Fluoride Crystal Structures. Part 32.[1] Triantimony Nonachloride Tetrafluoride Oxide

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The title compound has been prepared as a minor component in the reaction of chlorine with antimony trifluoride. Its structure has been determined from *X*-ray diffractometer data and refined by full-matrix least-squares methods to *R* 0.067 for 3 379 reflections. Crystals are triclinic, space group $P\bar{1}$, $a = 9.79$, $b = 13.24$, $c = 6.94$ Å, $\alpha = 93.1$, $\beta = 105.3$, $\gamma = 91.1°$. In the structure each antimony atom has octahedral co-ordination, two with three terminal chlorine atoms, two bridging fluorine atoms, and a bridging oxygen atom, and the third with three terminal chlorine atoms and two bridging and one terminal fluorine atoms. Two antimony atoms are linked together by a double bridge, consisting of an oxygen and a fluorine atom, and are also linked to the third antimony atom by single fluorine bridges.

MIXED chloride fluorides of antimony have been shown by *X*-ray crystallography to have a variety of structures. Both antimony tetrachloride fluoride[2] and antimony trichloride difluoride[3] have a tetrameric arrangement, with approximately linear fluorine bridges, similar to the pentafluorides of niobium, tantalum, molybdenum, and tungsten.[4] The compound ' $SbCl_2F_3$ ', however, is best described[5] in terms of the ions $[SbCl_4]^+$ and $[Sb_2Cl_2F_9]^-$ and the related compound[6] $Sb_3Cl_4F_{11}$ also contains the $[SbCl_4]^+$ cation and the $[Sb_2F_{11}]^-$ anion. A different, trimeric, arrangement has recently been reported for the compound[7] $Sb_3Cl_{11}F_4$, with three single fluorine bridges linking the antimony atoms. The compound was prepared by the interaction of SbF_5 and $SbCl_5$ in SO_2 solution, followed by vacuum sublimation.

In an attempt to prepare a sample of $SbCl_2F_3$ by the published method,[8] we sublimed crystals from the product of the reaction of chlorine with SbF_3 and determined the structure of one crystal obtained. The structure analysis here reported showed that the compound is also trimeric, with a structure closely related to that of $Sb_3Cl_{11}F_4$, but corresponding to $Sb_3Cl_9F_4O$ which can be considered as an initial reaction product of the trimeric chloride fluoride.

EXPERIMENTAL

Antimony trifluoride (B.D.H.) was recrystallised from 40% aqueous hydrofluoric acid and stored in a desiccator over phosphorus pentaoxide. Chlorine (I.C.I.) was dried by passing over P_4O_{10} and was passed over SbF_3 in a Pyrex glass apparatus. On gentle heating, reaction occurred to produce a solid product melting at *ca.* 60 °C. Samples of this product were sealed in Pyrex glass capillaries *in vacuo* and crystals were grown by sublimation in a temperature gradient. Only one single crystal suitable for *X*-ray examination was found.

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[1] Part 31, A. J. Edwards, D. R. Slim, J. E. Guerchais, and R. Kergoat, *J.C.S. Dalton*, preceding paper.

[2] H. Preiss, *Z. Chem.*, 1966, **6**, 350.

[3] J. G. Ballard, T. Birchall, and D. R. Slim, *J.C.S. Chem. Comm.*, 1976, 653.

[4] A. J. Edwards, *J. Chem. Soc.* (*A*), 1969, 909 and refs. therein.

[5] H. Preiss, *Z. anorg. Chem.*, 1972, **389**, 254.

[6] H. B. Miller, H. W. Baird, C. L. Bramlett, and W. K. Templeton, *J.C.S. Chem. Comm.*, 1972, 262.

[7] J. G. Ballard, T. Birchall, and D. R. Slim, *Canad. J. Chem.*, 1977, **55**, 743.

[8] L. Kolditz and W. von der Lieth, *Z. anorg. Chem.*, 1961, **310**, 236.

Unit-cell and space-group data were obtained photographically and intensity data with a diffractometer.

Crystal Data.—$Cl_9F_4OSb_3$, $M = 776$, Triclinic, $a = 9.79(2)$, $b = 13.24(3)$, $c = 6.94(2)$ Å, $\alpha = 93.1(4)$, $\beta = 105.3(4)$, $\gamma = 91.1(4)°$, $U = 873$ Å^3, $Z = 2$, $D_c = 2.96$ g cm^{-3}, $F(000) = 700$. Space group $P\bar{1}$ (C_i^1 no. 2). Mo-K_α radiation (λ 0.7107 Å, μ 60.4 cm^{-1}).

