X-Ray Crystal Structure of Tetra-antimony(v) Tridecachloride Heptafluoride, $(Sb_2Cl_{6.5}F_{3.5})_2$

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The title compound has been prepared and characterised by single-crystal *X*-ray crystallography. Crystals are monoclinic with a = 12.921(4), b = 7.423(4), c = 12.921(4) Å, β = 90.10(3), and Z = 4. The structure has been refined in the non-standard space group $I2$ to give a final agreement index R' of 0.116 for 1 129 independent reflections. The structure consists of *cis*-fluorine-bridged tetramers of $SbCl_3F_2$ with two antimony atoms having a chlorine atom partially substituted by fluorine. The problem of disorder in the $SbCl_xF_{5-x}$ species is discussed.

THE synthesis of the first antimony chloride fluoride, reported by Swartz in 1895,[1] involved the reaction of SbF_3 and $SbCl_5$ with an excess of chlorine gas, producing a compound which was identified by elemental analysis as $SbCl_3F_2$. Ruff *et al.*,[2] who prepared other chloride fluorides from the reaction of appropriate mixtures of $SbCl_5$ and SbF_5, characterised the following by elemental analysis: $3SbCl_5{\cdot}SbF_5$, $SbCl_5{\cdot}SbF_5$, and $SbCl_5{\cdot}3SbF_5$. Since this early work the usefulness of the antimony(v) chloride fluorides as powerful Lewis-acid catalysts and as oxidising and halogenating agents has resulted in renewed interest in these materials. The synthesis of $SbCl_4F$, from $SbCl_5$ and AsF_3, was first reported by Kolditz [3] and subsequently shown [4] to be a *cis*-fluorine-bridged tetramer. This compound has also been prepared by the solvolysis of $SbCl_5$ in anhydrous HF, a procedure which also yielded $SbCl_3F_2$ (m.p. 68 °C) and $SbCl_2F_3$.[5] We have prepared $SbCl_3F_2$ (m.p. 62—63 °C) and shown it to be a *cis*-fluorine-bridged tetramer.[6] Since the initial report of $SbCl_2F_3$ by Henne and Trott [7] several groups have claimed its isolation and attributed differing properties and a number of structures to it.[8-10] Preiss [11] has reported the crystal structure of $SbCl_2F_3$ and shown it to be $[Sb^{V}Cl_4][Sb_2^{V}Cl_2F_9]$, but it is difficult to decide whether the earlier workers had indeed prepared this compound. We have recently presented Mössbauer evidence for this compound and confirmed its identity by measuring its unit-cell dimensions.[12] Reaction of $SbCl_5$ and SbF_5 resulted in $[Sb^{V}Cl_4][Sb^{V}_2F_{11}]$,[13] but the m.p. range of the bulk material (69—81 °C) suggests that it contains more than one compound. Other ratios of $SbCl_5$ and SbF_5 have resulted in the novel trimer $Sb_3Cl_{10.7}F_{4.3}$,[12] while other combinations of these reactants have been reported to yield $SbClF_4$.[14]

It is apparent from the above summary that a variety of antimony(v) chloride fluorides can be isolated from the reaction between $SbCl_5$ and SbF_5, or related compounds. The fact that these materials are extremely hygroscopic, coupled with the problems of analysing accurately for fluorine, makes identification of the final products difficult. Even isolation of a single crystal is no guarantee that a stoicheiometric material is present, for the trimer reported by us [12] can be considered to be a mixture of two trimers namely $Sb_3Cl_{11}F_4$ and $Sb_3Cl_{10}F_5$. To add further to the problem we here report the analysis by single-crystal *X*-ray diffraction of $(Sb_2Cl_{6.5}F_{3.5})_2$.

