Crystal and Molecular Structure of
Tetrachlorobis-[o-phenylenebis(dimethylarsino)]molybdenum(V) Triiodide

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Crystals of the title compound are triclinic, space group $P\bar{1}$, $a=12\cdot58$ (1), $b=12\cdot32$ (1), $c=14\cdot33$ (1) Å, $\alpha=114\cdot0$ (1), $\beta=95\cdot0$ (1), $\gamma=116\cdot9$ (1)°, $Z=2$. The intensities of 1997 independent reflexions above background were collected by counter methods and refined to $R=0\cdot070$. The cation has dodecahedral D_{2d} symmetry within experimental error with mean bond lengths Mo–As $2\cdot653$ (5) and Mo–Cl $2\cdot451$ (11) Å. The arsenic atoms occupy the A sites and the chlorine atoms the B sites in the polyhedron, an arrangement equivalent to that found for the analogous titanium(IV) complex. The geometry of the cation is dependent upon the minimizing of 16 close Cl $\cdots$ Me intramolecular repulsions rather than any electronic effect. Geometric parameters for the dodecahedron are $\theta_A=37\cdot8$, $\theta_B=72\cdot6°$, $(M-A)/(M-B)=1\cdot08$. The triiodide anion has dimensions $2\cdot912$ (4), $2\cdot890$ (5) Å, $179\cdot7$ (1)°.

Introduction

During studies of the seven-coordinate complexes of molybdenum(II) and tungsten(II) (Drew & Wilkins, 1973), we prepared the complex $[Mo(CO)_2(diars)_2I]^+I^-$ {diars $=o$-phenylenebis(dimethylarsine)} by the method of Nigam, Nyholm & Stiddard (1960) and obtained satisfactory analyses and spectra. We then recrystallized the compound in chloroform and obtained two distinct types of red crystals, one belonging to the orthorhombic and the other to the triclinic system. A structure analysis on the orthorhombic crystals (Drew & Wilkins, 1973) has established that they contain $[Mo(CO)_2(diars)_2Cl]^+I_3^-$. 2CHCl$_3$, the formation of the cation being probably attributable to traces of phosgene in the chloroform. In any event, the preparation could not be repeated. We were intrigued to discover the substituents of the triclinic crystals and have therefore carried out a single-crystal X-ray analysis on them which we report here. The crystals contain $[MoCl_4(diars)_2]^+I_3^-$.

Crystal data

Crystals are triclinic, space group $P\bar{1}$, confirmed by the successful structure determination.

$C_{20}H_{32}As_4Cl_4I_3Mo$, $M=1192\cdot7$, $a=12\cdot58^w(1)$, $b=12\cdot32$ (1), $c=14\cdot33$ (1) Å, $\alpha=114\cdot0$ (1), $\beta=95\cdot0$ (1), $\gamma=116\cdot9$ (1)°, $U=1704\cdot7$ Å^3, $Z=2$, $d_m=2\cdot33$, $d_c=2\cdot31$ g cm^{-3}, $F(000)=1106$, Mo $K\alpha$ radiation, $\lambda=0\cdot7107$ Å, $\mu=75\cdot1$ cm^{-1}.

Experimental

A crystal with dimensions *ca.* $0\cdot25\times0\cdot10\times0\cdot25$ mm was mounted with the (011) planes perpendicular 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 reflexions seriously affected by the streaking of other orders. For other reflexions backgrounds were taken from plots of background as a function of 2θ. Several standard reflexions were measured repeatedly during the course of the experiment but no significant change in intensity was detected. 3329 independent reflexions were measured with $2\theta<40°$. The standard deviation $\sigma(I)$ of the reflexions was taken to be $[I+2E+(0\cdot03I^2)]^{1/2}$, where E is the estimated background of the reflexion. 1997 independent reflexions with $I>2\sigma(I)$ were used in subsequent calculations. An absorption correction was applied with the program *ABSORB* in the X-RAY system of programs (Stewart, 1972). Transmission factors varied between $0\cdot20$ and $0\cdot48$. No extinction correction was applied.