Structure Determination.—Intensity data were collected about the *c* axis (layers *hk*0—6) with a Stoe two-circle computer-controlled diffractometer as described previously.[9] Within the range $0.1 < (\sin \theta)/\lambda \leqslant 0.70$, 3 379 independent reflections having $I > 3\sigma(I)$ were observed. Data were corrected for Lorentz and polarisation factors but not for absorption. Although the absorption factor is rather high, and the crystal was large (dimensions *ca.* 0.5 mm), it was found impossible to define crystal faces accurately enough to apply a satisfactory absorption correction, particularly as a considerable part of the crystal was in contact with the curved surface of the capillary tube. However, the block shape of the crystal should minimise any absorption errors.

The structure was solved by conventional Patterson–Fourier techniques. Scattering factors used were those for neutral atoms[10] with all the light atoms assigned those of fluorine. Corrections were applied to those of antimony for the effects of anomalous dispersion.[11] Refinement was carried out on the positional and isotropic temperature parameters and layer scale factors by full-matrix least-squares methods, minimising the function $\Sigma w(|F_o|-|F_c|)^2$, initially with unit weights and using only the first three layers of data to reduce computing time.

TABLE 1

Final atomic positional parameters with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Sb(1)	−0.266 7(1)	0.101 8(1)	−0.193 9(2)
Sb(2)	−0.360 4(1)	0.307 6(1)	−0.401 2(2)
Sb(3)	0.059 4(1)	0.287 1(1)	−0.196 7(2)
Cl(1)	−0.363 4(6)	0.463 2(4)	−0.259 1(8)
Cl(2)	−0.489 5(4)	0.037 3(4)	−0.241 8(7)
Cl(3)	0.149 6(6)	0.428 0(4)	−0.296 4(9)
Cl(4)	−0.190 5(5)	0.084 4(4)	0.140 6(7)
Cl(5)	−0.175 1(5)	−0.032 2(4)	−0.327 5(7)
Cl(6)	−0.595 5(4)	0.269 5(4)	−0.496 9(7)
Cl(7)	0.260 1(5)	0.204 5(4)	−0.062 2(9)
Cl(8)	0.033 0(6)	0.355 7(4)	0.098 2(8)
Cl(9)	−0.343 2(6)	0.346 5(4)	−0.715 7(7)
F(1)	0.035 2(10)	0.218 3(7)	−0.457 3(14)
F(2)	−0.062 6(10)	0.170 0(7)	−0.153 5(14)
F(3)	−0.140 0(11)	0.334 5(7)	−0.322 0(15)
O,F(1)	−0.307 9(10)	0.164 1(7)	−0.459 6(15)
O,F(2)	−0.315 9(11)	0.246 4(8)	−0.146 4(15)

For the final cycles of refinement with all the data included, the layer scale factors were held constant and anisotropic thermal parameters, for all the atoms, of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$ were introduced. In the final stages of refinement, weights derived from the counting statistics were found appropriate, giving a satisfactory analysis of the variation of $\omega\Delta^2$ with increasing $(\sin \theta)/\lambda$ and with increasing fractions of $|F_o|$. Final parameter shifts were $<0.3\sigma$ and the final R was 0.067.

Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22091 (23 pp.)* and the final positional parameters, with their estimated standard deviations, are in Table 1. Interatomic distances and angles are given in Table 2.

