Inorg. Chem. **2008**, *47*, 7068−7070

Inorganic Chemistry

Communication

$AEuAsS_3$ (A = Li, K, Rb, and Cs): New As^{3+} Species from an Arsenic-Rich Polysulfide Flux

Tarun K. Bera and Mercouri G. Kanatzidis*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208

Received June 3, 2008

Four europium compounds, $LiEuAsS_3$ (**I**), $KEuAsS_3$ (**IIa**), $RbEuAsS_3$ (**IIb**), and $CsEuAsS_3$ (**IIc**), containing As^{3+} were synthesized in molten alkali-metal polysulfide salts. An As-rich flux was found to be necessary to stabilize the pyramidal building unit $[AsS_3]^{3-}$. All crystallize in the monoclinic space group $P2_1/c$ with two new structure types. Compound **I** features a new coordination mode for the $[AsS_3]^{3-}$ unit and three-dimensional $[Eu(AsS_3)]^-$ framework. Compounds **IIa**−**c** are isostructural and feature a layer of $[Eu(AsS_3)]^-$ with an unusual μ_5-sulfide anion in a *umbrella-like* geometry. The compounds are paramagnetic semiconductors with an energy gap of ~2.0 eV.

The reactivity of rare-earth elements with the molten alkali-metal polychalcophosphate salts has been studied extensively,[1,2] and a wide variety of compounds with interesting structures and physical properties[3] have been synthesized. The corresponding polychalcoarsenate system also merits investigation because it could lead to new materials and also teach us a great deal about similarities and differences between P and As chemistry.[4] Moreover, the different redox behavior of P and As gives compounds with different structural motifs and physical properties. Initial studies on the RE/As/Q and A/RE/As/Q systems (A = alkali metals, RE = rare earths, and Q = S, Se, and Te) reported recently have revealed novel species.[5] Our investigations of the reactivity of several main-group and transition metals (Sn, Pb, Mn, Cd, etc.) with the alkali-metal polychalcoarsenate flux showed that divalent metals (e.g., Pb^{2+}, Mn^{2+}, Cd^{2+}, etc.) favor As^{5+} species in a wide composition range.[4] The highly Lewis acidic tetravalent metals (e.g., Sn^{4+}), however, favor As^{3+} species. The stereochemically active 4s lone pair of electrons on As^{3+} could act as an enhancement factor for nonlinear optical properties[6] and also can increase the glass formation tendency.[7] It would be useful therefore to understand the flux chemistry and controlling factors for stabilizing As^{5+} vis-à-vis As^{3+} species in the compounds.

Here we describe new chemistry involving the reactivity of Eu metal and four new compounds: $LiEuAsS_3$ (**I**), $KEuAsS_3$ (**IIa**), $RbEuAsS_3$ (**IIb**), and $CsEuAsS_3$ (**IIc**). The compounds contain the pyramidal $[AsS_3]^{3-}$ as the building unit, which is unknown in the corresponding P system. The compounds formed under flux conditions designed to inhibit As^{5+}.

The red crystalline compounds **I** and **IIa**−**c** were synthesized from the A_2S/Eu/As/S mixtures (A = Li, K, Rb, and Cs).[8] The relatively As-rich flux ratio of 1/2/2/4 led to compound **I**, while compounds **IIa**−**c** were prepared from a flux ratio of 1/1/3/4. Here a flux ratio with a lower As content (e.g., 1/1/1/4) was unable to produce the title phases; instead, we observed As^{5+}-containing compounds A_4Eu-

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* To whom correspondence should be addressed. E-mail: m-kanatzidis@northwestern.edu.

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$(AsS_4)_2$ (A = K, Rb, and Cs), which are isostructural with the chalcophosphates.[1c] Lowering the flux basicity by decreasing the A_2S/S ratio also failed to stabilize the As^{3+} phases. It seems that the less oxidizing As-rich flux is necessary to stabilize the As^{3+} species in the A_2S/Eu/As/S system.

Single-crystal X-ray diffraction analysis showed that the compounds $LiEuAsS_3$ (**I**), $KEuAsS_3$ (**IIa**), $RbEuAsS_3$ (**IIb**), and $CsEuAsS_3$ (**IIc**) crystallize in the monoclinic space group $P2_1/c$.[9] The structure of **I** is built of slabs of $[Eu(AsS_3)]^-$ (shaded region in Figure 1a) interconnected in the third dimension via Eu−S bonds to give a dense 3-D framework, leaving a 1-D channel for the tiny Li^+ ions. Two notable features in this structure are (i) the unusual coordination mode of the $[AsS_3]^{3-}$ anion to Eu and (ii) the coordination environment of S3. Each $[AsS_3]^{3-}$ anion bridges to five Eu atoms, four within the slab and one from a neighboring slab (Figure 2a). Among the three S atoms in the asymmetric unit, the coordination environment of S1 and S2 is normal, whereas S3 has an unusual "flattened umbrella-like" geometry similar to that in α-$Na_6Pb(PS_4)_4$[10] (Figure 3a).

