The Preparation and Crystal Structure of $5SbF_3 \cdot 3SbF_5$ †

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$5SbF_3 \cdot 3SbF_5$ was prepared by the reduction of $SbF_3 \cdot SbF_5$ or SbF_5 with a stoicheiometric amount of PF_3 in arsenic trifluoride solution. A single-crystal *X*-ray diffraction study of $5SbF_3 \cdot 3SbF_5$ shows that it is orthorhombic, space group *Pnma* with cell dimensions, $a = 19.187(9)$, $b = 15.890(2)$, $c = 15.713(3)$ Å, and $Z = 8$. The structure was refined to a final *R* of 0.057 for 3 718 reflections. The structure consists of a three-dimensional cross-linked polymeric $(Sb_5F_{12})_n^{3n+}$ cation and SbF_6^- anions with significant cation–anion interactions. The polymeric cation can be viewed as being built of strongly interacting $Sb_2F_5^+$, SbF_3, and $Sb_2F_3^{3+}$ units. The various configurations of $Sb_2F_5^+$ cations are described and discussed. The planar eclipsed $Sb_2F_3^{3+}$ cation has not been observed in other binary fluorides of antimony. The geometries of the fluorine atoms in the several co-ordination spheres about the various antimony(III) species are described. A rationale is advanced for the existence of a variety of polymeric antimony(III) fluorocations formed between SbF_3 and SbF_5, in contrast to AsF_3 and SbF_5, which form an adduct that can be described as $AsF_2^+SbF_6^-$. The Raman spectrum of $5SbF_3 \cdot 3SbF_5$ is reported.

Arsenic and antimony pentafluoride have both proved to be very useful in the synthesis of a wide variety of salts of novel non-metal cations, including graphite salts, and those of various polymers,[1] *e.g.* polyacetylene, chalcogen homoatomic cations,[2 8] and sulphur- and selenium-iodine cations.[7,9] An example[7] is given in equation (*i*). The analogous reaction, using

$$3AsF_5 + \tfrac{1}{2}S_8 \xrightarrow[SO_2(l)]{\text{trace } Br_2} S_4^{2+}(AsF_6^-)_2 + AsF_3 \qquad (i)$$

antimony pentafluoride is more complicated, in that complex fluoroanions can be formed [*e.g.* $Sb_2F_{11}^-$], and the reduced product is rarely SbF_3 in SO_2 or AsF_3 solution.[10] In order more fully to understand these reactions, SbF_5 was systematically reduced with PF_3 and I_2, and the reduced products identified. Thus, $SbF_3 \cdot SbF_5$,[11] (β)$6SbF_3 \cdot 5SbF_5$,[12] and $3SbF_3 \cdot SbF_5$[13] have been prepared and identified. In addition, the new binary fluoride of antimony, $5SbF_3 \cdot 3SbF_5$ was identified and its crystal structure determined by *X*-ray crystallography, and is the subject of this paper.

Ruff and Plato,[14] in 1904, were the first to prepare compounds of this type. Antimony pentafluoride and antimony trifluoride were reacted together to give $2SbF_3 \cdot SbF_5$ and $5SbF_3 \cdot SbF_5$, and they suggested that $4SbF_3 \cdot SbF_5$ and $3SbF_3 \cdot SbF_5$ were formed also.

At the present time the binary fluorides of antimony include, as well as the tri-[15] and penta-fluoride,[16,17] $3SbF_3 \cdot 4SbF_5$,[18] $SbF_3 \cdot SbF_5$,[11] (β)$6SbF_3 \cdot 5SbF_5$,[12] (α)$6SbF_3 \cdot 5SbF_5$,[19] $2SbF_3 \cdot SbF_5$,[20] $3SbF_3 \cdot SbF_5$,[13] and $5SbF_3 \cdot 3SbF_5$ which is reported below. The structures of all these compounds have been determined by *X*-ray crystallography. They all contain SbF_6^- anions and complex Sb^{III} fluorocations with varying degrees of cation–anion interaction. The structures are of interest in that they present a wide variety of stereochemical arrangements of the fluorine atoms about Sb^{III}; the Sb^{III}–F bond lengths vary from 1.858 to 3.55 Å, the sum of the van der Waals radii for Sb and F, thus covering a wide range of bond orders. They therefore are of interest in terms of the current ideas on secondary bonding and stereochemistry.[21–26] The compound $5SbF_3 \cdot 3SbF_5$ is a particularly good source of structural information, in that it contains seven crystallographically different Sb^{III} atoms. A full discussion of the structure of $5SbF_3 \cdot 3SbF_5$ is reported below. The existence of a wide variety of salts formed between SbF_3 and SbF_5, containing polymeric antimony(III) fluorocations is in contrast to the situation for AsF_3 and SbF_6, where only one adduct is formed that can be described as $AsF_2^+SbF_6^-$,[27] containing the isolated AsF_2^+ fluorine bridged to SbF_6^-. Suggestions as to why this is the case are proposed, in the context of the model of interaction in the solid state developed by Brown.[22,23]

Experimental

Reagents and Apparatus.—The apparatus, chemicals, and techniques, unless otherwise specified, are described in refs. 28 and 13. Raman spectra were obtained using a Spex Ramalab spectrometer and Spectra Physics 2 W krypton–argon or 2 W argon-ion lasers, both with the 5 145 Å exciting line. $SbF_3 \cdot SbF_5$ was prepared according to ref. 28.

Preparation of $5SbF_3 \cdot 3SbF_5$.—*Method 1.* In one of the reactions carried out in order to obtain the most reduced product of SbF_5, the adduct $SbF_3 \cdot SbF_5$[11] (6.303 g, 15.94 mmol) was reacted with PF_3 (2.643 g, 30.04 mmol) in AsF_3 (14.733 g) in a Pyrex vessel equipped with a Teflon and glass valve at room temperature [Table 1, reaction 1(i)]. The reaction was stopped after 4 d, before the reaction was complete, when well formed crystals appeared. The volatile [PF_3, PF_5, AsF_3 (i.r.)] materials were removed, leaving behind a product that contained well formed translucent crystals (*ca.* 15%) and a microcrystalline bulk material. Raman spectra of the well formed crystals identified them as $3SbF_3 \cdot SbF_5$[13] and the microcrystalline material gave a Raman spectrum very similar to the spectrum in Figure 1 and Table 2 and different from that of any known antimony fluoride. The elemental analysis of the bulk material was consistent with $5SbF_3 \cdot 3SbF_5$ (Found: F, 36.2; Sb, 63.3. Calc. for $5SbF_3 \cdot 3SbF_5$: F, 36.9; Sb, 63.1%).

In order to confirm the identity of the microcrystalline bulk material obtained from reaction 1(i), an attempt was made to obtain single crystals of $5SbF_3 \cdot 3SbF_5$ by reaction 1(ii), Table 1.

