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Hydrothermal Assembly of Novel Covalent, Extended Structures Based on $[As_xS_y]^{n-}$ Building Blocks Derived from Condensation of AsS_3^{3-}. Isolation of $(Ph_4P)_2[InAs_3S_7]$ and $(Me_4N)_2Rb[BiAs_6S_{12}]$

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Several important classes of solid-state compounds such as silicate, borate, and phosphate minerals contain building blocks which are assembled from the condensation of elementary units like SiO_4^{4-}, BO_3^{3-}, PO_4^{3-}, etc.[1] This condensation gives rise to a large variety of rings, chains, and layers and results in great structural diversity among these minerals. By comparison, condensation in main-group thiometalates is less common. Examples include ternary thioborates,[2] thiogermanates,[3] and thioarsenates.[4] An elementary structural unit which may have great potential for condensation is the pyramidal AsS_3^{3-} unit. Condensation of AsS_3^{3-} is exhibited in species such as $[As_8S_{13}]^{2-}$,[5] $[As_4S_6]^{2-}$,[6] and $[As_3S_6]^{2-}$.[7] Similar units were recently reported to occur in the molecular compounds $[M(CO)_2(As_3Se_3)_2]^{2-}$ (M = Mo, W),[8] $[Mo_2O_2As_4S_{14}]^{2-}$,[9] $[MoAs_2Se_{10}]^{2-}$, and $[W_2As_2Se_{13}]^{2-}$,[10] where they exhibit unusual binding modes. Using the hydrothermal synthesis approach, we initiated exploration of the systems R_4E^+ (R = alkyl, Ph; E = N, P)/M^{n+}/AsS_3^{3-} with the aim of obtaining novel open frameworks containing either AsS_3^{3-} or its condensates. Open chalcogen-based frameworks could be interesting semiconducting analogs of zeolites. We report here our initial results from this promising approach[11] which include the isolation of two novel polymeric compounds, $(Ph_4P)_2[InAs_3S_7]$ and $(Me_4N)_2Rb[BiAs_6S_{12}]$.

$(Ph_4P)_2[InAs_3S_7]$ was prepared by heating $InCl_3$ with K_3AsS_3[12] and Ph_4PBr in H_2O at 120 °C.[13] The compound does not dissolve in common organic solvents. The structure was determined by X-ray single-crystal diffraction analysis.[14a] The macroanion $[InAs_3S_7]_n^{2n-}$ has an unusual one-dimensional polymeric structure composed of In^{3+} ions and $[As_3S_7]^{5-}$ units formed by corner-sharing pyramidal $[AsS_3]^{3-}$ units (Figure 1). The $[As_3S_7]^{5-}$ units engage in a remarkably complex multidentate coordination with two In^{3+} centers, using all five of their terminal sulfur atoms. To the best of our knowledge, the $[As_3S_7]^{5-}$ unit represents a new thioarsenate anion with potentially rich coordination chemistry. The In^{3+} ion is in a distorted trigonal bipyramidal environment with the axial bond angle, S3–In–S4, at 171.4(1)°. The average distance between the In and the axial S atoms (2.649(4) Å) is significantly longer than that between the equatorial S atoms (2.492(4) Å). The $[InAs_3S_7]_n^{2n-}$ chains lie parallel to the *c* axis and are separated by Ph_4P^+ cations (Figure 1B). There are two types of As–S bonds in $[As_3S_7]^{5-}$. The average As–S distance of the type As–S–In (2.216(4) Å) is slightly shorter than that of the As–S–As type (2.279(4) Å). The S–As–S angles range from 95.3(1) to 107.8(1)°. The bond distances and angles are comparable to those found in $[Mo_2O_2As_4S_{14}]^{2-}$ and $[Mo_4O_4As_4S_{14}]^{4-}$.[9] The electronic spectrum of $(Ph_4P)_2[InAs_3S_7]$ shows a steep absorption edge, characteristic of an optical bandgap of 3.1 eV.

