The Crystal Structure of the 1:1 Adduct of Antimony Trifluoride and Antimony Pentafluoride

By **Ronald J. Gillespie,* David R. Slim,** and **John E. Vekris,** Department of Chemistry, McMaster University, Hamilton, Ontario, Canada

A single-crystal *X*-ray diffraction study of the compound $(SbF_4)_4$ shows that it is monoclinic with the following unit-cell dimensions: $a = 9.32(1)$, $b = 12.07(1)$, $c = 11.60(1)$ Å, $\beta = 107.1(3)°$, space group $P2_1/c$, and $Z = 4$. Refinement by full-matrix least-squares methods of all parameters with anisotropic temperature factors on the heavy atoms gave an *R* of 0.071 for 2 048 observed reflections. The asymmetric unit consists of an $[Sb_2F_4]^{2+}$ cation and two $[SbF_6]^-$ anions. When the longer Sb^{III}–F contacts are considered then the structure must be described as an infinite three-dimensional polymer.

RECENTLY we have shown that the reaction of S_4N_4 with AsF_5 in SO_2 gives a black compound $[S_3N_2][AsF_6]$.[1] In an analogous reaction of S_4N_4 with SbF_5 we obtained a white crystalline solid which proved to be a 1 : 1 adduct of SbF_3 and SbF_5. Two different forms, A and B, of an adduct which was believed to be $SbF_3{\cdot}SbF_5$ have been previously reported by Birchall *et al.*,[2] but their structures were not determined. Recently one of these, form B, has been shown by Edwards and Slim [3] to have the composition $6SbF_3{\cdot}5SbF_5$ or $Sb_{11}F_{43}$. The structure was described as consisting of the polymeric cation $[Sb_6F_{13}]^{5+}$ and 5 $[SbF_6]^-$ anions. If only the shorter Sb–F distances are considered the cation $[Sb_6F_{13}]^{5+}$ may be considered to consist of 4 $[SbF_2]^+$ ions and an $[Sb_2F_5]^+$ ion. In the same paper Edwards and Slim mentioned that they had obtained preliminary *X*-ray data for another $SbF_3{\cdot}SbF_5$ adduct. This compound was later shown to be $2SbF_3{\cdot}SbF_5$.[4] We now report the structure of the first 1 : 1 SbF_3–SbF_5 adduct to have been definitely characterized.

EXPERIMENTAL

Tetrasulphur tetranitride was prepared and purified in a similar manner to that described previously.[1] Antimony pentafluoride (Ozark–Mahoning) was purified by a double distillation in an all-glass apparatus. Sulphur dioxide (Matheson) was repeatedly distilled from, and kept over, phosphorus pentaoxide before use.

In a typical experiment S_4N_4 (2.96 mmol) was placed into one arm of a rigorously dried Pyrex double ampoule inside the dry-box. SbF_5 (27.59 mmol) was syringed into the other arm of the ampoule. The apparatus was connected to the vacuum line and an excess of sulphur dioxide was condensed into the SbF_5 at −196 °C. On warming to room temperature the SbF_5–SO_2 mixture was vigorously stirred and on addition of this to the S_4N_4 a black solution appeared immediately. After several hours the colour of the solution changed to a red-brown and a fine precipitate appeared. After 48 h the solution was filtered to the other arm of the ampoule and the precipitate was washed several times with SO_2 to give a white powder, presumably SbF_3. The red-brown solution was set aside for several months at room temperature. A large number of well-formed colourless crystals appeared. These were separated from the mother liquor, washed several times with SO_2, and pumped to dryness. Suitable crystals for *X*-ray studies were selected in a dry-box equipped with a microscope and were sealed inside thin-walled quartz capillaries.

