The Crystal Structure of $HgCl_2 \cdot 2(C_6H_5)_3AsO$

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The crystal structure of $HgCl_2 \cdot 2(C_6H_5)_3AsO$ has been determined and refined from three-dimensional X-ray data. The crystals are monoclinic (space-group $P\ 2_1/c$) with four molecules in a unit cell with the dimensions $a = 18.40$ Å, $b = 10.58$ Å, $c = 18.23$ Å and $\beta = 106.0°$. The structure comprises discrete $HgCl_2 \cdot 2(C_6H_5)_3AsO$ molecules with a highly distorted tetrahedral configuration around the mercury atom. The mean bond-lengths are: $Hg-Cl = 2.33$ Å, $Hg-O = 2.35$ Å, $As-O = 1.69$ Å, $As-C = 1.92$ Å and $C-C = 1.40$ Å. The bond angles subtended at the mercury atom are: $Cl-Hg-Cl = 146.5°$, $Cl-Hg-O = 101.5°$ (mean value) and $O-Hg-O = 92.5.°$ The bond angle subtended at the oxygen atom is $135.5°$ (mean value). The two crystallographically different $(C_6H_5)_3AsO$-groups of the molecule exhibit small deviations from three-fold rotation symmetry around the As-O vector, the deviations being different in the two groups.

Addition compounds formed between metal halides and oxygen donor molecules have been extensively studied at this Institute during the last five years [1]. The structural study of $HgCl_2 \cdot 2(C_6H_5)_3AsO$ described below was undertaken as part of these investigations.

From a study of the infrared spectra Sheldon and Tyree [2] concluded that the oxygen atoms in this compound function as donor atoms. A spectroscopic investigation of the similar adduct between $HgCl_2$ and $(C_6H_5)_3PO$ has been carried out by Lindqvist et al.[3]

CRYSTAL DATA

Single crystals of the compound $HgCl_2 \cdot 2(C_6H_5)_3AsO$ were kindly provided by Tyree who has already described the preparation of the compound [2]. The unit cell dimensions of the monoclinic crystals were determined from powder photographs recorded in a camera of the Guinier type using $CrK\alpha_1$-radiation with silicon ($a = 5.4306$) as an internal standard.

The values are:
$a = 18.40 \pm 0.02$ Å, $b = 10.58 \pm 0.01$ Å, $c = 18.23 \pm 0.02$ Å and $\beta = 106.0° \pm 0.2°$.

The value 2.2896 Å was assumed for the wave-length of $CrK\alpha_1$-radiation.

A crystal was cut in the form of a needle with the dimensions $0.06 \times 0.14 \times 0.02$ mm, the crystallographic b-axis being coincident with the needle axis. With the crystal rotating about this axis, Weissenberg photographs for the nine zones $0 \le k \le 8$ were recorded using the multiple-film technique and $CuK\alpha$ radiation. In order to correlate the individual layer-lines a second crystal was mounted and rotated around the c-axis and four zones ($0 \le l \le 3$) were recorded in a similar way. These reflections were used for scaling purposes only.

A visual estimate of 1864 independent intensities was made and the data were corrected for Lorentz and polarization effects. Observed extinctions were l odd for $h0l$ and k odd for $0k0$ reflections. It was assumed that the structure belongs to the space-group $P\,2_1/c$.

A density determination by the flotation method using a mixture of CCl_4 and CH_3I gave a value of approximately 1.8 g $\cdot$ cm^{-3}. The density, calculated on the basis of a unit cell containing four molecules of $HgCl_2 \cdot 2(C_6H_5)_3AsO$, is 1.78 g $\cdot$ cm^{-3}.

DETERMINATION OF THE ATOMIC POSITIONS

Since there are four molecules in the unit cell it was assumed that all the atoms in the molecule $HgCl_2 \cdot 2(C_6H_5)_3AsO$ occupy general position 4(e) in the space-group $P\,2_1/c$. A three-dimensional Patterson function $P_1(x, y, z)$ was calculated on the electronic computer BESK in Stockholm using a programme devised by Westman et al. [4] From this function approximate parameters for the mercury and the two arsenic atomic positions could easily be derived by locating the corresponding vectors. As the y-coordinate of Hg is very near 0.25 no unique solution of the arsenic positions could be derived from the Hg—As vectors alone. (These vectors are identical for positions x_{As}, y_{As}, z_{As} and x_{As}, y_{As}, $z_{As} + \frac{1}{2}$.) However, by locating the unsymmetrical As—As vector a unique solution was obtained.

