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Preparation and Crystal Structures of Compounds Containing the $Te_xS_{6-x}^{2+}$ and $Te_xSe_{6-x}^{2+}$ Cations

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Reactions between Se/Te mixtures and AsF_5 or SbF_5 and between $Se_4(AsF_6)_2$ and $Te_4(AsF_6)_2$ have been investigated with the aim of preparing new "mixed" Se/Te cations. Among the crystalline products isolated and characterized by X-ray crystallography were $(Te_2Se_4)(Sb_3F_{14})(SbF_6)$ (**1**), $(Te_{2.7}Se_{3.3})(SbF_6)_2$ (**2**), $(Te_{3.4}Se_{2.6})(SbF_6)_2$ (**3**), and new crystal forms of $(Te_2Se_4)(MF_6)_2$ [M = As (**4**), Sb (**5**)]. Similar reactions of Te/S mixtures gave the compound $(Te_{2.1}S_{3.9})(SbF_6)_2$ (**6**), which is isomorphous with **5** and contains the cation $Te_2S_4^{2+}$. Compounds **2** and **3** are isomorphous with the previously reported form of $(Te_2Se_4)(SbF_6)_2$. In all six compounds the cations are six-membered rings in the boat conformation with two tellurium atoms forming a cross-ring bond, that is, a bicyclo[3.1.0]hexane type arrangement. Occupational disorder in compounds **2** and **3** and anion–cation interactions are discussed. Crystal data are as follows: **1**, orthorhombic, space group *Pbca*, $a = 15.288$ (5) Å, $b = 17.189$ (5) Å, $c = 17.300$ (5) Å, $V = 4546$ Å^3; **2**, orthorhombic, $P2_12_12_1$, $a = 12.192$ (2) Å, $b = 8.770$ (2) Å, $c = 15.817$ (2) Å, $V = 1697$ Å^3; **3**, orthorhombic, $P2_12_12_1$, $a = 12.266$ (3) Å, $b = 8.828$ (3) Å, $c = 15.884$ (4) Å, $V = 1720$ Å^3; **4**, orthorhombic, $Pna2_1$, $a = 23.775$ (6) Å, $b = 8.663$ (3) Å, $c = 15.168$ (4) Å, $V = 3124$ Å^3; **5**, orthorhombic, *Pbcn*, $a = 12.124$ (4) Å, $b = 18.493$ (6) Å, $c = 29.503$ (7) Å, $V = 6614$ Å^3; **6**, orthorhombic, *Pbcn*, $a = 11.988$ (3) Å, $b = 18.220$ (6) Å, $c = 29.096$ (8) Å, $V = 6355$ Å^3.

Introduction

The square-planar cations Te_4^{2+} and Se_4^{2+} have been prepared with a variety of anions,[2] and ^{125}Te and ^{77}Se NMR spectroscopy has given additional evidence for the mixed species $TeSe_3^{2+}$, *cis*- and *trans*-$Te_2Se_2^{2+}$, and Te_3Se^{2+} in solution.[3,4] In attempts to prepare solid crystalline derivatives of these mixed species by the reaction of Te/Se mixtures with SbF_5 in SO_2, we have characterized the *trans*-$Te_2Se_2^{2+}$ cation in an X-ray crystallographic study of $(Te_2Se_2)(Sb_3F_{14})(SbF_6)$[5] and evidence for the Te_3Se^{2+} cation has been obtained in the disordered structure $(Te_{3.0}Se_{1.0})(Sb_3F_{14})(SbF_6)$.[5] An analogous reaction with a Te:Se ratio of 1:3, however, unexpectedly gave a new salt of the $Te_2Se_4^{2+}$ cation, namely $(Te_2Se_4)(Sb_3F_{14})(SbF_6)$, and a new form of $(Te_2Se_4)(SbF_6)_2$[6] was obtained as a second crop of crystals in the $(Te_{3.0}Se_{1.0})(Sb_3F_{14})(SbF_6)$ preparation.

In the present work attempts to prepare $(Te_3Se_3)(SbF_6)_2$ and $(Te_4Se_2)(SbF_6)_2$ resulted in the compounds $(Te_{2.7}Se_{3.3})(SbF_6)_2$ and $(Te_{3.4}Se_{2.6})(SbF_6)_2$, in which two atom sites in the cation are partially occupied by both tellurium and selenium. Similar occupational disorder has been observed in $(Te_{3.0}Se_{1.0})(Sb_3F_{14})(SbF_6)$[5] and $(Te_{3.7}Se_{6.3})(AsF_6)_2$.[7] Both of these new $Te_xSe_{6-x}^{2+}$ salts are isostructural with the previously reported form of $(Te_2Se_4)(SbF_6)_2$.[6] The reaction between $Se_4(AsF_6)_2$ and $Te_4(AsF_6)_2$ and reactions of Te/Se mixtures with sufficient AsF_5 to produce $Te_xSe_{4-x}^{2+}$ cations gave instead a second form of $(Te_2Se_4)(AsF_6)_2$.[6] Oxidation of Te/S mixtures with SbF_5 gave $(Te_3S_3)(SbF_6)_2$ and $(Te_{2.1}S_{3.9})(SbF_6)_2$. The former is isostructural with $(Te_3S_3)(AsF_6)_2$,[6] and the latter, with the form of $(Te_2Se_4)(SbF_6)_2$ reported here. In this paper we report details of the preparation and characterization of these compounds and discuss the structures and occupational disorder of these and related cations as well as the anion–cation interactions.

Experimental Section

Materials. Tellurium metal (99.7%, K & K, ICN Pharmaceuticals Inc.), selenium metal ("Baker Analyzed", J. T. Baker Chemical Co.), and sulfur (BDH) were dried overnight under vacuum at 22 °C. Arsenic pentafluoride (Ozark Mahoning Co.) was used directly from the cylinder, while SbF_5 (Ozark Mahoning Co.) was doubly distilled in an atmosphere of dry nitrogen before use. Anhydrous SO_2 (Canadian Liquid Air) was distilled from a glass vessel containing P_4O_{10}, over which it had been stored for at least 24 h. Sulfuryl chloride fluoride (Columbia Organic Chemicals Ltd.) was stored over NaF.

Preparations. Reactions were carried out in double-bulb vessels, with SO_2 as the solvent, as previously described.[8] The compound $(Te_{2.1}S_{3.9})(SbF_6)_2$ was too soluble for a good crystalline sample to be obtained from SO_2, so, in this case, a 4:1 SO_2/SO_2ClF solvent mixture was used. Reagent stoichiometries and reaction times for all of the preparations are summarized in Table I.

X-ray Crystallography. All crystals were selected and sealed in Lindemann capillaries in a drybox equipped with a microscope. Preliminary precession photographs were used to determine crystal quality and to obtain cell and symmetry information. Accurate unit cell dimensions were then obtained on the diffractometer at room temperature (298 K) (Table II). Data were collected under the conditions given in Table III. Lorentz and polarization corrections were applied to all data collected. Absorption corrections were applied at a later stage in the refinements when the composition of each crystal had been established. Each structure was solved as indicated (Table III). Least-squares refinement (block-diagonal or full-matrix) then converged to the residuals in Table III.

For all structures, neutral-atom scattering factors in the analytical form were taken from ref 9. Calculations were performed on a CDC 6400 computer using programs in the SHELX[10] and XRAY[11] systems and some local programs. Interatomic distances and angles, occupational parameters, and the final atomic positional parameters are given in Tables IV–VI.

