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The Molecular Structure of an Adduct of 10-Phenoxarsine Chloride: $C_{12}H_8OAsClOSbCl_5$

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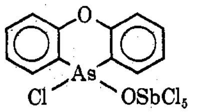
The crystal and molecular structure of the antimony pentachloride adduct of 10-chlorophenoxarsine oxide, $C_{12}H_8OAsClOSbCl_5$, has been determined by single-crystal X-ray diffraction methods. The unit cell is monoclinic: a = 8.795 (1), b = 17.470 (3), c = 13.533 (2) Å, β = 117.90 (1)°, d_{measd} = 2.12 (1) gcm^{-3}, and d_{calcd} (Z = 4) = 2.145 (1) g/cm^{-3}. The space group is $P2_1/c$ (C_{2h}^5; No. 14). Manual diffractometer methods (Mo radiation, λ 0.71069 Å) were used to obtain 813 observed ($I \geq 2\sigma(I)$) reflections at 23°. Final full-matrix least-squares refinement using anisotropic thermal parameters for As, Cl, and Sb and assigned positional and thermal parameters for the hydrogen atoms gave an R index of 0.035. The As–Cl, As–O, and As–C bond distances are 2.100 (6), 1.73 (1), and 1.83 (2) Å, and the $SbCl_5$ moiety is in a slightly distorted octahedral geometry with Sb–Cl distances of 2.34 (1) Å. The bond angles at the approximately tetrahedral arsenic atom vary from 98.0 to 117.2°. The two C_6H_4AsO "halves" of the phenoxarsine system are planar within experimental error, and the angle of fold at the As···O line is 167.7°.

Introduction

The most striking feature of the molecular structure of 10-phenoxarsine chloride is a nearly planar configuration of the *o*-phenylene groups, which suggests some delocalized bond character for the central ring as discussed in the preceding paper.[1] As a means of illustrating the sensitivity of the structural features of these condensed ring molecules to electronic effects, we report here the structure of the $OSbCl_5$ adduct of 10-phenoxarsine chloride (**1**).



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Experimental Section

The subject adduct was prepared by adding 0.23 ml (1.8 mmol) of $SbCl_5$ to a solution of 0.538 g (1.9 mmol) of 10-phenoxarsine chloride in 20 ml of benzene. Upon addition of the pentachloride the solution turned red. Subsequent heating to reflux without any special precautions to exclude atmospheric air resulted in the solution changing to a dark green color; we suspect it was this step which introduced the oxygen to the reaction. Light green crystals of the product ($C_{12}H_8OAsClOSbCl_5$) were obtained by slow evaporation of the benzene solution, and the product was identified by its mass spectrum. Suitable crystals were obtained by slow evaporation of benzene solutions. The approximately parallelpiped crystal used for the diffractometer data collection measured 0.08 × 0.31 × 0.28 mm (all ±0.01 mm) in the [010], [100], and [001] directions. The crystal was mounted on a glass fiber with the a axis approximately parallel to the ϕ axis.

The diffractometer used was a Ge XRD-5 manually operated quarter circle system, with Mo Kα (λ 0.71069 Å) radiation filtered by a 1-mil thickness of zirconium foil. A scintillation counter was used with a pulse height analyzer set for a 90% window. Least-squares refinement[2] of the setting angles of 27 carefully centered reflections gave, at 23°: a = 8.795 (1), b = 17.470 (3), c = 17.533 (2) Å, and β = 117.90 (1)°. The crystal density, measured by suspension in a mixture of ethyl iodide and 1,2-dibromo-1,1-dichloroethane, is 2.21 (1) g/cm^{-3}, which compares with 2.145 (1) g/cm^{-3} calculated for four formula units per cell. Four molecules/cell in space group $P2_1/c$ (indicated by absences for $h0l$, l odd, and $0k0$, k odd) imposes no crystallographic symmetry on the molecules of the structure.