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† *Supplementary data available* (No. SUP 56677, 19 pp.): Raman spectrum of cubic phase, description of the geometries of the fluorine atoms around the antimony(III) atoms (< 3.55 Å) and bond angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Various preparations of $5SbF_3 \cdot 3SbF_5$ (weight of compounds in g, values in parentheses in mmol)

$$3(SbF_3 \cdot SbF_5) + PF_3 \xrightarrow[r.t.]{AsF_3} 2(2SbF_3 \cdot SbF_5) + PF_5 \quad (1)$$

	$SbF_3 \cdot SbF_5/PF_3$[a]							
	calc.	obs.	$SbF_3 \cdot SbF_5$	PF_3	AsF_3	Time (d)	SbF_x	x[b]
(i)	3.00	0.53	6.303 (15.94)	2.643 (30.04)	14.7	4	5.906	3.34
(ii)[c]	3.00	2.97[a]	0.741 1.87	0.055 (0.63)	6.6	19	0.705	3.50[d]

$$8SbF_5 + 5PF_3 \xrightarrow[r.t.]{AsF_3} 5SbF_3 \cdot 3SbF_5 + 5PF_5 \quad (2)$$

	SbF_5/PF_3[a]							
	calc.	obs.	SbF_5	PF_3	AsF_3	Time (d)	SbF_x	x
(i)[c]	1.60	1.71	4.595 (21.20)	0.092 (12.41)	4.7	13	4.148	3.89
(ii)[c]	1.60	1.63	5.109 (23.57)	1.272 (14.46)	12.7	10	4.579	3.82
(iii)[c]	1.60	1.62	3.027 (13.97)	0.760 (8.64)	17.3	11	2.705	3.79
(iv)[c]	1.60	1.52	4.275) (19.73)	1.147 (13.03)	13.0	13	3.804	3.74

[a] Mole ratios calculated correspond to that expected according to the appropriate equation. [b] For $5SbF_3 \cdot 3SbF_5$ calculated value of x is 3.75. [c] At the end of the reaction the i.r. of the volatile material showed it to contain PF_5, AsF_3, very small amounts of $P(O)F_3$, and a trace of PF_3. [d] The value of x is low relative to the calculated value. Similar low values have been obtained in other related reactions and reasons why this might be the case are discussed in refs. 12 and 13.

Table 2. Raman spectra[a] of $5SbF_3 \cdot 3SbF_5$ and the 'cubic' phase

$5SbF_3 \cdot 3SbF_5$[b] (single crystal)	Cubic phase[c] (single crystal)	$LiSbF_6$[d] Raman	$LiSbF_6$[d] I.r.	$H_3O^+SbF_6^-$[e]	Tentative assignments
				265 (sh)	*f*
278 (0.3) (sh)					*f*
				280 (4.1)	*f*
284 (0.9) (sh)					*f*
				287 (sh)	*f*
294 (3.2)	*g*	294 (4.4)			SbF_6^- ν_5
			350		SbF_6^- ν_4
	395 (0.5)				cation
	412 (1.4)				cation
				450 (sh)	
				490 (0.6) br	
523 (1.2)					*f* or cation
	558 (2.2)	558 (2.1)		558 (0.8)	SbF_6^- ν_2
567 (sh)					*f* or cation
572 (3.7)					SbF_6^- ν_2
				590 (sh) br	
611 (0.4)					*f* or cation
629 (1.4)					*f* or cation
635 (sh)					*f*
646 (10.0)					SbF_6^- ν_1
	647 (3.5)				*f* or cation
	662 (10.0)	668 (10.0)		663 (10.0)	SbF_6^- ν_1
676 (3.7)			669		SbF_6^- ν_3
686 (1.3)					*f*

[a] Raman spectra taken in various orientations of the crystal in the laser beam were almost, but *not* absolutely, identical. Intensities in parentheses; sh = shoulder, br = broad, s = strong. [b] Actual spectrum shown in Figure 1. [c] The actual spectrum of one cubic phase crystal is included in SUP No. 56677. [d] G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, 1967, **6**, 2212. [e] Ref. 29(*a*). [f] Possibly attributable to SbF_6^- arising from slight distortions from octahedral symmetry. [g] Spectrum not obtained below 300 cm^{-1} due to very high fluorescence.

The Raman spectrum of the bulk material was consistent with it being a mixture of $3SbF_3 \cdot SbF_5$ and $5SbF_3 \cdot 3SbF_5$. Single crystals were not obtained.

Method 2. Reduction of SbF_5 with PF_3 in AsF_3 (reaction 2, Table 1) was also carried out to obtain single crystals of $5SbF_3 \cdot 3SbF_5$. The product of reaction 2(i) (Table 1) was highly crystalline. Raman spectra of (*ca.* 12) individual crystals showed that this product contained three different phases; (β)$6SbF_3 \cdot 5SbF_5$,[12] $5SbF_3 \cdot 3SbF_5$ (the Raman spectra is shown in Figure 1 and frequencies listed in Table 2), and a phase with a cubic unit cell [a = 10.1(1) Å determined by precession photography]. Raman spectra of the single crystals are given in Table 2, and compared with that of $H_3O^+SbF_6^-$.[29a] The product from reaction 2(ii) (Table 1) contained well formed crystals (*ca.* 20%) and a microcrystalline bulk product. Raman spectra of the crystals identified them as $3SbF_3{\cdot}SbF_5$ while Raman spectra of the bulk material were similar to $5SbF_3{\cdot}3SbF_5$.

The product of reaction 2(iii) was highly crystalline. Raman spectra of (*ca.* 12) individual crystals showed that it contained two different types of crystals: (β)$6SbF_3{\cdot}5SbF_5$[12] and $5SbF_3{\cdot}3SbF_5$. A single crystal for *X*-ray diffraction study was selected from this preparation. The product of reaction 2(iv) contained well formed crystals (*ca.* 20%) which were identified as $3SbF_3{\cdot}SbF_5$[13] by their Raman spectra. The Raman spectrum of the bulk material was very similar to the single-crystal spectrum of $5SbF_3{\cdot}3SbF_5$.

Crystal Data.—$5SbF_3{\cdot}3SbF_5$, $M = 1\,543.9$, orthorhombic, space group *Pnma*, $a = 19.187(9)$, $b = 15.890(2)$, $c = 15.713(3)$ Å, $U = 4\,790.6$ Å^3, $Z = 8$, $D_c = 4.28$ Mg m^{-3}, $F(000) = 5\,424$, $\mu(\text{Mo-}K_\alpha) = 9.21$ mm^{-1}, $\lambda = 0.710\,69$ Å, $2\theta_{\text{max.}} = 50°$; 4 316 unique reflections, 3 718 observed reflections [$I \geqslant 2\sigma(I)$], crystal size 0.26 × 0.34 × 0.40 mm.

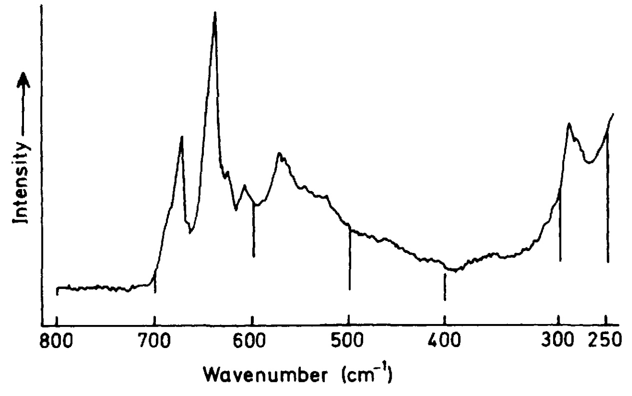


Figure 1. Single crystal Raman spectrum of $5SbF_3{\cdot}3SbF_5$

A suitable crystal was sealed in a glass capillary tube under an atmosphere of dry N_2. The crystal was initially aligned on a precession camera after which it was transferred to a Picker FACS-1 diffractometer equipped with graphite-monochromated Mo-K_α radiation. Cell parameters and an orientation matrix were determined by a least-squares fit to the centred co-ordinates of 43 reflections in the range $35 \leqslant 2\theta \leqslant 45°$. Intensity data were collected using ω–2θ scans at 2°(2θ) min^{-1}. Background intensity was estimated by a standing count of one-tenth of the scan time at each end of the scan; if the reflection was considered significant [$I > 2\sigma(I)$] an analysis of the peak profile was performed.