Results and Discussion

Reactions. In most of the reactions in Table I it is apparent that there is a strong preference for the formation and crystallization of $Te_xSe_{6-x}^{2+}$ or $Te_xS_{6-x}^{2+}$ cations. In reactions 1 and 2, for example, the amounts of reagents used could have led to salts of the $TeSe_3^{2+}$ or $Te_2S_6^{2+}$ cations, respectively, but the resulting crystalline products were salts containing $Te_2Se_4^{2+}$ and $Te_2S_4^{2+}$, although ^{77}Se NMR spectra indicated that the $TeSe_3^{2+}$

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Table I. Preparations

reagents									
Te		Se		S		MF_5			
mg	mmol	mg	mmol	mg	mmol	mg	mmol	reacn time	product
785.5	6.156	486.1	6.156			1569	9.24	24 h	$(Te_2Se_4)(AsF_6)_2$[a]
636.3	4.987	393.8	4.987			1627	7.505	1 week	$(Te_2Se_4)(SbF_6)_2$[a]
644.4	5.050	1196	15.15			1642	7.575	1 week	$(Te_2Se_4)(SbF_6)_2$[b]
720.9	5.650	1338	16.94			4904	22.62	1 week	$(Te_2Se_4)(Sb_3F_{14})(SbF_6)$[a]
1089	8.535	674.4	8.541			1848	8.527	4 h	$(Te_{2.7}Se_{3.3})(SbF_6)_2$[a]
1651	12.94	512.3	6.488			2104	9.709	4 h	$(Te_{3.4}Se_{2.6})(SbF_6)_2$[a]
858.4	6.727			647.1	20.18	2181	10.06	24 h	$(Te_{2.1}S_{3.9})(SbF_6)_2$[a,c]
1814	14.22			455.4	14.20	1541	7.110	24 h	$(Te_3S_3)(SbF_6)_2$[a,d]
1206	9.451			302.6	9.437	1534	7.079	5 h	$(Te_3S_3)(SbF_6)_2$[e]

[a] Sample for which crystallographic data are reported. All other products characterized from precession photographs. [b] Approximately equal quantity of $(Te_2Se_8)(SbF_6)_2$ obtained in preparation.[16] [c] 4:1 SO_2/SO_2ClF solvent mixture. All other reactions in SO_2. [d] Cell dimensions only obtained on the diffractometer. Since the structure was not solved, a composition of the type $(Te_xS_{6-x})(SbF_6)_2$ cannot be ruled out. [e] Large quantity of $Te_4(SbF_6)_2$ also obtained.[2a]

Table II. Crystal Data

compd[a]	*a*, Å	*b*, Å	*c*, Å	*β*, deg	*V*, Å^3	fw	*Z*	D_{calcd}, g cm^{-3}	space group	reflns in cell detn (no./2*θ* range)
$(Te_2Se_4)(AsF_6)_2$[b]	8.640 (7)	12.012 (7)	15.272 (9)		1585	948.9	4	3.98	$P2_12_12_1$	
$(Te_2Se_4)(AsF_6)_2$[c]	23.775 (6)	8.663 (3)	15.168 (4)		3124 (2)	948.9	8	4.03	$Pna2_1$[d]	15/24.3–26.6°
$(Te_2Se_4)(SbF_6)_2$[b]	12.117 (11)	8.748 (6)	15.772 (5)		1672	1042.5	4	4.14	$P2_12_12_1$	
$(Te_2Se_4)(SbF_6)_2$[c]	12.124 (4)	18.493 (6)	29.503 (7)		6614 (3)	1042.5	16	4.19	*Pbcn*	15/28.4–32.1°
$(Te_2Se_4)(Sb_3F_{14})(SbF_6)$[c]	15.288 (5)	17.189 (5)	17.300 (5)		4546 (2)	1438.0	8	4.20	*Pbca*	15/25.5–29.1°
$(Te_{2.7}Se_{3.3})(SbF_6)_2$[c]	12.192 (2)	8.770 (2)	15.817 (2)		1697 (7)	1076.6	4	4.23	$P2_12_12_1$	15/11–22°
$(Te_{3.4}Se_{2.6})(SbF_6)_2$[c]	12.266 (3)	8.828 (3)	15.884 (4)		1720 (1)	1110.6	4	4.29	$P2_12_12_1$	15/11–22°
$(Te_{2.1}S_{3.9})(SbF_6)_2$[c]	11.988 (3)	18.220 (6)	29.096 (8)		6355 (3)	854.9	16	3.57	*Pbcn*	15/27–30°
$(Te_3S_3)(AsF_6)_2$[b]	8.421 (6)	11.828 (4)	15.279 (3)	90.92 (5)	1522	856.8	4	3.74	$P2_1/n$	
$(Te_3S_3)(SbF_6)_2$[c]	8.689 (8)	12.217 (1)	15.732 (1)	91.59 (5)	1669 (2)	950.5	4	3.78	$P2_1/n$	15/20–34°

[a] All compounds crystallize in the orthorhombic system with the exception of $(Te_3S_3)(AsF_6)_2$ and $(Te_3S_3)(SbF_6)_2$ (monoclinic). [b] Reference 6. [c] This work. [d] Or *Pnam* (*Pna*2_1 by analysis).

cation was the major cation component in the solution obtained from reaction 1.

$$\mathrm{Te} + 3\mathrm{Se} + 4\mathrm{SbF_5} \begin{array}{l} \not\nearrow\ (\mathrm{TeSe_3})(\mathrm{Sb_3F_{14}})(\mathrm{SbF_6}) \\ \searrow\ (\mathrm{Te_2Se_4})(\mathrm{Sb_3F_{14}})(\mathrm{SbF_6}) \end{array} \tag{1}$$

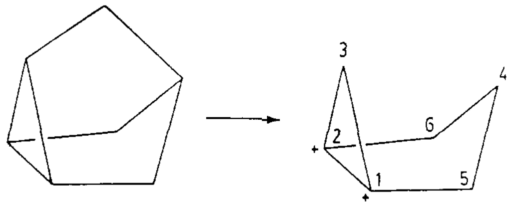
$$2\mathrm{Te} + 6\mathrm{S} + 3\mathrm{SbF_5} \begin{array}{l} \not\nearrow\ (\mathrm{Te_2S_6})(\mathrm{SbF_6})_2 + \mathrm{SbF_3} \\ \searrow\ (\mathrm{Te_2S_4})(\mathrm{SbF_6})_2 \end{array} \tag{2}$$

In a separate set of reactions, $Te_4(AsF_6)_2$ and $Se_4(AsF_6)_2$, prepared by previously described methods,[8] were combined in various ratios in SO_2 solutions, and the products were examined by X-ray crystallography. With Te_4^{2+}:Se_4^{2+} ratios of 1:3 and 2:2, the compound $(Te_2Se_4)(AsF_6)_2$ (form reported here) was produced. With a ratio of 3:1, however, the product obtained had a different space group, *Pcmm*, *Pc2m*, or *Pcm*2_1, cell dimensions 8.644 (3) × 15.410 (4) × 24.012 (8) Å, and a slightly larger cell volume, 3198 (2) Å^3. The crystals were very thin red-brown plates, and it was not possible to obtain a sufficiently good data set to resolve the space group ambiguity and obtain a satisfactory structure solution. The unit cell volume and reaction conditions suggest, however, that the crystals contained a cation isostructural with $Te_2Se_4^{2+}$, but with a higher ratio of Te, as was observed in $(Te_{2.7}Se_{3.3})(SbF_6)_2$ and $(Te_{3.4}Se_{2.6})(SbF_6)_2$. Oxidation–reduction obviously occurs in all of the reactions between Se_4^{2+} and Te_4^{2+} rather than exchange to produce mixed square-planar cations. The Se_4^{2+} cation acts as the oxidant, and it is probable that Te_6^{4+} is another product.

Crystal Structures

The $Te_xSe_{6-x}^{2+}$ Cations. Contrary to a previous report,[6] $(Te_2Se_4)(AsF_6)_2$ crystallizes in the space group *Pna*2_1 with a cell that has twice the volume of that reported (space group $P2_12_12_1$). However, there is a systematic weakness for all reflections *hkl* with $h = 2n$ in the data collected on this new cell. Furthermore, $(Te_2Se_4)(SbF_6)_2$ has been obtained in a second form that crystallizes in the space group *Pbcn* with two independent ion pairs in the asymmetric unit and a cell volume 4 times as large as that reported (space group $P2_12_12_1$).[6] A comparison of the cation dimensions in the three new $Te_2Se_4^{2+}$ structures with those previously reported, however, suggests that the cations in the previously described compounds have some occupational Te/Se disorder (see below). The larger size of the disordered cations and differences in anion–cation interactions probably lead to the different space groups observed. The present disordered compounds $(Te_{2.7}Se_{3.3})(SbF_6)_2$ and $(Te_{3.4}Se_{2.6})(SbF_6)_2$ are isostructural with the forms of $(Te_2Se_4)(AsF_6)_2$ and $(Te_2Se_4)(SbF_6)_2$ reported earlier (Table II).