$(Me_4N)_2Rb[BiAs_6S_{12}]$ was synthesized by heating $BiCl_3$ with Rb_3AsS_3 and Me_4NCl in H_2O at 120 °C.[14b,15] The anionic $[BiAs_6S_{12}]_n^{3n-}$ possesses a two-dimensional layered structure with trigonal symmetry consisting of octahedral Bi^{3+} ions and $[As_3S_6]^{3-}$ cyclic units formed by three corner-sharing trigonal pyramidal $[AsS_3]^{3-}$ units (Figure 2). The $[As_3S_6]^{3-}$ ligand was first observed as a discrete molecule in $(enH_2)_3(As_3S_6)_2$.[16] The $[As_3S_6]^{3-}$ fragment in $(Me_4N)_2Rb[BiAs_6S_{12}]$ is sitting on a 3-fold axis with three As atoms and three S atoms forming a six-membered ring in a chair conformation. In $[As_3S_6]^{3-}$ the As–S bonds are separated into two types. The intra-ring As–S distance (2.312(2) Å) is significantly longer than the other As–S distance (2.189(3) Å). Similar distances were also observed in the free $[As_3S_6]^{3-}$.[16] The Bi^{3+} ion is in a nearly perfect octahedral geometry. The overall organization of the Bi^{3+} and the $[As_3S_6]^{3-}$ ions is $CdCl_2$-type with the cations in the Cd^{2+} and the anions in the Cl^- sites, respectively. The Bi–S bond distance (2.830(2) Å), is in the normal range.[17] The Me_4N^+ and the Rb^+ cations are sitting between the $[BiAs_6S_{12}]_n^{3n-}$ layers, which are spaced 9.445 Å apart. The Rb^+ and $[As_3S_6]^{3-}$ ions share a common C_3 axis so that each Rb^+ ion is coordinated to six bridging S atoms from two $[As_3S_6]^{3-}$ units, one above and one below, in a trigonal antiprismatic fashion. The Rb···S distance is 3.458(2) Å.

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(12) A_3AsS_3 (A = K, Rb, Cs) were synthesized using stoichiometric amounts of alkali metal, arsenic sulfide (As_2S_3), and sulfur in liquid ammonia. The reaction gives a yellow-brown powder upon evaporation of ammonia.

(13) A Pyrex tube (~4 mL) containing $InCl_3$ (55 mg, 0.25 mmol), K_3AsS_3 (144 mg, 0.5 mmol), Ph_4PBr (419 mg, 1.0 mmol), and 0.5 mL of water was sealed under vacuum and kept at 120 °C for 2 days. The large pale yellow transparent chunky crystals were isolated in water and washed with methanol and ether (yield 74.5% based on In).

(14) (a) Crystal data for $(Ph_4P)_2[InAs_3S_7]$: single-crystal X-ray diffraction data were collected at 23 °C on a Rigaku AFC6 diffractometer; monoclinic $P2_1/c$ (No. 14); a = 19.059(3) Å, b = 14.436(3) Å, c = 19.325(6) Å, β = 106.02(1)°, Z = 4, V = 5111(2) Å^3, d_{calc} = 1.615 g/cm^3; μ = 94.61 cm^{-1}, $2\theta_{max}$(Mo Kα) = 45.00°; total data collected 8427, unique data 8374, data with $F_o^2 > 3\sigma(F_o^2)$ 3604; final R = 5.5% and R_w = 5.7%. (b) Crystal data for $(Me_4N)_2Rb[BiAs_6S_{12}]$: single-crystal X-ray diffraction data were collected at 23 °C on a computer-controlled four-circle Nicolet (Siemens) autodiffractometer; trigonal space group $R\bar{3}$ (No. 148); a = 9.978(1) Å, c = 28.337(5) Å, V = 2356(1) Å^3, Z = 3, d_{calc} = 2.700 g/cm^3; μ = 141.34 cm^{-1}, $2\theta_{max}$(Mo Kα) = 58.7°; total number of reflections collected 1233, unique data 1157, number of reflections having $F_o^2 > 3\sigma(F_o^2)$ 906; final R = 3.1% and R_w = 2.5%. The structures were solved using software described elsewhere.[20]

(15) $BiCl_3$ (63 mg, 0.2 mmol) was mixed with 2 equiv of $Rb_3As_3S_3$ (171 mg, 0.4 mmol) and 4 equiv of Me_4NCl (88 mg, 0.8 mmol), and the mixture was sealed under vacuum with 0.3 mL of H_2O in a Pyrex tube (~4 mL). The reaction was run at 120 °C for 1 week. Washing the reaction mixture with methanol and ether afforded dark red cubelike single crystals of $(Me_4N)_2Rb[BiAs_6S_{12}]$ (45 mg, yield of 30% based on As).

(16) (a) en = ethylenediamine. (b) Sheldrick, W. S.; Kaub, J. *Z. Naturforsch.* **1985**, *40B*, 19–21.

