Contribution from the Department of Chemistry,
McMaster University, Hamilton, Ontario, Canada

# Preparation and Crystal Structures of $Te_3S_3(AsF_6)_2$, $Te_2Se_4(SbF_6)_2$, and $Te_2Se_4(AsF_6)_2$

R. J. GILLESPIE,* W. LUK, E. MAHARAJH, and D. R. SLIM

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The compounds $Te_3S_3(AsF_6)_2$, $Te_2Se_4(SbF_6)_2$, and $Te_2Se_4(AsF_6)_2$ have been prepared and their crystal structures determined by three-dimensional x-ray counter measurements. Crystals of $Te_3S_3(AsF_6)_2$ are monoclinic with $a = 8.421$ (6) Å, $b = 11.828$ (4) Å, $c = 15.279$ (3) Å, and $\beta = 90.92$ (5)°. The structure has been refined in the space group $P2_1/n$ to a final agreement index $R_2$ of 0.088 for 1292 independent reflections. Crystals of $Te_2Se_4(SbF_6)_2$ are orthorhombic with $a = 12.117$ (11), $b = 8.748$ (6), and $c = 15.772$ (5) Å. The structure has been refined in the space group $P2_12_12_1$ to a final agreement index $R_2$ of 0.117 for 1465 independent reflections. Crystals of $Te_2Se_4(AsF_6)_2$ are orthorhombic with $a = 8.640$ (7), $b = 12.012$ (7), and $c = 15.272$ (9) Å. The structure has been refined in the space group $P2_12_12_1$ to a final agreement index $R_2$ of 0.144 for 838 independent reflections. The structures of the three compounds consist of discrete ions in which the cations can be described as consisting of a three-membered ring and a five-membered ring fused together or as a boat-shaped six-membered ring with a cross-ring bond, i.e., as a bicyclo[3.1.0]hexane type structure.

## Introduction

In continuance of our studies of the cationic species $Ch_n^{2+}$, where Ch is one or more of the chalcogens sulfur, selenium, and tellurium,[1] we have prepared and determined the crystal structures of three new compounds: $Te_3S_3(AsF_6)_2$, $Te_2Se_4(SbF_6)_2$, and $Te_2Se_4(AsF_6)_2$.

These compounds contain the new interchalcogen cations $Te_3S_3^{2+}$ and $Te_2Se_4^{2+}$ with a novel type of structure which can be described as consisting of a three-membered ring and a five-membered ring fused together or as a boat-shaped six-membered ring with a cross-ring bond. The first of these compounds was prepared by a new type of method, i.e., the reaction between two different homonuclear cations, in this case $S_8^{2+}$ and $Te_4^{2+}$, in solution in $SO_2$, as well as by two other methods that we have used previously, namely, the reaction of a 1:1 Te–S "alloy" or a 1:1 Te–S mixture with $AsF_5$ in $SO_2$ solution.[1] The other two compounds were prepared by the reaction of a 1:1 Te–Se mixture with either $AsF_5$ or $SbF_5$ in $SO_2$ as solvent.

## Experimental Section

**Tritellurium Trisulfur Bis(hexafluoroarsenate(VI)), $Te_3S_3(AsF_6)_2$.** This compound was prepared by three different methods, all of which gave an identical product.

**(i) Reaction between $Te_4(AsF_6)_2$ and $S_8(AsF_6)_2$.** $Te_4(AsF_6)_2$ and $S_8(AsF_6)_2$ were prepared as described previously.[2,3] In a typical experiment anhydrous $SO_2$ (40 mL) was distilled onto a mixture of $Te_4(AsF_6)_2$ (0.900 g, 0.001 mol) and $S_8(AsF_6)_2$ (0.325 g, 0.0005 mol). On allowing the reaction to proceed at room temperature, the deep blue color of the solution, due to $S_8^{2+}$, rapidly changed to a deep orange-red. The reaction mixture was stirred for several hours and then filtered. On allowing the solution to stand for 1 day, at room temperature, red-black crystals were deposited. These were filtered, washed with a small amount of $SO_2$, and pumped under vacuum to remove any adhering solvent. Other products, which have not yet been identified, remained in solution.

**(ii) Reaction of a 1:1 Te–S "Alloy" with $AsF_5$ in $SO_2$.** In a typical experiment arsenic pentafluoride (2.29 g, 0.0143 mol) was condensed onto a powdered 1:1 Te–S "alloy" (2.86 g, 0.0179 mol) and excess $SO_2$ at −196 °C. On allowing the mixture to warm up to room temperature, there was an immediate reaction resulting in a red solution, the color of which intensified to a very deep black-red on stirring for 24 h. The solution was allowed to stand for 48 h, at room temperature, during which time a large quantity of red-black crystals formed. These were filtered and any remaining volatile material was removed by pumping under vacuum.

**(iii) Reaction of an Equimolar Mixture of S and Te with $AsF_5$.** In a typical experiment $AsF_5$ (2.55 g, 0.0150 mol) was condensed onto a powdered 1:1 Te–S mixture (3.22 g, 0.0202 mol) and excess $SO_2$ at −196 °C. On warming, a blue solution was obtained, but as the temperature approached 20 °C, the color changed, with stirring, to a red-brown which slowly became much darker. After about 72 h the stirring was stopped and the mixture was filtered to remove unreacted sulfur and tellurium and any other insoluble material. On allowing this solution to stand for 2 days at room temperature, a large quantity of red-black crystals was obtained.

Anal. Calcd for $Te_3S_3As_2F_{12}$: S, 11.23; F, 26.61. Found: S, 11.48; F, 26.61.

**$Te_2Se_4(SbF_6)_2$.** In a typical experiment 3.642 g of a finely powdered 1:1 mixture of selenium and tellurium was mixed with 4.023 g of $SbF_5$ in liquid $SO_2$ at −63 °C. On warming to room temperature a green solution was obtained which changed to a black-brown solution after stirring for 0.5 h. The solution, after being filtered to remove unreacted Se and Te, was allowed to stand at room temperature. After 2–3 h a large quantity of black crystals was obtained.