TABLE 2

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

(*a*) Distances			
Sb(1)–Cl(2)	2.261(4)	Sb(2)–Cl(1)	2.265(4)
Sb(1)–Cl(4)	2.269(4)	Sb(2)–Cl(6)	2.259(4)
Sb(1)–Cl(5)	2.266(4)	Sb(2)–Cl(9)	2.256(4)
Sb(1)–F(2)	2.120(8)	Sb(2)–F(3)	2.100(9)
Sb(1)–O,F(1)	2.007(9)	Sb(2)–O,F(1)	2.013(9)
Sb(1)–O,F(2)	2.014(9)	Sb(2)–O,F(2)	1.988(9)
Sb(3)–Cl(3)	2.267(4)	Sb(3)–F(1)	1.935(9)
Sb(3)–Cl(7)	2.270(4)	Sb(3)–F(2)	2.023(9)
Sb(3)–Cl(8)	2.273(5)	Sb(3)–F(3)	2.042(9)
O,F(1) · · · O,F(2)	2.40(1)	O,F(1) · · · F(2)	2.75(1)
O,F(1) · · · F(3)	2.74(1)	O,F(2) · · · F(2)	2.71(1)
O,F(2) · · · F(3)	2.65(1)	F(2) · · · F(3)	2.56(1)
F(1) · · · F(2)	2.64(1)	F(1) · · · F(3)	2.64(1)
(*b*) Angles			
Cl(2)–Sb(1)–Cl(4)	97.8(2)	Cl(6)–Sb(2)–Cl(9)	97.3(2)
Cl(2)–Sb(1)–Cl(5)	98.1(2)	Cl(1)–Sb(2)–Cl(6)	98.8(2)
Cl(4)–Sb(1)–Cl(5)	103.5(2)	Cl(1)–Sb(2)–Sl(9)	101.6(2)
O,F(1)–Sb(1)–O,F(2)	73.2(4)	O,F(1)–Sb(2)–O,F(2)	73.7(4)
O,F(1)–Sb(1)–F(2)	83.6(3)	O,F(1)–Sb(2)–F(3)	83.5(4)
O,F(2)–Sb(1)–F(2)	81.8(4)	O,F(2)–Sb(2)–F(3)	80.6(4)
Cl(2)–Sb(1)–O,F(1)	94.4(3)	Cl(6)–Sb(2)–O,F(1)	93.7(3)
Cl(2)–Sb(1)–O,F(2)	95.3(3)	Cl(6)–Sb(2)–O,F(2)	96.7(3)
Cl(4)–Sb(1)–O,F(1)	105.1(7)	Cl)9)–Sb(2)–O,F(2)	101.1(7)
Cl(4)–Sb(1)–F(2)	83.6(3)	Cl(9)–Sb(2)–O,F(1)	90.9(3)
Cl(5)–Sb(1)–O,F(2)	81.8(4)	Cl(1)–Sb(2)–O,F(2)	90.6(3)
Cl(5)–Sb(1)–F(2)	94.3(3)	Cl(1)–Sb(2)–F(3)	83.4(3)
Cl(7)–Sb(3)–Cl(8)	96.1(2)	F(1)–Sb(3)–F(2)	83.6(4)
Cl(3)–Sb(3)–Cl(8)	97.3(2)	F(1)–Sb(3)–F(3)	93.2(4)
Cl(3)–Sb(3)–Cl(7)	101.2(2)	F(2)–Sb(3)–F(3)	78.1(3)
Cl(3)–Sb(3)–F(1)	91.4(3)	Cl(3)–Sb(3)–F(3)	89.2(3)
Cl(7)–Sb(3)–F(1)	92.5(3)	Cl(7)–Sb(3)–F(2)	91.3(3)
Cl(8)–Sb(3)–F(2)	85.6(3)	Cl(8)–Sb(3)–F(3)	86.3(3)
Sb(1)–O,F(1)–Sb(2)	106.2(4)	Sb(1)–F(2)–Sb(3)	149.2(4)
Sb(1)–O,F(2)–Sb(2)	106.9(4)	Sb(2)–F(3)–Sb(3)	150.4(5)
(*c*) Contacts <3.6 Å			
O,F(2) · · · Cl(9^{I})	3.28	O,F(1) · · · Cl(4^{I})	3.40
F(1) · · · Cl(4^{I})	3.45	Cl(3) · · · Cl(9^{II})	3.49
Cl(4) · · · Cl(5^{III})	3.57	F(1) · · · Cl(5^{IV})	3.31
O,F(1) · · · Cl(2^{V})	3.52		

Roman numerals as superscripts refer to atoms in the following equivalent positions:

I $x, y, 1 + z$
II $-x, 1 - y, -1 - z$
III $-x, -y, -z$
IV $-x, -y, -1 - z$
V $-1 - x, -y, -1 - z$

RESULTS AND DISCUSSION

When the structure analysis was started the identity of the compound was unknown, although elemental analysis had shown a Cl : Sb ratio of *ca.* 3 : 1 for some of the reaction product, suggesting a compound other than the reported $SbCl_2F_3$. The identity of the three antimony atoms, and the associated sets of three chlorine atoms, was easily established during the course of the analysis. After these atoms had been identified the five light atoms were found and their positions gave an approximately octahedral co-ordination for each antimony atom. It therefore appeared that the expected oxidation of the original Sb^{III} to Sb^{V} had taken place.

