34(5)
Mo(1)–Cl(1)	2·575(11)	C(12)–C(13)	1·49(5)
Mo(1)–C(1)	1·92(5)	C(13)–C(14)	1·43(6)
Mo(1)–C(2)	1·87(6)	C(14)–C(15)	1·33(6)
C(1)–O(1)	1·18(7)	C(15)–C(16)	1·33(6)
C(2)–O(2)	1·23(8)	C(16)–C(11)	1·47(5)
As(1)–C(3)	1·95(4)	C(7)–Cl(2)	1·64
As(1)–C(4)	2·05(5)	C(7)–Cl(3)	1·68
As(1)–C(11)	1·95(4)	C(8)–Cl(4)	1·70(6)
As(2)–C(5)	1·92(4)	C(8)–Cl(5)	1·79(5)

(*b*) Angles (°)

IO(2)–IO(1)–IO(2^{I}) [a]	176·9(2)
Cl(1)–Mo(1)–As(1)	81·2(2)[3·38] [b]
Cl(1)–Mo(1)–As(2)	82·2(2)[3·41]
Cl(1)–Mo(1)–C(1)	145·3(16)[4·29]
Cl(1)–Mo(1)–C(2)	147·0(18)[4·27]
C(1)–Mo(1)–As(1)	118·3(7)[3·91]
C(1)–Mo(1)–As(2)	76·3(9)[2·85]
C(1)–Mo(1)–C(2)	67·7(24)]2·11]
C(2)–Mo(1)–As(1)	78·1(11)[2·88]
C(2)–Mo(1)–As(2)	116·6(9)[3·84]
As(1)–Mo(1)–As(2)	75·6(1)[3·21]
As(1)–Mo(1)–As(1^{I})	101·6(2)[4·05]
As(1)–Mo(1)–As(2^{I})	163·4(2)[5·15]
As(2)–Mo(1)–As(2^{I})	102·2(2)[4·07]
Mo(1)–C(2)–O(2)	171(5)
Mo(1)–C(1)–O(1)	176(4)
Mo(1)–As(1)–C(11)	109·5(10)
Mo(1)–As(1)–C(3)	119·1(12)
C(3)–As(1)–C(4)	103·5(19)
C(3)–As(1)–C(11)	104·3(16)
C(4)–As(1)–C(11)	102·8(18)
Mo(1)–As(1)–C(4)	115·9(15)
Mo[1]–As(2)–C(5)	118·7(13)
Mo(1)–As(2)–C(6)	115·5(11)
Mo(1)–As(2)–C(12)	110·0(11)
As(1)–C(11)–C(12)	116·7(27)
As(1)–C(11)–C(16)	118·6(25)
C(12)–C(11)–C(16)	125(3)
C(11)–C(12)–C(13)	116(3)
As(2)–C(12)–C(11)	121·7(27)
As(2)–C(12)–C(13)	121·9(26)
C(12)–C(13)–C(14)	117(3)
Cl(2)–C(7)–Cl(3)	119
Cl(3)–C(7)–Cl(3^{I})	114
Cl(4)–C(8)–Cl(5)	102(3)
Cl(5)–C(8)–Cl(5^{I})	107(4)
C(5)–As(2)–C(6)	104·3(17)
C(5)–As(2)–C(12)	104·0(17)
C(6)–As(2)–C(12)	102·6(15)
C(13)–C(14)–C(15)	120(4)
C(14)–C(15)–C(16)	126(4)
C(15)–C(16)–C(11)	115(3)

[a] See footnote to Table 4. [b] In square brackets is the distance L · · · L, corresponding to the angle L–M–L.

