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Hg_3AsE_4X (E = S, Se; X = Cl, Br, I), a Family of Isotypic Compounds with an Acentric, Layered Structure

Johannes Beck,* Sylvia Hedderich, and Klaus Köllisch

Institut für Anorganische Chemie der Rheinischen Friedrich-Wilhelms-Universität,
Gerhard-Domagk Strasse 1, 53121 Bonn, Germany

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Four isotypic compounds Hg_3AsS_4Cl, Hg_3AsS_4Br, Hg_3AsSe_4Br, and Hg_3AsSe_4I were synthesized in the quaternary system mercury/arsenic/chalcogen/halogen by vapor transport reactions from As, Hg(II) halide, Hg(II) chalcogenide, and elemental chalcogen at temperatures between 250 and 310 °C. Their structures were solved by single-crystal X-ray diffraction analyses. The compounds crystallize in the hexagonal system with the acentric space group $P6_3mc$ and the following lattice parameters: $a = 7.431(5)$ Å, $c = 9.003(8)$ Å for Hg_3AsS_4Cl, $a = 7.430(5)$ Å, $c = 9.364(5)$ Å for Hg_3AsS_4Br, $a = 7.707(8)$ Å, $c = 9.47(2)$ Å for Hg_3AsSe_4Br, and $a = 7.6902(7)$ Å, $c = 9.968(1)$ Å for Hg_3AsSe_4I, and $Z = 2$. All compounds are air-stable and form hexagonal prismatic crystals. The colors vary from yellow (Hg_3AsS_4Cl) to red (Hg_3AsSe_4I). The structures consist of ${}^{2}_{\infty}[Hg_3AsE_4]^+$ polycationic layers built of six-membered Hg_3E_3 and Hg_2AsE_3 rings in chair and boat conformations. Alternatively, the structure of the layers can be described as composed of $[AsE_3]^{3-}$ and $[Hg_3E]^{4+}$ ions both forming regular trigonal pyramids. The halide ions are intercalated between the layers and have only weak bonds to the mercury atoms. The acentricity of the structures was confirmed through SHG measurements using IR laser radiation ($\lambda = 1064$ nm).

Introduction

In the ternary system group 12 metal/pentele/halogen, phases with different compositions have been synthesized and structurally characterized. Often, these compounds contain polyanionic parts built by pentelide ions. For example, phases of the composition M_2YX_2 (M = Cd, Hg; Y = P, As, Sb; X = Cl, Br)[1] or $M_7Y_4X_6$ (M = Cd, Hg; Y = P,Sb; X = Cl, Br)[2] contain Y_2^{4-} dumbbells which are coordinated octahedrally by cadmium or mercury atoms. By the interconnection of these M_6Y_2 units, three-dimensional cationic networks are formed. In the compounds M_2Y_3X (M = Cd, Hg; Y = P, As; X = Cl, Br, I)[3] another polyanionic structure is realized. The pentelide ions build infinite ${}^{1}_{\infty}[Y^-]$ chains that are surrounded by metal atoms. In this way, a tunnel-like structure with intercalated halide ions is formed. Another ternary system, mercury/chalcogen/halogen, was the subject of several structural investigations. Here, the cubic compounds $Hg_3E_2X_2$ (E = S, Se, Te; X = Cl, Br, I)[4] are dominating. Their structural characteristics are trigonal Hg_3E pyramids that are interconnected by edges to form a three-dimensional network. Holes in this cationic network are occupied by halide counterions. A known quaternary phase is $Cd_{13}P_4S_{22}I_2$, which can be obtained by the reaction of I_2 with $Cd_{14}P_4S_{24}$.[5] It has a complicated structure with icosahedra of 12 sulfide ions that are centered by sulfide ions. Iodide ions are statistically distributed over some of the S atom positions. In our investigations the interest was focused on the quaternary system mercury/pentele/chalcogen/halogen to look for the structural principles that will be realized. We succeeded in synthesizing four isotypic compounds Hg_3AsE_4X (E = S, Se; X = Cl, Br, I) with an acentric, layered structure, which we will report here.

