Fluoride Crystal Structures. Part XXI.[1] Trifluorotellurium(IV) μ-Fluoro-bis[pentafluoroantimonate(V)]

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The interaction of tellurium tetrafluoride and antimony pentafluoride gives the title compound as a minor product. Crystals are monoclinic, space group $P2_1/c$, $a = 7{\cdot}48 \pm 0{\cdot}01$, $b = 14{\cdot}29 \pm 0{\cdot}02$, $c = 9{\cdot}72 \pm 0{\cdot}01$ Å, $\beta = 91{\cdot}0° \pm 0{\cdot}2°$. The structure was solved by Patterson and Fourier methods and refined by three-dimensional least-squares methods to R 0·095 for 824 reflections measured photographically. Although the atomic arrangement is consistent with the ionic formulation $[TeF_3]^+$ $[Sb_2F_{11}]^-$ there is considerable interaction between the ions through fluorine bridging. The cation has C_{3v} symmetry, with a mean Te–F distance of 1·84 Å, and there are three long contacts of 2·54, 2·55, and 2·69 Å to bridging fluorine atoms to give a much distorted octahedral co-ordination for tellurium, very similar to that found for selenium in $[SeF_3]^+$ $[Nb_2F_{11}]^-$.

TELLURIUM tetrafluoride can act as either a fluoride-ion donor or acceptor to form the trifluorotellurium(IV) cation or pentafluorotellurate(IV) anion. The solid-state structures of the tetrafluoride [2] and of potassium pentafluorotellurate(IV) [3] have been determined previously by X-ray crystallography, but the only previous investigations of compounds containing the cation have been by Raman spectroscopy.[4]

The interaction of tellurium tetrafluoride and antimony pentafluoride has been reported [5] to yield the 1 : 1 adduct, TeF_4,SbF_5. In a Raman spectroscopic study [4] of SF_4,SbF_5, SeF_4,SbF_5, SeF_4,AsF_5, and TeF_4,SbF_5 it was concluded that the first three compounds were essentially ionic $[MF_3]^+[MF_6]^-$ but that there was a more covalent interaction for the tellurium compound.

The adducts SeF_4,NbF_5 and $SeF_4,2NbF_5$ have been studied by X-ray crystallography [6] and formulated as being predominantly ionic $[SeF_3]^+[NbF_6]^-$ and $[SeF_3]^+$-$[Nb_2F_{11}]^-$, but with considerable interionic fluorine bridging. The crystal structure [7a] of the adduct SF_4,BF_3 shows a much smaller degree of fluorine bridging and a close approach to the ionic formulation $[SF_3]^+[BF_4]^-$.

This is consistent with the order of fluoride-ion acceptor strength of the cations $(SF_3)^+ < (SeF_3)^+$, since BF_3 is a weaker fluoride ion acceptor [7b] than NbF_5.

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[1] Part XX, A. J. Edwards, *J.C.S. Dalton*, 1972, 2325.

[2] A. J. Edwards and F. I. Hewaidy, *J. Chem. Soc.* (*A*), 1968, 2977.

[3] A. J. Edwards and M. A. Mouty, *J. Chem. Soc.* (*A*), 1969, 703; S. H. Mastin, R. R. Ryan, and L. B. Asprey, *Inorg. Chem.*, 1970, **9**, 2100.

[4] J. A. Evans and D. A. Long, *J. Chem. Soc.* (*A*), 1968, 1688.

[5] N. Bartlett and P. L. Robinson, *J. Chem. Soc.*, 1961, 3417.

[6] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), 1970, 1491.

[7] (*a*) D. D. Gibler, C. J. Adams, M. Fischer, A. Zalkin, and N. Bartlett, *Inorg. Chem.*, 1972, **11**, 2325; (*b*) R. J. Gillespie and A. Whitla, *Canad. J. Chem.*, 1970, **48**, 657.

In the present work the previously unreported title compound has been characterised by X-ray single-crystal structure analysis, and the interaction between the ions investigated.