Structure determination

Although we were uncertain as to the stoichiometry of the compound, we inferred the presence of the triiodide anion and indeed located this distinctive linear grouping with some difficulty in the Patterson function. Further Fourier analyses located all atoms and established the structure as $[MoCl_4(diars)_2]I_3^-$. Scattering factors for iodine, molybdenum, arsenic, chlorine and carbon atoms were taken from *International Tables for X-ray Crystallography* (1965) as were the corrections for the real and imaginary part of the anomalous dispersion for all atoms bar carbon. The isotropic temperature factor was defined as exp $(-8\pi^2$ $U\sin^2\theta/\lambda^2)$ and the anisotropic thermal parameters as $\exp(-2\pi^2\sum_i\sum_j h_ih_jb_ib_jU_{ij}$;

$i,j=1,2,3)$: b_i is the ith reciprocal-lattice dimension. Programs used were part of the X-RAY system (Stew-

art, 1972) and were run on an ICL 1906A at S.R.C. Chilton and a CDC 7600 at the University of London Computer Centre. Iodine, arsenic, molybdenum and chlorine atoms were refined anisotropically and carbon atoms isotropically to $R = 0.070$. The weighting scheme was $\sqrt{w} = 1$ for $F_o < 125$ and $\sqrt{w} = 125/F_o$ for $F_o > 125$. This scheme gave average values of $w\Delta^2$ for groups of reflexions independent of the value of $\sin\theta/\lambda$ and F_o. In the final cycle of refinement no shift was $> 0.050\sigma$. The 1332 reflexions given zero weight in the refinement showed no large discrepancies. The final difference map showed no significant peaks. The final lists of positional coordinates and thermal parameters, together with their standard deviations, are given in Tables 1 and 2. The bond distances and angles are given in Table 3.*

* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30424 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\times 10^3$) with estimated standard deviations in parentheses*

	x	y	z	U
IO(1)	−160 (2)	3363 (3)	589 (2)	*
IO(2)	1508 (2)	3626 (2)	2320 (2)	*
IO(3)	3170 (2)	3902 (3)	4042 (2)	*
Mo(1)	3329 (3)	701 (3)	7381 (2)	*
As(1)	5519 (3)	1719 (4)	8803 (3)	*
As(2)	3042 (3)	1749 (4)	9299 (3)	*
As(3)	1889 (3)	−1813 (3)	5608 (3)	*
As(4)	2922 (3)	1245 (4)	5833 (3)	*
Cl(1)	4817 (8)	401 (9)	6458 (7)	*
Cl(2)	1188 (7)	264 (9)	7150 (6)	*
Cl(3)	2818 (8)	−1142 (9)	7834 (7)	*
Cl(4)	4484 (8)	3247 (8)	8097 (7)	*
C(11)	5603 (36)	2551 (38)	10316 (29)	67 (10)
C(12)	6645 (34)	3204 (37)	11118 (30)	61 (10)
C(13)	6646 (38)	3820 (41)	12195 (32)	77 (12)
C(14)	5618 (38)	3815 (40)	12436 (31)	73 (11)
C(15)	4497 (32)	3141 (35)	11535 (27)	55 (9)
C(16)	4530 (28)	2598 (30)	10518 (23)	39 (8)
C(18)	6990 (33)	3117 (36)	8765 (27)	59 (10)
C(19)	5962 (42)	357 (46)	8759 (35)	91 (13)
C(28)	2692 (31)	3223 (34)	9598 (26)	54 (9)
C(29)	1669 (34)	417 (38)	9546 (29)	66 (11)
C(31)	1501 (30)	−1635 (34)	4371 (25)	50 (9)
C(32)	744 (32)	−2890 (35)	3364 (27)	56 (9)
C(33)	487 (40)	−2800 (35)	2379 (34)	84 (12)
C(34)	859 (34)	−1487 (38)	2546 (30)	61 (10)
C(35)	1627 (32)	−278 (35)	3533 (26)	54 (9)
C(36)	1972 (29)	−390 (32)	4488 (24)	44 (8)
C(38)	192 (39)	−3071 (43)	5605 (39)	83 (12)
C(39)	2571 (33)	−2952 (36)	5284 (33)	60 (10)
C(48)	2099 (39)	2277 (43)	6048 (39)	81 (12)
C(49)	4428 (37)	2437 (41)	5579 (37)	75 (11)

* Anisotropic thermal parameters given in Table 2.

