Preparation of Antimony(v) Trichloride Difluoride and its Characterization by Means of *X*-ray Crystallography, Antimony-121 Mössbauer, and Raman Spectroscopy

By **Jack G. Ballard, Thomas Birchall,*** and **David R. Slim**, Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, Ontario L8S 4M1, Canada

Antimony trichloride difluoride has been prepared by the reaction of $SbCl_4F$ and SbF_5 in liquid SO_2 and has been characterized by single-crystal *X*-ray diffraction studies and by Raman and Mössbauer spectroscopy. Crystals are tetragonal with $a = 12.81(1)$, $c = 7.282(7)$ Å, $U = 1\,194.6$ Å^3, $Z = 8$, and $D_c = 2.96$ g cm^{-3}. The structure has been refined in the space group $I4$ to a conventional R' index 0.073 for 265 independent reflections. The structure consists of *cis*-fluorine-bridged tetramers with each antimony having a distorted octahedral arrangement of three chlorines and three fluorines.

ELEMENTS of Group 5 form a wide variety of compounds with the halogens. A number of the pentachlorides and pentafluorides are powerful Lewis-acid catalysts and have a wide variety of industrial applications. Perhaps the most important of these is antimony pentafluoride which has a polymeric fluorine-bridged structure in the liquid state[1,2] and a *cis*-fluorine-bridged tetrameric structure in the solid state.[3] The tetrachloride fluorides of antimony,[4] niobium,[5] and tantalum[6] also have a tetrameric structure. We have recently reported preliminary evidence for antimony trichloride difluoride[7] and now present complete *X*-ray crystallographic evidence, together with Raman and Mössbauer spectroscopic data, which shows that this molecule also has a fluorine-bridged cyclic tetrameric structure.

EXPERIMENTAL

In a typical experiment $SbCl_4F$ (0.719 g) was added to one half of a dry Pyrex double ampoule in a dry-box; SbF_5 (0.206 g) was added to the other half and the vessel was evacuated. Sulphur dioxide (25 cm^3) was condensed on to the SbF_5, cooled to −196 °C, and the vessel was sealed. After warming to room temperature the SO_2–SbF_5 solution was poured on to the $SbCl_4F$. The mixture was stirred for 8 h and the solution was filtered. The SO_2 was evaporated yielding a colourless crystalline solid, m.p. 62—63 °C. Suitable crystals for *X*-ray studies were obtained by vacuum sublimation at 50 °C in a thin-walled quartz capillary. The Mössbauer spectrum was recorded at 4 K and was analyzed by procedures already described.[8,9] Raman spectra were recorded using an argon-ion (5 145 Å) laser with a Spex 1400 spectrophotometer system.

TABLE 1

Final positional and thermal * parameters ($\times 10^4$) for $SbCl_3F_2$

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb	−473(2)	2 214(2)	0	361(20)	361(20)	1 051(30)	38(16)	31(44)	−212(36)
				U/Å^2					
Cl(1)	−2 026(10)	2 979(11)	−356(27)	671(41)					
Cl(2)	−596(11)	2 624(11)	368(33)	785(44)					
Cl(3)	−393(23)	1 846(20)	3 077(29)	948(79)					
F(1)	802(17)	1 234(17)	−319(49)	433(67)					
F(2)	−410(27)	2 027(23)	−2 614(43)	474(79)					

* The anisotropic temperature factors are given by the expression $\exp[-2\pi^2(a^{*2}h^2U_{11} + b^{*2}k^2U_{22} + c^{*2}l^2U_{33} + 2a^*b^*hkU_{12} + 2a^*c^*hlU_{13} + 2b^*c^*klU_{23})]$.