All the $Te_xSe_{6-x}^{2+}$ cations described above are six-membered rings in the boat conformation with two tellurium atoms forming a cross-ring bond (Figure 1). As described previously,[6,12] the structure of this cation may be obtained from the "birdcage" structure of molecules such as P_4S_3,[13] $As_3Se_4^+$,[14] and Sb_7^{3-}[15] by removal of an atom bridging one of the edges of the tetrahedron of P, As(Se), or Sb atoms. The valence structure I can then be drawn.



I

In $(Te_{2.7}Se_{3.3})(SbF_6)_2$ and $(Te_{3.4}Se_{2.6})(SbF_6)_2$ the apical selenium positions of the boat (Se(3) and Se(4) of I) are partially

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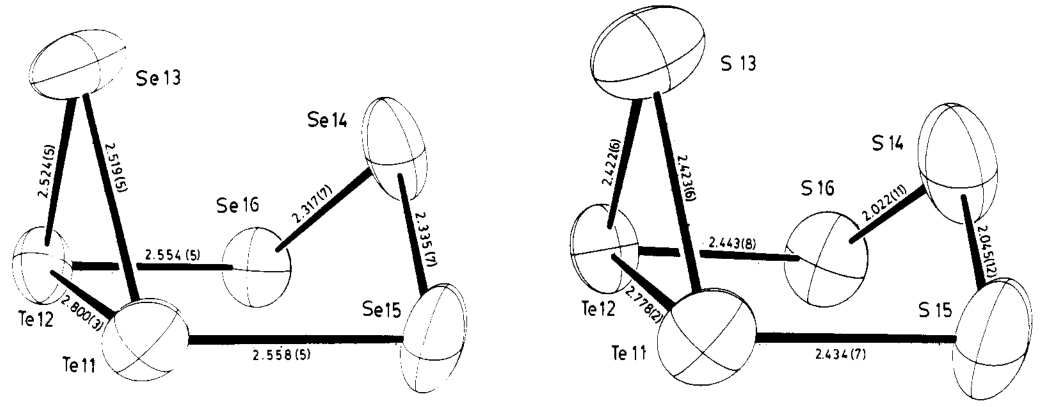

Figure 1. ORTEP diagrams of a $Te_2Se_4^{2+}$ cation in $(Te_2Se_4)(SbF_6)_2$ and a $Te_{2.1}S_{3.9}^{2+}$ cation in $(Te_{2.1}S_{3.9})(SbF_6)_2$.

Table III. Details of Data Collection[a] and Structure Refinements

	(Te_2Se_4)-$(AsF_6)_2$[b]	(Te_2Se_4)-$(SbF_6)_2$[c]	(Te_2Se_4)-$(Sb_3F_{14})(SbF_6)$[c]	$(Te_{2.7}Se_{3.3})$-$(SbF_6)_2$[c]	$(Te_{3.4}Se_{3.6})$-$(SbF_6)_2$[c]	$(Te_{2.1}S_{3.9})$-$(SbF_6)_2$[d]
			Data Collections			
scan range, deg	$(K\alpha_1 - 0.85)$ to $(K\alpha_2 + 0.85)$	$(K\alpha_1 - 0.75)$ to $(K\alpha_2 + 0.75)$	$(K\alpha_1 - 0.9)$ to $(K\alpha_2 + 0.9)$	$(K\alpha_1 - 1.0)$ to $(K\alpha_2 + 1.0)$	$(K\alpha_1 - 1.0)$ to $(K\alpha_2 + 1.0)$	$(K\alpha_1 - 1.0)$ to $(K\alpha_2 + 1.0)$
scan speed,[e] deg/min	2.0–29.3	3.5–29.3	3.5–29.3	3.0–29.3	3.0–29.3	3.0–29.3
std reflns,[f] no./interval	3/47	3/77	3/67	3/67	3/67	3/77
quadrant collcd	$(h,k,\pm l)$	(h,k,l)	(h,k,l)	$(h,k,\pm l)$	$(h,k,\pm l)$	(h,k,l)
max 2θ, deg	45	50	52.5	55	50	50
abs cor (dist in cm)	spherical ($\mu R = 1.725$; $R = 0.0093$)	ABSORB, ($\{1,0,0\}$, 0.0075; $\{0,1,0\}$, 0.0125; $\{0,0,1\}$, 0.0125)	ABSORB ($\{1,0,0\}$, 0.0155; (0,0,1), 0.0050; $(0,\bar{1},0)$, 0.0050; (0,1,1), 0.0053)	ABSORB ($\{1,0,0\}$, 0.0120; $(0,\bar{1},\bar{1})$, (0,1,1), 0.0036; $(0,1,\bar{1})$, $(0,\bar{1},1)$, 0.0090)	ABSORB ($\{1,0,0\}$, 0.0160; (0,1,1), $(0,\bar{1},\bar{1})$, 0.0050; $(0,1,\bar{1})$, $(0,\bar{1},1)$, 0.0070)	ABSORB ($\{1,0,0\}$, 0.0125; $\{0,1,0\}$, 0.0070; $\{0,0,1\}$, 0.0070)
grid		10 × 7 × 7	6 × 10 × 10	5 × 10 × 10	5 × 10 × 10	6 × 10 × 10
A^*		7.32–42.62	3.72–22.46	2.69–16.76	3.24–9.97	2.51–2.93
μ, cm^{-1}		164.6	144.1	157.1	150.6	77.9
			Structure Refinements			
structure soln	Patterson[g]	direct methods (SHELX)	direct methods (SHELX)	*h*	*h*	*i*
no. of data						
$I > 3\sigma(I)$	2171	2440	1908	2080	2440	3084
$I > 1\sigma(I)$	3139	4027	3081			
R factors						
$3\sigma(I)$: R_1 (R_2)	0.052 (0.062)	0.071 (0.085)	0.072 (0.091)	0.054 (0.056)	0.054 (0.060)	0.049 (0.054)
$1\sigma(I)$: R_1 (R_2)	0.072 (0.076)	0.119 (0.113)	0.117 (0.123)	NA	NA	NA
max shift/error	0.21	0.19	0.20	0.06	0.20	0.25
weighting scheme		$\sigma^2(F) + 0.0017F^2$	$\sigma^2(F) + 0.003F^2$	$\sigma^2(F) + 0.0021F^2$	$\sigma^2(F) + 0.0079F^2$	$\sigma^2(F) + 0.0021F^2$
diff Fourier[j]						
max peak, e Å^{-3}	+2.2	+2.3	+3.3	+2.2	+2.9	+1.6
min trough, e Å^{-3}	−1.6	−1.6	−2.3	−1.4	−3.0	−1.0

