Charge-transfer Interactions in the Square-planar Chalcogen Cations, M_4^{2+}: Preparation and Crystal Structures of the Compounds $(Se_4^{2+})(Sb_2F_4^{2+})(Sb_2F_5^{+})(SbF_6^{-})_5$, $(Se_4^{2+})(AlCl_4^{-})_2$, and $(Te_4^{2+})(SbF_6^{-})_2$

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The solid-state structures of the compounds (1) $(Se_4^{2+})(Sb_2F_4^{2+})(Sb_2F_5^{+})(SbF_6^{-})_5$, (2) $(Te_4^{2+})(SbF_6^{-})_2$, and (3) $(Se_4^{2+})(AlCl_4^{-})_2$ are reported. The first compound was initially isolated from the reaction of a 1 : 3 sulphur–selenium alloy with a SbF_5–SO_2 solution and the second by the reaction of a mixture of tellurium and germanium, with a SbF_5–SO_2 solution. They have also been prepared by the direct oxidation of Se and Te with SbF_5 in SO_2. Crystals of (1) are monoclinic, space group $P2_1/c$, with a = 15.739(3), b = 13.498(2), c = 17.040(4) Å, β = 92.26(2)°, and Z = 4. The dark red plates of (2) are triclinic, space group $A\bar{1}$, with a = 5.700(2), b = 16.252(6), c = 8.076(2) Å, α = 100.56(3), β = 102.67(3), γ = 97.47(3)°, and Z = 2. Compound (3) is orthorhombic, space group $Pbam$, with a = 13.245(3), b = 13.223(3), c = 9.266(2) Å, and Z = 4. The structures of compounds (1) and (2) have been solved by direct methods and compound (3) by a Patterson function. They were refined by least squares to final agreement indices of R = 0.052 (R' = 0.062), 0.051 (0.064), and 0.042 (0.046) for 3 634, 709, and 912 observed reflections respectively. In these three compounds, the approximately square-planar chalcogen cations Se_4^{2+} and Te_4^{2+} were found to have crystallographic inversion symmetry with average Se–Se and Te–Te distances of 2.260(4) (1), 2.688(3) (2), and 2.286(2) Å (3). These values are close to the distances observed in the other examples of these cations. The packing of these and other examples of the M_4^{2+} cations, the anion–cation charge-transfer interactions, and the stereochemistry of the fluorine contacts to the antimony(III) atoms in the $Sb_2F_4^{2+}$ and $Sb_2F_5^{+}$ ions and related species are discussed.

ALTHOUGH the mixed chalcogen cationic species $Te_2Se_2^{2+}$,[1] $Te_3S_3^{2+}$,[2] $Te_2Se_4^{2+}$,[2] and $Te_2Se_8^{2+}$ [3] have been prepared and characterised by X-ray structural determinations, no mixed sulphur–selenium cationic species are at present known. We have been investigating the synthesis of mixed sulphur–selenium cations by the reaction of sulphur–selenium mixtures or alloys with Lewis acids such as AsF_5 or SbF_5 and in a reaction of a 1 : 3 S : Se alloy with SbF_5 in SO_2 a yellow-green crystalline product was obtained which it was hoped might have been a mixed sulphur–selenium cation. A single-crystal X-ray study, however, has established the composition of this product as the compound $(Se_4^{2+})(Sb_2F_4^{2+})(Sb_2F_5^{+})(SbF_6^{-})_5$, and independently we were able to prepare this compound directly from selenium metal and excess of SbF_5 in sulphur dioxide. Similarly, in attempting to prepare mixed cations of the chalcogens with other non-metals, the reaction of a mixture of tellurium and germanium with SbF_5 in sulphur dioxide was observed to give a variety of products, one of which has been identified by X-ray crystallography as the compound $Te_4(SbF_6)_2$. It is an interesting feature of the packing of the Se_4^{2+} and Te_4^{2+} cations in both of these compounds that there are some highly stereospecific anion–cation contacts which are significantly shorter than van der Waals distances. These contacts are, in fact, common to all the square-planar chalcogen cations M_4^{2+} so far characterised. In order to gain some additional information on these contacts we have also determined the structure of the compound $Se_4(AlCl_4)_2$.

In this paper we report the preparations of $(Se_4^{2+})(Sb_2F_4^{2+})(Sb_2F_5^{+})(SbF_6^{-})_5$ and $Te_4(SbF_6)_2$ and details of all three structure determinations. The charge-transfer interactions involving the M_4^{2+} cations and the stereochemistry of the $Sb^{III} \cdots F$ interactions involving the $Sb_2F_4^{2+}$ and $Sb_2F_5^{+}$ ions are discussed.

EXPERIMENTAL

Sulphur powder (B.D.H.), selenium powder 99.95% (Koch-Light Laboratories), tellurium powder ⩾99.7% (Koch-Light), and germanium powder 99.999% (Laramie Chemicals Co.) were used as received. Antimony pentafluoride (Ozark-Mahoning) was purified by double distillation in an all-glass apparatus. Sulphur dioxide (Canadian Liquid Air Ltd.) was distilled from, and kept over, phosphorus pentaoxide before use.

(*a*) *Preparation of* $(Se_4^{2+})(Sb_2F_4^{2+})(Sb_2F_5^{+})(SbF_6^{-})_5$.—Finely powdered sulphur and selenium, in the molar ratio 1 : 3 respectively, were placed in a thick-walled Pyrex glass tube. The contents of the tube were pumped to dryness for 24 h on a vacuum line and the tube was sealed. The materials were thoroughly mixed by shaking and then heated to 450 °C for 18 h. The melt, after cooling to room temperature, gave a dark glassy material which was pulverised in a porcelain mortar.

In a typical experiment S : 3Se ' alloy ' (6.552 mmol) was placed in one arm of a double ampoule and SbF_5 (20.582 mmol) was syringed into the other. Approximately 20 cm³ of SO_2 were condensed into each arm of the ampoule at −196 °C and the apparatus was sealed. On warming to room temperature, the SbF_5–SO_2 solution was thoroughly mixed and added to the S : 3Se–SO_2 suspension. On stirring the mixture, a dark green solution appeared which changed to a viscous emerald-green solution after a few days of stirring. This solution was filtered and left standing for *ca.* 2 weeks. A number of greenish yellow crystals were formed which were isolated from the mother-liquid.

Crystal data and an initial X-ray crystallographic structure showed that these crystals were the compound $(Se_4)(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$. Confirmation of the absence of sulphur in the compound was obtained when it was independently prepared by the direct reaction of selenium metal with excess of SbF_5 heated to 75—80 °C in SO_2. On cooling, a slightly greenish yellow powder containing some large crystals was obtained. These crystals were shown by their unit-cell parameters to be the same compound as that prepared above. The final crystallographic data set was collected on one of these latter crystals.

(b) *Preparation of* $(Te_4^{2+})(SbF_6^-)_2$.—In a typical experiment a solution of SbF_5 (21.63 mmol) in sulphur dioxide (*ca.* 35 cm^3) was added to a suspension of Te (12.33 mmol) and Ge (12.35 mmol), in SO_2 (30 cm^3) at 0 °C. The reactants were stirred at −15 °C for 3 h and then for 20 d at room temperature. A brown-yellow precipitate formed which eventually disappeared giving finally a dark red precipitate and a wine-red solution. All soluble products were extracted to the other side of the ampoule and upon evaporation of the volatiles a dark red powder together with a large number of dark red crystals were obtained.

Although crystal data and *X*-ray intensity measurements for the compound $(Te_4^{2+})(SbF_6^-)_2$ were collected from a crystal selected from the above preparation, the same compound was also prepared by the direct reaction of elemental tellurium (25.35 mmol) and antimony pentafluoride (15.01 mmol) in liquid sulphur dioxide. The product was a dark red powder mixed with dark red crystals. The Raman spectrum showed only the presence of the Te_4^{2+} ion.[4]

X-*Ray Crystallography*.—Crystals of the selenium compound $(Se_4)(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$ from both preparations were greenish yellow although larger crystals appear dark green. Plate-shaped crystals originally obtained from the reaction of the 1 : 3 S : Se alloy with SbF_5 were initially used. Crystals were selected and sealed in Lindemann capillaries (diameter 0.2—0.3 mm) under a dry nitrogen atmosphere in a dry-box equipped with a microscope. Virtually all examination of these crystals was by the use of a Syntex $P2_1$ diffractometer (graphite monochromator) and Mo-$K_{\bar{\alpha}}$ radiation ($\lambda = 0.710\ 69$ Å). Preliminary examination of several crystals showed that, although reflections selected from an initial ϕ rotation photograph centred well, the subsequent autoindexing routines found very few axial vectors which suggested that these crystals were probably twinned.

For one particular crystal it was found from peak profiles that all reflections with the exception of the *h*00 reflections were split into two overlapping components of unequal intensity. Close optical examination of this crystal then showed a small indentation in a small $(00\bar{1})$ face of the crystal parallel to the *a* axis indicating that the crystal was formed by the parallel growth of two components with a very small angle between the lattices of each component. However, the separation in 2θ of reflections from each component was sufficiently small at most values of 2θ that it was possible to treat this crystal as if it were single and a data set collected from this crystal was used to obtain a reasonably good initial structure solution. Subsequently when crystals from the reaction of selenium with excess of SbF_5 were obtained and identified from their cell parameters as the same compound, it was possible to shape a small approximately spherical crystal of radius 0.075 mm from a much larger crystal that was definitely single. An improved data set was collected using this crystal, and this is reported.

Crystals of the tellurium compound $Te_4(SbF_6)_2$ occur as very thin dark red plates. The majority of these crystals were found to be too small for *X*-ray studies. Eventually a thin plate of dimensions 0.0076 × 0.125 × 0.130 mm in the [0,1,1], [1,0,0], and [0,1,−1] directions was found among the reaction products and was sealed in a Lindemann capillary with the aid of some very dry fluorocarbon grease. This crystal was used throughout. Preliminary precession photographs indicated no symmetry higher than triclinic and the following crystal data were obtained using the diffractometer and Mo-$K_{\bar{\alpha}}$ radiation ($\lambda = 0.710\ 69$ Å).

Crystals of the selenium compound $Se_4(AlCl_4)_2$ which had been prepared by a published procedure[5] were kindly provided by Dr. R. C. Burns. Crystals occur as orange blocks or needles and were selected and sealed in Lindemann capillaries in the dry-box. The crystal used throughout was an approximately rectangular block described by the forms {0,0,1}, {0,1,0}, and {1,0,0}, and the face (0,3,1) which were respectively 0.14, 0.09, 0.115, and 0.086 mm from an origin within the crystal. Precession photographs gave preliminary cell and symmetry information and the following crystal data were obtained using the diffractometer and Mo-$K_{\bar{\alpha}}$ radiation.

Crystal data. $F_{39}Sb_9Se_4$ $M = 2151.9$, Monoclinic, $a = 15.739(3)$, $b = 13.498(2)$, $c = 17.040(4)$ Å, $\beta = 92.26(2)°$, $U = 3\ 617(1)$ Å^3, $D_c = 4.0$ g cm^{-3}, $Z = 4$, $F(000) = 3\ 444$, Mo-$K_{\bar{\alpha}}$ radiation ($\lambda = 0.710\ 69$ Å), μ(Mo-$K_{\bar{\alpha}}$) = 118.2 cm^{-1}. Systematic absences, *h0l*, $l = 2n$ and *0k0*, $k = 2n$, indicate that the space group is $P2_1/c$ (no. 14).

$Al_2Cl_8Se_4$, $M = 653.4$, Orthorhombic, $a = 13.245(3)$, $b = 13.223(3)$, $c = 9.266(2)$ Å, $U = 1\ 622.8(6)$ Å^3, $D_c = 2.67$ g cm^{-3}, $Z = 4$, $F(000) = 1\ 192$, μ(Mo-K_α) = 110.9 cm^{-1}. Systematic absences, *h0l*, $h = 2n$, *0kl*, $k = 2n$, indicate space group *Pbam* or $Pba2_1$. The centrosymmetric space group was initially assumed and confirmed by the satisfactory refinement. A previous report[5] of the unit-cell parameters for this compound gives $a \approx 12.8$, $b \approx 12.7$, $c \approx 9.1$ Å, where it was also noted that the relationship $a \approx b \approx \sqrt{2}\, c$ gives the powder pattern a pseudo-cubic appearance. Similarly it may be noted that a pseudo-tetragonal cell 13.169(4) × 13.171(4) × 9.354(2) Å with $\gamma = 89.45(2)°$ may be obtained from the cell above. The two cells are related by the matrix shown below, or its inverse.

$$\begin{pmatrix} -\frac{1}{2} & -\ \frac{1}{2} & -\ 1 \\ -\frac{1}{2} & -\ \frac{1}{2} & 1 \\ -\frac{1}{2} & +\ \frac{1}{2} & 0 \end{pmatrix}$$

$F_{12}Sb_2Te_4$, $M = 981.8$, Triclinic, $a = 5.700(2)$, $b = 16.252(6)$, $c = 8.076(2)$ Å, $\alpha = 100.56(3)$, $\beta = 102.67(3)$, $\gamma = 97.47(3)°$, $U = 706.2(4)$ Å^3, $D_c = 4.62$ g cm^{-3}, $Z = 2$, $F(000) = 836$, μ(Mo-$K_{\bar{\alpha}}$) = 123.8 cm^{-1}. Systematic absences, *hkl*, $k + l = 2n$, indicate the non-standard space groups $A\bar{1}$ or $A1$. The centrosymmetric space group was initially assumed and confirmed by the satisfactory refinement.

X-*Ray intensity measurements*. The options used in the data collections for each compound are summarised in Table 1. For each data set, Lorentz, polarisation, and absorption corrections were applied to all reflections. Subsequent averaging and exclusion of reflections which were systematically absent or had observed structure amplitudes equal to zero gave the final numbers of independent observed data given in Table 1.

