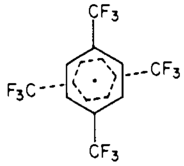
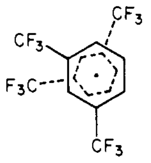
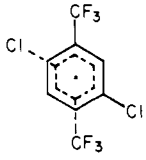
of the CF_3 substituents in opposite rings. The orientation of the two π-arene rings with respect to one another are illustrated in **1**–**3**. In **1** the rotation of 17° results in F---F intramolecular contacts that are all greater than normal estimates of van der Waal distances.[22] However, in the meta-substituted case, **2**, simple rotation cannot alleviate all of these interactions, and one interaction distance (F_2---F_{11}) is 2.89 Å. This is close to the estimated van der Waals contact of 2.94 Å considering that the large thermal ellipsoids observed for the fluorines would result in an underestimation of these distances. Further, C_{16} is displaced from the mean plane of the ring by ~0.08 Å away from the chromium while displacement of the CF_3 carbon in **1** and **3** is 0.01 Å or less. The absence of a second CF_3 group in **3** allows the carbons of the two rings to eclipse, with all intramolecular contacts of the substituents being greater than van der Waals distances.



1



2



3

An analysis of the intermolecular packing interactions reveals normal contact distances in **3**. In **1**, an F---F interaction of 2.80 Å, occurring at F_3---F_3^{I} where I = $^1/_2 - x$, $^1/_2 - y$, $1 - z$, is shorter than the normal[22] 2.94 Å distance. Similarily an F---H contact of 2.51 Å occurs between F_2---H_8^{II} and F_8---H_6^{III} where II = $-1 + x, y, z$ and III = $x, y, -1 + z$. Comparatively, the estimated F---H van der Waals distance is 2.67 Å.[22] Of course, the large thermal motion of the F atoms combined with the crude determination of hydrogen atomic positions produces a relatively large error in these distances.

Acknowledgment. Support of this work from the Research Corp. is acknowledged with gratitude. Acknowledgment is also made to the University of North Dakota for computer time.

Registry No. **1**, 53966-06-6; **2**, 53966-05-5; **3**, 78166-85-5.

Supplementary Material Available: Listings of the structure factor amplitudes (35 pages). Ordering information is given on any current masthead page.

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Preparation, X-ray Crystal Structures, and Vibrational Spectra of Some Salts of the $As_3S_4^+$ and $As_3Se_4^+$ Cations

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Received July 28, 1980

The reactions of α- and β-As_4S_4 and some arsenic–selenium melts with various oxidants in SO_2 as solvent are reported. It is shown by X-ray crystallography that the reactions of As_4S_4 and a 1:1 As–Se melt with the Lewis acids AsF_5 and SbF_5 in a 1:3 molar ratio in SO_2 give the hexafluoroarsenate and hexafluoroantimonate salts of the novel arsenic chalcogen cations $As_3S_4^+$ and $As_3Se_4^+$. Crystals of $(As_3S_4)(SbF_6)$ are yellow plates which crystallize in the orthorhombic space group *Pcam* with $a = 20.453$ (4) Å, $b = 5.990$ (1) Å, $c = 9.609$ (2) Å, $U = 1177.3$ (4) Å^3, and $d_c = 3.32$ g cm^{-3} for $Z = 4$. Crystals of the isomorphous $(As_3S_4)(AsF_6)$ are dark yellow prisms and rhombs with cell dimensions $a = 19.962$ (4) Å, $b = 5.930$ (1) Å, $c = 9.441$ (3) Å, $U = 1115.8$ (5) Å^3, and $d_c = 3.22$ g cm^{-3} for $Z = 4$. The compound $(As_3Se_4)(SbF_6)$ forms orange diamond-shaped plates which crystallize in the monoclinic space group $P2_1/m$ with $a = 6.224$ (3) Å, $b = 9.564$ (5) Å, $c = 10.643$ (5) Å, $\beta = 92.65$ (4)°, $U = 632.9$ (5) Å^3, and $d_c = 4.07$ g cm^{-3} for $Z = 2$. The structure of the compound $(As_3S_4)(SbF_6)$ was solved by using the Patterson function and refined by least-squares methods to final agreement indices $R_1 = 0.036$ and $R_2 = 0.043$ for 699 observed data. The isomorphous compound $(As_3S_4)(AsF_6)$ has similarly been refined by least-squares methods to final agreement indices $R_1 = 0.043$ and $R_2 = 0.052$ for 546 observed data. The structure of the compound $(As_3Se_4)(SbF_6)$ was solved by using direct methods and has been refined by least-squares to final agreement indices $R_1 = 0.064$ and $R_2 = 0.082$ for 620 observed reflections. The two cations $As_3S_4^+$ and $As_3Se_4^+$ are isostructural with crystallographic mirror symmetry and an overall symmetry of C_s. The cage structure of the two cations can be derived by bridging three edges of a tetrahedron of three arsenic and one sulfur or selenium atoms by the remaining sulfur or selenium atoms. Bond distances, bond angles and some significant interionic contact distances in these compounds are discussed. In addition, the Raman and IR spectra of these cations as well as the Raman spectrum of As_4S_3 and an improved Raman spectrum of the compound α-As_4S_4 are reported.

Introduction

Although the reactions of S_4N_4 and related compounds with various oxidizing agents and Lewis acids and the reactions of S_4N_4 in reducing media such as potassium/liquid ammonia solutions have been observed to give various new cations and anions,[1-6] the analogous reactions of the structurally related compounds As_4S_4[7-10] and As_4Se_4[11-14] have previously not been studied in any depth. The only ionic derivative of As_4S_4 that has been definitely characterized is the $As_4S_6^{2-}$ anion which

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[10] It should be noted, however, that an isomeric form of As_4S_4 has been found, the structure of which is based on an edge-bridged cube with one vertex missing. Kutoglu, A. *Z. Anorg. Allg. Chem.* **1976**, *419*, 176.

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has been studied as a piperidinium salt.[15]

Following our earlier work on the oxidation of sulfur–nitrogen compounds to give SN cations,[1-3] we have begun a systematic investigation of the reactions of the arsenic sulfides and selenides with group 5 pentahalides and other oxidants. Reported here are the preparation and characterization by X-ray crystallography and other physical methods of the arsenic–sulfur cation $As_3S_4^+$ as its hexafluoroantimonate and hexafluoroarsenate salts and the isostructural $As_3Se_4^+$ cation as its hexafluoroantimonate salt.

Experimental Section

Materials. Elemental selenium (Fisher) and sublimed sulfur (BDH) were both heated under vacuum overnight before use. Arsenic metal (99.5%, Alfa Inorganics) was heated at 200 °C under vacuum to sublime out any arsenic(III) oxide. Antimony pentafluoride (Ozark Mahoning Co.) was doubly distilled in a Pyrex still in an atmosphere of dry nitrogen. It was then distilled under vacuum and stored in an FEP bottle. Anhydrous sulfur dioxide (99.98%, Canadian Liquid Air), bromine (Reagent ACS, Fisher Scientific Co.) and carbon disulfide were distilled onto and stored over P_4O_{10} prior to use. Chlorine (99.5%, Canadian Liquid Air) was purified by passage through calcium oxide, two sulfuric acid (95%) traps, and a P_4O_{10} trap before being distilled through traps at −78.5, −96.7, −130, and −196 °C. The fraction in the trap at −130 °C was used. Phosphorus pentachloride (99.0%, BDH) was sublimed in an evacuated tube, and antimony pentachloride (100%, Baker Chemical Co.) was vacuum distilled before use. Arsenic pentafluoride was prepared directly from the elements. Methylene chloride was dried for 24 h over anhydrous calcium chloride and then stored over P_4O_{10}. Acetonitrile and arsenic trifluoride (City Chemical Co. or prepared directly from the elements) were stored over molecular sieves and NaF, respectively. Fluorosulfuric acid (technical grade, Baker and Adamson) and sulfuryl chlorofluoride (Allied Chemical) were purified by using standard procedures.[17,18] All other reagents or solvents were of reagent quality and were used directly. All reactions involving air-sensitive materials were carried out under vacuum in flame-sealed, double-bulb ampules fitted with medium glass frits. Solid transfers were done in nitrogen-filled dryboxes.

The compound $S_8(AsF_6)_2$ was prepared according to the method of Dean, Gillespie, and Ummat.[19] The starting materials β-As_4S_4, As_4S_3, and the 1:1 and 4:3 As–Se melts were obtained by adding the dry-weighed elements to Pyrex tubes which were evacuated, sealed, and heated to 360–450 °C for at least 4 days. α-As_4S_4 and β-As_4S_3 were obtained by subliming, respectively, β-As_4S_4 and the amorphous As_4S_3 obtained from the melt. CS_2 extractions of a quick-quenched 1:1 As–S melt produced a few crystals of α-As_4S_3.

Preparation of $(As_3S_4)(AsF_6)$. In a typical experiment arsenic pentafluoride (0.699 mmol) was condensed into a vessel containing powdered As_4S_4 (α or β, 0.233 mmol) under about 14 cm^3 of frozen SO_2 at −196 °C. As the reaction mixture was warmed to room temperature, a bright yellow solution immediately formed which lightened in color in about 5 min. After 0.5 h the formation of a light yellow precipitate was observed. The reaction was allowed to stir for at least 12 h. After the precipitate had been allowed to settle, the solution was carefully poured through the frit at the same time that the other side was cooled. The SO_2 was then distilled back and the extraction repeated many times because of the low solubility of the product. Varying amounts of sulfur were mixed with the final crystalline product. In addition, the reaction with β-As_4S_4 also gave an unidentified insoluble yellow powder.

The compound $As_3S_4(AsF_6)$ can also be made by using $S_8(AsF_6)_2$ as oxidant. An SO_2 solution of 0.3355 mol of $S_8(AsF_6)$ poured onto 0.6709 mmol of β-As_4S_4 immediately gave a pale yellow solution. The Raman spectrum of the resultant solid showed the presence of the compound $(As_3S_4)(AsF_6)$, a large amount of sulfur, and unreacted β-As_4S_4.

