

Preparation and Crystal Structures of $(\text{Te}_2\text{Se}_2)(\text{Sb}_3\text{F}_{14})(\text{SbF}_6)$ Containing the *trans*- $\text{Te}_2\text{Se}_2^{2+}$ Cation and $(\text{Te}_{3.0}\text{Se}_{1.0})(\text{Sb}_3\text{F}_{14})(\text{SbF}_6)$ Containing a Disordered Mixture of the Cations $\text{Te}_3\text{Se}^{2+}$, Te_4^{2+} , and $\text{Te}_2\text{Se}_2^{2+}$

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The compounds $(\text{Te}_2\text{Se}_2)(\text{Sb}_3\text{F}_{14})(\text{SbF}_6)$ (1) and $(\text{Te}_{3.0}\text{Se}_{1.0})(\text{Sb}_3\text{F}_{14})(\text{SbF}_6)$ (2) have been prepared by the oxidation of a 1:1 Te-Se alloy and 1:1 and 3:1 Te-Se mixtures with SbF_5 in SO_2 solution. Crystals of 1 are orthorhombic, space group *Pbcm*, with cell dimensions $a = 8.293$ (2) Å, $b = 16.337$ (3) Å, $c = 15.811$ (4) Å, $V = 2142.2$ (8) Å³, and $D_c = 3.97$ g cm⁻³ for $Z = 4$ at 22 °C; $R_1 = 0.074$ and $R_2 = 0.095$ for 1491 reflections with $I > 3\sigma(I)$. The compound contains the ions $\text{Te}_2\text{Se}_2^{2+}$, $\text{Sb}_3\text{F}_{14}^-$, and SbF_6^- . The *trans*- $\text{Te}_2\text{Se}_2^{2+}$ cation has crystallographic inversion symmetry with Te-Se bond lengths of 2.446 (4) and 2.481 (4) Å and Se-Te-Se and Te-Se-Te angles of 89.1 (1) and 90.9 (1)°, respectively. Compound 2 crystallizes in the orthorhombic space group *Pn2₁a*, with cell dimensions $a = 16.594$ (8) Å, $b = 11.634$ (4) Å, $c = 11.128$ (3) Å, $V = 2148$ (1) Å³, and $D_c = 4.11$ g cm⁻³ for $Z = 4$; $R_1 = 0.046$ and $R_2 = 0.052$ for 4467 reflections with $I > \sigma(I)$. The $\text{Te}_{3.0}\text{Se}_{1.0}^{2+}$ cation consists of a disordered mixture of the $\text{Te}_3\text{Se}^{2+}$, Te_4^{2+} , and *trans*- $\text{Te}_2\text{Se}_2^{2+}$ cations so that the average composition is $\text{Te}_{3.02(2)}\text{Se}_{0.98(2)}^{2+}$. The $\text{Sb}_3\text{F}_{14}^-$ anion in both compounds consists of two $\text{Sb}^{\text{V}}\text{F}_6^-$ octahedra linked by strong fluorine bridges to an $\text{Sb}^{\text{III}}\text{F}_2^{2-}$ ion. The coordination of each Sb(III) atom is completed by several weak Sb(III)⋯F contacts to fluorine atoms in other anions.

Introduction

In recent years, a number of cations such as S_4^{2+} , S_8^{2+} , S_{19}^{2+} , Se_4^{2+} , Se_8^{2+} , Se_{10}^{2+} , Te_4^{2+} , and Te_6^{4+} have been prepared by oxidation of the elements S, Se, and Te with suitable oxidizing agents such as HSO_3F , $\text{S}_2\text{O}_8\text{F}_2$, AsF_5 , and SbF_5 .¹⁻⁶ Among these cations the three tetraatomic species S_4^{2+} , Se_4^{2+} , and Te_4^{2+} have all been shown by vibrational spectroscopy and X-ray crystallography to have square-planar structures.⁷⁻¹⁰ Recently we have prepared and characterized several heterochalcogen cationic species,^{6,11-13} but only ¹²⁵Te and ⁷⁷Se NMR evidence has been obtained for the mixed species $\text{Te}_x\text{Se}_{4-x}^{2+}$ in solution.^{14,15} Accordingly we have attempted to prepare crystalline compounds containing mixed cations of this type in order to obtain further information on the bond-length-bond-order relationships in these cations and to further study the strong anion-cation interactions that have been observed in the homopolyatomic species M_4^{2+} .⁹ We now report the preparation and structural characterization

of $(\text{Te}_2\text{Se}_2)(\text{Sb}_3\text{F}_{14})(\text{SbF}_6)$, which contains the *trans*- $\text{Te}_2\text{Se}_2^{2+}$ cation, and $(\text{Te}_{3.0}\text{Se}_{1.0})(\text{Sb}_3\text{F}_{14})(\text{SbF}_6)$, which contains a disordered mixture of the $\text{Te}_3\text{Se}^{2+}$, Te_4^{2+} , and *trans*- $\text{Te}_2\text{Se}_2^{2+}$ cations.

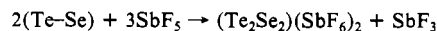
Experimental Section

Apparatus and Materials. All reactions were carried out under vacuum in flame-sealed double-bulb vessels fitted with medium glass frits. Manipulations involving moisture-sensitive reactants and products were performed in a drybox under an atmosphere of nitrogen. Sulfur dioxide (Canadian Liquid Air) was stored over P_2O_5 . Antimony pentafluoride (Ozark Mahoning) was doubly distilled under dry nitrogen and stored in a FEP bottle in the drybox. Selenium and tellurium powders (Koch-Light Laboratories Ltd.) were dried under vacuum at 22 °C overnight.