The structure was solved using the MULTAN-80 system[30] of direct methods programs. After correction of the data for absorption the structure was refined by block-matrix least-squares techniques using weights derived from counter statistics. Scattering factors were taken from ref. 31 and corrected for anomalous dispersion; the function minimised was $\Sigma w(\Delta|F|)^2$. All atoms were assigned anisotropic thermal parameters. The final residuals were $R = (\Sigma\Delta|F|/\Sigma|F|) = 0.057$ and $R' = [\Sigma w(\Delta|F|)^2/\Sigma w|F|^2] = 0.098$ (including unobserved reflections, 0.066 and 0.103 respectively). Atomic co-ordinates are given in Table 3. The programs used were those of Larson and Gabe[32] for the PDP8/A computer.

Discussion

Preparation of $5SbF_3{\cdot}3SbF_5$.—The reaction of $SbF_3{\cdot}SbF_5$ and SbF_5 in AsF_3 solution, with stoicheiometric amounts of PF_3 according to equations (1) and (2) in Table 1, lead to a mixture of products that included single crystals of $5SbF_3{\cdot}3SbF_5$ which were identified by *X*-ray crystallography and Raman spectroscopy (Figure 1 and Table 2). Other products were identified as (β)$6SbF_3{\cdot}5SbF_5$,[12] $3SbF_3{\cdot}SbF_5$,[13] and a cubic phase [$a = 10.1(1)$ Å], which may be $H_3O^+SbF_6^-$ [29b] [$a = 10.130(8)$ Å]. However, the Raman spectra of single crystals of this material differed from that reported for $H_3O^+SbF_6^-$ (see Table 2)[29a] and it could also possibly be a new binary fluoride of antimony. We were unable to prepare a homogeneous sample of highly crystalline $5SbF_3{\cdot}3SbF_5$, although a microcrystalline

Table 3. Final atomic positional parameters (fractional × 10^4) for $5SbF_3{\cdot}3SbF_5$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Sb(1)	5 704.6(4)	4 035.2(5)	221.9(5)
Sb(2)	7 639.7(4)	3 781.6(5)	5 234.8(5)
Sb(3)	7 349.7(5)	2 500	1 216.2(7)
Sb(4)	7 127.0(6)	2 500	−1 375.2(7)
Sb(5)	10 076.9(5)	188.9(6)	7 523.2(5)
Sb(6)	6 060.4(8)	7 500	2 031.8(10)
Sb(7)	10 701.7(6)	2 500	8 572.3(8)
Sb(8)	6 193.5(6)	2 500	3 532.3(7)
Sb(9)	7 663.4(4)	4 901.6(5)	2 457.4(5)
Sb(10)	−841.9(7)	2 500	3 585.8(8)
Sb(11)	6 101.1(4)	5 898.4(5)	4 755.2(5)
F(11)	6 392(5)	4 881(5)	122(6)
F(12)	5 548(4)	4 386(4)	1 382(4)
F(13)	5 000	5 000	0
F(21)	6 829(4)	3 425(5)	5 857(4)
F(22)	8 261(4)	3 398(5)	6 190(5)
F(23)	7 734(5)	2 500	4 975(6)
F(31)	6 623(4)	3 335(5)	914(5)
F(41)	6 515(6)	3 306(9)	−946(5)
F(42)	7 471(5)	2 500	−139(6)
F(51)	10 552(4)	564(5)	6 529(4)
F(52)	9 353(4)	1 072(4)	7 215(5)
F(53)	10 539(4)	1 159(4)	8 162(4)
F(61)	9 564(6)	2 500	6 128(6)
F(71)	11 269(7)	2 500	7 562(7)
F(72)	9 828(5)	2 500	7 853(7)
F(80)	5 628(5)	3 346(6)	3 122(6)
F(81)	6 823(4)	3 338(4)	3 928(5)
F(82)	5 787(8)	2 500	4 620(9)
F(83)	6 661(6)	2 500	2 461(6)
F(84)	6 729(4)	4 838(6)	2 654(6)
F(85)	7 302(5)	3 944(5)	7 658(5)
F(86)	7 915(5)	4 653(6)	3 566(5)
F(87)	8 616(4)	4 919(5)	2 172(5)
F(88)	7 655(4)	3 759(4)	2 151(5)
F(89)	7 458(4)	5 154(5)	1 290(4)
F(90)	−643(5)	1 678(7)	2 810(6)
F(91)	107(7)	2 500	3 951(9)
F(92)	−1 003(6)	1 672(6)	4 422(6)
F(93)	−1 775(7)	2 500	3 272(8)
F(94)	5 688(4)	5 286(5)	3 889(5)
F(95)	5 362(7)	6 660(7)	4 625(7)
F(96)	6 807(6)	5 106(8)	4 792(7)
F(97)	5 621(6)	5 306(7)	5 599(6)
F(98)	6 597(7)	6 514(7)	3 911(6)
F(99)	6 546(6)	6 516(6)	5 597(6)

Table 4. Bond distances (Å), corresponding bond valences,[a] and their correlation to structure types in $5SbF_3\cdot3SbF_5$

$Sb^{III}(1)$	F(11)	F(12)	F(13)	F(31)	F(41)	F(51)	F(91)[b]	F(92)[b]	Total bond valence
Bond valence	0.79	0.73	0.56	0.35	0.22	0.18	0.14		2.97
Bond length	1.891(9)	1.930(7)	2.0735(9)	2.351(8)	2.669(8)	2.838(7)	2.993(8)	3.509(11)[c]	
Structural type[d]			AX_3E	AX_4E		AXY_5E		$AXY_5Y'_2E$ or AX_4Y_4E	

$Sb^{III}(2)$	F(21)	F(22)	F(23)	F(89)[b]	F(81)[b]	F(96)[b]	F(11)	F(92)[b]	F(86)[b]	Total bond valence
Bond valence	0.74	0.63	0.55	0.34	0.22	0.20	0.18	0.14	0.14	3.14
Bond length	1.922(7)	2.011(7)	2.085(2)	2.376(7)	2.677(8)	2.732(11)	2.829(9)	2.988(10)	3.012(8)[c]	
Structural type[d]			AX_3E	AX_4E		AXY_5E			$AXY_5Y'_3E$	

$Sb^{III}(3)$	F(31)	F(31′)	F(42)	F(83)[b]	F(88)[b]	F(88′)[b]	F(99)[b]	F(99′)[b]	Total bond valence
Bond valence	0.66	0.66	0.50	0.35	0.26	0.26	0.18	0.18	3.05
Bond length	1.982(7)	1.982(7)	2.142(10)	2.360(10)	2.551(7)	2.551(7)	2.807(10)	2.807(10)[c]	
Structural type[d]			AX_3E	AX_4E				AX_4Y_4E	