The absorption coefficient of $C_{12}H_8O_2AsSbCl_6$ for Mo Kα radiation is 43.5 cm^{-1}. A general correction for absorption, using the method of Busing and Levy,[3] was applied. A 2 × 6 × 6 summation was made, and the transmission factors (for F) varied from 0.60 to 0.84. No correction was made for extinction.

For intensity data collection a θ–2θ scan of 2.0° in 2θ was made at a speed of 2°/min with a take-off angle of 3°. Stationary crystal–stationary counter background readings were taken for 10 sec at each end of the scans. All reflections with $0 < 2\theta < 40°$ were examined (1708). Of these, 813 reflections had $I \geq 2\sigma(I)$; these were used for the solution and refinement of the structure. Four reflections, measured periodically during the six day data collection, indicated crystal and electronic stability ($\Delta I < 3\%$).

The standard deviations for I were calculated by $\sigma(I) = (S + BT^2 + 0.0016\ I^2)^{1/2}$ [where S = total scan count, B = sum of the background counts, T = (scan time)/(total background time), and $I = S - BT$], except for a small number of reflections for which the two background readings differed by more than twice the calculated σ due to tailing of the reflection peak. For the latter reflections the standard deviations were set equal to the deviation of the background readings from the mean background value.

Scattering factors for neutral atoms were calculated from the analytical functions of Cromer and Waber,[4] and real and imaginary anomalous dispersion corrections were made for As, Sb, and Cl using the values given by Cromer.[5] All calculations were done with the IBM 360/50 computer at the University of Arkansas Computer Center, using the programs previously described.[1]

Solution and Refinement of the Structure

The eight heavy atoms were located by analysis of a three-dimensional sharpened Patterson map, and the phenylene rings were subsequently located by Fourier methods and refined originally as rigid groups. When the rigid group constraints were removed and all nonhydrogen atoms were refined with isotropic thermal motion R_1 $(=\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ was 0.057 and R_2 $(=[\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2})$ was 0.062.

In the least-squares refinement, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where w is $1/\sigma(F)$. When the hydrogen atoms were positioned in calculated positions and the antimony, arsenic, and chloride atoms were refined with anisotropic thermal parameters, R_1 and R_2 became 0.035 and 0.040, respectively. This final refinement consisted of 129 parameters and 813 reflections. The standard deviation of an observation of unit weight is 0.69, and no $\Delta F/\sigma$ values were greater than 3.3.[6] In the final cycle all of the atoms had positional and thermal factor shifts of less than 0.36σ except C(4), C(5), C(8), and C(11), which had total posi-

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[1] J. E. Stuckey, A. W. Cordes, L. B. Handy, R. W. Perry, and C. K. Fair, *Inorg. Chem.*, **11**, 1846 (1972).

[2] A. Foust, Program ANGSET, University of Wisconsin, 1968.

[3] W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

[4] D. T. Cromer and J. T. Waber, Los Alamos Scientific Laboratory, private communications.

[5] D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

[6] A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W. Washington, D. C. 20036, by referring to code number INORG-72-1849. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

tional shifts of 0.94, 1.58, 0.65, and 1.61σ, respectively. Because of the expense of the refinement (42-min IBM 360/50 computing/cycle) and the lack of any special interest in distances or angles involving these atoms, refinement was terminated. A final difference map did not have any peaks which were interpretable chemically; the highest electron density was 0.50 e/Å,^{3} which is equal to 9% of the maximum electron density of a carbon atom on a regular electron density map. Inspection of the reflection list of the final least squares did not reveal any $\Delta F/\sigma$ dependence on either F or θ values.

The final positional and isotropic thermal parameters are given in Table I, and Table II gives the final anisotropic thermal parameters.