EXPERIMENTAL

Tellurium tetrafluoride was prepared by the interaction of selenium tetrafluoride and tellurium dioxide.[8] After removal of the volatile seleninyl difluoride produced and the excess of selenium tetrafluoride, by pumping at room temperature, the tellurium tetrafluoride was purified by vacuum sublimation. Antimony pentafluoride was prepared by direct fluorination of the element at 200 °C. An excess of antimony pentafluoride was distilled on a sample of tellurium tetrafluoride in a rigorously dried Pyrex glass apparatus. The tetrafluoride dissolved on warming to *ca.* 100° and excess of antimony pentafluoride was removed by pumping under vacuum at room temperature. The white solid product was powdered under vacuum, the powder transferred into thin-walled Pyrex capillaries, already attached to the apparatus, and these capillaries sealed under vacuum. Single crystals were obtained by sublimation in a temperature gradient in the evacuated capillaries, as described previously.[6] Two types of crystal were observed. The bulk of the material consisted of very thin plates, unsuitable for crystallographic investigation; these were assumed to be TeF_4,SbF_5. A small number of multifaceted block crystals were isolated in a small section of capillary. By cooling one crystal with water and heating the remainder to *ca.* 150° that crystal was grown sufficiently large for X-ray investigation.

Crystal Data.—$TeSb_2F_{14}$, $M = 637$, Monoclinic, $a = 7{\cdot}48 \pm 0{\cdot}01$, $b = 14{\cdot}29 \pm 0{\cdot}02$, $c = 9{\cdot}72 \pm 0{\cdot}01$ Å, $\beta = 91{\cdot}0 \pm 0{\cdot}2°$, $U = 1039$ Å^3, $Z = 4$, $D_c = 3{\cdot}29$ g cm^{-3}, $F(000) = 1120$. Space group $P2_1/c$ (C_{2h}^5, No. 14) from systematic absences: $0k0$ when $k \neq 2n$ and $h0l$ when $l \neq 2n$. Cu-K_α ($\lambda = 1{\cdot}5418$ Å) and Mo-K_α ($\lambda = 0{\cdot}7107$ Å, $\mu = 83{\cdot}0$ cm^{-1}) radiations. Single-crystal precession and Weissenberg photographs.

The density of the crystal was not measured, but $Z = 4$ was assumed since the volume per fluorine atom is then 18·6 Å^3, similar to the value of 20 Å^3 found[6] for $[SeF_3]^+$-$[Nb_2F_{11}]^-$.

Structure Determination.—Integrated intensities were collected about the c axis (layers $hk0$—6) by use of Mo-K_α radiation and a Nonius integrating camera. The relative intensities of 824 independent reflections were measured with a photometer of similar design to that described by Jeffery,[9] and were corrected for Lorentz and polarisation factors. Since the crystal was very small (dimensions *ca.* 0·05 mm) and the many faces were extremely difficult to assign, no absorption corrections were applied.

A three-dimensional Patterson synthesis was calculated and interpreted to give the positions of three heavy atoms in general positions. Structure factors were calculated by use of scattering factors for neutral atoms from ref. 10, with the three atoms given antimony scattering factors at this stage, for simplicity. The heavy atoms alone gave R 0·19.

Three-dimensional electron-density maps and difference maps, based on these positions, showed the presence of the fourteen independent fluorine atoms. The identity of the tellurium atom was inferred from the geometry of its fluorine-atom co-ordination, and the scattering factor assigned accordingly. Refinement of the positional and isotropic temperature parameters, and layer scale-factors, was continued by full-matrix least-squares methods. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimised, at first with unit weights and, in the final stages of the refinement with $\sqrt{w} = 1$ when $|F_o| \leqslant 85$, and $\sqrt{w} = 85/|F_o|$ when $|F_o| > 85$. The final parameter shifts were $< 0{\cdot}1\sigma$ and an analysis of the variation of $w\Delta^2$ with increasing $\sin\theta/\lambda$ and with increasing fractions of $|F_o|$ was satisfactory. The final R was 0·095. Observed and calculated structure factors are listed in Supplementary Publication No. 20760 (10 pp., 1 microfiche),* and the final positional parameters and isotropic temperature factors, with their estimated standard deviations, in Table 1. Interatomic distances and angles are given in Table 2.