EXPERIMENTAL

Doubly distilled (142—143 °C) SbF_5 (2.41 g) was added to one side of a dry reaction vessel, and freshly sublimed $SbCl_4F$ (3.15 g) was added to the other, separated by a glass frit. All the additions were made in dry nitrogen in a glove-box. Sulphur dioxide, previously dried over P_4O_{10}, was condensed onto the SbF_5 at 196 °C and, when allowed to warm, the SbF_5 dissolved completely. The SbF_5–SO_2 solution was then added to the $SbCl_4F$ which reacted immediately, producing a clear solution. The solution was stirred for 2 h after which the SO_2 was slowly distilled to the other side of the reaction vessel leaving a clear oil. The oil was placed in an evacuated sublimation apparatus, the cold finger of which was cooled with solid carbon dioxide–acetone. A white solid, m.p. 49—54 °C, formed on the cold finger. A suitable single crystal was grown by application of a temperature gradient of 30—60 °C to a sample of this material in a glass capillary.

Crystal Data.—$Cl_{13}F_7Sb_4$, Monoclinic, $M = 540.7$, $a = 12.921(4)$, $b = 7.423(4)$, $c = 12.921(4)$ Å, $\beta = 90.10\ (3)°$, $U = 1\,239.3$ Å^3, $Z = 4$, $D_c = 2.90$ g cm^{-3}, $F(000) = 976$, $\lambda(\text{Mo-}K_\alpha) = 0.710\ 69$ Å, and $\mu(\text{Mo-}K_\alpha) = 53.0$ cm^{-1}. The unit-cell parameters were obtained from a least-squares refinement of 15 reflections in the region $15 < 2\theta < 20°$. The diffractometer data indicated that reflections were absent for hkl when $h + k + l = 2n + 1$, characteristic of the space groups $I2$, Im, and $I2/m$. The structure was successfully refined in $I2$, which is an alternative setting for the standard space group $C2$ (no. 5).[15] The equivalent positions for $I2$ are: x,y,z; $\bar{x}, y, \bar{z}$; $\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$. The body-centred space group was chosen because of its similarity to that of $SbCl_3F_2$ and $SbCl_4F$, namely $I4$.

X-Ray Intensity Measurements.—The crystal, which was an irregular sphere of diameter *ca.* 0.2 mm, was sealed in a quartz capillary and mounted on a syntex $P\bar{1}$ automatic diffractometer so that its c axis was approximately coincident with the ϕ axis of the diffractometer. Intensities were measured with graphite-monochromated radiation, using a θ—2θ scan, with a scan rate varying from 8.0 to 24.0° min^{-1} in 2θ so that weaker reflections were examined more slowly to minimise counting errors. Stationary background counts, with a time equal to half the scan time for each reflection, were made at the end of the scan range. One standard reflection was monitored regularly to check the stability and alignment of the crystal, but no significant change in intensity was observed. Data were collected in the triclinic cell: $a = 9.856(6)$, $b = 9.864(6)$, $c = 7.432(7)$ Å, $\alpha = 112.08(6)$, $\beta = 112.19(5)$, and $\gamma = 81.87(5)°$. In this cell a total of 3 810 reflections was measured within the range $2\theta < 50°$. Subsequent averaging resulted in a total of 3 618 independent reflections of which 2 214 had intensities greater than three times their standard error, based on counting statistics. Lorentz, polarisation, and spherical absorption corrections were applied to the observed intensities. On applying a Delaunay reduction to this cell a pseudo-body-centered tetragonal cell (a 12.924, c 7.423 Å) was obtained. However, on transposing the data into this cell, reflections of the type hkl and $h\bar{k}l$ were not equivalent. Hence the true cell was body-centered monoclinic, the accurate cell dimensions of which were determined from the automatic indexing program using the same reflections as had been used for the triclinic cell. It was not possible to re-collect the data in the monoclinic cell because the crystal had decomposed.