**$Te_2Se_4(AsF_6)_2$.** In a typical experiment 2.591 g of arsenic pentafluoride was condensed onto 4.245 g of a finely powdered equimolar mixture of selenium and tellurium and excess sulfur dioxide at −196 °C. On warming to room temperature a green solution was obtained but on stirring for about 0.5 h the color changed to a red-brown which slowly became very dark over a period of 24 h. The mixture was then filtered to remove unreacted selenium and tellurium and the solution allowed to stand at room temperature to crystallize. After 48 h a large quantity of black crystals was obtained. These crystals were filtered and any remaining solvent and other volatile material was removed by pumping under vacuum.

Anal. Calcd for $Te_2Se_4AsF_6$: Te, 26.90; Se, 33.29; As, 15.78; F, 24.03. Found: Te, 26.43; Se, 33.05; As, 16.09; F, 23.77.

## Crystal Data

$Te_3S_3(AsF_6)_2$ is monoclinic with $a = 8.421$ (6) Å, $b = 11.828$ (4) Å, $c = 15.279$ (3) Å, $\beta = 90.92$ (5)°, $Z = 4$, $d_{calcd} = 3.74$ g/cm³, fw 856.6, $F(000) = 1512$, $\lambda$(Mo K$\bar{\alpha}$) 0.71069 Å, and $\mu$(Mo K$\bar{\alpha}$) = 163 cm$^{-1}$. The unit cell parameters were obtained from a least-squares refinement of 15 reflections in the region $20° < 2\theta < 25°$. Weissenberg and precession photographs indicated that reflections were absent for $h0l$ when $h + l = 2n + 1$ and for the $0k0$ when $k = 2n + 1$, characteristic of the nonstandard space group $P2_1/n$, which is an alternative setting for $P2_1/c$ (No. 14).[4] The general positions of this space group are $x, y, z$; $-x, -y, -z$; $^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$; $^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$.

$Te_2Se_4(SbF_6)_2$ is orthorhombic with $a = 12.117$ (11) Å, $b = 8.748$ (6) Å, $c = 15.772$ (5) Å, $V = 1672$ Å³, $Z = 4$, $d_{calcd} = 4.09$ g/cm³, fw 1030.7, $F(000) = 1800$, $\lambda$(Mo K$\bar{\alpha}$) 0.71069 Å and $\mu$(Mo K$\bar{\alpha}$) = 163 cm$^{-1}$. The unit cell parameters were obtained from a least-squares refinement of 15 reflections in the range $20° < 2\theta < 25°$. Weissenberg and precession photographs indicated that reflections were absent for $h00$ when $h = 2n + 1$, $0k0$ when $k = 2n + 1$, and $00l$ when $l = 2n + 1$, characteristic of the space group $P2_12_12_1$ (No. 19).[4]

$Te_2Se_4(AsF_6)_2$ is orthorhombic with $a = 8.640$ (7) Å, $b = 12.012$ (7) Å, $c = 15.272$ (9) Å, $V = 1585$ Å³, $Z = 4$, $d_{calcd} = 3.93$ g/cm³, fw 937.1, $F(000) = 1656$, $\lambda$(Mo K$\bar{\alpha}$) 0.71069 Å, and $\mu$(Mo K$\bar{\alpha}$) = 182 cm$^{-1}$. The unit cell parameters were obtained from a least-squares refinement of 15 reflections in the range $20° < 2\theta < 25°$. Weissenberg and precession photographs indicated that reflections were absent for $h00$ when $h = 2n + 1$, $0k0$ when $k = 2n + 1$, and $00l$ when $l = 2n + 1$, characteristic of the space group $P2_12_12_1$ (No. 19).[4]

## X-Ray Intensity Measurements

**$Te_3S_3(AsF_6)_2$.** The crystal, which was an irregular block of approximate dimensions 0.35 × 0.20 × 0.14 mm, was sealed in a quartz capillary and mounted on a Syntex $P\bar{1}$ diffractometer with its 0.35-mm edge, which was perpendicular to the (100) face, almost coincident with the $\phi$ axis of the diffractometer. Intensities were measured with graphite-monochromated radiation, using a $\theta$–$2\theta$ scan, with a scan rate varying from 8.0 to 24.0°/min in $2\theta$, so that the weaker reflections were examined more slowly to minimize counting errors. Stationary-background counts, with a time equal to half the scan time for each reflection, were made at each end of the scan range. One standard reflection was regularly checked to monitor the stability of the crystal and its alignment, but no significant variation was observed. A total of 1658 reflections within a unique quadrant with $2\theta < 45°$ were measured. Subsequent averaging resulted in a total of 1292 independent reflections, of which 845 had intensities greater than 3 times their standard error, based on counting statistics. Lorentz and polarization corrections were applied to the observed intensities.

**$Te_2Se_4(SbF_6)_2$.** The crystal, which was an irregular block of approximate dimensions 0.42 × 0.21 × 0.14 mm, was sealed in a quartz capillary and mounted on a Syntex $P\bar{1}$ diffractometer with its 0.42-mm edge, which was perpendicular to the (010) face, almost coincident with the $\phi$ axis of the diffractometer. Data were collected in a manner similar to that described above. A total of 2382 reflections within a quadrant with $2\theta < 50°$ were measured. After averaging of equivalent reflections, 1465 independent reflections were obtained of which 1179 had intensities greater than 3 times their standard error, based on counting statistics. Lorentz and polarization corrections were applied.