Crystal Data.—Sb_4F_{16}, $M = 790.4$, Monoclinic, with $a = 9.32(1)$, $b = 12.07(1)$, $c = 11.60(1)$ Å, $\beta = 107.1(3)°$, $U = 1\,247$ Å^3, $Z = 4$, $D_c = 4.21$ g cm^{-3}, $F(000) = 1\,392$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, and $\mu(\text{Mo-}K_\alpha) = 88.4$ cm^{-1}. The unit-cell parameters were obtained from a least-squares refinement of 15 reflections in the region $20 < 2\theta < 25°$. Weissenburg and precession photographs indicated that reflections were absent for $h0l$ when $l = 2n + 1$ and for $0k0$ when $k = 2n + 1$, characteristic of the space group $P2_1/c$ [No. 14].[5]

X-Ray Intensity Measurements.—The crystal which was an irregular block of approximate dimensions $0.42 \times 0.28 \times 0.19$ mm was sealed in a thin-walled quartz capillary and mounted on a Syntex $P\bar{1}$ diffractometer with its 0.42 mm edge, which was approximately perpendicular to the (100) face, almost coincident with the ϕ axis of the diffractometer. Intensities were measured using graphite-monochromated Mo-K_α radiation, with a θ—2θ scan and a scan rate varying from 8.0 to 24.0° min^{-1} in 2θ so that weaker reflections were examined more slowly to minimize counting errors. Stationary background counts, with a time equal to half the scan time for each reflection, were made at each end of the scan range. The scan width varied from 2° at low 2θ to 2.5° for high angle reflections. One standard reflection was regularly checked to monitor the stability of the crystal and its alignment, but no significant variation was observed. Of 2 218 independent reflections measured within a unique quadrant with $2\theta < 50°$, 2 048 reflections had intensities with $I > 3\sigma(I)$ based on counting statistics. Lorentz, polarization, and absorption corrections were applied to the observed intensities.

Structure Determination.—The positions of four independent heavy atoms were located from the three-dimensional Patterson function. These atoms were assumed to be antimony. The scattering factors for neutral antimony were corrected for anomalous dispersion using values for the real and imaginary parts from refs. 5 and 6. Full-matrix least-squares refinement of positional and isotropic temperature parameters gave an *R* of 0.22. Subsequent difference-electron-density maps revealed the positions of 16 fluorine atoms. Anisotropic temperature factors were introduced for the heavy atoms leading to a value of $R'\{R' = [\Sigma\omega(|F_o|^2 - |F_c|^2)|\Sigma\omega F_o^2]^{1/2}\}$ of 0.076 9, where w is given by the expression $w = [6.56 + 0.098F_o + 0.007\,6F_o^2]^{-1/2}$. The largest shift Δ/σ in the final cycle was 0.1. The final *R* was 0.071 0 and a final difference Fourier showed no significant peaks. Observed and calculated structure factors are listed

---

[1] R. J. Gillespie, P. R. Ireland, and J. E. Vekris, *Canad. J. Chem.*, 1975, **53**, 21.

[2] T. Birchall, P. A. W. Dean, B. Della Valle, and R. J. Gillespie, *Canad. J. Chem.*, 1973, **51**, 667.

[3] A. J. Edwards and D. R. Slim, *J.C.S. Chem. Comm.*, 1974, 178.

[4] A. J. Edwards and D. R. Slim, personal communication.

[5] 'International Tables for *X*-ray Crystallography,' vol. 1, Kynoch Press, Birmingham, U.K., 1965.

[6] 'International Tables for *X*-ray Crystallography,' vol. 4, Kynoch Press, Birmingham, U.K., 1975.

TABLE 1

Final atomic positional and thermal parameters ($\times 10^4$) for Sb_4F_{16}, with standard deviations in parentheses *

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb(1)	1 988(1)	934(1)	2 910(1)	267(6)	179(6)	280(8)	−34(4)	145(5)	−31(4)
Sb(2)	3 913(1)	1 515(1)	3 520(1)	232(6)	241(6)	283(8)	−12(4)	113(5)	−19(5)
Sb(3)	2 414(1)	772(1)	−591(1)	266(6)	163(5)	251(8)	−22(4)	145(5)	−6(4)
Sb(4)	2 267(1)	6 604(9)	461(1)	251(6)	143(5)	385(9)	14(4)	171(5)	11(4)

