

Hydrothermal Synthesis and Characterization of $(\text{Me}_4\text{N})[\text{HgAsSe}_3]$, $(\text{Et}_4\text{N})[\text{HgAsSe}_3]$, and $(\text{Ph}_4\text{P})_2[\text{Hg}_2\text{As}_4\text{Se}_{11}]$: Novel 1-D Mercury Selenoarsenates¹

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Three new mercury thioarsenates, $(\text{Me}_4\text{N})[\text{HgAsSe}_3]$, $(\text{Et}_4\text{N})[\text{HgAsSe}_3]$, and $(\text{Ph}_4\text{P})_2[\text{Hg}_2\text{As}_4\text{Se}_{11}]$, with one-dimensional structures were synthesized hydrothermally from mixtures of $\text{HgCl}_2/3\text{K}_3\text{AsSe}_3/4(\text{Me}_4\text{NCl}, \text{Et}_4\text{NBr}, \text{Ph}_4\text{PBr})$, respectively, in sealed Pyrex tubes. The structures were determined by single-crystal X-ray diffraction analysis. $(\text{Me}_4\text{N})[\text{HgAsSe}_3]$ and $(\text{Et}_4\text{N})[\text{HgAsSe}_3]$ both crystallize in the monoclinic space group $P2_1/n$ (No. 14) with $a = 7.115(1) \text{ \AA}$, $b = 17.464(5) \text{ \AA}$, $c = 9.356(2) \text{ \AA}$, $\beta = 91.34(1)^\circ$, $Z = 4$, $V = 1162.2(7) \text{ \AA}^3$ for the former and $a = 7.175(2) \text{ \AA}$, $b = 18.907(4) \text{ \AA}$, $c = 10.897(3) \text{ \AA}$, $\beta = 99.56(2)^\circ$, $Z = 4$, $V = 1457(1) \text{ \AA}^3$ for the latter. They have the same one-dimensional chain-like anionic framework with trigonal planar Hg^{2+} and $[\text{AsSe}_3]^{3-}$ units. $(\text{Ph}_4\text{P})_2[\text{Hg}_2\text{As}_4\text{Se}_{11}]$ crystallizes in the triclinic space group $P-1$ (No. 2) with $a = 10.329(2) \text{ \AA}$, $b = 17.017(3) \text{ \AA}$, $c = 17.485(3) \text{ \AA}$, $\alpha = 92.70(1)^\circ$, $\beta = 105.73(1)^\circ$, $\gamma = 103.71(1)^\circ$, $Z = 2$, $V = 2853(1) \text{ \AA}^3$. $[\text{Hg}_2\text{As}_4\text{Se}_{11}]^{2-}$ also possess a one-dimensional chain-like structure consisting of both trigonal-planar and tetrahedral Hg^{2+} ions. It contains a unique $[\text{As}_4\text{Se}_{11}]^{6-}$ ligand which binds to four Hg^{2+} ions. The optical absorption and thermal properties of these compounds are reported. © 1996 Academic Press, Inc.

INTRODUCTION

The hydro(solvo)thermal technique has been shown to be a useful synthetic tool for the synthesis of novel transition and main group metal polychalcogenides including many which are inaccessible by traditional solution methods (1–3). Given the isoelectronic relationship of polychalcogenides and polychalcoarsenates, we have extended our

solventothermal polychalcogenide chemistry to chalcoarsenates (i.e., $[\text{AsS}_3]^{3-}$) in the presence of organic counterions R_4E^+ ($E = \text{P}, R = \text{Ph}; E = \text{N}, R = \text{alkyl}$). We have demonstrated its potential by successfully synthesizing and characterizing several new metal thioarsenate compounds, including $[\text{InAs}_3\text{S}_7]^{2-}$, $[\text{BiAs}_6\text{S}_{12}]^{3-}$ (4), $[\text{SnAs}_4\text{S}_9]^{2-}$, $[\text{NiAs}_4\text{S}_8]^{2-}$, $[\text{Mo}_2\text{O}_2\text{As}_2\text{S}_7]^{2-}$ (5), $[\text{HgAs}_3\text{S}_6]^-$, $[\text{Hg}_2\text{As}_4\text{S}_9]^{2-}$ (6), $[\text{Pt}(\text{As}_3\text{S}_5)_2]^{2-}$, and $[\text{Pt}_3(\text{As}_4)_3]^{3-}$ (7). The structures of these compounds range from molecular clusters to one-dimensional chains to two-dimensional layers. The $[\text{AsS}_3]^{3-}$ anion in these systems shows a remarkably facile condensation ability which results in the high nuclearity $[\text{As}_x\text{S}_y]^{n-}$ units which are found coordinated to the metal cations. This self-condensation properties appear to be influenced by the acidity of the solutions and the nature of the solvent. Clearly, this chemistry is applicable to any cation/metal/ As_xQ_y ($\text{Q} = \text{S}, \text{Se}$) system. To date, we have paid less attention to the Se analogs of these compounds, but given the significant differences in basicity between $[\text{AsS}_3]^{3-}$ and $[\text{AsSe}_3]^{3-}$, one would predict that the solution behavior of the selenide analog, with respect to the above self-condensation reactions, would be considerably different. Indeed, with Hg^{2+} in the reaction medium we find that entirely different phases form with $[\text{AsSe}_3]^{3-}$ compared to the corresponding sulfur system (6). Here we describe the synthesis and characterization of three new mercury selenoarsenates, $(\text{Me}_4\text{N})[\text{HgAsSe}_3]$, $(\text{Et}_4\text{N})[\text{HgAsSe}_3]$, and $(\text{Ph}_4\text{P})_2[\text{Hg}_2\text{As}_4\text{Se}_{11}]$.