Structure solutions. (*a*) $(Se_4^{2+})(Sb_2F_4^{2+})(Sb_2F_5^+)(SbF_6^-)_5$ (1). Since the nature of the compound was unknown at the start of the structure determination a probable composition was assumed and the solution was attempted using the direct methods routines of the program SHELX.[6] Several of the highest peaks in the best *E* map were initially assumed to be antimony or sulphur. Several subsequent cycles of Fourier and least-squares calculations identified all remaining atoms in the structure and from a consideration of thermal parameters and bond lengths the composition of the crystal was established as $(Se_4^{2+})(Sb_2F_4^{2+})(Sb_2F_5^+)$-

$(SbF_6^-)_5$. Block-diagonal least-squares refinement (two blocks) of the positional and isotropic thermal parameters of all atoms in the structure converged to give $R = 0.078$ for 3 205 observed $[I/\sigma(I) > 3.0]$ reflections in the first data set $(R = \Sigma||F_o|-|F_c||/\Sigma F_o)$.

TABLE 1

Details of *X*-ray intensity measurements [a]

	$(Se_4)(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$	$Se_4(AlCl_4)_2$	$Te_4(SbF_6)_2$
Reflections used in unit-cell determination (no./2θ range)	15/(25 < 2θ < 29°)	15/(24 < 2θ < 30°)	14/(21 < 2θ < 27°)
Max. 2θ, scan type	47.5, θ—2θ	55.0, θ—2θ	45.0, θ—2θ
Scan speed (° min^{-1}) (dependent on intensity of a 2 s prescan)	3.5—29.3	2.5—29.3	1.2—29.3
Scan range	$(K_{\alpha1} - 0.8°)$—$(K_{\alpha2} + 0.8°)$	$(K_{\alpha1} - 0.9°)$—$(K_{\alpha2} + 0.9°)$	$(K_{\alpha1} - 0.9°)$—$(K_{\alpha2} + 0.9°)$
Standard reflections (no./interval)	3/77	3/47	3/57
Quadrants collected	$h,k,\pm l$	$h,\pm k,\pm l$	$h,\pm k,\pm l$
No. of data collected (including standards) [b]	6 273	4 308	1 962
Absorption correction	Spherical $\mu R = 0.9$	ABSORB [c] 8 × 9 × 7 grid (A^*: 4.28—12.37)	ABSORB [c] 5 × 10 × 10 grid (A^*: 1.10—3.57)
No. of independent data	5 219 [d]	1 858 [e]	874
No. of observed data with $F > 6\sigma(F)$	3 634	912	709
No. of data with $F > 2\sigma(F)$	4 715	1 543	823

[a] Radiation: Mo-$K_{\bar{\alpha}}$ (graphite monochromator). Background measurements: stationary counter stationary crystal background counts of a ¼ scan time at each end of the scan. [b] No decline in intensities of standards observed during data collection. [c] Ref. 8. [d] $R_{merge} = 0.02$ for 723 equivalent pairs. [e] $R_{merge} = 0.033$ for 1 290 equivalent pairs (*N.B.* $R_{merge} = 0.045$ before absorption corrections).

Using these parameters further refinement was with the data set collected on the single crystal from the direct reaction of selenium and excess of SbF_5. After allowing anisotropic thermal motion for the heavy atoms R refined to 0.074 (unit weights) for 4 715 reflections with $F > 2.0\sigma(F)$. At this point it was noted that the data were suffering badly from the effects of secondary extinction and on refining an approximate extinction correction for the data there was a significant improvement in the residual to give $R = 0.070$. Due to some significant correlations between both the scale factor and the overall thermal parameter with the extinction correction factor g, the value of g had to be fixed in subsequent cycles of least squares. Further cycles of block-diagonal least-squares (two blocks) then converged (maximum shift to error = 0.13) to the final residuals $R = 0.052$ $[R' = 0.062$, $R' = (\Sigma w|F_o - F_c|^2/\Sigma w F_o^2)^{\frac{1}{2}}]$ for 3 634 observed $[F > 6.0\sigma(F)]$ reflections and $R = 0.070$ $(R' = 0.075)$ for 4 715 reflections with $F > 2.0\sigma(F)$. The final value of the extinction correction g as defined by the *X*-ray system was 3.94×10^{-5}. The weights used in the final cycle were given by the expressions $w = x$ where $x = F/80$ if $F < 80$, or $x = 150/F$ if $F > 150$, otherwise $x = 1.0$. A final comparison of the average $w||F_o|-|F_c||^2$ as a function of $F_{obs.}$ and sinθ after the use of this scheme showed no systematic trends. A final difference-Fourier contained maximum peaks of *ca.* 3.0 e Å^{-3} close to several of the antimony atoms and some residual peaks of *ca.* 1—2 e Å^{-3} close to the fluorine atoms in the anion $Sb(9)F_6^-$. The minimum trough was −2.1 e Å^{-3}.

(*b*) $Se(AlCl_4)_2$ (3). The structure of this compound was solved using the Patterson function to locate the selenium atoms on the special positions of symmetry *2* and *m* such that each Se_4^{2+} cation has $2/m$ ($\equiv \bar{T}$) symmetry at several of the centres of symmetry in the unit cell. The tetrachloroaluminate anions were then located in subsequent Fourier maps. Least-squares refinement with all atoms having anisotropic thermal parameters converged to give the residual $R = 0.073$. Application of absorption corrections to all the data, re-averaging, and further least-squares refinement then reduced R to 0.051. There was no evidence of any extinction effects in the data and the least-squares refinement converged (maximum shift to error = 0.18) to give the final residuals $R = 0.042$ $(R' = 0.046)$ for 912 observed data with $F > 6.0\sigma(F)$ and $R = 0.087$ $(R' = 0.070)$ for 1 543 data with $F > 2.0\sigma(F)$. The weights used in the final cycle were given by the expressions $w = 0.000\,01$ if $0.20F_{obs.} \geqslant |F_{calc.}|$, or $w = xy$ where $x = F/46$ if $F < 46$ or $x = 46/F$ if $F > 46$, otherwise $x = 1.0$ and $y = \sin\theta/0.27$ if $\sin\theta < 0.27$ or $y = 0.31/\sin\theta$ if $\sin\theta > 0.31$, otherwise $y = 1.0$. A final comparison of the average $w||F_o|-|F_c||^2$ as a function of $F_{obs.}$ or sinθ after the use of this scheme showed no systematic trends. A final difference-Fourier contained no peak or trough greater than 1.3 or −1.9 e Å^{-3} respectively.

(*c*) $Te_4(SbF_6)_2$ (2). As with (1) above, the composition of the crystal was initially uncertain although the composition $2[Te_4(SbF_6)_2]$ for the unit cell was likely and was assumed in the calculation of normalised structure factors for the data. The direct methods routines of the program SHELX were then used to give positions for the three heavy atoms in the structure. Least-squares refinement assuming these atoms to be tellurium gave $R = 0.177$ and a subsequent difference-Fourier gave the positions of six fluorine atoms around one of the atoms which established the compound as the salt $Te_4(SbF_6)_2$.

Least-squares refinement allowing anisotropic thermal motion for the heavy atoms converged to give $R = 0.075$ for 709 observed data. The data set was then corrected for the effects of absorption and R dropped to 0.051. There was no evidence of any extinction effects in the data and further refinement converged (maximum shift to error = 0.06) to give the final residuals $R = 0.051$ $(R' = 0.064)$ for 709 observed data with $F > 6.0\sigma(F)$, and $R = 0.059$ $(R' = 0.069)$ for 823 data with $F > 2.0\sigma(F)$. The weights used were given by the expressions $w = 0.000\,01$ if $0.25\ F_{obs.} \geqslant |F_{calc.}|$, or $w = 150/F$ if $F > 150$, otherwise $w = 1.0$. This scheme gave unit weights to the majority of the data. A final comparison of the average $w||F_o|-|F_c||^2$ as a function of $F_{obs.}$ or sinθ after the use of this scheme showed no systematic trends. A final difference-Fourier contained no peak greater than 2.0 e Å^{-3} or any trough less than −1.3 e Å^{-3}.

For all three structures, neutral atom scattering factors in the analytical form were taken from ref. 7. All calculations were performed on a CDC 6400 computer using programs in the *X*-RAY [8] and SHELX [6] systems and some local programs. The final atomic positional co-ordinates for all three compounds are given in Table 2 and Table 3 includes

TABLE 2

Final atomic positional parameters (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
(*a*) $(\mathrm{Se_4}^{2+})(\mathrm{Sb_2F_4}^{2+})(\mathrm{Sb_2F_5}^{+})(\mathrm{SbF_6}^{-})_5$, (1)			
Se(1)	78(2)	3 855(2)	5 228(2)
Se(2)	698(2)	4 865(2)	4 355(2)
Se(3)	4 845(2)	4 014(2)	5 505(2)
Se(4)	4 016(2)	5 271(2)	5 019(2)
Sb(1)	−317(1)	4 532(1)	900(1)
Sb(2)	5 355(1)	5 608(1)	853(1)
Sb(3)	1 977(1)	3 756(1)	2 131(1)
Sb(4)	3 113(1)	6 484(1)	2 066(1)
Sb(5)	5 324(1)	8 141(1)	2 446(1)
Sb(6)	−318(1)	2 249(1)	2 686(1)
Sb(7)	−2 676(1)	2 917(1)	609(1)
Sb(8)	7 647(1)	7 132(1)	475(1)
Sb(9)	2 421(1)	206(1)	1 868(1)
F(11)	674(7)	5 205(9)	314(7)
F(12)	80(8)	3 312(10)	511(8)
F(21)	4 343(7)	4 836(9)	289(7)
F(22)	4 955(7)	6 759(9)	349(7)
F(31)	920(8)	4 364(9)	1 690(7)
F(32)	1 772(8)	4 446(10)	3 063(8)
F(34)	2 516(8)	5 093(9)	1 775(7)
F(41)	4 092(7)	5 912(9)	1 572(7)
F(42)	3 455(8)	5 849(10)	2 991(8)
F(51)	4 213(11)	7 618(13)	2 436(10)
F(52)	6 423(10)	8 665(12)	2 461(9)
F(53)	5 685(9)	7 009(11)	1 910(9)
F(54)	4 921(12)	9 226(15)	2 968(12)
F(55)	5 584(14)	7 532(18)	3 387(13)
F(56)	5 070(13)	8 729(16)	1 496(12)
F(61)	812(11)	2 663(13)	2 531(10)
F(62)	−1 401(10)	1 807(12)	2 869(10)
F(63)	−310(14)	1 472(17)	1 810(13)
F(64)	−315(15)	3 059(18)	3 552(14)
F(65)	−671(9)	3 314(11)	2 055(9)
F(66)	102(11)	1 224(14)	3 292(11)
F(71)	−2 764(10)	3 168(12)	−472(10)
F(72)	−2 570(9)	2 656(11)	1 682(8)
F(73)	−3 618(10)	2 077(12)	539(9)
F(74)	−1 724(9)	3 756(11)	674(9)
F(75)	−1 952(12)	1 872(15)	435(11)
F(76)	−3 384(10)	3 975(12)	809(9)
F(81)	6 899(12)	8 153(14)	212(11)
F(82)	8 375(9)	6 094(11)	740(9)
F(83)	6 713(9)	6 277(11)	608(8)
F(84)	8 577(11)	7 974(13)	349(10)
F(85)	7 585(9)	7 488(11)	1 529(9)
F(86)	7 697(10)	6 724(12)	−561(10)
F(91)	1 689(28)	62(34)	1 053(27)
F(92)	3 081(21)	316(26)	2 814(20)
F(93)	2 660(14)	−1 129(16)	1 794(13)
F(94)	2 192(14)	1 552(17)	1 858(13)
F(95)	3 379(19)	499(24)	1 370(18)
F(96)	1 582(27)	−33(32)	2 546(26)
(*b*) $\mathrm{Se_4(AlCl_4)_2}$			
Se(1)	0(0)	0(0)	1 741(2)
Se(2)	1 213(1)	126(1)	0(0)
Se(3)	0(0)	5 000(0)	3 254(2)
Se(4)	253(1)	3 803(1)	5 000(0)
Al(1)	1 757(3)	1 000(4)	5 000(0)
Al(2)	1 164(4)	3 329(3)	0(0)
Cl(1)	2 118(3)	92(3)	6 838(3)
Cl(2)	191(3)	1 319(3)	5 000(0)
Cl(3)	2 630(5)	2 324(5)	5 000(0)
Cl(4)	295(3)	2 887(2)	1 841(3)
Cl(5)	1 321(3)	4 934(3)	0(0)
Cl(6)	2 560(5)	2 593(5)	0(0)
(*c*) $\mathrm{Te_4(SbF_6)_2}$			
Sb	3 941(3)	3 315(1)	5 103(2)
Te(1)	1 559(3)	4 042(1)	9 616(2)
Te(2)	715(3)	5 318(1)	8 018(2)
F(1)	1 985(30)	3 320(10)	2 918(21)
F(2)	1 215(30)	2 845(11)	5 729(22)
F(3)	4 573(30)	2 237(11)	4 304(22)
F(4)	3 256(39)	4 382(13)	5 969(27)
F(5)	6 594(32)	3 820(11)	4 473(24)
F(6)	5 754(38)	3 408(13)	7 320(28)

TABLE 3

Bond lengths (Å), selected interionic contact distances (Å), and related bond angles (°) with standard deviations in parentheses *