	x/a	y/b	z/c	U		x/a	y/b	z/c	U
F(1)	3 293(13)	−189(9)	2 742(11)	325(25)	F(9)	3 557(13)	−401(10)	140(11)	372(27)
F(2)	3 469(12)	1 979(9)	2 582(10)	286(23)	F(10)	3 842(12)	1 781(9)	384(10)	288(23)
F(3)	3 388(13)	1 112(9)	4 604(11)	325(24)	F(11)	3 459(12)	5 348(9)	1 279(11)	306(24)
F(4)	1 829(12)	1 578(9)	3 996(11)	313(25)	F(12)	1 398(15)	5 592(11)	−799(12)	405(30)
F(5)	1 414(13)	791(10)	581(12)	378(27)	F(13)	3 745(14)	6 849(11)	−285(12)	433(29)
F(6)	1 382(14)	2 044(10)	−1 296(12)	391(28)	F(14)	852(15)	6 191(12)	1 190(13)	468(31)
F(7)	929(16)	−90(12)	−1 615(13)	456(33)	F(15)	1 119(16)	7 764(12)	−335(13)	509(35)
F(8)	3 533(13)	841(9)	−1 715(11)	319(25)	F(16)	3 308(17)	7 460(13)	1 736(14)	545(36)

* Anisotropic temperature factors ($U_{ij} \times 10^4$ Å^2) in the expression: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$

in Supplementary Publication No. SUP 22004 (12 pp., 1 microfiche).* Final atomic co-ordinates and thermal parameters are given in Table 1.

TABLE 2

Bond lengths (Å) and bond angles (°) in $(SbF_4)_4$, with standard deviations in parentheses

Lengths			
Sb(1)–F(1)	1.876(14)	Sb(3)–F(5)	1.862(17)
Sb(1)–F(2)	1.985(14)	Sb(3)–F(6)	1.859(13)
Sb(1)–F(3)	2.012(12)	Sb(3)–F(7)	1.857(15)
Sb(1)–F(5)	2.600(15)	Sb(3)–F(8)	1.901(16)
Sb(1)–F(6)	2.729(14)	Sb(3)–F(9)	1.829(13)
Sb(1)–F(7)	2.874(15)	Sb(3)–F(10)	1.905(11)
Sb(1)–F(12)	2.544(16)	Sb(4)–F(11)	1.946(12)
Sb(2)–F(2)	2.154(14)	Sb(4)–F(12)	1.875(15)
Sb(2)–F(3)	2.325(14)	Sb(4)–F(13)	1.856(16)
Sb(2)–F(4)	1.849(13)	Sb(4)–F(14)	1.837(18)
Sb(2)–F(8)	2.361(16)	Sb(4)–F(15)	1.837(16)
Sb(2)–F(10)	2.418(13)	Sb(4)–F(16)	1.825(16)
Sb(2)–F(11)	2.291(12)		
Angles			
F(1)–Sb(1)–F(2)	86.5(6)	F(2)–Sb(2)–F(3)	135.2(5)
F(1)–Sb(1)–F(3)	85.0(5)	F(2)–Sb(2)–F(4)	77.8(5)
F(1)–Sb(1)–F(5)	77.6(5)	F(2)–Sb(2)–F(8)	71.6(5)
F(1)–Sb(1)–F(6)	152.9(6)	F(2)–Sb(2)–F(10)	69.3(5)
F(1)–Sb(1)–F(7)	103.4(5)	F(2)–Sb(2)–F(11)	140.1(5)
F(1)–Sb(1)–F(12)	78.2(5)	F(3)–Sb(2)–F(4)	78.6(6)
F(2)–Sb(1)–F(3)	80.6(5)	F(3)–Sb(2)–F(8)	140.5(5)
F(2)–Sb(1)–F(5)	77.6(6)	F(3)–Sb(2)–F(10)	72.1(5)
F(2)–Sb(1)–F(6)	73.8(5)	F(3)–Sb(2)–F(11)	71.8(5)
F(2)–Sb(1)–F(7)	136.7(6)	F(4)–Sb(2)–F(8)	81.9(6)
F(2)–Sb(1)–F(12)	149.1(5)	F(4)–Sb(2)–F(10)	87.1(5)
F(3)–Sb(1)–F(5)	153.1(6)	F(4)–Sb(2)–F(11)	82.0(5)
F(3)–Sb(1)–F(6)	73.5(6)	F(8)–Sb(2)–F(10)	140.8(5)
F(3)–Sb(1)–F(7)	142.0(5)	F(8)–Sb(2)–F(11)	71.7(5)
F(3)–Sb(1)–F(12)	72.2(6)	F(10)–Sb(2)–F(11)	143.6(4)
F(5)–Sb(1)–F(6)	114.3(6)	F(11)–Sb(4)–F(12)	85.2(6)
F(5)–Sb(1)–F(7)	63.9(7)	F(11)–Sb(4)–F(13)	87.7(7)
F(5)–Sb(1)–F(13)	110.4(6)	F(11)–Sb(4)–F(14)	87.1(6)
F(6)–Sb(1)–F(7)	103.7(7)	F(11)–Sb(4)–F(15)	177.8(7)
F(6)–Sb(1)–F(12)	73.5(5)	F(11)–Sb(4)–F(16)	87.9(6)
F(7)–Sb(1)–F(12)	73.5(6)	F(12)–Sb(4)–F(13)	87.1(7)
F(5)–Sb(3)–F(6)	90.3(6)	F(12)–Sb(4)–F(14)	88.9(7)
F(5)–Sb(3)–F(7)	92.0(7)	F(12)–Sb(4)–F(15)	92.6(7)
F(5)–Sb(3)–F(8)	175.3(5)	F(12)–Sb(4)–F(16)	172.7(7)
F(5)–Sb(3)–F(9)	91.0(6)	F(13)–Sb(4)–F(14)	173.7(7)
F(5)–Sb(3)–F(10)	88.5(6)	F(13)–Sb(4)–F(15)	92.2(7)
F(6)–Sb(3)–F(7)	89.2(6)	F(13)–Sb(4)–F(16)	89.2(7)
F(6)–Sb(3)–F(8)	88.8(6)	F(14)–Sb(4)–F(15)	92.9(8)
F(6)–Sb(3)–F(9)	175.0(6)	F(14)–Sb(4)–F(16)	94.2(8)
F(6)–Sb(3)–F(10)	84.9(5)	F(15)–Sb(4)–F(16)	94.3(7)
F(7)–Sb(3)–F(8)	92.6(7)		
F(7)–Sb(3)–F(9)	95.6(6)	Sb(1)–F(2)–Sb(2)	148.3(6)
F(7)–Sb(3)–F(10)	174.1(6)	Sb(1)–F(3)–Sb(2)	154.0(6)
F(8)–Sb(3)–F(9)	89.5(6)		
F(8)–Sb(3)–F(10)	86.7(6)		
F(9)–Sb(3)–F(10)	90.2(5)		

