Fluoride Crystal Structures. Part XXV.[1] Trifluorobis(4-methoxypyridine *N*-oxide)antimony(III) Hydrate

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The structure of the title compound has been determined by the heavy-atom method from 1 265 reflections, measured with a diffractometer, and refined by full-matrix least-squares methods to *R* 0.042. Crystals are orthorhombic, space group *Pnma*, a = 14.91(2), b = 16.38(2), c = 6.52(1) Å, Z = 4. In the discrete molecules of the complex the antimony atom lies 0.29 Å below the basal plane of a distorted square pyramid. The apical Sb–F distance [1.905(5) Å] is shorter than the basal Sb–F distances [1.968(6) Å]; basal Sb–O(ligand) distances are 2.305(5) Å. There is only weak hydrogen bonding involving the water molecule of crystallisation.

ALTHOUGH the acceptor character of antimony trifluoride is well established, with the fluoride ion as donor, in the formation of the anions SbF_4^- (ref. 2), SbF_5^{2-} (ref. 3), $Sb_2F_7^-$ (ref. 4), and $Sb_2F_9^{3-}$ (ref. 5), there is only one report[6] of the characterisation of a neutral complex, $SbF_3[(C_6H_5)_3PO]_2$. We have prepared a series of such complexes with various donor molecules and we describe here the crystallographic structure determination of one of them.

EXPERIMENTAL

Air-stable colourless single crystals were obtained by recrystallisation from ethanol (Found: C, 32.2; H, 3.55; F, 13.1; N, 6.2; Sb, 27.5. $C_{12}H_{16}F_3N_2O_5Sb$ requires C, 32.24; H, 3.60; F, 12.75; N, 6.26; Sb, 27.24%). Unit-cell and space group data were obtained photographically and intensity data with a diffractometer.

Crystal Data.—$C_{12}H_{16}F_3N_2O_5Sb$, $M = 447$, Orthorhombic, $a = 14.91(2)$, $b = 16.38(2)$, $c = 6.52(1)$ Å, $U = 1\,592$ Å^3, $D_m = 1.90$, $Z = 4$, $D_c = 1.86$, $F(000) = 880$. Space group *Pnma* (D_{2h}^{1}, No. 62) or $Pn2_1a$ (C_{2v}^{9}, No. 33) from systematic absences: $0kl$ when $k + l \neq 2n$ and $hk0$ when $h \neq 2n$, the former confirmed by the successful structure refinement. Mo-K_α radiation ($\lambda = 0.7107$ Å; $\mu = 18$ cm^{-1}). Single-crystal precession and Weissenberg photographs and diffractometer data.

TABLE 1

Atomic positional and thermal parameters (×10³), with least-squares estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb	0.607 31(4)	$\frac{1}{4}$	0.401 91(8)	39.8(4)	39.7(4)	39.7(3)	0	−2.8(2)	0
F(1)	0.5104(3)	0.3314(4)	0.3893(6)	70(3)	80(3)	79(3)	31(3)	−8(2)	18(3)
F(2)	0.5832(4)	$\frac{1}{4}$	0.6888(7)	57(3)	46(3)	42(2)	0	4(2)	0
O(1)	0.6979(3)	0.3567(3)	0.5030(6)	58(3)	48(3)	48(2)	−12(2)	5(2)	−9(2)
O(2)	0.6145(3)	0.5516(3)	1.1505(6)	60(3)	48(3)	43(2)	3(2)	−2(2)	−0.4(20)
O(3)	0.3276(7)	$\frac{1}{4}$	0.3879(15)	86(7)	107(8)	114(7)	0	37(6)	0
N	0.6735(4)	0.4046(3)	0.6631(7)	45(3)	35(3)	44(2)	−10(2)	0(2)	3(2)
C(1)	0.7007(4)	0.3844(4)	0.8524(9)	44(4)	46(4)	47(3)	2(3)	−9(2)	4(2)
C(2)	0.6791(4)	0.4344(4)	1.0160(9)	47(3)	49(4)	44(3)	−6(3)	−6(3)	6(3)
C(3)	0.6312(4)	0.5055(4)	0.9831(9)	38(3)	36(3)	42(3)	−7(3)	−5(2)	6(2)
C(4)	0.6030(4)	0.5259(4)	0.7852(9)	50(4)	47(4)	46(3)	−9(3)	0(2)	5(3)
C(5)	0.6257(4)	0.4726(4)	0.6266(8)	48(4)	40(3)	41(2)	−8(3)	−3(2)	4(2)
C(6)	0.5735(6)	0.6305(5)	1.1238(12)	64(5)	48(4)	77(4)	6(4)	4(4)	−13(4)