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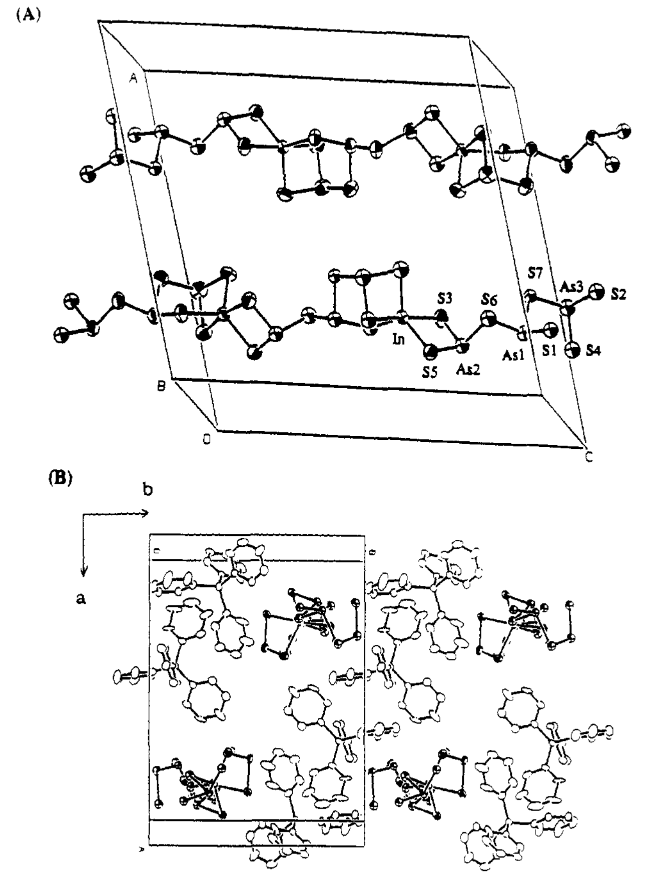

Figure 1. (A) Structure and labeling scheme of $[InAs_3S_7]_n^{2n-}$. Selected bond distances (Å) and angles (deg): In–S1 = 2.474(4), In–S2 = 2.496(4), In–S3 = 2.589(3), In–S4 = 2.696(4), In–S5 = 2.499(4), As1–S1 = 2.214(4), As1–S6 = 2.276(4), As1–S7 = 2.271(5), As2–S3 = 2.189(4), As2–S5 = 2.234(4), As2–S6 = 2.285(4), As3–S2 = 2.251(4), As3–S4 = 2.192(5), As3–S7 = 2.287(4); S1–In–S2 = 110.6(1), S1–In–S3 = 91.8(1), S1–In–S4 = 95.3(1), S1–In–S5 = 123.8(1), S2–In–S3 = 102.1(1), S2–In–S4 = 79.8(1), S2–In–S5 = 125.3(1), S3–In–S4 = 171.4(1), S3–In–S5 = 82.2(1), S4–In–S5 = 89.9(1), S1–As1–S6 = 95.3(1), S1–As1–S7 = 107.8(1), S6–As1–S7 = 97.3(1), S3–As2–S5 = 98.3(1), S3–As2–S6 = 104.0(1), S5–As2–S6 = 99.1(1), S2–As3–S4 = 97.2(1), S2–As3–S7 = 101.0(1), S4–As3–S7 = 102.7(1). (B) Packing diagram of $[InAs_3S_7]_n^{2n-}$

The lone pair on Bi^{3+} is stereochemically inactive and apparently is delocalized around the Bi nucleus. This is common for octahedral Bi^{3+} sites and has been found earlier in other Bi–S compounds such as $KBiS_2$.[18] $(Me_4N)_2Rb[BiAs_6S_{12}]$ absorbs light strongly thoughout the visible region with a λ_{max} of 520 nm. Its electronic spectrum reveals an optical bandgap of 1.1 eV, which is within the range appropriate for efficient solar energy collection and suggests possible photoconductivity in this material. The nature of the electronic absorption may be due to charge-transfer excitations from sulfur to bismuth orbitals.

Remarkably, although the arsenic/sulfide source in both reactions is $[AsS_3]^{3-}$, we do not observe such discrete units in the structures. Rather, in $[InAs_3S_7]^{2-}$ and $[BiAs_6S_{12}]^{3-}$, we find respectively the unusual chainlike $[As_3S_7]^{5-}$ and cyclic $[As_3S_6]^{3-}$ fragments, both formed from corner-sharing $[AsS_3]^{3-}$ units. These units result from condensation reactions in water in which several equilibria of the type shown in eqs 1–3 must exist.