RESULTS

The interatomic bond lengths and bond angles are given in Table 2, and the atomic arrangement is given in Figure 1. The asymmetric unit contains an $[Sb_2F_4]^{2+}$ cation, shown in Figure 2, and two slightly distorted $[SbF_6]^-$ octahedral anions. If only the shorter Sb^{III}–F bonds (<2.01 Å) are considered then the cation can be described as consisting of an SbF_3 molecule and an $[SbF]^{2+}$ cation; however, this division of the $[Sb_2F_4]^+$ ion must be regarded as rather artificial.

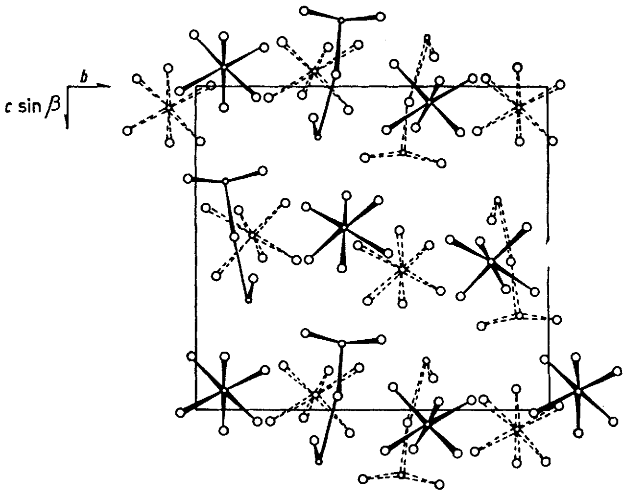

FIGURE 1 A projection of the structure down the *a* axis

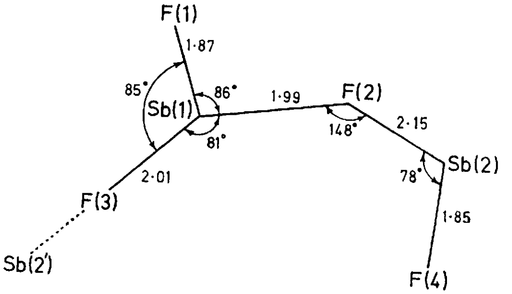

FIGURE 2 The $[Sb_2F_4]^{2+}$ cation. Bond lengths in Å

The Sb(1),F(1),F(2),F(3) unit has a pyramidal AX_3E

---

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

co-ordination similar to that found in SbF_3 itself.[7] The Sb(1)–F(1) bond length (1.88 Å) is similar to that found in SbF_3 (1.90 Å) but the Sb(1)–F(2) and Sb(1)–F(3) bond lengths (1.99 and 2.01 Å respectively) are significantly longer due to bridging interactions with the Sb(2) and Sb(2′) atoms respectively. The Sb(1),F(1),-F(2),F(3) unit is linked by an angular asymmetric fluorine bridge to the Sb(2),F(4) group forming the $[\text{Sb}_2\text{F}_4]^{2+}$ cation. The Sb(2)–F(4) bond, where F(4) is the fluorine that is not involved in further bridging, has a similar length to the Sb(1)–F(1) bond where F(1) is also a terminal fluorine.

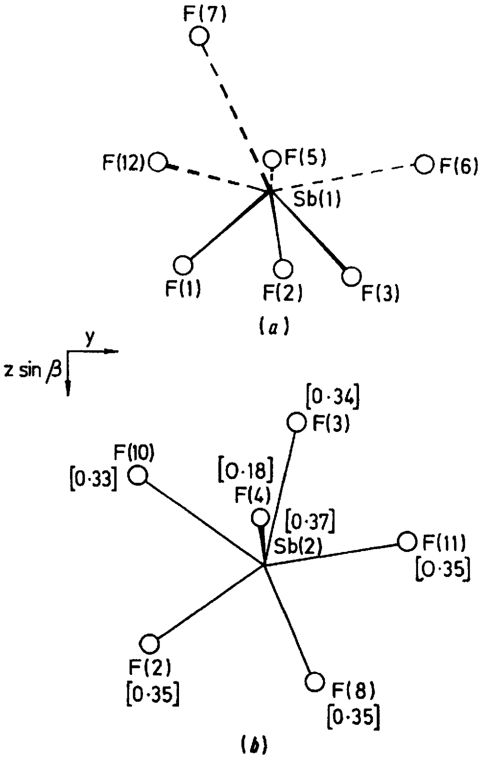

FIGURE 3 (*a*) Projection of the Sb(1)F_7 unit down the *c* axis. (*b*) Projection of the Sb(2)F_6 unit down the *a* axis. The *x*-co-ordinate for each atom is given in parentheses

The $[\text{Sb}_2\text{F}_4]^{2+}$ ions could be considered to be held together by the Sb(2)–F(3′)–Sb(1′) bridge to form an infinite chain cation $[(\text{Sb}_2\text{F}_4)_n]^{2n+}$ but this is rather artificial since there are other equally strong interactions between Sb^{III} atoms and fluorine atoms of the $[\text{SbF}_6]^-$ anions which link all the 'cations' and 'anions' together into a cross-linked three-dimensional polymeric structure. In this connection it is interesting to consider the