Hg—Cl vectors were then located. A unique solution for the positions of the Cl-atoms could not be obtained from a study of the As—Cl vectors in this function since these are of the same order of magnitude as the Hg—C vectors. Mercury does not contribute, however, to $F^2(h, k, l)$ if l is odd. These reflections where therefore used as Fourier coefficients to calculate the new three-dimensional Patterson function $P_2(x, y, z)$. In this function the As—Cl vectors were easily found and unique z-coordinates could be assigned to the two chlorine atomic positions.

The coordinates which had been determined at this stage were then employed in the calculation of one F_c-synthesis, using the programmes devised by Liminga et al. [5] for the Swedish electronic computer FACIT EDB. One F_o synthesis was also calculated, the signs of the coefficients being the same as those used in the F_c synthesis. Only those parts of the maps necessary for locating the mercury, arsenic and chlorine atomic positions were calculated. A back-shift correction was applied to the coordinates of these atoms. The scale factors and the vibration parameters were adjusted by means of two cycles of least-squares refinement using the programme devised by Åsbrink

and Brandén [6] (see below). The atomic positions obtained following the application of the back-shift corrections were used for the calculation of the matrix elements. The parameters refined at this stage were nine scale-factors, one for each layer-line, and the individual isotropic temperature factors for one mercury, two chlorine and two arsenic atoms.

Using these parameters a three-dimensional difference synthesis was calculated using $(F_o - (F_{Hg} + F_{As} + F_{Cl}))$ as Fourier coefficients. Atomic scattering factors for the elements in this and the following calculations were obtained from the following references; mercury and arsenic from Thomas

Table 1. Final atomic parameters and their e.s.d.'s.

Atom	x	$\sigma(x)$ Å	y	$\sigma(y)$ Å	z	$\sigma(z)$ Å	B Å^2	$\sigma(B)$ Å^2
Hg(1)	0.1985	0.002	0.2425	0.002	0.1179	0.002	4.22	0.03
Cl(2)	0.0711	0.011	0.2039	0.011	0.0579	0.011	5.57	0.22
Cl(3)	0.2964	0.011	0.3882	0.012	0.1428	0.011	5.93	0.23
O(4)	0.2098	0.023	0.1488	0.023	0.2357	0.023	4.26	0.48
O(5)	0.2601	0.024	0.0719	0.026	0.0760	0.024	5.36	0.55
As(6)	0.2059	0.004	0.1966	0.004	0.3232	0.004	3.79	0.07
As(7)	0.2889	0.004	0.9269	0.004	0.1109	0.004	4.47	0.08
C(8)	0.2999	0.035	0.2554	0.036	0.3867	0.033	4.64	0.66
C(9)	0.3483	0.036	0.3246	0.039	0.3514	0.035	4.97	0.79
C(10)	0.4206	0.035	0.3521	0.036	0.3918	0.035	4.90	0.79
C(11)	0.4464	0.040	0.3273	0.043	0.4686	0.040	6.39	0.92
C(12)	0.3949	0.039	0.2628	0.040	0.5016	0.038	6.02	0.84
C(13)	0.3290	0.037	0.2202	0.036	0.4652	0.036	5.17	0.82
C(14)	0.1342	0.037	0.3332	0.039	0.3207	0.037	4.77	0.77
C(15)	0.1479	0.035	0.4089	0.036	0.3843	0.035	4.76	0.80
C(16)	0.0906	0.040	0.5075	0.041	0.3861	0.039	6.10	0.90
C(17)	0.0277	0.040	0.5070	0.043	0.3159	0.040	6.37	0.93
C(18)	0.0213	0.041	0.4417	0.044	0.2572	0.042	6.85	0.97
C(19)	0.0773	0.038	0.3456	0.037	0.2552	0.037	5.28	0.83
C(20)	0.1709	0.034	0.0580	0.036	0.3696	0.033	4.42	0.75
C(21)	0.1794	0.039	−0.0616	0.041	0.3440	0.038	5.77	0.89
C(22)	0.1509	0.044	−0.1721	0.045	0.3823	0.043	7.34	1.02
C(23)	0.1180	0.039	−0.1509	0.039	0.4341	0.038	5.55	0.86
C(24)	0.1060	0.037	−0.0257	0.037	0.4584	0.036	5.06	0.83
C(25)	0.1332	0.035	0.0821	0.038	0.4266	0.036	4.89	0.80
C(26)	0.3183	0.035	−0.1693	0.038	0.0345	0.035	4.85	0.78
C(27)	0.3202	0.032	−0.0979	0.033	−0.0296	0.032	3.88	0.69
C(28)	0.3444	0.041	−0.1627	0.043	−0.0883	0.040	6.47	0.95
C(29)	0.3594	0.042	−0.2816	0.042	−0.0812	0.041	6.85	0.99
C(30)	0.3553	0.044	−0.3600	0.044	−0.0209	0.044	7.47	1.10
C(31)	0.3341	0.039	−0.2989	0.038	0.0392	0.038	5.57	0.85
C(32)	0.3794	0.032	−0.0591	0.035	0.1993	0.033	4.26	0.73
C(33)	0.4336	0.041	−0.1604	0.044	0.2116	0.043	6.88	1.01
C(34)	0.4988	0.040	−0.1462	0.040	0.2763	0.038	6.32	0.93
C(35)	0.5030	0.040	−0.0403	0.041	0.3237	0.041	6.53	0.96
C(36)	0.4448	0.038	0.0514	0.038	0.3099	0.036	5.38	0.84
C(37)	0.3770	0.039	0.0404	0.038	0.2482	0.038	5.59	0.87
C(38)	0.2117	0.031	−0.1651	0.033	0.1378	0.030	3.63	0.68
C(39)	0.1402	0.032	−0.1409	0.032	0.1048	0.031	3.67	0.68
C(40)	0.0841	0.040	−0.2049	0.041	0.1217	0.038	6.06	0.94
C(41)	0.0974	0.032	−0.3179	0.035	0.1671	0.032	3.97	0.69
C(42)	0.1725	0.044	−0.3486	0.044	0.1962	0.044	7.65	1.08
C(43)	0.2356	0.040	−0.2751	0.039	0.1865	0.038	5.99	0.88