$Sb^{III}(4)$	F(41)	F(41′)	F(42)	F(71)	F(85)[b]	F(85′)[b]	F(98)[b]	F(98′)[b]	Total bond valence
Bond valence	0.83	0.83	0.58	0.28	0.19	0.19	0.15	0.15	3.20
Bond length	1.864(9)	1.864(9)	2.052(10)	2.489(11)	2.772(8)	2.772(8)	2.941(10)	2.941(10)[c]	
Structural type[d]			AX_3E	AX_4E				AX_4Y_4E	

$Sb^{III}(5)$	F(51)	F(52)	F(53)	F(12)	F(87)[b]	F(94)[b]	F(90)[b]	F(97)[b]	F(80)[b]	F(84)[b]	Total bond valence
Bond valence	0.77	0.60	0.59	0.28	0.25	0.24	0.11	0.11	0.09		3.04
Bond length	1.905(7)	2.033(7)	2.042(7)	2.506(7)	2.589(9)	2.605(7)	3.202(11)	3.228(9)	3.360(8)	3.515(9)[c]	
Structural type[d]			AX_3E			AX_3Y_3E				$AX_3Y_3Y'_4E$	

$Sb^{III}(6)$	F(61)	F(72)	F(22)	F(22′)	F(52)	F(52′)	F(98)[b]	F(98′)[b]	Total bond valence
Bond valence	0.84	0.50	0.36	0.36	0.32	0.32	0.08	0.08	2.86
Bond length	1.858(11)	2.139(10)	2.342(7)	2.342(7)	2.421(7)	2.421(7)	3.498(12)	3.498(12)[c]	
Structural type[d]		AX_2E				AXY_5E		$AXY_5Y'_2E$	

Table 4 (*continued*)

$Sb^{III}(7)$	F(71)	F(72)	F(53)	F(53′)	F(21)	F(21′)	F(82)[b]	F(95)[b]	F(95′)[b]	Total bond valence
Bond valence	0.74	0.61	0.41	0.41	0.19	0.19	0.17	0.15	0.15	3.02
Bond length	1.924(11)	2.021(10)	2.248(7)	2.248(7)	2.765(7)	2.765(7)	2.845(14)	2.947(11)	2.947(11)[c]	

Structural type[d]
AX_2E
AX_4E
AXY_5E
$AXY_5Y'_3E$

Bond distances and the corresponding bond valences in the SbF_6^- anions:

$Sb^V(8)$	F(80)	F(80′)	F(81)	F(81′)	F(82)	F(83)		
Bond valence	0.95	0.95	0.75	0.75	0.82	0.74		4.96
Bond length	1.844(8)	1.844(8)	1.902(7)	1.902(7)	1.879(13)	1.908(10)[c]		
$Sb^V(9)$	F(84)	F(85)	F(86)	F(87)	F(88)	F(89)		
Bond valence	1.03	0.88	0.92	0.82	0.83	0.71		5.19
Bond length	1.823(8)	1.862(8)	1.850(8)	1.882(8)	1.878(7)	1.918(7)[c]		
$Sb^V(10)$	F(90)	F(90′)	F(91)	F(92)	F(92′)	F(93)	F(23)	
Bond valence	1.01	1.01	0.74	0.81	0.81	0.90		5.28
Bond length	1.827(9)	1.827(9)	1.908(12)	1.885(9)	1.885(9)	1.857(13)	3.497(10)[c]	
$Sb^V(11)$	F(94)	F(95)	F(96)	F(97)	F(98)	F(99)		
Bond valence	0.92	0.84	0.92	0.86	0.75	0.91		5.20
Bond length	1.851(7)	1.875(11)	1.850(10)	1.868(8)	1.903(9)	1.855(9)[c]		

[a] All bond valences less than 0.08 are omitted. Bond valence units (v.u.) are defined in refs. 22 and 23. [b] Anionic fluorine atom bridge to a cationic antimony atom. [c] Sb ··· F contacts up to 3.55 Å included. [d] Designation of geometry follows that of Gillespie in refs. 24 and 25.

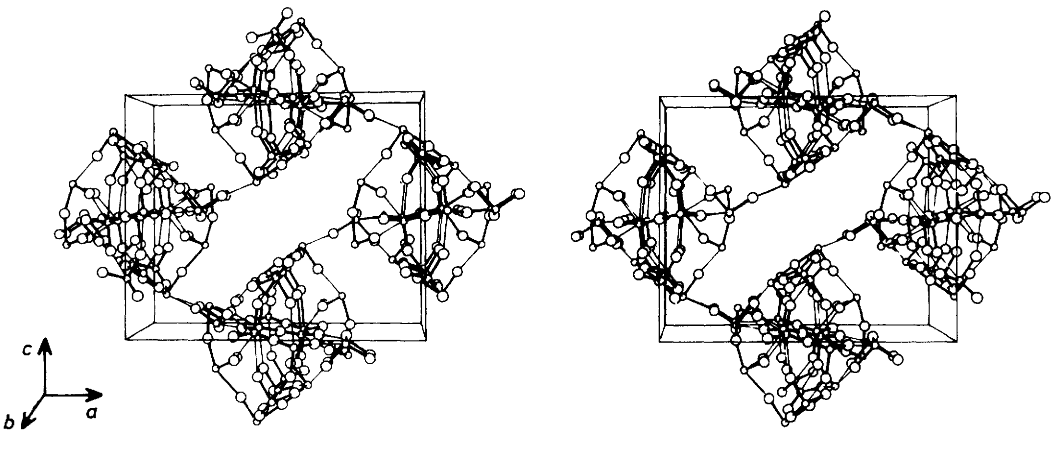


Figure 2. Stereoscopic view of the polymeric cation, $(Sb_5F_{12})_n^{3n+}$ as viewed down the *b* axis

product of a reaction of SbF_5 and PF_3 [Table 1, 2(ii) and (iii)] had a Raman spectrum that was very similar to that of single crystals of $5SbF_3{\cdot}3SbF_5$, and an elemental analysis that was also consistent with this formulation. However we note that the expected analysis results for $2SbF_3{\cdot}SbF_5$ and $5SbF_3{\cdot}3SbF_5$ are very similar indeed, and are both within the expected experimental error of the method. We have been able to identify $SbF_3{\cdot}SbF_5$,[11] (β)$6SbF_3{\cdot}5SbF_3$,[12] $5SbF_3{\cdot}3SbF_5$, and $3SbF_3{\cdot}SbF_5$[13] as reduction products of SbF_5 in AsF_3 or SO_2 solution, but not (α)$6SbF_3{\cdot}5SbF_5$,[19] or $2SbF_3{\cdot}SbF_5$[20] that are prepared by the direct fluorination of antimony metal.

X-Ray Crystal Structure of $5SbF_3{\cdot}3SbF_5$.—The crystal structure of $5SbF_3{\cdot}3SbF_5$ is a complex three-dimensional infinite polymeric network. The bond distances are given in Table 4 and the bond angles are shown in the corresponding figures. The various geometries of the fluorine atoms around the antimony(III) atoms are also listed in Table 4, the description of the geometries following those of Gillespie.[24,25] If only the shorter bond lengths (2.15 Å) are considered, the structure can be considered to be made up of one $Sb_2F_5^+$ cation in the Wyckoff position 4(b) of space group *Pnma*, two different $Sb_2F_5^+$ cations in 4(c), one SbF_3 unit in 8(d), one $Sb_2F_3^{3+}$ cation in 4(c), two SbF_6^- anions in 4(c), and two SbF_6^- anions in 8(d) sites. This cut-off limit (2.15 Å) has been used by other workers[11] to define discrete Sb–F units.