Experimental Section

Materials. Mercury sulfide (red, powder, >99%, Merck), mercury selenide (prepared from yellow mercury oxide powder, >99%, Merck), mercury(II) chloride, mercury(II) bromide, mercury(II) iodide (>99%, Fluka), sulfur (powder, >99%, Riedel-de-Häen), selenium (powder, >99.5%, Merck), and arsenic (powder, >95,5%, Alpha, purified by sublimation) were used as starting materials. HgSe was obtained by reduction of a solution of yellow HgO and elemental Se in nitric acid using hydrazinium sulfate in concentrated aqueous ammonia.[6] The precipitate of HgSe was filtered, rinsed, and dried under vacuum. The purity of the product was checked by X-ray powder patterns recorded by the Guinier method.

Synthesis of Hg_3AsS_4X (X = Cl, Br). Both compounds were synthesized by a solid-state reaction. A total of 1 mmol (0.2326 g) of HgS, 0.6 mmol (0.0192 g) of S, 0.4 mmol (0.0299 g) of As, and 0.2 mmol (0.0543 g) of $HgCl_2$ or 0.2 mmol (0.0721 g) of $HgBr_2$ were put in glass ampules and sealed under vacuum. After heating in a temperature gradient from 310 to 305 °C for 1−2 days, the products were transported to the colder parts of the ampule and obtained in yields

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* To whom correspondence should be addressed. Fax: +49 228/735660. E-mail: j.beck@uni-bonn.de.

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Table 1. Crystallographic Data for Hg_3AsS_4X and Hg_3AsSe_4X (X = Cl, Br, I)

	Hg_3AsS_4Cl	Hg_3AsS_4Br	Hg_3AsSe_4Br	Hg_3AsSe_4I
fw	840.41	884.86	1072.44	1119.44
space group	$P6_3mc$ (No. 186)	$P6_3mc$ (No. 186)	$P6_3mc$ (No. 186)	$P6_3mc$ (No. 186)
a, Å	7.431(5)	7.430(5)	7.707(8)	7.6902(7)
c, Å	9.003(8)	9.364(5)	9.47(2)	9.968(1)
vol, Å^3	430.5(3)	447.7(3)	487.0(8)	510.50(8)
Z	2	2	2	2
temp, K	293(2)	293(2)	293(2)	293(2)
λ, Å	0.7107	0.7107	0.7107	0.7107
ρ_{calc}, g cm^{-3}	6.483	6.564	7.313	7.283
μ (Mo Kα), cm^{-1}	583.6	602.9	695.1	645.2
R,^{a} R_w^{b}	0.0370, 0.099	0.0314, 0.095	0.041, 0.114	0.033, 0.106

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters [Å^2]

	x	*y*	*z*	U_{eq}
		Hg_3AsS_4Cl		
Hg	0.49589(5)	−0.00821(9)	0.2473(2)	0.0288(4)
As	0	0	0.2246(2)	0.0148(9)
S1	0.2972(5)	0.1486(3)	0.3614(6)	0.0179(7)
S2	$^1/_3$	$-^1/_3$	0.1086(8)	0.018(1)
Cl	$^2/_3$	$^1/_3$	0.0279(8)	0.026(1)
		Hg_3AsS_4Br		
Hg	0.4954(1)	−0.00919(9)	0.2458(2)	0.0347(4)
As	0	0	0.2278(4)	0.0232(9)
S1	0.2967(5)	0.1488(2)	0.3606(5)	0.0243(7)
S2	$^1/_3$	$-^1/_3$	0.1088(8)	0.027(2)
Br	$^2/_3$	$^1/_3$	0.0242(5)	0.0283(6)
		Hg_3AsSe_4Br		
Hg	0.49672(7)	−0.0065(2)	0.2453(3)	0.0340(5)
As	0	0	0.2238(5)	0.020(1)
Se1	0.2996(3)	0.1498(2)	0.3647(4)	0.0219(5)
Se2	$^1/_3$	$-^1/_3$	0.1052(5)	0.0217(9)
Br	$^2/_3$	$^1/_3$	0.0252(5)	0.0310(9)
		Hg_3AsSe_4I		
Hg	0.4965(1)	−0.0070(2)	0.2443(2)	0.0327(4)
As	0	0	0.2318(5)	0.0189(8)
Se1	0.3020(3)	0.1510(2)	0.3632(3)	0.0201(5)
Se2	$^1/_3$	$-^1/_3$	0.1083(4)	0.0209(8)
I	$^2/_3$	$^1/_3$	0.0224(3)	0.0232(7)