EXPERIMENTAL

Chemicals in this work, other than solvents, were used as obtained: (i) selenium powder, ~100 mesh, 99.5% purity, mercury chloride, HgCl_2 , 99.5% purity, tetraphenylphosphonium bromide, Ph_4PBr , 99% purity, tetramethylammonium chloride, Me_4NCl , 99% purity, tetraethylammonium bromide, Et_4NBr , 99% purity, Aldrich Chemical Company, Inc., Milwaukee, WI; (ii) arsenic selenide, As_2Se_3 , 200 mesh, 99% purity, Cerac Inc. Milwaukee WI; (iii) potassium metal, analytical reagent, Mallinckrodt Inc., Paris,

¹ See NAPS document No. 05290 for 67 pages of supplementary materials. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 up to 20 pages plus \$3.00 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15. Foreign orders add \$4.50 for postage and handling, for the first 20 pages, and \$1.00 for additional 10 pages of material, \$1.50 for postage of any microfiche orders.

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KY; (iv) methanol, anhydrous, Mallinckrodt Inc., Paris, KY; (v) diethyl ether, ACS anhydrous, EM Science, Inc., Gibbstown, NJ.

Physical Measurements

FT-IR spectra of these compounds were recorded as solids in a CsI matrix. The spectra were recorded in the far-IR region ($600\text{--}100\text{ cm}^{-1}$, 4 cm^{-1} resolution) with a Nicolet 740 FT-IR spectrometer. Optical diffuse reflectance measurements were made at room temperature with a Shimadzu UV-3101PC double beam, double-monochromator spectrophotometer. Thermal gravimetric analysis (TGA) was performed on a Shimadzu TGA-50. The samples were heated to 800°C at a rate of $10^\circ\text{C}/\text{min}$ under a steady flow of dry N_2 gas.

Syntheses

All syntheses were carried out under a dry nitrogen atmosphere in a vacuum atmosphere Dri-Lab glovebox except where specifically mentioned.

K_3AsSe_3 . K_3AsSe_3 was synthesized by using stoichiometric amounts of alkali metal, arsenic selenide, and selenium in liquid ammonia. The reaction gives a orange brown powder upon evaporation of ammonia.

$(\text{Me}_4\text{N})[\text{HgAsSe}_3]$. Amounts of 0.03 g (0.1 mmol) HgCl_2 , 0.13 g (0.3 mmol) K_3AsSe_3 , and 0.07 g (0.6 mmol) Me_4NCl were thoroughly mixed and sealed in a thick-wall Pyrex tube with 0.3 ml of H_2O . The reaction was run at 110°C for 2 days. The products were isolated by dissolving the excess starting material and KCl with H_2O and methanol and then washing with anhydrous ether to give 0.05 g of yellow rod-like crystals (85% yield based on Hg). Semi-quantitative microprobe analysis on single crystals gave $\text{Hg}_1\text{As}_{1.2}\text{Se}_{3.3}$ as its formula. The presence of the tetramethylammonium cations was confirmed by infrared spectroscopy.

$(\text{Et}_4\text{N})[\text{HgAsSe}_3]$. Amounts of 0.031 g (0.11 mmol) HgCl_2 , 0.13 g (0.3 mmol) K_3AsSe_3 , and 0.13 g (0.6 mmol) Et_4NBr were thoroughly mixed and sealed in a thick-wall Pyrex tube with 0.3 ml of H_2O . The reaction was run at

TABLE 1
Crystallographic Data for $(\text{Me}_4\text{N})[\text{HgAsSe}_3]$ (I), $(\text{Et}_4\text{N})[\text{HgAsSe}_3]$ (II),
and $(\text{Ph}_4\text{P})_2[\text{Hg}_2\text{As}_4\text{Se}_{11}]$ (III)

	I	II	III
Formula	$\text{C}_4\text{H}_{12}\text{NHgAsSe}_3$	$\text{C}_8\text{H}_{20}\text{NHgAsSe}_3$	$\text{C}_{48}\text{H}_{40}\text{P}_2\text{Hg}_2\text{As}_4\text{Se}_{11}$
F. w.	586.40	642.40	2247.45
$a(\text{\AA})$	7.115(1)	7.175(2)	10.329(2)
$b(\text{\AA})$	17.464(5)	18.907(4)	17.017(3)
$c(\text{\AA})$	9.356(2)	10.897(3)	17.485(3)
$\alpha(\text{deg.})$	90.00	90.00	92.70(1)
$\beta(\text{deg.})$	91.34(1)	99.56(2)	105.73(1)
$\gamma(\text{deg.})$	90.00	90.00	103.71(1)
$Z, V(\text{\AA}^3)$	4, 1162.2(7)	4, 1457(1)	2, 2853(1)
Space group	$P2_1/n$ (No 14)	$P2_1/n$ (No. 14)	$P-1$ (No. 2)
color, habit	yellow, block	yellow, block	red, block
$D_{\text{cal}}(\text{g}/\text{cm}^3)$	3.35	2.93	2.62
Radiation	$\text{MoK}\alpha$	$\text{MoK}\alpha$	$\text{MoK}\alpha$
$\mu(\text{cm}^{-1})$	253.12	201.93	147.06
$2\theta_{\text{max}}(\text{deg.})$	45.00	45.00	45.00
Absorption	ψ scan	ψ scan	ψ scan
Correction			
Transmission	0.85–1.22	0.71–1.28	0.94–1.03
Factors			
Index ranges	$0 \leq h \leq 8,$ $0 \leq k \leq 19,$ $-11 \leq l \leq 11$	$0 \leq h \leq 8,$ $0 \leq k \leq 21,$ $-12 \leq l \leq 12$	$-12 \leq h \leq 12,$ $0 \leq k \leq 19,$ $-19 \leq l \leq 19$
No. of data coll.	1785	2222	8126
Unique	1161	1991	4277
Reflections			
Data used	772	1574	4277
$(F_o^2 > 3\sigma(F_o^2))$			
No. of variables	66	82	364
Final $R^a/R_w^b(\%)$	3.5/2.6	3.0/3.1	6.7/7.1

$$^a R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|.$$

$$^b R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}.$$

110°C for 2 days. The products were isolated as above to give 0.064 g of yellow-orange rod-like crystals (yield = 98% based on Hg). Semi-quantitative microprobe analysis of several single crystals gave $\text{Hg}_1\text{As}_{1.2}\text{Se}_{3.3}$. The presence of the tetraethylammonium cations was confirmed by infrared spectroscopy.