The light atoms could not all be assigned as fluorine

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* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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

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

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

atoms, as this would have implied an oxidation state of IV for one antimony atom. A very careful search of a difference-Fourier map was made at this stage, since a compound $[Sb_3Cl_9F_5]F$ would satisfy the requirements for quinquevalent antimony and the geometry of the trimeric unit. However, no peak was found that could be assigned to the anion of such an arrangement and the map showed only some small features close to the chlorine-atom positions.

We therefore assumed that one of the light atoms was an oxygen atom. This could not be distinguished from fluorine by *X*-ray methods, in the presence of the heavy antimony and chlorine atoms, but should give a characteristically different antimony to light-atom distance. However, as can be seen from Table 2, the various antimony to light-atom distances are all similar, and all longer than the expected values for Sb–O, either terminal or bridge. We therefore further assume that the double bridge between Sb(1) and Sb(2) consists of a fluorine plus an oxygen atom in a disordered arrangement. The four antimony–bridge atom distances are the same within experimental error (Sb-O,F 2.005 Å) and this value is approximately the mean of Sb–F (bridge) distances [3,7] of 2.08 Å and Sb–O (bridge) distances [12] of 1.92 Å, which supports our hypothesis of disorder. The anisotropic temperature factors for the two disordered atoms are not significantly different from those of the fluorine atoms in the structure, although they might have been expected to be larger. This may be due to their relatively small contribution to the scattering added to the inability to apply an absorption correction.

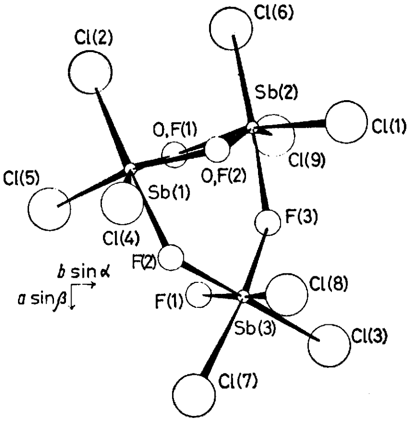

FIGURE 1 Projection of the structural unit down [001] showing the atom numbering

The compound is therefore formulated as triantimony nonachloride tetrafluoride oxide, where the oxygen atom is assumed to be derived from the Pyrex glass apparatus. Since the F : Sb ratio in the compound is 4 : 3 and in the starting material was 3 : 1, some fluorine must have been lost, probably by formation of $SbCl_{(5-n)}F_n$ ($n > 3$). By interaction with the glass apparatus these chloride fluorides could have caused the incorporation of oxygen in the product. We have shown previously [13] that such incorporation of oxygen from Pyrex glass apparatus can occur in systems containing antimony pentafluoride and chlorine as components.

This formulation is further supported by the close similarity of the present structure to that [7] of the trimeric $Sb_3Cl_{11}F_4$. In this chloride fluoride the three octahedrally co-ordinated antimony atoms are linked into a trimer by single fluorine bridges. The co-ordination of one antimony atom is identical with that of Sb(3), with bond lengths and bond angles the same within experimental error. The other two antimony atoms have four terminal chlorine atoms and two bridging fluorine atoms in their octahedral arrangements, and replacement of one chlorine atom on each antimony atom by a bridging oxygen atom would convert the chloride fluoride into our oxide derivative. Thus the oxide compound could be formulated as the first hydrolysis product of $Sb_3Cl_{11}F_4$, as in equation (1), although we do not believe that it was formed by this reaction in the present case.

$$Sb_3Cl_{11}F_4 + H_2O \longrightarrow Sb_3Cl_9F_4O + 2HCl \quad (1)$$

Interatomic distances and angles are directly comparable with those in other antimony compounds, particularly $Sb_3Cl_{11}F_4$ (1) and $SbCl_3F_2$ (2). Thus the mean Sb–Cl bond distance (2.265 Å) is very similar to those of 2.26 Å in (1) and 2.25 Å in (2), and the terminal Sb–F distance (1.935 Å) compares with 1.92 Å in (2) and 1.87 Å in (1). This Sb–F distance is long compared with terminal distances in various fluoroantimonate(V) anions [13-15] where the mean value is 1.83 Å, and where the distance might have been expected to be longer due to the overall negative charge. Since the bridging Sb–F distances (mean 2.07 Å) are also longer than the corresponding distances in the anions (mean 2.02 Å), the lengthening may be due to the presence of the chlorine atoms in positions *trans* to the Sb–F bonds. In (1) and (2), where this effect should also be observed, bridging Sb–F distances are 2.08 and 2.07 Å, the same as the present value, supporting this correlation.