TABLE 1

Final atomic positional and thermal parameters, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	B/Å^2
Te	0·7847(4)	0·2309(2)	0·4760(4)	1·59(6)
Sb(1)	1·1006(4)	0·4453(2)	0·2592(4)	1·21(6)
Sb(2)	0·6700(4)	0·6081(2)	0·2310(4)	1·39(6)
F(1)	0·6358(54)	0·1723(31)	0·5957(54)	4·8(9)
F(2)	0·8985(49)	0·2851(26)	0·6276(46)	3·7(7)
F(3)	0·6375(39)	0·3327(22)	0·4590(40)	2·6(6)
F(4)	0·9684(39)	0·3563(21)	0·3560(40)	2·4(6)
F(5)	0·9865(36)	0·4019(21)	0·0994(37)	2·2(5)
F(6)	0·4701(38)	0·6846(21)	0·1859(39)	2·4(6)
F(7)	1·1705(40)	0·4975(22)	0·4241(42)	2·7(6)
F(8)	1·1877(43)	0·5485(24)	0·1618(43)	3·2(7)
F(9)	1·2981(28)	0·3728(16)	0·2370(31)	0·7(4)
F(10)	0·8778(36)	0·5275(21)	0·2791(39)	2·2(6)
F(11)	0·7204(42)	0·6745(24)	0·3935(42)	2·9(6)
F(12)	0·6447(40)	0·5398(22)	0·0790(41)	2·6(6)
F(13)	0·8351(41)	0·6795(23)	0·1453(40)	2·9(6)
F(14)	0·5363(39)	0·5178(22)	0·3261(41)	2·7(6)

TABLE 2

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

(*a*) Distances

Te–F(1)	1·83(5)	Te · · · F(4)	2·55(3)
Te–F(2)	1·86(4)	Te · · · F(5^{I})	2·69(3)
Te–F(3)	1·83(3)	Te · · · F(6^{II})	2·54(3)
Sb(1)–F(4)	1·87(3)	Sb(2)–F(11)	1·87(4)
Sb(1)–F(5)	1·87(3)	Sb(2)–F(12)	1·78(4)
Sb(1)–F(9)	1·82(2)	Sb(2)–F(13)	1·82(3)
Sb(1)–F(7)	1·84(4)	Sb(2)–F(14)	1·89(3)
Sb(1)–F(8)	1·88(4)	Sb(2)–F(6)	1·90(3)
Sb(1)–F(10)	2·05(3)	Sb(2)–F(10)	1·98(3)
F(1) · · · F(2)	2·56(6)	F(4) · · · F(10)	2·64(4)
F(1) · · · F(3)	2·65(6)	F(6) · · · F(11)	2·73(5)
F(2) · · · F(3)	2·62(5)	F(10) · · · F(11)	2·66(5)
F(2) · · · F(4)	2·89(6)	F(6) · · · F(12)	2·67(5)
F(3) · · · F(4)	2·71(4)	F(10) · · · F(12)	2·60(5)
F(4) · · · F(5)	2·58(5)	F(6) · · · F(13)	2·77(4)
F(4) · · · F(7)	2·60(4)	F(10) · · · F(13)	2·55(5)
F(5) · · · F(8)	2·64(5)	F(11) · · · F(13)	2·58(5)
F(7) · · · F(8)	2·66(6)	F(12) · · · F(13)	2·53(5)
F(4) · · · F(9)	2·75(4)	F(6) · · · F(14)	2·79(5)
F(5) · · · F(9)	2·70(4)	F(10) · · · F(14)	2·61(4)
F(7) · · · F(9)	2·73(4)	F(11) · · · F(14)	2·70(5)
F(8) · · · F(9)	2·74(4)	F(12) · · · F(14)	2·57(5)
F(5) · · · F(10)	2·64(4)	F(5) · · · F(12)	3·23(4)
F(7) · · · F(10)	2·62(5)	F(8) · · · F(13)	3·24(5)
F(8) · · · F(10)	2·62(5)	F(3) · · · F(14)	3·03(5)

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[8] R. Campbell and P. L. Robinson, *J. Chem. Soc.*, 1956, 785.