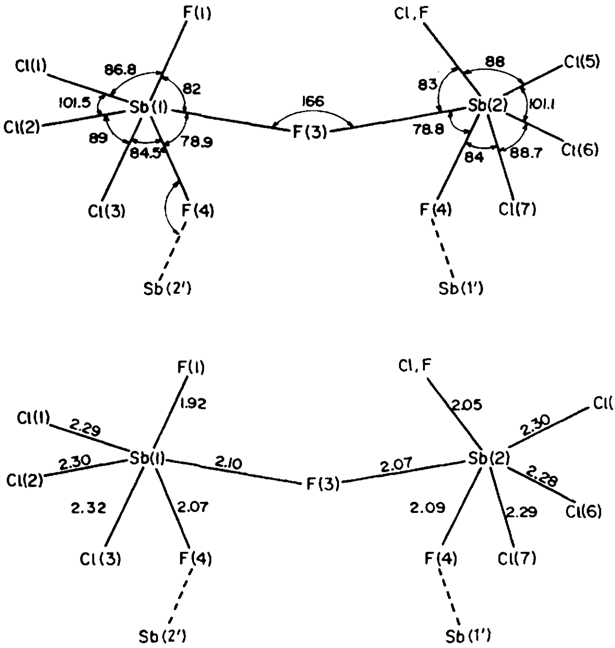

FIGURE 1 The octahedral co-ordination of light atoms about each antimony with bond lengths and selected bond angles

Solution and Refinement of the Structure.—Since the unit-cell dimensions were similar to those of $SbCl_3F_2$ with b and c interchanged the atomic co-ordinates of that cell were used as trial parameters. Since $Z = 8$ for $SbCl_3F_2$ and 4 for the present compound an extra molecular unit was placed at $-z, y, x$. Scattering curves for neutral atoms were applied, with those of antimony corrected for anomalous dispersion using the values for the real and imaginary parts given in the International Tables. Least-squares refinement of positional and isotropic thermal parameters gave a conventional R index of 0.135. Examination of the geometry indicated that one of the Sb–F bond lengths was longer than the generally accepted value but was shorter than a normal Sb–Cl bond. This suggested that this atom was partially substituted by chlorine. Hence an atom having a variable chlorine : fluorine ratio was put into this site and the occupational parameters only were varied. The R index was reduced to 0.128 with the occupational parameters being effectively unchanged. Anisotropic temperature factors were introduced for the antimony atoms and further refinement led to a final $R' = [\Sigma w(|F_o|^2 - F_c^2)|/\Sigma wF_o^2]^{\frac{1}{2}} = 0.116$ for the 1 129 reflections where $w^{\frac{1}{2}} = (117.6 - 1.87F_o + 0.001F_o^2)^{-1}$. The largest shift Δ/σ in the final cycle was 0.1, and a final difference electron-density map revealed no peak >0.45 e Å^{-3}. A list of observed and calculated structure factors and thermal parameters is available as Supplementary Publication No. SUP 22351 (13 pp.).* The final atomic parameters, bond lengths, and bond angles are given in Tables 1 and 2 respectively, the geometries about the two distinct antimony atoms are in Figure 1, and the packing diagram is in Figure 2. Computations were carried out using programs from the '*X*-Ray '71' system and a locally written program CUDLS.

TABLE 1

Final positional parameters for $(Sb_2Cl_{6.5}F_{3.5})_2$

	x/a	y/b	z/c
Sb(1)	−472(2)	0 000	221.5(2)
Sb(2)	−221.4(2)	−47.1(2)	1.5(1)
Cl(1)	−204(1)	−34(2)	301(1)
Cl(2)	60(1)	43(2)	361(1)
Cl(3)	−37(1)	306(2)	187(1)
Cl(5)	−302(1)	−31(2)	−205(1)
(Cl,F)	−207(3)	−273(2)	−42(3)
Cl(6)	−361(1)	44(2)	59(1)
Cl(7)	−190(2)	305(3)	−39(2)
F(1)	−45(2)	−257(6)	209(2)
F(3)	79(2)	−16(6)	120(2)
F(4)	−122(2)	−14(6)	80(2)

TABLE 2

Interatomic bond lengths and bond angles for $(Sb_2Cl_{6.5}F_{3.5})_2$

(*a*) Bond lengths (Å)