DISCUSSION

The structure of the cation [Mo(diars)$_2$(CO)$_2$Cl]$^+$ (I) is shown in Figure 1, together with the atomic numbering scheme. The cation has crystallographic m symmetry, the mirror planes at $y = 1/4$, $3/4$ containing the molybdenum and chlorine atoms and two carbonyl groups. In addition, there is an approximately mirror plane running through the molybdenum and chlorine atoms and perpendicular to this first plane. Thus the molecule as a whole has approximate C_{2v} symmetry. The co-ordination sphere of the metal atom is thus almost a perfect capped trigonal prism, the chlorine atom occupying the unique capping position, the four arsenic atoms the capped quadrilateral face, and the two carbonyl groups making up the remaining edge. Thus there is an exact correspondence between the stoicheiometry of this MXY_4Z_2 cation and the 1,4,2-capped trigonal prism. This is rare: other seven-co-ordinate complexes with this stoicheiometry have different geometries; NbX(OMe)$_2$(dedtc)$_2$ (dedtc = diethyl dithiocarbamate, X = Cl or Br) is a pentagonal bipyramid with two oxygens in the axial positions and four sulphurs and one halogen in the pentagonal girdle;[6] MeTaCl$_2$(MeN$_2$O$_2$)$_2$ is also a pentagonal bipyramid but with the chlorine atoms in the axial positions and four oxygens and one methyl group in the girdle.[7] In both compounds, the five atoms in the girdle (X and 4Y) are of a similar size which is different from that of the axial atoms (2Z). It is therefore not surprising that these molecules attain the D_{5h} geometry of the MY_5Z_2 type stoicheiometry, exemplified by [UO$_2$F$_5$]$^{3-}$.[8] * The correspondence between stoicheiometry and geometry is discussed with numerous examples in ref. 9. More recent examples are [W(CO)$_4$Br$_3$]$^+$,[10] and MoX$_4$(PMe$_2$-

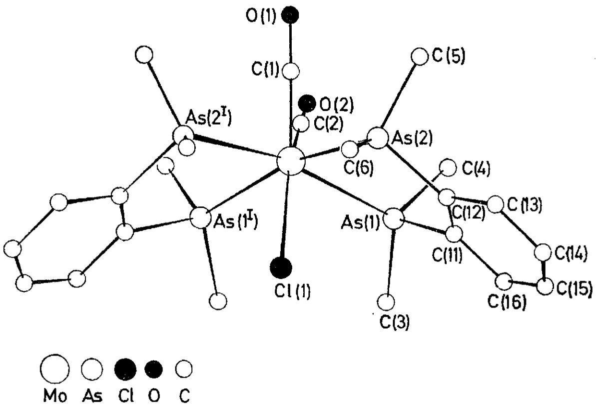

FIGURE 1 The cation

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* It is true that the X (= Cl) and 4Y (= As) atoms in (I) are of similar size but a pentagonal bipyramidal structure of the MY_5Z_2 type can be ruled out because of the repulsions between the methyl groups on adjacent diars groups in the girdle. We show in the text that the particular geometry obtained for (I) is favoured by symmetry considerations, ligand–ligand repulsions and the steric constraints of the diars ligands. This is only a qualitative judgement, however, and this is not to say that other geometries would not be sterically stable. From models, it would appear that less symmetric arrangements (such as a pentagonal bipyramid with one diars in the girdle, the other spanning an axial and an equatorial site, or a capped octahedron with one diars in the uncapped face, the other spanning sites in the capped and uncapped face) would not contain excessive steric contacts.

[6] J. W. Moncrief, D. C. Pantaleo, and N. E. Smith, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 255.

[7] M. G. B. Drew and J. D. Wilkins, *J. Organometallic Chem.*, in the press.

[8] W. H. Zachariasen, *Acta Cryst.*, 1954, **7**, 783.

[9] D. F. Lewis and S. J. Lippard, *Inorg. Chem.*, 1972, **11**, 621.

[10] M. G. B. Drew and A. P. Wolters, *Chem. Comm.*, 1972, 457.

Ph)$_3$ (X = Br [2] or Cl [11]) which have capped octahedral symmetry. From this data, it can be concluded that such correspondence is of secondary importance in fixing the geometry of a seven-co-ordinate complex.