**$Te_2Se_4(AsF_6)_2$.** The crystal, which was an irregular block of approximate dimensions 0.65 × 0.22 × 0.10 mm, was sealed in a quartz capillary and mounted on a Syntex $P\bar{1}$ diffractometer with its 0.65-mm edge, which was perpendicular to the (100) face, almost coincident with the $\phi$ axis of the diffractometer. Data were collected in a manner similar to that described above. A total of 1885 reflections within a quadrant with $2\theta < 50°$ for $k \leq 5$ and $2\theta < 35°$ for $k > 5$ were measured.[5] After averaging of equivalent reflections, 838 independent reflections were obtained of which 732 had intensities greater than 3 times their standard error, based on counting statistics. Lorentz and polarization corrections were applied.

## Structure Determinations

**$Te_3S_3(AsF_6)_2$.** The structure factors were put on an absolute scale by calculating accurately the statistical distribution of the $E$ values for all of the intensities. The resulting reflection statistics were of the type usually found in hypercentric crystal structures. The average computed values were $|E|_{av} = 0.806$, $|E|^2_{av} = 1.016$, $|E^2 - 1|_{av} = 0.988$, $|E^2 - 1|^2_{av} = 1.984$, and $|E^2 - 1|^3_{av} = 7.773$. A total of 148 reflections had $E$ values above 1.4. The most consistent set of signs for 127 of these was determined using the direct-methods programs SINGEN and PHASE from the X-ray 71 system.[6] An $E$ map was computed using the calculated phases. The map revealed positions of five independent heavy atoms, three of which were at the corners of an approximate equilateral triangle of side 2.7 Å. These atoms were assumed to be tellurium, and the other two atoms, arsenic. The scattering factors for neutral heavy atoms were all corrected for anomalous dispersion using values for the real and imaginary parts, given in ref 7. Full-matrix least-squares refinement of positional and isotropic temperature parameters gave a conventional agreement index $R_1$ of 0.29. The positions of three sulfur atoms attached to one side of the $Te_3$ triangle and 12 fluorine atoms were located from subsequent electron density maps. Least-squares refinement gave an $R_1$ index of 0.186. An absorption correction was applied and anisotropic temperature factors were introduced for the heavy atoms. This led to a final $R_2$ $(=[\sum w(|F_o|^2 - |F_c|^2)/\sum wF_o^2]^{1/2})$ of 0.0883 where $w = 1/\sigma^2$, $\sigma$ being the standard error from counting statistics, and a final $R_1$ index of 0.1048. The largest shift $\Delta/\sigma$ in the final cycle was 0.2 and a final difference electron density map showed no peaks greater than 0.5 e $Å^{-3}$.

**$Te_2Se_4(SbF_6)_2$.** The positions of five heavy atoms were obtained from the three-dimensional Patterson function. These atoms were all assumed to be tellurium and least-squares refinement of positional and isotropic temperature parameters gave an $R_1$ index of 0.38. Examination of the temperature factors suggested that one of the tellurium atoms was probably selenium. The positions of three more heavy atoms were obtained from a three-dimensional electron density map. These atoms were assumed to be selenium since they formed a six-atom species similar to that found in the $Te_3S_3^{2+}$ cation. The other two atoms were thus assumed to be antimony. The scattering factors for the heavy atoms were all corrected for anomalous dispersion using values for the real and imaginary parts given in ref 7. Least-squares refinement gave an $R_1$ index of 0.21. The positions of all the fluorine atoms were located from a three-dimensional electron density map. Least-squares refinement gave an $R_1$ index of 0.18. An absorption correction was applied and anisotropic temperature factors were introduced for the heavy atoms, leading to a final $R_2$ $(=[\sum w(|F_o|^2 - |F_c|^2)/\sum wF_o^2]^{1/2})$ of 0.117 where $w^{1/2} = (64.00 + 0.65F_o - 0.000\,96F_o^2)^{-1}$, and a final $R_1$ index of 0.1094. The largest shift $\Delta/\sigma$ was 0.2 and a final difference electron density map showed no peaks greater than 0.5 e $Å^{-3}$.

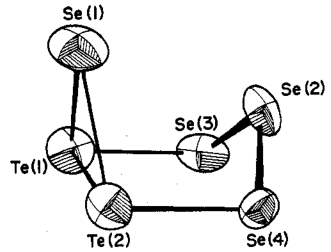

**Figure 1.** The $Te_2Se_4^{2+}$ cation.

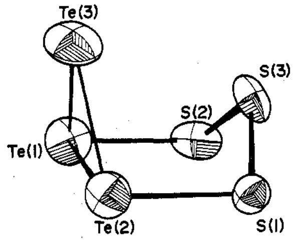

**Figure 2.** The $Te_3S_3^{2+}$ cation.

**$Te_2Se_4(AsF_6)_2$.** Since the unit cell dimensions were very similar to those of the previous compound (with $a$ and $b$ interchanged), the atomic parameters of that compound were used except that arsenic scattering curves were applied instead of antimony. Least-squares refinement gave an $R_1$ index of 0.22. The crystal was corrected for absorption and anisotropic temperature factors were introduced for the heavy atoms; this led to an $R_1$ index of 0.138. Examination of the molecular geometry around the arsenic atoms indicated that the fluorines refined to "unreasonable" positions. This may have been due to disorder and/or to a considerable thermal motion (libration) of the $AsF_6^-$ groups since there were smears of electron density with maxima of 0.7 e $Å^{-3}$ around these atoms in a difference Fourier. An attempt was made to overcome these problems by refining the $AsF_6$ units as rigid groups. This approach had the added advantage of reducing the number of parameters; however, the best $R_1$ index that could be obtained was 0.168 and therefore we considered that this approach was too artificial and hence rejected it. Probably the most important reason for the difficulties encountered in refining the structure was the relatively low number of reflections.[5] Data were, therefore, also collected on another better formed, smaller crystal, in order to reduce the effects of absorption but fewer observed reflections were obtained. Since the cation is very similar to the $Te_2Se_4^{2+}$ cation in $Te_2Se_4(AsF_6)_2$, we consider that the structure of the cation is essentially correct despite the poor geometry of the anions. The final $R_1$ index was 0.138 and final $R_2$ $(=[\sum 1/\sigma^2(|F_o|^2 - |F_c|^2)/\sum 1/\sigma^2F_o^2]^{1/2})$ was 0.144. The largest shift $\Delta/\sigma$ was 0.4 and a final difference electron density map showed no peaks greater than 0.5 e $Å^{-3}$ around the heavy atoms.

