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Hydrothermal Synthesis of $(Ph_4P)_2[Hg_2As_4S_9]$ and $(Me_4N)[HgAs_3S_6]$. Extended Chains and Layers Based on the Condensation of $[AsS_3]^{3-}$ Units

Jun-Hong Chou and Mercouri G. Kanatzidis*,[†]

Department of Chemistry and
Center for Fundamental Materials Research
Michigan State University
East Lansing, Michigan 48824

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The incorporation of main-group thiometallates in the solid state extended frameworks containing transition and other main-group metals promises to yield new solids with properties varying from semiconductivity to microporosity. The latter property may be achieved with large organic templates (e.g., Ph_4P^+ and R_4N^+, etc.) around which an open structure can assemble. Although there is substantial precedent for hydrothermal (or solvothermal) synthesis of solids with thio and chalcogeno anions in the lattice,[1-3] the use of the basic $[AsS_3]^{3-}$ anion has been limited. Recently, we have shown that hydrothermal synthetic investigations of the systems R_4E^+ (E = P, R = Ph; E = N, R = alkyl)/M^{n+}/$[AsS_3]^{3-}$ (where M is a main-group element) lead to novel polymeric materials containing thioarsenate anions as building blocks. These compounds include $(Ph_4P)_2[InAs_3S_7]$ and $(Me_4N)_2Rb[BiAs_6S_{12}]$.[4] The former has a one-dimensional chain structure and contains unusual chainlike $[As_3S_7]^{5-}$ units while the latter is a mixed salt with a two-dimensional layered structure featuring cyclic $[As_3S_6]^{3-}$ units. In these hydrothermal reactions the $[AsS_3]^{3-}$ anion shows a facile condensation ability resulting in higher nuclearity $[As_xS_y]^{n-}$ units, see eqs 1–4, which are found coordinated to the metal centers.

$$[AsS_3]^{3-} + [AsS_3]^{3-} \rightarrow [As_2S_5]^{4-} + S^{2-} \qquad (1)$$

$$[As_2S_5]^{4-} + [AsS_3]^{3-} \rightarrow [As_3S_7]^{5-} + S^{2-} \qquad (2)$$

$$[As_3S_7]^{5-} + [AsS_3]^{3-} \rightarrow [As_4S_9]^{6-} + S^{2-} \qquad (3)$$

$$[As_3S_7]^{5-} \rightarrow [As_3S_6]^{3-} + S^{2-} \qquad (4)$$

To investigate further this tendency for condensation and being aware of the wealth of different structure types exhibited by other condensable units (e.g., $[SiO_4]^{4-}$,[5] $[PO_4]^{3-}$ [6]), we explored the hydrothermal behavior of the $R_4E^+/Hg^{2+}/[AsS_3]^{3-}$ (E = P, R = Ph; E = N, R = Me) system. Here we report the first examples using transition metals, namely, the two novel low-dimensional compounds $(Ph_4P)_2[Hg_2As_4S_9]$ and $(Me_4N)[HgAs_3S_6]$. As found in the $(Ph_4P)_2[InAs_3S_7]$ and $(Me_4N)_2Rb[BiAs_6S_{12}]$, the mercury compounds also feature striking higher order $[As_xS_y]^{n-}$ units derived from the condensation of the $[AsS_3]^{3-}$ anion. These compounds are two new members of a rare but rapidly growing group of crystalline inorganic solid state compounds containing organic cations.[7-9]