higher than 80%. The byproducts were identified as As_4S_4 in the form of glassy solidified droplets, Hg(II) halides, Hg(II) chalcogenides, and small amounts of the respective ternary phases $Hg_3S_2X_2$. The crystals of Hg_3AsS_4X could easily be separated mechanically. Both compounds Hg_3AsS_4Cl and Hg_3AsS_4Br are yellow with a characteristic hexagonal, columnlike crystal shape.

Synthesis of Hg_3AsSe_4X (X = Br, I). Single crystals of Hg_3AsSe_4X (X = Br, I) were prepared analogous to Hg_3AsS_4X (X = Cl, Br). The starting materials $HgSe/HgX_2/Se/As$ were mixed in a ratio 5/1/3/2, placed in annealed glass ampules, and sealed under vacuum. After the mixture was heated to 350 °C for Hg_3AsSe_4Br and 250 °C for Hg_3AsSe_4I with a temperature gradient of about 10 °C, the products were obtained with similar yields and crystal shape as for Hg_3AsS_4X (X = Cl, Br) but were dark-red.

Crystallographic Studies. Suitable single crystals were placed in sealed glass capillaries (diameter 0.3 mm) and mounted on a STOE imaging plate diffraction system (IPDS) using graphite monochromated Mo Kα radiation (λ = 71.073 pm). The crystallographic data are given in Table 1 and the positional parameters and equivalent isotropic displacement factors in Table 2. All diffracted intensities were corrected for Lorentz and polarization effects. Systematic absences ($hh\overline{2h}l$ ($l = 2n$), $000l$ ($l = 2n$)) were in accordance with three possible space groups $P6_3mc$ (No. 186), $P\bar{6}2c$ (No. 190), and $P6_3/mmc$ (No. 194). The crystal structures were solved by direct methods[7] and refined against F^2 by full-matrix least-squares methods.[8] Stable refinements were only possible in the space group $P6_3mc$. The acentricity of the structures was confirmed by second harmonic generation experiments and *Flack* parameters, which were refined to values of zero within three standard deviations for all four data sets. Because of the high absorption coefficients, numerical absorption corrections using the program HABITUS[9] were applied to all data sets. Drawings were produced with the program DIAMOND.[10] Four X-ray crystallographic files, in CIF format, are available in Supporting Information.

Vibrational Spectra. FT-IR spectra of all four compounds were recorded with powdered samples in the far-IR region (600−20 cm^{-1}, resolution 5 cm^{-1}) with a Polytec model 30 far-IR spectrometer.

Differential Thermal Analysis/Thermogravimetry. DTA/TG experiments were performed with a NETZSCH STA 429 simultaneous TG-DTA thermal analyzer. Powdered samples of Hg_3AsSe_4Br (220 mg) and Hg_3AsSe_4I (110 mg) were placed in Al_2O_3 crucibles and heated to 500 °C at a rate of 5 K/min. Empty Al_2O_3 crucibles of equal mass were used as reference.

Study of Nonlinear Optic Properties. Powdered samples (ungraded) of Hg_3AsS_4Br and Hg_3AsSe_4I placed in glass tubes that are 5 mm in diameter were irradiated with pulsed IR laser light (λ = 1064 nm, pulse width 10 ns). The intensity of the reflected green light (λ = 532 nm) was detected. A filter with an absorption edge at 550 nm inserted between sample and the detector was used to suppress the doubled frequency.

Magnetic Properties. The magnetic properties of Hg_3AsS_4Br were determined on a 80 mg sample in the temperature range −197 to 27 °C (76−300 K) with a Faraday balance. The measured forces were corrected for the susceptibility of the quartz container. The balance was calibrated with $HgCo(SCN)_4$.