Sb(1)–F(1)	1.92(2)	Sb(2)–Cl,F	2.05(2)
Sb(1)–F(3)	2.10(2)	Sb(2)–Cl(5)	2.30(1)
Sb(1)–F(4)	2.07(2)	Sb(2)–Cl(6)	2.29(2)
Sb(1)–Cl(1)	2.29(1)	Sb(2)–Cl(7)	2.28(2)
Sb(1)–Cl(2)	2.30(1)	Sb(2)–F(3)	2.07(2)
Sb(1)–Cl(3)	2.32(1)	Sb(2)–F(4)	2.10(2)

(*b*) Bond angles (°)

F(1)–Sb(1)–F(2)	82(1)	Cl,F–Sb(2)–F(3)	83(1)
F(1)–Sb(1)–F(4)	83(1)	Cl,F–Sb(2)–F(4)	82(1)
F(1)–Sb(1)–Cl(1)	86.8(4)	Cl,F–Sb(2)–Cl(5)	88(1)
F(1)–Sb(1)–Cl(2)	101.4(4)	Cl,F–Sb(2)–Cl(6)	101(1)
F(1)–Sb(1)–Cl(3)	163.2(5)	Cl,F–Sb(2)–Cl(7)	164(1)
F(3)–Sb(1)–F(4)	78.9(8)	F(3)–Sb(2)–F(4)	78.8(1)
F(3)–Sb(1)–Cl(1)	164.5(9)	F(3)–Sb(2)–Cl(5)	89.5(7)
F(3)–Sb(1)–Cl(2)	91.8(7)	F(3)–Sb(2)–Cl(6)	168.9(8)
F(3)–Sb(1)–Cl(3)	83.8(1.1)	F(3)–Sb(2)–Cl(7)	86(1)
F(4)–Sb(1)–Cl(1)	88.7(7)	F(4)–Sb(2)–Cl(5)	165.6(1)
F(4)–Sb(1)–Cl(2)	169.1(8)	F(4)–Sb(2)–Cl(6)	91.1(8)
F(4)–Sb(1)–Cl(3)	84.5(1.1)	F(4)–Sb(2)–Cl(7)	84(1)
Cl(1)–Sb(1)–Cl(2)	101.5(4)	Cl(5)–Sb(2)–Cl(6)	101.1(5)
Cl(1)–Sb(1)–Cl(3)	104.3(6)	Cl(5)–Sb(2)–Cl(7)	103.1(8)
Cl(2)–Sb(1)–Cl(3)	89.0(6)	Cl(6)–Sb(2)–C(7)	88.7(6)
Sb(1)–F(3)–Sb(2)	166(1)		
Sb(1)–F(4)–Sb(2)	168(1)		

DISCUSSION

In the atomic arrangement (Figure 1) each antimony atom has an octahedral co-ordination of halogens. The antimony atoms are linked by symmetrical *cis*-fluorine bridges to form a tetramer as in $SbCl_3F_2$,[6] $SbCl_4F$,[4] and other pentafluorides and tetrachloride fluorides of antimony, niobium, and tantalum.[16-19] Two of the antimony atoms opposite each other in the tetramer have, in addition to two bridging fluorines, three chlorine atoms and a fluorine to complete their distorted octahedral

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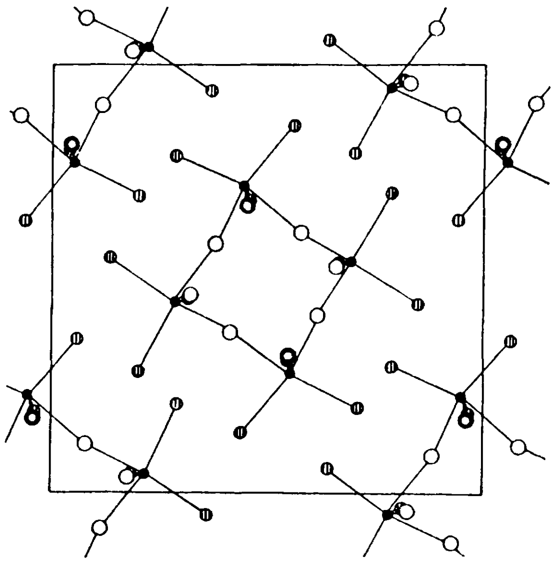
* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