[a] Data collected on a Syntex $P2_1$ diffractometer in the θ:2θ mode using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). Backgrounds: stationary crystal–stationary counter at each end of scan, each for one quarter of time taken for scan. [b] Crystals from Te_4^{2+}/Se_4^{2+} reactions were small, thin, dark red-brown plates. Those from reactions of mixed elements with AsF_5 were bricks and needles. Crystals used were shaped until approximately spherical. [c] Crystals of other Te/Se salts were dark brown plates, prisms, or needles. [d] Crystals were dark, amber needles. [e] Dependent on intensity of a 2-s prescan. [f] No systematic trends in the intensities of the standard reflections were observed for any of the data sets. [g] Statistics calculated by assuming the compound to be $(Te_2Se_2)(AsF_6)_2$ indicated that the space group was centrosymmetric (*Pnam*). Large overlaps in Patterson function caused direct methods to fail. Eventual solution achieved by using phasing model from several heavy-atom positions in *Pna2₁*. Strong similarity to previously reported cell for $(Te_2Se_4)(AsF_6)_2$ noted. [h] Isostructural with the previously reported form of $(Te_2Se_4)(SbF_6)_2$.[6] Atomic positions from this structure used in initial refinement. From bond length considerations it appeared that the cations in these compounds might be disordered, and in the final cycles, occupancy factors of all atoms in the cations were allowed to refine. [i] Isostructural with the present form of $(Te_2Se_4)(SbF_6)_2$. [j] In $(Te_2Se_4)(AsF_6)_2$ and $(Te_{3.3}Se_{2.7})(SbF_6)_2$ some residual electron density was observed close to some of the fluorine atoms; otherwise the largest residual peaks were close to the heavy atoms (notably Sb). (In view of the large absorptions required for this class of compounds these residual peaks are considered normal.)

occupied by tellurium. In both cases the tellurium concentration is higher at site 4 (Table V). The bonds to the partially Te-substituted positions are significantly longer than the average Te–Se and Se–Se bonds in the structures with simple $Te_2Se_4^{2+}$ cations (Table IV). Analogous bonds in different $Te_2Se_4^{2+}$ cations show some small variations as well. These differences may be accounted for by thermal effects on the bond lengths and by the different anion environments of each $Te_2Se_4^{2+}$ cation, that is, by some of the significant Te···F and Se···F charge-transfer contacts observed in each structure. The bond lengths to Se(3) and Se(4) in the published structures[6] of "$(Te_2Se_4)(AsF_6)_2$" and "$(Te_2Se_4)(SbF_6)_2$", however, are significantly longer than the analogous mean bond lengths in the present $Te_2Se_4^{2+}$ salts (Table IV), probably indicating partial tellurium substitution at these sites.

The cross-ring Se(3)···Se(4) distances in the $Te_xSe_{6-x}^{2+}$ structures are comparable in magnitude to cross-ring distances

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Table IV. Bond Lengths (Å) and Bond Angles (deg) in the $Te_xSe_{6-x}^{2+}$ and $Te_xS_{6-x}^{2+}$ Cations

Bond Lengths[a]

compd	1–2	1–3	1–5	2–3	2–6	4–5	4–6	3···4	5···6	ref
$(Te_2Se_4)(AsF_6)_2$[b]	2.812 (5)	2.547 (6)	2.566 (6)	2.530 (6)	2.527 (8)	2.327 (8)	2.285 (8)	3.350 (8)	3.384 (8)	*c*
	2.794 (4)	2.563 (5)	2.545 (5)	2.568 (5)	2.543 (6)	2.314 (7)	2.323 (7)	3.390 (7)	3.451 (7)	
$(Te_2Se_4)(SbF_6)_2$[b]	2.800 (3)	2.519 (4)	2.558 (5)	2.524 (5)	2.554 (5)	2.335 (7)	2.317 (6)	3.364 (6)	3.469 (6)	*c*
	2.809 (4)	2.520 (5)	2.553 (5)	2.504 (5)	2.551 (6)	2.305 (6)	2.298 (6)	3.374 (6)	3.429 (6)	
$(Te_2Se_4)(Sb_3F_{14})(SbF_6)$	2.770 (4)	2.460 (5)	2.522 (6)	2.466 (5)	2.494 (5)	2.268 (7)	2.280 (7)	3.344 (6)	3.372 (7)	*c*
mean $Te_2Se_4^{2+}$[d]	2.798	2.522	2.549	2.518	2.534	2.310	2.301	3.364	3.421	
$(Te_{2.7}Se_{3.3})(SbF_6)_2$	2.793 (2)	2.558 (3)	2.552 (3)	2.567 (4)	2.546 (3)	2.385 (4)	2.400 (4)	3.453 (4)	3.491 (4)	*c*
$(Te_{3.4}Se_{2.6})(SbF_6)_2$	2.802 (2)	2.646 (3)	2.579 (3)	2.646 (3)	2.567 (3)	2.445 (3)	2.469 (3)	3.543 (3)	3.531 (3)	*c*
"$(Te_2Se_4)(AsF_6)_2$"[e]	2.82 (2)	2.56 (2)	2.58 (2)	2.59 (2)	2.57 (2)	2.38 (2)	2.33 (2)	3.49 (2)	3.42 (2)	6
"$(Te_2Se_4)(SbF_6)_2$"[f]	2.786 (7)	2.525 (11)	2.539 (9)	2.539 (10)	2.532 (9)	2.346 (11)	2.346 (10)	3.412 (11)	3.445 (10)	6
$(Te_{2.1}S_{3.9})(SbF_6)_2$[b]	2.779 (2)	2.425 (5)	2.432 (6)	2.422 (6)	2.448 (6)	2.047 (10)	2.007 (9)	3.178 (9)	3.139 (9)	*c*
	2.782 (2)	2.451 (5)	2.440 (6)	2.416 (5)	2.433 (6)	2.020 (9)	2.028 (9)	3.217 (9)	3.137 (9)	
$(Te_3S_3)(AsF_6)_2$	2.787 (4)	2.665 (6)	2.468 (10)	2.684 (4)	2.443 (12)	2.105 (16)	2.098 (15)	3.391 (12)	3.213 (16)	6

Bond Angles

compd	2–1–3	2–1–5	3–1–5	1–2–3	1–2–6	3–2–6	1–3–2	5–4–6	1–5–4	2–6–4	ref
$(Te_2Se_4)(AsF_6)_2$[b]	56.1 (1)	96.9 (2)	99.4 (2)	56.7 (2)	95.9 (2)	101.0 (2)	67.3 (2)	94.4 (3)	96.7 (2)	97.2 (3)	*c*
	57.1 (1)	97.7 (1)	99.7 (2)	56.9 (1)	97.0 (2)	101.3 (2)	66.1 (1)	96.1 (2)	97.4 (2)	96.7 (2)	
$(Te_2Se_4)(SbF_6)_2$[b]	56.4 (1	98.9 (1)	99.7 (2)	56.2 (1)	96.0 (1)	100.7 (2)	67.4 (1)	96.4 (2)	96.6 (2)	97.0 (2)	*c*
	55.7 (1)	97.4 (1)	99.8 (2)	56.3 (1)	96.5 (1)	101.0 (2)	68.0 (1)	96.3 (2)	97.3 (2)	97.0 (2)	
$(Te_2Se_4)(Sb_3F_{14})(SbF_6)$	55.9 (1)	96.0 (2)	100.5 (2)	55.7 (1	97.8 (2)	100.8 (2)	68.4 (1)	95.7 (2)	97.8 (2)	97.7 (2)	*c*
mean $Te_2Se_4^{2+}$[d]	56.2	97.4	99.8	56.4	96.5	101.0	67.4	95.8	97.2	97.1	
$(Te_{2.7}Se_{3.3})(SbF_6)_2$	57.1 (1)	96.9 (1)	101.4 (1)	56.8 (1)	98.8 (1)	100.0 (1)	66.0 (1)	93.7 (1)	98.0 (1)	98.3 (1)	*c*
$(Te_{3.4}Se_{2.6})(SbF_6)_2$	58.0 (1)	97.0 (1)	101.7 (1)	58.0 (1)	99.2 (1)	100.9 (1)	63.9 (1)	91.9 (1)	98.4 (1)	98.4 (1)	*c*
"$(Te_2Se_4)(AsF_6)_2$"[e]	59 (1)	96 (1)	99	57 (1)	99 (1)	101 (1)	64 (1)	94 (1)	99 (1)	98 (1)	6
"$(Te_2Se_4)(SbF_6)_2$"[f]	56.9 (2)	98.0 (3)	99.9 (3)	56.4 (3)	96.8 (2)	101.8 (3)	66.8 (9)	94.3 (4)	98.1 (3)	97.5 (3)	6
$(Te_{2.1}S_{3.9})(SbF_6)_2$[b]	55.0 (1)	95.3 (2)	96.9 (2)	55.1 (1)	93.1 (1)	98.3 (2)	70.0 (1)	101.5 (4)	99.0 (3)	98.7 (3)	*c*
	54.6 (1)	94.4 (2)	97.2 (2)	55.7 (1)	93.8 (1)	99.2 (2)	69.7 (1)	101.6 (4)	99.8 (3)	98.8 (3)	
$(Te_3S_3)(AsF_6)_2$	58.9 (1)	95.4 (3)	99.5 (3)	58.3 (1)	94.6 (3)	100.3 (3)	62.8 (1)	99.7 (6)	98.2 (5)	98.7 (4)	6

[a] Numbering as in structure I. [b] Two independent cations in the structure. [c] This work. [d] Mean of five unique cation dimensions above. [e] Proposed composition based on 3···4 distance: $(Te_{3.0}Se_{3.0})(AsF_6)_2$. [f] Proposed composition based on 3···4 distance: $(Te_{2.4}Se_{3.6})(SbF_6)_2$.