The fluorine bridges between Sb(3) and the other two antimony atoms are significantly asymmetric [mean Sb(3)–F 2.03 Å and Sb(1)- or Sb(2)–F 2.11 Å]. This leads to a closer association of the bridging fluorine atoms with Sb(3) than with Sb(1) and Sb(2), and therefore we can consider that there is a contribution to the structure from the ionic form $[Sb_2Cl_6FO][SbCl_3F_3]$ although the covalently bridged trimeric form predominates. The asymmetry of the bridges (ratio of Sb–F distances = 1.04 : 1) is less than that found [15] in the $[Sb_3F_{16}]^-$ anion (ratio 1.07 : 1) where a contribution to the structure from the doubly solvated monomeric anion $[SbF_6]^- \cdot 2SbF_5$ is considered.

The pyramidal $SbCl_3$ units have very similar Cl–Sb–Cl angles, all >90°, as do those in (1) and (2), presumably

[12] W. Haase, *Acta Cryst.*, 1974, **B30**, 2465, 2508.

[13] A. J. Edwards and R. J. C. Sills, *J.C.S. Dalton*, 1974, 1726.

[14] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), 1969, 1467; A. J. Edwards and R. J. C. Sills, *ibid.*, 1970, 2697; 1971, 942; A. J. Edwards and P. Taylor, *J.C.S. Dalton*, 1973, 2150.

[15] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), 1971, 2318.

due to the repulsive interactions between the large chlorine atoms being greater than those between the smaller oxygen and fluorine atoms. In all the three units the F–Sb–F or F–Sb–O,F angles are <90° with the angles between the O,F bridging atoms for Sb(1) and Sb(2) at 73° and the F bridges for Sb(3) at 78°, significantly smaller than the remainder (mean 82.7°). The F–Sb–F bridge angles average 150° and are smaller than those of 158° in (1), due to the double bridge between Sb(1) and Sb(2). This double Sb–O,F–Sb bridge is the first example of such a system, although a symmetric di-μ-fluoro-bridge has been characterised in the structure [16] of vanadium trifluoride oxide.

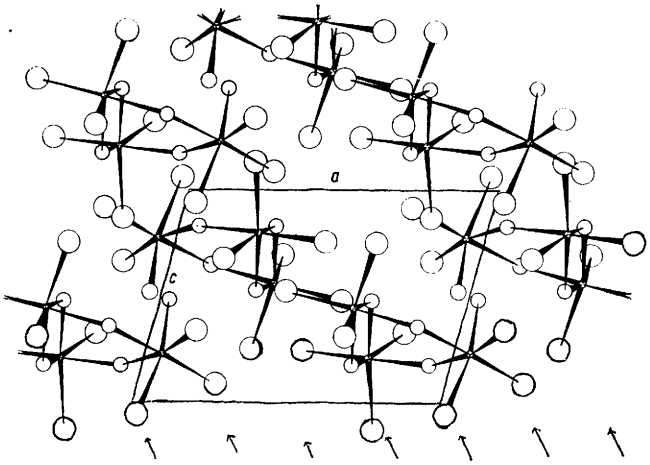

FIGURE 2 Projection of the structure down [010] with arrows indicating the approximation to close-packed layers

The packing arrangement is shown in Figure 2. There are no very close contacts between the trimeric molecular units [Table 2(*c*)]. The volume per non-metal atom of 31.1 Å^3 is almost the same as the corresponding value for (1) of 30.9 Å^3. The approach to close-packed planes of non-metal atoms is indicated in Figure 2. This can only be very approximate due to the incompatibility of the distances from antimony to chlorine or to oxygen and fluorine.

All the calculations were carried out on an ICL 1906A computer, using the SHELX-76 program,[17] and we thank the staff at Birmingham University Computer Centre for their assistance.

[7/345 *Received, 28th February,* 1977]

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[16] A. J. Edwards and P. Taylor, *Chem. Comm.*, 1970, 1474.

[17] SHELX-76, ' Program for Crystal Structure Determination,' G. M. Sheldrick, University of Cambridge, 1975.