Table 2. *Anisotropic thermal parameters ($\times 10^3$) with estimated standard deviations in parentheses*

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
IO(1)	51 (2)	86 (2)	61 (2)	38 (1)	15 (1)	32 (1)
IO(2)	48 (1)	60 (2)	47 (1)	26 (1)	20 (1)	22 (1)
IO(3)	69 (2)	83 (2)	67 (2)	40 (2)	23 (1)	48 (1)
Mo(1)	25 (2)	25 (2)	30 (2)	14 (1)	14 (1)	10 (1)
As(1)	34 (2)	45 (2)	48 (2)	24 (2)	17 (2)	21 (2)
As(2)	31 (2)	44 (2)	45 (2)	20 (2)	16 (2)	17 (2)
As(3)	40 (2)	36 (2)	45 (2)	19 (2)	18 (2)	16 (2)
As(4)	45 (2)	43 (2)	46 (2)	24 (2)	22 (2)	22 (2)
Cl(1)	45 (5)	57 (5)	53 (5)	32 (4)	20 (4)	19 (4)
Cl(2)	38 (5)	57 (5)	45 (5)	26 (5)	13 (4)	15 (4)
Cl(3)	51 (5)	52 (5)	66 (6)	26 (5)	23 (5)	36 (5)
Cl(4)	52 (5)	39 (5)	61 (5)	22 (4)	16 (4)	19 (4)

Table 3. *Molecular dimensions*

Bond distances

IO(1)—IO(2)	2·912 (4) Å	IO(2)—IO(3)	2·890 (5) Å
Mo(1)–As(1)	2·668 (5)	Mo(1)–As(3)	2·652 (3)
Mo(1)–As(2)	2·656 (5)	Mo(1)–As(4)	2·638 (6)
Mo(1)–Cl(1)	2·460 (11)	Mo(1)–Cl(3)	2·437 (13)
Mo(1)–Cl(2)	2·458 (11)	Mo(1)–Cl(4)	2·448 (9)
As(1)—C(18)	1·90 (4)	As(3)—C(38)	1·99 (4)
As(1)—C(19)	1·97 (6)	As(3)—C(39)	1·88 (5)
As(1)—C(11)	1·95 (4)	As(3)—C(31)	1·92 (4)
As(2)—C(28)	1·95 (4)	As(4)—C(48)	1·93 (6)
As(2)—C(29)	1·95 (4)	As(4)—C(49)	1·98 (4)
As(2)—C(16)	1·95 (4)	As(4)—C(36)	1·86 (3)
C(11) –C(12)	1·31 (5)	C(31) –C(32)	1·41 (5)
C(12) –C(13)	1·41 (6)	C(32) –C(33)	1·48 (6)
C(13) –C(14)	1·37 (7)	C(33) –C(34)	1·37 (7)
C(14) –C(15)	1·45 (5)	C(34) –C(35)	1·38 (4)
C(15) –C(16)	1·35 (5)	C(35) –C(36)	1·48 (6)
C(16) –C(11)	1·43 (6)	C(36) –C(31)	1·30 (6)

Angles

As(1)–Mo(1)–As(2)	75·7 (1)°
As(3)–Mo(1)–As(4)	75·5 (1)
Edges a: mean	75·6, mean As···As 3·25 Å
As(1)–Mo(1)–As(3)	128·0 (2)°
As(1)–Mo(1)–As(4)	129·0 (2)
As(3)–Mo(1)–As(2)	130·9 (2)
As(2)–Mo(1)–As(4)	126·5 (2)
Mean	128·6
As(1)–Mo(1)–Cl(3)	77·5 (3)°
As(1)–Mo(1)–Cl(4)	75·3 (3)
As(3)–Mo(1)–Cl(1)	75·8 (2)
As(3)–Mo(1)–Cl(2)	76·3 (2)
As(2)–Mo(1)–Cl(3)	76·9 (3)
As(2)–Mo(1)–Cl(4)	75·4 (3)
As(4)–Mo(1)–Cl(1)	77·5 (3)
As(4)–Mo(1)–Cl(2)	76·5 (3)
Edges g: mean	76·4, mean As···Cl 3·17 Å
As(1)–Mo(1)–Cl(2)	145·3 (3)°
As(2)–Mo(1)–Cl(1)	144·6 (2)
As(3)–Mo(1)–Cl(4)	144·9 (3)
As(4)–Mo(1)–Cl(3)	145·3 (2)
Mean	145·0
As(1)–Mo(1)–Cl(1)	68·9 (2)°
As(2)–Mo(1)–Cl(2)	69·7 (2)
As(3)–Mo(1)–Cl(3)	70·0 (2)
As(4)–Mo(1)–Cl(4)	69·6 (3)
Edges m: mean	69·6, mean As···Cl 2·92 Å
Cl(3)–Mo(1)–Cl(2)	92·1 (4)°
Cl(3)–Mo(1)–Cl(1)	96·9 (4)
Cl(4)–Mo(1)–Cl(1)	93·5 (3)
Cl(4)–Mo(1)–Cl(2)	97·9 (4)
Edges b: mean	95·1, mean Cl···Cl 3·61 Å
Cl(3)–Mo(1)–Cl(4)	145·0 (3)°
Cl(1)–Mo(1)–Cl(2)	145·7 (3)
Mean	145·3