If the discrete SbF_6^- anions are discounted, the rest of the structure can be considered as a polymeric cation, $(Sb_5F_{12})_n^{3n+}$, as shown in Figures 2 and 3, consisting of linked $Sb_2F_5^+$, $Sb_2F_3^{3+}$, and SbF_3 units. The weak bonds between these units are in the range 2.248–2.838 Å (including all contacts < 3.55 Å, sum of van der Waals radii[33]). In addition, there are numerous strong contacts between the 'cation', $(Sb_5F_{12})_n^{3n+}$, and the anionic SbF_6^- units in the range 2.36—3.55 Å, although in general any particular antimony(III) atom forms the strongest of its contacts with other antimony(III) fluorine atoms, and the weakest with $Sb^VF_6^-$ anions.

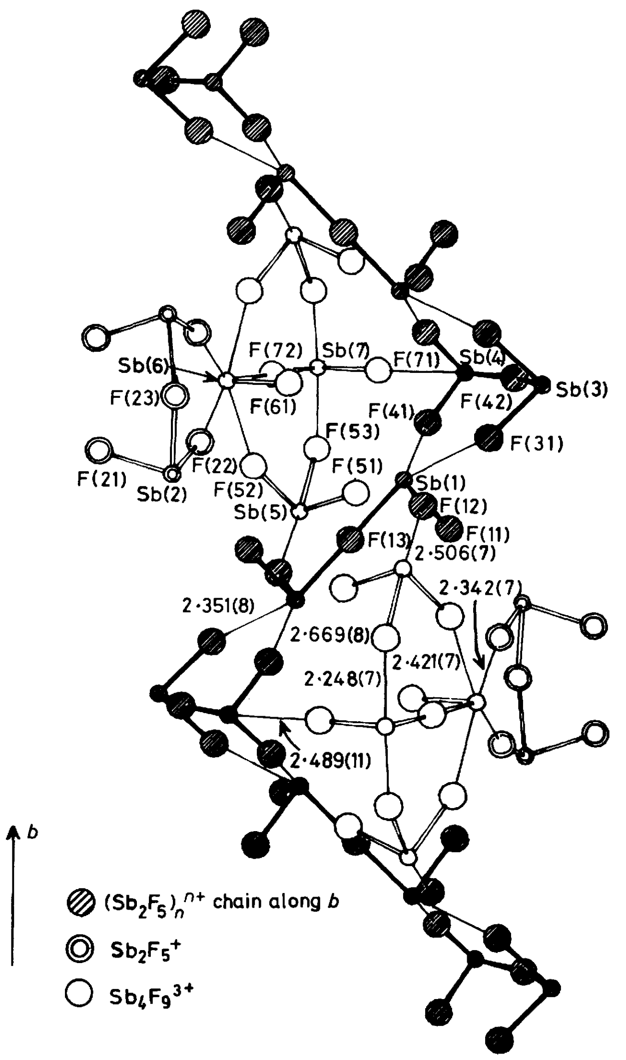


Figure 3. $(Sb_5F_{12})_n^{3n+}$ polymeric cation along the *b* axis in $5SbF_3{\cdot}3SbF_5$ with Sb–F distances (Å) < 2.7 Å

The bond valences for individual bonds as defined by Brown[22,23] are included in Table 4. The total bond valences for antimony atoms are *ca.* 5 or 3 and each fluorine is 1. Most of the fluorine atoms are bonded to two antimony atoms, generally one bond being stronger than the other. Consistently, the variations of the primary Sb–F bond distances are related to the secondary contacts, *i.e.* stronger secondary contacts lead to longer primary bonds. The three bond valences of the Sb^{III} cations are distributed over the various strong and weak Sb–F bonds, and the presence of oxygen (which can be mistaken for F) can be ruled out.

$Sb_2F_5^+$ *Units*. The three different types of $Sb_2F_5^+$ units in $5SbF_3{\cdot}3SbF_5$ are shown in Figure 4 and their shapes and bridging angles are compared with other known $Sb_2F_5^+$ units in $(\alpha)6SbF_3{\cdot}5SbF_5$,[19] $3SbF_3{\cdot}SbF_5$,[13] $(Se_4^{2+})(Sb_2F_4^{2+})(Sb_2F_5^+)(SbF_6^-)_5$,[8] and $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$[34] and related species in Table 5.

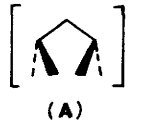
The $Sb_2F_5^+$ unit in Figure 4(*a*) is very similar to the $Sb_2F_5^+$ unit in $(\alpha)6SbF_3{\cdot}5SbF_5$[19] and $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$.[34] Both units have the *trans* configuration and a bridging fluorine at a centre of symmetry ($\bar{1}$). The other two $Sb_2F_5^+$ units [Figure 4(*b*) and (*c*)], although different, both consist of two eclipsed SbF_2 units joined by bridging fluorines. The configurations of all the known $Sb_2F_5^+$ cations and related species are different from each other and are compared in Table 5. The F–Sb–F bond angles and Sb–F bond distances around the antimony atoms for all the $Sb_2F_5^+$ units are very similar (Figure 4), with the bridging fluorine bond angles being either linear or *ca.* 150°. In addition, the two SbF_2 units, joined by the bridging fluorine, are either eclipsed, *trans* or near *trans* to each other.

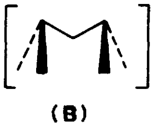
The fact that $Sb_2F_5^+$ cations adopt different configurations and have either bent or linear bridging fluorine bonds leads us to assume that there are small energy differences between the structures. It is likely that the particular configuration adopted minimises the energy of the total solid system. The relative size of bond angles and distances within the $Sb_2F_5^+$ cations (and other units in $5SbF_3{\cdot}3SbF_5$) are in accordance with valence-shell electron-pair repulsion (v.s.e.p.r.) theory[25] within experimental uncertainty, *i.e.* the larger bond angles are associated with shorter bond distances.

SbF_3 *Unit*. The structure of the SbF_3 unit, AX_3E, in $5SbF_3{\cdot}3SbF_5$ is shown in Figure 5. The average bond distances

Table 5. Comparison of $Sb_2F_5^+$ units and related species with Sb–F–Sb bond angles and configurations

Unit	Compound	Bridging bond angles (°)	Configurations
$Sb_2F_5^+$	$5SbF_3{\cdot}3SbF_5$ [a]	180	*trans*
		155.3(5)	Eclipsed } (A)
		155.0(6)	Eclipsed } (A)
	$3SbF_3{\cdot}SbF_5$ [b]	147.4(3)	Eclipsed (**B**)
	$(\alpha)6SbF_3{\cdot}5SbF_5$ [c]	180	*trans*
	$(Se_4^{2+})(Sb_2F_4^{2+})(Sb_2F_5^+)(SbF_6^-)_5$ [d]	149.8(6)	Near *trans*
	$(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$ [e]	180	*trans*
$Sb_2F_5^-$ [f]	$NaSb_2F_5$ [g]	134(2)	Staggered
I_2O_5 [f]	I_2O_5 [h]	139(1)	*gauche*, O-bridging
Sb_2F_4O [f]	$[(NH_2)_2CO]_2Sb_2F_4O$ [i]	125.9	Close to semi-eclipsed, O-bridging


(A)


(B)

[a] This work. [b] Ref. 13. [c] Ref. 19. [d] Ref. 8. [e] Ref. 34. [f] All units have same number of valence electrons (44), and the structures are determined in the solid state. [g] R. R. McDonald, A. C. Larson, and D. T. Cromer, *Acta Crystallogr.*, 1964, **17**, 1104. [h] K. Selte and A. Kjekshus, *Acta Chem. Scand.*, 1970, **24**, 1912. [i] M. Bourgault, R. Fourcade, and G. Mascherpa, *J. Solid State Chem.*, 1981, **36**, 214.