TABLE I[a]

FINAL ATOMIC POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR $C_{12}H_8OAsClOSbCl_5$

Atom	X	Y	Z	B, Å^2
Sb	−0.1585 (2)	0.6145 (1)	0.2117 (1)	
As	−0.0498 (3)	0.4331 (1)	0.1770 (2)	
Cl(1)	−0.1921 (8)	0.7262 (4)	0.2954 (5)	
Cl(2)	−0.2377 (7)	0.6777 (4)	0.0435 (4)	
Cl(3)	−0.0750 (7)	0.5433 (3)	0.3767 (4)	
Cl(4)	0.1308 (7)	0.6422 (3)	0.2691 (5)	
Cl(5)	−0.4455 (7)	0.5790 (4)	0.1507 [5)	
Cl(6)	−0.0812 (7)	0.3905 (4)	0.0235 (4)	
O(1)	0.108 (2)	0.3628 (7)	0.413 (1)	3.5 (3)
O(2)	−0.134 (2)	0.5233 (7)	0.132 (1)	3.2 (3)
C(1)	−0.161 (2)	0.371 (1)	0.235 (1)	2.4 (4)
C(2)	−0.332 (3)	0.350 (1)	0.170 (2)	3.7 (5)
C(3)	−0.406 (3)	0.304 (1)	0.220 (2)	4.4 (5)
C(4)	−0.311 (3)	0.281 (1)	0.333 (2)	3.8 (5)
C(5)	−0.146 (3)	0.301 (1)	0.394 (2)	3.3 (5)
C(6)	−0.065 (3)	0.346 (1)	0.343 (2)	2.9 (5)
C(7)	0.221 (2)	0.392 (1)	0.382 (1)	2.2 (4)
C(8)	0.393 (2)	0.388 (1)	0.464 (2)	3.3 (4)
C(9)	0.523 (3)	0.416 (1)	0.447 (2)	4.0 (5)
C(10)	0.478 (3)	0.450 (1)	0.343 (2)	5.0 (6)
C(11)	0.312 (4)	0.457 (1)	0.261 (2)	3.6 (5)
C(12)	0.176 (2)	0.429 (1)	0.282 (1)	2.3 (4)
H(1)[b]	−0.404	0.369	0.082	5.0
H(2)	−0.539	0.289	0.172	5.0
H(3)	−0.368	0.246	0.373	5.0
H(4)	−0.071	0.282	0.484	5.0
H(5)	0.425	0.362	0.544	5.0
H(6)	0.659	0.411	0.511	5.0
H(7)	0.577	0.472	0.328	5.0
H(8)	0.279	0.485	0.178	5.0

[a] The numbers in the parentheses in all tables, unless otherwise noted, are the estimated standard deviations for the last digit of the preceding parameter. [b] The hydrogen atom positions were calculated from the carbon positions, and the temperature factors were assigned the 5.0 value. These parameters were not refined.

TABLE II

ANISOTROPIC THERMAL PARAMETERS FOR $C_{12}H_8OAsClOSbCl_5$

Atom	$10^4\beta_{11}$[a]	$10^4\beta_{22}$	$10^4\beta_{33}$	$10\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Sb	125 (3)	18 (1)	59 (1)	5 (2)	36 (2)	5 (1)
As	134 (5)	18 (1)	52 (2)	0 (2)	41 (3)	1 (1)
Cl(1)	299 (18)	32 (3)	91 (6)	31 (6)	75 (9)	−1 (4)
Cl(2)	160 (13)	35 (3)	68 (5)	4 (5)	27 (7)	24 (3)
Cl(3)	215 (14)	22 (3)	54 (5)	12 (5)	49 (7)	8 (3)
Cl(4)	114 (13)	40 (4)	102 (7)	−3 (5)	37 (8)	10 (3)
Cl(5)	118 (12)	51 (4)	127 (7)	−5 (6)	63 (7)	20 (4)
Cl(6)	242 (14)	35 (3)	65 (5)	0 (6)	70 (7)	−7 (3)

Rms displacements

	Major	Intermediate	Minor
Sb	0.21	0.20	0.16
As	0.20	0.19	0.17
Cl(1)	0.32	0.26	0.19
Cl(2)	0.29	0.22	0.16
Cl(3)	0.26	0.21	0.16
Cl(4)	0.30	0.23	0.18
Cl(5)	0.34	0.25	0.17
Cl(6)	0.27	0.24	0.19