Results and Discussion

Synthesis of Hg_3AsE_4X. The quaternary phases Hg_3AsE_4X are formed in reactions according to the stoichiometry

$$5HgE + 3E + HgX_2 + 2As \rightarrow 2Hg_3AsE_4X$$

These reactions take place under the conditions of chemical vapor transport at temperatures between 250 and 350 °C, applying a temperature gradient of 5−10 °C along the evacuated reaction ampule, and lead almost quantitatively to the quaternary phases. Crystals of Hg_3AsE_4X are deposited in the colder part of the ampule with a typical shape of obelisk-like needles with one flat and one acute end and a hexagonal cross section. All four compounds are stable toward air and light. The colors vary with the composition; Hg_3AsS_4Cl is yellow, $HgAsS_4Br$ dark-yellow, Hg_3AsSe_4Br red, and Hg_3AsSe_4I dark-red. Various

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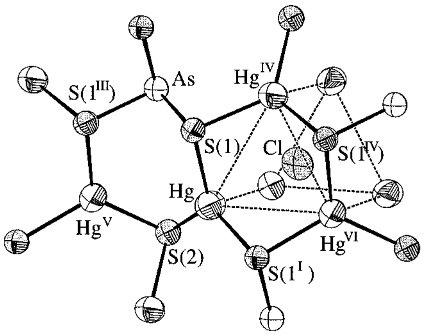

Figure 1. Section of the structure of Hg_3AsS_4Cl as a representative for the structure type Hg_3AsE_4X (E = S, Se; X = Cl, Br, I). The two different rings that form the two-dimensional polycationic $[Hg_3AsE_4]^+$ layers and one of the intercalated halide ions are shown. Three Hg atoms of the next layer are included in the figure to accentuate the trigonal prismatic coordination environment of the halide ions. Thermal ellipsoids are scaled to enclose 90% probability. The uppercase roman letters symbolize the symmetry operations for the generation of equivalent atoms: I = $-y + 1, x - y, z$; II = $-y, x - y, z$; III = $-x + y, -x, z$; IV = $(-x + y) + 1, -x + 1, z$; V = $-y, (x - y) - 1, z$; VI = $-y + 1, x - y, z$.

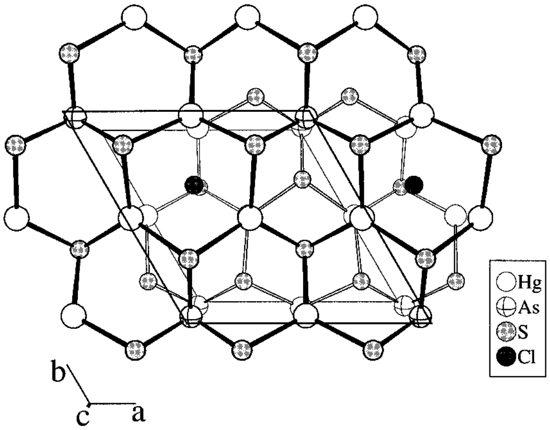

Figure 2. Unit cell of Hg_3AsE_4X in along the *c* axis. The unit cell contains two $[Hg_3AsE_4]$ layers that are stacked in the way that As and Hg atoms of neighbored layers are eclipsed and E(2) atoms are positioned in the projection of the centers of two Hg_3E_3 rings.

synthetic efforts to obtain additional compounds of this structure type were unsuccessful. Reactions involving Hg/As/S/I yielded only $Hg_3S_2I_2$, HgI_2, and As_2S_3 as the identifiable products. When Hg/As/Se/Cl reacted, large amounts of $AsCl_3$ were formed. All our attempts to substitute As for Sb led to the formation of $HgSb_4S_8$ and volatile SbX_3. Quaternary phases in the system Hg/As, Sb/Te/Br, I were also not obtained.