(Ph_4P)₂[$\text{Hg}_2\text{As}_4\text{Se}_{11}$]. Amounts of 0.03 g (0.1 mmol) HgCl_2 , 0.14 g (0.3 mmol) K_3AsSe_3 , and 0.24 g (0.6 mmol) Ph_4PBr were thoroughly mixed and sealed in a thick-wall Pyrex tube with 0.5 ml of H_2O . The reaction was run at 110°C for 1 week. The dark-red chunky crystals were isolated as above (0.076 g, yield = 34%, based on Hg). Semi-quantitative microprobe analysis of several single crystals gave $\text{P}_1\text{Hg}_1\text{As}_{2.8}\text{Se}_{7.3}$.

X-ray Crystallography

The single-crystal X-ray diffraction data of all three compounds were collected with a Nicolet P3 four-circle automated diffractometer with a graphite-crystal monochromator at -100°C . The data were collected in the $\theta - 2\theta$ scan mode. None of the crystals showed any significant intensity decay as judged by three check reflections measured every 150 reflections throughout the data collection. The monoclinic space groups were determined from systematic absences and intensity statistics. The structures were solved by directed methods of SHELXS-86 (8) and refined by full-matrix least-squares techniques of the TEXSAN (9) software package of the crystallographic program. An empirical absorption correction based on ψ -scans was applied to each data set, followed by a DIFABS (10) correction to the isotropically refined structures. All nonhydrogen atoms except carbon and nitrogen were eventually refined anisotropically. All calculations were performed on a VAXstation 3100/76 computer. Complete data collection

TABLE 2
Fractional Atomic Coordinates and B_{eq}^a Values for (Me_4N) [HgAsSe_3] with Estimated Standard Deviations (esd's) in Parentheses

Atom	X	Y	Z	B_{eq}^a (Å ²)
Hg	0.13217(9)	0.95396(6)	0.1684(1)	1.27(4)
As	-0.3584(2)	0.9499(1)	0.1158(2)	1.1(1)
Se(1)	0.4031(2)	0.8567(1)	0.1456(2)	1.3(1)
Se(2)	-0.1535(2)	0.9060(1)	0.3058(2)	1.3(1)
Se(3)	-0.1813(2)	0.9077(1)	-0.0860(2)	1.3(1)
N	0.633(2)	0.167(1)	0.389(2)	1.1(3)
C(1)	0.583(2)	0.087(2)	0.428(3)	2.8(4)
C(2)	0.678(2)	0.171(2)	0.243(3)	2.7(5)
C(3)	0.470(2)	0.217(1)	0.415(3)	2.5(4)
C(4)	0.790(3)	0.193(2)	0.481(3)	3.0(5)

$$^a B_{\text{eq}} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}].$$

TABLE 3
Fractional Atomic Coordinates and B_{eq}^a Values for (Et_4N) [HgAsSe_3] with Estimated Standard Deviations (esd's) in Parentheses

Atom	X	Y	Z	B_{eq}^a (Å ²)
Hg	0.15460(6)	0.53578(2)	0.14957(5)	0.84(2)
As	-0.3457(1)	0.53887(6)	0.1045(1)	0.54(4)
Se(1)	0.4274(2)	0.62365(6)	0.1415(1)	0.92(5)
Se(2)	-0.1051(2)	0.56705(6)	0.2776(1)	0.76(5)
Se(3)	0.2009(2)	0.41131(6)	0.0591(1)	0.77 β (5)
N	0.239(1)	0.1731(5)	0.831(1)	0.9(2)
C(1)	0.252(2)	0.1645(6)	0.695(1)	1.0(2)
C(2)	0.136(1)	0.1077(6)	0.868(1)	0.8(2)
C(3)	0.438(2)	0.1790(6)	0.911(1)	1.1(2)
C(4)	0.137(2)	0.2410(6)	0.854(1)	0.7(2)
C(5)	0.344(2)	0.2260(6)	0.640(1)	1.6(2)
C(6)	0.107(2)	0.1047(7)	1.000(1)	2.2(3)
C(7)	0.572(2)	0.1196(6)	0.899(1)	1.4(2)
C(8)	-0.064(2)	0.2447(7)	0.787(1)	2.0(3)

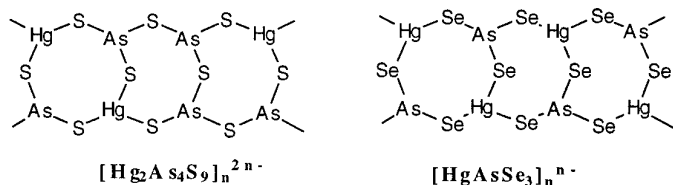
$$^a B_{\text{eq}} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}].$$

parameters and details of the structure solution and refinement are given in Table 1. The fractional atomic coordinates, average temperature factors, and their estimated standard deviations are given in Tables 2–4.