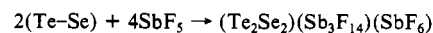
Nuclear Magnetic Resonance Spectroscopy. ⁷⁷Se and ¹²⁵Te NMR spectra were obtained on natural-abundance samples with a Bruker WH-90 and a Bruker WM-250 Fourier-transform multinuclear spectrometer, respectively. Samples were prepared in 10-mm-o.d. precision glass NMR tubes (Wilmad) joined by 1/4-in.-o.d. standard wall tubing. The appropriate solvent was pipetted onto the solute before the tubes were flame-sealed under vacuum. Spectra were referenced to saturated aqueous solutions of H_2SeO_3 and $\text{Te}(\text{OH})_6$.

Preparation of $(\text{Te}_2\text{Se}_2)(\text{Sb}_3\text{F}_{14})(\text{SbF}_6)$. A 1:1 Te-Se alloy was prepared by placing 40 g of finely powdered Te and 25 g of finely powdered Se in a stout glass tube and mixing thoroughly by shaking for several hours. The mixture was melted by heating it to 530 °C and it was maintained at this temperature for 12 h. After cooling, the resulting shiny black alloy was finely powdered in a mortar. In a typical experiment 1.033 g (5 mmol) of the 1:1 Te-Se alloy was placed in one bulb of a double-bulb reaction vessel. Antimony pentafluoride (2.167 g, 10 mmol) was added to the other bulb, and ca. 30 mL of SO_2 was condensed onto the SbF_5 . After being warmed to room temperature, the SbF_5 - SO_2 solution was poured into the bulb containing the Te-Se alloy. There was an immediate reaction producing a red solution, the color of which intensified very considerably on stirring for several hours. After 1 week, the solution was a deep blood red, almost black, in color. The insoluble reaction products were filtered off, and the solution was allowed to stand for 48 h at room temperature, during which time a large quantity of black crystals was deposited. The ⁷⁷Se NMR spectrum of these crystals dissolved in 30% oleum is the same as that obtained earlier for the *trans*- $\text{Te}_2\text{Se}_2^{2+}$ cation.¹⁴

If less oxidant is used, for example the amount required for



rather than the amount used in the present case



the crystalline product is the previously identified $(\text{Te}_2\text{Se}_4)(\text{SbF}_6)_2$ ^{11,13} and not the expected $(\text{Te}_2\text{Se}_2)(\text{SbF}_6)_2$.

In another experiment, 5 mmol of a finely powdered 1:1 mixture of selenium and tellurium was reacted with 10 mmol of SbF_5 by the procedure described above. Initially a green solution was obtained, but after

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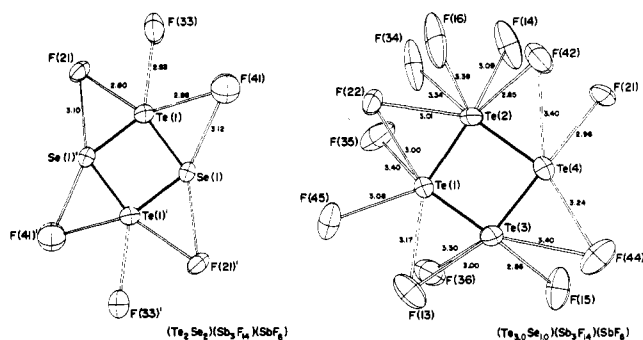


Figure 1. *trans*-Te₂Se₂²⁺ and Te_{3.0}Se_{1.0}²⁺ cations showing some of the shorter anion-cation contacts as unfilled bonds.

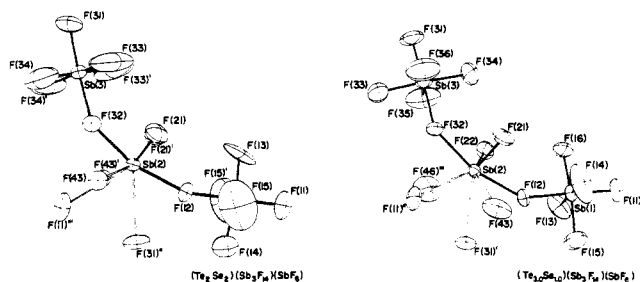


Figure 2. Sb₃F₁₄⁻ anions in the compounds (Te₂Se₂)(Sb₃F₁₄)(SbF₆) and (Te_{3.0}Se_{1.0})(Sb₃F₁₄)(SbF₆). The weaker secondary Sb(III)---F contacts out to the van der Waals limit (3.55 Å) are indicated as unfilled bonds.

being stirred for 0.5 h it began to change to the blood red color described above. After being stirred for 1 week, the mixture was filtered and the solution was allowed to stand at room temperature to crystallize. The composition of the crystals was shown to be (Te₂Se₂)(Sb₃F₁₄)(SbF₆) by the structure determination and by chemical analysis.

Anal. Calcd for Te₂Se₂Sb₄F₂₀: Te, 19.94; Se, 12.34; Sb, 38.04; F, 29.68. Found: Te, 20.2; Se, 12.3; Sb, 39.3; F, 27.5.

Preparation of (Te_{3.0}Se_{1.0})(Sb₃F₁₄)(SbF₆). In a typical experiment, 1.8163 g (14.23 mmol) of Te powder and 0.3747 g (4.745 mmol) of Se powder were mixed and reacted with SbF₅ (4.108 g, 18.95 mmol) in 30 mL of SO₂ with the procedure described above. A green solution was initially obtained, which turned red within a few minutes. After being stirred for 3.5 h, the solution was filtered and allowed to stand at room temperature for 24 h, resulting in a large crop of black crystals. The ¹²⁵Te NMR spectrum of these crystals dissolved in 100% H₂SO₄ showed the presence in solution of the Te₃Se²⁺, Te₄²⁺, and *trans*-Te₂Se₂²⁺ cations.^{14,15} The composition of these crystals was shown to be (Te_{3.0}Se_{1.0})(Sb₃F₁₄)(SbF₆) by the structure determination. If the same procedure was followed except that a reaction time of 1 week was allowed, as for (Te₂Se₂)(Sb₃F₁₄)(SbF₆), the crystalline product was (Te₂Se₂)(Sb₃F₁₄)(SbF₆).^{11,13}

X-ray Crystallography. All crystals used in the structure determinations were selected and sealed in Lindemann capillaries in a specially designed drybox equipped with a microscope under a dry nitrogen atmosphere. Preliminary precession and Weissenberg photographs were used to check crystal quality and to obtain cell and symmetry information. Crystal data and details of the intensity measurement and structure refinements are included in Table I. Final atomic positional parameters for both structures are included in Table II; significant bond lengths, bond angles, and contact distances are given in Table III. Views of the environments of the Te₂Se₂²⁺ and Te_{3.0}Se_{1.0}²⁺ cations, the Sb₃F₁₄⁻ anions, and the overall crystal packing of both structures are given in Figures 1–3, 5, and 6 (Figures 5 and 6 are supplementary material).