Preparation of $As_3Se_4(AsF_6)$. By use of similar amounts and conditions as described above, the reaction of a 1:1 or 4:3 As–Se melt and AsF_5 gave a light green-yellow solution that quickly gave a bright yellow-orange solution. After a few minutes a bright orange precipitate formed. Extraction with consequent crystal formation was carried out as described above. The compound was not very stable, darkening in color in usually less than 2 days. A black soluble unidenfitied product was also present.

Preparation of $As_3S_4(SbF_6)$ and $As_3Se_4(SbF_6)$. For $As_3S_4(SbF_6)$, 0.3727 mmol of As_4S_4 powder and 1.1181 mmol of SbF_5 were added to different sides of the double ampule vessel, SO_2 was condensed onto the SbF_5, and the mixture was warmed and poured through the frit. For $As_3Se_4(SbF_6)$, corresponding amounts of 1:1 or 4:3 As–Se melts with the necessary amount of SbF_5 were used. The reactions proceeded in the same manner as described above, but both compounds are more stable than the hexafluoroarsenate salts. Both reactions gave yellow insoluble products as well.

Anal. Calcd for $As_3S_4(SbF_6)$: As, 38.18; S, 21.78; Sb, 20.68; F, 19.36. Found: As, 39.94; S, 20.88; Sb, 18.20; F, 18.64. Calcd for $As_3Se_4(SbF_6)$: As, 28.95; Se, 40.68; Sb, 15.68; F, 14.68. Found: As, 27.22;, Se, 40.50; Sb, 17.94; F, 13.92. Analyses were carried out by Butterworths.

Reaction of As_4S_4 with Other Oxidants. By use of the same amounts, stoichiometric ratios, and conditions as above, the reaction between β-As_4S_4 and PF_5 in SO_2 gave only α-As_4S_4. Antimony pentafluoride in SO_2 as oxidant, however, reacted to give $SbCl_3$, $AsCl_3$, sulfur, and unreacted β-As_4S_4. No reaction was observed between β-As_4S_4 and PCl_5 in methylene chloride. As_4S_4 and chlorine gave $AsCl_3$, S_2Cl_2, and sulfur. Bromine gave the corresponding bromides and sulfur.

Spectra

Raman spectra were obtained on the instrument previously described.[20] The samples were in the preparation vessel or were sealed in $^1/_4$ in. o.d. Pyrex tubes.

Infrared spectra over the range 1000–200 cm^{-1} were recorded on a Perkin-Elmer grating infrared spectrometer, Type 283. The samples were mounted as Nujol mulls between CsI plates with the edges sealed with Teflon tape. The Nujol had been dried and stored over sodium. Infrared spectra in the range 700 to about 100 cm^{-1} were recorded by using a Nicolet 7199 FT IR system. The samples were mounted as above or as Nujol mulls in heat-sealed polyethylene packets. Raman and FT IR spectra as recorded are accurate to ±1 cm^{-1} while the grating spectrometer is accurate to ±5 cm^{-1} over the range of interest.

Absorption spectra were recorded on a Cary 14 instrument with a reference cell containing solvent. The quartz UV cells were attached by a graded glass seal to a sidearm in which the reaction could take place. Samples were introduced through a Rotoflow valve.

X-ray Crystallography

Crystals of $(As_3S_4)(SbF_6)$ were obtained as clear yellow platelets while those of the isomorphous $(As_3S_4)(AsF_6)$ were darker yellow in appearance and were irregular prisms and rhombs. The major crystal form found for $(As_3Se_4)(SbF_6)$ was orange diamond-shaped plates. These were mostly too small for the X-ray studies, but a few larger, slightly more irregular crystals were also present, and the structure was eventually solved by using one of these larger crystals. All crystals used in the structure determinations were sealed in Lindemann capillaries under a dry-air atmosphere. Crystals of $(As_3Se_4)(SbF_6)$ sealed in capillaries tended to darken in color from orange to dark red. This appears to be a surface effect, as the diffraction patterns are unaffected by these color changes, and is presumably due to traces of moisture/oxygen in the atmosphere of the drybox in which the crystals were sealed. Crystals that are left in the reaction vessel do not exhibit any color changes. Similar marked changes of color of sulfur–nitrogen cations have also been observed.[2,3]

Precession photographs were used to check crystal quality and to obtain preliminary cell and symmetry information. Further work with a Syntex P2$_1$ diffractometer and graphite-monochromatized Mo K$\bar{\alpha}$

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radiation ($\lambda = 0.71069$ Å) gave the following crystal data on each compound. Unit cell dimensions for each compound were obtained from least-squares refinements of 2θ, w, and x for 15 high-angle ($24° < 2\theta < 31°$ for the $As_3S_4^+$ cations, $25° < 2\theta < 29°$ for the $As_3Se_4^+$ cation) reflections on the diffractometer.

Crystal Data

$(As_3S_4^+)(SbF_6^-)$ is orthorhombic with $a = 20.453$ (4) Å, $b = 5.990$ (1) Å, $c = 9.609$ (2) Å, $U = 1177.3$ (4) Å^3, $Z = 4$. $d_c = 3.32$ g/cm^3, fw 588.8, $F(000) = 1072$; Mo $K\bar{\alpha}$ radiation ($\lambda = 0.71069$ Å), μ(Mo $K\bar{\alpha}$) = 120.5 cm^{-1}. Systematic absences ($h0l$, $h = 2n$; $0kl$, $l = 2n$) indicate space groups *Pcam* (a nonstandard setting [*bac*̄] of No. 57 *Pbcm*) or $Pca2_1$ (No. 29). The distribution of the normalized structure factors and the satisfactory structure solution shows that the correct space group is *Pcam*.

The isomorphous $(As_3S_4^+)(AsF_6^-)$ is orthorhombic with $a = 19.962$ (4) Å, $b = 5.930$ (1) Å, $c = 9.441$ (3) Å, $U = 1115.8$ (5) Å^3, $Z = 4$, $d_c = 3.22$ g/cm^3, fw 541.9, $F(000) = 1000$; Mo $K\bar{\alpha}$ radiation ($\lambda = 0.71069$ Å), μ(Mo $K\bar{\alpha}$) = 132.6 cm^{-1}; space group *Pcam*.

$(As_3Se_4^+)(SbF_6^-)$ is monoclinic with $a = 6.224$ (3) Å, $b = 9.564$ (5) Å, $c = 10.643$ (5) Å, $\beta = 92.65$ (4)°, $U = 632.9$ (5) Å^3, $Z = 2$, $d_c = 4.07$ g/cm^3, fw 776.4, $F(000) = 680$; Mo $K\bar{\alpha}$ radiation ($\lambda = 0.71069$ Å), μ(Mo$K\bar{\alpha}$) = 226.8 cm^{-1}. The systematic absence ($0k0$, $k = 2n$) indicated space groups $P2_1/m$ or $P2_1$. The distribution of the normalized structure factors and the satisfactory structure solution show that the space group is $P2_1/m$.

X-ray Intensity Measurements

(a) $(As_3S_4)(SbF_6)$. The crystal used in the data collection was an approximately hexagonal shaped plate of dimensions 0.125 × 0.21 × 0.24 mm in the *a*, *b*, and *c* directions which was bounded principally by the planes {100}, {110}, and {112}, although other smaller faces were also developed.

Data were collected by using θ–2θ scans over a scan range of $K\alpha_1 - 0.85°$ to $K\alpha_2 + 0.85°$ with variable scan rates of 3–29.3°/min, depending on the intensity of a preliminary 2-s count. Stationary background counts were recorded at each end of the scan, each for one quarter of the scan time. The intensities of the three standard reflections that were monitored after every 45 reflections showed no significant changes over the period of the data collection. A total of 4110 reflections (including standards) in the quadrants ($\pm h,\pm k,l$) with $2\theta < 47.5°$ were collected.

Lorentz and polarizaton corrections were applied to all data. Absorption corrections were calculated at a later stage in the structure refinement by using the program ABSORB and a 12 × 6 × 6 grid.[21] (A^* values varied from 4.24 to 8.55.) After averaging equivalent data and excluding reflections which are systematically absent or have observed structure amplitudes equal to zero, a final data set of 954 reflections was obtained. Of these, 703 were considered observed ($F/\sigma(F) > 6.0$).

(b) $(As_3S_4)(AsF_6)$. The crystal used in the data collection was somwehat irregular, and no identification of crystal faces was possible. The shape of the crystal was approximately a truncated tetrahedron of size 0.24 × 0.20 × 0.20 mm.

Data were collected by using θ-2θ scans over a scan range of $K\alpha_1 - 0.6°$ to $K\alpha_2 + 0.6°$ with variable scan rates of 3–29.3°/min, depending on the intensity of a preliminary 2-s count. The intensities of three standard reflections which were collected after every 37 reflections each showed a gradual loss in intensity over the period of the data collection. Other conditions were the same as in part a. A total of 3742 reflections (including standards) in the quadrants ($h,\pm k,\pm l$) with $2\theta < 47.5°$ were collected.

After the data were rescaled for the slight crystal decomposition by using the linear equation $I_{cor} = I_{obsd}(1 + 0.0038218t)$ (t = time in hours), Lorentz and polarization corrections were applied to all the data. No absorption corrections were made due to the irregular nature of the crystal and the slight decomposition observed during the data collection. After equivalent reflections were averaged and reflections which are systematically absent or have observed structure amplitudes equal to zero were excluded, a final data set of 904 reflections was obtained. Of these, 546 were considered observed ($F/\sigma(F) > 6.0$).

(c) $(As_3Se_4^+)(SbF_6^-)$. The crystal used throughout was a thick approximately hexagonal plate bound by the planes {001}, {011}, and {101} and the faces (111), $(11\bar{1})$, $(\bar{1}\bar{1}\bar{1})$, and $(\bar{1}\bar{1}1)$, which are 0.0055, 0.0085, 0.0009, 0.0085, 0.0085, 0.0085 and 0.0085 cm from an origin within the crystal.