Crystal Data.—$SbCl_3F_2$, Tetragonal, $a = 12.81(1)$, $c = 7.282(7)$ Å, $U = 1\,194.6$ Å^3, $Z = 8$, $D_c = 2.96$ g cm^{-3}, F.W. = 266.1, $F(000) = 960$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, and $\mu(\text{Mo-}K_\alpha) = 59$ cm^{-1}. The unit-cell parameters were obtained from a least-squares refinement of 15 reflections in the range $20 \leqslant 2\theta \leqslant 25°$. Weissenberg and precession photographs revealed the systematic absences hkl when $h + k + l \neq 2n$ which are characteristic of the space groups $I4$, $I\bar{4}$, and $I4/m$. The structure was successfully refined in the space group $I4$ (no. 79 C_4^5).[10]

X-*Ray Measurements.*—A crystal of dimensions *ca.* 0.20 × 0.12 × 0.12 mm was examined on a four-circle Syntex PT automatic diffractometer with a fine-focus molybdenum anode tube and a graphite monochromator [$\lambda(\text{Mo-}K_\alpha)$ 0.710 69 Å]. The crystal was mounted with its 0.20-mm edge, which was perpendicular to the c axis, approximately coincident with the ϕ axis of the diffractometer. Data were collected in a similar manner to that described previously.[11] A total of 875 reflections was collected within an octant with $2\theta \leqslant 50°$. Subsequent averaging resulted in 265 independent reflections, of which 185 had intensities greater than three times their standard deviation based on counting statistics. Structure factors were calculated by application of Lorentz and polarization corrections.

Solution and Refinement of the Structure.—The three-dimensional Patterson function, which could only be satisfactorily interpreted by assuming the space group to be $I4$, revealed the position of one independent antimony atom. Two cycles of least-squares refinement using an overall scale factor and positional and isotropic thermal parameters gave an R index of 0.32. Scattering curves for neutral antimony were corrected for anomalous dispersion using the values for the real and imaginary parts given in the International Tables.[12] The positions of five light atoms were located from a three-dimensional electron-density map. Two of these atoms were *ca.* 2.0 Å from the antimony and were assumed to be fluorine; the other atoms were *ca.* 2.3 Å and were assumed to be chlorine. Full-matrix least-squares refinement gave an R index of 0.13. An absorption correction was applied and anisotropic temperature factors were introduced for the antimony. This led to a final $R'\{= [\Sigma w(|F_o|^2 - |F_c|^2)/\Sigma w F_o^2]^{\frac{1}{2}}\}$ of 0.0732 for the 265 reflections, where $w = (96.6 - 0.62|F_o| + 0.003|F_o|^2)^{-\frac{1}{2}}$. The final R index was 0.0622 and the largest shift Δ/σ was 0.1 in the final cycle of refinement. A final difference electron-density map showed no significant peaks. Observed and calculated structure factors are given in Supplementary Publication No. SUP 22050 (3 pp.).* Final positional and thermal parameters are listed in Table 1 and interatomic bond lengths and angles in Table 2. The geometry about each antimony is given in Figure 1 and the packing diagram in Figure 2.

DISCUSSION

Each antimony is surrounded by three *cis*-chlorine atoms and three *cis*-fluorine atoms, including two bridging fluorines, giving it octahedral co-ordination.

---

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

[1] C. J. Hoffman and W. L. Jolly, *J. Phys. Chem.*, 1958, **62**, 364.

[2] J. Bacon, P. A. W. Dean, and R. J. Gillespie, *Canad. J. Chem.*, 1970, **48**, 3413.

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

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

[5] H. Preiss and P. Reich, *Z. anorg. Chem.*, 1968, **19**, 362.

[6] H. Preiss, *Z. anorg. Chem.*, 1966, **272**, 346.

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

[8] T. Birchall and A. F. Reid, *J. Solid-State Chem.*, 1975, **13**, 351.

[9] J. G. Ballard, T. Birchall, R. Fourcade, and G. Masherpa, *J.C.S. Dalton*, 1976, 2409.

[10] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 1.

[11] R. J. Gillespie, D. R. Slim, and J. E. Vekris, *J.C.S. Dalton*, 1977, 971.