Discussion

Preparations. The compound (Te₂Se₂)(Sb₃F₁₄)(SbF₆) was obtained from both a 1:1 alloy of Se and Te and a simple 1:1 mixture of the two elements. However, the different colors observed during the two reactions strongly suggests that they proceed by different pathways. The alloy gave an immediate red-brown color on reaction with SbF₅, while the mixture gave initially a green solution, which only later became red-brown. In the case of the mixture it seems probable that selenium and tellurium cations such as Se₃²⁺ (green), Se₄²⁺ (yellow), and Te₄²⁺ (red) are formed initially, which then react with each other to give Te₂Se₂²⁺ (red-brown).

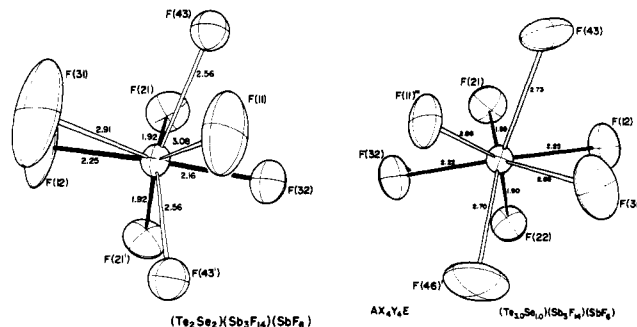
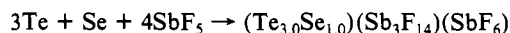


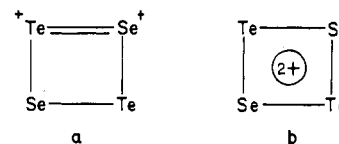
Figure 3. Overall arrangements of the primary and secondary Sb(III)-F bonds in the two examples of the Sb₃F₁₄⁻ anion. Primary bonds out to ca. 2.4 Å are filled bonds and secondary bonds out to 3.55 Å are the unfilled bonds. The view in each case is directly toward the assumed position of maximum electron density of the lone pair.

The compound (Te_{3.0}Se_{1.0})(Sb₃F₁₄)(SbF₆) was obtained by the reaction of a 3:1 mixture of tellurium and selenium with an equimolar amount of SbF₅. The overall equation for the reaction is



Crystal Structures. (a) The *trans*-Te₂Se₂²⁺ Cation. *trans*-Te₂Se₂²⁺ has crystallographic inversion symmetry with Te–Se bond lengths of 2.446 (4) and 2.481 (4) Å and Se–Te–Se' and Te–Se–Te' angles of 89.1 (1) and 90.9 (1)°, respectively. The cation is therefore significantly distorted from “square-planar” *D*_{2h} symmetry (Figure 1). This can be related to the different sizes of Te and Se and to the significant differences in the anion-cation interactions to the tellurium and selenium atoms in the cation (see below). The average Te–Se distance of 2.464 (4) Å is, however, almost exactly the mean of the Te–Te distances of 2.660–2.699 Å found for the Te₄²⁺ cation^{8,9} and the Se–Se distances of 2.247–2.283 Å found for the Se₄²⁺ cation.^{7,9} In some of these examples of the Se₄²⁺ and Te₄²⁺ cations, small but nonetheless significant distortions from square-planar *D*_{4h} symmetry were also observed.⁹ The Te–Se bond lengths in Te₂Se₂²⁺ are considerably shorter than the Te–Se bonds in the Te₂Se₄²⁺,^{11,13} and Te₂Se₈²⁺,^{12,19} cations which range from 2.525 to 2.539 and 2.579 to 2.644 Å, respectively. This is consistent with the bonds in the Te₂Se₂²⁺ cation having some double bond character.

The bonding in the *trans*-Te₂Se₂²⁺ cation can be described in terms of four resonance structures of the type a and a corresponding bond order of 1.25 or equivalently by the single structure b, where the circle indicates an aromatic sextet of π electrons.



However, as has been pointed out for the homopolyatomic cations M₄²⁺ this may be an oversimplified description of the bonding since in all cases there are appreciable anion-cation interactions.⁹

(b) The Te_{3.0}Se_{1.0}²⁺ Cation. The refined population parameters indicate that the composition of this ion is, on average, Te₃Se²⁺ but that it is disordered with Se atoms being found on all four sites though not with equal frequency (Table IV). Hence the average composition is Te_{3.02(2)}Se_{0.98(2)}²⁺.

The different occupation of the sites accounts for the difference in the four bond lengths. There is a linear correlation between the relative proportions of Se and Te atoms on a given pair of sites and the length (*R*) of the bond between them. The relation *R* = 2.26 + 0.4*x*_{Te} where *x*_{Te} is the average proportion of Te on both sites reproduces the observed lengths (Å) of the Se–Se (2.26), Se–Te (2.46), and Te–Te (2.66) bonds in the cations Se₄²⁺, *trans*-Te₂Se₂²⁺, and Te₄²⁺, respectively. Using this relation, it is

(19) Collins, M. J.; Gillespie, R. J.; Sawyer, J. F., unpublished data.