[9] J. W. Jeffery, *J. Sci. Instr.*, 1963, **40**, 494.

[10] 'International Tables for X-Ray Crystallography', vol. III, Kynoch Press, Birmingham, p. 202.

TABLE 2 (*continued*)

(*b*) Angles

F(4)–Sb(1)–F(9)	96·4(1·2)	F(10)–Sb(2)–F(11)	87·2(1·4)
F(5)–Sb(1)–F(9)	94·1(1·2)	F(10)–Sb(2)–F(12)	87·0(1·4)
F(7)–Sb(1)–F(9)	96·7(1·3)	F(10)–Sb(2)–F(13)	84·1(1·4)
F(8)–Sb(1)–F(9)	95·6(1·3)	F(10)–Sb(2)–F(14)	84·7(1·3)
F(4)–Sb(1)–F(10)	84·5(1·3)	F(6)–Sb(2)–F(11)	92·8(1·5)
F(5)–Sb(1)–F(10)	84·7(1·3)	F(6)–Sb(2)–F(12)	93·0(1·5)
F(7)–Sb(1)–F(10)	84·5(1·4)	F(6)–Sb(2)–F(13)	96·3(1·4)
F(8)–Sb(1)–F(10)	83·5(1·4)	F(6)–Sb(2)–F(14)	94·9(1·4)
F(4)–Sb(1)–F(5)	87·4(1·4)	F(11)–Sb(2)–F(13)	88·5(1·5)
F(4)–Sb(1)–F(7)	89·0(1·5)	F(11)–Sb(2)–F(14)	91·9(1·6)
F(8)–Sb(1)–F(5)	89·9(1·6)	F(12)–Sb(2)–F(13)	89·5(1·6)
F(8)–Sb(1)–F(7)	91·4(1·6)	F(12)–Sb(2)–F(14)	88·9(1·5)
F(1)–Te–F(2)	87·8(2·0)	F(4)–Te–F(5^{I})	113·3(0·9)
F(1)–Te–F(3)	92·8(1·7)	F(4)–Te–F(6^{II})	107·7(1·1)
F(2)–Te–F(3)	90·3(1·6)	F(5^{I})–Te–F(6^{II})	81·6(0·7)
F(1)–Te–F(5^{I})	74·7(1·5)	F(2)–Te–F(5^{I})	72·3(1·4)
F(1)–Te–F(6^{II})	79·4(1·6)	F(2)–Te–F(6^{II})	80·0(1·5)
F(3)–Te–F(4)	73·4(1·2)	F(3)–Te–F(6^{II})	73·0(1·2)
Sb(1)–F(10)–Sb(2)	160·9(2·1)	Te–F(4)–Sb(1)	177·0(1·9)
Te–F(5^{I})–Sb(1^{I})	148·2(1·7)	Te–F(6^{II})–Sb(2^{II})	142·7(1·0)