Table 2. Final weight analysis.

sin Θ interval	$\overline{w\Delta^2}$	Number of reflexions
0 -0.45	0.99	571
0.45 -0.57	0.89	483
0.57 -0.65	1.12	351
0.65 -0.71	1.15	214
0.71 -0.77	0.98	123
0.77 -0.82	1.00	68
0.82 -0.86	0.81	30
0.86 -0.90	0.70	12
0.90 -0.97	0.72	10

F_o $-$ interval	$\overline{w\Delta^2}$	Number of reflexions
0 $-$ 40	1.27	164
40 $-$ 80	1.02	880
80 $-$ 120	0.85	457
120 $-$ 160	0.95	182
160 $-$ 200	0.87	104
200 $-$ 240	1.24	40
240 $-$ 280	1.35	21
280 $-$ 400	2.33	14

and Umeda [7], chlorine from Tomiie and Stam [8], oxygen from Berghuis *et al.* [9] and carbon from Freeman [10]. The scattering factor of mercury was corrected for the real part of the anomalous dispersion effect [11].

From this difference synthesis it was possible to assign approximate coordinates to all the carbon atoms in the six phenyl rings and to the two oxygen atoms.

REFINEMENT OF THE PARAMETERS

The atomic parameters were refined by the least squares method using the programme devised by Åsbrink and Brändén [6] for FACIT EDB. The main outlines of this programme have been briefly described in another paper [12]. The parameters refined were the atomic coordinates, the individual isotropic vibration parameters and the nine separate scale-factors, one for each layer-line. The weights, w, were calculated according to an equation suggested by Cruickshank *et al.* [13] as follows; $w = 1/(a + |F_o| + c|F_o|^2)$. The final values of a and c were 63 and 0.0045, respectively. Only observed reflections were included in the refinement. At the end of each cycle a weight analysis was computed. The mean value of $w(|F_o| - |F_c|)^2$ was calculated at intervals of increasing F_o and $\sin\Theta$. The values of a and c were adjusted between the refinement cycles so that this mean value was constant at all intervals.