$(Ph_4P)_2[Hg_2As_4S_9]$ was prepared by heating $HgCl_2$ with K_3AsS_3[10] and Ph_4PBr in H_2O at 130 °C.[11a] The structure was determined by X-ray single-crystal analysis.[12a] The compound contains one-dimensional chains consisting of trigonal-planar Hg^{2+} ions and $[As_4S_9]^{6-}$ units formed by corner sharing of the pyramidal $[AsS_3]^{3-}$ units; see Figure 1. The $[Hg_2As_4S_9]_n^{2n-}$ chains are parallel to the crystallographic *a* axis and separated by Ph_4P^+ cations. The chains can also be viewed as assembled by fused $Hg_2As_2S_4$ eight-membered puckered rings arranged side-by-side. Inside each ring resides a center of symmetry. The Hg^{2+} is in the trigonal-planar environment with bond angles of S2–Hg–S3 at 119.01(3)°, S2–Hg–S4 at 121.69(3)°, S3–Hg–S4 at 119.28(2)°. The average As–S distance of 2.277(8) Å, and the average S–As–S angles at 100.1(3)° are well within the normal range found in other arsenic/sulfide compounds.[13] The average Hg–S bonding distance is normal at 2.470(4) Å.

$(Me_4N)[HgAs_3S_6]$[11b,12b] has a unique two-dimensional layered structure where slabs of $[HgAs_3S_6]_n^{n-}$ covalent framework sandwich Me_4N^+ cations. The interlayer distance is 9.303 Å. The $[HgAs_3S_6]_n^{n-}$ framework is composed of distorted tetrahedral Hg^{2+} atoms and

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[†] A. P. Sloan Foundation Fellow, 1991–93, and Camille and Dreyfus Teacher Scholar, 1993–95.

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(10) A_3AsS_3 (A = K, Rb, Cs) were synthesized using a stoichiometric amount of alkali metal, arsenic sulfide (As_2S_3), and sulfur in liquid ammonia. The reactions give yellow brown powder upon evaporation of ammonia.

(11) (a) A Pyrex tube (~4 mL) containing $HgCl_2$ (0.087 g, 0.5 mmol), K_3AsS_3 (0.144 g, 0.5 mmol), Ph_4PBr (0.419 g, 1 mmol), and 0.3 mL of water was sealed under vacuum and kept at 130 °C for 1 week. Large pale-yellow rodlike crystals were obtained by washing with water, MeOH, and anhydrous ether. Semiquantitative microprobe analysis on single crystals gave $P_2Hg_2As_{3.5}S_{8.5}$ (average of three data acquisitions). Yield = 84.5%, based on Hg. (b) A mixture of $HgCl_2$ (0.87 g, 0.5 mmol), K_3AsS_3 (0.144 g, 0.5 mmol) and Me_4NCl (0.110 g, 1 mmol) was sealed under vacuum with 0.3–0.5 mL of water in a Pyrex tube (~4 mL). The reaction was run at 130 °C for 1 week. Large pale yellow transparent crystals were isolated and washed with H_2O methanol and anhydrous ether. Semiquantitative microprobe analysis on single crystals gave $HgAs_{2.6}S_{5.5}$. Yield = 75.7% based on Hg.

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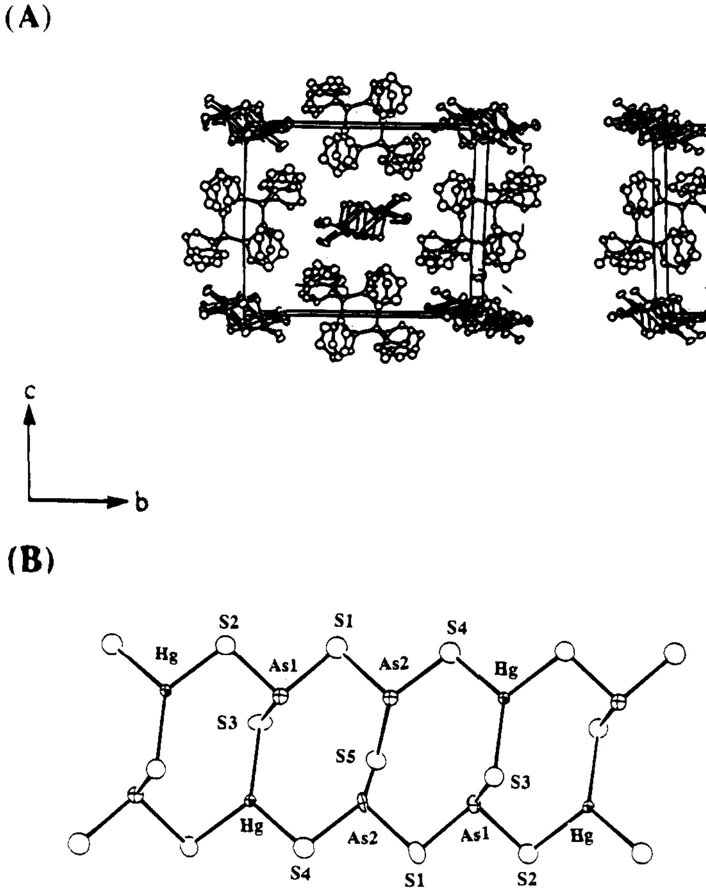
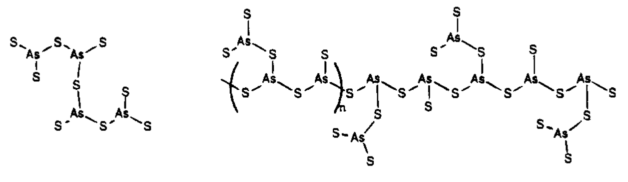