environments. These sites resemble those in $SbCl_3F_2$.[6] The remaining two antimony atoms also have three terminal chlorines and two bridging fluorines while the sixth position consists of 50% (47 ± 3) chlorine and of 50% fluorine. As in $SbCl_3F_2$ [6] and $Sb_3Cl_{10\cdot7}F_{4\cdot3}$,[12] the terminal fluorines and the disorder positions are all on the same side of the tetramer (Figure 1).

The mean Sb–Cl bond length (2.30 Å) is insignificantly different to that found for $SbCl_4F$ (2.29 Å) [4] but is slightly larger than the corresponding bond lengths in $SbCl_3F_2$,[6] $Sb_3Cl_{10\cdot7}F_{4\cdot3}$,[12] and $Sb_3Cl_9F_4O$ [20] of 2.25, 2.26, and 2.26 Å respectively. The terminal Sb–F bond length (1.92 Å) is the same as that found in $SbCl_3F_2$,[6] which falls between the values found for $Sb_3Cl_{10\cdot7}F_{4\cdot3}$ (1.87 Å) [12] and $Sb_3Cl_9F_4O$ (1.94 Å).[20] This is much larger than in other antimony–fluorine systems [11,21,22] and has already been attributed to the effect of the relatively bulky chlorine atoms.[6]



● Sb, ◍ Cl, ○ F, (Cl,F) ○

FIGURE 2 Projection of the structure down the *b* axis

The Sb–F bridge bonds are symmetric at 2.09 Å and are comparable to the mean values in the other chloride fluoride structures, [4,6,12] although in $SbCl_4F$,[4] and in one position in $Sb_3Cl_{10\cdot7}F_{4\cdot3}$, the bridge is asymmetric. Once again these bridging Sb–F distances are larger than those found in the $[Sb_2F_{11}]^-$ (ref. 21) and $[Sb_2Cl_2F_9]^-$ anions.[11] This is surprising since the negative charge on the anions might have been expected to lengthen these bonds. Undoubtedly, the presence of the bulky chlorine atoms is a more dominant effect.

As with the $SbCl_3F_2$ tetramer [6] the title molecule also shows distortion of the octahedral arrangement of the halogens about each antimony. Two of the Cl–Sb–Cl angles are opened up to 102—103° while the remaining angle is 89°. This opening of these angles of necessity results in a corresponding closing down, from 90°, of the F–Sb–F angles: these range from 79 to 83°, *i.e.* slightly greater than in $SbCl_3F_2$.[6] Again we see two Cl–Sb–F angles less than 80° with the third at 101°. The surprising feature of the angular arrangements at each antimony site is their similarity. Since the Sb(2)–F(terminal) position is 50% substituted by chlorine one might have expected that the angular arrangements at Sb(2) would be between those at Sb(1) and those found in $SbCl_4F$.[4] However, the angular arrangements at Sb(1) and Sb(2) are virtually identical and are much more distorted than in the $SbCl_4F$ tetramer. It is also found that the Sb–F–Sb angles (167°) resemble those in $SbCl_3F_2$ (164°) [6] rather than the 173° found for $SbCl_4F$.[9] It has been suggested that Sb–F–Sb angles of *ca.* 170° are indicative of a somewhat distorted, cubic, close-packed arrangement of halogens.[15] The title compound fits this general description with the deviation from the idealised 180° being the result of the two different halogen sizes, *i.e.* the bridging angle decreases with increasing chlorine content of the tetramer.