Data were collected by using θ–2θ scans over a scan range $K\alpha_1 -1.1°$ to $K\alpha_2 + 1.1°$ with a variable scan rate of 3–29.3°/min, depending on the intensity of a preliminary 2-s count. The intensities of three standard reflections were monitored after every 37 reflections and showed no significant losses in intensities over the period of the data collection. Other conditions were the same as in parts a and b. A total of 3457 reflections (including standards) in the quadrants ($h,\pm k,\pm l$) with $2\theta < 55°$ were collected.

Lorentz and polarization corrections were applied to all data. Absorption corrections were calculated at a late stage in the structure refinement by using the program ABSORB and a 7 × 7 × 10 grid.[21] (A^* values varied from 6.902 to 28.410.) After equivalent reflections were averaged and reflections which are systematically absent or have observed structure amplitudes equal to zero were excluded, a final data set of 1429 reflections was obtained. Of these 620 were considered observed ($F/\sigma(F) > 6.0$).

Structure Solutions

(a) $(As_3S_4)(SbF_6)$. The positions of the antimony and two arsenic atoms in the structure were eventually obtained from the Patterson function after several attempts due to some overlapping vectors in the original map. Least-squares refinement of the positional and thermal parameters of these atoms gave $R_1 = 0.317$,[22] and all the remaining sulfur and fluorine atoms in the structure were located in two subsequent Fourier maps. Least-squares refinement of these atoms gave $R_1 = 0.091$ with isotropic thermal parameters and $R_1 = 0.046$ when anisotropic thermal parameters were introduced for all atoms.

After the data were corrected for absorption effects, two further cycles of refinement gave some improvement in the residual. Inspection of the low-angle data showed that the four strongest reflections in the data set were being badly affected by secondary extinction, and it was decided to omit these reflections from further refinement. After introducing a weighting scheme, two further cycles of least-squares refinement with the above reflections excluded converged to final agreement indices $R_1 = 0.036$ and $R_2 = 0.043$[22] for 699 observed data (73 parameters refined). Refinement using all 950 nonzero data gave $R_1 = 0.054$ and $R_2 = 0.056$, but with some improvement in the standard deviations of the model so that the results of this refinement have been included in the final tables. In the final cycle of least-squares refinement no parameter shifted by more that 5% of its standard error. The most significant feature in a final difference Fourier map was some residual electron density (<1.0 e/Å^3) around the atom S(2) in the cation which had been refined with fairly anisotropic temperature factors. The minimum trough in the map was −0.8 e/Å^3. The weights used in the final cycles were given by the expressions $w = xy$ where (1) $x = F/26$ if $F < 26$ or $x = 42/F$ if $F > 42$, otherwise $x = 1.0$, and (2) $y = \sin\theta/0.29$ if $\sin\theta < 0.29$, otherwise $y = 1.0$. A final comparison of the average $w\|F_o| - |F_c\|^2$ as a function of F_{obsd} and $\sin\theta$ revealed no systematic trends, indicating the suitability of this scheme.

(b) $(As_3S_4)(AsF_6)$. By use of the final atomic coordinates of the isomorphous hexafluoroantimonate salt, but with the scattering curve for arsenic replacing that of antimony, two cycles of full-matrix, least-squares refinement with all atoms having anisotropic thermal parameters gave $R_1 = 0.057$ with unit weights. There was no evidence of any extinction effects in the data, and further cycles of refinement converged to give $R_1 = 0.043$ ($R_2 = 0.052$) for 546 observed reflections and $R_1 = 0.076$ ($R_2 = 0.075$) for all 904 nonzero data (73 parameters refined). In the final cycle of the refinement with all the data no parameter shifted by more than 24% of its standard error, and the weights used were given by the expressions $w = xy$ where (1) $x = F/29$ if $F < 29$ or $x = 48/F$ if $F > 48$, otherwise $x = 1.0$, and (2) $y = \sin\theta/0.25$ if $\sin\theta < 0.25$ or $y = 0.29/\sin\theta$ if $\sin\theta > 0.29$, otherwise $y = 1.0$. A final comparison of the average $w\|F_o| - |F_c\|^2$ as a function of F_{obsd} and $\sin\theta$ after using these weights in the refinement showed no systematic trends. The most significant feature in the final difference Fourier was again some residual electron density near S(2) of ca. 1.3 e/Å^3; the minimum trough was −0.6 e/Å^3.

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(21) "XRAY (1976) System of Crystallographic Programs"; Technical Report TR-446; Computer Science Center: University of Maryland, Baltimore, MD; 1976.

(22) $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$; $R_2 = [\sum w\|F_o| - |F_c\|^2/\sum w|F_o|^2]^{1/2}$.

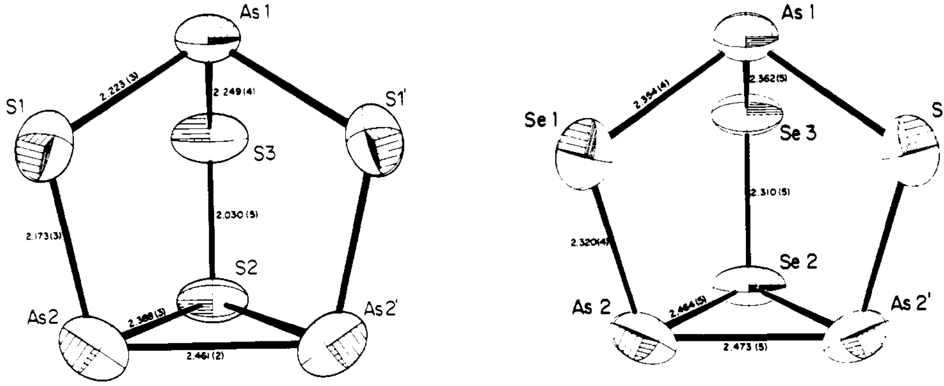

Figure 1. Cations $As_3S_4^+$ and $As_3Se_4^+$ showing the atomic numbering used in the structure determinations. Distances shown for the $As_3S_4^+$ cation are for the hexafluoroantimonate salt.

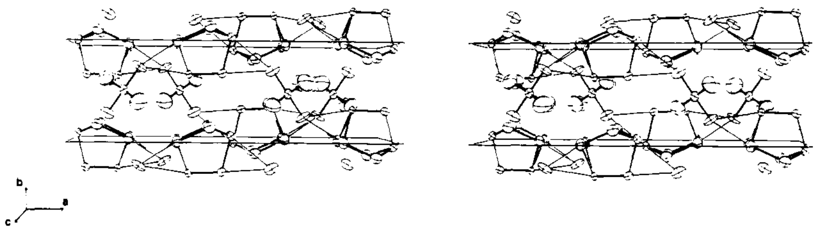

Figure 2. Packing diagram for the compound $(As_3S_4)(SbF_6)$ as viewed down *c*.

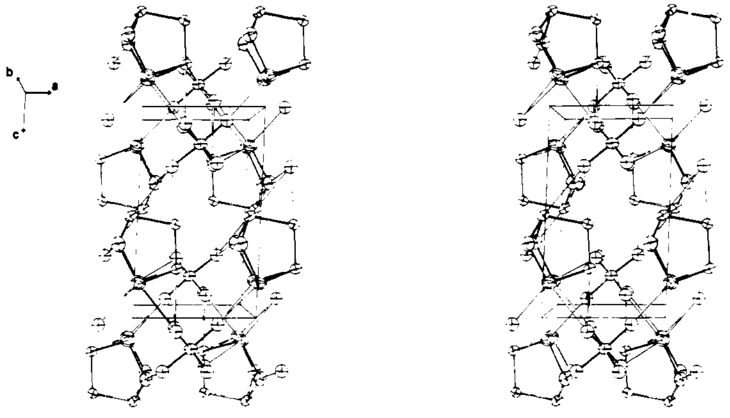

Figure 3. Packing diagram for the compound $(As_3Se_4)(SbF_6)$ as viewed down *b*.

(c) $(As_3Se_4)(SbF_6)$. As with the $As_3S_4^+$ cation above, the value of Z (=2) in the space group $P2_1/m$ indicates that the anion and cation in this compound have crystallographic mirror symmetry. The positions of the antimony and all five independent atoms in the cation were found by using a combination of direct methods (SHELX[23]) and the Patterson function. Initially all atoms in the cation were assumed to be selenium and least-squares refinement using a subset of the data gave $R_1 = 0.312$. The positions of the remaining fluorine atoms were found in a subsequent difference Fourier map. The correct atomic assignments in the cation were made on the basis of the structure of the $As_3S_4^+$ cation since crystallographic evidence in the form of temperature factors and residual peaks in the difference Fourier was inconclusive in resolving the arsenic and selenium positions. Accordingly, the two directly bonded selenium atoms were assumed to lie in the mirror plane, and the remaining selenium atom was assumed to bridge the apical and basal arsenic atoms. At this point in the refinement the data were corrected for absorption effects. Further least-squares refinement cycles, with Sb, As, and Se all having anisotropic temperature factors, eventually converged to final agreement indices $R_1 = 0.064$ and $R_2 = 0.082$ for 620 observed reflections and $R_1 = 0.128$ and $R_2 = 0.162$ for all 1429 nonzero reflections. In the final cycle of refinement with the observed data no parameter shifted by more than 14% of its standard error. The weighting scheme used in the final refinement gave reflections with $F > 45$ weights $w = (45/F)^2$ otherwise $w = 1.0$. Most reflections were given unit weights. A final difference Fourier map contained maximum peaks of ca. 2.0 e/Å^3 within 1 Å of atoms Sb(1), Se(3), and F(4) in the mirror plane at $y = {}^1/_4$. The minimum trough in the map was −2.0 e/Å^3 and was close to Sb(1).

For all three compounds, neutral atom scattering factors in the analytical form were taken from ref 24. All calculations were performed on a CDC 6400 computer with the series of programs in the XRAY71 and XRA76 systems,[21] the program SHELX,[23] and some local programs. The final atomic positional and thermal parameters for each compound are given in Table I and bond lengths and bond angles in Table II.