(*a*) $\mathrm{(Se_4)(Sb_2F_4)(Sb_2F_5)(SbF_6)_5}$

(*i*) The $\mathrm{Se_4}^{2+}$ cation

Se(1)–Se(2)	2.266(4)	Se(3)–Se(4)	2.276(4)
Se(1)–Se(2$^{\mathrm{V}}$)	2.247(4)	Se(3)–Se(4$^{\mathrm{V}}$)	2.252(4)
Se(1) · · · F(84$^{\mathrm{VIII}}$)	2.65(2)	Se(3) · · · F(73$^{\mathrm{XI}}$)	2.83(2)
Se(1) · · · F(63$^{\mathrm{XII}}$)	2.82(2)	Se(3) · · · F(95$^{\mathrm{XII}}$)	2.86(3)
Se(1) · · · F(12$^{\mathrm{XII}}$)	2.97(1)	Se(3) · · · F(55$^{\mathrm{III}}$)	2.91(2)
Se(1) · · · F(64)	3.09(2)	Se(3) · · · F(81$^{\mathrm{VIII}}$)	3.18(2)
Se(1) · · · F(91$^{\mathrm{XII}}$)	3.20(4)	Se(4) · · · F(73$^{\mathrm{IX}}$)	2.68(2)
Se(2) · · · F(84$^{\mathrm{VIII}}$)	2.83(2)	Se(4) · · · F(95$^{\mathrm{XII}}$)	2.75(3)
Se(2) · · · F(32)	2.88(1)		
Se(2) · · · F(63$^{\mathrm{IX}}$)	2.99(2)		
Se(2) · · · F(64)	3.19(2)		

Se(2$^{\mathrm{V}}$)–Se(1)–Se(2)	89.9(1)
Se(1)–Se(2)–Se(1$^{\mathrm{V}}$)	90.1(2)
Se(2)–Se(1)–F(84$^{\mathrm{VIII}}$)	69.8(4)
Se(2)–Se(1)–F(63$^{\mathrm{XII}}$)	146.7(5)
Se(2)–Se(1)–F(12$^{\mathrm{XII}}$)	134.6(3)
Se(2)–Se(1)–F(64)	71.2(5)
Se(2)–Se(1)–F(91$^{\mathrm{XII}}$)	70.1(8)
Se(2$^{\mathrm{V}}$)–Se(1)–F(84$^{\mathrm{VIII}}$)	156.1(4)
Se(2$^{\mathrm{V}}$)–Se(1)–F(63$^{\mathrm{XII}}$)	71.2(5)
Se(2$^{\mathrm{V}}$)–Se(1)–F(12$^{\mathrm{XII}}$)	134.8(3)
Se(2$^{\mathrm{V}}$)–Se(1)–F(64)	117.9(5)
Se(2$^{\mathrm{V}}$)–Se(1)–F(91$^{\mathrm{XII}}$)	86.6(8)
Se(1)–Se(2)–F(84$^{\mathrm{VIII}}$)	61.5(4)
Se(1)–Se(2)–F(32)	131.6(3)
Se(1)–Se(2)–F(63$^{\mathrm{IX}}$)	142.2(5)
Se(1)–Se(2)–F(64)	66.5(4)
Se(1$^{\mathrm{V}}$)–Se(2)–F(84$^{\mathrm{VIII}}$)	148.9(4)
Se(1$^{\mathrm{V}}$)–Se(2)–F(32)	137.2(3)
Se(1$^{\mathrm{V}}$)–Se(2)–F(63$^{\mathrm{IX}}$)	63.4(4)
Se(1$^{\mathrm{V}}$)–Se(2)–F(64)	117.0(5)
Se(1$^{\mathrm{VII}}$)–F(84)–Se(2$^{\mathrm{VII}}$)	48.7(3)
Se(1$^{\mathrm{XIII}}$)–F(63)–Se(2$^{\mathrm{X}}$)	45.4(4)
Se(1)–F(64)–Se(2)	42.2(3)
Se(4$^{\mathrm{V}}$)–Se(3)–Se(4)	89.4(1)
Se(3)–Se(4)–Se(3$^{\mathrm{V}}$)	90.6(1)
Se(4)–Se(3)–F(73$^{\mathrm{XI}}$)	150.7(4)
Se(4)–Se(3)–F(95$^{\mathrm{XII}}$)	63.6(6)
Se(4)–Se(3)–F(55$^{\mathrm{III}}$)	128.8(5)
Se(4)–Se(3)–F(81$^{\mathrm{VIII}}$)	70.1(4)
Se(4$^{\mathrm{V}}$)–Se(3)–F(73$^{\mathrm{XI}}$)	62.5(3)
Se(4$^{\mathrm{V}}$)–Se(3)–F(95$^{\mathrm{XII}}$)	140.9(7)
Se(4$^{\mathrm{V}}$)–Se(3)–F(55$^{\mathrm{III}}$)	140.6(5)
Se(4$^{\mathrm{V}}$)–Se(3)–F(81$^{\mathrm{VIII}}$)	133.8(4)
Se(3)–Se(4)–F(73$^{\mathrm{IX}}$)	158.3(4)
Se(3)–Se(4)–F(95$^{\mathrm{XII}}$)	68.7(7)
Se(3$^{\mathrm{V}}$)–Se(4)–F(73$^{\mathrm{IX}}$)	69.4(4)
Se(3$^{\mathrm{V}}$)–Se(4)–F(95$^{\mathrm{XII}}$)	144.7(6)
Se(3$^{\mathrm{XIII}}$)–F(95)–Se(4$^{\mathrm{XIII}}$)	47.8(5)
Se(3)–F(73)–Se(4)	48.1(3)

TABLE 3 (*continued*)

(*ii*) The $Sb_2F_4^{2+}$ cation

Sb(1)–F(11)	2.09(1)	Sb(2)–F(21)	2.10(1)
Sb(1)–F(11$^{\mathrm{VI}}$)	2.15(1)	Sb(2)–F(21$^{\mathrm{IV}}$)	2.11(1)
Sb(1)–F(12)	1.89(1)	Sb(2)–F(22)	1.87(1)
Sb(1)–F(31)	2.33(1)	Sb(2)–F(41)	2.41(1)
Sb(1)–F(65)	2.64(2)	Sb(2)–F(53)	2.65(2)
Sb(1)–F(74)	2.47(2)	Sb(2)–F(83)	2.37(1)
Sb(1)–F(66$^{\mathrm{IX}}$)	2.68(2)	Sb(2)–F(54$^{\mathrm{VIII}}$)	2.79(2)
Sb(1)–F(82$^{\mathrm{II}}$)	2.95(2)	Sb(2)–F(76$^{\mathrm{I}}$)	2.97(2)

F(11)–Sb(1)–F(11$^{\mathrm{VI}}$)	69.0(4)
F(11)–Sb(1)–F(12)	87.0(5)
F(11)–Sb(1)–F(31)	72.4(4)
F(11)–Sb(1)–F(65)	144.0(4)
F(11)–Sb(1)–F(74)	142.4(5)
F(11)–Sb(1)–F(66$^{\mathrm{IX}}$)	78.1(5)
F(11)–Sb(1)–F(82$^{\mathrm{II}}$)	100.2(4)
F(11$^{\mathrm{VI}}$)–Sb(1)–F(12)	83.3(5)
F(11$^{\mathrm{VI}}$)–Sb(1)–F(31)	138.7(4)
F(11$^{\mathrm{VI}}$)–Sb(1)–F(65)	139.8(4)
F(11$^{\mathrm{VI}}$)–Sb(1)–F(74)	73.8(5)
F(11$^{\mathrm{VI}}$)–Sb(1)–F(66$^{\mathrm{IX}}$)	112.1(5)
F(11$^{\mathrm{VI}}$)–Sb(1)–F(82$^{\mathrm{II}}$)	68.8(4)
F(12)–Sb(1)–F(31)	80.7(5)
F(12)–Sb(1)–F(65)	78.5(5)
F(12)–Sb(1)–F(74)	83.3(5)
F(12)–Sb(1)–F(66$^{\mathrm{IX}}$)	152.3(6)
F(12)–Sb(1)–F(82$^{\mathrm{II}}$)	146.0(5)
F(31)–Sb(1)–F(65)	72.9(4)
F(31)–Sb(1)–F(74)	140.5(5)
F(31)–Sb(1)–F(66$^{\mathrm{IX}}$)	72.6(5)
F(31)–Sb(1)–F(82$^{\mathrm{II}}$)	133.3(4)
F(65)–Sb(1)–F(74)	68.7(5)
F(65)–Sb(1)–F(66$^{\mathrm{IX}}$)	100.0(5)
F(65)–Sb(1)–F(82$^{\mathrm{II}}$)	110.3(4)
F(74)–Sb(1)–F(66$^{\mathrm{IX}}$)	122.4(5)
F(74)–Sb(1)–F(82$^{\mathrm{II}}$)	70.7(5)
F(66$^{\mathrm{IX}}$)–Sb(1)–F(82$^{\mathrm{II}}$)	60.8(5)
Sb(1)–F(11)–Sb(1$^{\mathrm{VI}}$)	111.0(5)
F(21)–Sb(2)–F(21$^{\mathrm{IV}}$)	68.4(4)
F(21)–Sb(2)–F(22)	88.1(5)
F(21)–Sb(2)–F(41)	72.1(4)
F(21)–Sb(2)–F(53)	142.1(5)
F(21)–Sb(2)–F(83)	141.2(5)
F(21)–Sb(2)–F(54$^{\mathrm{VIII}}$)	82.1(5)
F(21)–Sb(2)–F(76$^{\mathrm{I}}$)	96.7(4)
F(21$^{\mathrm{IV}}$)–Sb(2)–F(22)	84.0(5)
F(21$^{\mathrm{IV}}$)–Sb(2)–F(41)	137.6(4)
F(21$^{\mathrm{IV}}$)–Sb(2)–F(53)	141.7(5)
F(21$^{\mathrm{IV}}$)–Sb(2)–F(83)	73.0(5)
F(21$^{\mathrm{IV}}$)–Sb(2)–F(54$^{\mathrm{VIII}}$)	121.5(5)
F(21$^{\mathrm{IV}}$)–Sb(2)–F(76$^{\mathrm{I}}$)	65.8(4)
F(22)–Sb(2)–F(41)	79.8(5)
F(22)–Sb(2)–F(53)	76.9(5)
F(22)–Sb(2)–F(83)	83.8(5)
F(22)–Sb(2)–F(54$^{\mathrm{VIII}}$)	145.8(6)
F(22)–Sb(2)–F(76$^{\mathrm{I}}$)	144.8(5)
F(41)–Sb(2)–F(53)	71.1(4)
F(41)–Sb(2)–F(83)	142.3(5)
F(41)–Sb(2)–F(54$^{\mathrm{VIII}}$)	66.0(5)
F(41)–Sb(2)–F(76$^{\mathrm{I}}$)	134.9(4)
F(53)–Sb(2)–F(83)	72.2(5)
F(53)–Sb(2)–F(54$^{\mathrm{VIII}}$)	91.1(5)
F(53)–Sb(2)–F(76$^{\mathrm{I}}$)	115.7(4)
F(83)–Sb(2)–F(54$^{\mathrm{VIII}}$)	123.3(5)
F(83)–Sb(2)–F(76$^{\mathrm{I}}$)	70.7(5)
F(54$^{\mathrm{VIII}}$)–Sb(2)–F(76$^{\mathrm{I}}$)	69.2(5)
Sb(2)–F(21)–Sb(2$^{\mathrm{IV}}$)	111.6(5)

(*iii*) The $Sb_2F_5^+$ cation

Sb(3)–F(31)	1.98(1)	Sb(4)–F(34)	2.15(1)
Sb(3)–F(32)	1.88(1)	Sb(4)–F(41)	1.95(1)
Sb(3)–F(34)	2.09(1)	Sb(4)–F(42)	1.86(1)
Sb(3)–F(61)	2.47(2)	Sb(4)–F(51)	2.38(2)
Sb(3)–F(86$^{\mathrm{IV}}$)	2.82(2)	Sb(4)–F(71$^{\mathrm{VI}}$)	2.79(2)
Sb(3)–F(52$^{\mathrm{VIII}}$)	2.59(2)	Sb(4)–F(62$^{\mathrm{IX}}$)	2.74(2)
Sb(3)–F(85$^{\mathrm{VIII}}$)	2.91(1)	Sb(4)–F(72$^{\mathrm{IX}}$)	2 82(1)
Sb(3)–F(94)	3.03(2)		

TABLE 3 (*continued*)