Structure Determination.—Intensity data were collected about the c axis (layers $hk0$—7) with a Stoe two-circle computer-controlled diffractometer as previously described.[7] Within the range $0.1 < \sin\theta/\lambda \leqslant 0.65$ 1 265 independent reflections having $I > 3\sigma(I)$ were observed. Data were corrected for Lorentz and polarisation factors but not for absorption.

The structure was solved by conventional Patterson–Fourier techniques. Scattering factors used were those for neutral atoms,[8] with corrections for the effects of anomalous dispersion[9] applied to those for antimony. Initial refinement by full-matrix least-squares methods was with layer scale factors refined separately, and all atoms vibrating isotropically. Refinement was continued with the layer scale factors held constant[10] and with the introduction of anisotropic thermal parameters, for all atoms, of the form $\exp[-2\pi^2 \; (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. In the final stages of refinement the weighting scheme[11] $w = [\sigma^2(F_o) + (0.04|F_o|)^2]^{-1}$ was found appropriate, giving a satisfactory analysis of the variation of $w\Delta^2$ with increasing $\sin\theta/\lambda$ and with increasing fractions of $|F_o|$. At convergence no parameter

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[1] Part XXIV, A. J. Edwards and P. Taylor, *J.C.S. Dalton*, 1975, 2174.

[2] S. H. Mastin and R. R. Ryan, *Inorg. Chem.*, 1971, **10**, 1757.

[3] R. R. Ryan and D. T. Cromer, *Inorg. Chem.*, 1972, **11**, 2322.

[4] R. R. Ryan, S. H. Mastin, and A. C. Larson, *Inorg. Chem.*, 1971, **10**, 2793.

[5] D. R. Schroeder and R. A. Jacobson, *Inorg. Chem.*, 1973, **12**, 515.

[6] W. Hewertson, 1970, GP 1,960,732.

[7] J. C. Dewan, A. J. Edwards, D. R. Slim, J. E. Guerchais, and R. Kergoat, *J.C.S. Dalton*, 1975, 2171.

[8] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[9] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[10] E. C. Lingafelter and J. Donohue, *Acta Cryst.*, 1966, **20**, 321.

[11] G. H. Stout and L. H. Jensen, '*X*-Ray Structure Determination,' Macmillan, London, 1969, p. 456.

shift was $>0.001\sigma$ and a final difference-Fourier map showed no significant features. The final R was 0.042 and R' $\{=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ was 0.058. Hydrogen atoms could not be located.

Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21452 (5 pp., 1 microfiche), * the final positional parameters and anisotropic temperature factors, with their estimated standard deviations in Table 1, and interatomic distances and angles in Table 2.

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Intramolecular distances

Sb–F(1)	1.968(6)	C(3)–O(2)	1.351(8)
Sb–F(2)	1.905(5)	C(4)–C(5)	1.395(9)
Sb–O(1)	2.305(5)	C(6)–O(2)	1.439(10)
N–O(1)	1.356(7)	F(1) ··· F(1^{I})	2.667(9)
N–C(1)	1.341(8)	F(1) ··· O(1)	2.922(8)
N–C(5)	1.344(9)	F(1) ··· F(2)	2.602(7)
C(1)–C(2)	1.383(9)	F(2) ··· O(1)	2.729(6)
C(2)–C(3)	1.382(9)	O(1) ··· O(1^{I})	3.495(8)
C(3)–C(4)	1.398(8)		

(*b*) Angles

F(1)–Sb–F(2)	84.4(2)	C(1)–N–C(5)	121.9(5)
F(1)–Sb–O(1)	85.9(2)	N–C(1)–C(2)	119.6(6)
F(1)–Sb–F(1^{I})	85.3(2)	C(1)–C(2)–C(3)	120.0(5)
F(1)–Sb–O(1^{I})	162.9(2)	C(2)–C(3)–C(4)	120.0(6)
F(2)–Sb–O(1)	80.2(2)	C(2)–C(3)–O(2)	116.2(5)
O(1)–Sb–O(1^{I})	98.6(2)	C(4)–C(3)–O(2)	123.8(6)
Sb–O(1)–N	120.1(4)	C(3)–C(4)–C(5)	117.5(6)
O(1)–N–C(1)	119.0(5)	C(4)–C(5)–N	121.1(5)
O(1)–N–C(5)	119.1(4)	C(3)–O(2)–C(6)	118.9(5)