RESULTS AND DISCUSSION

Structure of (Me_4N)[HgAsSe_3] and (Et_4N)[HgAsSe_3]

Both compounds have the same one-dimensional anionic chains composed of trigonal planar Hg^{2+} ions and [AsSe_3]³⁻ units; see Figs. 1 and 2. In order to maintain the same anionic framework and accommodate the larger Et_4N^+ cations, the b and c lattice constants of the Et_4N^+ salt expand by about 1.5 Å, while the a axis remains almost unchanged. The β angle of (Et_4N)[HgAsSe_3], at $99.56(2)^\circ$, also differs from that of the (Me_4N)[HgAsSe_3], at $91.34(2)^\circ$. The Hg^{2+} centers in [HgAsSe_3]_{*n*}^{*n-*} have a trigonal-planar environment with bond angles of Se1–Hg–Se2 at $115.25(6)^\circ$, Se1–Hg–Se3 at $119.34(5)^\circ$, and Se2–Hg–Se3 at $124.70(5)^\circ$ for the Me_4N^+ salt. The average As–S distance of 2.391(3) Å and the average S–As–S angles at $96.79(6)^\circ$ are well within the normal range found in other arsenic/selenide compounds (11). Selected bond distances and bond angles are given in Table 5. The common [HgAsSe_3]_{*n*}^{*n-*} anion has a one-dimensional chain-like structure (see Fig. 3), which is related to that found in [$\text{Hg}_2\text{As}_4\text{S}_9$]_{*n*}^{*n-*} (6). Both structures contain the $\text{Hg}_2\text{As}_2\text{Q}_4$ eight-membered puckered rings; see scheme 1. The relationship lies in the fact that the structural motif in the [HgAsSe_3]_{*n*}^{*n-*} can be derived from that of [$\text{Hg}_2\text{As}_4\text{S}_9$]_{*n*}^{*n-*} by substitution of one fourth on the arsenic atoms for Hg.



SCHEME 1

TABLE 4
Fractional Atomic Coordinates and B_{eq}^a Values for
(Ph₄P)₂[Hg₂As₄Se₁₁] with Estimated Standard Deviations (esd's)
in Parentheses

Atom	<i>X</i>	<i>Y</i>	<i>Z</i>	B_{eq}^a (Å ²)
Hg(1)	0.2290(1)	0.13758(8)	0.36837(8)	2.30(5)
Hg(2)	0.2230(1)	0.33493(9)	0.24541(9)	3.09(6)
As(1)	-0.0881(3)	0.2007(2)	0.3865(2)	2.0(1)
As(2)	-0.1573(3)	0.3269(2)	0.2369(2)	1.8(1)
As(3)	0.5554(3)	0.1267(2)	0.3187(2)	2.5(1)
As(4)	0.4518(3)	0.2530(2)	0.1624(2)	2.5(1)
Se(1)	0.0100(3)	0.0924(2)	0.4149(2)	2.6(1)
Se(2)	0.0973(3)	0.3249(2)	0.4349(2)	2.5(1)
Se(3)	0.2872(3)	0.3090(2)	0.3911(2)	2.0(1)
Se(4)	-0.1121(3)	0.1940(2)	0.2469(2)	2.3(1)
Se(5)	0.0109(3)	0.3891(2)	0.1748(2)	2.0(1)
Se(6)	-0.3453(3)	0.2963(2)	0.1153(2)	2.7(1)
Se(7)	0.3794(4)	0.3727(2)	0.1525(2)	4.0(2)
Se(8)	0.5528(3)	0.2670(2)	0.3049(2)	2.4(1)
Se(9)	0.3617(3)	0.0595(2)	0.2071(2)	2.9(1)
Se(10)	0.1818(3)	0.1233(2)	0.2111(2)	2.4(1)
Se(11)	0.4725(3)	0.1135(2)	0.4292(2)	2.2(1)
P(1)	0.5671(7)	0.3389(4)	0.6809(4)	1.4(3)
P(2)	0.1153(7)	0.1936(4)	0.8649(4)	1.4(4)
C(1)	0.700(2)	0.364(2)	0.632(2)	1.3(5)
C(2)	0.677(3)	0.321(2)	0.555(2)	1.5(2)
C(3)	0.778(3)	0.346(2)	0.518(2)	2.1(6)
C(4)	0.899(3)	0.412(2)	0.549(2)	1.7(5)
C(5)	0.914(3)	0.453(2)	0.623(2)	2.2(6)
C(6)	0.815(3)	0.430(2)	0.664(2)	2.3(6)
C(7)	0.457(3)	0.407(2)	0.660(2)	1.6(5)
C(8)	0.448(3)	0.448(2)	0.593(2)	2.3(6)
C(9)	0.360(3)	0.500(2)	0.577(2)	3.0(7)
C(10)	0.285(3)	0.513(2)	0.632(2)	2.4(6)
C(11)	0.293(3)	0.472(2)	0.696(2)	3.4(7)
C(12)	0.379(3)	0.419(2)	0.710(2)	3.2(7)
C(13)	0.645(3)	0.350(2)	0.786(2)	1.6(5)
C(14)	0.703(3)	0.432(2)	0.826(2)	1.9(6)
C(15)	0.772(3)	0.439(2)	0.907(2)	2.8(6)
C(16)	0.776(3)	0.373(2)	0.949(2)	2.6(6)
C(17)	0.716(3)	0.296(2)	0.909(2)	3.5(7)
C(18)	0.649(3)	0.282(2)	0.832(2)	2.0(6)
C(19)	0.478(3)	0.232(2)	0.649(2)	1.8(6)
C(20)	0.549(3)	0.178(2)	0.652(2)	1.8(6)
C(21)	0.475(3)	0.095(2)	0.630(2)	3.4(7)
C(22)	0.334(3)	0.074(2)	0.613(2)	2.4(6)
C(23)	0.258(3)	0.130(2)	0.607(2)	2.7(6)
C(24)	0.326(3)	0.213(2)	0.627(2)	2.3(6)
C(25)	0.250(3)	0.138(3)	0.878(2)	2.1(6)