Figure 1. (A) Packing diagram of $(Ph_4P)_2[Hg_2As_4S_9]$. View down the *a*-axis showing chain cross section. (B) View of a single $[Hg_2As_4S_9]_n^{2n-}$ chain. Selected bond distances (Å): Hg–S2: 2.475(6), Hg–S3: 2.465(7), Hg–S4: 2.470(8), As1–S1: 2.287(8), As1–S2: 2.236(8), As1–S3: 2.272(6), As2–S1: 2.325(9), As2–S4: 2.22(2), As2–S5: 2.32(1). Selected bond angles (deg): S2–Hg–S3: 119.01(3), S2–Hg–S4: 111.22(3), S3–Hg–S4: 128.04(3), S1–As1–S2: 98.0(3), S1–As1–S3: 100.9(2), S2–As1–S3: 101.9(2), As2–S4: 94.9(6), S1–As2–S5: 100.3(4), S4–As2–S5: 123.1(8).

polymeric $[As_3S_6]_n^{3n-}$ units formed by corner-sharing AsS_3^{3-} units; see Figure 2. The bond angles around the Hg atoms vary widely from 94.1(2)° to 138.2(3)°. The Hg–S bond distances are divided into a set of two long bonds at 2.620(8) and 2.768(8) Å and a set of two short bonds at 2.445(9) and 2.431(8) Å. The Hg–Hg distance is 3.674(3) Å.

Both compounds feature striking new thioarsenate polyanions. Both the finite $[As_4S_9]^{6-}$ and infinite $[As_3S_6]_n^{3n-}$ which are shown schematically below are new species, whose formation results from condensation of the simpler building block $[AsS_3]^{3-}$. On the basis of the findings reported here and on two different thioarsenate anions found in $(Ph_4P)_2[InAs_3S_7]$ and $(Me_4N)_2Rb[BiAs_6S_{12}]$, it appears that relative solubilities of various products determine the actual $[As_xS_y]^{n-}$ species to be crystallized from a complex, "primordial soup"-like mixture. This behavior is reminiscent of polychalcogenide complexes, where metal preference, product solubility and solvent are key factors in product crystallization.[14] The condensation equilibria shown in eqs