Table V. Occupation of the Sites in the $Te_xSe_{6-x}^{2+}$ Cation[a]

	$(Te_{2.71(5)}Se_{3.29(5)})(SbF_6)_2$				$(Te_{3.45(4)}Se_{2.55(4)})(SbF_6)_2$			
site[b]	*K*[c]	no. of electrons	% Te[d]	% Se[d]	*K*[c]	no. of electrons	% Te[d]	% Se[d]
1	1.01 (1)	52.3 (4)	100	0	1.00 (1)	51.8 (4)	100	0
2	1.03 (1)	53.5 (5)	100	0	0.99 (1)	51.7 (5)	100	0
3	1.12 (1)[e]	38.0 (4)	22 (2)	78 (2)	0.87 (1)[f]	45.4 (4)	64 (2)	36 (2)
4	0.82 (1)[f]	42.7 (4)	49 (3)	51 (3)	0.94 (1)[f]	48.7 (4)	81 (2)	19 (2)
5	1.01 (1)	34.5 (4)	0	100	1.03 (1)	34.9 (4)	0	100
6	0.98 (1)	33.3 (4)	0	100	0.99 (1)	33.7 (4)	0	100

[a] In the $Te_{2.11(1)}S_{3.89(1)}^{2+}$ cations the population parameters of site 3 (refined as sulfur atoms) were 1.21 (2) and 1.29 (2). In a separate refinement where all population parameters of the Te and S atoms in the two cations were refined the results were as follows: Te(11), 0.993 (5); Te(12), 0.978 (5); Te(21), 0.990 (5); Te(22), 0.980(5); S(13), 1.21 (2); S(14), 1.03 (2); S(15), 0.95 (2); S(16), 1.02 (2); S(23), 1.29 (2); S(24), 0.98 (2); S(25), 1.04 (2); S(26), 1.09 (2). [b] Numbering as in structure I. [c] Population parameter from refinement with the program SHELX. [d] Sites where the number of electrons is within 3σ of 34 (Se) or 52 (Te) are considered to be 100% Se or Te. [e] Refined as Se. [f] Refined as Te.

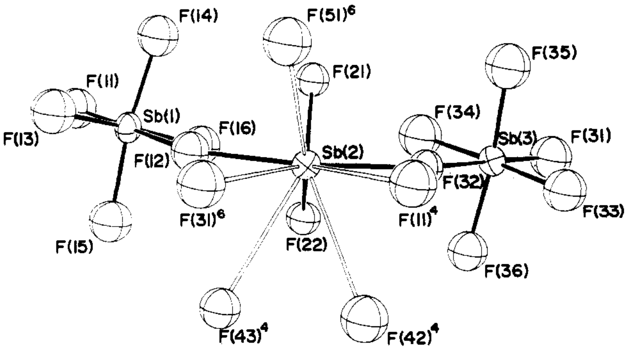

Figure 2. The $Sb_3F_{14}^-$ anion in $(Te_2Se_4)(Sb_3F_{14})(SbF_6)$. Contacts to fluorine atoms on adjacent anions (unfilled bonds) surround the assumed position of the lone pair of electrons on Sb(2).

in the $Te_2Se_6^{2+}$, $Te_xSe_{10-x}^{2+}$, and Se_{10}^{2+} cations[16,17] and may indicate weak bonding interactions. The observation that the Se(3) and Se(4) sites in the $Te_xSe_{6-x}^{2+}$ cation are preferentially occupied over the Se(5) and Se(6) sites by the larger, more polarizable tellurium atoms (Table V) lends some support to this argument. A plot of the Se(3)···Se(4) distance (*d*) as a function of total tellurium occupation at these two positions (X_{Te}) for the mean $Te_2Se_4^{2+}$ cation ($X_{Te} = 0$) and the mixed $(Te_{2.7}Se_{3.3})(SbF_6)_2$ and $(Te_{3.4}Se_{2.6})(SbF_6)_2$ structures ($X_{Te} = 0.7$ and 1.4, respectively) gives a straight line, $X_{Te} = (d - 3.364)/0.128$. On the basis of this plot, the 3···4 distances in the published structures of "$(Te_2Se_4)(AsF_6)_2$" and "$(Te_2Se_4)(SbF_6)_2$" indicate that these compounds might be better described as $(Te_{3.0}Se_{3.0})(AsF_6)_2$ and $(Te_{2.4}Se_{3.6})(SbF_6)_2$ respectively. The bond angles in the $Te_2Se_4^{2+}$ and $Te_xSe_{6-x}^{2+}$ cations (Table IV) are sensitive to changes in the tellurium content of the cation as well. The Te(1)–Se(3)–Te(2) and Se(5)–Se(4)–Se(6) angles in the $Te_{3.4}Se_{2.6}^{2+}$ cation, where the Se(3) and Se(4) sites are partially occupied by tellurium, are nearly 4° smaller than the analogous angles in the mean $Te_2Se_4^{2+}$ cation.

The $Te_xS_{6-x}^{2+}$ Cation. Compound **6**, which is isomorphous with the form of $(Te_2Se_4)(SbF_6)_2$ reported here, has the overall com-

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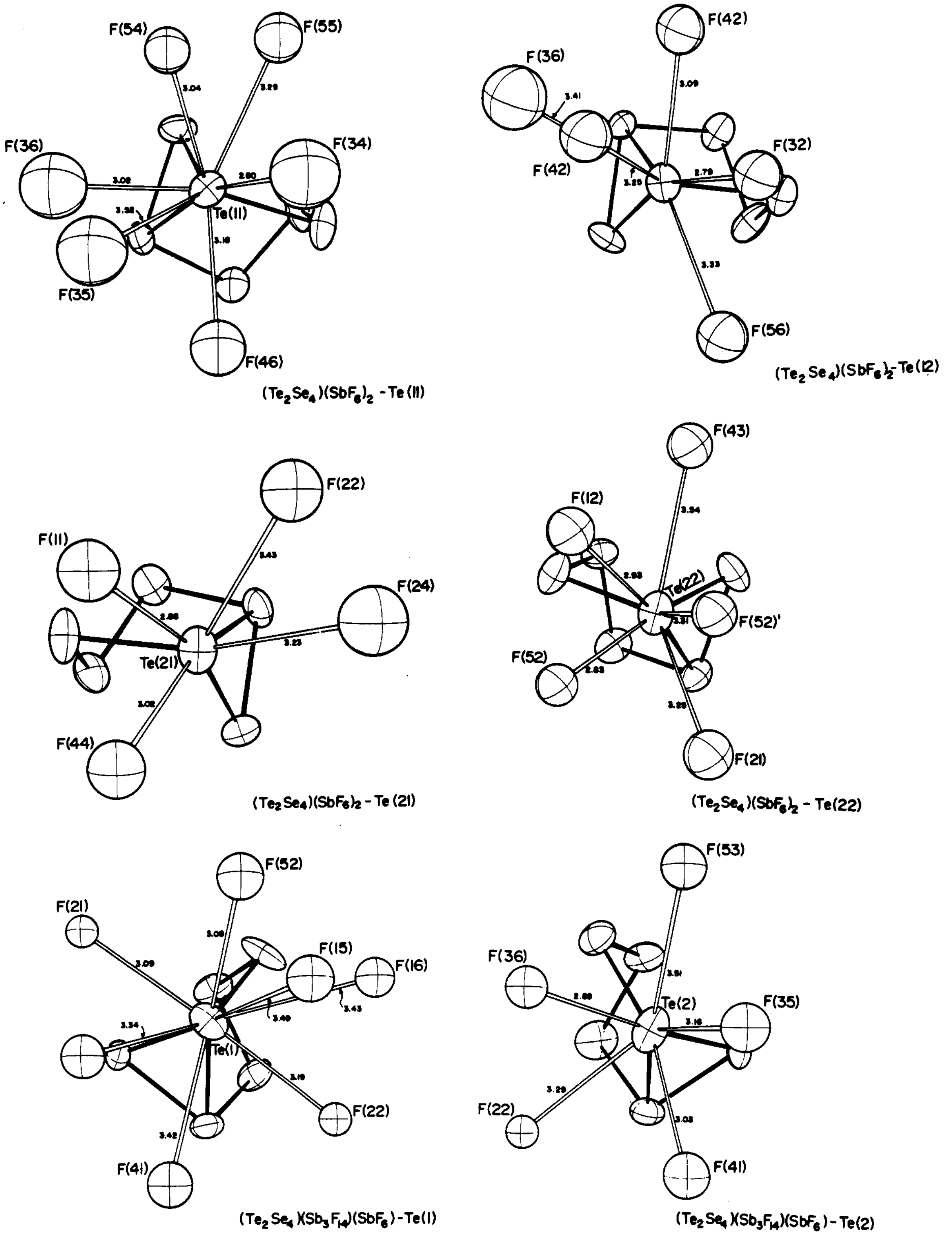

