The Preparation and Crystal Structure of the 1 : 2 Adduct of Phosphorus Trifluoride Oxide and Antimony Pentafluoride †

Anthony J. Edwards * and Khalaf I. Khallow
Chemistry Department, University of Birmingham, P.O. Box 363, Birmingham B15 2TT

The structure of the title adduct has been determined by the heavy-atom method from 2 140 reflections, measured with a diffractometer, and refined by full-matrix least-squares methods to R 0.041. Crystals are monoclinic, space group $P2_1/c$, with unit-cell dimensions a = 7.318(2), b = 14.725(4), c = 10.377(10) Å, β = 97.73(5)°, and Z = 4. The solid adduct exists as a monomer, with a tetrahedrally co-ordinated phosphorus atom linked through a bridging oxygen atom to complete the octahedral co-ordination of one antimony atom in the Sb_2F_{10} unit.

Adducts of phosphoryl chloride (PCl_3O) with chloride acceptor molecules, such as $SbCl_5$ and $NbCl_5$, have been characterised crystallographically.[1] Corresponding adducts of phosphoryl fluoride with fluoride acceptor molecules have been investigated only using spectroscopic techniques,[2,3] and no crystallographic results have been obtained. In earlier work [4] we found that the compound prepared by the interaction of an excess of phosphoryl fluoride with antimony pentafluoride was the 1 : 1 adduct, m.p. 39 °C, and crystals of this adduct had a small rhombohedral unit cell (a = 5.70 Å, α = 96.0°), probable space group $R3m$, corresponding to one formula unit. *X*-Ray analysis showed the antimony atom to be at the origin, with the phosphorus atom in a two-fold disordered position on the three-fold symmetry axis, and a P–Sb separation of 3.51 Å. No light-atom positions could be established and were obviously disordered.

In an attempt to obtain crystallographic data for an adduct of phosphoryl fluoride, the 1 : 1 compound was treated with excess antimony pentafluoride and a very volatile compound, m.p. 28 °C, was formed. An *X*-ray crystal-structure determination has now confirmed that this product is the 1 : 2 adduct, $PF_3O{\cdot}2SbF_5$.

Experimental

Antimony pentafluoride (Ozark Mahoning) was purified by repeated vacuum distillation. Phosphoryl fluoride was prepared by the reaction of concentrated sulphuric acid with an intimate mixture of calcium fluoride and phosphorus pentoxide and purified by fractional distillation.

Preparation of the 1 : 2 *Adduct*.—Excess SbF_5 was distilled onto a sample of the 1 : 1 adduct.[4] A clear colourless solution was formed and colourless crystals readily sublimed when the excess SbF_5 was removed by pumping under vacuum. The product was volatile at room temperature and proved difficult to separate from the excess SbF_5. Samples were sublimed directly into thin-walled Pyrex capillaries attached to the evacuated apparatus and single crystals formed spontaneously on standing at room temperature. A suitable crystal was sealed in a short length of tube using a microflame.

X-*Ray Structure Analysis*.—Unit-cell and space-group data were initially investigated photographically, and intensity data and accurate cell dimensions subsequently measured with a diffractometer at room temperature (20 °C).

Crystal data. $F_{13}OPSb_2$, M = 537.6, monoclinic, a = 7.318(2), b = 14.725(4), c = 10.377(10) Å, β = 97.73(5)°, U = 1 108 Å^3, Z = 4, D_c = 3.22 g cm^3, $F(000)$ = 968, space group $P2_1/c$ (C_{2h}^5, no. 14) (from systematic absences $h0l$ when $l \neq 2n$ and $0k0$ when $k \neq 2n$), Mo-K_α radiation (λ = 0.710 7 Å, μ = 48 cm^{-1}).