[a] The form of the thermal correction used was $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

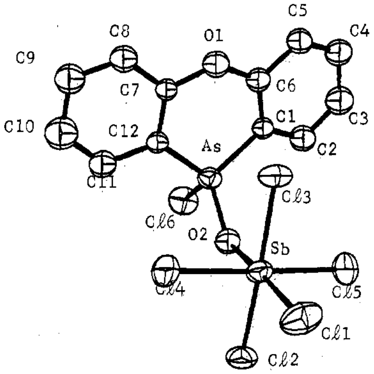

Figure 1.—ORTEP drawing of $C_{12}H_8OAsClOSbCl_5$, showing the anisotropic thermal ellipsoids.

TABLE III

BOND DISTANCES AND BOND ANGLES IN $C_{12}H_8OAsClOSbCl_5$

Bonds	Dist, Å	Angles	Deg
Sb–Cl(1)	2.343 (6)	Cl(1)–Sb–Cl(2)	91.8 (2)
Sb–Cl(2)	2.342 (7)	Cl(1)–Sb–Cl(3)	92.0 (2)
Sb–Cl(3)	2.354 (6)	Cl(1)–Sb–Cl(4)	91.7 (2)
Sb–Cl(4)	2.339 (7)	Cl(1)–Sb–Cl(5)	91.9 (2)
Sb–Cl(5)	2.344 (7)	Cl(ax)–Sb–Cl(eq) av[a]	91.8 (1)
Sb–Cl av[a]	2.34 (1)	Cl(2)–Sb–Cl(4)	90.4 (2)
Sb–O(2)	1.99 (1)	Cl(4)–Sb–Cl(3)	89.3 (2)
As–O(2)	1.73 (1)	Cl(3)–Sb–Cl(5)	90.0 (2)
As–Cl(6)	2.100 (6)	Cl(5)–Sb–Cl(2)	90.1 (2)
As–C(1)	1.86 (2)	Cl(ax)–Sb–Cl(ax) av[a]	90.0 (5)
As–C(1)	1.82 (3)	O(2)–Sb–Cl(2)	84.8 (4)
O(1)–C(6)	1.39 (3)	O(2)–Sb–Cl(3)	91.5 (4)
O(1)–C(7)	1.35 (2)	O(2)–Sb–Cl(4)	88.3 (4)
C(1)–C(2)	1.39 (3)	O(2)–Sb–Cl(5)	88.1 (4)
C(2)–C(3)	1.39 (3)	O(2)–Sb–Cl(ax) av[a]	88 (2)
		Cl(1)–Sb–O(2)	176.5 (4)
		Cl(2)–Sb–Cl(3)	176.2 (2)
		Cl(4)–Sb–Cl(5)	176.2 (2)
C(3)–C(4)	1.41 (3)	Sb–O(2)–As	132.7 (3)
C(4)–C(5)	1.34 (3)	O(2)–As–C(1)	117.2 (7)
C(5)–C(6)	1.43 (3)	O(2)–As–C(12)	116.3 (8)
C(6)–C(1)	1.37 (3)	O(2)–As–Cl(6)	98.0 (5)
C(7)–C(8)	1.39 (3)	Cl(6)–As–C(1)	111.0 (6)
C(8)–C(9)	1.36 (3)	Cl(6)–As–C(12)	110.6 (7)
C(9)–C(10)	1.41 (4)	C(6)–As–C(12)	103.8 (9)
C(10)–C(11)	1.37 (4)	C(6)–O(1)–C(7)	127 (1)
C(11)–C(12)	1.45 (3)	O(1)–C(6)–C(1)	126 (1)
C(12)–C(7)	1.38 (3)	O(1)–C(7)–C(12)	124 (1)
C–C av[a]	1.39 (3)	As–C(1)–C(6)	117 (2)
C–H (assigned)	1.09	As–C(12)–C(7)	120 (1)
		C(1)–C(2)–C(3)	117 (2)
		C(2)–C(3)–C(4)	121 (2)
		C(3)–C(4)–C(5)	121 (2)
		C(4)–C(5)–C(6)	119 (1)
		C(5)–C(6)–C(1)	119 (1)
		C(6)–C(1)–C(2)	122 (2)
		C(7)–C(8)–C(9)	123 (2)
		C(8)–C(9)–C(10)	117 (2)
		C(9)–C(10)–C(11)	123 (2)
		C(10)–C(11)–C(12)	118 (2)
		C(11)–C(12)–C(7)	118 (2)
		C(12)–C(7)–C(8)	121 (2)
		C–C–C av	120 (2)
		C–C–H (assigned)	120