TABLE 4—Continued

Atom	<i>X</i>	<i>Y</i>	<i>Z</i>	B_{eq}^a (Å ²)
C(26)	0.335(3)	0.138(2)	0.956(2)	1.9(6)
C(27)	0.442(3)	0.101(2)	0.968(2)	2.5(6)
C(28)	0.460(3)	0.058(2)	0.900(2)	3.9(8)
C(29)	0.373(3)	0.055(2)	0.826(2)	3.1(7)
C(30)	0.269(3)	0.093(2)	0.814(2)	3.0(7)
C(31)	0.012(2)	0.160(2)	0.932(2)	1.4(5)
C(32)	0.005(2)	0.215(2)	0.992(2)	1.5(5)
C(33)	-0.075(3)	0.186(2)	1.040(2)	2.2(6)
C(34)	-0.141(3)	0.106(2)	1.037(2)	1.9(6)
C(35)	-0.126(3)	0.050(2)	0.979(2)	3.4(7)
C(36)	-0.050(3)	0.079(2)	0.925(2)	2.9(7)
C(37)	0.193(2)	0.302(1)	0.889(1)	0.7(5)
C(38)	0.108(3)	0.354(2)	0.877(2)	2.3(6)
C(39)	0.167(3)	0.437(2)	0.888(2)	3.7(7)
C(40)	0.310(3)	0.468(2)	0.910(2)	3.4(7)
C(41)	0.401(3)	0.420(2)	0.922(2)	2.7(6)
C(42)	0.335(3)	0.333(2)	0.909(2)	2.7(6)
C(43)	0.016(3)	0.177(2)	0.763(2)	1.7(5)
C(44)	0.042(3)	0.232(2)	0.709(2)	1.9(6)
C(45)	-0.028(3)	0.219(2)	0.632(2)	2.9(7)
C(46)	-0.134(3)	0.150(2)	0.598(2)	2.9(7)
C(47)	-0.163(3)	0.096(2)	0.651(2)	2.2(6)
C(48)	-0.093(3)	0.107(2)	0.730(2)	3.1(7)

$$^a B_{\text{eq}} = (4/3)[a^2 B_{11} + b^2 B_{22} + c^2 B_{33} + ab(\cos \gamma) B_{12} + ac(\cos \beta) B_{13} + bc(\cos \alpha) B_{23}].$$

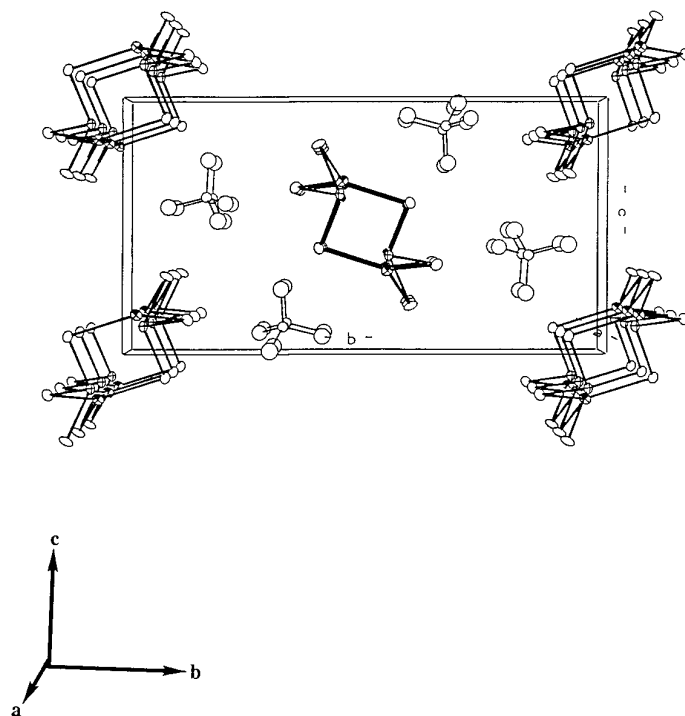


FIG. 1. Packing diagram of (Me₄N)[HgAsSe₃] viewed down the [100] direction. Within a chain, open circles represent S atoms, cross circles As atoms, and shaded circles Hg atoms.

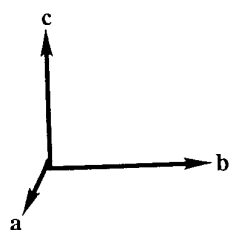
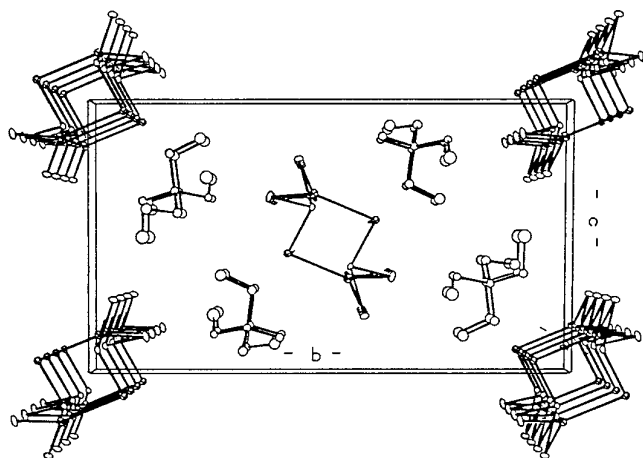


FIG. 2. Packing diagram of $(\text{Et}_4\text{N})[\text{HgAsSe}_3]$ viewed down the $[100]$ direction.