[12] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

The $SbCl_3F_2$ units are linked by symmetric *cis*-fluorine bridges to form a tetramer. In this respect the compound resembles the pentafluorides and tetrachloride fluorides of antimony, niobium, and tantalum.[3-6,13]

The mean Sb–Cl bond length (2.25 Å) is comparable to the corresponding means (2.26 Å) in both $Sb_3Cl_{10\cdot7}F_{4\cdot3}$ [14] and $Sb_3Cl_9F_4O$.[15] Other antimony chloride fluorides, namely $[SbCl_4][Sb_2F_{11}]$ [16] and $[SbCl_4][Sb_2Cl_2F_9]$ [17] have mean Sb–Cl distances of 2.18 and 2.23 Å respectively. However, the former compound has not been refined to a satisfactory level, while in the latter compound one might have expected to find two Sb–Cl distances, one for the cation and another, somewhat larger, value for the anion, but this was not observed.

TABLE 2

Bond lengths (Å) and angles (°) in $SbCl_3F_2$

Sb–Cl(1)	2.23(1)	Cl(1)–F(1′)	2.97(3)
Sb–Cl(2)	2.28(2)	Cl(1)–F(2)	2.91(4)
Sb–Cl(3)	2.29(2)		
Sb–F(1)	2.07(2)	F(1)–F(1′)	2.67(3)
Sb–F(1′)	2.07(2)	F(1)–F(1″)	2.67(3)
Sb–F(2)	1.92(3)	F(1)–F(2)	2.50(4)
		F(1)–F(2″)	2.52(4)
Cl(1)–Sb–Cl(2)	101.6(5)	Cl(3)–Sb–F(1)	87(1)
Cl(1)–Sb–Cl(3)	104.1(9)	Cl(3)–Sb–F(1′)	87(1)
Cl(1)–Sb–F(1)	163(1)	Cl(3)–Sb–F(2)	160(1)
Cl(1)–Sb–F(1′)	87.2(7)		
Cl(1)–Sb–F(2)	88(1)	F(1)–Sb–F(1′)	80.2(9)
		F(1)–Sb–F(1′)	77(1)
Cl(2)–Sb–Cl(3)	91.2(9)		
Cl(2)–Sb–F(1)	91.1(7)	F(1′)–Sb–F(2)	78(1)
Cl(2)–Sb–F(1′)	171.1(7)		
Cl(2)–Sb–F(2)	100.9(9)	Sb–F(1)–Sb′	164(2)

The Sb–F(terminal) bond length (1.92 Å) is similar to the corresponding distances found in $Sb_3Cl_{10\cdot7}F_{4\cdot3}$ [14] and $Sb_3Cl_9F_4O$,[15] *i.e.* 1.87 and 1.94 Å. All these bond lengths are longer than those found for the $[Sb_2F_{11}]^-$ ion in $[ClO_2][Sb_2F_{11}]$ (1.82 Å) [18] and for the $[SbF_6]^-$ ion in $[ClF_2][SbF_6]$ (1.8 Å).[19] These observed increases in length may be attributed to the relatively bulky chlorine atoms causing a drift of electrons towards the more electronegative fluorine atoms.

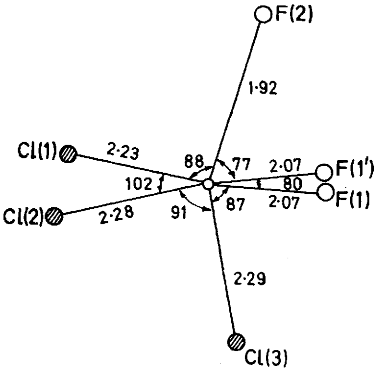

FIGURE 1 The octahedral co-ordination of light atoms about antimony with bond lengths (Å) and selected bond angles (°)