(*c*) Contacts $< 3·5$ Å

F(1) ··· F(5^{I})	2·83(5)	F(1) ··· F(12^{I})	3·03(6)
F(2) ··· F(4^{I})	3·04(5)	F(2) ··· F(5^{I})	2·77(5)
F(6) ··· F(1^{II})	2·84(6)	F(6) ··· F(3^{II})	2·66(5)
F(12) ··· F(1^{II})	3·28(5)	F(6) ··· F(9^{III})	3·28(4)
F(8) ··· Te^{III}	2·94(4)	F(8) ··· F(1^{III})	3·36(6)
F(11) ··· F(9^{III})	3·11(4)	F(13) ··· Te^{III}	3·18(3)
F(13) ··· F(4^{III})	2·92(4)	F(13) ··· F(9^{III})	3·16(4)
F(2) ··· F(7^{IV})	3·19(5)	F(2) ··· F(8^{IV})	3·21(6)
F(2) ··· F(10^{IV})	3·28(5)	F(2) ··· F(11^{IV})	2·92(5)
F(2) ··· F(13^{IV})	2·99(6)	F(3) ··· F(7^{IV})	3·03(5)
F(4) ··· F(7^{IV})	3·18(5)	F(4) ··· F(11^{IV})	3·37(5)
F(7) ··· F(7^{IV})	2·97(7)	F(7) ··· F(10^{IV})	2·94(6)
F(7) ··· F(11^{IV})	3·13(5)	F(7) ··· F(14^{IV})	3·25(5)
F(3) ··· F(9^{V})	3·35(4)	F(6) ··· F(8^{V})	2·88(5)
F(14) ··· F(7^{V})	2·93(5)	F(14) ··· F(8^{V})	3·06(5)
F(14) ··· F(9^{V})	2·86(4)	F(1) ··· F(6^{VI})	3·06(6)
F(1) ··· F(11^{VI})	3·45(5)	F(2) ··· F(6^{VI})	3·36(5)
F(3) ··· F(11^{VI})	3·06(5)	F(3) ··· F(14^{VI})	3·27(5)
F(14) ··· F(14^{VI})	3·47(8)	F(5) ··· F(5^{VII})	3·41(6)
F(5) ··· F(8^{VII})	2·92(5)	F(5) ··· F(12^{VII})	3·39(5)
F(5) ··· F(13^{VII})	2·98(5)	F(8) ··· F(12^{VII})	2·96(5)
F(9) ··· F(12^{VII})	3·35(5)	F(11) ··· F(13^{VIII})	3·32(5)
F(12) ··· F(12^{IX})	2·87(6)	F(1) ··· F(9^{X})	2·97(5)

Roman numerals as superscripts refer to atoms in the positions:

I $x, \frac{1}{2} - y, \frac{1}{2} + z$
II $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
III $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$
IV $2 - x, 1 - y, 1 - z$
V $-1 + x, y, z$
VI $1 - x, 1 - y, 1 - z$
VII $2 - x, 1 - y, - z$
VIII $x, \frac{3}{2} - y, \frac{1}{2} + z$
IX $1 - x, 1 - y, - z$
X $-1 + x, \frac{1}{2} - y, \frac{1}{2} + z$

DISCUSSION

The crystal structure analysis has established the existence of the adduct $TeF_4,2SbF_5$. The interaction of the component fluorides had been reported previously to yield only the 1 : 1 adduct.[4,5] The existence of both 1 : 1 and 1 : 2 adducts with pentafluorides has now been established for such fluoride-ion donor molecules as SeF_4 (ref. 6), IF_5 (ref. 11), and XeF_2 (ref. 12), and the $M_2F_{11}^-$ anion appears to form readily for most pentafluorides.

In the atomic arrangement found for the adduct (Figure 1), the nearest fluorine atom neighbours to the tellurium and antimony atoms define the ions TeF_3^+ and $Sb_2F_{11}^-$. However, interionic fluorine bridging leads to a complex, three-dimensional structural network.

Within experimental error the TeF_3^+ ion has C_{3v} symmetry, with a mean Te–F(terminal) distance of 1·84 Å and a F–Te–F angle of 90·3°. The next-nearest neighbours to the tellurium atom are three fluorine atoms from $Sb_2F_{11}^-$ anions at 2·54, 2·55, and 2·69 Å, which complete a distorted octahedral co-ordination of the tellurium atom. These three long contacts are grouped around the position assumed for the non-bonding electron pair on tellurium, and the total co-ordination, including the non-bonding pair, can be described as monocapped octahedral, very similar to that previously described for SeF_3^+ in $[SeF_3]^+[Nb_2F_{11}]^-$ (ref. 6) and $[SeF_3]^+[NbF_6]^-$ (ref. 13), and for SF_3^+ in $[SF_3]^+[BF_4]^-$ (ref. 7).