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

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

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

These reactions parallel those found in the condensation of SiO_4^{4-} and PO_4^{3-} units.[1] Therefore, as in these systems, one would expect that a variety of $[As_xS_y]^{n-}$ species might be possible.

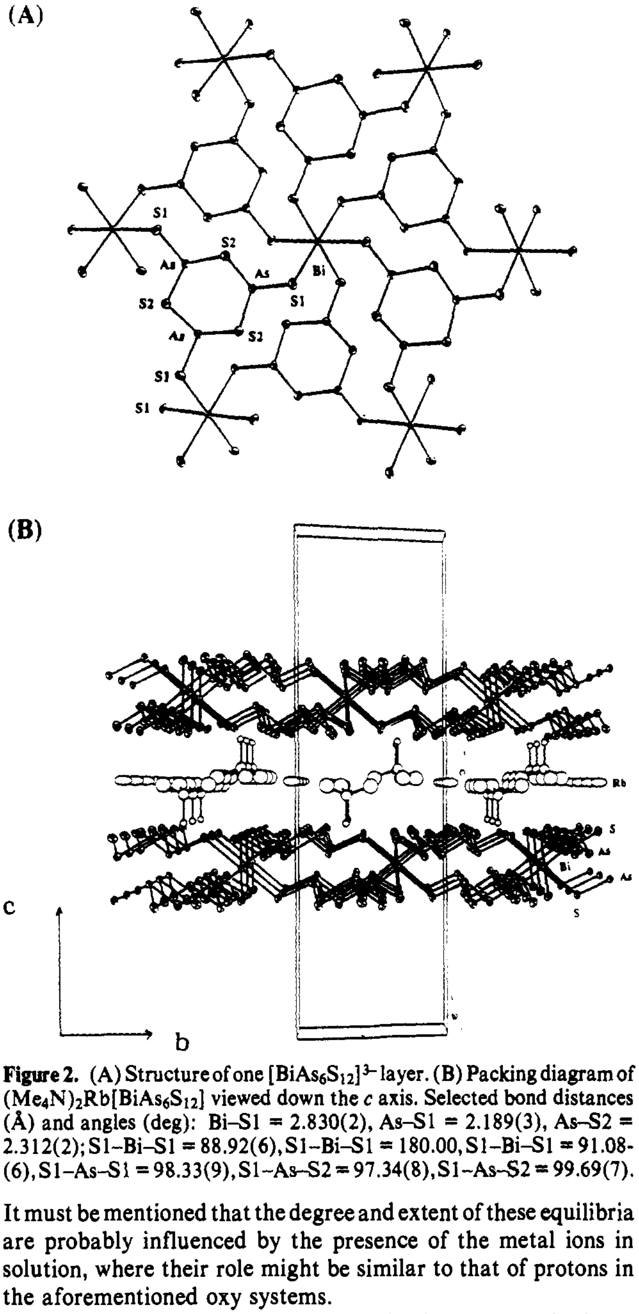

Figure 2. (A) Structure of one $[BiAs_6S_{12}]^{3-}$ layer. (B) Packing diagram of $(Me_4N)_2Rb[BiAs_6S_{12}]$ viewed down the *c* axis. Selected bond distances (Å) and angles (deg): Bi–S1 = 2.830(2), As–S1 = 2.189(3), As–S2 = 2.312(2); S1–Bi–S1 = 88.92(6), S1–Bi–S1 = 180.00, S1–Bi–S1 = 91.08(6), S1–As–S1 = 98.33(9), S1–As–S2 = 97.34(8), S1–As–S2 = 99.69(7).

It must be mentioned that the degree and extent of these equilibria are probably influenced by the presence of the metal ions in solution, where their role might be similar to that of protons in the aforementioned oxy systems.

In conclusion, the successful hydrothermal synthesis of $(Ph_4P)_2[InAs_3S_7]$ and $(Me_4N)_2Rb[BiAs_6S_{12}]$ using AsS_3^{3-} as starting material opens exciting possibilities for the further exploration of the metal/arsenic/sulfide and related systems. Key to this is the complex condensation equilibria which exist among various $[As_xS_y]^{n-}$ species in the reaction medium. As in other labile systems, the size of the countercations is expected to influence the structure of the covalent framework.[19,20] Although the controlled synthesis of specific $[As_xS_y]^{n-}$ ligands may be challenging, the above equilibria should undoubtedly be exploited for the synthesis of new thioarsenates and related compounds.

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Supplementary Material Available: Tables of positional parameters, bond distances and angles, and anisotropic and isotropic thermal parameters (18 pages). Ordering information is given on any current masthead page.

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