Because of the limited storage of the computer the coordinates of only 35 of the 43 Hg, Cl, C, As or O atoms could be refined during each cycle. In each cycle, therefore, a different set of eight atoms was excluded from the refinement.
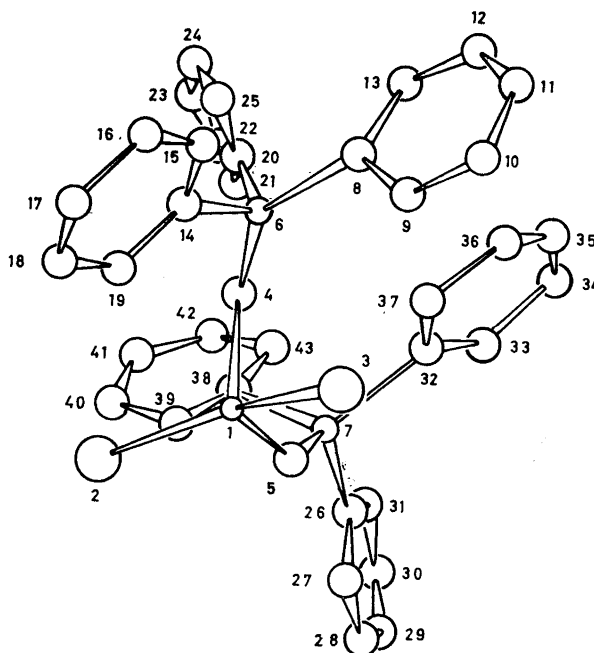
Fig. 1. The structure of HgCl$_2$ · 2(C$_6$H$_5$)$_3$AsO.

After four cycles of refinement the discrepancy factor R for the observed reflections had fallen from 0.236 to 0.139. A difference synthesis was calculated and some of the carbon atoms were given shifts according to the results of this synthesis. Using these parameters another ten cycles of least squares refinement were computed. In the last two cycles all the shifts of the positional parameters were less than one half of their estimated standard deviations. The final R value was 0.092 for the observed independent reflections. A difference synthesis was finally calculated, in which no spurious peaks were observed.

One feature of the refinement which needs further comment is the wide range of values obtained for the temperature factors of the carbon atoms. Due to the large shifts obtained in the early stage of the refinement these temperature factors were given artificial shifts to the value of 4.5 in every other cycle except for the last three cycles. Although the final values range between 3.6 and 7.6 it is probably wrong to associate these with any physical difference between the thermal vibration of the atoms, since systematic errors in the intensity data due, for example, to absorbtion effects might influence the values of the temperature factors.

The final atomic parameters are listed in Table 1 together with their estimated standard deviations. The weight analysis obtained from the last cycle of refinement is given in Table 2. Lists of the observed and calculated F-values can be obtained from this Institute on request.

Table 3. Bond distances and bond angles in $HgCl_2 \cdot 2(C_6H_5)_3AsO$.

Bond distances, (Å):

Hg(1)—Cl(2)	2.33	C(20)—C(21)	1.37
Hg(1)—Cl(3)	2.32	C(21)—C(22)	1.53
Hg(1)—O(4)	2.32	C(22)—C(23)	1.28
Hg(1)—O(5)	2.37	C(23)—C(24)	1.43
As(6)—O(4)	1.69	C(24)—C(25)	1.43
As(7)—O(5)	1.69	C(25)—C(20)	1.42
As(6)—C(8)	1.90	C(26)—C(27)	1.40
As(6)—C(14)	1.95	C(27)—C(28)	1.44
As(6)—C(20)	1.89	C(28)—C(29)	1.29
As(7)—C(26)	1.92	C(29)—C(30)	1.39
As(7)—C(32)	1.98	C(30)—C(31)	1.42
As(7)—C(38)	1.90	C(31)—C(26)	1.40
C(8)—C(9)	1.44	C(32)—C(33)	1.44
C(9)—C(10)	1.36	C(33)—C(34)	1.44
C(10)—C(11)	1.37	C(34)—C(35)	1.41
C(11)—C(12)	1.43	C(35)—C(36)	1.42
C(12)—C(13)	1.29	C(36)—C(37)	1.44
C(13)—C(8)	1.43	C(37)—C(32)	1.39
C(14)—C(15)	1.37	C(38)—C(39)	1.31
C(15)—C(16)	1.49	C(39)—C(40)	1.34
C(16)—C(17)	1.47	C(40)—C(41)	1.44
C(17)—C(18)	1.25	C(41)—C(42)	1.38
C(18)—C(19)	1.46	C(42)—C(43)	1.45
C(19)—C(14)	1.36	C(43)—C(38)	1.46

Bond angles (degrees):