$(Te_2Se_4)(SbF_6)_2$ - Te(11)

$(Te_2Se_4)(SbF_6)_2$ - Te(12)

$(Te_2Se_4)(SbF_6)_2$ - Te(21)

$(Te_2Se_4)(SbF_6)_2$ - Te(22)

$(Te_2Se_4)(Sb_3F_{14})(SbF_6)$ - Te(1)

$(Te_2Se_4)(Sb_3F_{14})(SbF_6)$ - Te(2)

Figure 3. Anion–cation interactions (unfilled bonds) at the tellurium atoms in $(Te_2Se_4)(SbF_6)_2$ and $(Te_2Se_4)(Sb_3F_{14})(SbF_6)$. All views are toward the assumed position of the lone pair on Te.

position $(Te_{2.1}S_{3.9})(SbF_6)_2$, based on the refined population parameters. The cation probably represents a 9:1 mixture of the cations $Te_2S_4^{2+}$ and $Te_3S_3^{2+}$. The $Te_2S_4^{2+}$ cation has not been previously characterized. The averaged cation in **6** is isostructural with $Te_2Se_4^{2+}$, with the two tellurium atoms forming a cross-ring bond (Figure 1), and the partial tellurium substitution is at site 3 in both independent cations. This same cation site is completely occupied by tellurium in $(Te_3S_3)(AsF_6)_2$.[6] As observed for "$(Te_2Se_4)(AsF_6)_2$" and "$(Te_2Se_4)(SbF_6)_2$",[6] the bond lengths to S(4) in the published structure of $(Te_3S_3)(AsF_6)_2$ are significantly longer than the bond lengths to the analogous S(14) and S(24) atoms in $(Te_{2.1}S_{3.9})(SbF_6)_2$, indicating that there is probably some tellurium substitution at S(4) of $(Te_3S_3)(AsF_6)_2$ as well (Table IV). The Te–S bonds of the Te_2S_3 ring have the same length in both structures. The analogous Te–Se bonds of the Te_xSe_{6-x} cations are also all of equal length (Table IV).

It is a common feature in both the $Te_xSe_{6-x}^{2+}$ and $Te_xS_{6-x}^{2+}$ structures that the two three-coordinate positions are essentially entirely occupied by tellurium while the remaining two atoms in the plane (5 and 6) are either selenium or sulfur. If the cation contains more than two tellurium atoms, then it is sites 3 and 4 that are partially occupied. This is in accord with calculations

Table VI. Final Atomic Positional (×10⁴) Parameters (×10³ for F Atoms in (A) and (C))