Observed and calculated structure factors are available upon request.[8]

## Discussion

The final atomic parameters and bond lengths and bond angles for the three structures are given in Tables I–VI, and Figures 1 and 2 show the structures of the two cations. These are remarkably similar and they may be described as having a three-membered ring fused to a three-atom sulfur or selenium chain forming an overall six-membered ring with a boat conformation. Alternatively, they may be described as having a bicyclo[3.1.0]hexane type of structure.

**Table I.** Final Atomic Parameters ($\times 10^4$) for $Te_3S_3(AsF_6)_2$[a]

| Atom | $x/a$ | $y/b$ | $z/c$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Te(1) | 1976 (4) | 8519 (2) | 5332 (2) | 784 (25) | 598 (21) | 552 (17) | 97 (20) | −101 (16) | 228 (15) |
| Te(2) | 910 (4) | 7358 (2) | 6798 (2) | 743 (26) | 662 (22) | 507 (16) | 62 (20) | 100 (15) | −49 (14) |
| Te(3) | 3906 (4) | 8073 (3) | 6701 (2) | 688 (27) | 1012 (27) | 732 (26) | 118 (23) | −271 (20) | 18 (18) |
| S(1) | 1208 (13) | 5458 (8) | 6156 (7) | 566 (86) | 302 (63) | 784 (66) | −66 (62) | 1 (61) | −69 (53) |
| S(2) | 2365 (15) | 6813 (10) | 4459 (6) | 720 (92) | 982 (98) | 424 (53) | 20 (85) | −91 (56) | −139 (57) |
| S(3) | 3289 (15) | 5756 (9) | 5444 (6) | 818 (100) | 555 (73) | 535 (57) | 249 (73) | −45 (60) | −79 (51) |
| As(1) | 2709 (5) | 2033 (4) | 5623 (2) | 528 (35) | 584 (31) | 497 (23) | −87 (31) | −55 (23) | −47 (22) |
| As(2) | 3044 (5) | 4727 (4) | 2292 (2) | 526 (35) | 509 (29) | 301 (19) | 21 (28) | −40 (21) | 40 (19) |

| Atom | $x/a$ | $y/b$ | $z/c$ | $B$, Å$^2$ | Atom | $x/a$ | $y/b$ | $z/c$ | $B$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| F(1) | 1266 (33) | 2720 (23) | 6147 (16) | 1093 (90) | F(7) | 2540 (36) | 6051 (25) | 2368 (17) | 1207 (97) |
| F(2) | 1430 (34) | 1100 (23) | 5219 (16) | 1048 (88) | F(8) | 3645 (33) | 3444 (22) | 2233 (15) | 994 (81) |
| F(3) | 2273 (39) | 2797 (28) | 4766 (19) | 1436 (113) | F(9) | 4141 (88) | 4983 (59) | 1463 (40) | 3102 (296) |
| F(4) | 3076 (37) | 1155 (24) | 6487 (17) | 1168 (96) | F(10) | 4804 (90) | 5074 (58) | 2795 (43) | 3115 (314) |
| F(5) | 3998 (41) | 2953 (26) | 6017 (18) | 1271 (101) | F(11) | 1551 (60) | 4532 (39) | 1588 (25) | 2129 (174) |
| F(6) | 4070 (41) | 1268 (26) | 5125 (18) | 1318 (109) | F(12) | 1897 (76) | 4437 (52) | 3157 (32) | 2863 (259) |

[a] Anisotropic temperature factors $U_{ij}$ are expressed in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

**Table II.** Final Atomic Parameters ($\times 10^4$) for $Te_2Se_4(SbF_6)_2$

| Atom | $x/a$ | $y/b$ | $z/c$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Te(1) | 1404 (3) | 2816 (7) | 2942 (3) | 414 (21) | 959 (35) | 639 (25) | −99 (26) | −150 (20) | 110 (29) |
| Te(2) | 2558 (4) | 2822 (8) | 4366 (3) | 518 (24) | 1218 (44) | 556 (25) | 11 (31) | 34 (22) | −209 (30) |
| Se(1) | 1812 (6) | 1141 (11) | 4221 (5) | 582 (42) | 917 (57) | 798 (48) | −77 (44) | 177 (38) | 328 (45) |
| Se(2) | 4177 (5) | 1151 (8) | 3047 (5) | 521 (35) | 593 (38) | 704 (40) | 232 (33) | 132 (34) | 33 (38) |
| Se(3) | 3069 (7) | 2320 (11) | 2013 (4) | 799 (46) | 1022 (59) | 462 (33) | −45 (50) | 53 (37) | 49 (42) |
| Se(4) | 4497 (6) | 3422 (10) | 3800 (5) | 374 (34) | 1023 (67) | 875 (49) | 53 (39) | 14 (35) | −119 (47) |
| Sb(1) | 7948 (3) | 2332 (6) | 3044 (3) | 431 (20) | 662 (30) | 696 (26) | −6 (22) | 20 (21) | 58 (25) |
| Sb(2) | 4672 (4) | 7905 (6) | 5185 (3) | 494 (23) | 653 (30) | 546 (22) | −6 (25) | 13 (20) | 42 (23) |