A view of the $As_3S_4^+$ and $As_3Se_4^+$ cations is given in Figure 1, and the packing in the structures of $(As_3S_4)(SbF_6)$ and $(As_3Se_4)(SbF_6)$ are shown in Figures 2 and 3. Final structure factor tables for all three compounds are available on request.[25]

Results and Discussion

Reactions of As_4S_4 and As–Se Alloys with Various Oxidizing Agents. The oxidation of As_4S_4 and As–Se alloys was studied by using PF_5, AsF_5, SbF_5, PCl_5, $SbCl_5$, $(S_8)(AsF_6)_2$, Cl_2, and Br_2 in SO_2 as solvent, except in the case of PCl_5 where methylene chloride was used.

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(23) Sheldrick, G. M. "SHELX. Program for Crystal Structure Determination"; University of Cambridge: Cambridge, England, 1976.

(24) "International Table for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1965.

(25) Supplementary material.

Table I. Final Atomic Positional (× 10^4) and Thermal Parameters (× 10^3)[a] with Standard Deviations in Parentheses

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
				(a) $[As_3S_4][MF_6^-]$, M = Sb, As					
Sb	3357.0 (4)	5119 (2)	2500 (0)	30.2 (5)	41.2 (5)	45.6 (6)	1.7 (4)	0	0
As	3354.4 (9)	5154 (3)	2500 (0)	32.1 (10)	39.5 (11)	46.0 (11)	4.6 (8)	0	0
As(1)	98.6 (6)	543 (2)	2500 (0)	32.7 (7)	37.8 (8)	55.3 (9)	5.6 (6)	0	0
	85.5 (9)	519 (3)	2500 (0)	29.7 (10)	33.1 (10)	50.0 (11)	6.4 (8)	0	0
As(2)	1700.0 (5)	55 (2)	1219 (1)	43.3 (6)	54.7 (7)	54.5 (7)	−1.5 (4)	12.8 (5)	−2.4 (6)
	1728.7 (7)	8 (3)	1197 (2)	41.0 (8)	54.3 (10)	58.0 (10)	−3.3 (6)	12.5 (7)	−3.3 (8)
S(1)	750 (1)	1486 (5)	743 (3)	58 (1)	50 (1)	38 (1)	2 (1)	−4 (1)	6 (1)
	758 (2)	1473 (6)	712 (4)	54 (2)	47 (2)	36 (2)	−1 (2)	−2 (2)	5 (2)
S(2)	1353 (2)	−3150 (7)	2500 (0)	30 (2)	28 (2)	79 (3)	4 (1)	0	0
	1377 (2)	−3255 (7)	2500 (0)	17 (3)	25 (2)	74 (3)	2 (2)	0	0
S(3)	361 (2)	−3103 (6)	2500 (0)	40 (2)	34 (2)	101 (3)	−3 (2)	0	0
	350 (2)	−3149 (8)	2500 (0)	35 (2)	27 (2)	102 (5)	−3 (2)	0	0
F(1)	3858 (6)	6482 (16)	1142 (10)	152 (8)	90 (6)	87 (6)	−13 (6)	46 (6)	22 (5)
	3850 (5)	6285 (18)	1235 (11)	93 (6)	81 (7)	71 (6)	−13 (6)	19 (6)	20 (6)
F(2)	2880 (7)	3722 (20)	1143 (15)	186 (11)	107 (8)	193 (12)	−13 (8)	−135 (10)	−25 (9)
	2875 (7)	4015 (23)	1235 (16)	129 (10)	103 (9)	131 (11)	−16 (8)	−71 (9)	−8 (9)
F(3)	3915 (6)	2695 (19)	2500 (0)	99 (8)	64 (7)	104 (9)	41 (6)	0	0
	3833 (7)	2778 (22)	2500 (0)	82 (9)	52 (8)	87 (10)	22 (7)	0	0
F(4)	2791 (7)	7517 (23)	2500 (0)	85 (8)	73 (8)	215 (18)	43 (7)	0	0
	2879 (8)	7517 (24)	2500 (0)	80 (10)	45 (8)	218 (22)	39 (7)	0	0
				(b) $[As_3Se_4^+][SbF_6^-]$					
Sb(1)	4978 (4)	2500	8324 (2)	53 (2)	63 (2)	34 (1)	0	1 (1)	0
Se(1)	−3495 (6)	2500	2228 (4)	44 (2)	102 (4)	31 (2)	0	−3 (2)	0
Se(2)	1461 (4)	647 (3)	3484 (3)	55 (2)	44 (2)	63 (2)	8 (1)	3 (1)	4 (1)
Se(3)	−3195 (6)	2500	4399 (3)	37 (2)	99 (3)	30 (2)	0	5 (1)	0
As(1)	564 (6)	2500	4819 (4)	45 (2)	59 (3)	36 (2)	0	−9 (2)	0
As(2)	−305 (5)	1207 (4)	1583 (3)	68 (2)	65 (2)	40 (1)	−2 (2)	7 (1)	−15 (1)

atom	x	y	z	U	atom	x	y	z	U
F(1)	3645 (40)	3863 (27)	7352 (23)	115 (8)	F(3)	−3612 (47)	1203 (32)	9261 (27)	143 (10)
F(2)	7283 (49)	2500	7233 (29)	92 (9)	F(4)	2849 (70)	2500	9513 (42)	149 (15)

[a] Anisotropic temperature factors U_{ij} are expressed in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + ... + 2klb^*c^*U_{23})]$.

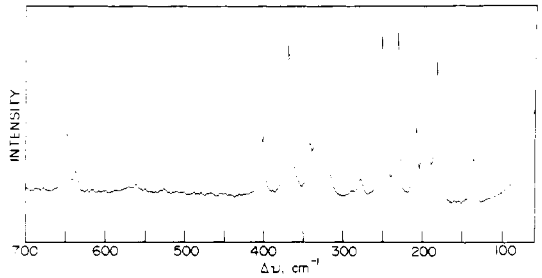

Figure 4. Raman spectrum of $(As_3S_4)(SbF_6)$.

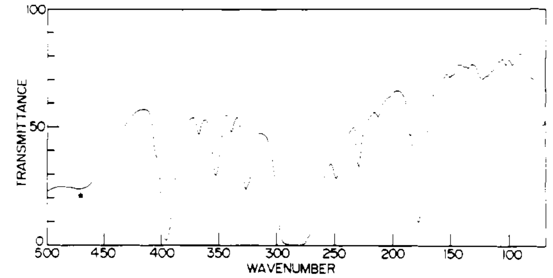

Figure 5. Infrared spectrum of $(As_3S_4)(SbF_6)$; asterisked peak is polyethylene.

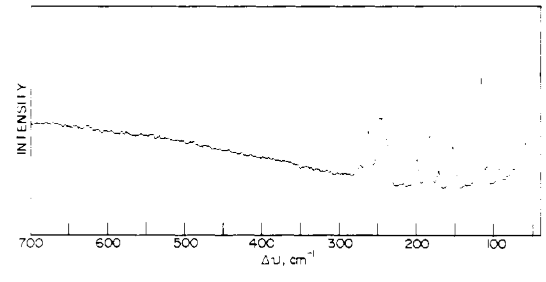

Figure 6. Raman spectrum of $(As_3Se_4)(AsF_6)$.

The reaction of PF_5 with β-As_4S_4 gave only α-As_4S_4, which seems to suggest that a very weak donor–acceptor complex is formed which is an intermediate in the rearrangement of the As_4S_4. The reactions of AsF_5 and SbF_5 with As_4S_4 in the molar ratio of 3:1 led to the preparation of the hexafluoroarsenate and hexafluoroantimonate salts of the $As_3S_4^+$ cation. These reactions gave a transient bright yellow solution which may be due to an intermediate product. However, if the SO_2 was quickly removed from the AsF_5/As_4S_4 reaction and a Raman spectrum run, only the spectra of $As_3S_4(AsF_6)$ and sulfur were observed. The UV spectrum of a 1:3 As_4S_4/AsF_5 mixture in SO_2 run immediately after warming of the mixture to room temperature showed only the characteristic absorption curve of the $As_3S_4^+$ cation. The use of larger amounts of AsF_5 produced the sulfur cations S_{19}^{2+} and S_8^{2+}.[26]

When $(S_8)(AsF_6)_2$ was used as the oxidant, the oxidation of the β-As_4S_4 was complete within about 1 min. This was evident by the rapid disappearance of the characteristic dark blue color of the $(S_8)(AsF_6)_2$. Although this oxidation was faster than that with arsenic and antimony pentafluorides, a large amount of contaminating elemental sulfur was deposited.

Since PCl_5 reacts with SO_2 to give $SOCl_2$ and $OPCl_3$, the reaction of As_4S_4 and PCl_5 was attempted in methylene chloride. No reaction was detected.

The reactions of $SbCl_5$, Cl_2, and Br_2 with As_4S_4 in SO_2 in the molar ratio of 3:1 produced AsX_3, S_2X_2 (X = Cl, Br), sulfur, and unreacted As_4S_4.

By use of a molar ratio of 3:1 or less the reactions of AsF_5 and SbF_5 with various As–Se alloys led to the preparation of

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(26) Burns, R. C.; Gillespie, R. J.; Sawyer, J. F. *Inorg. Chem.* **1980**, *19*, 1423 and references therein.

(27) Gordy, W. J. *J. Chem. Phys.* **1946**, *14*, 305.