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
(A) $(Te_2Se_4)(AsF_6)_2$											
Te(11)	5036 (1)	4433 (3)	−1130 (2)	F(11)	704 (1)	606 (4)	575 (2)	F(31)	899 (1)	189 (4)	392 (4)
Te(12)	4378 (1)	3153 (4)	226 (3)	F(12)	675 (1)	860 (3)	520 (2)	F(32)	946 (1)	374 (3)	300 (2)
Se(13)	4578 (2)	1778 (6)	−1212 (3)	F(13)	788 (1)	626 (3)	484 (2)	F(33)	858 (2)	430 (5)	355 (3)
Se(14)	5725 (2)	1255 (6)	36 (4)	F(14)	757 (1)	881 (3)	427 (2)	F(34)	821 (1)	217 (4)	285 (2)
Se(15)	5997 (2)	3658 (6)	−501 (4)	F(15)	694 (1)	673 (3)	413 (2)	F(35)	870 (2)	395 (5)	199 (3)
Se(16)	5195 (3)	2248 (6)	1157 (4)	F(16)	768 (1)	837 (4)	584 (2)	F(36)	924 (2)	150 (5)	240 (3)
Te(21)	7474 (1)	5764 (3)	2448 (3)	F(21)	573 (1)	368 (3)	598 (2)	F(41)	637 (2)	363 (5)	421 (3)
Te(22)	8107 (1)	6785 (3)	1007 (2)	F(22)	469 (1)	139 (3)	667 (2)	F(42)	574 (3)	152 (8)	355 (4)
Se(23)	7897 (2)	8481 (5)	2357 (3)	F(23)	488 (1)	281 (4)	531 (2)	F(43)	587 (3)	360 (9)	296 (5)
Se(24)	6723 (2)	8573 (5)	1090 (3)	F(24)	488 (1)	404 (4)	674 (2)	F(44)	692 (2)	293 (5)	299 (3)
Se(25)	6503 (2)	6298 (5)	1811 (5)	F(25)	558 (1)	221 (4)	723 (2)	F(45)	648 (2)	135 (5)	416 (3)
Se(26)	7283 (2)	7451 (5)	9 (4)	F(26)	555 (1)	106 (3)	580 (2)	F(46)	620 (2)	88 (7)	259 (4)
As(1)	7323 (2)	7396 (4)	5016 (4)								
As(2)	5225 (2)	2535 (4)	6291 (4)								
As(3)	8865 (2)	2830 (6)	2950 (3)								
As(4)	6332 (3)	2199 (6)	3284 (4)								
(B) $(Te_2Se_4)(SbF_6)_2$											
Te(11)	2710 (2)	1181 (1)	4364 (1)	F(11)	809 (26)	563 (15)	2212 (10)	F(41)	3028 (24)	−295 (14)	1260 (9)
Te(12)	1526 (2)	−117 (1)	4315 (1)	F(12)	−845 (23)	−829 (13)	2785 (8)	F(42)	1005 (23)	−160 (13)	325 (9)
Se(13)	2182 (4)	579 (2)	3630 (1)	F(13)	−952 (34)	−115 (19)	2022 (12)	F(43)	1285 (24)	−1075 (13)	1005 (9)
Se(14)	4413 (4)	−337 (2)	3990 (2)	F(21)	5000 (0)	1574 (20)	2500 (0)	F(44)	1098 (24)	372 (14)	1146 (9)
Se(15)	5350 (4)	−661 (2)	5535 (2)	F(22)	3511 (27)	599 (16)	2632 (10)	F(45)	2777 (27)	570 (16)	596 (10)
Se(16)	3177 (4)	−947 (2)	4452 (2)	F(23)	5000 (0)	−463 (32)	2500 (0)	F(46)	2863 (28)	−851 (16)	419 (10)
Te(21)	2328 (2)	1453 (1)	1772 (1)	F(24)	4607 (31)	596 (19)	1908 (12)	F(51)	2131 (23)	2181 (13)	3008 (8)
Te(22)	3508 (2)	2717 (1)	1930 (1)	F(31)	−21 (31)	2906 (18)	460 (12)	F(52)	3830 (20)	2993 (11)	2863 (7)
Se(23)	3117 (4)	2303 (3)	1138 (1)	F(32)	805 (23)	1351 (13)	−229 (8)	F(53)	2080 (24)	3561 (13)	3229 (8)
Se(24)	769 (4)	3102 (2)	1493 (1)	F(33)	1615 (47)	2012 (26)	433 (17)	F(54)	2119 (21)	2555 (12)	3856 (8)
Se(25)	392 (4)	1982 (2)	1799 (2)	F(34)	863 (37)	2720 (21)	−345 (14)	F(55)	3876 (25)	2049 (14)	3519 (9)
Se(26)	1831 (4)	3512 (2)	2084 (2)	F(35)	−1065 (37)	2151 (19)	−134 (13)	F(56)	3879 (25)	3401 (14)	3697 (9)
Sb(1)	0 (0)	−139 (2)	2500 (0)	F(36)	−287 (38)	1524 (22)	541 (14)				
Sb(2)	5000 (0)	546 (2)	2500 (0)								
Sb(3)	359 (2)	2138 (1)	106 (1)								
Sb(4)	1992 (2)	−246 (1)	795 (1)								
Sb(5)	3000 (2)	2808 (1)	3365 (1)								
(C) $(Te_2Se_4)(Sb_3F_{14})(SbF_6)$											
Te(1)	−51 (2)	1235 (1)	2525 (2)	F(11)	225 (1)	−34 (1)	404 (2)	F(33)	257 (1)	280 (1)	−76 (2)
Te(2)	−90 (2)	2280 (2)	1306 (2)	F(12)	231 (1)	−29 (1)	182 (1)	F(34)	267 (1)	264 (1)	136 (2)
Se(3)	−1323 (2)	2045 (2)	2194 (2)	F(13)	248 (2)	−136 (2)	291 (2)	F(35)	384 (2)	268 (1)	26 (2)
Se(4)	21 (3)	3240 (2)	3151 (3)	F(14)	348 (1)	−12 (1)	295 (2)	F(36)	140 (1)	272 (1)	37 (1)
Se(5)	733 (3)	2123 (3)	3456 (3)	F(15)	111 (1)	−50 (1)	280 (2)	F(41)	55 (2)	−68 (2)	−66 (2)
Se(6)	654 (3)	3386 (2)	1966 (3)	F(16)	206 (1)	73 (1)	296 (2)	F(42)	−86 (1)	−73 (1)	20 (2)
Sb(1)	2280 (1)	−324 (1)	2972 (1)	F(21)	332 (1)	93 (1)	144 (1)	F(43)	−68 (1)	35 (1)	−82 (1)
Sb(2)	2435 (1)	499 (1)	824 (1)	F(22)	157 (1)	107 (1)	138 (1)	F(51)	−102 (2)	−30 (1)	450 (2)
Sb(3)	2626 (1)	2752 (1)	297 (1)	F(31)	263 (1)	381 (1)	40 (2)	F(52)	36 (2)	39 (1)	405 (2)
Sb(4)	5000 (0)	0 (0)	5000 (0)	F(32)	259 (1)	163 (1)	20 (1)	F(53)	−48 (2)	99 (1)	527 (2)
Sb(5)	0 (0)	5000 (0)	0 (0)								
(D) $(Te_{2.7}Se_{3.3})(SbF_6)_2$											
Te(1)	1396 (1)	2837 (2)	2949 (1)	F(1)	1301 (27)	7747 (39)	978 (3)	F(7)	3359 (17)	8942 (31)	5140 (16)
Te(2)	2563 (1)	3833 (3)	4365 (1)	F(2)	919 (17)	5995 (29)	2195 (19)	F(8)	4389 (22)	7505 (57)	6268 (11)
Te(4)	4193 (2)	1124 (3)	3035 (2)	F(3)	1305 (15)	8944 (24)	2477 (12)	F(9)	3943 (28)	6241 (38)	4868 (26)
Se(3)	1809 (2)	1114 (4)	4214 (2)	F(4)	2790 (19)	5819 (24)	1377 (17)	F(10)	4973 (30)	8430 (45)	4078 (19)
Se(5)	3055 (3)	2328 (4)	2006 (2	F(5)	2595 (23)	6637 (36)	2968 (16)	F(11)	5953 (24)	6820 (43)	5206 (23)
Se(6)	4502 (2)	3439 (4)	3809 (2)	F(6)	3108 (23)	8605 (27)	1672 (31)	F(12)	5395 (21)	9620 (36)	5492 (32)
Sb(1)	2058 (1)	7347 (2)	1962 (1)								
Sb(2)	4676 (1)	7903 (2)	5186 (1)								
(E) $(Te_{3.4}Se_{2.6})(SbF_6)_2$											
Te(1)	1414 (1)	2903 (2)	2938 (1)	F(1)	1289 (12)	8988 (20)	2472 (12)	F(7)	3815 (57)	6157 (81)	5163 (37)
Te(2)	2564 (1)	3847 (2)	4368 (1)	F(2)	3166 (20)	8663 (24)	1768 (25)	F(8)	4867 (19)	8105 (56)	4078 (10)
Te(3)	1792 (2)	1061 (3)	4219 (1)	F(3)	1385 (27)	7863 (37)	1003 (14)	F(9)	4489 (21)	7727 (71)	6258 (15)
Te(4)	4234 (1)	1116 (2)	3029 (1)	F(4)	857 (15)	5998 (24)	2168 (16)	F(10)	3346 (13)	8998 (29)	5143 (14)
Se(5)	3085 (2)	2401 (3)	1993 (1)	F(5)	2800 (17)	5927 (20)	1370 (12)	F(11)	5990 (23)	6912 (41)	5175 (16)
Se(6)	4518 (2)	3486 (3)	3824 (2)	F(6)	2587 (21)	6619 (32)	3000 (14)	F(12)	5295 (19)	9589 (37)	5415 (45)
Sb(1)	2054 (1)	7395 (2)	1967 (1)								
Sb(2)	4674 (1)	7926 (2)	5199 (1)								
(F) $(Te_{2.1}S_{3.9})(SbF_6)_2$											
Te(11)	2733 (1)	1156.3 (7)	4371.9 (5)	F(11)	4165 (12)	4199 (7)	2215 (5)	F(41)	3726 (14)	3973 (7)	1045 (6)
Te(12)	1566 (1)	−156.0 (7)	4298.2 (5)	F(12)	5851 (15)	5651 (7)	2770 (7)	F(42)	2241 (14)	5565 (9)	563 (7)
Te(21)	2328 (1)	1495.8 (7)	1739.7 (6)	F(13)	4045 (18)	4895 (11)	2994 (7)	F(43)	2160 (13)	4139 (10)	419 (5)
Te(22)	3524 (1)	2776.1 (8)	1909.2 (5)	F(21)	5000	1631 (11)	2500	F(44)	4019 (12)	4827 (9)	327 (5)
S(13)[a]	2242 (5)	561 (3)	3655 (2)	F(22)	3482 (11)	629 (10)	2626 (6)	F(45)	1946 (14)	4752 (11)	1271 (5)
S(14)	4322 (5)	−314 (4)	4053 (3)	F(23)	5000	−412 (13)	2500	F(46)	3844 (14)	5389 (8)	1146 (6)
S(15)	4554 (5)	586 (4)	4463 (3)	F(24)	4671 (14	624 (12)	1877 (6)	F(51)	2174 (11)	2139 (8)	2985 (5)
S(16)	3235 (5)	−901 (3)	4428 (2)	F(31)	861 (14)	8634 (7)	4769 (5)	F(52)	3812 (12)	3055 (7)	2847 (4)
S(23)[a]	3091 (4)	2317 (3)	1151 (2)	F(32)	−50 (17)	7060 (9)	5471 (7)	F(53)	1956 (13)	3564 (8)	3225 (5)