| Atom | $x/a$ | $y/b$ | $z/c$ | $B$, Å$^2$ | Atom | $x/a$ | $y/b$ | $z/c$ | $B$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| F(1) | 8715 (37) | 3823 (53) | 2451 (26) | 794 (118) | F(7) | 3659 (157) | 7028 (233) | 4654 (106) | 4348 (956) |
| F(2) | 6690 (47) | 3727 (62) | 3053 (34) | 1128 (164) | F(8) | 4684 (50) | 8009 (72) | 3894 (37) | 1234 (184) |
| F(3) | 8790 (64) | 2432 (100) | 4015 (46) | 1737 (295) | F(9) | 4516 (50) | 7723 (75) | 6294 (37) | 1330 (201) |
| F(4) | 8890 (51) | 1084 (73) | 2705 (36) | 1233 (190) | F(10) | 3357 (57) | 8693 (86) | 5146 (40) | 1419 (225) |
| F(5) | 7314 (71) | 985 (98) | 3423 (51) | 1936 (325) | F(11) | 5874 (54) | 6928 (81) | 5316 (40) | 1482 (231) |
| F(6) | 7689 (80) | 1850 (112) | 2070 (60) | 2221 (388) | F(12) | 4900 (46) | 9299 (67) | 5167 (34) | 1114 (169) |

**Table III.** Final Atomic Parameters ($\times 10^4$) for $Te_2Se_4(AsF_6)_2$

| Atom | $x/a$ | $y/b$ | $x/c$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Te(1) | 3198 (11) | 1341 (7) | 2919 (5) | 1094 (81) | 642 (47) | 606 (45) | −58 (53) | 227 (54) | −250 (42) |
| Te(2) | 4259 (12) | 2553 (10) | 4360 (6) | 1070 (82) | 1517 (96) | 611 (52) | −6 (84) | −117 (62) | 123 (65) |
| Se(1) | 1628 (14) | 1780 (12) | 4294 (7) | 433 (75) | 1333 (112) | 461 (61) | −129 (81) | 216 (64) | 111 (72) |
| Se(2) | 1421 (13) | 4147 (9) | 2974 (6) | 252 (62) | 888 (76) | 392 (48) | 245 (48) | −130 (53) | −93 (55) |
| Se(3) | 2517 (16) | 2995 (9) | 1937 (6) | 850 (90) | 766 (68) | 393 (55) | 529 (77) | 12 (70) | −84 (56) |
| Se(4) | 3823 (20) | 4498 (12) | 3691 (13) | 881 (130) | 669 (87) | 1703 (163) | −192 (91) | 95 (122) | −42 (104) |
| As(1) | 2584 (15) | 7902 (8) | 3102 (6) | 634 (79) | 378 (50) | 607 (61) | −95 (64) | 182 (68) | 80 (50) |
| As(2) | 7819 (18) | 4737 (8) | 5183 (6) | 1272 (126) | 477 (54) | 263 (47) | −252 (76) | 129 (69) | 38 (46) |

| Atom | $x/a$ | $y/b$ | $x/c$ | $B$, Å$^2$ | Atom | $x/a$ | $y/b$ | $x/c$ | $B$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| F(1) | 3623 (74) | 8661 (62) | 2890 (51) | 1672 (204) | F(7) | 7197 (99) | 3582 (79) | 5707 (80) | 3398 (477) |
| F(2) | 3702 (67) | 6804 (53) | 3410 (40) | 882 (183) | F(8) | 7840 (67) | 4713 (60) | 4014 (43) | 1393 (190) |
| F(3) | 2619 (102) | 8802 (87) | 4001 (81) | 3548 (487) | F(9) | 8102 (93) | 4691 (79) | 6446 (73) | 2482 (366) |
| F(4) | 1421 (50) | 8890 (42) | 2824 (27) | 453 (112) | F(10) | 8510 (77) | 3602 (18) | 5002 (40) | 1146 (177) |
| F(5) | 1691 (100) | 6944 (83) | 3333 (72) | 2545 (370) | F(11) | 7002 (77) | 5897 (65) | 5307 (53) | 1651 (212) |
| F(6) | 2602 (100) | 7111 (86) | 2197 (69) | 2571 (377) | F(12) | 8401 (102) | 5802 (87) | 4701 (73) | 2501 (382) |

In the $Te_3S_3^{2+}$ cation, the Te(1)–Te(2) bond length of 2.787 Å is slightly longer than twice the covalent radius for tellurium,[9] 2.74 Å, and appreciably longer than the Te(2)–Te(3) and Te(1)–Te(3) bond lengths (mean 2.67 Å) which are very close to the Te–Te bond lengths in the $Te_4^{2+}$ cation,[10] in which the bonds have a formal bond order of 1.25. This suggests that the resonance structures **2** and **3** are of some importance in addition to the single-bond structure **1** (see Figure 3). However, it must be noted that, in view of the very small angles of approximately 60° in the $Te_3$ triangle, the bonds are very likely to be bent and this curvature of the bonds may be responsible for their slightly lesser length. The somewhat longer Te(1)–Te(2) bond length is perhaps also understandable in view of the probable tendency of the bond angles, at sulfur, to open up toward the value of 104° found in the $S_8$ ring thus increasing the distances across the six-membered $Te_3S_3$ ring.