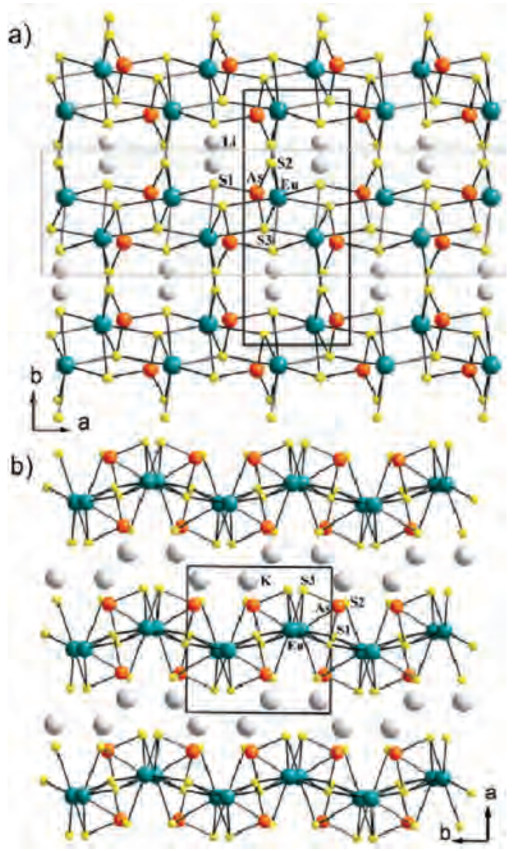

Figure 1. Extended unit cell view of (a) the 3-D framework structure of $LiEuAsS_3$ (the shaded part represents the $[Eu(AsS_3)]^-$ slab) and (b) the layered structure of $KEuAsS_3$ (**Ia**).

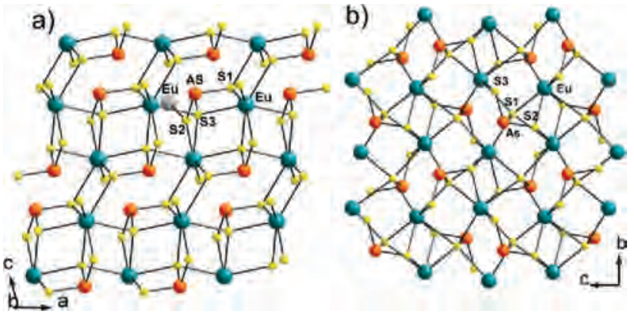

Figure 2. (a) View of the $[Eu(AsS_3)]^-$ slab in **I**. Each $[AsS_3]^{3-}$ anion is coordinated to four Eu atoms within the slab and one from the neighboring slab (gray atom connected to S2). (b) View of the single layer in the 2-D structures (**IIa−c**).

The coordination environment of Eu is distorted monocapped trigonal prismatic with all seven Eu−S distances in the range of 2.929(2)−3.139(2) Å (Figure 3a).[11] The EuS_7 monocapped trigonal prisms share only edges within the $[Eu(AsS_3)]^-$ slab (in the *ac* plane) and extend their coordination into the third dimension (along the *b* axis) through corner sharing (Figure 1a).

The Li atoms are in a distorted tetrahedral environment of S atoms (see Figure 3b). Those Li−S distances are in the range of 2.462(13)−2.624(13) Å.

The isostructural compounds **IIa−c** have ${}_\infty^{2}[Eu(AsS_3)]^-$ layers, which sandwich the large alkali-metal ions: K, Rb,