Intensity data. After preliminary photographic investigations, the crystal, sealed in the capillary tube under vacuum, was mounted on an Enraf-Nonius CAD-4 diffractometer of the Crystallography Unit, Universities of Aston and Birmingham. Accurate cell dimensions and the orientation matrix were obtained by least-squares methods from the setting angles of 25 reflections, measured using graphite-monochromated Mo-K_α radiation. Intensities were measured with an ω/2θ scan, a variable scan rate, and ω scan angle of (1.00 + 0.35 tan θ)°. Within the range $2 < 2\theta < 55°$, 2 140 independent reflections having $I > 2.5\sigma(I)$ were considered observed. Two standard reflections were measured every hour and showed no variation with time. Data were corrected for Lorentz and polarisation factors but not for absorption.

Structure determination. The structure was solved by conventional Patterson–Fourier techniques. Scattering factors used were those for neutral atoms.[5] Refinement by full-matrix least-squares methods was carried out initially with unit weights and with all atoms vibrating isotropically. All light atoms were assigned fluorine scattering factors, until the geometry was established, when the bridging atom between phosphorus and antimony was assigned as oxygen, as discussed below.

After this refinement was complete (R 0.106) anisotropic thermal parameters were introduced for all atoms and R was reduced to a final value of 0.041. In the final stages of refinement weights derived from counting statistics were found appropriate, giving a satisfactory analysis of the variation of $w\Delta^2$ with increasing sinθ/λ and with increasing fractions of $|F_o|$. Final parameter shifts were $<0.1\sigma$, the final R was 0.041 and $R'\{= [\Sigma w(|F_o| - |F_c|)^2]^{\frac{1}{2}}\}$ 0.040. Calculations were carried out on an ICL 1906A computer at Birmingham University Computer Centre and on a CDC 7600 computer at the University of Manchester Regional Computer Centre using the program [6] SHELX 76. Final positional parameters with their estimated standard deviations are listed in Table 1, and interatomic distances and angles in Table 2.

Discussion

The atomic arrangement is shown in the Figure. The structure consists of monomer units, $PF_3O{\cdot}2SbF_5$. The two antimony atoms have octahedral co-ordination and are linked by a bridging fluorine atom. The phosphorus atom has a tetrahedral arrangement of three terminal fluorine atoms and a

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† *Supplementary data available* (No. SUP 56013, 3 pp.): anisotropic thermal parameters, non-bonded interactions. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Final atomic positional parameters with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb(1)	0.216 81(6)	0.436 78(3)	0.210 20(5)
Sb(2)	−0.136 15(5)	0.256 36(3)	0.040 67(4)
P	0.237 3(2)	0.129 8(1)	0.162 8(2)
O	0.065 1(6)	0.180 5(3)	0.140 0(5)
F(1)	0.028 3(6)	0.274 8(3)	−0.075 9(4)
F(2)	−0.009 3(6)	0.358 8(3)	0.139 8(4)
F(3)	0.136 0(8)	0.416 4(4)	0.369 5(5)
F(4)	0.416 4(7)	0.504 3(4)	0.279 0(6)
F(5)	0.336 3(7)	0.327 4(4)	0.226 5(8)
F(6)	0.257 6(10)	0.448 4(4)	0.041 1(6)
F(7)	0.378 9(5)	0.160 7(3)	0.084 0(4)
F(8)	0.213 6(6)	0.031 7(3)	0.133 2(5)
F(9)	0.321 0(7)	0.134 9(4)	0.299 2(4)
F(10)	−0.236 4(7)	0.153 5(3)	−0.038 5(5)
F(11)	−0.255 3(6)	0.241 7(4)	0.184 4(5)
F(12)	−0.308 1(7)	0.336 2(3)	−0.037 7(5)
F(13)	0.055 3(7)	0.532 3(3)	0.188 2(5)

Table 2. Selected distances (Å) and angles (°) with estimated standard deviations in parentheses