A chemically related compound worth mentioning here is KHgSbS_3 , which is layered and contains pyramidal SbS_3^{3-} units (12). The counterions, K^+ , which are considerably smaller than the organic cations found in our com-

TABLE 5
Selected Distances (\AA) and Angles (Deg) in $(\text{Me}_4\text{N})[\text{HgAsSe}_3]$ and $(\text{Et}_4\text{N})[\text{HgAsSe}_3]$ with Standard Deviations in Parentheses

$(\text{Me}_4\text{N})[\text{HgAsSe}_3]$		$(\text{Et}_4\text{N})[\text{HgAsSe}_3]$	
Hg–Se1	2.582(2)	Hg–Se1	2.580(1)
Hg–Se2	2.572(2)	Hg–Se2	2.594(1)
As1–Se3	2.563(3)	Hg–Se3	2.575(1)
As–Se1	2.373(3)	As–Se1	2.366(2)
As–Se2	2.398(3)	As–Se2	2.400(2)
As–Se3	2.411(3)	As–Se3	2.396(2)
Se1–Hg–Se2	115.32(8)	Se1–Hg–Se2	115.18(4)
Se1–Hg–Se3	119.21(6)	Se1–Hg–Se3	119.47(4)
Se2–Hg–Se3	124.93(7)	Se2–Hg–Se3	124.47(4)
Se1–As–Se2	96.7(1)	Se1–As–Se2	96.72(5)
Se1–As–Se3	105.7(1)	Se1–As–Se3	91.43(5)
Se2–As–Se3	99.38(9)	Se2–As–Se3	90.81(5)
Hg–Se1–As	95.49(9)	Hg–Se1–As	104.81(6)
Hg–Se2–As	89.94(9)	Hg–Se2–As	98.15(6)
Hg–Se3–As	91.39(9)	Hg–Se3–As	98.82(6)

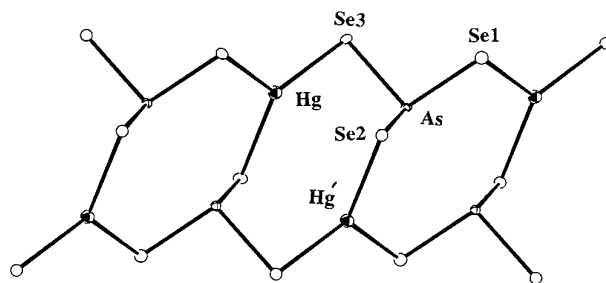


FIG. 3. Structure and labeling scheme of one $[\text{HgAsSe}_3]^{n-}$ chain.

pounds, reside between the layers. Here again, as in many other cases (13), we see a tendency for the covalent metal–chalcogen framework to increase its structural dimensionality in response to a significant decrease in the size of the counterion. An inspection of the KHgSbS_3 structure clearly suggests that there is inadequate space in the crystal to accommodate Me_4N^+ ions, if one wished to substitute K^+ for Me_4N^+ . A structural transition is necessary if the chemical composition is to be maintained.

Structure of $(\text{Ph}_4\text{P})_2[\text{Hg}_2\text{As}_4\text{Se}_{11}]$

This compound contains novel one-dimensional chains consisting of both trigonal-planar and tetrahedral Hg^{2+}

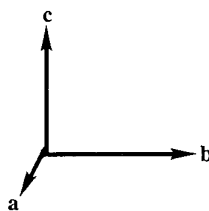
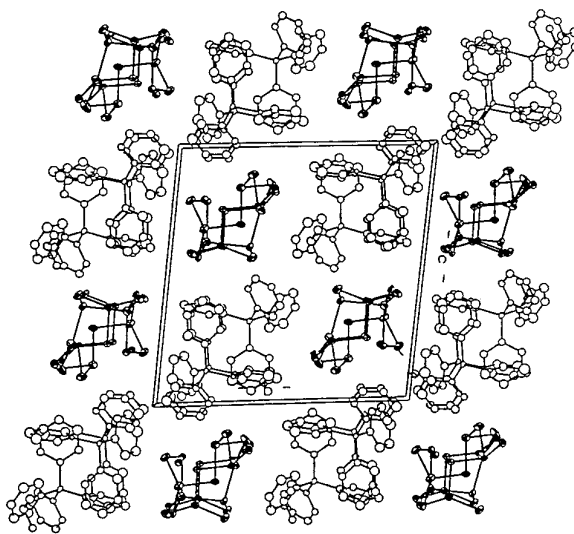


FIG. 4. Packing diagram of $(\text{Ph}_4\text{P})_2[\text{Hg}_2\text{As}_4\text{Se}_{11}]$ viewed down the $[100]$ direction.

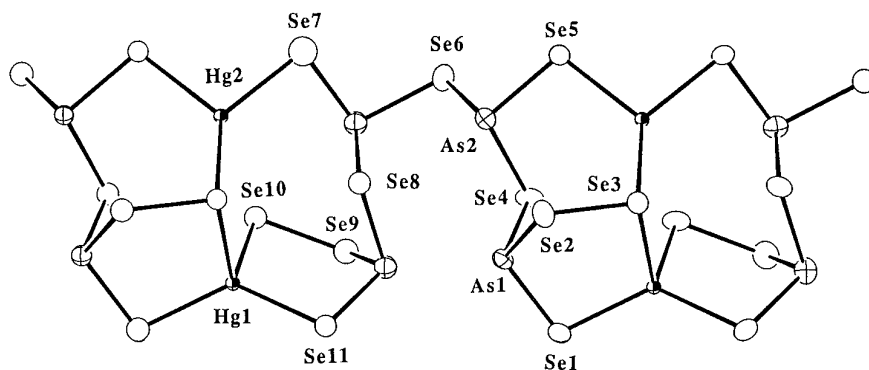


FIG. 5. Structure and labeling scheme of one $[\text{Hg}_2\text{As}_4\text{Se}_{11}]n^{2n-}$ chain.

ions and $[\text{As}_4\text{Se}_{11}]^{6-}$ units. The $[\text{Hg}_2\text{As}_4\text{Se}_{11}]n^{2n-}$ chains run parallel to the crystallographic a axis and are separated by Ph_4P^+ cations; see Fig. 4. These chains possess a unique structural arrangement. They can be viewed as assembled by connecting the clusters $\text{Hg}_2\text{As}_4\text{Se}_{10}$ through monoselenide Se(6); see Fig. 5. There are two kinds of Hg^{2+} ions in the chains. Hg(1) is coordinated in a distorted tetrahedral arrangement to four selenides with the Se–Hg–Se angles ranging from $96.5(1)^\circ$ to $128.2(1)^\circ$. Hg(2) is in a distorted trigonal-planar environment with bond angles of Se5–Hg–Se7 at $100.9(1)^\circ$, Se3–Hg–Se5 at $124.9(1)^\circ$, and Se3–Hg2–Se7 at $129.9(1)^\circ$. The average As–Se distance and the average Se–As–Se angle are within the normal range found in the other arsenic/selenide compounds (11). Selected bond distances and bond angles are contained in Tables 6 and 7.