TABLE 3

Unit-cell dimensions for a number of antimony chloride fluorides

	a	*b*	*c*			Volume per
		Å		β/°	*U*/Å³	halogen
SbF_5	19.00	14.10	5.29	94.0	1 414	17.7
$[Sb^VCl_4][Sb^V_2F_{11}]$	12.95	10.53	11.60	96.4	1 572	26.2
$[Sb^VCl_4][Sb^V_2Cl_2F_9]$	11.7	10.4	13.2	94.2	1 600	26.7
$SbCl_3F_2$	12.81	12.81	7.28	tetragonal	1 194	29.9
$(Sb_2Cl_{6\cdot5}F_{3\cdot5})_2$	12.92	7.42	12.92	90.1	1 239	30.9
$Sb_3Cl_{10\cdot7}F_{4\cdot3}$	12.37	16.48	9.39	103.96	1 856	30.9
$SbCl_4F$	12.87	12.87	7.84	tetragonal	1 298	32.5

In $SbCl_4F$, $SbCl_3F_2$, and the title compound it is apparent (Table 3) that the unit-cell dimensions are remarkably similar, in spite of the fact that the first two compounds are tetragonal while the latter is monoclinic. From this close similarity it is possible that the cell dimensions are determined by the close packing of the larger chlorines since replacing one terminal chlorine in the $SbCl_4F$ structure by a terminal fluorine has little effect on the unit-cell dimensions. Therefore we conclude that it is possible to obtain all the possible combinations of $SbCl_3F_2$ and $SbCl_4F$. Stated another way, the terminal fluorine in the $SbCl_3F_2$ tetramer could be systematically replaced by chlorine until $SbCl_4F$ is formed and the formulae should perhaps be represented as $Sb_4Cl_{12+x}F_{8-x}$ (x = 0—4). Since these three molecules are all prepared in similar ways and are closely similar in structure it is not surprising that so many different claims have appeared in the literature for $SbCl_3F_2$. The many differing melting points and the claimed changes on sublimation, *etc.* were undoubtedly due to the changing value of x in $Sb_4Cl_{12+x}F_{8-x}$.

We have also noted that disorder occurs in the only well documented trimeric molecule $Sb_3Cl_{10\cdot7}F_{4\cdot3}$ [12] in this series of chloride fluorides of antimony. In view of the above discussion it may be possible to isolate and characterise the molecules $Sb_3Cl_{11}F_4$ and $Sb_3Cl_{10}F_5$. Despite many attempts, we have not been able to accomplish this; $Sb_3Cl_{10\cdot7}F_{4\cdot3}$ appears to sublime unchanged and gives a constant melting point. Two other chloride fluorides have been reported, namely $[\mathrm{Sb^{V}Cl_4}][\mathrm{Sb^{V}_2Cl_2F_9}]$ [11] and $[\mathrm{Sb^{V}Cl_4}][\mathrm{Sb^{V}_2F_{11}}]$.[13] We have authenticated the former stoicheiometry by crystallography, Mössbauer spectroscopy,[22] and Raman spectroscopy [23] and have suggested that the antimony atoms are arranged so as to form a triangle, the cation and anion being associated through weak fluorine bridges.[12] The crystallographic evidence for $[\mathrm{Sb^{V}Cl_4}][\mathrm{Sb^{V}_2F_{11}}]$ is not particularly convincing, nor is the other physical evidence.[13] The unit-cell dimensions for this compound are very similar to those for the $[\mathrm{Sb_2Cl_2F_9}]^-$ analogue (Table 3) and it seems possible that there is, once again, a disorder problem with the $[\mathrm{Sb^{V}Cl_4}][\mathrm{Sb^{V}_2F_{11}}]$ salt. A terminal fluorine in the $[\mathrm{Sb_2F_{11}}]^-$ anion could easily be partially substituted by chlorine, in molecules of similar cell dimensions, to give a mixture of the $[\mathrm{Sb_2F_{11}}]^-$ and $[\mathrm{Sb_2Cl_2F_9}]^-$ anions and hence explain the large m.p. range.[13] We have obtained a material which we believe to be $[\mathrm{Sb^{V}Cl_4}][\mathrm{Sb^{V}_2F_{11}}]$ based on Mössbauer [22] and Raman spectroscopic data,[23] but we have so far been unable to obtain a single crystal in order to check unit-cell dimensions or the structure.

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