F(31)–Sb(3)–F(32)	86.8(5)
F(31)–Sb(3)–F(34)	82.9(5)
F(31)–Sb(3)–F(61)	74.3(5)
F(31)–Sb(3)–F(86$^{\mathrm{IV}}$)	85.2(5)
F(31)–Sb(3)–F(52$^{\mathrm{VIII}}$)	156.5(5)
F(31)–Sb(3)–F(85$^{\mathrm{VIII}}$)	135.3(5)
F(31)–Sb(3)–F(94)	116.5(6)
F(32)–Sb(3)–F(34)	84.4(5)
F(32)–Sb(3)–F(61)	84.8(6)
F(32)–Sb(3)–F(86$^{\mathrm{IV}}$)	163.6(5)
F(32)–Sb(3)–F(52$^{\mathrm{VIII}}$)	89.7(5)
F(32)–Sb(3)–F(85$^{\mathrm{VIII}}$)	70.9(5)
F(32)–Sb(3)–F(94)	129.8(6)
F(34)–Sb(3)–F(61)	155.3(5)
F(34)–Sb(3)–F(86$^{\mathrm{IV}}$)	80.3(5)
F(34)–Sb(3)–F(52$^{\mathrm{VIII}}$)	73.6(5)
F(34)–Sb(3)–F(85$^{\mathrm{VIII}}$)	130.3(4)
F(34)–Sb(3)–F(94)	138.8(5)
F(61)–Sb(3)–F(86$^{\mathrm{IV}}$)	106.8(5)
F(61)–Sb(3)–F(52$^{\mathrm{VIII}}$)	128.5(5)
F(61)–Sb(3)–F(85$^{\mathrm{VIII}}$)	65.7(5)
F(61)–Sb(3)–F(94)	62.9(6)
F(86$^{\mathrm{IV}}$)–Sb(3)–F(52$^{\mathrm{VIII}}$)	91.9(5)
F(86$^{\mathrm{IV}}$)–Sb(3)–F(85$^{\mathrm{VIII}}$)	124.2(4)
F(86$^{\mathrm{IV}}$)–Sb(3)–F(94)	66.6(5)
F(52$^{\mathrm{VIII}}$)–Sb(3)–F(85$^{\mathrm{VIII}}$)	64.2(5)
F(52$^{\mathrm{VIII}}$)–Sb(3)–F(94)	83.2(5)
F(85$^{\mathrm{VIII}}$)–Sb(3)–F(94)	61.3(5)
F(34)–Sb(4)–F(41)	84.3(5)
F(34)–Sb(4)–F(42)	84.4(5)
F(34)–Sb(4)–F(51)	158.6(5)
F(34)–Sb(4)–F(71$^{\mathrm{VI}}$)	81.6(5)
F(34)–Sb(4)–F(62$^{\mathrm{IX}}$)	74.1(5)
F(34)–Sb(4)–F(72$^{\mathrm{XI}}$)	121.5(4)
F(41)–Sb(4)–F(42)	88.6(5)
F(41)–Sb(4)–F(51)	77.8(6)
F(41)–Sb(4)–F(71$^{\mathrm{VI}}$)	77.0(5)
F(41)–Sb(4)–F(62$^{\mathrm{IX}}$)	151.6(5)
F(41)–Sb(4)–F(72$^{\mathrm{IX}}$)	145.1(4)
F(42)–Sb(4)–F(51)	83.6(6)
F(42)–Sb(4)–F(71$^{\mathrm{VI}}$)	160.8(5)
F(42)–Sb(4)–F(62$^{\mathrm{IX}}$)	107.0(5)
F(42)–Sb(4)–F(72$^{\mathrm{IX}}$)	72.7(5)
F(51)–Sb(4)–F(71$^{\mathrm{VI}}$)	105.2(5)
F(51)–Sb(4)–F(62$^{\mathrm{IX}}$)	126.5(6)
F(51)–Sb(4)–F(72$^{\mathrm{IX}}$)	71.2(5)
F(71$^{\mathrm{VI}}$)–Sb(4)–F(62$^{\mathrm{IX}}$)	81.7(5)
F(71$^{\mathrm{VI}}$)–Sb(4)–F(72$^{\mathrm{IX}}$)	126.1(4)
F(62$^{\mathrm{IX}}$)–Sb(4)–F(72$^{\mathrm{IX}}$)	63.3(4)
Sb(3)–F(34)–Sb(4)	149.8(6)
Sb(1)–F(31)–Sb(3)	158.4(7)
Sb(4)–F(41)–Sb(2)	166.2(6)

(*iv*) SbF_6^- anions

Sb–F bond distances: 1.78(4)—1.89(2)
F–Sb–F bond angles: *cis*, 87(1)—101(2)
trans, 169(2)—179.6(7)

(*v*) Fluorine bridge angles

Sb(5)–F(51)–Sb(4)	155.4(10)
Sb(5)–F(52)–Sb(3$^{\mathrm{VII}}$)	155.8(8)
Sb(5)–F(53)–Sb(2)	148.8(7)
Sb(5)–F(54)–Sb(2$^{\mathrm{VII}}$)	161.4(10)
Sb(5)–F(55)–Se(3$^{\mathrm{III}}$)	147.0(11)
Sb(6)–F(61)–Sb(3)	158.0(9)
Sb(6)–F(62)–Sb(4$^{\mathrm{X}}$)	167.6(9)
Sb(6)–F(63)–Se(1$^{\mathrm{XIII}}$)	151.6(12)
Sb(6)–F(63)–Se(2$^{\mathrm{X}}$)	162.4(11)
Sb(6)–F(64)–Se(1)	160.7(12)
Sb(6)–F(64)–Se(2)	141.7(11)
Sb(6)–F(65)–Sb(1)	147.3(8)
Sb(6)–F(66)–Sb(1$^{\mathrm{X}}$)	165.2(9)
Sb(7)–F(71)–Sb(4$^{\mathrm{VI}}$)	172.8(8)
Sb(7)–F(72)–Sb(4$^{\mathrm{X}}$)	146.3(7)
Sb(7)–F(73)–Se(3$^{\mathrm{XIV}}$)	173.4(8)
Sb(7)–F(73)–Se(4$^{\mathrm{X}}$)	138.5(8)
Sb(7)–F(74)–Sb(7)	167.1(8)
Sb(7)–F(76)–Sb(2$^{\mathrm{II}}$)	170.1(8)
Sb(8)–F(81)–Se(3$^{\mathrm{VIII}}$)	153.3(9)

TABLE 3 (*continued*)

Sb(8)–F(82)–Sb(1$^{\mathrm{I}}$)	169.8(8)
Sb(8)–F(83)–Sb(2)	164.6(8)
Sb(8)–F(84)–Se(1$^{\mathrm{VII}}$)	162.6(9)
Sb(8)–F(84)–Se(2$^{\mathrm{VII}}$)	146.9(9)
Sb(8)–F(85)–Sb(3$^{\mathrm{VII}}$)	152.3(7)
Sb(8)–F(86)–Sb(3$^{\mathrm{IV}}$)	171.1(8)
Sb(9)–F(91)–Se(1$^{\mathrm{XIII}}$)	140.3(22)
Sb(9)–F(94)–Sb(3)	169.7(11)
Sb(9)–F(95)–Se(3$^{\mathrm{XIII}}$)	176.9(16)
Sb(9)–F(95)–Se(4$^{\mathrm{XIII}}$)	130.6(15)

(*b*) $Se_4(AlCl_4)_2$

(*i*) The Se_4^{2+} cation

Se(1)–Se(2)	2.283(2) (× 4)
Se(1)–Se(1)	3.227(2)
Se(2)–Se(2)	3.231(2)
Se(1)–Cl(1$^{\mathrm{XVII,XX}}$)	3.101(3)
Se(1)–Cl(2$^{0,\mathrm{XVII}}$)	3.496(2)
Se(1)–Cl(4)	3.838(3)
Se(2)–Cl(1$^{\mathrm{XVI,XX}}$)	3.166(3)
Se(2)–Cl(5$^{\mathrm{XXV}}$)	3.275(4)
Se(2)–Cl(6)	3.717(7)
Se(2)–Cl(6$^{\mathrm{XXV}}$)	3.723(7)
Se(3)–Se(4)	2.288(2) (× 4)
Se(3)–Se(3)	3.235(2)
Se(4)–Se(4)	3.236(2)
Se(3)–Cl(4$^{0,\mathrm{XIX}}$)	3.111(3)
Se(3)–Cl(5$^{0,\mathrm{VI}}$)	3.488(2)
Se(3)–Cl(1$^{\mathrm{XXIII,XXVI}}$)	3.821(3)
Se(4)–Cl(4$^{0,\mathrm{XX}}$)	3.168(3)
Se(4)–Cl(2)	3.285(4)
Se(4)–Cl(3$^{0,\mathrm{XXIII}}$)	3.706(6)
Se(2$^{\mathrm{XVIII}}$)–Se(1)–Se(2)	90.08(7)
Se(1$^{\mathrm{XVIII}}$)–Se(2)–Se(1)	89.92(7)
Se(2)–Se(1)–Cl(1$^{\mathrm{XVII}}$)	159.97(8)
Se(2)–Se(1)–Cl(1$^{\mathrm{XX}}$)	70.15(7)
Se(2)–Se(1)–Cl(2^{0})	121.52(7)
Se(2)–Se(1)–Cl(2$^{\mathrm{XVII}}$)	134.24(7)
Cl(1$^{\mathrm{XVII}}$)–Se(1)–Cl(1$^{\mathrm{XX}}$)	129.75(10)
Cl(1$^{\mathrm{XVII}}$)–Se(1)–Cl(2^{0})	73.65(9)
Cl(1$^{\mathrm{XVII}}$)–Se(1)–Cl(2$^{\mathrm{XVII}}$)	63.14(9)
Cl(2^{0})–Se(1)–Cl(2$^{\mathrm{XVII}}$)	60.55(8)
Se(1)–Se(2)–Cl(1$^{\mathrm{XVI}}$)	156.82(9)
Se(1)–Se(2)–Cl(1$^{\mathrm{XX}}$)	67.12(7)
Se(1)–Se(2)–Cl(5$^{\mathrm{XXV}}$)	134.11(4)
Se(1)–Se(2)–Cl(6^{0})	113.69(8)
Se(1)–Se(2)–Cl(6$^{\mathrm{XXV}}$)	103.97(8)
Cl(1$^{\mathrm{XVI}}$)–Se(2)–Cl(1$^{\mathrm{XX}}$)	135.51(10)
Cl(1$^{\mathrm{XVI}}$)–Se(2)–Cl(5$^{\mathrm{XXV}}$)	67.77(7)
Cl(1$^{\mathrm{XVI}}$)–Se(2)–Cl(6^{0})	80.26(8)
Cl(1$^{\mathrm{XVI}}$)–Se(2)–Cl(6$^{\mathrm{XXV}}$)	79.76(9)
Cl(5$^{\mathrm{XXV}}$)–Se(2)–Cl(6^{0})	65.77(12)
Cl(5$^{\mathrm{XXV}}$)–Se(2)–Cl(6$^{\mathrm{XXV}}$)	59.69(12)
Cl(6^{0})–Se(2)–Cl(6$^{\mathrm{XXV}}$)	125.45(14)
Se(1$^{\mathrm{XVII}}$)–Cl(1)–Se(2$^{\mathrm{XV}}$)	42.72(6)
Se(4$^{\mathrm{V}}$)–Se(3)–Se(4)	90.03(7)
Se(3$^{\mathrm{V}}$)–Se(4)–Se(3)	89.97(7)
Se(4)–Se(3)–Cl(4^{0})	69.98(7)
Se(4)–Se(3)–Cl(4$^{\mathrm{XIX}}$)	159.65(8)
Se(4)–Se(3)–Cl(5^{0})	121.36(7)
Se(4)–Se(3)–Cl(5$^{\mathrm{VI}}$)	134.59(7)
Cl(4^{0})–Se(3)–Cl(4$^{\mathrm{XIX}}$)	130.20(10
Cl(4^{0})–Se(3)–Cl(5^{0})	63.29(9)
Cl(4^{0})–Se(3)–Cl(5$^{\mathrm{VI}}$)	73.82(9)
Cl(5^{0})–Se(3)–Cl(5$^{\mathrm{VI}}$)	60.32(8)
Se(3)–Se(4)–Cl(4^{0})	67.29(6)
Se(3)–Se(4)–Cl(4$^{\mathrm{XX}}$)	156.95(8)
Se(3)–Se(4)–Cl(2^{0})	133.47(4)
Se(3)–Se(4)–Cl(3^{0})	119.32(8)
Se(3)–Se(4)–Cl(3$^{\mathrm{XXIII}}$)	97.92(8)
Cl(4^{0})–Se(4)–Cl(4$^{\mathrm{XX}}$)	135.00(9)
Cl(4^{0})–Se(4)–Cl(2^{0})	67.56(6)
Cl(4^{0})–Se(4)–Cl(3^{0})	77.50(8)
Cl(4^{0})–Se(4)–Cl(3$^{\mathrm{XXIII}}$)	82.26(9)
Cl(2^{0})–Se(4)–Cl(3^{0})	59.58(12)
Cl(2^{0})–Se(4)–Cl(3$^{\mathrm{XXIII}}$)	65.36(12)
Cl(3^{0})–Se(4)–Cl(3$^{\mathrm{XXIII}}$)	124.94(14)
Se(3)–Cl(4)–Se(4)	42.73(5)

TABLE 3 (*continued*)

(*ii*) The $AlCl_4^-$ anions

Al(1)–Cl(1)	2.138(5)	Al(2)–Cl(4)	2.140(5)
Al(1)–Cl(1$^{\mathrm{XX}}$)	2.138(5)	Al(2)–Cl(4$^{\mathrm{XXI}}$)	2.140(5)
Al(1)–Cl(2)	2.117(6)	Al(2)–Cl(5)	2.132(6)
Al(1)–Cl(3)	2.097(8)	Al(2)–Cl(6)	2.090(8)

Cl(1)–Al(1)–Cl(1$^{\mathrm{XX}}$)	106.6(2)
Cl(1)–Al(1)–Cl(2)	109.3(2)
Cl(1)–Al(1)–Cl(3)	110.2(2)
Cl(2)–Al(1)–Cl(3)	111.9(3)
Al(1)–Cl(1)–Se(1$^{\mathrm{XVII}}$)	99.1(2)
Al(1)–Cl(1)–Se(2$^{\mathrm{XV}}$)	130.2(2)
Al(1)–Cl(1)–Se(3$^{\mathrm{XXII}}$)	102.9(2)
Al(1)–Cl(2)–Se(1)	88.4(1)
Al(1)–Cl(2)–Se(4)	100.1(2)
Al(1)–Cl(2)–Se(1$^{\mathrm{XVII}}$)	88.4(1)
Se(1)–Cl(2)–Se(4)	120.04(5)
Se(1)–Cl(2)–Se(1$^{\mathrm{XVII}}$)	119.46(10)
Al(1)–Cl(3)–Se(4)	88.4(2)
Al(1)–Cl(3)–Se(4$^{\mathrm{XXII}}$)	100.2(2)
Cl(4)–Al(2)–Cl(4$^{\mathrm{XXI}}$)	105.7(3)
Cl(4)–Al(2)–Cl(5)	109.0(2)
Cl(4)–Al(2)–Cl(6)	110.4(2)
Cl(5)–Al(2)–Cl(6)	112.2(3)
Al(2)–Cl(4)–Se(1)	107.9(2)
Al(2)–Cl(4)–Se(3)	99.1(2)
Al(2)–Cl(4)–Se(4)	129.9(2)
Al(2)–Cl(5)–Se(2$^{\mathrm{XXIV}}$)	100.1(2)
Al(2)–Cl(5)–Se(3)	88.6(1)
Al(2)–Cl(5)–Se(3$^{\mathrm{VI}}$)	88.6(1)
Se(2$^{\mathrm{XXIV}}$)–Cl(5)–Se(3)	119.89(6)
Se(3)–Cl(5)–Se(3$^{\mathrm{VI}}$)	119.68(11)
Al(2)–Cl(6)–Se(2)	89.1(2)
Al(2)–Cl(6)–Se(2$^{\mathrm{XXIV}}$)	88.1(2)