However, the actual polyhedron can usually be related to the minimisation of ligand–ligand repulsions and (I) is no exception. The chlorine atom occupies the least-crowded site, the unique capping position, thus no Cl–Mo–L (L = ligand) need be less than 81° (all other sites in this and the other polyhedra involve L–M–L angles of *ca.* 75°). The next sterically free positions are the four in the quadrilateral face which are occupied by the four arsenic atoms of the two diars ligands. In assessing the relative importance of particular L · · · L contacts in a polyhedron, the starting point is usually the van der Waals radii (Cl 1·80, As 2·00 Å [12]). However in $WOCl_4$(diars),[13] a structure which is pentagonal bipyramidal with three chlorine atoms and two arsenic atoms in the girdle, Cl–W–As angles are 67, 67° (Cl · · · As 2·81, 2·81 Å) and Cl–W–Cl angles are 76, 78° (Cl · · · Cl 2·95, 3·03 Å), suggesting that the chlorine atoms have a greater effect than the arsenic atoms in fixing the geometry of the co-ordination sphere. A similar conclusion has been drawn from a study of the co-ordination spheres of $MoX_2(dam)_2(CO)_2$ [dam = bis(diphenylarsino)methane; X = Br [14] or Cl [15]]. Thus, all things being equal, one would expect chlorine in preference to arsenic to occupy the unique capping position. The most sterically crowded positions in the polyhedron * are those in the remaining edge which are occupied by the smallest atoms C · · · C 2·11 Å (*cf.* contacts of *ca.* 2·25 Å reported in refs. 14 and 15).

In metal complexes containing a number of π accepting ligands, such ligands are often mutually *cis* in order to avoid competition for the metal electrons. The arrangement of ligands in (I) is consistent with this observation; the π accepting carbonyl groups are mutually *cis* and while the diars ligands are approximately *trans* to each other, the four arsenic atoms are *cis* to the more strongly π accepting carbonyl ligands. The chlorine atom which is approximately *trans* to the carbonyl groups (mean 146°) is not a π acceptor.

Unlike some other co-ordination polyhedra (*e.g.* octahedron, tetrahedron, *etc.*) the geometry of the capped trigonal prism is not totally fixed and variations in L–M–L angle which accommodate particular ligands are often found while C_{2v} symmetry is maintained. The geometry of (I) is compared with that of $[Mo(CNR)_6I]^+$ (R = Bu^t [9]) (II) in Figure 2. The positions of the crystallographic mirror planes in (I) and (II) are equivalent. In (II) the two independent bites in the quadrilateral face are different, bite *a* (between atoms in the same triangular face) being the longer. It is therefore consistent that the diars ligands in (I) occupy the shorter bites *b*. The As · · · As distance in diars is 3·21 Å in (I) [As–Mo–As 75·6(1)°], a value similar to those found [13,16] in $WOCl_4$(diars) and $[AuI_2(diars)_2]^+$. To compensate for the short chelating bite, the As–Mo–As^I *cis* angles are 101·6(2) and 102·2(2)°. As the Cl–Mo–As angles are equivalent [81·2(2) and 82·2(2)]° to those found in (II) (81·5°), the difference between the two geometries (Figure 2) is mainly confined to angles in the quadrilateral face, none of the other 17 angles in the respective co-ordination spheres, differing by more than 4°. The largest deviation is for the As–Mo–CO angles in the triangular face which are slightly greater [76·3(9) and 78·1(11)°] than the equivalent angles in (II) (74·6 and 74·5°). This may be ascribed to the greater size of the arsenic atoms in (I).