P–O	1.456(4)	P–F(8)	1.482(4)
P–F(7)	1.475(4)	P–F(9)	1.467(4)
Sb(2)–O	2.018(4)	Sb(2)–F(1)	1.838(4)
Sb(2)–F(2)	1.985(4)	Sb(2)–F(10)	1.829(4)
Sb(2)–F(11)	1.839(5)	Sb(2)–F(12)	1.831(4)
Sb(1)–F(2)	2.065(4)	Sb(1)–F(3)	1.854(5)
Sb(1)–F(4)	1.831(5)	Sb(1)–F(5)	1.830(5)
Sb(1)–F(6)	1.827(6)	Sb(1)–F(13)	1.832(5)
O–P–F(7)	114.2(3)	O–P–F(8)	113.0(3)
O–P–F(9)	111.7(3)	F(7)–P–F(8)	104.9(3)
F(7)–P–F(9)	106.6(3)	F(8)–P–F(9)	105.7(3)
O–Sb(2)–F(1)	85.4(2)	O–Sb(2)–F(2)	84.2(2)
O–Sb(2)–F(11)	85.1(2)	O–Sb(2)–F(10)	89.5(2)
F(1)–Sb(2)–F(12)	94.8(2)	F(2)–Sb(2)–F(12)	89.3(2)
F(10)–Sb(2)–F(12)	97.0(2)	F(11)–Sb(2)–F(12)	93.6(2)
F(1)–Sb(2)–F(2)	85.8(2)	F(2)–Sb(2)–F(11)	84.8(2)
F(11)–Sb(2)–F(10)	93.6(2)	F(10)–Sb(2)–F(1)	94.9(2)
F(2)–Sb(1)–F(3)	83.6(2)	F(2)–Sb(1)–F(5)	83.9(2)
F(2)–Sb(1)–F(6)	86.5(2)	F(2)–Sb(1)–F(13)	84.8(2)
F(4)–Sb(1)–F(3)	94.2(3)	F(4)–Sb(1)–F(5)	95.5(3)
F(4)–Sb(1)–F(6)	95.7(3)	F(4)–Sb(1)–F(13)	95.7(3)
F(3)–Sb(1)–F(5)	88.9(2)	F(5)–Sb(1)–F(6)	91.9(3)
F(6)–Sb(1)–F(13)	89.7(3)	F(13)–Sb(1)–F(3)	87.6(3)
P–O–Sb(2)	157.4(3)	Sb(2)–F(2)–Sb(1)	154.5(2)

bridging oxygen atom which completes the octahedral co-ordination of Sb(2).

The assignment of the oxygen atom to the bridging position has been made from the geometry of the system, since oxygen and fluorine could not be distinguished by *X*-ray means. Thus the Sb–O–P unit in the present adduct can be compared with that [1] in $PCl_3O\cdot SbCl_5$. The P–O and Sb–O bond distances are 1.456 and 2.018 Å in $PF_3O\cdot 2SbF_5$ compared to 1.47 and 2.17 Å in $PCl_3O\cdot SbCl_5$, thus providing good evidence for the designation of the bridging atom as oxygen. The bridge angle of 157.4° in the fluoride is larger than that of 145° in the chloride. This assignment is in agreement with previous Raman spectral studies [2,3] of molten $PF_3O\cdot SbF_5$ and $PF_3O\cdot AsF_5$, which showed a lowering of the P–O stretching frequency in the adducts compared with that for pure PF_3O. The bridging oxygen formulation is also supported by the P–O(bridge) distance of 1.456 Å being smaller than the P–F(terminal) distances, which average 1.475 Å.

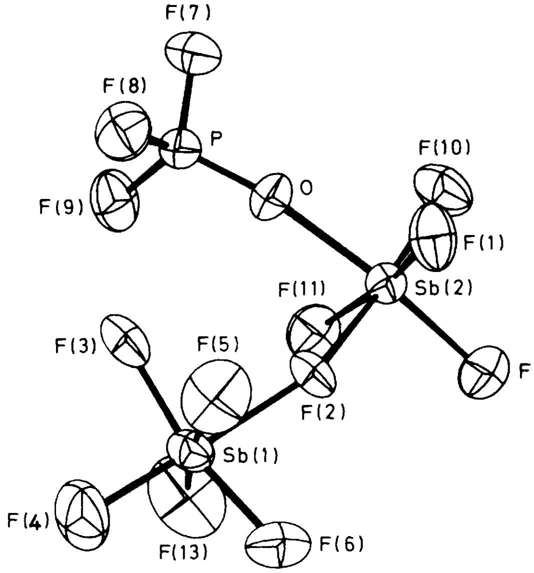

Figure. The molecular structure of $PF_3O\cdot 2SbF_5$ showing the atom numbering, with 50% thermal ellipsoids