A notable feature of this compound is the presence of the $[\text{As}_4\text{Se}_{11}]^{6-}$ ligand which contains a diselenide fragment. This ligand represents a new selenoarsenate polyanion. The Se–Se bond lengths are reasonable; see Table 7. The closest sulfide analog we have observed is $[\text{As}_4\text{S}_9]^{6-}$, found in $(\text{Ph}_4\text{P})_2[\text{Hg}_2\text{As}_4\text{S}_9]$ (6), however, we see no reason why the selenoarsenate ligand, $[\text{As}_4\text{Se}_9]^{6-}$, should not exist. The stabilization of $[\text{As}_4\text{Se}_{11}]^{6-}$ confirms that self-conden-

sation reactions between $[\text{AsSe}_3]^{3-}$ units occur just as they do in the S system.

In the context of the previously discovered cation/Hg/As/S phases, the isolation of the $(\text{Me}_4\text{N})[\text{HgAsSe}_3]$, $(\text{Et}_4\text{N})[\text{HgAsSe}_3]$, and $(\text{Ph}_4\text{P})_2[\text{Hg}_2\text{As}_4\text{Se}_{11}]$ underscores the fact that As_xSe_y polyanions behave quite differently from As_xS_y polyanions and thus one should not think of them simply as analogs to the sulfide species.

Physicochemical Studies

The infrared spectra of $(\text{Me}_4\text{N})[\text{HgAsSe}_3]$ and $(\text{Et}_4\text{N})[\text{HgAsSe}_3]$ are identical. The peaks at 268 and 249 cm^{-1} can be assigned to As–Se vibration modes. The remaining lower energy peak at 173 cm^{-1} might be a Hg–Se stretching vibration. A similar assignment can also be advanced for the $(\text{Ph}_4\text{P})_2[\text{Hg}_2\text{As}_4\text{Se}_{11}]$ compound. The peaks between 200 and 300 cm^{-1} are assigned to As–Se and Se–Se vibration modes and those at 181 and 162 cm^{-1} to Hg–Se modes.

TABLE 6
Selected Distances (Å) in $(\text{Ph}_4\text{P})_2[\text{Hg}_2\text{As}_4\text{Se}_{11}]$ with Standard Deviations in Parentheses

Hg1–Se1	2.570(3)	Se4–As2	2.420(5)
Hg1–Se3	2.820(3)	Se5–As2	2.362(4)
Hg1–Se10	2.648(4)	Se6–As2	2.396(4)
Hg1–Se11	2.589(3)	Se6–As4	2.423(4)
Hg2–Se3	2.540(4)	Se7–As4	2.329(5)
Hg2–Se5	2.602(3)	Se8–As3	2.417(5)
Hg2–Se7	2.587(4)	Se8–As4	2.403(5)
Se1–As1	2.317(5)	Se9–Se10	2.378(5)
Se2–Se3	2.357(4)	Se9–As3	2.389(5)
Se2–As1	2.425(4)	Se11–As3	2.316(5)
Se4–As1	2.381(5)		

TABLE 7
Selected Angles (Deg) in $(\text{Ph}_4\text{P})_2[\text{Hg}_2\text{As}_4\text{Se}_{11}]$ with Standard Deviations in Parentheses

Se1–Hg1–Se3	102.7(1)	Hg2–Se7–As4	93.6(1)
Se1–Hg1–Se10	114.6(1)	As3–Se8–As4	98.3(2)
Se1–Hg1–Se11	128.2(1)	Se10–Se9–As3	105.4(2)
Se3–Hg1–Se10	96.5(1)	Hg1–Se10–Se9	97.0(1)
Se3–Hg1–Se11	102.06(9)	Hg1–Se11–As3	99.4(1)
Se10–Hg1–Se11	106.8(1)	Se1–As1–Se2	107.3(2)
Se3–Hg2–Se5	124.9(1)	Se1–As1–Se4	98.7(2)
Se3–Hg2–Se7	129.9(1)	Se2–As1–Se4	100.3(2)
Se5–Hg2–Se7	100.9(1)	Se4–As2–Se5	100.3(1)
Hg1–Se1–As1	100.7(1)	Se4–As2–Se6	99.4(1)
Se3–Se2–As1	107.4(2)	Se5–As2–Se6	94.1(2)
Hg1–Se3–Hg2	98.8(1)	Se8–As3–Se9	100.2(2)
Hg1–Se3–Se2	100.5(1)	Se8–As3–Se11	97.8(2)
Hg2–Se3–Se2	104.4(1)	Se9–As3–Se11	105.3(2)
As1–Se4–As2	93.4(2)	Se6–As4–Se7	98.0(2)
Hg2–Se5–As2	102.0(1)	Se6–As4–Se8	102.4(2)
As2–Se6–As4	102.7(2)	Se7–As4–Se8	98.9(2)

TABLE 8
TGA Data for $(\text{Me}_4\text{N})[\text{HgAsSe}_3]$, $(\text{Et}_4\text{N})[\text{HgAsSe}_3]$,
and $(\text{Ph}_4\text{P})_2[\text{Hg}_2\text{As}_4\text{Se}_{11}]$

Compound	Temp. range (°C)	Weight loss (%)
$(\text{Me}_4\text{N})[\text{HgAsSe}_3]$	148–260	22.2
	260–610	76.0
$(\text{Et}_4\text{N})[\text{HgAsSe}_3]$	150–250	31.1
	250–550	67.1
$(\text{Ph}_4\text{P})_2[\text{Hg}_2\text{As}_4\text{Se}_{11}]$	310–630	98.2