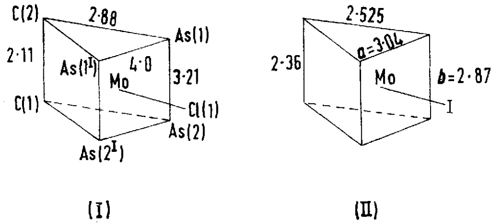

FIGURE 2 A comparison of the capped trigonal prisms found in (I) and (II), both with C_{2v} (*mm*) symmetry

In (I), the angle between the planes Mo(1), As(1), and As(2), and Mo(1), Cl(1), C(1), and C(2) is 79·5°. The planar As_2C_6 group intersects the Mo(1), As(1), and As(2) plane at an angle of 21·2°. Such a deviation is not unusual: angles of 28, 12·5, 9·0, and 10·4° have been recorded [16–19] for octahedral molecules, in which the diars ligands are mutually *trans* and the bends in the M(diars) grouping could be explained in terms of increasing the contacts between the methyl groups and the halogen atoms. This is shown in Figure 3 for $[AuI_2(diars)_2]^+$,[16] which is centrosymmetric, and for (I). For I(1), the 28° bend in diars A increases and the 28° bend in diars B decreases the I · · · Me contacts. To compensate for this, the mean I–Au–As angles are 82·8 and 97·2° such that all I · · · Me contacts are *ca.* 3·90 Å. In (I) the bends in the diars ligands can also be ascribed to repulsions between the methyl groups and the chlorine atom and also the carbonyl groups. Dimensions relating to these contacts are given in Table 4. The

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* This is true for an ML_7 polyhedron but not necessarily so in a complex with different ligands. In $[Mo(CNR)_6I]^+$,[9] the Mo–C bond lengths are non-equivalent: to carbon in the quadrilateral face 2·115(15) and to carbon in the edge 2·055(15) Å. The authors suggest that this is because steric crowding is less severe for the edge carbon atoms. This may be true but it is difficult to assess the relative importance of a I · · · C of 3·28 and C · · · C 2·36 Å distances on the Mo–C bond lengths and the overall geometry of the polyhedron. Perhaps π bonding effects are equally important.

[11] L. M. Muir, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 59.

[12] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.

[13] M. G. B. Drew and R. Mandyczewsky, *Chem. Comm.*, 1970, 292.

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

[15] M. G. B. Drew and A. P. Wolters, to be published.

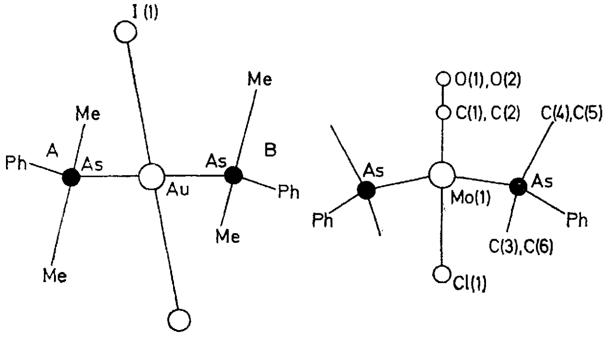
[16] V. F. Duckworth and N. C. Stephenson, *Inorg. Chem.*, 1969, **8**, 1661.

[17] N. C. Stephenson, *J. Inorg. Nuclear Chem.*, 1962, **24**, 791.

[18] N. C. Stephenson, *Acta Cryst.*, 1964, **17**, 1517.

[19] N. C. Stephenson, *Acta Cryst.*, 1964, **17**, 592.

dihedral angles Cl(1)–Mo(1)–As(1)–C(3), Cl(1)–Mo(1)–As(1)–C(12), Cl(1)–Mo(1)–As(1)–C(11), Cl(1)–Mo(1)–As-(2)–C(6) are *all* close to 60°. If the diars ligand were not bent out of the $MoAs_2$ plane, both C(3) and C(6) would be much closer to the chlorine atom. The Me · · · CO contacts, are also increased by the bend in the Mo(diars) group (Table 4), the corresponding Me–Mo–As–(CO) dihedral angles being −27·5 and 25·0°. An additional consequence is that the contacts between the methyl groups C(3) and C(6) across the mirror plane are decreased (Table 4). Although the hydrogen atoms on these carbon atoms will be eclipsed with respect to each other, H · · · H contacts would not be particularly short (*ca.* 2·5 Å). The variations observed in angles subtended at the arsenic atoms can also be related to steric effects. Angles of the type Mo–As–Me are the largest (mean 117·2°), compared to 109·8 for the other Mo–As–C angles and 103·5° for the C–As–C angles. This type of variation in angles is very often found for phosphorus and arsenic ligands [14,20] and can be attributed to an *s* orbital effect,[21] but is also consistent with an increase in intramolecular contacts involving the methyl groups.