(*c*) $Te_4(SbF_6)_2$

(*i*) The Te_4^{2+} cation

Te(1)–Te(2)	2.676(3)	Te(1)–Te(2$^{\mathrm{XXVII}}$)	2.669(3)
Te(1) · · · Te(1$^{\mathrm{XXVII}}$)	3.801(3)	Te(2) · · · Te(2$^{\mathrm{XXVII}}$)	3.757(3)
Te(1) · · · F(2)	3.33(2)	Te(2) · · · F(4)	2.80(2)
Te(1) · · · F(4)	3.41(2)	Te(2) · · · F(3$^{\mathrm{XXXI}}$)	3.42(2)
Te(1) · · · F(6)	3.48(2)	Te(2) · · · F(5$^{\mathrm{III}}$)	3.19(2)
Te(1) · · · F(1$^{\mathrm{XXVIII}}$)	3.08(2)	Te(2) · · · F(1$^{\mathrm{V}}$)	2.97(2)
Te(1) · · · F(6$^{\mathrm{II}}$)	3.34(2)		
Te(1) · · · F(3$^{\mathrm{XXIX}}$)	3.31(2)		
Te(1) · · · F(2$^{\mathrm{XXX}}$)	3.20(2)		

Te(2$^{\mathrm{XXVII}}$)–Te(1)–Te(2)	89.34(8)
Te(2)–Te(1)–F(2)	87.5(3)
Te(2)–Te(1)–F(4)	53.2(4)
Te(2)–Te(1)–F(6)	94.1(4)
Te(2)–Te(1)–F(1$^{\mathrm{XXVIII}}$)	149.1(3)
Te(2)–Te(1)–F(6$^{\mathrm{II}}$)	77.0(4)
Te(2)–Te(1)–F(3$^{\mathrm{XXIX}}$)	145.8(3)
Te(2)–Te(1)–F(2$^{\mathrm{XXX}}$)	135.5(3)
Te(2$^{\mathrm{XXVII}}$)–Te(1)–F(2)	148.9(3)
Te(2$^{\mathrm{XXVII}}$)–Te(1)–F(4)	142.5(4)
Te(2$^{\mathrm{XXVII}}$)–Te(1)–F(6)	166.5(3)
Te(2$^{\mathrm{XXVII}}$)–Te(1)–F(1$^{\mathrm{XXVIII}}$)	61.8(3)
Te(2$^{\mathrm{XXVII}}$)–Te(1)–F(6$^{\mathrm{II}}$)	80.2(4)
Te(2$^{\mathrm{XXVII}}$)–Te(1)–F(3$^{\mathrm{XXIX}}$)	117.8(3)
Te(2$^{\mathrm{XXVII}}$)–Te(1)–F(2$^{\mathrm{XXX}}$)	91.8(3)
Te(1$^{\mathrm{XXVII}}$)–Te(2)–Te(1)	90.66(9)
Te(1)–Te(2)–F(4)	76.9(5)
Te(1)–Te(2)–F(3$^{\mathrm{XXXI}}$)	121.3(3)
Te(1)–Te(2)–F(5$^{\mathrm{III}}$)	132.4(4)
Te(1)–Te(2)–F(1$^{\mathrm{V}}$)	154.1(4)
Te(1$^{\mathrm{XXVII}}$)–Te(2)–F(4)	167.6(5)
Te(1$^{\mathrm{XXVII}}$)–Te(2)–F(3$^{\mathrm{XXXI}}$)	85.7(3)
Te(1$^{\mathrm{XXVII}}$)–Te(2)–F(5$^{\mathrm{III}}$)	131.7(3)
Te(1$^{\mathrm{XXVII}}$)–Te(2)–F(1$^{\mathrm{V}}$)	110.5(4)

(*ii*) The SbF_6^- anion

Sb–F bond distances: 1.83(2)—1.87(2)
F–Sb–F bond angles: *cis*, 85.1(9)—93.8(9)
trans, 177.7(8)—179.3(9)

TABLE 3 (*continued*)

(*iii*) Bridge angles

Sb–F(1)–Te(1^{XVI})	146.3(8)	Sb–F(4)–Te(1)	100.9(9)
Sb–F(1)–Te(2^{V})	126.7(7)	Sb–F(4)–Te(2)	147.2(12)
Sb–F(2)–Te(1)	104.2(6)	Sb–F(5)–Te(2^{I})	112.2(7)
Sb–F(2)–Te(1^{XXX})	135.3(8)	Sb–F(5)–Te(2^{III})	155.0(8)
Sb–F(3)–Te(2^{XXXII})	129.6(8)	Sb–F(6)–Te(1)	99.4(9)
Sb–F(3)–Te(1^{XXIX})	140.4(7)	Sb–F(6)–Te(1^{I})	138.6(11)

* Roman numeral superscripts refer to atoms related to the position x,y,z by the transformations: 0 x,y,z; I $1+x,y,z$; II $-1+x,y,z$; III $1-x,1-y,1-z$; IV $1-x,1-y,-z$; V $-x,1-y,1-z$; VI $-x,1-y,-z$; VII $1-x,\frac{1}{2}+y,\frac{1}{2}-z$; VIII $1-x,-\frac{1}{2}+y,\frac{1}{2}-z$; IX $-x,\frac{1}{2}+y,\frac{1}{2}-z$; X $-x,-\frac{1}{2}+y,\frac{1}{2}-z$; XI $1+x,\frac{1}{2}-y,\frac{1}{2}+z$; XII $x,\frac{1}{2}-y,\frac{1}{2}+z$; XIII $x,\frac{1}{2}-y,-\frac{1}{2}+z$; XIV $-1+x,\frac{1}{2}-y,-\frac{1}{2}+z$; XV $x,y,1+z$; XVI $x,y,-1+z$; XVII $-x,-y,1-z$; XVIII $-x,-y,-z$; XIX $-x,1-y,z$; XX $x,y,1-z$; XXI $x,y,-z$; XXII $\frac{1}{2}+x,\frac{1}{2}-y,1-z$; XXIII $-\frac{1}{2}+x,\frac{1}{2}-y,1-z$; XXIV $\frac{1}{2}-x,\frac{1}{2}+y,z$; XXV $\frac{1}{2}-x,-\frac{1}{2}+y,z$; XXVI $\frac{1}{2}-x,\frac{1}{2}+y,1-z$; XXVII $-x,1-y,2-z$; XXVIII $x,y,1+z$; XXIX $1-x,\frac{1}{2}-y,\frac{3}{2}-z$; XXX $-x,\frac{1}{2}-y,\frac{3}{2}-z$; XXXI $x,\frac{1}{2}+y,\frac{1}{2}+z$; XXXII $x,-\frac{1}{2}+y,-\frac{1}{2}+z$.

information on the lengths and angles between all the primary covalent and additional short interionic contacts in these compounds (for bond lengths and angles and some contact distances in the hexafluoroantimonate and tetrachloroaluminate anions, see SUP 23216). Tabulations of observed and calculated structure factors, thermal parameters, and least-squares mean planes for each structure are available as Supplementary Publication No. SUP 23216 (61 pp.).*

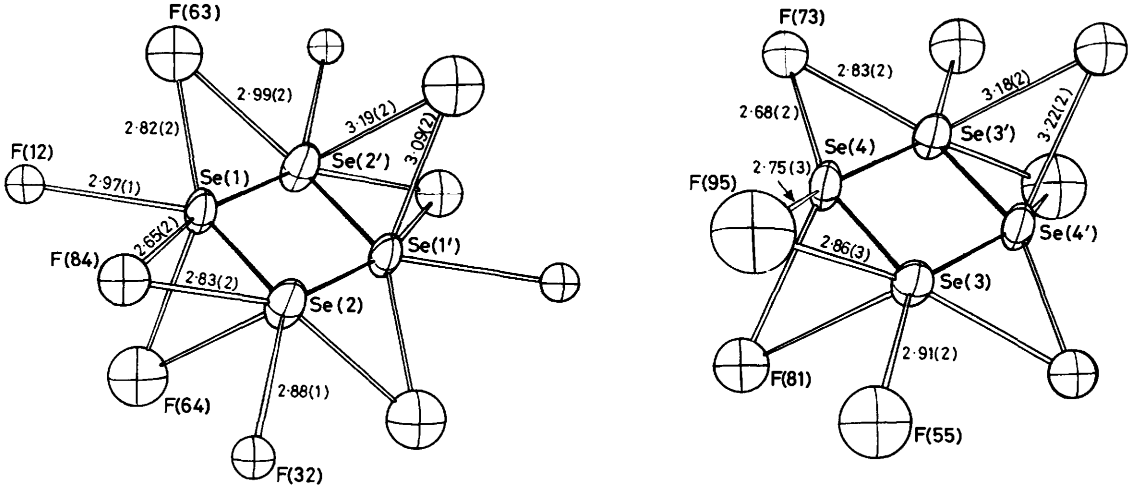

FIGURE 1 ORTEP views of the two Se_4^{2+} cations in $(Se_4)(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$ at the centres of symmetry at $(0,\frac{1}{2},\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, including all interionic Se · · · F interactions out to 3.2 Å as the unfilled bonds

RESULTS AND DISCUSSION

The structure determinations show that, instead of the anticipated heteroatomic cations, the two major crystalline products of the reactions contained the previously known Se_4^{2+} and Te_4^{2+} cations. The structures of these two ions have previously been shown to be approximately square planar by crystallographic determinations of the structures of $Se_4(HS_2O_7)_2$,[9] $Te_4(AlCl_4)_2$,[10] and $Te_4(Al_2Cl_7)_2$.[10]

The Se_4^{2+} *Cations.*—The Se_4^{2+} cations in the asymmetric unit of $(Se_4)(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$ are situated around the centres of symmetry at $(0,\frac{1}{2},\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. At $(0,\frac{1}{2},\frac{1}{2})$ the Se–Se bond lengths are 2.266(4) and 2.247(4) Å with Se–Se–Se′ angles of 89.9(1) and 90.1(2)°; similarly at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ the analogous bond lengths and bond angles are 2.276(4) and 2.252(4) Å, 89.4(1) and 90.6(1)°. The Se_4^{2+} cations are therefore planar and almost square (D_{2h} symmetry). The slight but nonetheless significant difference between the Se–Se bond lengths is possibly related to differences in the anion–cation contacts to each selenium in the cations (Figure 1). The average distance of 2.260(4) Å is slightly smaller than the average Se–Se distance of 2.283(4) Å in the compound $Se_4(HS_2O_7)_2$.[9]

The Se_4^{2+} cation in the asymmetric unit of $Se_4(AlCl_4)_2$ [compound (3)] is situated around the centres of symmetry at (0,0,0) and $(0,\frac{1}{2},\frac{1}{2})$. At (0,0,0) the independent Se–Se bond length is 2.283(2) Å (× 4), while that for the cation at $(0,\frac{1}{2},\frac{1}{2})$ is 2.288(2) Å (×4) (Figure 2). These Se–Se bond lengths are the same as those in $Se_4(HS_2O_7)_2$ although they are marginally longer than the distances in the cation in $(Se_4)(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$. The four independent Se–Se–Se′ angles in the two cations of $Se_4(AlCl_4)_2$ do not deviate significantly from 90°.