Table 3: Selected Bond Lengths and Bond Angles for Hg_3AsE_4X (E = S, Se; X = Cl, Br, I)

Selected Bond Lengths (Å)				
	Hg_3AsS_4Cl	Hg_3AsS_4Br	Hg_3AsSe_4Br	Hg_3AsSe_4I
Hg−X	2.955(5)	3.027(4)	3.081(5)	3.167(3)
Hg−E(1)	2.513(3)	2.534(3)	2.621(2)	2.634(2)
Hg−E(2)	2.437(4)	2.448(4)	2.553(4)	2.561(3)
As−E(1)	2.275(4)	2.283(5)	2.406(5)	2.400(4)

Selected Bond Angles (deg)				
	Hg_3AsS_4Cl	Hg_3AsS_4Br	Hg_3AsSe_4Br	Hg_3AsSe_4I
E(I)−Hg−E(2)	123.66(7)	124.3(1)	124.35(7)	125.26(5)
$E(I)-Hg-E(1)^{I\ a}$	110.1(2)	108.6(2)	108.1(2)	105.9(1)
Hg−E(1)−As	101.9(2)	101.0(2)	100.3(2)	99.6(1)
$Hg-E(1)-Hg^{IV\ a}$	98.5(2)	97.8(2)	97.1(2)	96.4(1)
$Hg-E(2)-Hg^{IV\ a}$	96.1(2)	95.1(2)	95.4(2)	94.6(1)
$E(1)-As-E(1)^{III\ a}$	93.5(2)	93.2(2)	92.2(2)	93.1(2)

[a] The uppercase numbers refer to symmetry-related atoms. For the symmetry operations see caption of Figure 1.

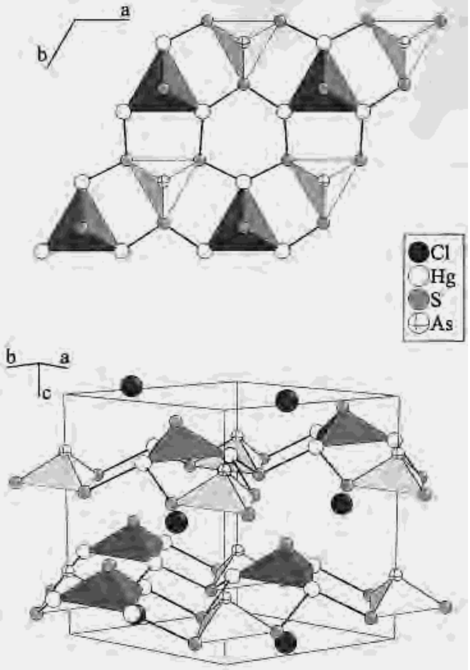

Figure 3. Structure of Hg_3AsE_4X depicted as interconnected trigonal pyramidal $(AsE_3)^{3-}$ (white) and $(Hg_3E)^{4+}$ (gray) units. On top a view along the *c* axis perpendicular to a $[Hg_3AsE_4]$ layer is given; below is a view of the unit cell slightly inclined in the [110] direction. The acentricity of the structure causes all pyramidal AsE_3 and Hg_3E groups to be oriented in the same direction with respect to the polar *c* axis.

Crystal Structures. As shown in Figures 1 and 2 the structure of Hg_3AsE_4X (E = S, Se; X = Cl, Br, I) is built of layers spreading along the *ab* plane. These layers are formed by two different kinds of six-membered rings. One is a Hg_2AsE_3 ring in the boat conformation, the other a Hg_3E_3 ring in the chair conformation. The layers are separated by halide ions. The Hg−X distances indicate only weak metal−halogen interactions, whereas the bond lengths (Table 3) within the layers are in good agreement with the respective sum of the covalent radii. These are 2.48 Å for Hg−S, 2.61 Å for Hg−Se, 2.25 Å for As−S, and 2.38 Å for As−Se bonds.[11] Therefore, the structure can be described as consisting of two-dimensional polycationic layers with predominant covalent bonds within these layers and discrete halide ions between them. This structural description corresponds to the formula ${}^{2}_{\infty}[Hg_3AsE_4]^+X^-$.