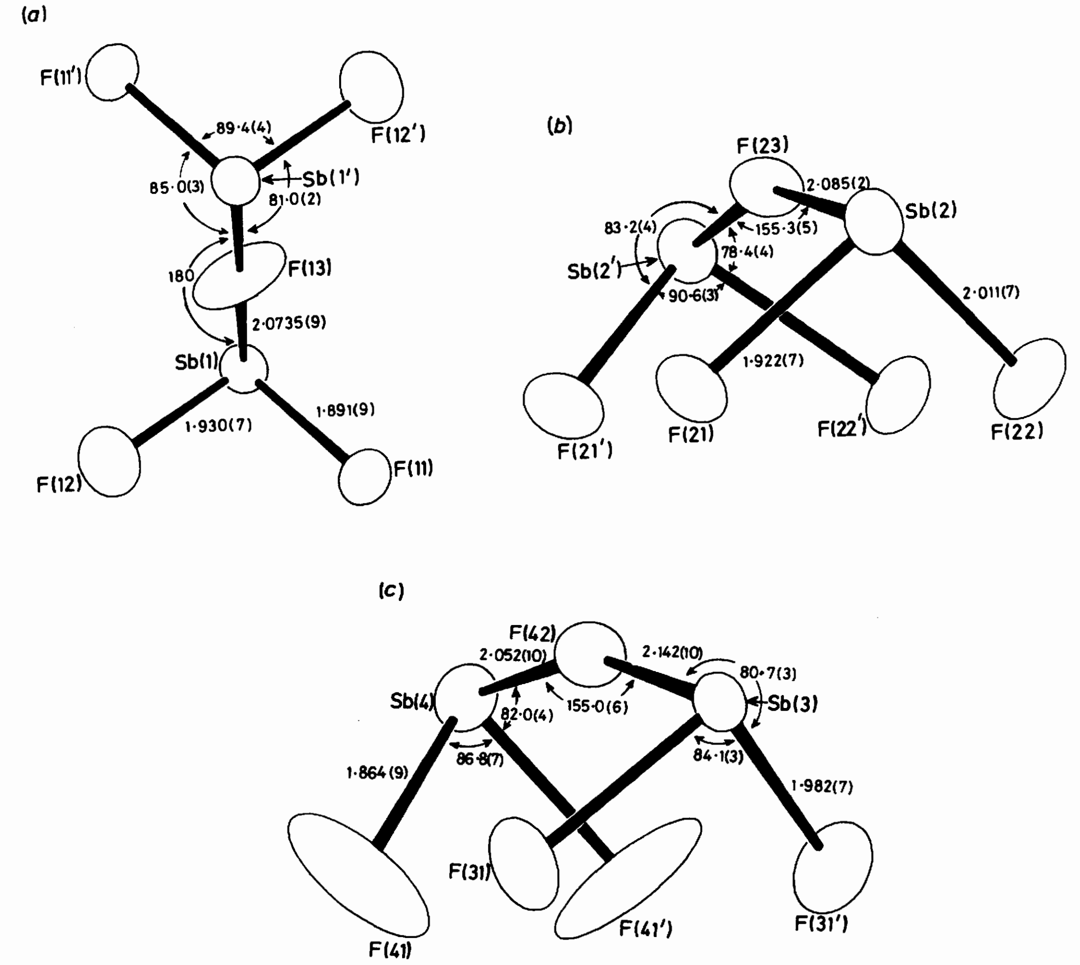


Figure 4. Geometry of (*a*) the centrosymmetric $Sb_2F_5^+$ cation; (*b*) the symmetric $Sb_2F_5^+$ cation; and (*c*) the symmetric $Sb_2F_5^+$ cation

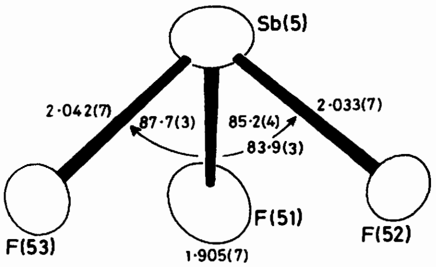


Figure 5. Geometry of the neutral SbF_3 unit

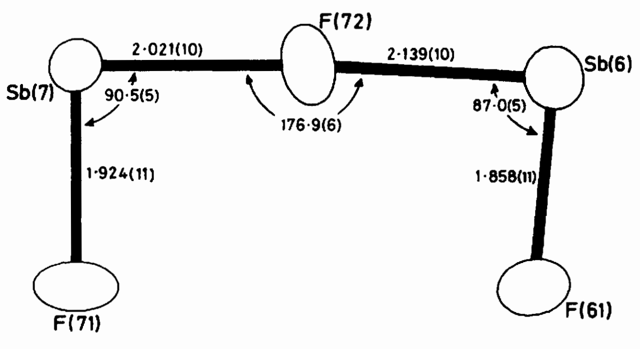


Figure 6. Geometry of the planar eclipsed $Sb_2F_3^{3+}$ cation

and angles [1.993(7) Å, 85.6(4)°] are similar to those of SbF_3 in $3SbF_3{\cdot}SbF_5$ [1.962(8) Å, 85.1(2)°][13] and SbF_3 itself in the solid state [1.93(2) Å, 84(2)°].[15]

$Sb_2F_3^{3+}$ *Cation.* This is the first example of an $Sb_2F_3^{3+}$ cation as far as we are aware and is shown in Figure 6. The Sb(6)F(61) and Sb(6)F(72) distances [1.858(11) and 2.139(10) Å] are shorter and longer than Sb(7)F(71) and Sb(7)F(72) [1.924(11) and 2.021(10) Å] respectively. This suggests that Sb(6) has more SbF^{2+} character [Sb(6)F(61)] while Sb(7) has more SbF_2^{2+} character [Sb(7)F(71)F(72)]. Presumably, a gaseous $Sb_2F_3^{3+}$ cation would adopt a *trans* planar configuration minimising repulsion between lone pairs in the antimony(III) atoms, and electrostatic repulsion between F(61) and F(71). Calculations have shown that the electrostatic repulsion between the two terminal iodine atoms of I_5^+ in $I_5(AsF_6)$[35] accounts for its *trans* planar structure.