Table I. Crystal Data, Details of Intensity Measurements, and Structure Refinements

compd system	(Te ₂ Se ₂)(Sb ₃ F ₁₄)(SbF ₆) orthorhombic	(Te _{3.0} Se _{1.0})(Sb ₃ F ₁₄)(SbF ₆) orthorhombic
<i>a</i> , Å	8.293 (2)	8.267 (2)
<i>b</i> , Å	16.337 (3)	16.200 (3)
<i>c</i> , Å	15.811 (4)	15.714 (4)
<i>V</i> , Å ³	2142.2 (8)	2104.6 (8)
<i>T</i> , K	295	248 ^a
fw	1280.2	1328.7
<i>Z</i>	4	4
<i>D_c</i> , g cm ⁻³	3.97	4.11
space group	<i>Pbcm</i> or <i>Pbc2₁</i> ^b	<i>Pnma</i> or <i>Pn2₁a</i> ^c
μ (Mo K α), cm ⁻¹	119.2	110.2
cryst dimens, cm	thick plate {0,1,0}: 0.08 (0,2,1): 0.14 (0,2, $\bar{1}$): 0.14 (0, $\bar{2}$,1): 0.14 ($\pm 2,3,1$): 0.15 ($\pm 2,3,\bar{1}$): 0.15	tabular shaped needle {1,0,0}: 0.048 (0,1,0): 0.450 (0, $\bar{1}$,1): 0.105 (0, $\bar{1}$, $\bar{1}$): 0.105 (1,0,1): 0.105 ($\bar{1}$,0,1): 0.105 ($\bar{1}$,0, $\bar{1}$): 0.034 (1,0, $\bar{1}$): 0.034
mode	$\theta:2\theta$; Mo K α radiation ($\lambda = 0.71069$ Å)(graphite monochromator)	
scan width, deg	(K $\alpha_1 - 0.75$) to (K $\alpha_2 + 0.75$)	(K $\alpha_1 - 1.0$) to (K $\alpha_2 + 1.0$)
scan rates, deg min ⁻¹	2.2-29.3	3.5-29.3
std. reflns (no./interval)	3/57	3/77
max 2 θ , deg	55	55
quadrants	(<i>h,k,l</i>)	(<i>h,$\pm k,l$)</i>
total no. of reflns colld	5732	5429
no. of data with $I > \sigma(I)$ ^d	2099	4467
no. of data with $I > 3\sigma(I)$	1491	N/A
structure soln	patterson and direct methods for heavy atoms ^e	patterson for 5 heavy atoms ^e
<i>R</i> factors		
<i>R</i> ₁ ($I > \sigma(I)$)	0.100	0.046
<i>R</i> ₂	0.122	0.052
<i>R</i> ₁ ($I > 3\sigma(I)$)	0.074	
<i>R</i> ₂	0.095	
max shift/error	0.35	0.74 (av 0.04)
residual electron density, eÅ ⁻³	± 2.6 (near Sb) ± 1.8 (near F's on Sb(4))	+1.8 -0.6
weighting scheme	<i>f</i>	<i>g</i>
programs	SHELX ¹⁸ and XRAY76 ¹⁶ on CDC6400 or CYBER72 computers	

^a After it was established in the room temperature refinement that several of the fluorine atoms in the anions had significantly anisotropic thermal parameters, a further data set was measured at 248 K. Refinement using this data set did not eliminate the problems with the anisotropy of many of the atoms in the structure. ^b Centric space group *Pbcm* was indicated by statistical tests. The anisotropy in the thermal parameters for this structure may be due in large degree to statistical disordering of the Sb₃F₁₄⁻ and SbF₆⁻ anions about the mirror plane and the 2-fold axis in *Pbcm*, respectively. An attempted refinement in *Pbc2₁* was unsuccessful due to correlation between the parameters of the heavy atoms, although we cannot rule out this space group with certainty. ^c *Pn2₁a* by statistical analysis and successful refinement.

^d Lorentz and polarization corrections were applied to all reflections. Absorption corrections (after compositions of crystals were established) were made by using ABSORB (XRAY71).¹⁶ Symmetry-equivalent data were averaged. Systematically absent data and data with $F < 2\sigma(F)$ were eliminated. ^e Alternative "hand" obtained by reversing signs of $\Delta f''$ for the anomalous scatterers.¹⁷ Refinement gave $R_1 = 0.047$ and $R_2 = 0.052$. ^f $w = xy$ where $x = F/33$ if $F < 33$ or $x = 55/F$ if $F > 55$; otherwise, $x = 1.0$ and $y = (\sin \theta)/0.31$ if $\sin \theta < 0.31$, otherwise $y = 1.0$. ^g $w = (\sigma^2(F) + 0.001F^2)^{-1}$.

possible to predict the bond lengths (within 0.02 Å) from the observed population parameters (Table V).

Although the occupation numbers and bond lengths are consistent with a disordered Te₃Se²⁺ cation, the crystallographic evidence does not exclude the possibility that the crystal contains a mixture of some, or all, of the cations Te₄²⁺, Te₃Se²⁺, *cis*- and *trans*-Te₂Se²⁺, TeSe₃²⁺, and Se₄²⁺. Both Te-Te (207, 215 cm⁻¹) and Te-Se (252, 266 cm⁻¹) stretching vibrations²⁰ are observed in the Raman spectrum of the crystalline sample, but a Se-Se stretch at around 320 cm⁻¹ is not seen, ruling out the presence of significant amounts of Se₄²⁺, TeSe₃²⁺, and *cis*-Te₂Se²⁺. The ¹²⁵Te NMR spectrum of the bulk sample dissolved in 100% H₂SO₄ (Figure 4) contains peaks assigned previously^{14,15} to the *trans*-Te₂Se²⁺ (2380 ppm), Te₃Se²⁺ (2292, 2221 ppm), and Te₄²⁺ (1948 ppm) cations. The intensity of the Te₂Se²⁺ resonance is roughly half that of the Te₄²⁺ resonance, indicating that since there are twice as many tellurium atoms in Te₄²⁺, the two species are present in roughly equal concentrations. None of the other Te-containing cations were observed, and a ⁷⁷Se NMR investigation revealed