The Te_4^{2+} *Cation.*—The Te_4^{2+} cation in $Te_4(SbF_6)_2$ is situated around a centre of symmetry at $(0,\frac{1}{2},0)$ with Te–Te bond lengths of 2.676(3) and 2.669(3) Å. However, as can be seen from the significant differences between the cross-ring Te · · · Te distances of 3.801(3) and 3.757(3) Å and between the Te–Te–Te′ angles of 89.34(8) and 90.66(9)°, the cation is significantly distorted and has D_{2h} symmetry compared with the expected D_{4h} symmetry. This small distortion in the shape of the Te_4^{2+} cation appears to be related to differences in the anion–cation contacts to the two independent tellurium atoms (Figure 3). The bond lengths in the present Te_4^{2+} cation are slightly longer than the average bond lengths of 2.668 and 2.661 Å observed in $Te_4(AlCl_4)_2$ [10] and $Te_4(Al_2Cl_7)_2$ [10] respectively.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

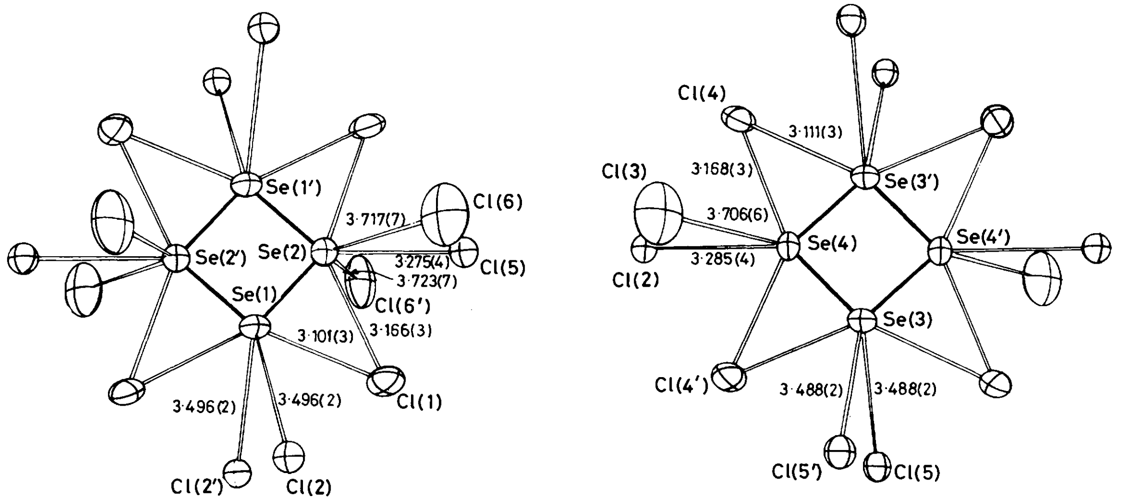


FIGURE 2 ORTEP views of the Se_4^{2+} cations in $Se_4(AlCl_4)_2$ at the centres of symmetry at (0,0,0) and (0,½,½), including all Se · · · Cl interactions out to 3.8 Å as the unfilled bonds

It has been proposed on the basis of simple valence-bond and molecular-orbital (m.o.) treatments of the isolated Se_4^{2+} and Te_4^{2+} cations that the bonds in these ions have bond orders of 1.25 and that they may be regarded as examples of 6π electron ' aromatic ' species.[9,11] This provided a reasonable explanation for the shortness of these bonds when compared to twice the accepted covalent radii for the elements (Se–Se 2.34, Te–Te 2.74 Å [12]). Recent more detailed m.o. calculations have however indicated that there are differences in the σ bonding in these cations and that in particular *s* orbitals make a smaller contribution to the σ bonds in Te_4^{2+} than in Se_4^{2+} and S_4^{2+}.[13] It has also been observed that there are considerable variations in the lengths of Te–Te and Se–Se single bonds. In particular the Te–Te bonds in diphenyl ditelluride [2.712(2) Å] [14] and di-*p*-tolyl ditelluride [2.697(3) Å] [15] and those in the related diselenides bis(pentafluorophenyl) diselenide [2.319(4) Å] [16] and bis(diphenylmethyl) diselenide [2.285(5) Å] [17] which are all nominally single bonds have lengths which are considerably shorter than the accepted values based on covalent radii and are in fact comparable to the bond lengths in Se_4^{2+} and Te_4^{2+}. Furthermore, the extent to which the relatively strong contacts with the anions, which are discussed below, affect the bond lengths in the present M_4^{2+} cations is uncertain. It is very difficult, therefore, to make reliable estimates of the bond orders in these M_4^{2+} cations from the observed bond lengths.

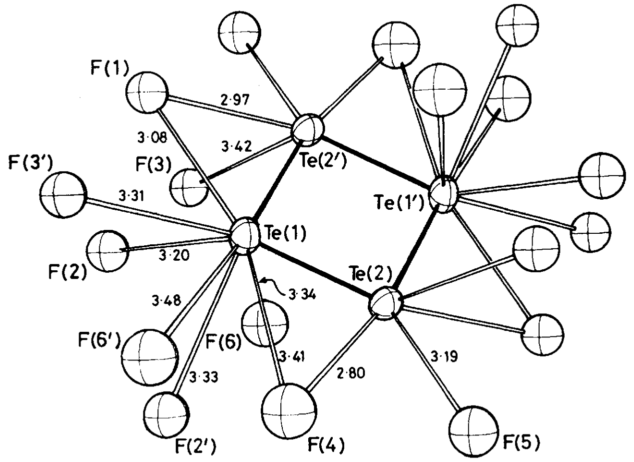


FIGURE 3 ORTEP view of the Te_4^{2+} cation in the compound $Te_4(SbF_6)_2$ almost down *a*. All Te · · · F interionic contacts (Å) out to 3.5 Å are shown as the unfilled bonds

The Charge-transfer Interactions with the M_4^{2+} *Cations.*—The slight deviation of the Se_4^{2+} cation in (1) and more particularly the Te_4^{2+} cations in (2) as well as those in $Te_4(AlCl_4)_2$ [10] and $Te_4(Al_2Cl_7)_2$ [10] from perfect squares, and the small bond-length differences, may be attributed in part to the charge-transfer interactions of the M_4^{2+} cations with the accompanying anions. These are a characteristic feature of the packing arrangements of these ions (Figures 1—4) and the patterns in these interactions may be correlated with the symmetries of the available lowest unoccupied m.o.s of the M_4^{2+} cations.

These interactions may best be described in terms of contacts which bridge the edges of the cation and contacts which lie along the extensions of the diagonals of the cation. A summary of the contact distances involved and the deviation of the interacting atoms from the planes of the cations is given in Table 4. In all cases, there is at least one atom bridging each edge of the approximately square cation. In some cases two edges are bridged by two atoms [*e.g.* $(Se_4)(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$, Figure 1] and in one case all four edges are bridged by two atoms [*e.g.* $(S_4^{2+})(S_7I^+)_4(AsF_6)_6$,[18] Figure 4(*b*)]. When there is only one bridging atom it normally lies in the plane of the ring and when there are two bridging atoms one lies above the plane and the other lies below the plane. These edge-bridging contacts are normally the shortest of the anion–cation contacts. The second

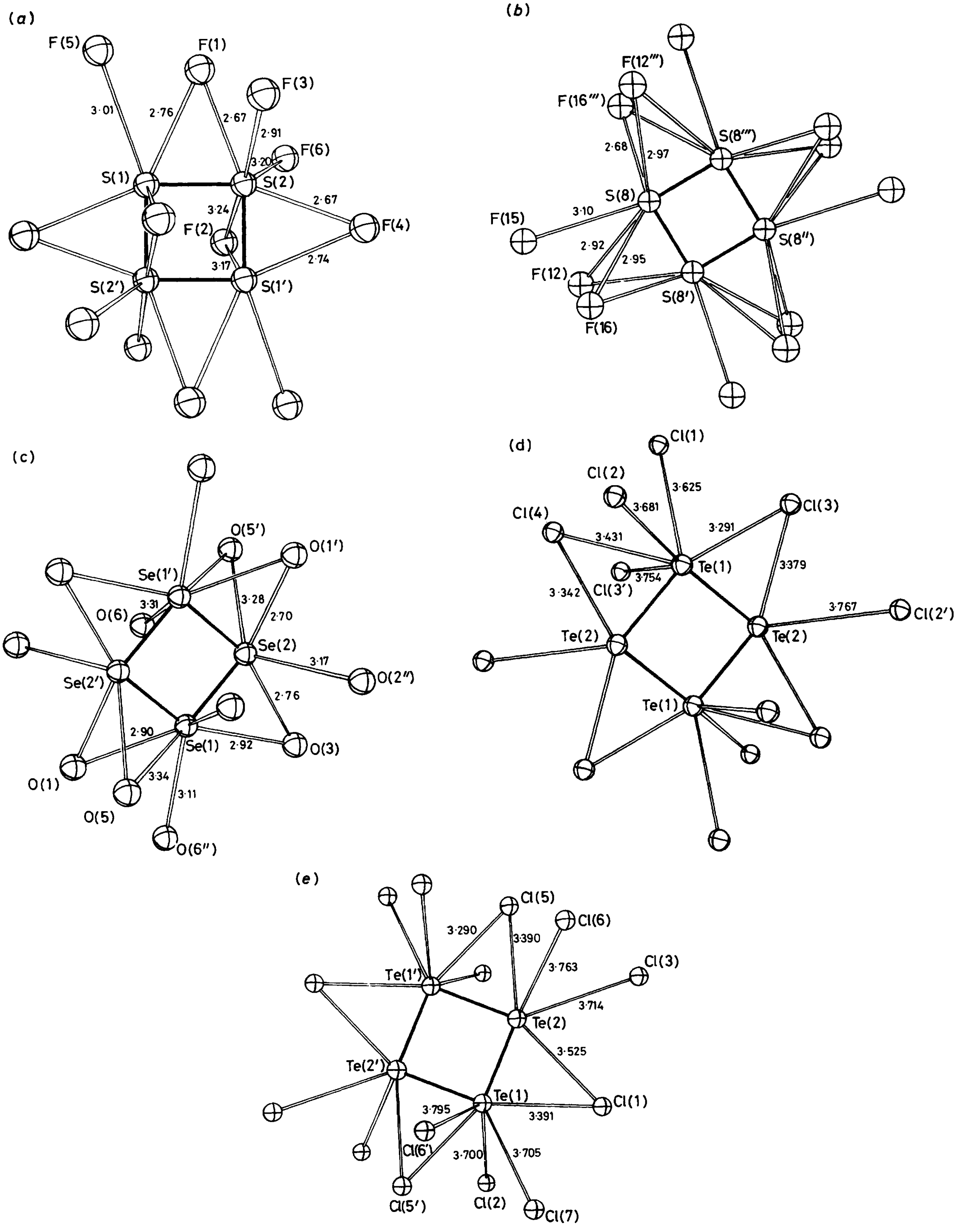


FIGURE 4 Charge-transfer interactions (Å) in the known examples of the tetrachalcogen dications, M_4^{2+}. The limiting values for the contacts are indicated in parentheses after the compound name. (*a*) $S_4(AsF_6)_2(SO_2)_{0.6}$ (3.20 Å) (redrawn from the co-ordinates in ref. 18); (*b*) $S_4(S_7I)_4(AsF_6)_6$ (3.25 Å) (redrawn from the co-ordinates in ref. 18); (*c*) $Se_4(HS_2O_7)_2$ (3.35 Å) (redrawn from the co-ordinates in ref. 9); (*d*) $Te_4(AlCl_4)_2$ (3.80 Å) (redrawn from the co-ordinates in ref. 10); (*e*) $Te_4(Al_2Cl_7)_2$ (3.80 Å) (redrawn from the co-ordinates in ref. 10)

set of contacts involve atoms which lie along the extensions of the diagonals of the cation. There may be up to three contacts along these diagonals, two of which lie above and below the plane with the third close to the plane of the cation [*e.g.* atom Se(2) of $Se_4(AlCl_4)_2$, Figure 2]. When there is only one edge-bridging atom in the plane of the cation the shortest ' diagonal ' contacts lie above and below the plane of the ring and, when the edge-bridging contacts deviate from the plane of the cation, the shortest ' diagonal ' contacts tend to lie close to the plane of the cation (Table 4).

TABLE 4

Charge-transfer interactions in the M_4^{2+} cations [a]

Compound	Interactions [b]					
	Bridging edges (Å)		Deviation (Å) from plane	Along diagonals (Å)		Deviation (Å) from plane
(*a*) $S_4(AsF_6)_2\cdot(SO_2)_{0.6}$	F(1)	2.762(5), 2.671(5)	±0.29	F(5)	3.010(6)	±1.01
	F(4)	2.736(6), 2.665(6)	±0.26	F(3)	2.909(5)	±2.47
				F(2)	3.170(6)	±3.02
(*b*) $S_4(S_7I^+)_4(AsF_6^-)_6$	F(12)	2.97(3), 2.92(3)	±1.18	F(15)	3.10(3)	±0.23
	F(16)	2.68(5), 2.95(4)	±1.04			
(*c*) $Se_4(HS_2O_7)_2$	O(1)	2.90(2), 2.70(2)	±0.52	O(6)	3.11(2)	
	O(3)	2.92(2), 2.76(1)	±0.18	O(2)	3.17(1)	
(*d*) $Se_4(Sb_2F_4^{2+})(Sb_2F_5^+)(SbF_6^-)_5$						
(*i*) Cation 1	F(63)	2.82(2), 2.99(2)	±1.23	F(12)	2.97(1)	±0.35
	F(84)	2.65(2), 2.83(2)	±0.57	F(32)	2.88(1)	±0.41
	F(64)	3.09(2), 3.19(2)	±2.56			
(*ii*) Cation 2	F(73)	2.68(2), 2.83(2)	±0.38	F(55)	2.91(2)	±0.37
	F(95)	2.75(3), 2.86(3)	±1.31			
	F(81)	3.18(2), 3.22(2)	±1.97			
(*e*) $Se_4(AlCl_4)_2$						
(*i*) Cation 1	Cl(1)	3.101(3), 3.166(3)	±0.17	Cl(5)	3.275(4)	±0.59
				Cl(2)	3.496(2)	±1.71
(*ii*) Cation 2	Cl(4)	3.111(3), 3.168(3)	±0.20	Cl(2)	3.285(4)	±0.76
				Cl(5)	3.488(2)	±1.69
(*f*) $Te_4(SbF_6)_2$	F(1)	3.08(2), 2.97(2)	±0.54	F(5)	3.19(2)	±0.97
	F(4)	2.80(2), 3.41(2)		F(2)	3.20	±2.24
	F(3)	3.31(2), 3.42(2)	±1.09	F(6)	3.48(2)	
				F(2)	3.33(2)	
(*g*) $Te_4(AlCl_4)_2$	Cl(3)	3.379(4), 3.291(4)	±0.04	Cl(1)	3.625(5)	±2.00
	Cl(4)	3.431(5), 3.342(5)	±0.82	Cl(2)	3.767(6)	±2.19
(*h*) $Te_4(Al_2Cl_7)_2$	Cl(1)	3.391(6), 3.525(6)	±0.01	Cl(3)	3.714(5)	±0.10
	Cl(5)	3.290(6), 3.390(6)	±0.16	Cl(2′)	3.700(6)	±2.99
	Cl(6)	3.763(6), 3.795(6)		Cl(7)	3.705(6)	[illegible]1.48

[a] All the M_4^{2+} cations have crystallographic inversion symmetry except the S_4^{2+} cation in the compound $S_4(S_7I^+)_4(AsF_6^-)_6$ which has crystallographic four-fold symmetry. [b] Sum of the neutral atom van der Waals radii: $S + F = 3.20$, $Se + O = 3.40$, $Se + F = 3.35$, $Te + F = 3.55$, $Te + Cl = 4.00$ Å.