(*c*) Intermolecular contacts <3.5 Å

O(3) ··· C(1^{II})	3.36(1)	O(1) ··· C(3^{VI})	3.407(8)
O(3) ··· F(1)	3.03(1)	O(2) ··· C(5^{VII})	3.368(8)
F(1) ··· C(6^{III})	3.47(1)	O(2) ··· N^{VIII}	3.243(8)
F(1) ··· C(4^{IV})	3.101(9)	O(2) ··· C(1^{VIII})	3.228(9)
F(2) ··· C(6^{III})	3.28(1)	N ··· C(3^{VI})	3.468(9)
O(1) ··· C(2^{V})	3.433(9)	C(2) ··· C(5^{VIII})	3.36(1)
O(1) ··· O(2^{VI})	3.318(7)		

Roman numeral superscripts refer to atoms in the following equivalent positions:

I	$x, \frac{1}{2}-y, z$	V	$x, y, -1+z$
II	$-\frac{1}{2}+x, \frac{1}{2}-y, \frac{3}{2}-z$	VI	$\frac{3}{2}-x, 1-y, -\frac{1}{2}+z$
III	$1-x, 1-y, 2-z$	VII	$x, y, 1+z$
IV	$1-x, 1-y, 1-z$	VIII	$\frac{3}{2}-x, 1-y, \frac{1}{2}+z$

DISCUSSION

The structure consists of discrete molecules of the complex (Figure 1) and water molecules of crystallisation in a 1 : 1 ratio, as shown in Figure 2. The closest contact to the water molecule is F(1) ··· O(3) of 3.03 Å, which is long for a hydrogen bond and must represent only a weak interaction between the molecules. However, F(1) and F(1^{I}), related by the mirror plane at $y=\frac{1}{4}$, are stereochemically positioned to interact with the two hydrogen atoms of the water molecule. The antimony atom, the apical fluorine atom F(2), and the oxygen atom of the water molecule O(3) lie on the mirror plane, with the five nearest-neighbour atoms to antimony in a distorted square-pyramidal arrangement. This stereochemistry can be described on VSEPR theory [12] as being derived from an octahedron, with one position occupied by the non-bonding electron pair.

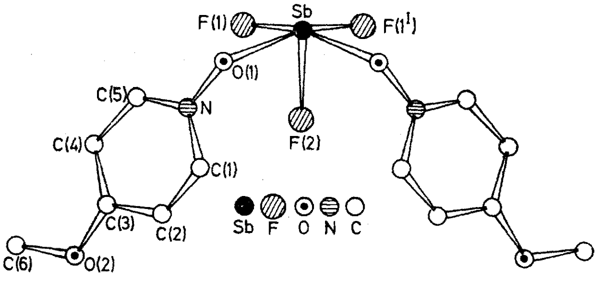

FIGURE 1 Projection of the molecule down [100]; the water molecule of crystallisation is not shown

Although the distortion in the square-pyramidal arrangement is partly due to the difference in the basal bond lengths to fluorine, and to oxygen (ligand), there are features in common with other antimony(III) fluoride compounds with the same arrangement. Thus the antimony atom lies 0.29 Å below the basal plane of the square pyramid, and the corresponding displacements are 0.382 Å in SbF_5^{2-} [in $(NH_4)_2SbF_5$][3] and 0.36 Å in $Sb_2F_9^{3-}$ [in the $Co(NH_3)_6^{3+}$ salt].[5] The Sb–F(apical) distance in the present case is 0.06 Å less than the Sb–F(basal) distance, and the differences for SbF_5^{2-} and $Sb_2F_9^{3-}$ are 0.16 and 0.11 Å, with a shortening of the bond opposite to the non-bonding electron pair.[12]