Table VI (Continued)

atom	x	y	z	atom	x	y	z	atom	x	y	z
S(24)	869 (5)	3080 (3)	1546 (2)	F(33)	−291 (20)	8523 (12)	5508 (7)	F(54)	2082 (13)	2526 (8)	3866 (5)
S(25)	508 (4)	2084 (3)	1812 (3)	F(34)	1671 (17)	7924 (14)	5402 (10)	F(55)	3947 (13)	2076 (8)	3510 (5)
S(26)	1859 (5)	3510 (3)	2043 (2)	F(35)	−987 (17)	7834 (13)	4840 (10)	F(56)	3771 (12)	3474 (8)	3709 (5)
Sb(1)	5000	4917.4 (9)	2500	F(36)	941 (26)	7223 (9)	4715 (10)				
Sb(2)	5000	581.8 (11)	2500								
Sb(3)	360 (1)	7850.7 (7)	5112.4 (5)								
Sb(4)	2985 (1)	4771.1 (7)	799.2 (5)								
Sb(5)	2946 (1)	2811.9 (7)	3359.5 (5)								

[a] Population parameters: S(13), 1.21 (2); S(23), 1.29 (2).

of the charge distributions in the P_7^{3-} and Sb_7^{3-} anions,[15,18] which indicate that the negative charge is concentrated primarily at the three two-coordinate sites of the anions. Two of these correspond to atoms 5 and 6 in the derived structure (I) for the $Te_xSe_{6-x}^{2+}$ or $Te_xS_{6-x}^{2+}$ cations and will therefore be favored by the more electronegative selenium or sulfur atoms. An obvious difference between the $Te_xS_{6-x}^{2+}$ and the $Te_xSe_{6-x}^{2+}$ cations is the preference for tellurium occupation of site 3 in the Te/S cations and site 4 in the Te/Se cations. In the Te/S case, site 3 may be preferentially occupied by tellurium to minimize angle strain. The 1–2–3 and 2–1–3 bond angles are particularly small in all of these structures as a result of the cross-ring Te(1)–Te(2) bond (Table IV), and these angles are smallest when site 3 is occupied by sulfur.

The Anions. In $(Te_2Se_4)(AsF_6)_2$ three anions appear to be ordered with an average As–F bond length of 1.70 Å and bond angles close to expected values.[19] The fourth anion is considerably distorted from an octahedral geometry, consistent with the significantly higher temperature factors for the fluorine atoms, and is probably disordered. A feature of the bond lengths in the ordered anions is the large range of values from 1.63 (3) to 1.79 (4) Å, with the longer bonds to the atoms involved in the shortest anion–cation interactions. Similar lengthening of the As–F bonds in an AsF_6^- anion as a consequence of significant interionic interactions has been observed in $SnF_2{\cdot}AsF_5$,[20] $(S_6N_4)(AsF_6)_2$,[21] $(Se_4S_2N_4)(AsF_6)_2$,[22] and *trans*-$[Mn(NSF_3)_4(AsF_6)_2]$.[23]

The anions in $(Te_2Se_4)(SbF_6)_2$ are approximately octahedral with an average Sb–F distance of 1.85 Å, comparable to that observed in $KSbF_6$ of 1.844 (7) Å.[24] However, the Sb–F distances again show a considerable variation (1.81 (3)–1.90 (4) Å).

The $Sb_3F_{14}^-$ anion in $(Te_2Se_4)(Sb_3F_{14})(SbF_6)$ has been found in several compounds[5,25] and consists of two SbF_6^- anions trans-bridged to an SbF_2^+ cation (Figure 2). When we exclude the two Sb(V)–F distances in the anions that are lengthened to 2.00 (2) and 1.94 (2) Å by the bridging interactions to the SbF_2^+ ion, other Sb(V)–F bonds range from 1.80 (2) to 1.91 (2) Å. Despite the relatively high standard deviations, many of these bond lengths are appreciably longer than those in $KSbF_6$, and there appears to be a correlation between the length of the Sb(V)–F bond and the number and lengths of the interionic contacts made by that fluorine atom.

In the SbF_2^+ cation the Sb(III)–F lengths are 1.88 (2) and 1.90 (2) Å. Completing the primary bonding of the Sb(III) atom are bridging interactions to two SbF_6^- anions of 2.20 (1) and 2.24 (2) Å in the axial positions of a trigonal-bipyramidal arrangement with two fluorines and the lone pair in the equatorial plane. The position of this lone pair is further defined by considering several additional interionic Sb(III)···F contacts (Figure 2). Two of the shortest Sb(III)···F contacts involve F atoms in the Sb(V)–F_6 groups of other $Sb_3F_{14}^-$ anions that are trans to the bridging atoms F(12) and F(32).

The SbF_6^- anion in this structure has crystallographic inversion symmetry with Sb–F bond lengths of 1.84 (3)–1.91 (2) Å and bond angles close to their expected values.

Interactions with the $Te_2Se_4^{2+}$ Cations. As well as the interactions with the Sb(III) atom in the $Sb_3F_{14}^-$ anion, several interionic contacts to the $Te_2Se_4^{2+}$ cations that are significantly shorter than the van der Waals limits (Te···F = 3.55 Å; Se···F = 3.35 Å) are in stereochemically meaningful positions (Figure 3). The contacts Te···F are shorter and more numerous than any of the Se···F contacts. These observations are consistent with the larger size of Te and with valence structures such as I, in which positive charge is localized on the Te atoms. The Te···F contacts in the present compounds are as short as 2.86 Å, which is 0.69 Å less than the van der Waals limit. We assume that these additional fluorine contacts are nucleophilic in nature and that, as with the contacts to the $Sb_3F_{14}^-$ anion above, they tend to form in directions that avoid the direction of maximum lone-pair electron density on the chalcogen atoms, while maximizing any charge-transfer overlap with presumably antibonding orbitals of the cation. The arrangement of bonds and contacts to Te(11) in $(Te_2Se_4)(SbF_6)_2$ produces an $AX_3Y_3Y'_3E$ tricapped trigonal prism, with the lone pair of electrons on tellurium presumably capping the triangular face of the prism (Figure 3).

The crystal packing of $(Te_2Se_4)(SbF_6)_2$ and $(Te_2Se_4)(Sb_3F_{14})(SbF_6)$ and some of the shorter anion–cation contacts are shown in supplementary Figures 4 and 5. The crystal packing of $(Te_2Se_4)(Sb_3F_{14})(SbF_6)$ is very similar to that of $(S_8)(Sb_3F_{14})(SbF_6)$.[26] These compounds have the same space group and similar cell dimensions. In both compounds, layers of $Sb_3F_{14}^-$ anions separated by $c/2$ are held together by the Sb(III)···F contacts involving the SbF_6^- anions. The cations are situated in cavities between these anions.

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Registry No. $(Te_2Se_4)(AsF_6)_2$, 61617-70-7; $(Te_2Se_4)(SbF_6)_2$, 61617-69-4; $(Te_2Se_4)(Sb_3F_{14})(SbF_6)$, 113379-59-2; $(Te_3S_3)(SbF_6)_2$, 113379-60-5; $(Te_2Se_8)(SbF_6)_2$, 107453-36-1; $Te_4(AsF_6)_2$, 12536-35-5; $Se_4(AsF_6)_2$, 53513-64-7; AsF_5, 7784-36-3; SbF_5, 7783-70-2; Te, 13494-80-9; Se, 7782-49-2; S, 7704-34-9.

Supplementary Material Available: Tables SI and SII, listing bond lengths and bond angles in the anions and atomic positional and thermal parameters, and Figures 4 and 5, showing crystal packing (14 pages); Table SIII, listing structure factor amplitudes (117 pages). Ordering information is given on any current masthead page.

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