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(12) (a) Crystal data for $(Ph_4P)_2[Hg_2As_4S_9]$: monoclinic $P2_1/n$ (No. 14); $a = 10.119(2)$ Å, $b = 18.010(4)$ Å, $c = 14.932(3)$ Å, $\beta = 103.98(2)°$, $Z = 4$, $V = 2640(2)$ Å^3, $D_{calc} = 2.098$ g/cm^3, $2\theta_{max} = 45.0°$. Single-crystal X-ray diffraction data were collected on a P3 Nicolet four-circle diffractometer using $\omega-2\theta$ scan mode and graphite monochromated Mo Kα radiation at −83 °C. Total data collected: 3989. Unique data: 3624. Data with $F_o^2 > 3\sigma(F_o^2)$: 2028. Final $R = 5.8\%$ and $R_w = 4.7\%$. During the structure refinement, we found the position of the S5 atom very close to the special position (1/2, 1, 1). However fixing the S5 atom in (1/2, 1, 1) resulted in a greatly increased temperature factor, with the As2–S5 bond distance becoming unreasonably short. A better refinement with more reasonable As–S distances was obtained if the S5 atom were displaced away from the special position. The S5 atom was set at 0.5 occupancy. As a result of the S5 atom positional disorder, atoms As2 and S4 were also found to be disordered between two sites. The occupancy of the two sites were refined to be 0.47 and 0.53, respectively (essentially equal occupancy). The positions of all hydrogen atoms were calculated using a C–H distance of 1 Å. The scattering contribution of the hydrogen atoms was included in the structure factor calculation but their positions were not refined. (b) Crystal data for $(Me_4N)[HgAs_3S_6]$: monoclinic space group $C2/c$ (No. 15); $a = 18.607(7)$ Å, $b = 7.126(1)$ Å, $c = 26.524(6)$ Å, $\beta = 91.87(2)°$, $Z = 8$, $V = 3515(3)$ Å^3, $D_{calc} = 2.615$ g/cm^3, $2\theta_{max} = 50°$. Single-crystal X-ray diffraction data were collected at −100 °C on a Rigaku AFC6 diffractometer (Mo Kα radiation). Total data collected: 3564. Unique data: 3483. Data with $F_o^2 > 3\sigma(F_o^2)$: 1820. Final $R = 7.2\%$ and $R_w = 9.3\%$. Both structures were solved by direct methods (SHELXS-86)[12c] and refined with the TEXSAN[12d] software package. An empirical absorption correction (DIFABS[12e]) was applied to the isotropically refined data. All non-hydrogen atoms except nitrogen and carbon were refined anisotropically. The hydrogen atoms were treated as described above. (c) Sheldrick, G. M. In Crystallographic Computing 3; Sheldrick, G. M., Gruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1985; pp 175–189. (d) TEXSAN: Single Crystal Structure Analysis Package, Version 5.0, Molecular Structure Corp., Woodland, TX. (e) Walker, N.; Stuard, D. *Acta. Crystallogr.* **1983**, *39A*, 158–166.

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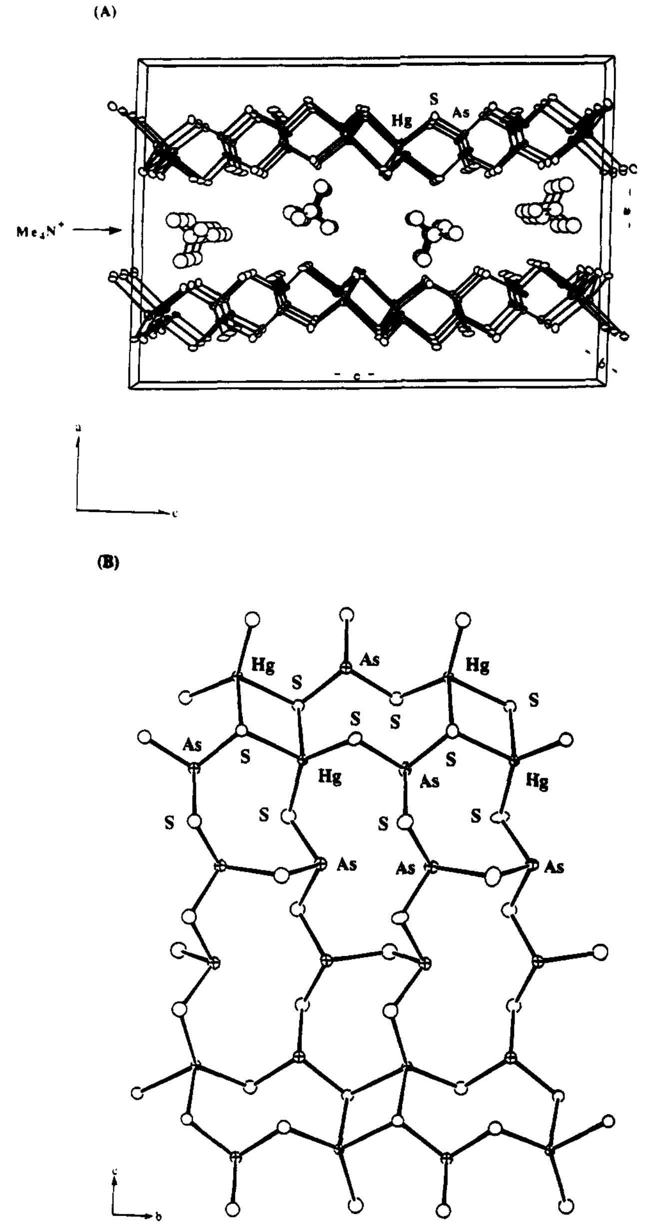