An alternative way to describe the structure of Hg_3AsE_4X is to focus on the coordination of the chalcogen and As atoms. E(2) is coordinated by three Hg atoms, and As is coordinated by three E(1) atoms, and in each case regular trigonal pyramids are formed (Figure 3). When the $[Hg_3AsE_4]$ layers are stacked in the [001] direction, the tops of these trigonal pyramidal units point in the same direction and the crystallographic *c* axis becomes polar (Figure 3). Since both kinds of pyramids are isolated, the chemical formula alternatively can be written as $\{(Hg_3E)^{4+}(AsE_3)^{3-}\}^+X^-$ with Hg in the oxidation state +2, As in +3, and S/Se in −2.

The observed diamagnetism for Hg_3AsS_4Br is in accordance with these formulations. The susceptibility of Hg_3AsS_4Br is

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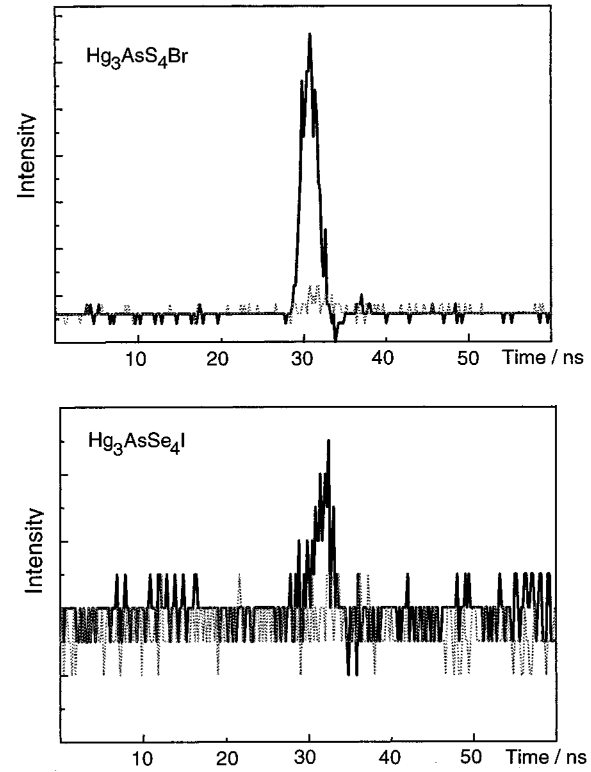

Figure 4. Emission of green light from powdered samples of Hg_3AsS_4Br (top) and Hg_3AsSe_4I (bottom) when irradiated with pulsed laser light ($\lambda = 1064$ nm). A superposition of 256 lights pulses as the response of the samples to the laser pulses of 10 ns width is shown. The emission was recorded without a filter (thick lines) and with a 550 nm band filter to suppress all shorter wavelengths (dotted line). This experimental technique ensures that the emitted light has a wavelength shorter than 550 nm.

temperature-independent with a value of $(-207 \pm 4) \times 10^{-6}$ cm^3/mol from −197 to 27 °C. The estimation of the diamagnetic susceptibility by the summation of the diamagnetic increments of the ions gives the comparable value of -346×10^{-6} cm^3/mol.[12]

Closely related to the anionic layers in the structure of Hg_3AsE_4X are the anionic structure parts of the compounds $(Me_4N)[HgAsSe_3]$, $(Et_4N)[HgAsSe_3]$,[13] $(Ph_4P)[Hg_2As_4S_9]$, and $(Me_4N)[HgAs_3Se_6]$.[14] Here, the structural motif is also a trigonal pyramidal trichalcogenoarsenate(III) unit $[AsE_3]^{3-}$. In the structures of $(Me_4N)[HgAsSe_3]$ and $(Et_4N)[HgAsSe_3]$ the trithioarsenate(III) ions are interconnected by Hg^{2+} ions, forming polyanions $[HgAsSe_3]_n^{n-}$. The Hg^{2+} ions are trigonal-planar-coordinated, and the polyanions therefore consist of chains of eight-membered, puckered $[Hg_2As_2Se_4]$ rings. Their As−Se distances (averaged 239 pm) and their Hg−Se distances (averaged 258 pm) are in the same range as found in Hg_3AsSe_4X (X = Br, I). The structure of the anion in $(Ph_4P)[Hg_2As_4S_9]$ can be derived from the structure of the $[HgAsSe_3]_n^{n-}$ ion by substitution of one-fourth of the As atoms by Hg atoms without changing the atomic arrangement. In $(Me_4N)[HgAs_3Se_6]$, two-dimensional layers of $[HgAs_3S_6]_n^{n-}$ are present that are formed from polymeric $[AsS_3]_n^{n-}$ units and Hg^{2+} ions with a distorted tetrahedral coordination. The $(Me_4N)^+$ cations are located between the layers. Here, the averaged As−S (228 pm) and Hg−S distances (247 pm) are very close to the distances found in Hg_3AsS_4X (X = Cl, Br).