[a] Average values are weighted averages, and uncertainties are rms errors.

Discussion

Tables III and IV list, and Figures 1 and 2 display, the structural parameters for the title molecule. The antimony chloride part of the molecule compares very closely to previous structures involving that group; *cf.* the structures of $POCl_3 \cdot SbCl_5$,[7] $(C_6H_5)_2SO \cdot SbCl_5$,[8]

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[7] C. I. Brandén and I. Lindquist, *Acta Chem. Scand.*, **17**, 353 (1963).

[8] I. Lindquist, "Inorganic Adduct Molecules of Oxocompounds," Springer-Verlag, West Berlin, 1963.

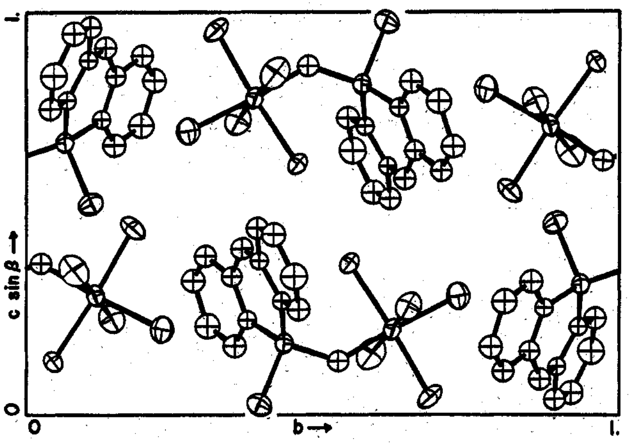

Figure 2.—View of the unit cell of $C_{12}H_8OAsClOSbCl_5$ down the *a* axis.

TABLE IV

DEVIATIONS (Å) FROM LEAST-SQUARES PLANES[a] IN $C_{12}H_8OAsClOSbCl_5$ AND DIHEDRAL ANGLES BETWEEN PLANES

	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5
As	−0.03	0.01	−0.01	0.02	
O(1)	0.02	0.00	0.00	−0.20	
C(1)	0.00				
C(2)	0.02				
C(3)	0.02				
C(4)	−0.02				
C(5)	−0.03				
C(6)	0.02				
C(7)		0.02			
C(8)		0.00			
C(9)		−0.01			
C(10)		0.01			
C(11)		0.00			
C(12)		−0.03			
O(2)			+0.01	0.09	
Sb			0.00	0.03	−0.061
Cl(1)				−0.05	
Cl(2)				−0.15	+0.016
Cl(3)				0.21	+0.016
Cl(4)					+0.014
Cl(5)					+0.014
Cl(6)				0.05	

Dihedral Angles (Deg)

	Plane 2	Plane 3	Plane 4	Plane 5
Plane 1	167.7	97.4	96.5	170.4
Plane 2		94.9	95.7	174.2
Plane 3			175.7	90.7
Plane 4				91.9

[a] Each atom whose distance to a plane is listed was used with unit weight in the calculation of that plane.