Cl(2)—Hg(1)—Cl(3)	146.6	C(9)—C(10)—C(11)	121.4
Cl(2)—Hg(1)—O(4)	100.4	C(10)—C(11)—C(12)	116.0
Cl(2)—Hg(1)—O(5)	103.0	C(11)—C(12)—C(13)	126.0
Cl(3)—Hg(1)—O(4)	103.6	C(12)—C(13)—C(8)	117.5
Cl(3)—Hg(1)—O(5)	98.9	C(19)—C(14)—C(15)	127.0
O(4)—Hg(1)—O(5)	92.5	C(14)—C(15)—C(16)	117.5
Hg(1)—O(4)—As(6)	136.7	C(15)—C(16)—C(17)	111.7
Hg(1)—O(5)—As(7)	134.4	C(16)—C(17)—C(18)	127.7
O(4)—As(6)—C(8)	113.8	C(17)—C(18)—C(19)	120.5
O(4)—As(6)—C(14)	113.8	C(18)—C(19)—C(14)	115.2
O(4)—As(6)—C(20)	107.3	C(25)—C(20)—C(21)	122.5
C(8)—As(6)—C(14)	105.5	C(20)—C(21)—C(22)	117.7
C(8)—As(6)—C(20)	110.3	C(21)—C(22)—C(23)	119.8
C(14)—As(6)—C(20)	105.9	C(22)—C(23)—C(24)	122.5
O(5)—As(7)—C(26)	109.3	C(23)—C(24)—C(25)	120.8
O(5)—As(7)—C(32)	110.2	C(24)—C(25)—C(20)	116.6
O(5)—As(7)—C(38)	112.6	C(31)—C(26)—C(27)	121.9
C(26)—As(7)—C(32)	106.8	C(26)—C(27)—C(28)	116.5
C(26)—As(7)—C(38)	107.3	C(27)—C(28)—C(29)	119.4
C(32)—As(7)—C(38)	110.5	C(28)—C(29)—C(30)	127.2
As(6)—C(8)—C(9)	117.9	C(29)—C(30)—C(31)	115.0
As(6)—C(8)—C(13)	123.3	C(30)—C(31)—C(26)	119.8
As(6)—C(14)—C(15)	116.5	C(37)—C(32)—C(33)	127.4
As(6)—C(14)—C(19)	116.5	C(32)—C(33)—C(34)	115.8
As(6)—C(20)—C(21)	118.6	C(33)—C(34)—C(35)	118.7
As(6)—C(20)—C(25)	118.8	C(34)—C(35)—C(36)	121.8
As(7)—C(26)—C(27)	113.3	C(35)—C(36)—C(37)	122.4
As(7)—C(26)—C(31)	124.8	C(36)—C(37)—C(32)	113.0
As(7)—C(32)—C(33)	117.6	C(43)—C(38)—C(39)	122.1
As(7)—C(32)—C(37)	114.4	C(38)—C(39)—C(40)	122.3
As(7)—C(38)—C(39)	120.6	C(39)—C(40)—C(41)	122.3
As(7)—C(38)—C(43)	116.5	C(40)—C(41)—C(42)	114.3
C(13)—C(8)—C(9)	118.2	C(41)—C(42)—C(43)	125.4
C(8)—C(9)—C(10)	120.1	C(42)—C(43)—C(38)	112.8

Table 4. Estimated standard deviations of the bond lengths and bond angles.

Bond	e.s.d. (Å)	Angle	e.s.d. (°)
Hg−Cl	0.01	Cl−Hg−Cl	0.4
Hg−O	0.03	Cl−Hg−O	0.7
As−O	0.03	O−Hg−O	0.9
As−C	0.04	Hg−O−As	1.4
C−C	0.06	C−As−C	1.7
		O−As−C	1.5
		As−C−C	2.9
		C−C−C	3.6

Table 5. Packing distances less than 4.0 Å in HgCl₂·2(C₆H₅)₃AsO.