Figure 2. Layered structure of (Me$_4$N)[HgAs$_3$S$_6$]. (A) Unit cell view down the *b* axis. (B) A closeup of the [HgAs$_3$S$_6$]$_n^{n-}$ framework. Selected bond distances (Å): Hg–S1: 2.620(8), Hg–S1: 2.768(8), Hg–S3: 2.445(9), Hg–S5: 2.431(8), As1–S2: 2.263(9), As1–S3: 2.206(9), As1–S4: 2.260(9), As2–S1: 2.239(8), As2–S5: 2.199(9), As2–S6: 2.324(9), As3–S2: 2.279(9), As3–S4: 2.285(9), As3–S6: 2.244(9). Selected bond angles (deg): S1–Hg–S1: 94.1(2), S1–Hg–S3: 114.8(3), S1–Hg–S5: 98.9(2), S1–Hg–S3: 94.0(3), S1–Hg–S5: 108.2(3), S3–Hg–S5: 138.2(3), S2–As1–S4: 101.0(4), S2–As1–S3: 91.6(3), S3–As1–S4: 103.1(4), S1–As2–S5: 96.4(3), S1–As2–S6: 101.2(3), S5–As2–S6: 95.7(3), S2–As3–S4: 97.6(3), S2–As3–S6: 93.1(3), S4–As3–S6: 102.0(3).

1–4 are most likely catalyzed by protonation reactions of the terminal sulfide groups. If true, different products are expected from similar reactions performed under aprotic solvents.

The optical properties of (Ph$_4$P)$_2$[Hg$_2$As$_4$S$_9$] and (Me$_4$N)[HgAs$_3$S$_6$] suggest that they are wide-bandgap semiconductors. The optical absorption spectrum of (Ph$_4$P)$_2$[Hg$_2$As$_4$S$_9$], shown in Figure 3A, exhibits an intense, steep absorption edge, revealing an optical bandgap of 2.9 eV. The spectrum of (Me$_4$N)[HgAs$_3$S$_6$] also shows a similar absorption edge with a corresponding bandgap very close to that of (Ph$_4$P)$_2$[Hg$_2$As$_4$S$_9$] at 2.8 eV, see Figure 3B. This intense absorption is probably due to charge-transfer transitions from a primarily sulfur-based filled valence band to a mainly mercury-based empty conduction band.