The geometry of the TeF_3^+ cation can be usefully compared with those of the corresponding sulphur and selenium cations (Table 3). There is an increase in bond length from SF_3^+ to TeF_3^+, reflecting the increase in size of the central atom, and the increases agree reasonably well with the differences in covalent radii (S 1·04, Se 1·17, and Te 1·37 Å). There is a corresponding decrease in bond angle, which, on valence-shell electron-pair repulsion theory, can be attributed to the closer association of the bond-pair electrons with the fluorine atoms, as the central atom becomes less electronegative, and the consequent more effective repulsion between the non-bonding electron pair and the bond pairs.

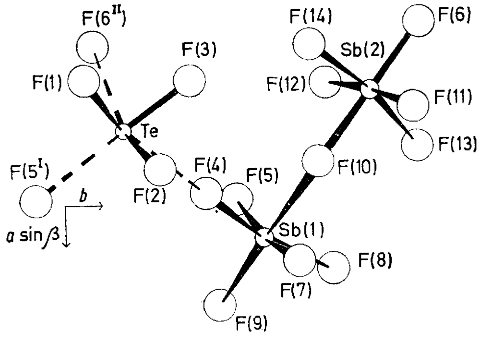

FIGURE 1 Projection of the structural unit down [001] showing the atom numbering and the co-ordination of the tellurium atom

TABLE 3

Species	Mean M–F (Å)	Mean F–M–F (°)	Mean M ··· F bridge (Å)	(M ··· F)/(M–F)
SF_3^+	1·496[a]	97·47	2·614	1·75
SeF_3^+	1·66[b]	94·2	2·43	1·46
TeF_3^+	1·84[c]	90·3	2·59	1·41
SbF_3	1·92[d]	87·3	2·61	1·36

[a] Ref. 6. [b] Ref. 5. [c] Present work. [d] Ref. 11.

Bond angles in isoelectronic pairs of cations and neutral molecules, such as SF_3^+ and PF_3, and SeF_3^+ and

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[11] H. W. Baird, and H. F. Giles, *Acta Cryst.*, 1969, *A*25, S 115; A. J. Edwards and P. Taylor, unpublished work.

[12] J. H. Holloway and J. G. Knowles, *J. Chem. Soc.* (*A*), 1969, 756; F. O. Sladky, P. A. Bulliner, and N. Bartlett, *ibid.*, p. 2179.

[13] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), 1970, 1891.

AsF_3, have been shown to be very similar.[6] This similarity is also found for TeF_3^+ and SbF_3, since the angle F–Te–F of 90·3° is not statistically significantly different from F–Sb–F of 87·3°.[14] There is a shortening in bond length of 0·08 Å between SbF_3 and TeF_3^+, presumably due to the combined effects of the positive charge and the decrease in size of the central atom. The corresponding shortening in the bond length of the cation compared with that of the neutral molecule is 0·04 Å in SF_3^+ and 0·05 Å in SeF_3^+. A variation of bond length, which can be correlated with a charge effect, is also found in the species TeF_3^+, TeF_4, and TeF_5^- with mean Te–F distances of 1·84, 1·86, and 1·92 Å, although the difference between the first two distances is not statistically significant.

If the bridging interaction of the ions is considered, the monocapped octahedral co-ordination for tellurium is apparently characteristic for species with three bonds and a non-bonding electron pair. As well as SeF_3^+ and SF_3^+, this arrangement has also been found[14-18] in SbF_3, $[AsF_2]^+[SbF_6]^-$, $SeOF_2$,NbF_5, $TeCl_4$, and $[TeCl_3]^+$-$[AlCl_4]^-$.

Bartlett *et al.*[7] consider that the arrangement in $[SF_3]^+[BF_4]^-$ results from an electrostatic interaction between the ions whereas some covalent interaction has been suggested[6,13] in the SeF_3^+ compounds, and in SbF_3.[14] Since the same geometrical arrangement will accommodate both proposals it appears difficult to decide the relative contributions of the electrostatic and covalent bridging effects.