The Sb–F(bridge) bond length (2.07 Å) is also longer than that found in $[ClO_2][Sb_2F_{11}]$ (2.01 Å) [18] but is similar to the mean values found in $Sb_3Cl_{10\cdot7}F_{4\cdot3}$ [14] and $Sb_3Cl_9F_4O$ [15] of 2.07 and 2.08 Å respectively. Once again crowding resulting from the presence of the chlorine atoms is probably responsible for these increases. In the $SbCl_4F$ tetramer [4] a similar lengthening of the bridge bonds is also noted, but the fluorine bridge is asymmetric with Sb–F distances of 2.05 and 2.18 Å. However, it should be pointed out that the errors are rather large in this structure.[4]

The $SbCl_3F_3$ octahedra also show considerable angular distortion. Two of the Cl–Sb–Cl′ angles are opened up from the 90° expected for an octahedron to 102°, whereas the third angle, Cl(2)–Sb–Cl(3), is 91°. All the Cl–Sb–F angles are *ca.* 90°, except Cl(2)–Sb–F(2) which is 101°, whilst the F–Sb–F′ angles average 79°. The crowding effect due to the presence of the large chlorines would tend to narrow the F–Sb–F′ angles. As mentioned above, the Cl(2)–Sb–Cl(3) and Cl(2)–Sb–F(2) angles are anomalous and are likely the result of packing considerations.

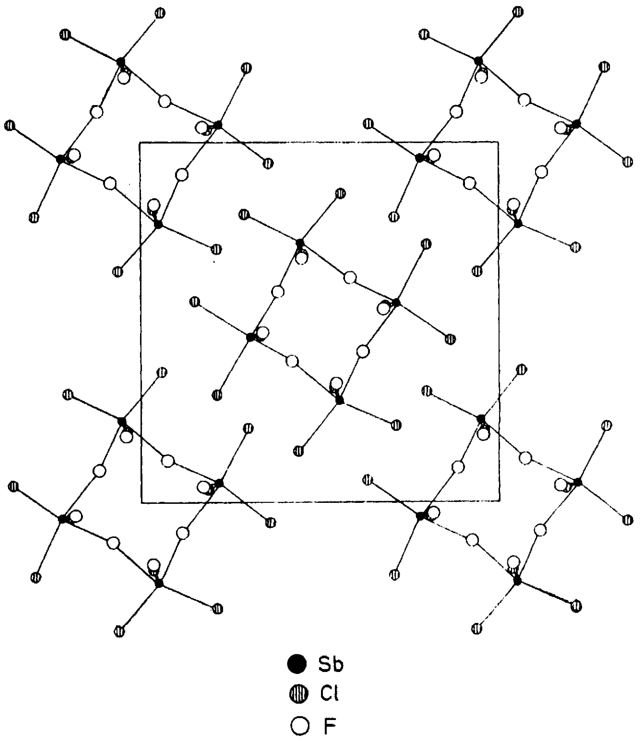

FIGURE 2 Projection of the structure down the *c* axis

In the tetramers, the narrowing of the F(1)–Sb–F(1)′ angle has a considerable influence on the Sb–F(1)–Sb′ angle. In the title compound, the former angle is 79 compared to 82.7° in $SbCl_4F$, while the corresponding angles at the bridging fluorine are 164 and 173° respec-

---

[13] A. J. Edwards, *J. Chem. Soc.*, 1964, 3714.

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

[15] A. J. Edwards and G. R. Jones, personal communication.

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

[17] H. B. Millar, H. W. Baird, C. C. Bramlett, and W. F. Templeton, *J.C.S. Chem. Comm.*, 1972, 262.