It is hardly surprising that $Sb_2F_5^+$ cations are found in $5SbF_3{\cdot}3SbF_5$ (nearly $2SbF_3{\cdot}SbF_5$). However, the existence of $Sb_2F_3^{3+}$ in the presence of SbF_3, a potential fluorine-ion donor, is unexpected at first sight. The problem may be created by the way in which the cations are defined, *i.e.* by ignoring contacts greater than 2.15 Å. In fact, $Sb_2F_3^{3+}$ strongly interacts with two SbF_3 units. If the cut-off limit is increased to 2.25 Å, then the new cation, $Sb_4F_9^{3+}$, is defined with two SbF_3 and one $Sb_2F_3^{3+}$ linked *via* Sb(7)F(53) at 2.248(7) Å, and with additional weaker contacts Sb(6)F(52) at 2.421(7) Å as shown in Figure 7. The sum of bond valence of the contacts between the two SbF_3 units and the $Sb_2F_3^{3+}$ is 1.46 v.u., which justifies the 'isolation' of the

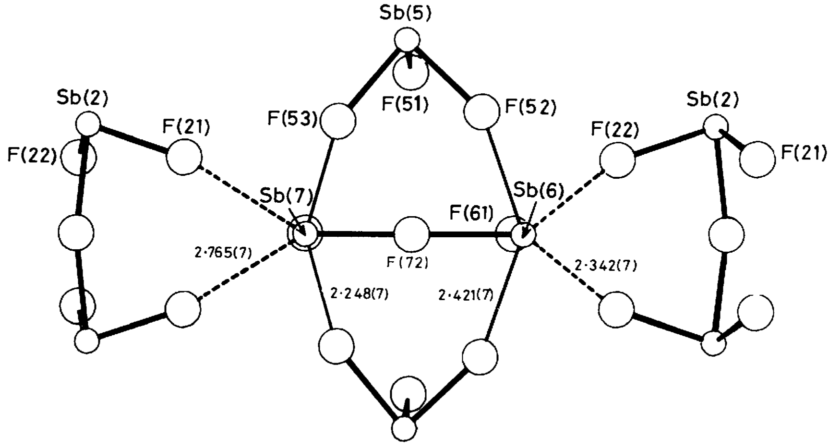


Figure 7. The $Sb_4F_9^{3+}$ cation with contacts (• • •) to two $Sb_2F_5^+$ cations

$Sb_4F_9^{3+}$ cation. With inclusion of contacts less than 2.80 Å, both Sb(6) and Sb(7) are surrounded by five planar fluorine atoms (Figure 7).

SbF_6^- *Anions.* The SbF_6^- anions have a slightly distorted octahedral structure with a mean Sb–F distance of 1.87(3) Å and F–Sb–F angle of 90°.

Polymeric cation, $(Sb_5F_{12})_n^{3n+}$. If only contacts within 2.70 Å are considered, the polymeric cation can be described as consisting of two of the three $Sb_2F_5^+$ cations [Figure 4(*a*) and (*c*)] linked together *via* contacts, Sb(1)F(31) [2.351(8) Å] and Sb(1)F(41) [2.669(8) Å] along the *b* axis to form infinite cation chains, $(Sb_2F_5)_n^{n+}$ (Figure 3). The $Sb_4F_9^{3+}$ cations (Figure 7) are joined to the $(Sb_2F_5)_n^{n+}$ chains through contacts, Sb(4)F(71) [2.489(11) Å] and Sb(5)F(12) [2.506(7) Å]. One of the remaining $Sb_2F_5^+$ cations [Figure 4(*b*)] is joined to the $Sb_4F_9^{3+}$ cation through two strong contacts, 2 × Sb(6)F(22) [2.342(7) Å] to complete the polymeric caton, $(Sb_5F_{12})_n^{3n+}$ as illustrated in Figure 3. Additional long contacts, Sb(7)F(21) [2.765(7) Å] cross-link the polymeric chains to form the infinite three-dimensional polymeric cation as shown in Figure 2.

Co-ordination of fluorine atoms about the various antimony(III) *atoms.* The primary co-ordination sphere around each antimony(III) atom can be defined as that which contains all the fluorine atoms within 2.15 Å. A secondary co-ordination sphere is identified when there is a noticeable gap in the bond lengths (hence bond valences) (see Table 4) as bond distance increases. The co-ordination sphere around each antimony(III) atom is completed by inclusion of contacts to fluorine atoms within 3.55 Å, the sum of the van der Waals radii for antimony and fluorine. The bond distances, bond valences, and the types of co-ordination spheres to which the fluorine atoms belong are listed in Table 4. The Sb^{III}–F distances in $5SbF_3{\cdot}3SbF_5$ and other antimony fluoride binary systems cover a large range. Various geometries of the halogen around the antimony(III) atoms have been extensively reviewed by Gillespie and Sawyer,[24] and our descriptions of the various geometries around the antimony(III) atoms (Table 4) follow this treatment.

Table 6. Fluorine accepting[a] and donating[b] strength of the units in $5SbF_3{\cdot}3SbF_5$

Unit	Sb^{III} atoms	Fluorine accepting strength (v.u.)		Fluorine donating strength (v.u.)	
$Sb_2F_3^{3+}$	Sb(6), Sb(7)	1.60		0.14	
$Sb_2F_5^+$	Sb(1) × 2	0.89	mean 1.07	0.23	mean 0.27
	Sb(2) × 2	1.22		0.28	
	Sb(3), Sb(4)	1.10		0.29	
SbF_3	Sb(5)	1.08		0.30	
SbF_6^-	Sb(8)	0		0.19	mean 0.18
	Sb(9)	0		0.20	
	Sb(10)	0		0.13	
	Sb(11)	0		0.19	

[a] The fluorine accepting strength of a unit is defined as the sum of the bond valences of the fluorine contacts to the antimony atoms in the unit per antimony atom in the unit. [b] The fluorine donating strength of a unit is defined as the sum of the bond valences of terminal fluorine contacts to other antimony atoms per donating fluorine atoms within the unit.

The geometry of the Sb(1) and the surrounding fluorine atoms within the complete co-ordination sphere (< 3.55 Å) can be described as either AX_4Y_4E or $AXY_5Y_2'E$ and it appears that the two geometries are related.* A similar situation has also been observed for one of the Sb^{III} atoms [Sb(2)] in $3SbF_3{\cdot}SbF_5$.[13] However, the geometries of the fluorine atoms around Sb(2), Sb(3), Sb(4), Sb(5), Sb(6), and Sb(7) can be defined unambiguously (see Table 4). In general, the variations of the bond angles are in accordance with v.s.e.p.r. theory.[25]

Suggestions as to why $5SbF_3{\cdot}3SbF_5$ *and other* SbF_3/SbF_5 *Adducts contain Polymeric Antimony*(III) *Fluorocations; and Reasons why* AsF_3 *and* SbF_5 *form an Adduct that can be described as* $AsF_2^+SbF_6^-$, *made in the Context of Brown's Model*[22,23] *of Interaction in the Solid State.*—Each unit in the polymeric cation, $(Sb_5F_{12})_n^{3n+}$, acts as both a fluorine acceptor (Lewis acid) and a fluorine donor (Lewis base). We define the fluorine donating strength of a unit (basicity) as the sum of the bond valences of the terminal fluorine contacts to the antimony atoms in other units per donating fluorine atoms within the unit (*e.g.* $Sb_2F_5^+$ has four donating fluorine atoms to other Sb^{III} containing units, the bridging fluorine atom within the $Sb_2F_5^+$ is not included). The fluorine accepting strength of a unit (acidity) can be defined as the sum of bond valences of the fluorine contacts to the antimony atoms in the unit per antimony atom.