Table II. Bond Distances (Å) and Bond Angles (Deg) with Standard Deviations in Parentheses[a]

	$[As_3S_4^+]$		$[As_3Se_4^+]$	
	$[SbF_6^-]$	$[AsF_6^-]$		
Cations				
Bond Lengths (Å)				
As(1)-S(1)	2.223(3)	2.230(4)	As(1)-Se(1)	2.354(4)
As(1)-S(3)	2.249(4)	2.239(5)	As(1)-Se(3)	2.362(5)
As(2)-As(2′)	2.461(2)	2.461(2)	As(2)-As(2′)	2.473(5)
As(2)-S(1)	2.173(3)	2.172(4)	As(2)-Se(1)	2.320(4)
As(2)-S(2)	2.388(3)	2.398(4)	As(2)-Se(2)	2.464(5)
S(2)-S(3)	2.030(5)	2.052(6)	Se(2)-Se(3)	2.310(5)
Bond Angles (Deg)				
S(1)-As(1)-S(1′)	98.83(11)	98.39(14)	Se(1)-As(1)-Se(1′)	97.65(17)
S(1)-As(1)-S(3)	95.96(10)	96.00(13)	Se(1)-As(1)-Se(3)	98.41(14)
S(1)-As(2)-As(2′)	102.17(8)	102.16(11)	Se(1)-As(2)-As(2′)	103.35(15)
S(1)-As(2)-S(2)	99.20(11)	99.80(14)	Se(1)-As(2)-Se(2)	103.19(15)
S(2)-As(2)-As(2′)	58.99(6)	59.12(7)	Se(2)-As(2)-As(2′)	59.87(11)
As(1)-S(1)-As(2)	106.00(12)	106.03(16)	As(1)-Se(1)-As(2)	103.68(16)
As(2)-S(2)-As(2′)	62.02(9)	61.75(12)	As(2)-Se(2)-As(2′)	60.26(14)
As(2)-S(2)-S(3)	106.60(15)	105.52(19)	As(2)-Se(2)-Se(3)	104.47(17)
As(1)-S(3)-S(2)	104.60(19)	105.40(24)	As(1)-Se(3)-Se(2)	102.86(20)
Anions				
Bond Lengths (Å)[b]				
M-F(1)	1.849(10) [1.904]	1.689(11) [1.725]	Sb-F(1)	1.84(3) [1.84]
-F(2)	1.831(14) [1.930]	1.673(14) [1.742]	-F(2)	1.89(3) [1.91]
-F(3)	1.847(12) [1.888]	1.702(14) [1.730]	-F(3)	1.80(3) [1.80]
-F(4)	1.845(14) [1.914]	1.693(15) [1.764]	-F(4)	1.87(5) [1.88]
Bond Angles (Deg)				
F(1)-M-F(2)	89.7(5)	89.5(6)	F(1)-Sb-F(2)	89(1)
-F(3)	90.3(4)	90.0(5)	-F(3)	178(1)
-F(4)	90.3(4)	90.0(5)	-F(4)	94(1)
-F(1′)	89.7(5)	90.0(5)	-F(1′)	90(1)
-F(2′)	178.5(5)	179.1(6)	-F(3′)	91(1)
F(2)-M-F(3)	88.3(5)	89.3(6)	F(2)-Sb-F(3)	89(1)

[a] Primed atoms are related to the corresponding unprimed atoms by reflection through the mirror plane. [b] Values in square brackets are thermally corrected bond lengths obtained by using a riding model.

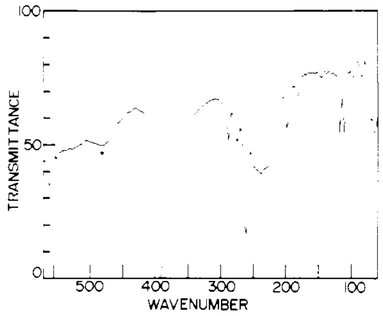

Figure 7. Infrared spectrum of $(As_3Se_4)(AsF_6)$; asterisked peak is polyethylene.

the corresponding hexafluoroarsenate (antimonate) salts of the $As_3Se_4^+$ cation. The use of a larger ratio of AsF_5 led to the formation of Se_8^{2+} and Se_4^{2+} as shown by their characteristic UV spectra.

Vibrational Spectra. The bands observed in the Raman and infrared spectra of $As_3S_4(AsF_6)$, $As_3S_4(SbF_6)$, $As_3Se_4(AsF_6)$, $As_3Se_4(SbF_6)$, α-As_4S_3, β-As_4S_3, and α-As_4S_4 are listed in Tables V and VI. Selected Raman and infrared spectra are also reproduced in Figures 4–7.

Since the crystallographic data has shown that both of the $As_3S_4^+$ and $As_3Se_4^+$ cations have C_s symmetry, 15 bands are expected for each species in both the infrared and Raman spectra. After assignment of the bands due to AsF_6^- and SbF_6^-, approximately this number of bands remains for each of the compounds. It was not possible, however, to make any detailed assignment of these bands. Such an assignment would have been aided by solution Raman spectra, but these could not be obtained because of the very low solubility of the compounds in a wide variety of solvents that were investigated. Although some solubility was found in SO_2, this was too small to enable Raman spectra to be obtained. As expected, the Raman spectra of $As_3S_4^+$ has many bands very close to those observed for α- and β-As_4S_3 and α-As_4S_4. The Raman spectrum of β-As_4S_3 agrees well with the previously reported infrared spectrum.[28] The previously reported band at 235 cm^{-1} in the Raman spectrum of α-As_4S_4[29,30] was not observed by us or by other workers.[10]

Discussion of Crystal Structures. The structure determinations show that the crystals of parts a and b consist of $As_3S_4^+$ cations and hexafluoroantimonate (arsenate) anions while those of part c contain the isostructural $As_3Se_4^+$ cation along with hexafluoroantimonate anions. The $As_3S_4^+$ and $As_3Se_4^+$ cations both have crystallographic mirror symmetry and overall C_s symmetry. The bond distances and angles of the $As_3S_4^+$ ion in the AsF_6^- and SbF_6^- salts show only very small differences. The structure of this cation can be considered to be derived from a tetrahedron of three arsenic atoms and one sulfur atom with three of its edges bridged by sulfur atoms. Similarly, the $As_3Se_4^+$ cation consists of a tetrahedron of three arsenic atoms and one selenium atom with three edges bridged by selenium atoms (Figure 1). This is a common structural type in cage compounds of the nonmetals and is found for the two forms of As_4S_3,[31,32] As_4Se_3,[33] P_4S_3,[34] P_4Se_3,[35] Sb_7^{3-},[36]

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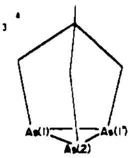
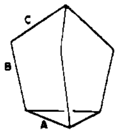
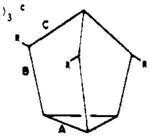
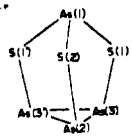
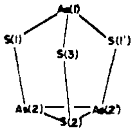
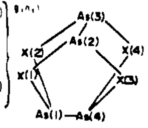
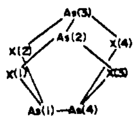
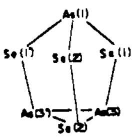
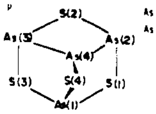
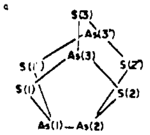
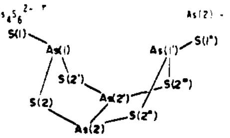
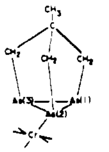
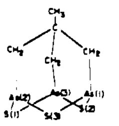
(28) Whitfield, H. J. *Aust. J. Chem.* **1971**, *24*, 697.
(29) Scheuermann, W.; Ritter, G. J. *Z. Naturforsch., A* **1969**, *24A*, 408.
(30) Forneris, R. *Am. Mineral.* **1969**, *54*, 1062.
(31) Whitfield, H. J. *J. Chem. Soc. A* **1970**, 1800.
(32) Whitfield, H. J. *J. Chem. Soc., Dalton Trans.* **1973**, 1737.
(33) Bastow, T. J.; Whitfield, H. J. *J. Chem. Soc., Dalton Trans.* **1977**, 959.
(34) Leung, Y. C.; Waser, J.; van Houten, S.; Vos, A.; Wiegers, G. A.; Wiebenga, E. H. *Acta Crystallogr.* **1957**, *10*, 574.

Table III. Arsenic–Arsenic, Arsenic–Sulfur, and Arsenic–Selenium Bond Lengths in Various Cluster Compounds

Compound		As-As	As-S(Se)
$CH_3C(CH_2As)_3$ [a]		As(1) - As(2) 2.405(5) As(1) - As(1') 2.422(5)	
As_7^{3-} [b]		A: 2.498 B: 2.399 C: 2.432	
$As_7(SiMe_3)_3$ [c]		A: 2.444(2) B: 2.427(2) C: 2.407(1)	
αAs_4S_3 [d,e]		As(2) - As(3) 2.445(6) As(3) - As(3') 2.450(10)	As(1) - S(1) 2.220(9) As(1) - S(2) 2.216(11) As(2) - S(2) 2.213(12) As(3) - S(1) 2.200(3)
βAs_4S_3		As(2) - As(3) 2.460(7) As(3) - As(3') 2.480(7)	As(1) - S(1) 2.230(8) As(1) - S(2) 2.234(16) As(2) - S(2) 2.221(12) As(3) - S(1) 2.218(10)
$As_3S_4^+$ [f]		As(2) - As(2') 2.459(2)	As(1) - S(1) 2.223(3) As(1) - S(3) 2.249(4) As(2) - S(1) 2.173(3) As(2) - S(2) 2.388(3)
$\alpha(As_4S_4)$ [g,h,i]	 X = S, Se	As(1) - As(4) 2.593(6) (≡ As(2) - As(3))	As(1) - S(1) 2.252(9) As(1) - S(3) 2.241(9) As(2) - S(2) 2.241(9) As(2') - S(3') 2.238(9)
$\beta(As_4S_4)$		As(1) - As(4) 2.571(1) As(2) - As(3) 2.566(1)	As(1) - S(1) 2.242(2) As(1) - S(2) 2.232(2) As(2) - S(1) 2.243(2) As(2) - S(3) 2.238(2) As(3) - S(2) 2.247(2) As(3) - S(4) 2.238(2) As(4) - S(3) 2.231(2) As(4) - S(4) 2.228(2)
As_2S_3 [j] (orpiment)			As(1) - S(1) 2.292(5) As(1) - S(2) 2.270(5) As(1) - S(3) 2.289(5) As(2) - S(1) 2.243(5) As(2) - S(2) 2.293(5) As(2) - S(3') 2.308(5)
As_4Se_4 [k l m n]	 X = S, Se	As(1) - As(4) 2.571(3) As(2) - As(3) 2.560(3)	As(1) - Se(1) 2.393(3) As(1) - Se(2) 2.381(3) As(2) - Se(1) 2.385(3) As(2) - Se(3) 2.384(3) As(3) - Se(2) 2.387(3) As(3) - Se(4) 2.386(3) As(4) - Se(3) 2.375(3) As(4) - Se(4) 2.378(3)
As_2Se_3 [o]			As(1) - Se(1) 2.37 As(1) - Se(2) 2.44 As(1) - Se(3) 2.56 As(2) - Se(1) 2.32 As(2) - Se(2) 2.37 As(2) - Se(3) 2.36
$As_3Se_4^+$ [f]		As(2) - As(2') 2.473(5)	As(1) - Se(1) 2.354(4) As(1) - Se(3) 2.362(5) As(2) - Se(1) 2.320(4) As(2) - Se(2) 2.464(5)
$As_4S_4(II)$ [p]		As(2) - As(4) 2.519(3) As(3) - As(4) 2.550(3)	As(1) - S(1) 2.263(4) As(1) - S(3) 2.235(4) As(1) - S(4) 2.260(4) As(2) - S(1) 2.226(4) As(2) - S(2) 2.257(4) As(3) - S(2) 2.269(4) As(3) - S(3) 2.240(4) As(4) - S(4) 2.199(4)
As_4S_5 [q]		As(1) - As(2) 2.546(11)	As(1) - S(1) 2.229(10) As(2) - S(2) 2.254(10) As(3) - S(1) 2.230(11) As(3) - S(2) 2.241(11) As(3) - S(3) 2.268(8)
$As_4S_6^{2-}$ [r]		As(2) - As(2') 2.579(9)	As(1) - S(1) 2.302(11) As(1) - S(2) 2.183(10) As(2) - S(2) 2.231(8)
$MeC(CH_2As)_3Cr(CO)_5$ [s]		As(1) - As(2) 2.406(2) - As(3) 2.462(2) As(2) - As(3) 2.408(2)	
$MeC(CH_2AsS)_3$ [t]			As(1) - S(2) 2.237(3) - S(3) 2.242(3) As(2) - S(3) 2.250(3) - S(1) 2.243(3) As(3) - S(1) 2.242(3) - S(2) 2.239(3)