We have previously used the ratio M–F(bridge) : M–F(terminal) to compare the strengths of bridging interactions, and values of this ratio are given in Table 3. There is a considerable difference between the value (1·75) for SF_3^+ and those (1·36—1·46) for the species involving the heavier elements. This may represent a change in the type of interaction involved, from a weak essentially electrostatic interaction in $[SF_3]^+[BF_4]^-$ to much stronger interactions, involving some covalency, for $[SeF_3]^+[Nb_2F_{11}]^-$ and $[TeF_3]^+[Sb_2F_{11}]^-$.

A direct comparison of the fluoride-ion donor character of SeF_4 and TeF_4 cannot be obtained from the results in Table 3, since the anion involved in the two cases is different. However, the crystal-structure determination[1] of the adduct NbF_5,SbF_5 has shown SbF_5 to be a stronger fluoride-ion acceptor than NbF_5. Since the ratio Te–F(bridge) : Te–F(terminal) of 1·41 is smaller than the corresponding ratio for selenium (1·46), despite the change to a stronger fluoride-ion acceptor, then TeF_4 is apparently a weaker fluoride ion donor than SeF_4.

Although the Nb–F(bridge) distances in the $Nb_2F_{11}^-$ anion are longer than the Nb–F(terminal) distances there is no significant corresponding lengthening in the $Sb_2F_{11}^-$ anion in the present case. The interionic linking in the two compounds $[SeF_3]^+[Nb_2F_{11}]^-$ and $[TeF_3]^+$-$[Sb_2F_{11}]^-$ is quite different. In $[SeF_3]^+[Nb_2F_{11}]^-$ the three Se–F–Nb bridges are all *cis* to the Nb–F–Nb bridge, with bridge angles within the range 167—177°. The ions are linked into zig-zag chains and these chains cross-linked through the third bridge to give a sheet arrangement. In the present compound the bridging atoms F(4) and F(5) are *cis*, whereas F(6) is *trans* to the Sb–F–Sb bridges. The bridge angles of 143 [F(6)], 148 [F(5)], and 177° [F(4)] lead to a different arrangement from that in the selenium compound and no sheet arrangement can be distinguished. Although the interionic linking is different in the two compounds, the configurations of the two anions are similar. The Sb–F–Sb angle of 161° is more distorted from linear than Nb–F–Nb of 166° and the $Sb_2F_{11}^-$ ion correspondingly has a slightly more distorted eclipsed configuration than the $Nb_2F_{11}^-$ ion.

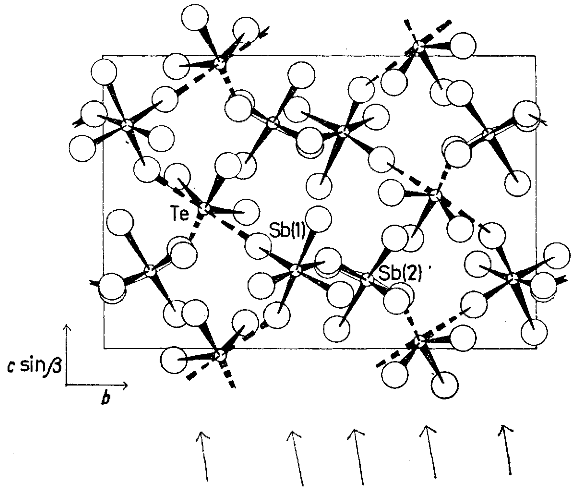

FIGURE 2 Projection of the structure down [100]; arrows indicate planes of approximately close-packed atoms

A comparison of the volume per fluorine atom in the two structures, 20 Å^3 in $[SeF_3]^+[Nb_2F_{11}]^-$ and 18·6 Å^3 in $[TeF_3]^+[Sb_2F_{11}]^-$, shows a more efficient packing in the latter case. The decrease in volume appears to be due to a nearer approach to close-packing of the fluorine atoms in the $[TeF_3]^+[Sb_2F_{11}]^-$ structure. Planes of approximately close packed atoms are indicated in Figure 2, although no layer sequence can be elucidated.

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