Table 3 (cont.)

|				
Mo(1)-As(1)-C(11)	114·5 (14)°		Mo(1)-As(3)-C(31)	110·8 (9)°
Mo(1)-As(1)-C(18)	116·1 (14)		Mo(1)-As(3)-C(38)	116·2 (12)
Mo(1)-As(1)-C(19)	117·3 (10)		Mo(1)-As(3)-C(39)	114·9 (8)
C(11)-As(1)-C(18)	104·8 (14)		C(31)-As(3)-C(38)	103·2 (18)
C(11)-As(1)-C(19)	98·6 (22)		C(31)-As(3)-C(39)	108·7 (18)
C(18)-As(1)-C(19)	103·2 (21)		C(38)-As(3)-C(39)	102·1 (20)
Mo(1)-As(2)-C(16)	113·4 (11)		Mo(1)-As(4)-C(36)	111·8 (14)
Mo(1)-As(2)-C(28)	113·9 (19)		Mo(1)-As(4)-C(48)	115·5 (16)
Mo(1)-As(2)-C(29)	116·3 (10)		Mo(1)-As(4)-C(49)	117·0 (15)
C(16)-As(2)-C(28)	105·0 (14)		C(36)-As(4)-C(48)	107·3 (17)
C(16)-As(2)-C(29)	103·7 (17)		C(36)-As(4)-C(49)	103·6 (15)
C(28)-As(2)-C(29)	103·2 (19)		C(48)-As(4)-C(49)	100·4 (22)
As(1)—C(11)-C(16)	117 (3)		As(3)—C(31)-C(36)	119 (2)
As(1)—C(11)-C(12)	122 (4)		As(3)—C(31)-C(32)	117 (3)
C(16)-C(11)-C(12)	121 (4)		C(36)-C(31)-C(32)	123 (4)
As(2)—C(16)-C(11)	120 (2)		As(4)—C(36)-C(31)	122 (3)
As(2)—C(16)-C(15)	119 (3)		As(4)—C(36)-C(35)	119 (3)
C(11)-C(16)-C(15)	121 (3)		C(31)-C(36)-C(35)	118 (3)
C(11)-C(12)-C(13)	119 (4)		C(31)-C(32)-C(33)	119 (4)
C(12)-C(13)-C(14)	123 (4)		C(32)-C(33)-C(34)	116 (3)
C(13)-C(14)-C(15)	117 (4)		C(33)-C(34)-C(35)	123 (5)
C(14)-C(15)-C(16)	119 (4)		C(34)-C(35)-C(36)	119 (4)
IO(1)-IO(2)-IO(3)	179·7 (1)			
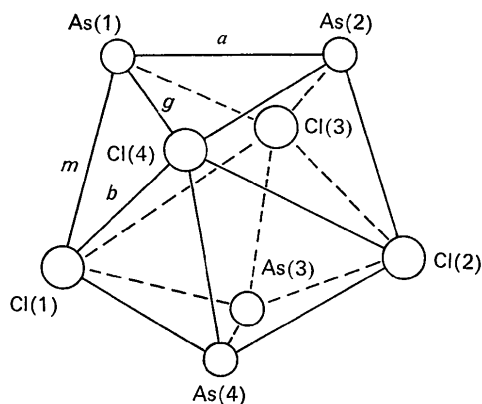
Fig. 1. The coordination sphere of (I) showing the shortest edges; mean values being m 2·92, b 3·61, g 3·17, a 3·25 Å.
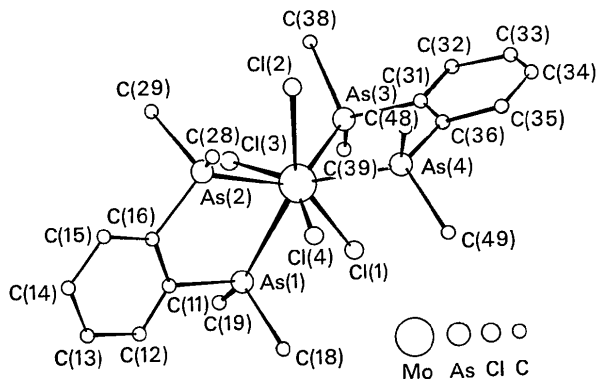

Fig. 2. The cation [MoCl₄(diars)₂]⁺.