Table 6 lists the fluorine accepting and donating strengths of each discrete unit in $5SbF_3{\cdot}3SbF_5$. The average fluorine accepting strengths in various units are in the following order, $Sb_2F_3^{3+}$ (1.60) > SbF_3 (1.08) ≈ $Sb_2F_5^+$ (1.07) > SbF_6^- (0

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* Description of the geometries of all the fluorine atoms around the Sb^{III} atoms within the complete co-ordination sphere (< 3.55 Å), with the corresponding figures, are included in the SUP No. 56677.

v.u.). The average fluorine donating strengths are in the following order, SbF$_3$ (0.30) > Sb$_2$F$_5^+$ (0.27) > SbF$_6^-$ (0.18) > Sb$_2$F$_3^{3+}$ (0.14 v.u.). Clearly, SbF$_6^-$ can act as a fluorine donor but not an acceptor, since no site for additional Sb$^V \cdots$ F contact is available. However, it is interesting to note that the Sb$_2$F$_5^+$, and Sb$_2$F$_3^{3+}$ cation as well as the SbF$_3$ neutral unit are both good fluorine donors and acceptors despite the formal positive charge on the antimony(III) atoms in the cationic units. Sb$_2$F$_3^{3+}$ has the highest fluorine accepting strength and lowest fluorine donating strength consistent with its high charge.

The fluorine accepting and donating strengths of the SbF$_3$ neutral units in 5SbF$_3$·3SbF$_5$ (1.08 and 0.30 v.u. respectively) and 3SbF$_3$·SbF$_5$[13] (0.98 and 0.30 v.u.) are significantly higher than SbF$_3$ itself in the solid state[15] (0.72 and 0.24 v.u.). Presumably, the high fluorine donating strengths of the neutral SbF$_3$ units in 5SbF$_3$·3SbF$_5$ and 3SbF$_3$·SbF$_5$ are enhanced by the presence of the cationic units such as Sb$_2$F$_5^+$ and Sb$_2$F$_3^{3+}$. The terminal fluorine atoms in the neutral SbF$_3$ unit form strong fluorine contacts to the antimony(III) atoms in the neighbouring cationic units. This decreases the sum of bond valence of the primary Sb–F bonds in the neutral SbF$_3$ units. In order to compensate for the decrease in sum of bond valence around the antimony(III) atom, the number and/or strength of the secondary fluorine contacts will be increased, *i.e.* increasing the fluorine accepting strength.

The synergic effect increases the effective accepting and donating strengths of the cations and SbF$_3$. In general, the strength of the contacts to any particular antimony(III) atom from SbF$_3$ or Sb$_2$F$_5^+$ is stronger than that from SbF$_6^-$ in 5SbF$_3$·3SbF$_5$ [except the weak Sb(2)F(11) contact at 2.829(9) Å]. The reason for this is that the donating strength of the SbF$_6^-$ anion is more or less evenly apportioned among all six fluorines, leading each fluorine atom to have an average donating strength of *ca.* 0.18 v.u. The donating strength for the other units, although lower, are spread over fewer fluorines giving greater donating power per fluorine contact, *e.g.* SbF$_3$, donating strength per unit, 0.91 v.u.; per fluorine, 0.30 v.u. Thus the strong fluorine contacts are between cations and SbF$_3$ units leading, as observed, to the three-dimensional cross-linked polymeric (Sb$_5$F$_{12}$)$_n^{3n+}$ cation in 5SbF$_3$·3SbF$_5$. The other SbF$_3$/SbF$_5$ adducts, for which full structures are known, also contain cations linked into polymeric units. 3SbF$_3$·SbF$_5$[13] contains the chain-like cation (Sb$_3$F$_8$)$_n^{n+}$, (α)6SbF$_3$·5SbF$_5$,[19] a chain of linked (Sb$_6$F$_{13}$)$^{5+}$ units, while (β)6SbF$_3$·5SbF$_5$[12] contains an isolated (Sb$_6$F$_{13}$)$^{5+}$ unit which consists of two fused eight-membered rings. In SbF$_3$·SbF$_5$,[11] the strongest contact to the Sb$_2$F$_4^{2+}$ cation is from the SbF$_6^-$ anion at 2.29(1) Å (0.39 v.u.), however, the strong contact between the Sb$_2$F$_4^{2+}$ cations at 2.33(1) Å (0.36 v.u.) is significant and gave rise to a polymeric chain cation, (Sb$_2$F$_4$)$_n^{2n+}$. Thus a great variety of cations can be envisaged, that are made up of SbF$_3$ and simple cations derived from SbF$_3$, *e.g.* SbF$_2^+$ and SbF^{2+}. This is in contrast to the situation for AsF$_3$/SbF$_5$ where solely AsF$_2^+$SbF$_6^-$[27] is known, and consists of an isolated AsF$_2^+$ cation fluorine-bridged to SbF$_6^-$ anions. Solid AsF$_3$[26] is a weaker acceptor and donor (0.45, 0.45 v.u.*) than solid SbF$_3$ (0.72, 0.72 v.u.).[15] Thus it is not surprising that the donating strength per fluorine atom in AsF$_2^+$ is less than that of SbF$_6^-$ leading to a non-polymeric cation AsF$_2^+$SbF$_6^-$ structure with strong cation–anion interaction.

It would therefore be expected that oxides and fluorides of other antimony and heavier *p* block elements would form a variety of polymeric cations. In fact a number of examples are known, including Sb$_6$O$_7^{4+}$ (bicyclic ring) in Sb$_6$O$_7$(SO$_4$)$_2$,[36] (IO)$_n^{n+}$ (helical infinite chain) in (IO)$_2$SO$_4$,[37] and (TeF$_3$·2TeF$_4$)$_n^{n+}$ (infinite chain) in Os(O)(OTeF$_5$)$_4$·F·TeF$_3$·2TeF$_4$.[38] The situation in the SnF$_2$/BF$_3$ system is reminiscent of that in the SbF$_3$/SbF$_5$ adduct system. For example, 2SnF$_2$·BF$_3$ forms an infinite polymeric cationic chain, (Sn$_2$F$_3$)$_n^{n+}$, and 3SnF$_2$·BF$_3$ consists of layers of connected Sn$_6$F$_{10}^{2+}$ rings.[39]

Packing of Fluorine Atoms.—The structure of 5SbF$_3$·3SbF$_5$ is approximately closely packed with a volume per fluorine of 20.0 Å^3, but the packing is not so efficient as in SbF$_5$[16] (volume per fluorine 17.8 Å^3). However, it has been shown that the lone pair on an Sb^{III} atom can be assumed to occupy a volume similar to that of a fluorine and then the volume per fluorine in 5SbF$_3$·3SbF$_5$ will be 17.1 Å^3, which is similar to that of SbF$_3$ itself (16.8 Å^3),[15] 3SbF$_3$·SbF$_5$ (16.6 Å^3),[13] SbF$_3$·SbF$_5$ (17.3 Å^3),[11] (α)6SbF$_3$·5SbF$_5$ (16.9 Å^3),[19] and (β)6SbF$_3$·5SbF$_5$ (17.1 Å^3).[12]

Acknowledgements

We thank the Natural Sciences and Engineering Research Council (Canada) for financial support.

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Received 23rd May 1986; *Paper* 6/1014