The general pattern of anion–cation contacts described above does however show considerable variation from compound to compound and must be partly influenced by the packing requirements of the rest of the structures. Moreover, as the size of the chalcogen increases many other longer weaker contacts are less than the sum of the neutral atom van der Waals limits but their geometry is less well defined. Similar bridging and ' diagonal ' contacts are observed to the heteropolyatomic cation $Te_2Se_2^{2+}$ in $(Te_2Se_2)(Sb_3F_{14})(SbF_6)$ [1] and the Te · · · F contacts in this case [2.79(1) 2.98(3), and 2.91(3) Å] are very comparable in strength to some of the contacts in $Te_4(SbF_6)_2$. Similarly, it may be noted that many of the shorter Se · · · Cl and Te · · · Cl contacts in $Se_4(AlCl_4)_2$ and $Te_4(AlCl_4)_2$ [10] are very similar in strength, as measured by the difference (up to 0.6—0.7 Å) from the van der Waals limits.

As has been noted by Corbett and co-workers [10] in he case of $Te_4(AlCl_4)_2$ and $Te_4(Al_2Cl_7)_2$ and by other workers [19,20] the interactions between the anions and the M_4^{2+} cations probably involve the lowest unoccupied m.o.s of both σ symmetry [(e_u) [10] or (a_{2g}) [19,20]] and of π symmetry (b_{2u}) which are relatively close in energy. It seems reasonable to suppose that the out-of-plane interactions are with the lowest unoccupied molecular orbital (l.u.m.o.) of π symmetry and that the in-plane interactions are with the l.u.m.o. of σ symmetry.

It does not seem possible to make any quantitative estimate of the relative strengths of the charge-transfer interactions between the known M_4^{2+} cations and oxygen, fluorine, and chlorine atoms in the accompanying anions. Qualitatively it appears that the degree of charge transfer increases slightly in the series $S_4^{2+} < Se_4^{2+} < Te_4^{2+}$ and this is consistent with the results of m.o. calculations which show that the h.o.m.o.–l.u.m.o. gap decreases in this order.[13]

It was found by Rothman *et al.*[20] in their pseudo-potential SCF–MO study of Te_4^{2+} that the calculated bond length was 0.054 Å shorter than that observed in $Te_4(AlCl_4)_2$ and $Te_4(Al_2Cl_7)_2$, but when the calculation was repeated simulating the 18 chlorine atoms which were closest to the cation in the crystal structure by point charges of $-\frac{1}{2}e$ the bond length in the Te_4^{2+} ion increased by 0.06 Å to a value very close to the experimental value. This result emphasises that the interactions discussed above might have a significant effect on the cation geometry.

The Anions.—The counter ions in the structure of the selenium compound (1) are also of some interest. For each Se_4^{2+} cation in the asymmetric unit there are nine antimony atoms, four of which are Sb^{III} and the remaining five Sb^{V} (as SbF_6^- anions). If only antimony–fluorine bonds shorter than 2.15 Å are considered, the compound may be formulated as $(Se_4^{2+})(Sb_2F_4^{2+})(Sb_2F_5^+)(SbF_6^-)_5$. Both of these $Sb_2F_4^{2+}$ and the $Sb_2F_5^+$ cations have been observed previously although there are some significant differences from the present examples.[21-23] Apart from the primary Sb^{III}–F bonds each Sb^{III} in the selenium compound also forms several slightly longer Sb · · · F contacts >2.3 Å which appear to be stereochemically specific in that they form in directions away from the primary bonds and avoiding the presumed space occupied by the lone pair. In fact, from the number, the lengths, and spatial arrangements of these additional contacts to each Sb^{III} it is possible to qualitatively estimate the position of the centroid of the lone pair on each antimony.

The $Sb_2F_4^{2+}$ *Cation.*—The $Sb_2F_4^{2+}$ cations in the asymmetric unit of the selenium compound are situated around the centres of symmetry at (0,½,0) and (½,½,0). At each of these centres the antimony(III) atoms form primary bonds to two fluorine atoms related by the centre of symmetry to give planar Sb_2F_2 rings (Figure 5). In these rings the average $Sb–F_{bridge}$ bond length is 2.11 Å and the average F–Sb–F′ and Sb–F–Sb′ angles are 68.7 and 111.3° respectively. The primary geometry of each Sb^{III} is completed by shorter Sb–F bonds of 1.89(1) [Sb(1)] and 1.87(1) Å [Sb(2)] which are approximately perpendicular to the plane of the Sb_2F_2 rings. The two $F_{bridge}–Sb–F_{apex}$ angles at each antimony are, however, slightly different [87.0(5) and 83.3(5)° at Sb(1) and 88.1(5) and 84.0(5)° at Sb(2)] possibly as a consequence of the asymmetry in further fluorine contacts to each antimony (Figure 5).

Of these further contacts, two are intermediate in length (2.32—2.46 Å) and two are much longer (2.62—2.79 Å) than the sum of the covalent radii for Sb and F. Differences between the environments of Sb(1) and Sb(2) are relatively small ($\leqslant$0.05 Å in related distances and $\leqslant$10° in analogous angles) and will not be discussed further. Inspection of Figure 5 and Tables 3 and 4 show that the short and long contacts around Sb(1) and Sb(2) fall into three groups. The first group includes the axial primary bond to atom F(12) [and F(22)] which is the shortest. The second group involves five contacts including the two fluorine atoms forming the Sb_2F_2 ring which range in lengths over 2.10—2.64 Å and which lie within 0.8 Å of an equatorial plane defined by the Sb_2F_2 ring (Table 4). Alternatively the antimony atom can be regarded as being *ca.* 0.3 Å out of the equatorial plane defined by these five fluorine atoms (see Table 4). The angles between the fluorine atoms in the equatorial plane (69—73°) are close to the angles of 72° required for a regular pentagonal planar arrangement of fluorines. Finally there are two further longer contacts (2.79—2.95 Å) below this equatorial plane which appeared to be avoiding a lone pair approximately *trans* to the apical bond.

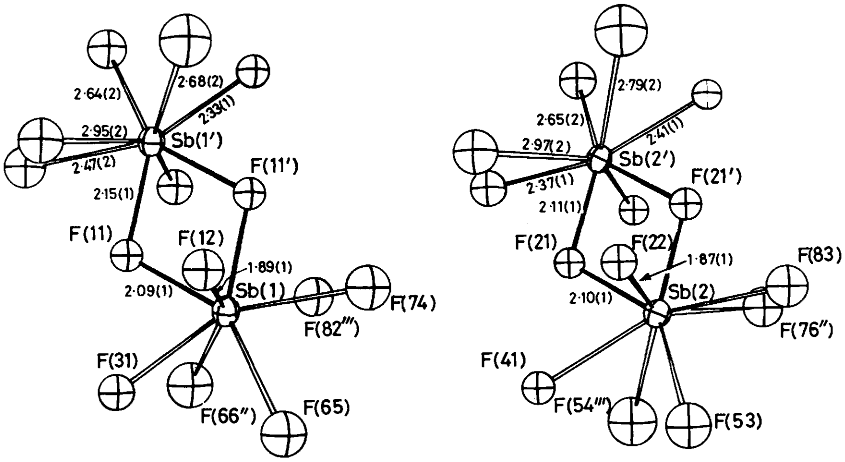


FIGURE 5 ORTEP views of the two $Sb_2F_4^{2+}$ cations at the centres of symmetry at (0,½,0) and (½,½,0) including all additional Sb^{III} · · · F interactions (Å) out to 3.0 Å as unfilled bonds (primary bonds $\leqslant$2.40 Å)

The geometries of Sb(1) and Sb(2) may then be considered to be $AXY_5Y'_2E$ based upon a pentagonal-bipyramidal arrangement AXY_5E with two further contacts to atoms Y′ approximately *trans* to the A–X bond and avoiding the lone pair E. These two longer bonds may be considered to be capping two of the triangular faces of the pentagonal bipyramid. Examples of non-metal complexes containing related pentagonal-bipyramidal geometries of primary and secondary bonds and stereoactive lone pairs have been discussed elsewhere.[24,25]

The other known example of an $Sb_2F_4^{2+}$ ion is in the compound $(Sb_2F_4^{2+})(SbF_6^-)_2$.[21] In this case the $Sb_2F_4^{2+}$ cation may be regarded as an SbF_3 molecule interacting with an $Sb–F^{2+}$ ion *via* an asymmetrical fluorine bridge and it does not contain the Sb_2F_2 ring found in the present case. This description is, however, again somewhat arbitrary as there are additional strong interactions to the antimony(III) atoms (2.15—2.42 Å).[21] In particular the environment of the SbF^{2+} unit is also based on a pentagonal bipyramid AXY_5E if all Sb^{III}–F contacts less than 2.5 Å are considered. Three even longer contacts (*ca.* 3 Å) which cap the lower faces of the pentagonal bipyramid are consistent with the presence of the lone pair in the axial position *trans* to the Sb–F axial bond.

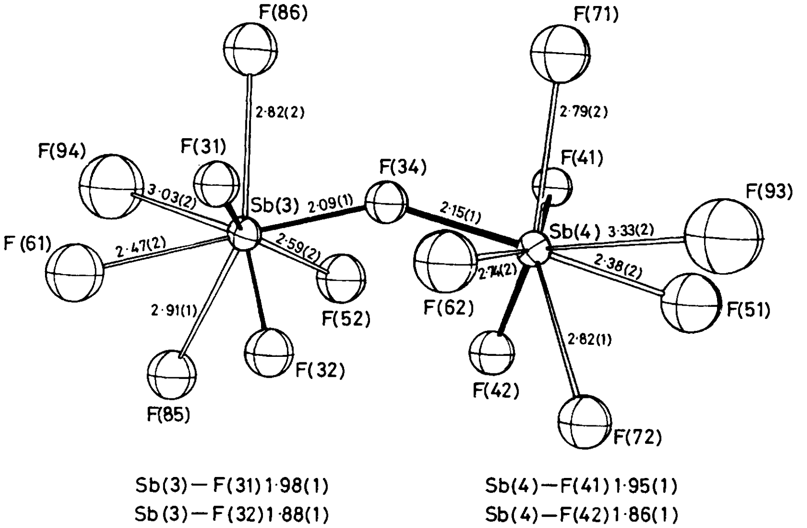


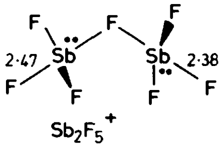
FIGURE 6 ORTEP view of the $Sb_2F_5^+$ cation including all additional $Sb^{III}\cdots F$ interactions (Å) out to 3.35 Å as unfilled bonds

The $Sb_2F_5^+$ *Cation.*—The $Sb_2F_5^+$ cation has an asymmetric fluorine bridge with Sb–F_{bridge} distances of 2.09(1) and 2.15(1) Å and an Sb–F–Sb angle of 149.8(6)° (Figure 6). The terminal Sb–F bonds are also significantly different, average values being 1.87(1) and 1.96(1) Å, with the longer of these bonds [to F(31) and F(41)] resulting from bridging interactions to other antimony(III) atoms. An $Sb_2F_5^+$ cation of very similar geometry is found in the compound $SbF_5(SbF_3)_3$.[23] In this example the $Sb_2F_5^+$ cation has a symmetric fluorine bridge (Sb–F_{bridge} 2.144 Å, Sb–F–Sb 147.8°) and the distances to the terminal fluorine atoms are 1.898 and 1.961 Å. An $Sb_2F_5^+$ cation can also be recognised at a crystallographic centre of symmetry in the compound $Sb_{11}F_{45}$ [equivalent to $(SbF_5)_6(SbF_3)_5$].[22] Here the Sb–F–Sb system is linear with an Sb–F_{bridge} bond of 2.06(2) Å and Sb–$F_{terminal}$ bonds of 1.85 and 2.06(2) Å.[22] In all three examples of these cations the FSbF angles between the primary bonds are in the range 80—89°, and are all markedly less than the tetrahedral value and close to the angles in SbF_3 [85.7(8) and 89.0(8)°].