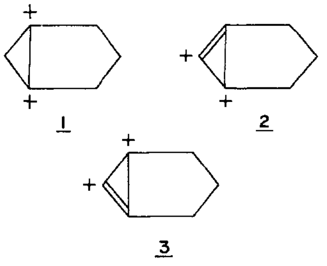

**Figure 3.** Resonance forms of the two cations.

**Table IV.** Interatomic Bond Lengths (Å) and Angles (deg) for $Te_3S_3(AsF_6)_2$

| | | | | |
|---|---|---|---|---|
| | | Cations | | |
| Te(1)-Te(2) | 2.787 (4) | | Te(2)-Te(1)-Te(3) | 58.3 (1) |
| Te(3) | 2.684 (4) | | Te(2)-Te(1)-S(2) | 94.6 (3) |
| S(2) | 2.443 (12) | | Te(3)-Te(1)-S(2) | 100.3 (3) |
| Te(2)-Te(3) | 2.665 (6) | | Te(1)-Te(2)-Te(3) | 58.9 (1) |
| S(1) | 2.468 (10) | | Te(1)-Te(2)-S(1) | 95.4 (3) |
| S(1)-S(3) | 2.105 (16) | | Te(3)-Te(2)-S(1) | 99.5 (3) |
| S(2)-S(3) | 2.098 (15) | | Te(1)-Te(3)-Te(2) | 62.8 (1) |
| | | | Te(2)-S(1)-S(3) | 98.2 (5) |
| | | | Te(1)-S(2)-S(3) | 98.7 (4) |
| | | | S(1)-S(2)-S(3) | 99.7 (6) |
| | | Anions | | |
| As(1)-F(1) | 1.68 (3) | | F(3)-As(1)-F(4) | 176 (2) |
| F(2) | 1.66 (3) | | F(5) | 94 (2) |
| F(3) | 1.63 (3) | mean | F(6) | 95 (2) |
| F(4) | 1.71 (3) | 1.66 | F(4)-As(1)-F(5) | 91 (1) |
| F(5) | 1.65 (3) | | F(6) | 84 (1) |
| F(6) | 1.65 (3) | | F(5)-As(1)-F(6) | 94 (2) |
| As(2)-F(7) | 1.63 (3) | | F(7)-As(2)-F(8) | 177 (2) |
| F(8) | 1.60 (3) | | F(9) | 92 (3) |
| F(9) | 1.61 (7) | mean | F(10) | 88 (3) |
| F(10) | 1.71 (7) | 1.64 | F(11) | 89 (2) |
| F(11) | 1.65 (5) | | F(12) | 89 (2) |
| F(12) | 1.68 (6) | | F(8)-As(2)-F(9) | 87 (3) |
| | | | F(10) | 89 (3) |
| F(1)-As(1)-F(2) | 92 (1) | | F(11) | 94 (2) |
| F(3) | 88 (1) | | F(12) | 92 (2) |
| F(4) | 93 (1) | | F(9)-As(2)-F(10) | 79 (3) |
| F(5) | 89 (1) | | F(11) | 87 (3) |
| F(6) | 176 (1) | | F(12) | 179 (4) |
| F(2)-As(1)-F(3) | 86 (1) | | F(10)-As(2)-F(11) | 166 (3) |
| F(4) | 90 (1) | | F(12) | 101 (3) |
| F(5) | 179 (1) | | F(11)-As(2)-F(12) | 92 (3) |
| F(6) | 85 (1) | | | |

**Table V.** Interatomic Bond Lengths (Å) and Angles (deg) for $Te_2Se_4(SbF_6)_2$

| | | | | |
|---|---|---|---|---|
| | | Cations | | |
| Te(1)-Se(1) | 2.539 (10) | | Te(2)-Te(1)-Se(1) | 56.4 (3) |
| Se(3) | 2.532 (9) | | Te(2)-Te(1)-Se(1) | 96.8 (2) |
| Te(2) | 2.786 (7) | | Se(1)-Te(1)-Se(3) | 101.8 (3) |
| Te(2)-Se(1) | 2.525 (11) | | Se(1)-Te(2)-Se(4) | 99.9 (3) |
| Se(4) | 2.539 (9) | | Te(1)-Te(2)-Se(4) | 98.0 (3) |
| Se(2)-Se(3) | 2.346 (10) | | Te(1)-Te(2)-Se(1) | 56.9 (2) |
| Se(4) | 2.346 (11) | | Te(1)-Se(1)-Te(2) | 66.8 (9) |
| | | | Se(3)-Se(2)-Se(4) | 94.3 (4) |
| | | | Te(1)-Se(3)-Se(2) | 97.5 (3) |
| | | | Te(2)-Se(4)-Se(2) | 98.1 (3) |
| | | Anions | | |
| Sb(1)-F(1) | 1.86 (5) | | F(3)-Sb(1)-F(4) | 85 (3) |
| F(2) | 1.96 (6) | | F(5) | 89 (4) |
| F(3) | 1.84 (7) | mean | F(6) | 155 (4) |
| F(4) | 1.67 (6) | 1.75 | F(4)-Sb(1)-F(5) | 88 (4) |
| F(5) | 1.53 (9) | | F(6) | 70 (4) |
| F(6) | 1.62 (10) | | F(5)-Sb(1)-F(6) | 94 (5) |
| Sb(2)-F(7) | 1.67 (20) | | F(7)-Sb(2)-F(8) | 62 (6) |
| F(8) | 1.99 (6) | | F(9) | 112 (6) |
| F(9) | 1.77 (6) | mean | F(10) | 60 (7) |
| F(10) | 1.74 (7) | 1.70 | F(11) | 118 (7) |
| F(11) | 1.70 (7) | | F(12) | 131 (7) |
| F(12) | 1.32 (7) | | F(8)-Sb(2)-F(9) | 174 (3) |
| | | | F(10) | 87 (3) |
| F(1)-Sb(1)-F(2) | 87 (2) | | F(11) | 98 (3) |
| F(3) | 96 (3) | | F(12) | 86 (3) |
| F(4) | 87 (3) | | F(9)-Sb(2)-F(10) | 88 (3) |
| F(5) | 172 (3) | | F(11) | 98 (3) |
| F(6) | 79 (4) | | F(12) | 86 (3) |
| F(2)-Sb(1)-F(3) | 113 (3) | | F(10)-Sb(2)-F(11) | 79 (4) |
| F(4) | 161 (3) | | F(12) | 171 (3) |
| F(5) | 95 (4) | | F(11)-Sb(2)-F(12) | 108 (3) |
| F(6) | 91 (4) | | | |