Discussion

The unit cell contains two cations of formula [MoCl$_4$(diars)$_2$]$^+$, (I), and two triiodide anions. This cation has not been previously prepared although Blight, Kepert, Mandyczewsky & Trigwell (1972) have tried. They could find no reason for not being able to prepare such a cation, particularly as [MCl$_4$(diars)$_2$]$^+$ ions with M = Tc, Re and MCl$_4$(diars)$_2$ complexes with M = Ti, Zr, Hf, V, Nb, Ta, U had been prepared; not surprisingly, they did not attempt to prepare the cation by the convoluted method which we inadvertently adopted.

In the cation the metal atom is eight-coordinate, being bonded to four chlorine atoms and four arsenic atoms of two bidentate diars ligands. We have followed the test of Lippard & Russ (1968) to distinguish the dodecahedron from other eight-coordinate polyhedra. As the dodecahedron may be described as being formed from two mutually orthogonal interlocking trapezoids, this test involves calculating the angle between the trapezoids. This is 87·7° for (I) (see Table 5), a value which confirms the polyhedron of the cation as a dodecahedron.

The geometry of the coordination sphere of the molybdenum atom is shown in Fig. 1, an adaptation of the diagram of Hoard & Silverton (1963). We have followed the nomenclature of that paper for sites (two types A and B) and edges (four types a, b, m, g) in the dodecahedron. The arsenic atoms occupy the A sites [bond lengths 2·668 (5), 2·656 (5), 2·652 (3), 2·638 (5) Å] and the chlorine atoms occupy the B sites [2·460 (11), 2·458 (11), 2·437 (13), 2·448 (9) Å]. The bidentate diars ligands occupy the two a edges in the polyhedron with As···As 3·25 Å [As–Mo–As 75·6°], normal values for this bidentate ligand. The cation has D$_{2d}$ symmetry within experimental error except possibly for the

Cl–Mo–Cl angles (see Table 3). In the table, equivalent distances and angles are listed together. The atomic numbering scheme is shown in Fig. 2, the y projection of the molecule.

The arrangement of atoms in the dodecahedron is equivalent to that observed, *via* a crystal structure analysis, in TiCl$_4$(diars)$_2$ by Clark, Lewis, Nyholm, Pauling & Robertson (1961). VCl$_4$(diars)$_2$ and NbCl$_4$-(diars)$_2$ have been shown by Clark, Kepert, Lewis & Nyholm (1965) to have powder patterns isomorphous with that of the titanium analogue. Orgel (1960) has suggested that complexes of the type MX$_4$Y$_4$ (M = d^n metal, $n \neq 0$, X = π non-bonding or π donor ligand, Y = π acceptor ligand) would adopt a dodecahedral structure with the π acceptor Y ligands in the B sites and the X ligands in the A sites. However, the arrangement of ligands in the present cation and the related complexes suggests that metal–ligand π-bonding is not a significant factor in determining the geometry of the coordination sphere. From our examination of the structure, detailed below, it is clear that steric effects are of greater import.

In our work on seven-coordinate polyhedra (Drew & Wilkins, 1973), we have noted that ligand···ligand repulsions involving chlorine had greater weight in fixing molecular geometry than those involving arsenic and phosphorus. Consistent with this is that the Cl···Cl contacts in (I) occupy the b edges (3·61 Å) and As···As the a edges (3·25 Å). This latter distance is suitable for the bidentate diars ligand; however, unlike Clark *et al.* (1961), we feel that it would be possible for the diars ligand to occupy g or m edges but this would lead to a lowering of symmetry and perhaps more importantly to closer Cl···Cl contacts. The present arrangement in [MoCl$_4$(diars)$_2$]$^+$ leads to 4 Cl···As contacts across the m edges of mean distance 2·92 Å (Cl–Mo–As 69·6°) compared with the sum of the van der Waals radii (3·75 Å, Pauling, 1960). There are precedents for this short distance; among them the other MCl$_4$(diars)$_2$ complexes and WOCl$_4$(diars)$_2$ (Drew & Mandyczewsky, 1970). In this seven-coordinate pentagonal bipyramidal molecule two arsenic

atoms and three chlorine atoms occupy the planar girdle with Cl–W–As angles of 66·9° (Cl···As 2·81 Å). There are close similarities between the two structures as in (I) each of the two trapezoids is equivalent in geometry to the WCl$_2$(diars) grouping in the girdle.