TABLE V

COMPARISON OF THE AVERAGE RING PARAMETERS OF $C_{12}H_8OAsCl$ AND $C_{12}H_8OAsClOSbCl_5$[a]

	Å				Deg			
	As–C	C–C	O–C	As–Cl	C–As–C	As–C–C	O–C–C	C–O–C
Parent	1.93 (2)	1.38 (1)	1.40 (2)	2.255 (5)	94.6 (7)	123 (3)	124 (2)	124 (1)
Adduct	1.84 (2)	1.37 (1)	1.37 (2)	2.100 (7)	103.8 (9)	119 (2)	125 (1)	127 (1)

[a] The carbon atoms in this table refer only to the four central ring carbon atoms.

$SeOCl_2 \cdot SbCl_5$,[8] $(CH_3)_2SO_2 \cdot SbCl_5$,[8] and $HCON(CH_3)_2 \cdot SbCl_5$.[9] These general features include Sb–Cl bonds which average 2.34 (1) Å, Sb–O distances which vary from 1.94 to 2.16 Å (1.99 (1) Å in the present structure), and a displacement of the antimony atom from the plane of the four equatorial chlorine atoms to the extent that the four Cl(ax)–As–Cl(eq) angles average about 92° (91.7 (2) to 92.0° (2) here). Table IV shows that in the present structure this displacement of the antimony atom from the chlorine plane is about 0.07 Å.

The As–O bond distance of 1.73 (1) Å in this structure is somewhat longer than the 1.62–1.69 Å values found for adducts of $(C_6H_5)_3AsO$.[8,10,11] In a discussion of the As–O bond lengths of $2H_3AsO_4 \cdot H_2O$, Worzala[12] has assigned a bond order of 1.0 for a 1.75-Å As–O bond length, 1.25 for a 1.69-Å bond length, and 1.5 for a 1.59-Å bond length.

There do not appear to be any special features of the relatively simple solid state packing scheme of the adducts (Figure 1). The only intermolecular contact shorter than normal nonbonding distances was a Cl(3) ···Cl(3) distance (related by $-x$, $1 - y$, $1 - z$) of 3.32 (1) Å.

With respect to the phenoxarsine portion of the adduct, Table V shows the comparison of the central ring parameters of the adduct to the corresponding distances and angles of 10-phenoxarsine chloride. This table shows that the largest structural changes are those associated with the arsenic atom. The As–C and As–Cl bonds have become shorter in the adduct (by 0.09 and 0.15 Å, respectively) as would be anticipated in considering the change from As(III) to As(V), and the C–As–C bond angle has increased from 94.6 (7)° to 103.8 (9)°. The C–O–C bond angle has increased slightly from 124 (1) to 127 (1)°. These changes, as well as the smaller decreases in the C–C and C–O distances and the increase in the As–C–C bond angles, are also consistent with an increase in the central ring π bonding. The shift toward a more planar phenoxarsine fragment (a dihedral angle increase from 156.3° in the chloride to 167.7° in the adduct) also suggests an increase in aromatic character caused by the electron-withdrawing effect of the $OSbCl_5$ group. The 167.7° value of the dihedral angle is obtained either by considering the best planes of the central ring only, or those of the two C_6H_4OAs fragments. It is interesting to note that only a small change in the CAsC and COC bond angles would be required for a completely planar phenoxarsine moiety (103.8 to 104.5° and 127 to 128.5°, respectively), since the bond angles change only slowly with the dihedral angle[13] near the planar configuration.

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[9] L. Brun and C. I. Branden, *Acta Crystallogr.*, **20**, 749 (1966).

[10] C. I. Branden, *Ark. Kemi*, **22**, 485 (1964).

[11] C. I. Branden, *Acta Chem. Scand.*, **17**, 1363 (1963).

[12] H. Worzala, *Acta Crystallogr., Sect. B*, **24**, 987 (1968).

[13] The bond angle (A) for a planar molecule and that (A') for a folded molecule are related to the dihedral angle B by $\sin (A'/2) = \sin (A/2) \cos ((180 - B)/2)$.