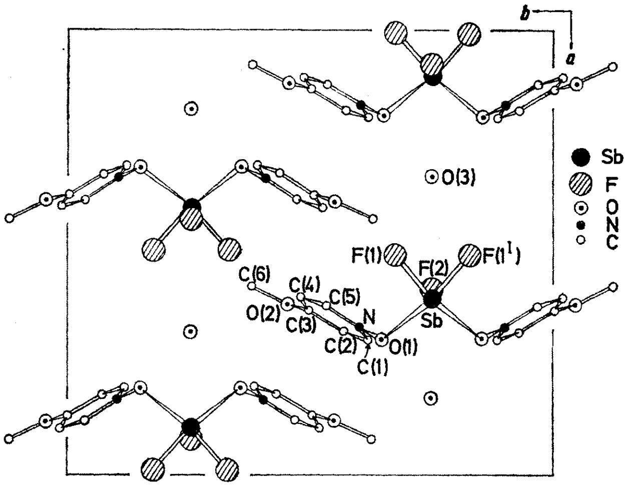

FIGURE 2 Projection of the structure down [001]. O(3) represents the oxygen atom of the water molecules of crystallisation

These effects are also observed for the structurally

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full-size copies).

[12] R. J. Gillespie, *J. Chem. Soc.*, 1963, 4672.

similar chloro-compound,[13] $SbCl_3(aniline)_2$, where the displacement below the plane is 0.25 Å and the difference in bond distance is 0.14 Å.

The structure of the complex can be usefully compared with that of SbF_3.[14] The trifluoride itself has a greatly distorted octahedral arrangement of fluorine atoms around antimony with three short Sb–F distances (1.92 Å) and mean F–Sb–F angle 87.3°, and three long distances of 2.61 Å. This structure can be described on VSEPR theory as being based on a distorted tetrahedral arrangement of three fluorine atoms and the non-bonding pair of electrons, with the three long contacts grouped around the non-bonding pair position, to give an overall, distorted, seven co-ordinate, monocapped octahedral geometry. The non-bonding electron pair is symmetrically placed with respect to the three equal Sb–F bonds. In the complex, the mean F–Sb–F angle of 84.7° is similar, but the bond distances are now different, with the bond opposite to the non-bonding pair position shorter than those in the neutral molecule.

The geometry of the ligand is normal. The pyridine ring is planar [plane (ii) Table 3] and O(1) lies 0.06 Å out of this plane, a similar distance to those reported previously for the pyridine *N*-oxide ligand.[15] The oxygen atom of the methoxy-group, O(2), is slightly displaced from the plane, on the same side as O(1). The Sb–O–N angle (120.1°), and the dihedral angle (89.3°) between the pyridine ring and the Sb, O(1), N plane [plane (iii) Table 3], are similar to corresponding angles in other complexes containing pyridine *N*-oxide co-ordinated to a metal.[16,17] The bonding in this system has been discussed in detail elsewhere.[17]

TABLE 3

Equations of least-squares planes in the form $Ax + By + Cz = D$, where x,y,z are the fractional co-ordinates of the defining atoms (italicised) in the direct cell. Atomic distances (Å) from each plane are in square brackets

	A	*B*	*C*	*D*	σ
Plane (i):	−3.82	0.0	6.30	0.50	—
[*F(1)*, *F(1^I)*, *O(1)*, *O(1^I)*, Sb −0.29, F(2) 1.61, N 1.10]					
Plane (ii):	12.68	8.30	−0.93	11.27	0.005
[*C(1)* 0.004, *C(2)* −0.008, *C(3)* 0.005, *C(4)* 0.001, *C(5)* −0.005, *N* 0.002, O(1) 0.06, O(2) 0.02, C(6) 0.18, Sb −1.88]					
Plane (iii):	−7.21	10.00	−4.09	−3.52	—
[*Sb*, *O(1)*, *N*, C(3) 0.004, O(2) −0.10, C(6) 1.09]					

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[13] R. Hulme, D. Mullen, and J. C. Scruton, *Acta Cryst.*, 1969, **A25**, S171.

[14] A. J. Edwards, *J. Chem. Soc.* (*A*), 1970, 2751.

[15] W. D. Horrocks, D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 1968, **7**, 1552, and refs. therein.

[16] D. L. Kepert, D. Taylor, and A. H. White, *J.C.S. Dalton*, 1973, 392.

[17] E. A. Blom, B. R. Penfold, and W. T. Robinson, *J. Chem. Soc.* (*A*), 1969, 913, and refs. therein.

[18] '*X*-Ray' System, Technical Report TR 192 of the Computer Science Centre, University of Maryland, June 1972.