The Te–S bonds are a little longer than the mean (2.42 Å) of the S–S bond in $S_8$ (2.10 Å)[9] and twice the sum of the covalent radius of Te (2.74 Å). The S–S bond lengths are similar to those found in $S_8$.[9]

**Table VI.** Interatomic Bond Lengths (Å) and Angles (deg) for $Te_2Se_4(AsF_6)_2$

| | | | |
|---|---|---|---|
| | Cations | | |
| Te(1)-Se(1) | 2.59 (2) | Te(2)-Te(1)-Se(1) | 57 (1) |
| Se(3) | 2.57 (2) | Te(2)-Te(1)-Se(1) | 99 (1) |
| Te(2) | 2.82 (2) | Se(1)-Te(1)-Se(3) | 101 (1) |
| Te(2)-Se(1) | 2.56 (2) | Se(1)-Te(2)-Se(4) | 99 (1) |
| Se(4) | 2.58 (2) | Te(1)-Te(2)-Se(4) | 96 (1) |
| Se(2)-Se(3) | 2.33 (2) | Te(1)-Te(2)-Se(1) | 59 (1) |
| Se(4) | 2.38 (2) | Te(1)-Se(1)-Te(2) | 64 (1) |
| | | Se(3)-Se(2)-Se(4) | 94 (1) |
| | | Te(1)-Se(3)-Se(2) | 98 (1) |
| | | Te(2)-Se(4)-Se(2) | 99 (1) |
| | Anions | | |
| As(1)-F(1) | 1.31 (5) | F(3)-As(1)-F(4) | 77 (5) |
| F(2) | 1.71 (3) | F(5) | 108 (9) |
| F(3) | 1.76 (11) | F(6) | 179 (9) |
| F(4) | 1.61 (3) | F(4)-As(1)-F(5) | 109 (5) |
| F(5) | 1.44 (9) | F(6) | 104 (5) |
| F(6) | 1.77 (9) | F(5)-As(1)-F(6) | 73 (8) |
| As(2)-F(7) | 1.81 (11) | F(7)-As(2)-F(8) | 116 (3) |
| F(8) | 1.53 (4) | F(9) | 62 (3) |
| F(9) | 1.70 (9) | F(10) | 57 (4) |
| F(10) | 1.96 (4) | F(11) | 117 (4) |
| F(11) | 1.53 (5) | F(12) | 179 (4) |
| F(12) | 1.59 (9) | F(8)-As(2)-F(9) | 172 (5) |
| | | F(10) | 78 (3) |
| F(1)-As(1)-F(2) | 102 (3) | F(11) | 104 (3) |
| F(3) | 77 (6) | F(12) | 63 (4) |
| F(4) | 82 (4) | F(9)-As(2)-F(10) | 96 (4) |
| F(5) | 109 (7) | F(11) | 83 (5) |
| F(6) | 103 (7) | F(12) | 119 (6) |
| F(2)-As(1)-F(3) | 105 (6) | F(10)-As(2)-F(11) | 174 (4) |
| F(4) | 176 (3) | F(12) | 122 (6) |
| F(5) | 67 (6) | F(11)-As(2)-F(12) | 63 (7) |
| F(6) | 74 (6) | | |

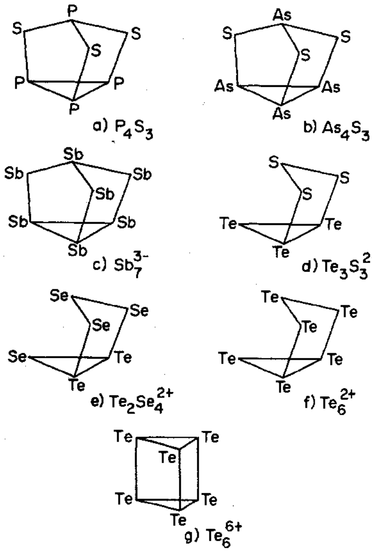

**Figure 4.** The structures of $P_4S_3$, $As_4S_3$, and $Sb_7^{3-}$ compared with the structures of $Te_3S_3^{2+}$ and $Te_2Se_4^{2+}$ and the postulated structure of $Te_6^{6+}$.

In the $Te_2Se_4^{2+}$ ion the Te(1)–Te(2) bond length is the same as the Te(1)–Te(2) bond length in $Te_3S_3(AsF_6)_2$. All of the Te–Se bond lengths are approximately equal, mean 2.53 Å, and are very close to the average (2.54 Å) of the Te–Te single-bond length and the Se–Se single-bond length (2.34 Å) as found in elemental selenium $Se_8$.[9] It seems that **1** is the only structure that needs to be considered in this case perhaps because there is a smaller tendency for the positive charge to be located on the less electropositive selenium as in structures **2** and **3**.

The three-membered $Te_3$ and $Te_2Se$ rings have not been previously observed in any other compounds and at first sight

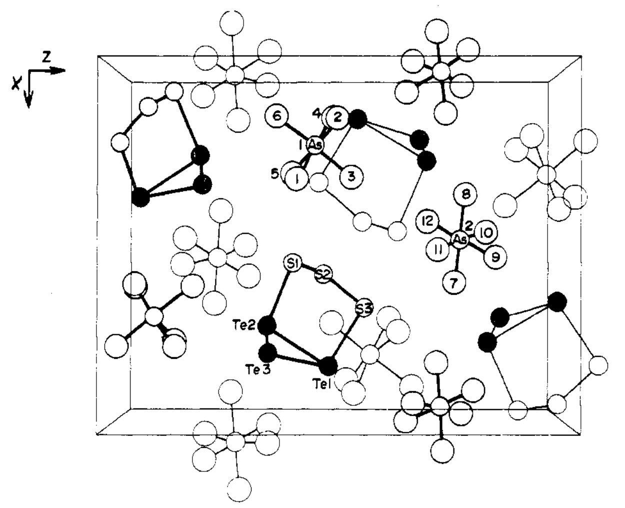

**Figure 5.** Perspective view of the structure of $Te_3S_3(AsF_6)_2$ down the *a* axis: •, Te; o, S.

the structures of these species are surprising. However, it may be seen from Figure 4 that their structures are closely related to those of $P_4S_3$,[11] $As_4S_3$,[12] and $Sb_7^{3-}$,[13] which contain three-membered $P_3$, $As_3$, and $Sb_3$ rings, respectively. Addition of an $M^{2+}$ ion to one of the $M_6^{2+}$ cations would give an $M_7^{4+}$ species isoelectronic with $P_4S_3$, $Sb_7^{3-}$, etc.