[a] Reference 39. [b] Reference 37. [c] Reference 60. [d] Reference 31. [e] Reference 32. [f] This work. [g] Reference 7. [h] Reference 9. [i] Reference 11. [j] References 11 and 16. [k] Reference 12. [l] Reference 13. [m] Reference 14. [n] Reference 15. [o] References 11 and 16. [p] Reference 10. [q] Reference 61. [r] Reference 15. [s] Reference 40. [t] Reference 59.

As_7^{3-},[37] and P_7^{3-} [38] and in the organocyclotriarsane 4-methyl-1,2,6-triarsatricyclo[2.2.1.0^{2,6}]heptane.[39] However, this is the first time that the triangular base of this structural type has been found to contain more than one kind of atom.

The arsenic–arsenic bond length in this base is 2.461 (2) Å for the $As_3S_4^+$ cation and 2.473 (5) Å for the $As_3Se_4^+$ cation and is comparable to the arsenic–arsenic bond lengths in the base of the As_7^{3-} [37] and α- and β-As_4S_3 structures[31,32] (Table III). In the organocyclotriarsane structure the As–As bonds in the base are noticeably shorter at 2.41–2.42 Å than that in $As_3S_4^+$, and it has been suggested that these bonds have some multiple bond character.[39] It should also be noted in this context that this compound has been found to form a complex with $Cr(CO)_5$ in which one of the basal arsenic atoms is coordinated to the chromium with As–As distances in this structure of 2.406 (2), 2.408 (2), and 2.462 (2) Å. It is interesting to note that the longest distance is between the two As atoms not coordinated to the chromium.[40] The As–As distances in the structures of As_4S_4, As_4S_5, and the anion $As_4S_6^{2-}$, which are based on the cuneane polyhedron, are, however, significantly longer at 2.55–2.59 Å.

In addition to those given in Table III, several other examples of arsenic–arsenic bonds have been characterized crystallographically. Of particular note is the very short As–As bond of 2.343 (7) Å in the complex $(CO)_4Mo(Me_2P-As(Me)-As(Me)-PMe_2)$.[41] Comparable short As–As bonds of 2.372, 2.273, 2.273, and 2.281 Å have been observed in $As_3Co(CO)_3$, $As_2Co_2(CO)_6$, and two μ_2-As_2Co_2 cluster compounds, respectively. However, these structures are based on tetrahedra of arsenic and cobalt atoms so that the actual bonds in these structures are expected to be "bent" and therefore shorter than a normal single bond.[42] Finally, the arsenic–arsenic bond lengths in pentameric arsenomethane, arsenobenzene $[PhAs]_6$, tetrameric $[AsCF_3]_4$, and the complex *cyclo*-1,4-bis(tetracarbonylchromium)-2,3,5,6-tetrakis(dimethylarsenic) are 2.428, 2.456, 2.454, and 2.442 Å, respec-

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Table IV. Selected Intra- and Interionic Contacts (Å) and Some Related Angles (Deg)

For $(As_3S_4)(SbF_6)$ and $(As_3S_4)(AsF_6)$[a,b]

	SbF_6	AsF_6		SbF_6	AsF_6
		Intraionic			
As(1)···As(2)	3.511 (2)	3.517 (2)	S(1)···S(1′)	3.817 (4)	3.745 (5)
As(1)···S(2)	3.389 (3)	3.415 (4)	S(1)···S(3)	3.320 (4)	3.321 (5)
As(2)···S(3)	3.550 (4)	3.549 (5)	S(1)···S(2)	3.475 (4)	3.498 (5)
As(2)···S(1′)	3.610 (3)	3.609 (4)			
		Interionic (As···F < 3.35 Å, S···F < 3.20 Å)[a]			
As(1)···F(3^{I})	3.107 (12)	3.174 (14)	S(1)–As(1)···F(3^{I})	128.7 (1)	129.1 (1)
			S(3)–As(1)···F(3^{I})	65.0 (2)	65.6 (3)
S(3)···F(3^{I})	2.968 (13)	3.036 (15)	As(1)–S(3)···F(3^{I})	71.6 (2)	72.7 (3)
			S(2)–S(3)···F(3^{I})	176.1 (3)	177.6 (4)
			As(1)···F(3^{I})···S(3)	43.4 (2)	42.2 (2)
As(2)···F(4^{II})	2.970 (12)	2.994 (14)	S(1)–As(2)···F(4^{II})	164.1 (2)	165.4 (2)
			As(2′)–As(2)···F(4^{II})	65.5 (1)	65.7 (1)
			As(2)···F(4^{II})···As(2′)	48.9 (2)	48.5 (2)
S(2)···F(4^{II})	2.965 (13)	3.032 (16)	S(3)–S(2)···F(4^{II})	171.6 (3)	169.6 (4)
			As(2)–S(2)···F(4^{II})	66.4 (4)	65.7 (2)
			As(2)···F(4^{II})···S(2)	47.5 (2)	46.9 (2)
			As(1)···F(3^{I})–M^{I}	166.9 (6)	162.2 (7)
			S(3)···F(3^{I})–M^{I}	123.5 (5)	120.0 (6)
			As(2)···F(4^{II})–M^{II}	150.7 (4)	147.0 (5)
			S(2)···F(4^{II})–M^{II}	121.4 (6)	115.4 (7)

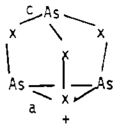
For $(As_3Se_4)(SbF_6)$[b]

			Intraionic				
As(1)···As(2)	3.676 (5)	As(2)···Se(3)	3.775 (5)	Se(1)···Se(1^{III})	3.544 (4)	Se(1)···Se(2)	3.750 (5)
As(1)···Se(2)	3.653 (5)	As(2)···Se(1^{III})	3.761 (4)	Se(1)···Se(3)	3.570 (4)		
			Interionic (Se···F and As···F < 3.5 Å)				
As(1)···F(2^{IV})	3.36 (3)	Se(1)–As(1)···F(2^{III})	129.2 (2)	Se(1)···F(2^{VII})	3.21 (11)	As(1)–Se(1)···F(2^{VII})	156.4 (6)
		Se(3)–As(1)···F(2)	60.8 (5)			As(2)–Se(1)···F(2^{VII})	96.9 (6)
As(2)···F(3^{V})	3.14 (3)	Se(1)–As(2)···F(2)	162.2 (6)	Se(2)···F(3^{V})	3.39 (3)	Se(3)–Se(2)···F(3^{V})	158.3 (5)
		Se(2)–As(2)···F(3)	73.3 (6)			As(2)–Se(2)···F(3^{V})	62.6 (5)
		As(2^{III})–As(2)···F(3)	67.7 (3)	Se(3)···F(2^{IV})	3.02 (3)	As(1)–Se(3)···F(2^{IV})	76.1 (6)
As(2)···F(4^{V})	3.26 (4)	As(2^{III})–As(2)···F(4)	67.7 (3)			Se(2)–Se(3)···F(2^{IV})	179.0 (6)
		Se(2)–As(2)···F(4)	121.1 (5)				
		Se(1)–As(2)···F(4)	113.6 (8)			As(2)···F(1^{VI})–Sb^{VI}	124.4 (11)
As(2)···F(1^{VI})	3.29 (3)	As(2^{III})–As(2)···F(1)	132.9 (5)			Se(3)···F(2^{IV})–Sb^{IV}	124.9 (13)
		Se(1)–As(2)···F(1)	79.8 (4)			Se(1)···F(2^{VII})–Sb^{VII}	110.3 (5)
		Se(2)–As(2)···F(1)	73.5 (5)			As(2)···F(3^{V})–Sb^{V}	136.2 (14)
						Se(2)···F(3^{V})–Sb^{V}	104.7 (12)
						As(2)···F(4^{V})–Sb^{V}	157.3 (5)

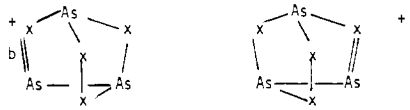
[a] N.B. no contacts to S(1). [b] I, $-\frac{1}{2} + x, -y, z$; II, $x, -1 + y, z$; III, $x, \frac{1}{2} - y, z$; IV, $-1 + x, y, z$; V, $x, y, -1 + z$; VI, $-x, -\frac{1}{2} + y, 1 - z$; VII, $1 - x, -y, 1 - z$.

tively.[43,44] All these distances are shorter than the As–As distances of 2.51 Å in metallic arsenic.[43] It appears, therefore, that the As–As bond in the triangular base of the $As_3S_4^+$ and $As_3Se_4^+$ cations is somewhat longer than most As–As bonds. This is somewhat surprising in view of the fact that these bonds are usually regarded as "bent" bonds.