environment of each Sb^{III} atom. For Sb(1) there are, in addition to the short bonds to F(1), F(2), and F(3), four long contacts to F(5), F(6), F(7), and F(12) in the range 2.54—2.87 Å. Figure 3(*a*) shows the projection of the Sb(1)F_7 unit down the *c* axis. The Sb(1) atom can be regarded as having an AX_7E stereochemistry with the four long contacts surrounding the lone pair (E). If a long contact is denoted by Y and a normal bond by X then the geometry of Sb(1) can be described as $\text{AX}_3\text{Y}_4\text{E}$. On this basis $[\text{IF}_4][\text{Sb}_2\text{F}_{11}]$ [8] and SbF_3 [7] can be regarded as $\text{AX}_4\text{Y}_4\text{E}$ and $\text{AX}_3\text{Y}_3\text{E}$ systems respectively. The $\text{AX}_3\text{Y}_3\text{E}$ and $\text{AX}_3\text{Y}_4\text{E}$ systems are very similar with the long contacts, Y, surrounding the lone pair. The atom Sb(2), in addition to the short bond to F(4), has five short contacts to F(2), F(3′), F(8), F(10), and F(11) in the range 2.10—2.42 Å. Figure 3(*b*) shows the projection of the Sb(2)F_6 unit down the *a* axis. The Sb(2) atom can be regarded as having an AXY_5E stereochemistry in the form of a pentagonal bipyramid with the lone pair occupying one of the axial positions. On the basis of VSEPR theory [9] it can be predicted that for a pentagonal bipyramid geometry the bonds in the equatorial plane will be longer than the axial bonds and that a lone pair would be expected to occupy an axial position as is observed. The atoms F(2),F(3),F(8),F(10), and F(11) are coplanar to within 0.08 Å. Because a lone pair has a greater repulsive effect than a bond pair, the equatorial plane is expected to be displaced towards the axial fluorine. This is observed, as all the F(4)–Sb(2)–F angles are less than 90°. Furthermore, the angles between neighbouring fluorine atoms are close to the 72° angle for a regular pentagon. The overall geometry of the Sb^{III} atoms is consistent with the description of the $[\text{Sb}_2\text{F}_4]^{2+}$ cation since Sb(2) would be expected to have much shorter contacts than Sb(1) as the former antimony has a larger formal positive charge and hence attracts the negative fluorines more strongly.