Thermal gravimetric analysis (TGA) results for all three compounds are summarized in Table 8 and the graphs are shown in Fig. 6. Above 650°C, all compounds completely evaporate. During pyrolysis, redox reactions must occur

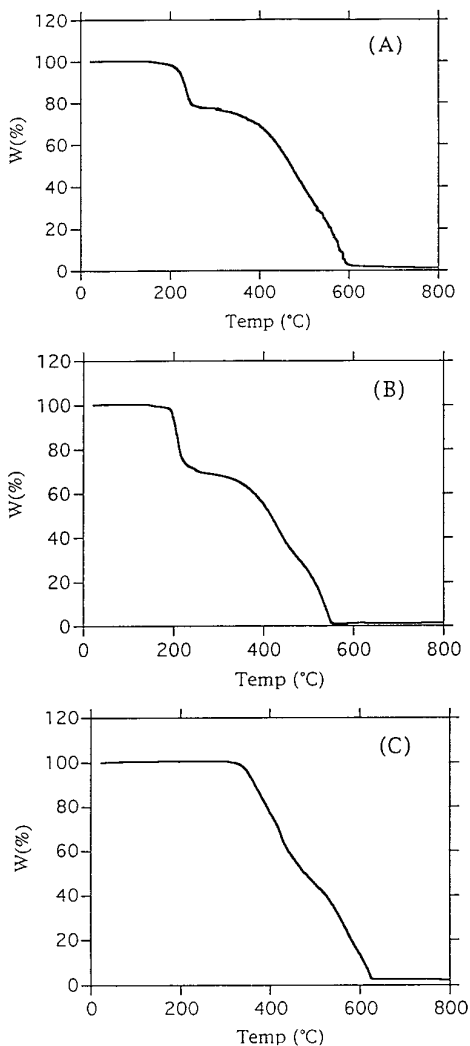


FIG. 6. TGA diagrams of (A) $(\text{Me}_4\text{N})[\text{HgAsSe}_3]$, (B) $(\text{Et}_4\text{N})[\text{HgAsSe}_3]$, and (C) $(\text{Ph}_4\text{P})_2[\text{Hg}_2\text{As}_4\text{Se}_{11}]$.

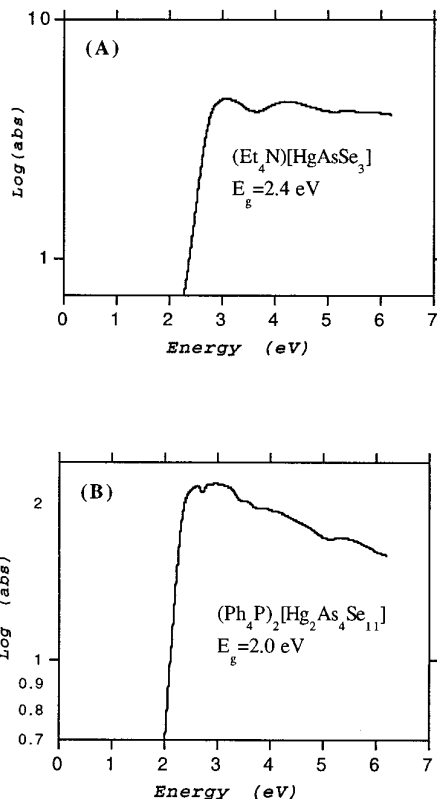


FIG. 7. Optical absorption spectra of (A) $(\text{Et}_4\text{N})[\text{HgAsSe}_3]$ and (B) $(\text{Ph}_4\text{P})_2[\text{Hg}_2\text{As}_4\text{Se}_{11}]$.

between Hg^{2+} metal ions and $[\text{As}_x\text{Se}_y]^{n-}$ to form volatile Hg and As_xSe_y species. For the compounds $(\text{Me}_4\text{N})[\text{HgAsSe}_3]$ and $(\text{Et}_4\text{N})[\text{HgAsSe}_3]$, there are two weight-loss steps. The first step is due to the loss of the organic cations, probably as R_3N and R_2Se , while the final step is due to the loss of Hg and As_xSe_y .

The optical absorption spectra indicate that these materials are wide bandgap semiconductors by revealing the presence of sharp optical gaps; see Fig. 7. The bandgaps are 2.4 eV for $(\text{R}_4\text{N})[\text{HgAsSe}_3]$ ($\text{R} = \text{Me}, \text{Et}$) and 2.0 eV for $(\text{Ph}_4\text{P})_2[\text{Hg}_2\text{As}_4\text{Se}_{11}]$. The absorption is probably due to a charge-transfer transition from a primarily selenium-based valence band to a mainly mercury-based conduction band.

CONCLUDING REMARKS

Based on the findings reported here, it appears that the relative solubilities of the various products determine the actual $[\text{As}_x\text{Se}_y]^{n-}$ species formed by self-condensation of $[\text{AsSe}_3]^{3-}$. This behavior is reminiscent of the polychalcogenide complexes mentioned earlier, where metal preference, product solubility, and solvent are the key factors that control product crystallization (14). The isolation of

the three compounds reported here demonstrates that the $[\text{As}_x\text{Se}_y]^{n-}$ anions behave differently from the $[\text{As}_x\text{S}_y]^{n-}$ anions. This observation parallels earlier observations made in chalcogenide chemistry where polysulfides, polyselenides, and polytellurides often possess individual structural and coordination chemistries. The self-condensation process also occurs in the $[\text{As}_x\text{Se}_y]^{n-}$ system but to a different extent than in the $[\text{As}_x\text{S}_y]^{n-}$ system, and the solubilities of different $[\text{As}_x\text{Se}_y]^{n-}$ polyanions are also probably different from those of the thio anions. These two factors alone could be primarily responsible for the departure of the chemistry of selenoarsenate anions from that of the thioarsenate ones. Similar considerations apply to other chalcogen anions.

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