$[AuI_2(diars)_2]^+$ (I)

FIGURE 3 A comparison of the bend in the M(diars) group in (I) and in $[AuI_2(diars)_2]^+$; both projections are along the As · · · As vector

TABLE 4

(*a*) Dihedral angles (°)

Cl(1)–Mo(1)–As(1)–C(11)	62·7
Cl(1)–Mo(1)–As(1)–C(3)	−57·0
Cl(1)–Mo(1)–As(1)–C(4)	178·4
Cl(1)–Mo(1)–As(2)–C(12)	−62·9
Cl(1)–Mo(1)–As(2)–C(5)	177·6
Cl(1)–Mo(1)–As(2)–C(6)	52·6
C(1)–Mo(1)–As(2)–C(5)	25·0
C(2)–Mo(1)–As(1)–C(4)	−27·5
C(3)–As(1)–C(11)–C(16)	−33·4
C(4)–As(1)–C(11)–C(16)	74·4
C(5)–As(2)–C(12)–C(13)	−65·4
C(6)–As(2)–C(12)–C(13)	43·1

(*b*) Intra- and inter-molecular distances (<3·75 Å) *

Cl(1) · · · C(11)	3·72	Cl(3) · · · $O(2^{II})$	3·59
Cl(1) · · · C(12)	3·74	C(14) · · · $C(5^{III})$	3·73
Cl(1) · · · C(3)	3·83	Cl(1) · · · $O(1^{III})$	3·55
Cl(1) · · · C(6)	3·73	Cl(5) · · · $O(1^{III})$	3·55
C(5) · · · C(1)	3·18	IO(1) · · · $Cl(4^{III})$	3·63
O(1) · · · C(5)	3·22	C(8) · · · $O(2^{III})$	3·41
C(2) · · · C(4)	3·24	Cl(2) · · · $C(14^{IV})$	3·70
O(2) · · · C(4)	3·23	Cl(5) · · · $IO(2^{V})$	3·64
C(3) · · · $C(3^{I})$	3·52	C(6) · · · $C(6^{I})$	3·41

* Roman numerals as superscripts refer to an atom in the following equivalent positions relative to the reference molecule (Table 1) at *x*, *y*, *z*:

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

Although the configuration of the molecule is affected by intramolecular contacts, none of these distances is particularly short. The Cl · · · C contacts are much longer than those (3·20 Å) reported in refs. 15 and 22, and however the hydrogen atoms on the methyl groups are orientated in (I), it is unlikely that H · · · Cl contacts could become unreasonably short. It can be deduced that a bromine or iodine atom would also fit into this capping position, and thus that cations analogous to (I), $[Mo(diars)_2(CO)_2X]^+$ (X = Br or I), would be isostructural. The Me · · · CO contacts in (I) of *ca.* 3·20 Å are equivalent to the shortest such contacts found in other seven-co-ordinate complexes.[20] The primary effect of the bend in the Mo(diars) groupings is to increase the Me · · · CO rather than the Me · · · Cl contacts.*

The bond distances in (I) are mostly as expected. The Mo–C distances are normal [20] within their limited accuracy. The Mo–As bond lengths are comparable with those found in the capped octahedral molecules $MoBr_2(CO)_2(dam)_2$ [14] and $MoCl_2(CO)_2(dam)_2$ [15] for Mo–As bonds not *trans* to Mo–CO bonds. The Mo–Cl(1) distance is somewhat longer than in $MoCl_2(CO)_2(PMe_2Ph)_3$ [22] and $MoCl_2(CO)_2(dam)_2$.[15] Of particular interest is a comparison with the Mo–I distance in ref. 9 (2·862 Å), which is only 0·29 Å greater than the Mo–Cl distance in (I), despite a difference of 0·41 Å in the atomic radii.[12]