no Se₄²⁺. To confirm that the product was not a mixture of crystals of separate fluoroantimonate salts of Te₄²⁺, Te₂Se₂²⁺, and TeSe₃²⁺ (disordered), the ¹²⁵Te NMR spectrum of a 100% H₂SO₄ solution of a single crystal from the same sample was obtained. The concentration of the solution was only 7×10^{-4} *m*. After an accumulation of 390 000 scans (acquisition time = 12.5 h), the peak due to *trans*-Te₂Se²⁺, the weakest peak observed for the bulk sample, could not be observed with certainty over the noise level, but the species Te₃Se²⁺ and Te₄²⁺ were clearly observed and in approximately the same ratio as in the bulk sample. It would appear that the product is not a mixture of crystals of separate compounds but is a single compound containing equal proportions of the cations *trans*-Te₂Se²⁺ and Te₄²⁺ in addition to Te₃Se²⁺ so that the average composition of the cation is Te_{3.0}Se_{1.0}²⁺.

The Sb₃F₁₄⁻ Anions. The anions in both compounds are the fluoroantimonate (III, V) anion Sb₃F₁₄⁻ and the hexafluoroantimonate anion SbF₆⁻. The Sb₃F₁₄⁻ anion has previously been found in (S₄N₄)(Sb₃F₁₄)(SbF₆),²¹ (Te₂Se₄)(Sb₃F₁₄)(SbF₆),¹³ and

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Table II. Final Atomic Positional Parameters ($\times 10^4$) with Estimated Standard Deviations in Parentheses

atom	x	y	z
(a) (Te ₂ Se ₂)(Sb ₃ F ₁₄)(SbF ₆)			
Sb(1)	10992 (2)	2341 (1)	2500
Sb(2)	6344 (2)	3156 (1)	2500
Sb(3)	6074 (3)	272 (1)	2500
Sb(4)	4864 (4)	2500	0
Te(1)	1655 (3)	163 (1)	671 (2)
Se(1)	-108 (4)	1036 (2)	-219 (2)
F(11)	13146 (29)	2201 (23)	2500
F(12)	8731 (26)	2513 (17)	2500
F(13)	11194 (70)	3375 (28)	2500
F(14)	10499 (51)	1254 (26)	2500
F(15)	10820 (49)	2267 (36)	1389 (24)
F(21)	7390 (18)	3832 (9)	1672 (10)
F(31)	6479 (48)	1375 (16)	2500
F(32)	4509 (24)	4100 (11)	2500
F(33)	4558 (55)	407 (14)	1717 (31)
F(34)	7592 (39)	51 (13)	1695 (21)
F(41)	3213 (35)	1777 (18)	296 (19)
F(42)	6206 (91)	1749 (46)	279 (49)
F(43)	4926 (50)	2811 (24)	1115 (24)
(b) (Te _{3.0} Se _{1.0})(Sb ₃ F ₁₄)(SbF ₆)			
Sb(1)	548.5 (4)	0 (0)	2570.9 (7)
Sb(2)	-1787.5 (4)	-876.2 (10)	2368.0 (6)
Sb(3)	-2904.7 (6)	-3336.0 (12)	515.3 (8)
Sb(4)	-2126.5 (5)	2261.6 (11)	581.5 (7)
Te(1) ^a	-873.0 (8)	5340.9 (14)	3430.0 (11)
Te(2) ^a	-163.3 (7)	5916.4 (13)	1478.2 (9)
Te(3) ^a	37.7 (12)	3650.4 (15)	3659.7 (13)
Te(4) ^a	792.9 (9)	4125.4 (16)	1718.2 (10)
F(11)	1646 (5)	131 (10)	2277 (9)
F(12)	-592 (4)	-131 (8)	2915 (8)
F(13)	731 (7)	-787 (11)	3978 (9)
F(14)	289 (7)	895 (15)	1291 (11)
F(15)	541 (7)	1300 (10)	3581 (13)
F(16)	480 (7)	-1336 (12)	1714 (13)
F(21)	-1348 (6)	-811 (9)	805 (6)
F(22)	-1203 (5)	-2257 (7)	2603 (8)
F(31)	-3125 (7)	-4629 (10)	-391 (10)
F(32)	-2703 (5)	-2004 (7)	1508 (8)
F(33)	-3939 (7)	-3337 (11)	1082 (12)
F(34)	-1833 (7)	-3282 (16)	49 (17)
F(35)	-2596 (11)	-4212 (11)	1839 (12)
F(36)	-3226 (10)	-2324 (11)	-664 (11)
F(41)	-1505 (8)	3460 (10)	1038 (12)
F(42)	-1285 (6)	1622 (10)	-316 (9)
F(43)	-1766 (7)	1430 (8)	1935 (8)
F(44)	-2993 (7)	2848 (11)	1420 (13)
F(45)	-2761 (7)	967 (11)	173 (13)
F(46)	-2490 (10)	3040 (14)	-776 (11)

^a All four "Te" sites are partially occupied by Se. PP: Te(1), 0.882 (4); Te(2), 0.968 (4); Te(3), 0.863 (4); Te(4), 0.947 (5).

(S₈)(Sb₃F₁₄)(SbF₆).²² The Sb₃F₁₄⁻ anion in (Te₂Se₂)(Sb₃F₁₄)(SbF₆) is, however, the only example with crystallographic mirror symmetry. This probably arises from a statistical disordering about the mirror plane in the space group (*Pbcm*), which would explain the large anisotropy in the thermal ellipsoids of some of the atoms in directions perpendicular to the mirror plane.