The geometry of the PF_3O unit in the adduct can be compared with that of the gaseous PF_3O molecule,[7] determined by electron diffraction. The P–F distance of 1.475 Å in the adduct is less than that of 1.524 Å in the molecule, whereas the P–O distance is longer in the adduct (1.456 Å) than in the molecule (1.435 Å). This presumably can be rationalised in terms of the bridging through oxygen weakening the P–O bond, moving the oxygen atom further from phosphorus, and allowing the fluorine atoms to approach phosphorus more closely. The increase in the F–P–F angle in the adduct, compared with the molecule, from 101.3 to 105.7°, and the concurrent decrease of F–P–O from 116.8 to 112.9° is a consequence of the changes in the bond distances. In terms of valence-shell electron-pair repulsion theory, the multiple bonding to oxygen has a greater repulsive effect and results in F–P–O being larger than F–P–F.

The O–Sb(2) bridge distance of 2.018 Å is comparable with the values for the symmetric bridges in the $[Sb_2F_{10}O]^{2-}$ (1.91 Å)[8] and $[Sb_3F_{12}O_3]^{3-}$ (1.92 Å)[9] ions and thus the adduct appears to be strongly bridged, although the P–O link may still retain some multiple bond character. Chen and Passmore[3] have suggested that the base strength of PF_3O is greater than that of SO_2 and our results, compared with the crystallographic results [10] on the adduct $SO_2\cdot SbF_5$ confirm this order. Thus, the Sb–O bond distance in the PF_3O adduct is 2.018 Å compared with 2.13 Å in the SO_2 adduct, and presumably represents a stronger interaction. The Sb(2)–O(bridge) (2.018 Å) and Sb(2)–F(bridge) (1.985 Å) bonds are in *cis* positions in the octahedral co-ordination of Sb(2), with the four terminal fluorine atoms at an average distance of 1.834 Å. The octahedral co-ordination is distorted, due to the longer bonds, with angles less than 90° between O and F(2) and the terminal fluorine atoms (average 86.6°) and angles greater than 90° between the terminal fluorine atoms themselves (average 94.8°).

In the linked SbF_6 octahedron the Sb(1)–F(2)(bridge) distance of 2.065 Å is longer than the terminal Sb–F distances which average 1.835 Å. The octahedron is again distorted, due to the single longer bond, with angles between the bridge bond and the four fluorine atoms *cis* to it less than 90° (average 84.7°) while angles between the opposite fluorine atom [F(4)] and the four *cis* fluorine atoms are greater than 90° (average 95.3°). The angles between the four *cis* fluorine atoms themselves are close to 90° (average 89.5°).

The difference in the Sb–F(bridge) distances (2.065 and 1.985 Å) at 0.08 Å is significant and the shorter bridge distance to Sb(2) may be a consequence of the attached PF_3O. The asymmetry in the bridge is similar to, but smaller than that in the $[Sb_3F_{16}]^-$ ion,[11] where the Sb–F(bridge) distances are 2.10 and 1.97 Å, and suggests that there is some contribution to the structure from a formulation as the solvated 1 : 1 adduct $F_3P{-}O{-}SbF_5{\cdot}SbF_5$.

The P–Sb distance (3.408 Å) in the 2 : 1 adduct is sufficiently close to that of 3.51 Å in the disordered structure of the 1 : 1 adduct for a similar oxygen bridged arrangement to be postulated in the 1 : 1 compound. The increase could arise from a larger P–O–Sb angle.

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