The bend in the Mo(diars) groupings has changed the Mo(1)–As(1)–C(11)–C and Mo(1)–As(2)–C(12)–C dihedral angles from the 60° which would be expected for a planar Mo(diars) grouping, so that the two smallest are 33·4 and 43·1°. The As(1)–C(11)–C(16) and As(2)–C(12)–C(13) angles are unaffected and are no larger than the other angles subtended at C(11) and C(12). The remaining dimensions of the benzene ring are as expected.

The I_3^- anion has crystallographically imposed *m* symmetry with IO(1)–IO(2) 2·903(2) Å and IO(2)–IO(1)–$IO(2^{I})$ 176·9(2)°. These atoms undergo much

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* These close Me · · · CO contacts may explain why seven-co-ordinate complexes containing two bidentate ligands of the type dam, dpe [=1,2-bis(diphenylphosphino)ethane] (or dpm, dae, the phosphorus and arsenic analogues) have not been prepared. We have built a model of (I) and replaced the diars ligands by dam and dae ligands but have not been able to find a configuration in which the phenyl rings are adequately separated from each other and from the other ligands.

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[21] M. A. Bush, A. D. U. Hardy, L. M. Muir, and G. A. Sim, *J. Chem. Soc.* (*A*), 1971, 1003.

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

higher thermal motion than does the cation and that motion is also much more anisotropic. The root-mean-square amplitudes of thermal vibration are for IO(1) 0·237, 0·314, and 0·396, and for IO(2) 0·287, 0·385, and 0·468 Å. Ref. 23 lists dimensions of tri-iodide anions in various compounds, showing that two significantly different I–I distances are invariably found except when crystallographic symmetry is imposed. For this reason in $(C_5H_4Me)_2Fe^+I_3^-$, in which the anion has imposed $\bar{1}$ symmetry, an attempt was made to resolve the anion into two equal asymmetric components.[23] The value of such a procedure is difficult to estimate in view of the high correlations between parameters and we have not attempted it. However, it is quite possible that two asymmetric tri-iodide anions occur and that the refined symmetric anion has average dimensions. Both chloroform molecules have crystallographically imposed *m* symmetry with a carbon, hydrogen, and one chlorine atom on the mirror plane. They undergo high thermal vibration and the dimensions of the groups are not very accurate. Indeed, one of the carbon atoms could not be successfully refined and was given fixed parameters. The packing diagram is shown in Figure 4. The constituents of the unit cells are held together by the normal van der Waals forces. All distances <3·75 Å are given in Table 4.

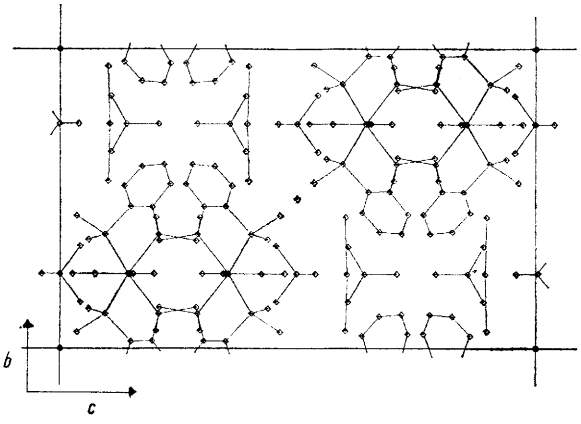

FIGURE 4 The unit cell of $[Mo(diars)_2(CO)_2Cl]^+I_3^-,2CHCl_3$ in the *a* projection

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[23] J. W. Bats, J. J. DeBoer, and D. Bright, *Inorg. Chim. Acta*, 1971, **5**, 605.