Table 4: Positions [cm^{-1}] and Relative Intensities (vst = Very Strong, st = Strong, w = Weak, vw = Very Weak) of the Significant Peaks in the IR Spectra of Hg_3AsE_4X (E = S, Se; X = Cl, Br, I)

Hg_3AsS_4Cl	340 (vst), 280 (st), 215 (st), 170 (w), 105 (st), 70 (w)
Hg_3AsS_4Br	335 (vst), 275 (st), 210 (st), 135 (w), 100 (st), 75 (st)
Hg_3AsSe_4Br	245 (vst), 195 (st), 145 (st), 110 (vw), 85 (st), 65 (st)
Hg_3AsSe_4I	240 (vst), 185 (st), 140 (st), 100 (w), 85 (st), 60 (st)

Vibrational Spectra. All four compounds show a similar pattern of absorption bands in the far-IR region between 340 and 60 cm^{-1}. The positions and the intensities are listed in Table 4. Comparing the spectra of pairs of compounds containing different halogens but the same type of chalcogen, Hg_3AsS_4Cl and Hg_3AsS_4Br as one pair and Hg_3AsSe_4Br and Hg_3AsSe_4I as the other, shows that the positions of the absorption peaks for each pair are almost unchanged, shifting generally by only 5 cm^{-1} to lower frequencies for the compound with the heavier halogen. The substitution of S against Se causes a strong shift of nearly all absorption bands to lower frequencies by up to 100 cm^{-1}. These observations indicate that the absorption bands under discussion are mainly caused by Hg−S, Hg−Se, As−S, and As−Se vibrations. Hereby, the IR spectra confirm the structural features derived from the crystallographic study, since they are in accordance with pronounced covalent Hg−E and As−E bonds within the layers and very weak bonds between mercury atoms of the polycationic layers and the intercalated halide ions.

Thermal Analysis. The thermal behavior of the two selenido compounds was investigated by combined differential calorimetry and thermogravimetry experiments. Both compounds decompose at temperatures above 380 °C for Hg_3AsSe_4Br and 320 °C for Hg_3AsSe_4I. The mass changes (−14.1% for Hg_3AsSe_4Br and −19.3% for Hg_3AsSe_4I) indicate that the halogen and As or Se evaporate. A black material remained in the crucibles. The compounds do not melt congruently. This is in accordance with the observation that the synthesis from a cooling melt is not possible. The only so far known way to obtain these compounds is chemical vapor deposition at a temperature below the decomposition points.

Second Harmonic Generation Experiments. Acentric crystals can show nonlinear optical effects by interaction with light. The generation of the second harmonic (SHG), which is the doubling of the frequency of the incident radiation, is the most striking effect. On irradiation with pulsed IR laser light, samples of Hg_3AsS_4Br and Hg_3AsSe_4I reflected green light of doubled frequency. When the reflected light was sent through an absorption filter with an absorption edge of 550 nm, the SHG light was totally suppressed. This showed that the emitted wavelength was shorter than 550 nm and that no artifacts had been detected. In Figure 4 an SHG light pulse of both examined compounds is shown. The SHG intensity of Hg_3AsS_4Br is much stronger in comparison with the intensity of Hg_3AsSe_4I. This can be attributed to the yellow color of the sulfide bromide, while the dark-red selenide iodide absorbs much of the generated light intensity.

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Supporting Information Available: Four X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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