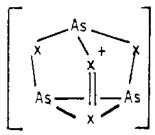
There are three independent arsenic–sulfur bonds in the $As_3S_4^+$ cation. The As–S bond in the base of the cation is longest at 2.388 (3) Å in the hexafluoroantimonate salt and 2.398 (4) Å in the hexafluoroarsenate salt. Intermediate in length are the two As–S bonds to As(1) which have an average length of 2.235 Å. [In the hexafluoroantimonate salt, however, these two bonds, As(1)–S(1) [2.223 (3) Å] and As(1)–S(3) [2.249 (4) Å], have significantly different lengths.] Finally, the distance As(2)–S(1) is the shortest at 2.173 (3) Å. The ordering of the arsenic sulfur distances in the $As_3S_4^+$ cation is the same as that found for the distances in the homopolyatomic analogues P_7^{3-}, As_7^{3-}, and Sb_7^{3-}. A good compilation of arsenic–sulfur bond lengths in a variety of compounds has been given by Draeger.[45] For three-coordinate arsenic, As–S distances range from 2.18 to 2.35 Å so that the distances As(2)–S(1) and As(2)–S(2) in the $As_3S_4^+$ cation are significantly shorter and longer, respectively, than most As–S distances. In α- and β-As_4S_4 and its isomeric form II the As–S bonds have essentially "normal" lengths in the range 2.199–2.269 Å.[9-11,16]



(I)



(II)



(X = S, Se)

(III)

The abnormally long and short As–S bonds can be accounted for if it is assumed that there is a tendency for the positive charge on the basal S atom in I to be delocalized onto the other nonadjacent S atoms. This would cause a lengthening of the As–S bonds in the triangular base and a shortening of the type b As–S bonds. Delocalization of charge onto the adjacent S atom can only occur as in III with the generation of a 4-valent S atom, and it is not unreasonable to assume

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Table V. Infrared and Raman Spectra (cm^{-1}) of Some Arsenic-Sulfur Compounds

$As_3S_4(AsF_6)$		$As_3S_4(SbF_6)$			β-As_4S_3		α-As_4S_3	α-As_4S_4	
Raman	IR	Raman	IR	assignments	Raman	IR[28]	Raman	Raman	IR[30]
682 (9)	684 s	648 (20)	653 s	ν_1, AsF_6^-, SbF_6^-					
670 (7)	671 s	637 (7)	633 s	ν_3, AsF_6^-, SbF_6^-					
		570 (2)							
561 (2)	561 m	561 (3)	560 w	ν_2, AsF_6^-, SbF_6					
		407 (6)	407 sh						
406 (10)		402 (21)	398 vs						
			388 sh				375 (5)	375 (5)	375 s
368 (26)									
364 (27)	372 sh	369 (54)	370 m		368 (10)	370 vs	367 (5)	368 (8)	369 s
	351 m		355 s		348 (26)		353 (18)	355 (100)	361 m
340 (16)	341 sh	344 (19)	342 m		340 (8)	340 vs	336 (7)	344 (30)	341 s
								340 (21)	
329 (71)	329 m	329 (74)	328 s					328 (4)	329 sh
389 (10)	399 vs	290 (3)	285	ν_4, AsF_6^-, SbF_6^-					
				ν_5, AsF_6^-, SbF_6^-					
	391 vs	278 (7)			271 (100)	273 m	272 (100)		
250 (64)	250 w	250 (59)	250 s				237 (2)		
229 (65)	231 w	231 (60)	230 s				231 (1)	224 (26)	225 s
					221 (16)	217 vw	214 (13)	221 (55)	
	214 vw		214 w		211 (31)		210 (28)	212 (3)	212 m
207 (24)		207 (26)	205 w		203 (28)	202 w	206 (33)	210 (1)	210 m
							204 (19)		
197 (100)		197 (100)			197 (17)		202 (14)	193 (77)	193 m
190 sh	186 sh		186 sh		184 (14)	185 w	182 (6)	183 (85)	183 m
182 (40)	182 s								
		181 (49)	179 vs		178 (35)	177 s	177 (14)		
177 (14)	178 s				174 (15)	173 s	171 (17)	172 (5)	169 m
							169 (18)	166 (5)	
							152 (7)		
136 (17)		135 (18)						143 (12)	141 vw
131 (2)									
					120 (1)		121 (7)	124 (2)	
					70 (0.5)				
								66 (7)	
							57 (6)	60 (22)	
					53 (5)			55 (17)	
					50 (3)			50 (15)	
							43 (48)	46 (47)	
					42 (4)			40 (4)	
					39 (3)				
					36 (5)		32 (15)		
					33 (6)		29 (14)		
					28 (13)		23 (5)	27 (38)	
					17 (3)				

Table VI. Infrared and Raman Spectra (cm^{-1}) for $As_3Se_4(AsF_6)$ and $As_3Se_4(SbF_6)$

$As_3Se_4(AsF_6)$		$As_3Se_4(SbF_6)$		
Raman	IR	Raman	IR	assignments
	681 s		654 s	ν_1, MF_6^-
	670 s		639 sh	ν_3, MF_6^-
	562 m		564 vw	ν_2, MF_6^-
	395 vs		287 vs	ν_4, ν_5, MF_6^-
	288 m		278 sh	
272 (11)	275 m	271 (6)	275 sh	
263 (44)	261 s	261 (45)	260 s	
247 (60)	249 sh	247 (55)	248 sh	
244 (58)	244 m	243 (53)	243 sh	
238 (40)	237 sh	240 (47)	237 m	
199 (25)	199 m	199 (30)	199 m	
183 (47)	182 m	183 (40)	176 m	
171 (16)		172 (32)		
153 (39)		152 (39)	151 w	
148 (11)	146 vw	144 (11)		
115 (100)	118 m	115 (100)	117 m	
109 (16)	111 m	109 (32)	110 m	
93 (15)	96 w	93 (13)	92 w	
59 (9)		60 (60)	63	
40 sh				

that this structure is not of great importance. This is consistent with the S–S bond length of 2.04 Å, which is very similar to the bond lengths of 2.048[46] and 2.04 Å[47] in S_8 and S_8^{2+}, respectively. The bonds in these latter molecules are always regarded as "normal" single bonds although it should be emphasized that there is no conclusive evidence that this is the case. For comparison the bond length in S_4^{2+}, which nominally has a bond order of 1.25, is 2.014 (3) Å.[48] Indeed, the relationships between bond length and bond order for bonds between heavy atoms such as sulfur and arsenic are very uncertain. Even in the neutral molecule As_4S_3 the As–As bonds in the triangular base are longer than "normal", and no satisfactory explanation for this has been given. It would seem that a given bond, e.g., an As–As single bond, can vary considerably in length with the nature and arrangement of the attached atoms.

Similarly, in the $As_3Se_4^+$ cation there are again three different arsenic–selenium bond lengths; that in the base is longest at 2.464 (5) Å, the two bonds to As(1) are intermediate in length (average of 2.358 (5) Å), and finally As(2)–Se(1) is shortest at 2.320 (4) Å. The ordering of the lengths of these bonds in terms of position in the structure is the same as in the $As_3S_4^+$ cation, although the differences between the three

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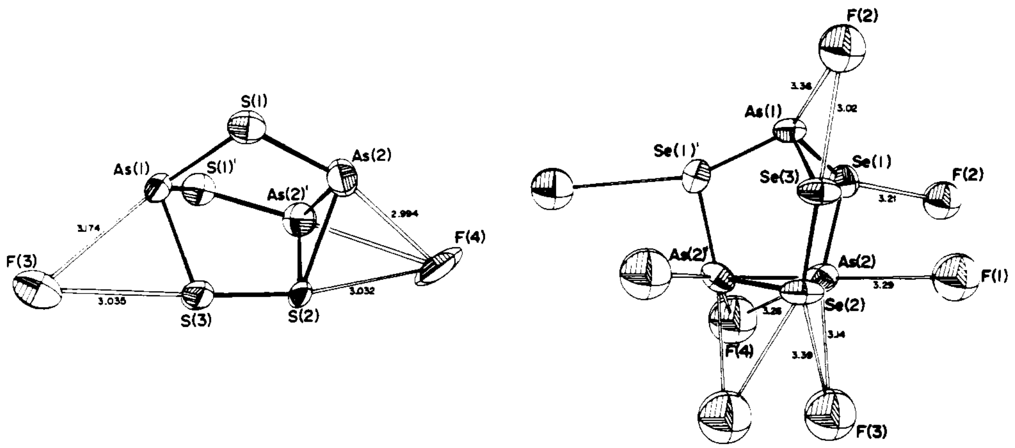

Figure 8. Views of the $As_3S_4^+$ and $As_3Se_4^+$ cations showing some interionic contact distances less than the van der Waals distances.

As–Se bond lengths in $As_3Se_4^+$ is less than those between the analogous As–S bond lengths in the $As_3S_4^+$ cation.