Distance	Å	Distance	Å
Cl(2)A−C(15)F	3.99	C(15)A−C(27)E	3.71
Cl(2)A−C(16)F	3.94	C(16)A−C(22)B	3.57
Cl(2)A−C(16)I	3.98	C(16)A−C(23)B	3.72
Cl(2)A−C(17)I	3.90	C(16)A−C(40)H	3.89
Cl(2)A−C(23)H	3.84	C(17)A−C(40)H	3.44
Cl(2)A−C(24)F	3.99	C(17)A−C(41)B	3.79
Cl(2)A−C(25)F	3.70	C(18)A−C(20)H	3.86
Cl(2)A−C(40)C	3.70	C(18)A−C(21)H	3.65
Cl(3)A−C(12)F	3.88	C(18)A−C(22)H	3.68
Cl(3)A−C(13)F	3.64	C(18)A−C(23)H	3.84
Cl(3)A−C(31)B	3.97	C(18)A−C(24)H	3.99
Cl(3)A−C(34)K	3.67	C(18)A−C(40)H	3.66
Cl(3)A−C(35)K	3.65	C(18)A−C(41)H	3.99
Cl(3)A−C(42)B	3.89	C(18)A−C(41)B	3.52
Cl(3)A−C(43)B	3.88	C(18)A−C(42)B	3.95
O(5)A−C(12)F	3.59	C(19)A−C(41)B	3.96
O(5)A−C(13)F	3.45	C(19)A−C(42)B	3.97
O(5)A−C(15)F	3.54	C(21)A−C(29)G	3.62
C(8)A−C(27)E	3.91	C(21)A−C(30)G	3.58
C(9)A−C(27)E	3.74	C(22)A−C(26)G	3.91
C(9)A−C(28)E	3.75	C(22)A−C(27)G	3.93
C(10)A−C(27)E	3.70	C(22)A−C(28)G	3.87
C(10)A−C(28)E	3.63	C(22)A−C(29)G	3.74
C(10)A−C(33)K	3.68	C(22)A−C(30)G	3.70
C(10)A−C(34)K	3.75	C(22)A−C(31)G	3.78
C(11)A−C(27)E	3.69	C(23)A−C(31)G	3.94
C(11)A−C(28)K	3.87	C(23)A−C(39)G	3.74
C(11)A−C(29)K	3.78	C(23)A−C(40)G	3.95
C(12)A−C(27)E	3.79	C(33)A−C(36)L	3.86
C(12)A−C(35)D	3.99	C(34)A−C(36)L	3.83
C(13)A−C(30)G	3.84		

The coordinates of the atoms of molecules B−L are related to those of molecule A by the following symmetry relations.

Molecule	Coordinates		
A	x	y	z
B	x	$1+y$	z
C	$-x$	$-y$	$-z$
D	$1-x$	$-y$	$1-z$
E	x	$1/2-y$	$1/2+z$
F	x	$1/2-y$	$-1/2+z$
G	x	$-1/2-y$	$1/2+z$
H	$-x$	$1/2+y$	$1/2-z$
I	$-x$	$-1/2+y$	$1/2-z$
K	$1-x$	$1/2+y$	$1/2-z$
L	$1-x$	$-1/2+y$	$1/2-z$

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure comprises discrete $HgCl_2 \cdot 2(C_6H_5)_3AsO$ molecules, one of which is shown in Fig. 1. The bond distances and bond angles in the molecule are listed in Table 3. The standard deviations of the different kinds of bond lengths and bond angles listed in Table 4 were calculated [14] after the following approximations had been made: The standard deviations of the positions of the atoms were assumed to be the same in all directions and equal to 0.002 Å for Hg, 0.004 Å for As, 0.012 Å for Cl, 0.025 Å for O and 0.040 Å for C. Table 5 lists packing distances less than 4.0 Å between symmetrically related molecules calculated on the basis of the atomic coordinates given in Table 1.

The mercury atom has a highly distorted tetrahedral coordination, the ligands being two chlorine atoms and two oxygen atoms, one from each $(C_6H_5)_3AsO$ molecule. The bond angles show marked deviations from the regular tetrahedral angle of 109°28', the values being Cl—Hg—Cl = 146.5°, Cl—Hg—O = 101.5° (mean value) and O—Hg—O = 92.5°. Construction of a model of the molecule demonstrated the difficulty of accounting for these deviations in terms of strain produced by the close proximity of two phenyl groups, at least so far as a hypothetical molecule with regular coordination is concerned. Deviations from the regular bond angle have been found in a number of adduct molecules with octahedral coordination around the acceptor atom [15]. These deviations have been explained as being due to two steric factors, the van der Waal radii of the ligand atoms and their distances from the central atom. In the present structure the operation of these steric factors would produce departures from the tetrahedral angle of the observed type. The deviations in this structure are, however, quite large although the distances between the ligand atoms exceed the sums of their van der Waal radii. Thus the distances are Cl—Cl = 4.45 Å, Cl—O = 3.62 Å (mean value) and O—O = 3.39 Å while the van der Waal radii given by Pauling [16] are 1.80 Å for chlorine and 1.40 Å for oxygen. In view of these large distances it is doubtful whether such steric factors are the main cause of the large deviations observed.