The arrangement of ligands found in (I) is thus compatible with a minimum of ligand···ligand repulsions. However, we believe that these are not the main factor in fixing the geometry of (I). It is often forgotten in discussions of high-coordination polyhedra that the steric effects from the total ligand must be considered. Indeed in (I) the geometry found also ensures that Cl···Me repulsions are minimized. Thus for the four m edges, which are the most sterically crowded at 2·92 Å, all Cl–Mo–As–Me dihedral angles are close to 60°. For the eight g edges, where As···Cl distances are slightly longer at 3·17 Å, the dihedral angles are *ca.* 40° and 160°. (A full list is given in Table 5.) This arrangement puts all 16 close Cl···Me contacts within the range 3·25 to 3·51 Å.

The Mo(diars) groupings are both planar within experimental error (see Table 4). This contrasts with the geometry of this moiety in other complexes such as [Mo(CO)$_2$(diars)$_2$Cl]$^+$ (Drew & Wilkins, 1973) and [AuI$_2$(diars)$_2$]$^+$ (Duckworth & Stephenson, 1969), where the angles between the planes of atoms MAs$_2$ and As$_2$C$_6$ are 21·1 and 28° respectively. Drew & Wilkins (1973) show that these bends minimize repulsions between the methyl groups and the remaining ligands in the metal coordination sphere. This would not be so for (I) as such a bend would increase one Cl···Me contact only at the expense of another.

The proximity of the Cl···Me contacts in (I) explains why compounds in which diars was replaced by ligands such as R$_2$PCH$_2$CH$_2$PR$_2$ do not yield eight-coordinate complexes (Chatt & Hayter, 1963) because a non-planar ring must of necessity lead to closer contacts. Similarly, attempts to prepare equivalent complexes to TiCl$_4$(diars)$_2$ with ethyl groups substituted for methyl groups were unsuccessful (Clark, Negrotti & Nyholm, 1966).

From models it would appear that the Cl···Me re-

Table 4. *Equations of least-squares planes in the form* $Ax + By + Cz = D$, *where* x, y, z *are the crystallographic coordinates*

Distances (Å) of contributing atoms from the planes are given.

Plane		A		B		C		D				
1		−1·48		11·55		−6·35		−4·38				
	Mo(1)	0·00,	As(1)	−0·04,	As(2)	0·04,	Cl(1)	0·03,	Cl(2)	−0·03		
2		12·28		−4·22		−4·30		0·61				
	Mo(1)	0·01,	As(3)	0·06,	As(4)	−0·06,	Cl(3)	−0·04,	Cl(4)	0·04		
3		−1·32		11·51		−6·60		−4·56				
	As(1)	−0·00,	As(2)	0·03,	C(11)	−0·05,	C(12)	0·03,				
	C(13)	0·03,	C(14)	−0·00,	C(15)	−0·03,	C(16)	0·01				
4		12·25		−3·78		−4·38		0·55				
	As(3)	−0·01,	As(4)	−0·00,	C(31)	−0·01,	C(32)	−0·02,				
	C(33)	0·06,	C(34)	−0·05,	C(35)	−0·00,	C(36)	0·04				

Angles between planes 1 and 2 87·7°, 1 and 3 1·2°, 2 and 4 2·3°.