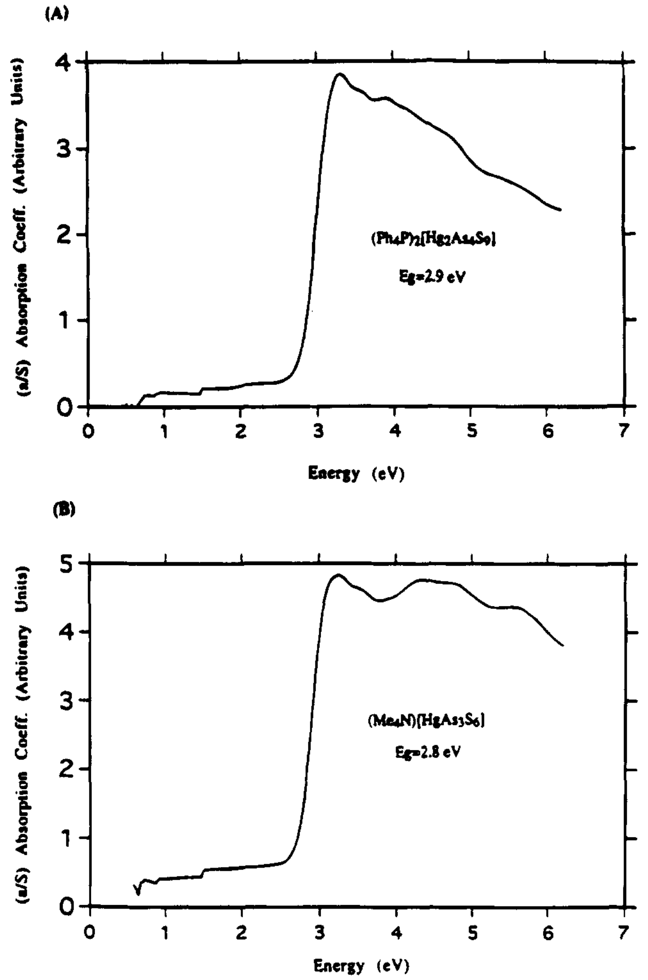

Figure 3. Solid-state electronic absorption spectra of (A) (Ph$_4$P)$_2$[Hg$_2$As$_4$S$_9$] and (B) (Me$_4$N)[HgAs$_3$S$_6$].

It is interesting to point out in these two compounds an interesting possible correlation between the counterion size and the metal coordination number. We notice that the large Ph$_4$P$^+$ cations afforded a one-dimensional chain structure with the Hg atoms in a trigonal-planar geometry, while the small Me$_4$N$^+$ cations produced a layered structure, where the Hg atoms assume tetrahedral coordination. This may be coincidental, but it is reminiscent of similar counterion size effects observed in silver polyselenides,[15] where, for example, the coordination number of Ag in [Ag$_x$Se$_y$]$^{n-}$ anions varies inversely with the size of counterion. More examples are needed to explore whether such tendencies actually exist in these systems. Furthermore, the dimensionality of the structures in (Ph$_4$P)$_2$[Hg$_2$As$_4$S$_9$] and (Me$_4$N)[HgAs$_3$S$_6$], as well as in (Ph$_4$P)$_2$[InAs$_3$S$_7$] and (Me$_4$N)$_2$Rb[BiAs$_6$S$_{12}$], is consistent with the view expressed earlier, where small cations *tend* to stabilize higher

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dimensionality anionic M/Q frameworks than corresponding large cations.[16] This, however, is not yet an established trend, and one can certainly find cases (especially in zeolites) where a given cation may give rise to different structure types or different cations give rise to the same framework. The cation size/structure correlation seems to be stronger when the stoichiometry of the anionic M/Q framework is the same from cation to cation.[17]

In summary, when applied to the "organic cation/M^{n+}/AsS_3^{3-}" system, the hydrothermal technique is a powerful tool that can successfully, and perhaps uniquely, produce novel metal/arsenic/sulfide covalent frameworks. Further investigations are in progress to explore the existence of other novel $[As_xS_y]^{n-}$ anions and to delineate the factors which influence the dimensionality of the final products and to achieve three-dimensional frameworks.

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Supplementary Material Available: Tables of crystal structure analysis, fractional atomic coordinates, and anisotropic and isotropic thermal parameters of all non-hydrogen atoms (13 pages); tables of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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