The mean value of the two Hg—Cl bond lengths is 2.33 Å and that of the two Hg—O bond lengths is 2.35 Å. There is no significant difference between the lengths of bonds of the same type. A detailed discussion of these bond distances is complicated by the difficulty of finding suitable distances for comparison. Thus all previous Hg—Cl and Hg—O bond distances relevant to the solid state have been evaluated from structures in which there is a distorted octahedral configuration about the mercury atom. It is evident, however, that there are two strong Hg—Cl bonds and two weaker Hg—O bonds. The Hg—Cl bond lengths are almost as short as those in free $HgCl_2$ (2.27 Å) and approximately equal to the short Hg—Cl bond lengths in complex mercury chlorides and in $HgCl_2$ adducts [17] exhibiting distorted octahedral coordination. The Hg—O bond length is significantly larger than the short linear Hg—O bonds (2.03 Å) found in the O—Hg—O chains of HgO [18], but shorter than the Hg—O acceptor-donor bond length (2.66 Å) found in the adduct $HgCl_2 \cdot C_4H_8O_2$ [19].

Table 6. Comparison of mean bond distances and bond angles of the $(C_6H_5)_3AsO$ molecules in $HgCl_2 \cdot 2(C_6H_5)_3AsO$ and $SbCl_3 \cdot 2(C_6H_5)_3AsO$.

$HgCl_2 \cdot 2(C_6H_5)_3AsO$	$HgCl_2 \cdot 2(C_6H_5)_3AsO$	$SbCl_3 \cdot 2(C_6H_5)_3AsO$
Molecule 1	Molecule 2	Mean value
As—O	1.69 Å	1.69 Å	1.66 Å
As—C	1.91 Å	1.93 Å	1.92 Å
C—C	1.40 Å	1.40 Å	1.40 Å
∧O—As—C	111.6°	110.9°	110.5°
∧C—As—C	107.2°	108.2°	108.4°
∧C—C—C	119.9°	119.9°	119.8°

The Hg—O—As bond angle is 135.5° (mean value). The bond angle subtended at the O-atom in adducts of this type depends largely on the distribution of the *s*-electrons of the oxygen atom. This has been discussed and exemplified by Lindqvist [1] who has shown that other factors, particularly steric factors, are also of importance in determining the magnitude of this angle.

The dimensions of the two $(C_6H_5)_3AsO$ groups are very similar to each other and to the $(C_6H_5)_3AsO$ ligands in the adduct $SbCl_3 \cdot 2(C_6H_5)_3AsO$ [20]. The mean bond distances and bond angles within each of the two groups in the present structure and the corresponding mean values of the two ligands of $SbCl_3 \cdot 2(C_6H_5)_3AsO$ are compared in Table 6. (The group comprising carbon atoms numbered 8—25 in Table 1 is referred to as molecule 1 in this discussion.) The mean bond distance and bond angle for the phenyl rings are in close agreement with the values found in other structures, although the individual bond lengths and angles vary considerably owing to the high standard deviations for the carbon-atom positions. The mean As—C bond lengths (1.92 Å) is not significantly different from that found in arsenobenzene [21]. The bond angles around arsenic are very close to the tetrahedral value, with the angle O—As—C slightly larger than C—As—C in both structures. The As—O bond distances of 1.69 Å and 1.66 Å are not significantly different. In a number of structure determinations of adducts in which R_3PO is the donor molecule [12,22,23] a significant change in the dimensions of the donor molecule on adduct formation has been found only in the presence of a very strong donor-acceptor interaction. This change was apparent only in the change in the P—O bond length. Since $(C_6H_5)_3AsO$ is a very similar donor molecule it seems reasonable to assume that, with the possible exception of the As—O distance, the bond lengths and bond angles given in Table 6 are not very different from those of free $(C_6H_5)_3AsO$.

The »best» planes for the atoms of each phenyl group were estimated from a least-squares fit of the C-atom coordinates, using the method suggested by Blow [24]. All atoms were given unit weight. The results are given in Table 7 which lists the equation of each plane (expressed in Cartesian coordinates), the distances of the carbon atoms from the plane, and the distance from the plane to the As atom bonded to the relevant phenyl group. The results show that within each ring the carbon atoms depart from the »best» plane by not

Table 7. Distances of atoms from the best planes.

Ring 1. Best plane through C(8), C(9), C(10), C(11), C(12), and C(13).
        $0.3567\ X - 0.8672\ Y - 0.3475\ Z + 2.361 = 0$
        Distances from this plane:

C(8) = −0.01 Å	C(11) = −0.01 Å	
C(9) = −0.03 Å	C(12) = −0.04 Å	As(6) = + 0.17 Å
C(10) = +0.04 Å	C(13) = +0.05 Å	

Ring 2. Best plane through C(14), C(15), C(16), C(17), C(18), and C(19).
        $0.5129\ X + 0.6633\ Y - 0.5450\ Z - 0.781 = 0$
        Distances from this plane:

C(14) = −0.04 Å	C(17) = −0.03 Å	
C(15) = +0.02 Å	C(18) = +0.02 Å	As(6) = −0.18 Å
C(16) = +0.02 Å	C(19) = +0.02 Å	

Ring 3. Best planes through C(20), C(21), C(22), C(23), C(24), and C(25).
        $-0.8780\ X + 0.0586\ Y - 0.4751\ Z + 5.392 = 0$
        Distances from this plane:

C(20) = −0.02 Å	C(23) = +0.01 Å	
C(21) = +0.02 Å	C(24) = +0.01 Å	As(6) = +0.01 Å
C(22) = −0.01 Å	C(25) = −0.00 Å	

Ring 4. Best plane through C(26), C(27), C(28), C(29), C(30), and C(31).
        $-0.9578\ X - 0.2098\ Y - 0.1965\ Z + 4.805 = 0$
        Distances from this plane:

C(26) = −0.02 Å	C(29) = −0.01 Å	
C(27) = +0.02 Å	C(30) = +0.01 Å	As(7) = −0.04 Å
C(28) = −0.01 Å	C(31) = +0.00 Å	

Ring 5. Best plane through C(32), C(33), C(34), C(35), C(36), and C(37).
        $0.4661\ X + 0.5268\ Y - 0.7109\ Z - 1.527 = 0$
        Distances from this plane:

C(32) = +0.06 Å	C(35) = +0.01 Å	
C(33) = −0.02 Å	C(36) = +0.01 Å	As(7) = +0.05 Å
C(34) = −0.01 Å	C(37) = −0.05 Å	

Ring 6. Best plane through C(38), C(39), C(40), C(41), C(42), and C(43).
        $0.0186\ X + 0.5602\ Y + 0.8282\ Z - 0.258 = 0$
        Distances from this plane:

C(38) = +0.03 Å	C(41) = +0.00 Å	
C(39) = −0.05 Å	C(42) = −0.03 Å	As(7) = −0.14 Å
C(40) = +0.04 Å	C(43) = +0.02 Å	

Coordinate system:
$$X = a \times x \times \sin\beta$$
$$Y = b \times y$$
$$Z = a \times x \times \cos\beta + c \times z$$

more than 1.5 times the e.s.d. Within one $(C_6H_5)_3AsO$ group the As atom is coplanar with one of the phenyl rings but departs by a significant amount from the planes of the other two. In the second group, the As atom is coplanar with two of the rings and departs by a significant amount from the plane of the third.

The orientation of the phenyl-rings within the two $(C_6H_5)_3AsO$-groups differs slightly. Both groups exhibit fairly small deviations from three-fold

Table 8.

1. Angles between the planes of the phenyl rings of each $(C_6H_5)_3AsO$ group.

Angle between rings:

1 and 2 = 102°	4 and 5 = 115°
1 and 3 = 101°	4 and 6 = 107°
2 and 3 = 99°	5 and 6 = 107°

2. Angles between normal n and the normals of the planes of the corresponding phenyl-rings.

Angle between n and normal of:

Ring 1 = 57°	Ring 4 = 80°
Ring 2 = 67°	Ring 5 = 61°
Ring 3 = 65°	Ring 6 = 72°

rotation symmetry around an axis approximately in the direction of the As—O vector. The deviations from strict symmetry were calculated for each group by rotating the normals to each plane through $\pm$ 120° around an axis n defined as the normal of the plane through the centroids of the three phenyl rings. The angles between the original set of normals and the rotated set were all found to be between 7 and 11 degrees, except in the case of the rotation of the normal to plane 4 through 240°, when the rotated line makes an angle of 20° with the normal to plane 5. This larger distortion is also reflected in the angles between the planes, which are listed in Table 8. The angle between planes 4 and 5 is eight degrees larger than the other two angles in group 2. All attempts to correlate this particular distortion with the way in which the molecules are packed have failed, probably as a result of the complicated nature of the packing.

The bond angles between the planes also reflect another difference between the two groups. These angles are all smaller for group 1 than for group 2. The structural implications of this are best seen when viewing the $(C_6H_5)_3AsO$-group down the axis n in the O—As direction. The greater the apparent departure of the phenyl-rings from the horizontal, the larger is the angle between the planes in the convention used here. The combined effect of the magnitude of this angle and the deviations from three-fold rotation symmetry is perhaps best reflected in the angles between the normals to the planes and the axis n of each group, listed in Table 8. In the symmetrical molecule tetra-phenylmethane [25] which exhibits strict three-fold rotation symmetry around each of the tetragonal bonds from the central carbon atom, this angle is 55°.

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