The Sb₃F₁₄⁻ anion can be considered to consist of an SbF₂⁺ cation trans linked to two SbF₆⁻ anions by asymmetric fluorine bridges (Figure 2). The Sb(III) atom thus has a trigonal-bipyramidal AX₄E configuration with the lone pair and bridging fluorine atoms in equatorial and axial positions respectively. The equatorial Sb(2)-F(21) or Sb(2)-F(22) bond lengths of 1.923 (15) and 1.891 (8) Å in (Te₂Se₂)(Sb₃F₁₄)(SbF₆) and (Te_{3.0}Se_{1.0})(Sb₃F₁₄)(SbF₆) respectively, are similar to those found for the SbF₂⁺ ion in Sb₁₁F₄₃ (1.87-1.92 Å)²³ and in the other Sb₃F₁₄⁻ anions (1.88-1.90 Å) (Table VI, supplementary material). The

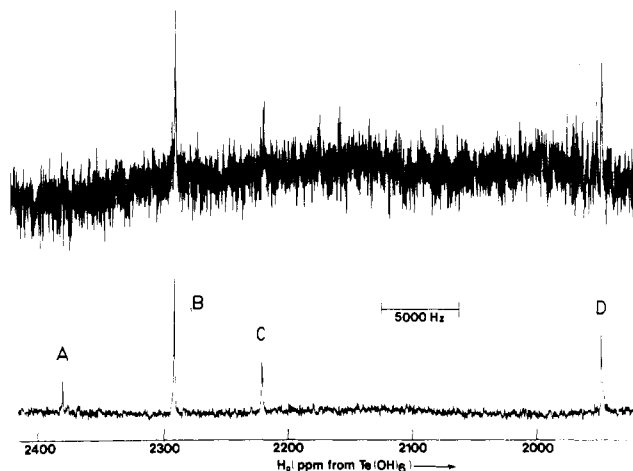


Figure 4. ¹²⁵Te NMR spectrum of (Te_{3.0}Se_{1.0})(Sb₃F₁₄)(SbF₆) dissolved in 100% H₂SO₄. Lower trace is for a bulk crystalline sample (78.97 MHz, 0.02 *m*, 20 000 scans, 7.6 Hz/point): (A) *trans*-Te₂Se₂²⁺; (B, C) Te₃Se₂²⁺; (D) Te₄²⁺. Upper trace is for a single crystal (7×10^{-4} *m*, 390 000 scans).

axial Sb(III)-F bond lengths are in the range 2.20-2.29 Å. The F(21)-Sb(2)-F(22) angles in the SbF₂⁺ ions are 86.0 (6)° and 88.0 (4)° in (Te₂Se₂)(Sb₃F₁₄) and (Te_{3.0}Se_{1.0})(Sb₃F₁₄), respectively. Consistent with the smaller angles between the equatorial fluorines, the angle between the axial fluorines of 162.6 (8) and 161.3 (3)° in the *trans*-Te₂Se₂²⁺ and Te_{3.0}Se_{1.0}²⁺ salts, respectively, are significantly larger than the analogous angles in other Sb₃F₁₄⁻ anions. Other F_{axial}-Sb(III)-F_{equatorial} bond angles are in the range 80-85°. Differences in the primary geometry of the Sb(III) atom in the Sb₃F₁₄⁻ anions in (Te₂Se₂)(Sb₃F₁₄)(SbF₆) and (S₄N₄)(Sb₃F₁₄)(SbF₆) are also indicated in their ¹²¹Sb Mössbauer spectra.²⁴

Another feature of these Sb₃F₁₄⁻ structures are the stereospecific Sb(III)···F contacts to other Sb₃F₁₄⁻ and SbF₆⁻ anions, which vary in length from 2.55 Å up to the sum of the van der Waals radii for Sb and F of 3.55 Å (Figure 3). A useful formalism²⁵ for discussing these additional interactions describes the Sb(III)···F secondary bonds as capping faces and bridging edges of the polyhedron describing the arrangement of the primary bonds and the nonbonded pair (a trigonal bipyramid in the present examples). These positions on the polyhedron are presumably minima in the electron density around the central Sb(III). The number of each of these two types of secondary contacts is summarized in Table VII.

The significance of these contacts in terms of their effects on the distortion of the primary geometry from a regular trigonal bipyramid is difficult to estimate.²⁶ Using the bond valence equation $S = S_0(R/R_0)^{-N}$ (with $S_0 = 0.5$, $R_0 = 2.137$, and $N = 3.7$ for Sb(III)···F bonds), it is possible to calculate individual bond valences for all the Sb-F interactions at less than the van der Waals distance.²⁷ The resulting summations then give values of 3.08, 3.15, 3.19, 3.17, and 3.16 for the Sb(III) atoms in the Sb₃F₁₄⁻ salts of the S₄N₄²⁺, S₈²⁺, Te₂Se₂²⁺, Te₂Se₄²⁺, and Te_{3.0}Se_{1.0}²⁺ cations, respectively, which are reasonably close to the theoretical value of 3.0.

The SbF₆⁻ Anions. In (Te₂Se₂)(Sb₃F₁₄)(SbF₆) the hexafluoroantimonate anion has crystallographic symmetry 2 and is a distorted octahedron with a mean Sb-F distance of 1.81 Å and cis and trans angles close to the expected values. However, the large thermal parameters of the fluorine atoms and the significant

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Table III. Bond Lengths (Å), Bond Angles (deg), and Significant Contact Distances (Å) for the $\text{Te}_2\text{Se}_2^{2+}$ and $\text{Te}_{3,0}\text{Se}_{1,0}^{2+}$ Cations^a