The Sb^{V}–F bond lengths appear to fall into three categories; first the fluorines F(8),F(10), and F(11), which make rather strong contacts with Sb(1), have rather long Sb^{V}–F bond lengths (mean 1.92 Å); second the fluorines F(5),F(6),F(7), and F(12), which make weaker contacts with Sb(2), have shorter Sb^{V}–F bond lengths (mean 1.86 Å); third, the fluorines F(9),F(13),-F(14),F(15), and F(16), which have no contacts with either Sb(1) or Sb(2) < 3 Å, have even short erSb^{V}–F distances (mean 1.84 Å). The bond weakening effect due to fluorine-bridge formation is also found for F(2) and F(3) since the Sb(1)–F(2) and Sb(1)–F(3) bond lengths are much longer than the terminal Sb(1)–F(1) and Sb(2)–F(4) bond lengths.

Although the structure is approximately close packed, the packing is not as efficient as in SbF_5,[10] since the volume per fluorine atom in the latter compound (17.8 Å^3) is less than that in $(\text{SbF}_4)_4$ (19.5 Å^3). However, this is not surprising since the lone pairs on the Sb^{III} atoms occupy considerable space in the structure. If the lone pairs on the two Sb^{III} atoms are assumed to occupy a volume similar to that of a fluorine atom,[11] then the volume per light atom is 17.3 Å^3, which is comparable to that found for SbF_5.[10]

The Raman spectrum of the bulk material and of the

---

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

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

[9] R. J. Gillespie, 'Molecular Geometry,' Van Nostrand Reinhold, London, 1972.

[10] A. J. Edwards and P. Taylor, *Chem. Comm.*, 1971, 1376.

[11] J. Galy, G. Meunier, S. Andersson, and A. Angstrom, *J. Solid-State Chem.*, 1975, **13**, 142.

single crystal were essentially identical. A detailed interpretation of the spectra is not possible in view of the complexity of the structure; however, they are identical with that of $SbF_3{\cdot}SbF_5$ (A) [2] and completely different from that of $SbF_3{\cdot}SbF_5$ (B) ($Sb_{11}F_{43}$) and the spectrum reported by Hewitt *et al.*[12] We conclude that $SbF_3{\cdot}SbF_5$ (A) is $(SbF_4)_4$. A mixture of a yellow and a white solid was obtained by Hewitt *et al.* on fluorination of antimony in a flow system. The Raman spectrum of the white solid, sublimed at 240 °C, was interpreted as indicating the presence of an $[Sb_2F_{11}]^-$ ion and the authors suggested that the compound was probably identical with the second of the $SbF_3{\cdot}SbF_5$ adducts reported by Edwards and Slim.[3] However, these authors later showed that this adduct had the composition $2SbF_3{\cdot}SbF_5$ and had a structure containing a polymeric cation $[Sb_4F_{10}]^{2+}$ and the $[SbF_6]^-$ anion.[4] Thus the nature of the white compound, prepared by Hewitt *et al.*, remains uncertain.

[6/1089 *Received, 7th June,* 1976]

---

[12] A. J. Hewitt, J. H. Holloway, and B. Frlec, *J. Fluorine Chem.*, 1975, **5**, 169.