In both $SbF_5(SbF_3)_3$ [23] and $(SbF_5)_6(SbF_3)_5$,[22] as well as the present selenium compound, the identification of $Sb_2F_5^+$ as constituent ions in the structure depends on a somewhat arbitrary division in the Sb–F bond lengths as the antimony(III) atoms and some of the terminal fluorine atoms of each $Sb_2F_5^+$ cation are involved in some quite short additional $Sb\cdots F$ secondary bonds/contacts. Thus in the present $Sb_2F_5^+$ cation the fluorine atoms F(31) and F(41) forming the longer terminal bonds are also involved in strong bridging interactions to the $Sb_2F_4^{2+}$ cations of 2.33(1) Å [Sb(1)–F(31)] and 2.41(1) Å [Sb(2)–F(41)] with bridge angles of 158.4(7)° [Sb(1)–F(31)–Sb(3)] and 166.2(6)° [Sb(2)–F(41)–Sb(4)]. In $SbF_5(SbF_3)_3$, the analogous fluorine atoms of the constituent $Sb_2F_5^+$ cation are also involved in strong bridging interactions, this time to the same Sb^{III} of an SbF_3 group.[23] The Sb–F bridging distance in this example is 2.409 Å and the Sb–F–Sb angle is only 134°.[23] Furthermore, in the $Sb_2F_5^+$ ion in $Sb_{11}F_{45}$, a bridging contact of 2.17(2) Å involving one of the terminal atoms is even stronger than the above examples and appears to be responsible for the lengthening of a terminal bond in this $Sb_2F_5^+$ ion to 2.07(2) Å. The bridge angle in this last example is 158°.[22]

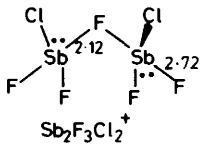
An analogous ion $Sb_2F_3Cl_2^+$ (II) may be considered to be a constituent of the antimony chloride fluoride '$Sb_2F_4Cl_5$'.[26] In this case, the $Sb_2F_3Cl_2^+$ ion has two-fold symmetry, the chlorine atoms occupy axial positions at each antimony and the fluorine bridge in the ion is symmetrical with Sb–F 2.12(2) Å and Sb–F–Sb′ 140°. The other axial Sb^{III}–F distance in this ion is 2.12(2) Å and this fluorine atom is also involved in a strong fluorine bridge to an antimony(V) atom of 2.04(2) Å (the Sb^{III}–F–Sb^{V} angle is 166°).[26]

Apart from the interactions involving the terminal fluorine atoms, each antimony(III) atom in the $Sb_2F_5^+$ cations also forms several characteristic stereospecific $Sb\cdots F$ contacts/secondary bonds. In the present cation there are some significant differences in the lengths of the additional contacts to each antimony(III) atom [particularly the difference of 0.29 Å in the contacts $Sb(3)\cdots F(94)$ and $Sb(4)\cdots F(93)$], although the arrangement of these additional contacts has an approximately two-fold symmetry about an axis through F(34) (Figure 6). Around Sb(3), the five additional contacts have lengths from 2.47 and 3.00 Å whilst the same five contacts around Sb(4) have lengths from 2.38 to 3.33 Å. When these contacts are included, the environment of Sb(3) and Sb(4) may be regarded as either AX_3Y_5E (Y = longer fluorine contact) or as AX_4Y_4E where one of the shorter Y contacts above [Sb(3)–F(61) 2.47 and Sb(4)–F(51) 2.38 Å] has been included in the description of the primary geometry. For AX_3Y_5E, the geometry is based on a tetrahedral arrangement of bond and lone pairs with five secondary contacts avoiding the lone pair E, whilst for AX_4Y_4E, the geometry is based on a trigonal-bipyramidal arrangement of bonding and lone pairs, with the four further fluorine contacts avoiding the lone pair which is in an equatorial position [F(34)–Sb(3)–F(61) 155.3(5), F(34)–Sb(4)–F(51) 158.6(5)°]. Figure 6 shows that the actual geometry is intermediate between AX_3Y_5E and AX_4Y_4E and is very similar to the geometry of the antimony(III) atom of the $Sb_3F_{14}^-$ anion in $(S_4N_4)(Sb_3F_{14})(SbF_6)$.[27,28]



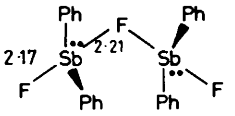
$Sb_2F_5^+$

(I)



$Sb_2F_3Cl_2^+$

(II)



Ph_2SbF

(III)

In both $SbF_5(SbF_3)_3$[23] and the $Sb_2F_3Cl_2^+$ ion of '$Sb_2F_4Cl_5$'[26] the arrangements of these additional secondary contacts are very similar to both the present $Sb_2F_5^+$ cation and the $Sb_3F_{14}^-$ anion and these can also be described as distorted AX_4Y_4E arrangements.[27] In $SbF_5(SbF_3)_3$ these additional interactions have lengths of 2.27 Å and 2.72—3.06 Å; in $Sb_2F_3Cl_2^+$ the contacts have lengths of 2.40—2.89 Å. [Complete details of the longer Sb · · · F^{III} contacts in $(SbF_5)_6(SbF_3)_5$ have not been published yet.] In the recently determined structure of diphenylantimony(III) fluoride[29] (III) the distorted trigonal-bipyramidal geometry of the Sb atom is somewhat analogous to that observed in the present $Sb_2F_5^+$ cations although no longer contacts around the equatorial lone pair are observed. The average bond order for the Sb–F bonds in this latter compound [2.166(5) and 2.221(5) Å] has been quoted as 0.37.[29]

Secondary Bonds to Sb^{III}.—It appears that in the solid-state structures of all fluoro- and halogenofluoro-complexes containing Sb^{III} there are in addition to normal covalent bonds interionic contacts that are significantly shorter than the sum of the van der Waals radii.[27] In many cases there is also a lengthening of some of the primary bonds as a consequence of these bridging interactions. To date, the only semi-quantitative treatments of these contacts have made use of Pauling's relationship $D(n') = D(1) - 0.71 \log n$, or bond-valence principles.[30-32]

Using the bond-valence equation $S = S_0(R/R_0)^{-N}$ with $S = 0.5$, $R_0 = 2.137$, and $N = 3.7$,[31] individual bond valencies for the 'bonds' from the antimony(III) atoms in the $Sb_2F_4^{2+}$ and $Sb_2F_5^+$ cations to all the fluorine atoms which were within the van der Waals limit (3.55 Å) were calculated and summed. The total valence sums, Σs, for these four antimony(III) atoms were 3.07 [Sb(1)], 3.10 [Sb(2)], 3.02 [Sb(3)], and 3.02 [Sb(4)]. These values are all reasonably close to the theoretical value of 3.0 and would argue in favour of the inclusion of these longer Sb^{III} · · · F interactions in the overall description of the geometry of antimony(III) and related atoms with stereoactive lone pairs. Using bond valences, Brown[31] has also defined, for compounds of Sb^{III} and several isoelectronic atoms, several characteristic arrangements of these additional contacts in terms of distance from the central atom which are all based on octahedral arrangements of strong, intermediate, and weak bonds. The overall stereochemistries of the contacts in the present and other antimony(III)–fluorine compounds are, however, even more complex than those discussed by Brown although they all exhibit the common features of a 'hole' in the co-ordination sphere of the Sb^{III} which can be attributed to the lone pair. The number, lengths, and spatial arrangement of these additional contacts to Sb^{III} are then useful as an indication of the stereoactivity and position of the lone pair on the central atom since these contacts are formed in directions which avoid the volume occupied by the lone pair(s) but which at the same time attempt to maximise the overlap of any orbitals involved in the charge-transfer interactions.[33] Taking the lone pair into account the overall geometries including the weak secondary contacts are consistent with the basic principles of valence shell electron-pair repulsion theory.[34] The overall geometries of these and related compounds are discussed more extensively elsewhere.[27]

The SbF_6^- *Anions*.—Bond distances and bond angles in the SbF_6^- anions of compounds (1) and (2) are comparable to values in other structures and because of the relatively high standard errors associated with individual values it is not possible to draw any conclusions regarding possible lengthening of the Sb^V–F bond lengths as a consequence of any bridging interactions although these correlations have been observed in other structures.[21] Although the bridge angles Sb–F · · · Sb(Se) have a considerable range of values over 147—173°, there is again no correlation between the strength of the con-

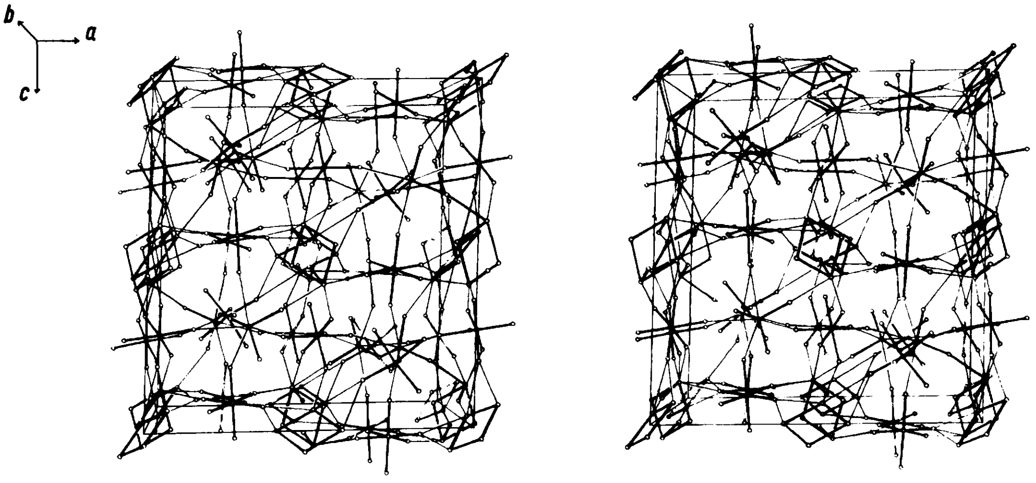


FIGURE 7 Stereoscopic view of the crystal packing in the compound $(Se_4^{2+})(Sb_2F_4^{2+})(Sb_2F_5^{+})(SbF_6^{-})_5$. Interionic contacts (Se · · · F and Sb · · · F) out to 3.1 Å indicated (primary bonds out to 2.35 Å)

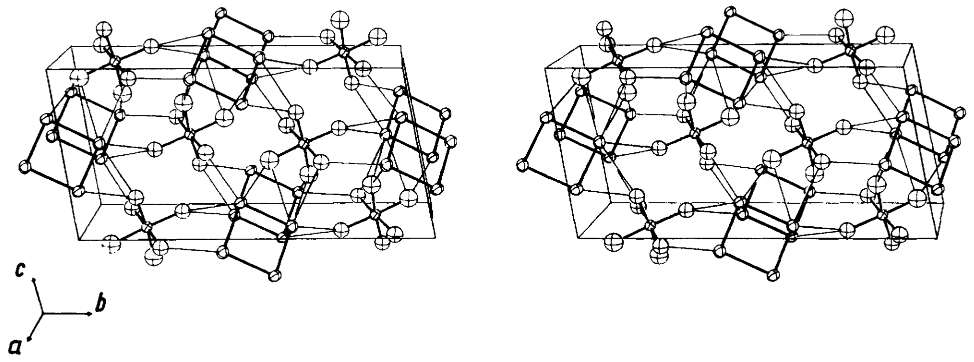


FIGURE 8 Stereoscopic view of the crystal packing in the compound $(Te_4^{2+})(SbF_6^{-})_2$. Interionic contacts out to 3.55 Å are indicated

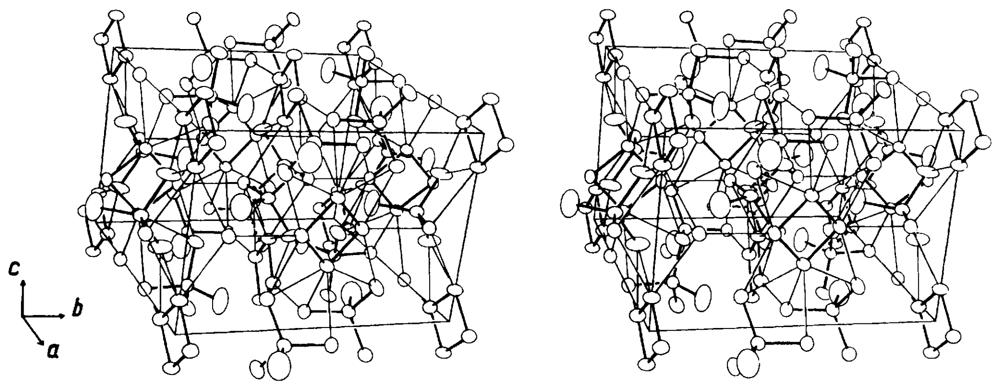


FIGURE 9 Stereoscopic view of the crystal packing in the compound $Se_4(AlCl_4)_2$. Interionic contacts out to 3.50 Å are indicated

tacts Sb · · · F (or Se · · · F) and these angles.* In (1) the interactions from F(95) to Se(2) and Se(4) and very long contacts to Sb(3) are the only short fluorine contacts formed by Sb(9)F_6^- and this anion is only weakly held in the lattice. Bond angles in all of the SbF_6^- anions are close to 90 and 180°. In the tellurium compound (2) the hexafluoroantimonate anion, is within the measured standard deviations, octahedral with an average Sb–F distance of 1.85(2) Å and *cis* and *trans* angles close to 90 and 180°.

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* However, in a series of compounds $M^+Sb_2F_7^-$ some correlation between the size of the cation, the strength of fluorine contacts to each Sb^{III}, and the asymmetry of the Sb–F–Sb bridge has been observed (D. Tichit, B. Ducourant, R. Fourcade, and G. Mascherpa, *J. Fluorine Chem.*, 1979, **13**, 45).

Views of the overall packing of both the selenium and tellurium compounds (1) and (2) are given in Figures 7 and 8 respectively. In (1) the packing consists of layers of strongly interacting anions and cations held together by some of the weaker fluorine bridging interactions. These layers are all canted with respect to the ***a****** direction, and the twinning observed in some crystals is a consequence of this layer arrangement.

The $AlCl_4^-$ *Anion.*—The tetrachloroaluminate anions in (3) have crystallographic mirror symmetry and are slightly flattened tetrahedra with an average Al–Cl bond length of 2.119 Å and Cl–Al–Cl bond angles of 105—106° perpendicular to the mirror plane and 112° in the mirror plane. As such, the dimensions and distortions of these anions are comparable to those of the anions in the salts with the Te_4^{2+} and Se_8^{2+} cations [10,35] and the cations Rb^+, Cs^+, NO^+, NH_4^+, and K^+.[36] No appreciable lengthening of the Al–Cl bond lengths due to the charge-transfer interactions to the M_4^{2+} cations (M = Se or Te) is observable after riding corrections to the bond lengths have been applied. The thermal parameters for the two atoms bridging the edges of the Se_4^{2+} cation are, however, significantly smaller than those for the other chlorine atoms in the anion. A view of the packing in compound (3) is given in Figure 9.

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[1/892 *Received, 2nd June*, 1981]

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