The structure of the $Te_6^{2+}$ cation[2] has never been determined, but it seems reasonable to suppose that it has the analogous structure f (Figure 4). The previous suggestion[2] that the cation $Te_n^{n+}$, whose structure has also not been determined, could have the closely related trigonal-prism structure $Te_6^{6+}$ (g) (Figure 4) now has some justification.

Of course it cannot be said that the structure of $P_4S_3$ or that of any of the phosphorus sulfides is well understood. While they can all be well represented by apparently reasonable single-bond structures, it is not understood why they differ so remarkably from the phosphorus oxides. It is hoped that the discovery of analogous compounds among the heteroatomic chalcogen cations will eventually lead to a better understanding of these structures. Although a three-valent $Te^+$ or $Se^+$ atom is formally isoelectronic with a phosphorus or other group 5 atom, direct analogues of the phosphorus and arsenic sulfides, e.g., $Te_4S_3^{4+}$, have not yet been discovered among the chalcogen heteropolyatomic cations.

The $SbF_6^-$ and $AsF_6^-$ anions are somewhat distorted due to thermal motion and/or disorder but the mean Sb–F and As–F distances, 1.73 and 1.64 Å respectively, are similar to those found in other species containing these ions.

Figures 5 and 6 show packing diagrams for $Te_3S_3(AsF_6)_2$ and $Te_2Se_4(SbF_6)_2$. All interionic distances are greater than 2.9 Å and the compounds can therefore be considered to consist of discrete ions. Although some of the contacts between F atoms and the cations are a little shorter than van der Waals distances, they would correspond to only rather weak interactions, and in view of the uncertainties in the coordinates of the fluorine atoms it does not seem justifiable to discuss these possible weak interactions.

It is interesting that three different methods of preparation gave the same product $Te_3S_3(AsF_6)_2$. In the reaction between $S_8^{2+}$ and $Te_4^{2+}$ the characteristic blue color of $S_8^{2+}$ was observed at low temperature and this changed to a deep red color on allowing the solution to warm to room temperature. Presumably $S_8^{2+}$ is more soluble at low temperature in the $SO_2$ solvent than $Te_4^{2+}$. Since the stoichiometry of the products does not correspond to that of the reactants, it is clear that there were other products in the reaction which were not isolated or characterized. In the reaction of the mixture of selenium and tellurium with $AsF_5$ the same sequence of color changes was observed which suggests that sulfur is oxidized to soluble $S_8^{2+}$ even at low temperature and that subsequently $Te_4^{2+}$ is formed which reacts with $S_8^{2+}$ to give $Te_3S_3^{2+}$. In the reaction of the 1:1 Te–S "alloy" a red solution was obtained immediately, suggesting that a cation or cations containing both S and Te were formed directly from the "alloy".

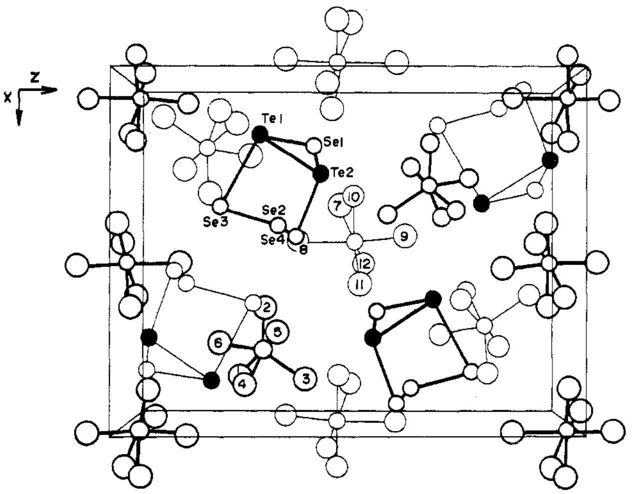

**Figure 6.** Perspective view of the structure of $Te_2Se_4(SbF_6)_2$ down the *b* axis: •, Te; o, Se.

In the preparation of $Te_2Se_4(SbF_6)_2$ and $Te_2Se_4(AsF_6)_2$ by the reaction of a mixture of selenium and tellurium with $AsF_5$ or $SbF_5$, a green solution was obtained initially, suggesting that $Se_8^{2+}$ is first formed in solution and that this then reacts with a tellurium cation, presumably $Te_4^{2+}$, which is formed subsequently. Again there are undoubtedly other products in these reactions which were not isolated. It must be admitted that our understanding of the details of all of these preparative reactions is, at present, very limited and much further work is needed.

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**Registry No.** $Te_3S_3(AsF_6)_2$, 61617-68-3; $Te_2Se_4(SbF_6)_2$, 61617-69-4; $Te_2Se_4(AsF_6)_2$, 61617-70-7; $Te_4(AsF_6)_2$, 12536-35-5; $S_8(AsF_6)_2$, 33248-05-4; $AsF_5$, 7784-36-3; $SbF_5$, 7783-70-2.

**Supplementary Material Available:** Listings of calculated and observed structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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