The lengths of these As–Se bond lengths may be compared to the sum of the covalent radii for As and Se of 2.38 Å and the average As–Se distances of 2.384 (5) Å in As_4Se_4[11–14] and the As–Se distances of 2.32–2.56 Å calculated for polycrystalline As_2Se_3 by a Monte Carlo fitting technique.[11] Apart from these values, the few other As–Se distances that have been reported in the literature are for compounds containing $AsSe_3^{3-}$ and related ions; for example, the As–Se distance in Ag_3AsSe_3 is 2.411 Å.[49]

The unique Se–Se bond in the $As_3Se_4^+$ cation, of length 2.310 (5) Å, is slightly shorter than the Se–Se bonds in several forms of cyclooctaselenium (2.335 Å)[50] and the bonds in dimorpholinodiselane [2.346 (1) Å] and dimorpholinotriselane [2.352 (1) Å][51] which may be regarded as "normal" single bonds. However, this bond is still considerably longer than the Se–Se bonds of 2.283 (4) and 2.236 (8) Å observed for the Se_4^{2+} cation which, on the basis of simple valence bond and MO treatments, has a bond order of 1.25.[52,53] It has been noted previously[54] that, in compounds containing chains of sulfur and selenium atoms, adjacent bonds can interact to produce an alternation in bond lengths along the chain. This effect is more pronounced when one of the S or Se atoms is positively charged as in the Se_{10}^{2+} cation.[54] The bond adjacent to the positive charge is always observed to be long, and then the bonds are alternately short and long, the effect diminishing with increasing distance from the positive charge. A similar effect is noted in the $As_3S_4^+$ and $As_3Se_4^+$ cations.

The $As_3Se_4^+$ ion has a more regular structure than that of $As_3S_4^+$. The angles in the triangular base are all equal to 60° in $As_3Se_4^+$ whereas in $As_3S_4^+$ there are two angles of 59° and one of 62°. All the other bond angles are slightly smaller than 109.5°, and those at S are slightly larger than those at Se. That the $As_3S_4^+$ cation is more distorted than the $As_3Se_4^+$ cation can be readily seen by comparing some internal contact distances. Thus in $As_3Se_4^+$ the contacts As(1)⋯As(2) and As(1)⋯Se(2) are very similar at 3.676 (5) and 3.653 (5) Å, respectively, while in the two $As_3S_4^+$ cations the As(1)⋯As(2) and As(1)⋯S(2) contacts are respectively 3.511 (2) and 3.389 (3) Å for the hexafluoroantimonate salt and 3.517 (2) and 3.415 (4) Å for the hexafluoroarsenate salt. The significant difference in the two As(1)⋯S(2) contacts in these two salts may be related to the different strengths of several short interionic contacts which are significantly less than the neutral-atom van der Waals distances (As⋯F ≤ 3.35 Å, S⋯F ≤ 3.20 Å).

In the structures of $(As_3S_4)(AsF_6)$ and $(As_3S_4)(SbF_6)$ there are three contacts of note (Figure 8, Table IV). In particular the fluorine atom F(4) forms short contacts of approximately the same length to all three atoms in the base of the cation. In the hexafluoroantimonate structure the contacts, of lengths 2.940 (12) [As(2)⋯F(4′) ×2] and 2.965 (13) Å [S(2)⋯F(4′)], are 0.41 and 0.23 Å less than the van der Waals limits. In the hexafluoroarsenate structure the corresponding contacts are of lengths 2.994 (14) (×2) and 3.032 (16) Å, or 0.36 and 0.17 Å less than the van der Waals limits. Furthermore, these As⋯F and S⋯F contacts are approximately colinear with the S(1)–As(2) and S(3)–S(2) bonds [for example, the S(1)–As(2)⋯F(4′) and S(3)–S(2)⋯F(4′) angles are 164.1 (2) and 171.6 (3)°, respectively, for the hexafluoroantimonate salt]. The related Sb(As)–F(4)⋯As(2) and Sb(As)–F(4)⋯S(2) angles are 150° and 121°, respectively.

The remaining short interionic contacts in the $As_3S_4^+$ structure involve atom F(3) of a second SbF_6^- anion which appears to be bridging the As(1)–S(3) bond of the cation. These contacts in the hexafluoroantimonate structure are of lengths 3.107 (12) [As(1)⋯F(3″)] and 2.968 (13) Å [S(3)⋯F(3″)], ca. 0.24 Å less than the respective van der Waals limits. [In the AsF_6^- structure the analogous contacts are of lengths 3.174 (14) and 3.036 (15) Å.] Of note also is the S(2)–S(3)⋯F(3) angle which is 176.1 (3)° in the SbF_6^- salt and 177.6 (4)° in the AsF_6^- salt. That these contacts are approximately colinear with primary bonds in the cation suggests that they are weak charge-transfer interactions involving transfer of electron density on fluorine to σ^* orbitals associated with the σ bonding orbitals of the cation. In $(As_3S_4)(SbF_6)$ and $(As_3S_4)(AsF_6)$ the average SbF and AsF bond lengths in the anions are 1.843 (13) and 1.689 (13) Å, respectively [1.909 and 1.740 Å after application of a riding correction to the bond lengths by using the local program STREP], and are close to the distances of 1.844 (7) and 1.719 (3) Å observed in the crystal structures of $K(SbF_6)$[55] and $K(AsF_6)$,[56] respectively. As the Sb(As)–F(3) and Sb(As)–F(4) bond lengths are not significantly different from the other Sb–F and As–F bond lengths, it appears that charge transfer to the cations is relatively weak. Cis and trans angles in the hexafluoroarsenate and hexafluoroantimonate anions of the $As_3S_4^+$ structures also do not deviate significantly from 90° and 180°. As a result

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of the interactions of fluorine atoms in the anions with the apex and base of the $As_3S_4{}^+$ cations, the packing of these compounds consists of rows of alternating anions and cations along *a* (Figure 2).

In $As_3Se_4{}^+SbF_6{}^-$ the positions of the fluorine atoms in the hexafluoroantimonate anion are not as well defined as those in the anions with the $As_3S_4{}^+$ cation so that some of the contact distances in the former structure are not as reliable. However, from the change in the symmetry of the structure and the geometry of the contacts listed in Table IV it may be noted that there are some subtle differences in the contacts to the $As_3Se_4{}^+$ cation from those in the $As_3S_4{}^+$ cation (Figure 8). In particular, the three atoms in the base of the cation are involved in three unsymmetrical fluorine bridges to the fluorine atoms in two anions. These contacts are weaker than those to the $As_3S_4{}^+$ cations and are close to the van der Waals limits [As(2)···F(3) = 3.14 Å, Se(2)···F(3) = 3.39 Å, and As(2)···F(4) = 3.26 Å (×2)]. It is also worthy of note that the angles Se(1)–As(2)···F(3) and Se(3)–Se(2)···F(3) are 162° and 158°, respectively. The shortest interionic contact in the $As_3Se_4(SbF_6)$ structure of length 3.02 Å is to the bridging selenium atom Se(3) and is collinear with the Se(2)–Se(3) primary bond [Se(2)–Se(3)···F(2) is 179.0 (6)°]. A similar contact to the other bridging selenium atom Se(1) is, however, poorly defined [Se(1)···F(2) = 3.21 (11) Å, As(1)–Se(1)···F(2) = 156°]. Another feature of the contacts to the $As_3Se_4{}^+$ cation is the absence of any short contacts to the apical arsenic atom As(1). The short anion–cation contacts observed in the present structures are analogous to those observed in the sulfur–nitrogen cations $S_3N_2{}^{+\cdot}$, $S_6N_4{}^{2+}$, and $S_4N_3{}^+$ (all of which principally involve the S–S bond in each ring[57]), the mixed S–Se–N cation $Se_4S_2N_4{}^{2+}$ (involving the diselenide bond),[58] and the homo- and heteropolyatomic cations of the group 6 elements. These charge-transfer contacts usually reflect the charge distribution in the cation and presumably play a small but nonetheless significant role in the stabilization of the cations involved.

The average antimony–fluorine bond length in the anion of $(As_3Se_4)(SbF_6)$ is 1.85 (4) Å which is similar to the bond length in $K(SbF_6)$;[55] cis and trans angles in this anion deviate by up to 5° from 90° to 180°. A view of the packing of $(As_4Se_4)(SbF_6)$ is given in Figure 3.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

Registry No. $As_3S_4(AsF_6)$, 77846-58-3; $As_3S_4(SbF_6)$, 77825-63-9; $As_3Se_4(AsF_6)$, 77825-65-1; $As_3Se_4(SbF_6)$, 77825-66-2; α-As_4S_3, 12512-13-9; α-As_4S_4, 12279-90-2; AsF_5, 7784-36-3; SbF_5, 7783-70-2; $S_8(AsF_6)_2$, 33248-05-4.

Supplementary Material Available: Listings of structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

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Transition-Metal Complexes of Poly(1-pyrazolyl)borate Ligands. 2.[1] Crystal and Molecular Structure of (Hydrotris(3,5-dimethyl-1-pyrazolyl)borato)dicarbonyl(*p*-chlorobenzenethiolato)molybdenum(II) Acetone Solvate

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Received November 24, 1980

Crystals of the acetone solvate of $HB(Me_2pz)_3Mo(CO)_2SC_6H_4Cl$, a formally 16-electron Mo(II) complex, are triclinic, space group $P\bar{1}$, with two formula units in a unit cell of dimensions a = 10.355 (1) Å, b = 12.100 (1) Å, c = 13.433 (1) Å, α = 103.43 (1)°, β = 94.31 (1)°, and γ = 113.74 (1)°. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to a final R value of 0.038 for 3247 reflections with $I > 3.0\sigma(I)$. The molybdenum atom has slightly distorted octahedral coordination with the pyrazolylborate ligand occupying three *facial* sites. The Mo–S distance 2.305 (1) Å is indicative of considerable double-bond character; other dimensions include Mo–C = 1.969 and 1.977 (3) Å, Mo–N(trans to S) = 2.169 Å, and Mo–N(trans to CO) = 2.220 and 2.221 (1) Å. The acetone of solvation is present with partial occupancy and lies in cavities between the molecules of the complex.

Introduction

An interesting aspect of the chemistry of poly(1-pyrazolyl)borate ligands[3] is that the introduction of appropriate substituents onto the carbon atoms of the pyrazole rings can effect major changes in the electronic characteristics and steric demand of the ligands while leaving the symmetry unchanged.[4] In the earliest investigation of this phenomenon Trofimenko demonstrated that the carbonyl anion $HB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_3{}^-$ reacted in an anomalous fashion with allyl halides,[5] arenediazonium cations,[4] and arenesulfonyl

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