(a) The <i>trans</i> - $\text{Te}_2\text{Se}_2^{2+}$ Cation			
Bond Lengths			
Te(1)-Se(1)	2.480 (4)	Te(1)···F(21) ^{III}	2.80 (2)
Te(1)-Se(1) ^I	2.448 (4)	Se(1)···F(41)	3.12 (3)
Te(1)···Te(1) ^I	3.511 (3)	[···F(15) ^{II}	3.33 (5)]
Se(1)···Se(1) ^I	3.458 (4)	[···F(42) ^{II}	3.37 (8)]
Te(1)···F(41)	3.00 (3)	···F(21) ^{IV}	3.10 (2)
···F(33)	2.95 (5)		
[···F(14) ^{II}	3.53 (2)]		
Bond Angles			
Se(1) ^I -Te(1)-Se(1)	89.1 (1)	Te(1)-Se(1)-F(41)	63.5 (5)
Te(1)-Se(1)-Te(1) ^I	90.9 (1)	-F(21) ^{IV}	148.7 (3)
Se(1)-Te(1)-F(41)	68.6 (6)	Te(1) ^I -Se(1)-F(41)	148.3 (5)
-F(33)	136.2 (5)	-F(21) ^{IV}	59.2 (3)
-F(21) ^{III}	158.9 (3)		
Se(1) ^I -Te(1)-F(41)	150.7 (6)		
-F(33)	134.4 (5)		
-F(21) ^{III}	72.1 (3)		
Te(1) ^I -Te(1)-F(33)	176.7 (9)		
(b) The $\text{Te}_{3,0}\text{Se}_{1,0}^{2+}$ Cation			
Bond Lengths			
Te(1)-Te(2)	2.560 (2)	Te(2)-Te(4)	2.633 (2)
-Te(3)	2.493 (2)	Te(3)-Te(4)	2.558 (2)
Te(1)···F(22) ^V	2.992 (8)	Te(3)···F(15)	2.860 (12)
···F(35) ^V	3.403 (18)	···F(13) ^{VI}	2.995 (10)
···F(13) ^{VI}	3.178 (11)	···F(36) ^{VII}	3.300 (16)
···F(45) ^{VII}	3.070 (13)	···F(44) ^X	3.400 (12)
Te(2)···F(16) ^V	3.381 (14)	Te(4)···F(21) ^{VIII}	2.956 (8)
···F(22) ^V	3.009 (9)	···F(42) ^{VIII}	3.397 (11)
···F(34) ^V	3.328 (14)	···F(44) ^X	3.250 (13)
···F(14) ^{VIII}	3.089 (12)		
···F(42) ^{VIII}	2.850 (11)		
···F(33) ^{IX}	3.501 (13)		
Bond Angles			
Te(2)-Te(1)-Te(3)	90.83 (7)	Te(1)-Te(3)-Te(4)	92.29 (7)
Te(1)-Te(2)-Te(4)	89.09 (6)	Te(2)-Te(4)-Te(3)	87.79 (7)
Te(2)-Te(1)-F(22) ^V	65.1 (2)	Te(1)-Te(3)-i ^v (15)	158.1 (3)
-F(35) ^V	84.6 (3)	-F(13) ^{VI}	70.1 (2)
-F(13) ^{VI}	147.6 (2)	-F(36) ^{VII}	75.1 (2)
-F(45) ^{VII}	144.4 (3)	-F(44) ^X	142.8 (2)
Te(3)-Te(1)-F(22) ^V	151.5 (2)	Te(4)-Te(3)-F(15)	92.2 (3)
-F(35) ^V	133.1 (2)	-F(13) ^{VI}	154.6 (3)
-F(13) ^{VI}	62.4 (2)	-F(36) ^{VII}	135.5 (2)
-F(45) ^{VII}	124.7 (3)	-F(44) ^X	64.3 (2)
Te(1)-Te(2)-F(16) ^V	109.1 (2)	Te(2)-Te(4)-F(21) ^{VIII}	94.1 (2)
-F(22) ^V	64.4 (2)	-F(42) ^{VIII}	54.7 (2)
-F(34) ^V	95.5 (3)	-F(44) ^X	143.2 (2)
-F(14) ^{VIII}	144.4 (3)	Te(3)-Te(4)-F(21) ^{VIII}	163.8 (2)
-F(42) ^{VIII}	148.0 (2)	-F(42) ^{VIII}	133.7 (2)
-F(33) ^{IX}	71.0 (2)	-F(44) ^X	70.5 (2)
Te(4)-Te(2)-F(16) ^V	123.4 (2)		
-F(22) ^V	149.5 (2)		
-F(34) ^V	140.5 (3)		
-F(14) ^{VIII}	97.8 (3)		
-F(42) ^{VIII}	76.5 (2)		
-F(43) ^{IX}	76.6 (2)		

^a Roman numerals as superscripts refer to the atom *x*, *y*, *z* at the following symmetry related positions: (I) $-x, -y, -z$; (II) $-1 + x, y, z$; (III) $1 - x, -1/2 + y, z$; (IV) $-1 + x, 1/2 - y, -z$; (V) $x, 1 + y, z$; (VI) $-x, 1/2 + y, 1 - z$; (VII) $-1/2 - x, 1/2 + y, 1/2 + z$; (VIII) $-x, 1/2 + y, -z$; (IX) $1/2 + x, 1 + y, 1/2 - z$; (X) $1/2 + x, y, 1/2 - z$.

Table IV. Occupation of the Four Sites in the $\text{Te}_{3,0}\text{Se}_{1,0}^{2+}$ Cation

site 1	0.66 (1) Te + 0.34 (1) Se
site 2	0.91 (1) Te + 0.09 (1) Se
site 3	0.60 (1) Te + 0.40 (1) Se
site 4	0.85 (1) Te + 0.15 (1) Se
total	3.02 (2) Te + 0.98 (2) Se

anisotropy of the Sb atom would indicate that, like the $\text{Sb}_3\text{F}_{14}^-$ anion, the SbF_6^- ion is probably statistically disordered about its crystallographic site. In $(\text{Te}_{3,0}\text{Se}_{1,0})(\text{Sb}_3\text{F}_{14})(\text{SbF}_6)$, the hexafluoroantimonate has no crystallographic symmetry and is a fairly

Table V. Bond Lengths (Å) in $\text{Te}_{3,0}\text{Se}_{1,0}^{2+}$

	predicted	obsd
1-2	2.57	2.56
2-4	2.61	2.63
3-4	2.55	2.56
3-1	2.51	2.49

regular octahedron with an average Sb-F bond length of 1.860 Å.