Table 5. *Chlorine· · ·methyl intramolecular contacts*: *dihedral angles* (°) *and distances* (Å)*

m edges

Cl(1)–Mo(1)–As(1)–C(18)	56·5	3·28
Cl(1)–Mo(1)–As(1)–C(19)	−66·3	3·51
Cl(2)–Mo(1)–As(2)–C(28)	−62·0	3·37
Cl(2)–Mo(1)–As(2)–C(29)	57·9	3·35
Cl(3)–Mo(1)–As(3)–C(38)	60·1	3·41
Cl(3)–Mo(1)–As(3)–C(39)	−59·0	3·31
Cl(4)–Mo(1)–As(4)–C(48)	−62·3	3·38
Cl(4)–Mo(1)–As(4)–C(49)	55·5	3·31

g edges (only angles < 60° are listed, the others are *ca.* ±160°)

Cl(1)–Mo(1)–As(3)–C(39)	43·9	3·29
Cl(1)–Mo(1)–As(4)–C(49)	−43·0	3·31
Cl(2)–Mo(1)–As(3)–C(38)	−37·3	3·29
Cl(2)–Mo(1)–As(4)–C(48)	41·6	3·30
Cl(3)–Mo(1)–As(1)–C(19)	36·2	3·36
Cl(3)–Mo(1)–As(2)–C(29)	−39·4	3·33
Cl(4)–Mo(1)–As(1)–C(18)	−43·1	3·31
Cl(4)–Mo(1)–As(2)–C(28)	42·3	3·25

* Distances between atoms *i* and *l* relevant to the dihedral angle *i*–Mo–*k*–*l*.

pulsions are minimized by this arrangement in the dodecahedron rather than any arrangement in any of the other eight-coordinate polyhedra. Geometric parameters for the dodecahedron in (I) are $\theta_A = 37\cdot8$, $\theta_B = 72\cdot6°$, $(M-A)/(M-B) = 1\cdot08$. These values compare with 36·3, 72·8° in TiCl$_4$(diars)$_2$ and with 34·6, 72·8°, ideal angles calculated for sp^3d^4 hybridization by Racah (1943).

In WOCl$_4$(diars), in which the steric crowding is similar to that of (I), W–Cl is 2·41, W–As 2·67 Å. As in TiCl$_4$(diars)$_2$, Ti–Cl is 2·46, Ti–As 2·71 Å, the difference between the M–Cl and M–As (M being a d^0 metal) bond lengths is 0·25 Å. In (I) this difference is only 0·20 Å; and the lesser value, if significant, may relate to some amount of metal-to-arsenic π donation. In octahedral complexes, Mo(V)–Cl bond lengths of 2·26, 2·25 Å are found in MoOCl$_3$ (Drew & Tomkins, 1970) and Mo$_2$Cl$_{10}$ (Sands & Zalkin, 1958), for ter-

minal bonds. The increase of *ca.* 0·20 Å in Mo–Cl bonds is not unusual for eight *versus* six-coordination. The Mo–As bonds in (I) are slightly shorter than the W–As bonds in WOCl$_4$(diars), 2·71 Å.
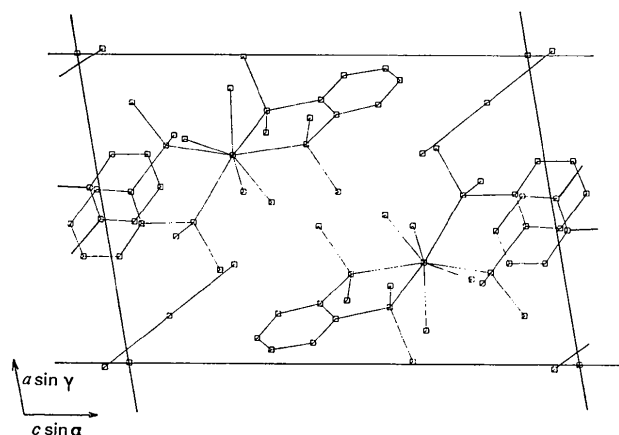
The remaining dimensions in the molecule are unremarkable; As–C bond lengths average 1·94 Å and there is no significant difference between As–Me and As–C$_{ring}$ distances. Of the six angles subtended at each arsenic atom, those involving the metal atom are, as usual, much larger (mean 114·8°) than those involving pairs of carbon atoms (103·6°). The ring carbon bond lengths are all as expected, taking into account the standard deviations. The dimensions of the triiodide anion are somewhat more symmetric than is usually found. A list of dimensions for this anion in various environments is given by Bats, DeBoer & Bright (1971). Intramolecular distances are not particularly short. All values less than 3·8 Å are given in Table 6. Fig. 3 shows the unit cell in the *b* projection.