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

[19] A. J. Edwards and R. J. C. Sills, *J. Chem. Soc.* (*A*), 1970, 2697.

tively for the two compounds. In the antimony pentafluoride tetramer two different Sb–F–Sb′ angles were found, namely 170 and 141°. It was suggested[3] that these different angles were a consequence of the structure consisting of a mixture of cubic and hexagonal close-packed arrays of fluorine atoms. If this analogy can be continued to the chloride fluoride structures, it suggests that both $SbCl_3F_2$ and $SbCl_4F$ consist of approximately cubic close-packed arrays of halogen atoms. Since the halogens are not all of the same kind, one would expect distortions from the ideal close-packed arrangements, and since $SbCl_4F$ contains a higher percentage of close-packed atoms of the same size than does $SbCl_3F_2$ one would anticipate the latter structure to deviate more from the cubic close-packed arrangement than $SbCl_4F$. This deviation is reflected in the smaller Sb–F–Sb′ angle in $SbCl_3F_2$ than in $SbCl_4F$.

Comparisons with the $NbCl_4F$ and $TaCl_4F$ structures[6,20] bear out these generalizations. The F–Nb–F′ angle of 81° is between those for $SbCl_3F_2$ (79°) and $SbCl_4F$ (82.7°) and the angle at the bridging fluorine (Nb–F–Nb′) is 171°, again between the values for the two antimony chloride fluorides. The F–Ta–F′ angle is close to 90 and the bridge angle has opened up to 180°.[6] Both these molecules, $NbCl_4F$ and $TaCl_4F$, can therefore be considered as cubic close-packed arrays.

The ^{121}Sb Mössbauer spectrum of the title compound consisted of a single resonance showing considerable distortion. Analysis of the spectrum gave an isomer-shift value, relative to InSb, of $+6.84$ mm s^{-1} and an e^2qQ_g value of $+9.75$ mm s^{-1}. In order to obtain a satisfactory fit to this spectrum it was also necessary to vary the asymmetry parameter η: the computer fit gave a best value for η of 0.88. The isomer shift is more positive than that found for $SbCl_4F$.[21] This is to be expected since replacement of a chlorine atom by the more electronegative fluorine would result in more s-electron density being removed from the antimony. The nuclear term $\delta r/r$ in the isomer-shift expression is negative for ^{121}Sb so that a reduction in s-electron density causes a shift to more positive isomer shifts. The relatively large quadrupole-coupling constant and large asymmetry parameter are clearly consistent with the distorted environment about the antimony discussed above.

Table 3 contains a summary of the bands observed in the Raman spectrum of this compound together with a tentative assignment. This is based on the Raman study of $SbCl_4F$ reported by Beattie *et al.*[22] Two bands, at 649 and 621 cm^{-1}, are observed in the region normally attributed to Sb–F vibrations and a weak band at 488 cm^{-1} is assigned to the Sb–F–Sb bridging mode; in $SbCl_4F$ this occurs at 446 cm^{-1}. Very strong Sb–Cl stretches are observed at 406, 380, and 349 cm^{-1}. The first two are attributed to ν(Sb–Cl)(equatorial), while the latter is the ν(Sb–Cl)(axial) vibration. Lower-frequency vibrations are tentatively assigned to ring deformations and lattice modes.

TABLE 3

Raman spectrum (cm^{-1}) of $SbCl_3F_2$

	Assignment *
649(11)	ν(Sb–F)
621(8)	
488(2)br	ν(Sb $\cdots$ F $\cdots$ Sb)
406(73 (sh)	ν(Sb–Cl) (equatorial)
380 (100)	
349(73)	ν(Sb–Cl) (axial)
240(4)	Ring deformations
161(50)	
152(36) (sh)	
139(37) (sh)	
125(48)	
93(24)	Lattice mode

* Made on the basis of $SbCl_4F$.[22]

We thank the National Research Council of Canada for support.

[6/2232 *Received*, *6th December*, 1976]

---

[20] H. Preiss, *Z. anorg. Chem.*, 1966, **362**, 13.

[21] J. G. Ballard and T. Birchall, *J. Phys.*, 1976, **37**, C6–513.

[22] I. R. Beattie, K. M. S. Livingston, G. A. Ozin, and D. J. Reynolds, *J. Chem. Soc.* (*A*), 1969, 958.