Anion-Cation Interactions. Apart from the Sb(III)···F interactions discussed above, several anion-cation contacts are also

Table VII. Secondary Contacts to the Sb(III) AX₄E Polyhedron in Sb₃F₁₄⁻ Anions

compound	face capping	edge bridging
(S ₄ N ₄)(Sb ₃ F ₁₄)(SbF ₆) ^a	4	0
(S ₈)(Sb ₃ F ₁₄)(SbF ₆) ^b	4	2
(Te ₂ Se ₂)(Sb ₃ Fe ₁₄)(SbF ₆) ^c	0	4
(Te ₂ Se ₄)(Sb ₃ F ₁₄)(SbF ₆) ^d	3	2
(Te _{3,0} Se _{1,0})(Sb ₃ F ₁₄)(SbF ₆) ^c	4	0

^aReference 21. ^bReference 22. ^cThis work. ^dReference 13.

less than the sum of the appropriate van der Waals radii.²⁸ As in all of the homopolyatomic M₄²⁺ cations all four edges of the cations are bridged by fluorine atoms, and there are also several contacts approximately along the diagonals of the square-planar cations (Figure 1). In (Te₂Se₂)(Sb₃F₁₄)(SbF₆) the edge-bridging contacts are unsymmetrical and involve atoms F(21) and F(41), which are 0.46 and 0.93 Å respectively out of the plane of the *trans*-Te₂Se₂²⁺ cation. In addition the contact Te(1)⋯F(33) is along the extension of the Te⋯Te diagonal of the cation [Te(1)⋯Te(1)⋯F(33) is 176.7 (9)°] with the atom F(33) 0.17 Å out of the plane of the cation. These contacts are ca. 0.75–0.55 Å shorter than the sum of the neutral-atom van der Waals radii. The edges of the averaged cation Te_{3,0}Se_{1,0}²⁺ are symmetrically bridged by the atoms F(13), F(22), F(42), and F(44). These

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bridging distances vary from 2.85 to 3.40 Å and are quite similar in length to the contacts in Te₄(SbF₆)₂.⁹ They do however, lie significantly (0.73–1.54 Å) out of the average plane of the cation. The remaining contacts are more irregular (Figure 1). The contacts Te(1)⋯F(45), Te(3)⋯F(15), and Te(4)⋯F(12) could possibly be regarded as being analogous to the "diagonal" contacts in Te₂Se₂²⁺. These anion-cation contacts can be regarded as being nucleophilic and involve the donation of electron density from fluorine atoms into the lowest unoccupied MO's of the cation. The analogous interactions in the homopolyatomic cations M₄²⁺ (M = S, Se and Te) are discussed more extensively elsewhere.⁹

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Registry No. *trans*-(Te₂Se₂)(Sb₃F₁₄)(SbF₆), 68791-83-3; (Te_{3,0}Se_{1,0})(Sb₃F₁₄)(SbF₆), 98587-07-6; Te, 13494-80-9; Se, 7782-49-2; SbF₅, 7783-70-2.

Supplementary Material Available: A comparison of the geometries of the known Sb₃F₁₄⁻ anions (Table VI), listings of anisotropic thermal parameters (Table VIII), bond distances and bond angles in the Sb₃F₁₄⁻ and SbF₆⁻ anions (Table IX), and final structure factor amplitudes (Table X), and drawings of the crystal packing in (Te₂Se₂)(Sb₃F₁₄)(SbF₆) (Figure 5) and (Te_{3,0}Se_{1,0})(Sb₃F₁₄)(SbF₆) (Figure 6) (51 pages). Ordering information is given on any current masthead page.

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Preparation and Characterization of Silver(I) Teflate Complexes: Bridging OTeF₅ Groups in the Solid State and in Solution

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The preparations of AgOTeF₅·CH₂Cl₂ and [AgOTeF₅(C₆H₅CH₃)₂]₂ are reported. The latter compound crystallizes in the monoclinic system, space group *P*2₁/*c* (No. 14). Unit cell parameters are *a* = 9.363 (2) Å, *b* = 18.109 (4) Å, *c* = 10.514 (2) Å, β = 112.89 (2)°, and *Z* = 2. The centrosymmetric dimeric molecules contain planar Ag₂O₂ cores, with two OTeF₅ groups bridging two silver atoms. A molecular weight determination demonstrates that the compound is also dimeric in toluene solution. The Ag–O and Ag–O' bond distances are 2.396 (3) and 2.368 (3) Å, respectively. The Ag–O–Ag' and O–Ag–O' bond angles are 101.4 (1) and 78.6 (1)°, respectively. Structural and spectroscopic data indicate that the silver(I)-oxygen bonds in this compound have a large amount of ionic character. Spectroscopic data indicate that AgOTeF₅·CH₂Cl₂ and the literature compound AgOTeF₅(CH₃CN)_x also contain bridging OTeF₅ groups in the solid state. These data provide the first evidence that the OTeF₅ group can bridge two elements in the solid state and in solution. Our structure also demonstrates that teflate is a much stronger ligand than perchlorate in this type of complex. This is the first direct comparison of the ligating ability of teflate to another monovalent oxoanion.

Introduction

Pentafluoroorthotellurate (OTeF₅⁻), or teflate, has only recently been used as a ligand for high-valent¹ and low-valent^{2,3} transition-metal chemistry. This bulky^{4–6} and electronegative⁷ pseu-

dohalide holds the promise of inducing coordinative unsaturation by means of nonbonded interactions with other ligands in a metal complex. In addition, coordinative unsaturation may be realized because of the inability of this bulky, unidentate anion to form extended lattices. To facilitate the synthesis of a wide variety of metal teflates, we have prepared silver(I) teflate, AgOTeF₅, as a halide/OTeF₅⁻ metathesis reagent. A material prepared earlier by Sladky et al.^{8,9} and formulated by them as AgOTeF₅(CH₃CN)_x is less useful for generating coordinatively unsaturated complexes because it contains several equivalents of the two-electron donor acetonitrile.

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