Table 6. *Intermolecular contacts* < 3·8 Å

C(48)· · ·C(14^I)	3·74
C(13)· · ·Cl(3^{II})	3·64
C(12)· · ·Cl(3^{II})	3·70
C(33)· · ·C(18^{III})	3·80
C(34)· · ·Cl(2^{IV})	3·50
C(35)· · ·Cl(2^{IV})	3·60

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	$1-x, 1-y, 2-z$
II	$1-x, -y, 2-z$
III	$1-x, -y, 1-z$
IV	$-x, -y, 1-z$

We are grateful to A. W. Johans for measuring the intensity data.

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Fig. 3. The unit cell of [MoCl$_4$(diars)$_2^+$]I$_3^-$ in the *b* projection.

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The Crystal and Molecular Structure of Pseudoivalin Bromoacetate

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The crystal structure at 25°C of the bromoacetate of the guaianolide pseudoivalin, $C_{17}H_{21}O_4Br$, has been determined from three-dimensional X-ray diffractometer data by heavy atom and Fourier methods. The crystal is orthorhombic, space group $P2_12_12_1$ with four molecules per unit cell. The cell dimensions are $a = 13\cdot219$ (3), $b = 8\cdot835$ (4), $c = 14\cdot367$ (4) Å. All hydrogen atoms have been located and the structure refined by least-squares calculations to an R of $0\cdot076$. The absolute stereochemistry has been determined from the X-ray data, and this is in accord with the strong negative Cotton effect observed in the optical rotatory dispersion. The cyclopentane ring is highly puckered and the cycloheptene ring has a flattened twist-boat conformation.

Introduction

The isolation from a chemical race of *Iva microcephala* Nutt. of microcephalin (I) (Herz, Högenauer & de Vivar, 1964) and pseudoivalin (II*a*) (Herz, de Vivar & Lakshmikantham, 1964) has so far remained the only instance in which a guaianolide has been found to co-occur with a eudesmanolide. While the stereochemistry of microcephalin was established by chemical and physical means, the assignment of stereochemistry (II*a*) to pseudoivalin was speculative and based primarily on the assumption that a common ten-membered ring precursor was involved. The nature of this precursor has been discussed (Parker, Roberts & Ramage, 1967).

To place speculations concerning the biogenetic origin of these and other sesquiterpene lactones (Herz, 1971) on a firmer footing, we undertook an X-ray crystallographic analysis of pseudoivalin bromoacetate (II*b*), the results of which confirm formula (II*a*) and support the hypothesis that (I) and (II*a*) are formed by processes simulating Markownikow and anti-Markownikow oriented cyclization of the same (*cis*-$\Delta^{1,10}$?) germacradienoid precursor.
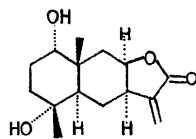
(I)
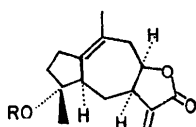
(II)
(*a*) R=H
(*b*) R=-CO.CH₂Br

Experimental

Crystallization was from methanol solution. A fairly equidimensional fragment (0·5mm diameter) was selected for study. Weissenberg and precession photography were used to determine the space group and approximate cell dimensions. The density was determined by flotation in aqueous potassium iodide. The crystal, mounted with the [010] direction approximately parallel to the goniometer axis, was then transferred to a Hilger and Watts four-circle automatic diffractometer and the cell constants refined by least-squares calculations on the observed angles for 11 reflections. Crystal data are given in Table 1.

Table 1. *Crystal data*

$C_{17}H_{21}O_4Br$	$M = 369\cdot264$
Orthorhombic	Systematic absences:
$a = 13\cdot219$ (3) Å	$h00,\ h = 2n + 1$
$b = 8\cdot835$ (4)	$0k0,\ k = 2n + 1$
$c = 14\cdot367$ (4)	$00l,\ l = 2n + 1$
$V = 1677\cdot9$ Å³	Space group:
$Z = 4$	$P2_12_12_1$
$F(000) = 760$	$D_{exp} = 1\cdot47$ (2) g cm⁻³
$\mu(\text{Mo } K\alpha) = 26$ cm⁻¹	$D_{calc} = 1\cdot462$

Intensity data were collected to a 2θ value of 60° by the $\omega/2\theta$ scan technique, with Zr-filtered Mo $K\alpha$ radiation, scintillation counter and pulse-height discrimination. Beyond a 2θ value of 39·0° a rapid sampling method was used to avoid measuring reflections for which $I < B + 3\cdot5\sigma(B)$, where I is the intensity,