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(8) **$LiEuAsS_3$ (I).** A mixture of Li_2S (0.029 g, 0.63 mmol), Eu (0.190 g, 1.25 mmol), As (0.094 g, 1.25 mmol), and S (0.080 g, 2.50 mmol) was loaded into a fused-silica tube in a nitrogen-filled glovebox. It was flame-sealed under vacuum (~10^{-4} mbar) and then heated to 650 °C in 10 h. After 60 h at 650 °C, it was cooled down to 250 °C in 80 h followed by rapid cooling to room temperature. A mixture of red and black crystals (1:9) was obtained after dissolution of the excess flux in degassed DMF. The red crystalline phase (<10% yield) was identified as **I**, and the black material was mostly As. Several attempts to make pure $LiEuAsS_3$ have failed so far. **$KEuAsS_3$ (IIa).** A red crystalline product was isolated as a single phase in >70% yield from the mixture of K_2S (0.072 g, 0.66 mmol), Eu (0.100 g, 0.66 mmol), As (0.150 g, 2.00 mmol), and S (0.084 g, 2.61 mmol) using a procedure similar to that above. Semiquantitative energy-dispersive (EDS) analysis gave an average composition of $K_{1.1}Eu_{1.0}As_{1.0}S_{3.2}$. **$RbEuAsS_3$ (Ib).** It was isolated from the mixture of Rb_2S (0.100 g, 0.49 mmol), Eu (0.075 g, 0.49 mmol), As (0.111 g, 1.48 mmol), and S (0.063 g, 1.97 mmol) using a procedure similar to that above. Red crystals, single phase with >75% yield, and EDS analysis gave the composition $Rb_{1.0}Eu_{1.0}As_{1.1}S_{3.2}$. **$CsEuAsS_3$ (IIc).** A single-phase red crystalline compound with >70% yield was achieved from the mixture of Cs_2S (0.120 g, 0.40 mmol), Eu (0.061 g, 0.40 mmol), As (0.090 g, 1.22 mmol), and S (0.052 g, 1.62 mmol) as described above. EDS analysis gave an average composition of $Cs_{1.0}Eu_{1.0}As_{1.1}S_{3.3}$.

(9) Single-crystal X-ray diffraction data were collected at 100 K using a STOE imaging-plate diffraction system (IPDS-2) with graphite-monochromatized Mo Kα radiation. A numerical absorption correction was applied. Direct methods and full-matrix least-squares refinements against F^2 were performed with the *SHELXTL* package. Crystal data for $LiEuAsS_3$ (**I**): monoclinic $P2_1/c$, $Z = 4$, $a = 5.6862(5)$ Å, $b = 13.1187(11)$ Å, $c = 7.1735(6)$ Å, $\beta = 104.858(7)°$, $V = 517.22(8)$ Å^3, θ_{max}(Mo Kα) = 29.18°, total reflections = 4715, unique reflections $[F_o^2 > 2\sigma(F_o^2)] = 1387$, number of variables = 56, $\mu = 19.503$ mm^{-1}, $D_c = 4.238$ g cm^{-3}, $R_{int} = 3.37\%$, GOF = 1.427, $R_1 = 2.45\%$, $R_w = 5.23$ for $I > 2\sigma(I)$. $KEuAsS_3$ (**IIa**): $P2_1/c$, $Z = 4$, $a = 8.8306(8)$ Å, $b = 8.3455(9)$ Å, $c = 8.6224(9)$ Å, $\beta = 106.591(8)°$, $V = 608.98(11)$ Å^3, θ_{max}(Mo Kα) = 29.24°, total reflections = 5750, unique reflections $[F_o^2 > 2\sigma(F_o^2)] = 1581$, number of variables = 56, $\mu = 17.252$ mm^{-1}, $D_c = 3.950$ g cm^{-3}, $R_{int} = 9.06\%$, GOF = 1.017, $R_1 = 2.32\%$, $R_w = 4.53$ for $I > 2\sigma(I)$. $RbEuAsS_3$ (**IIb**): $P2_1/c$, $Z = 4$, $a = 9.0795(8)$ Å, $b = 8.3669(8)$ Å, $c = 8.6752(8)$ Å, $\beta = 105.844(7)°$, $V = 633.99(10)$ Å^3, θ_{max}(Mo Kα) = 29.03°, total reflections = 7053, unique reflections $[F_o^2 > 2\sigma(F_o^2) = 2047$, number of variables = 56, $\mu = 23.543$ mm^{-1}, $D_c = 4.280$ g cm^{-3}, $R_{int} = 4.07\%$, GOF = 1.168, $R_1 = 2.10\%$, $R_w = 4.12$ for $I > 2\sigma(I)$. $CsEuAsS_3$ (**IIc**): $P2_1/c$, $Z = 4$, $a = 9.3953(19)$ Å, $b = 8.4407(17)$ Å, $c = 8.7702(18)$ Å, $\beta = 105.12(3)°$, $V = 671.4(2)$ Å^3, θ_{max}(Mo Kα) = 29.14°, total reflections = 6184, unique reflections $[F_o^2 > 2\sigma(F_o^2)] = 1800$, number of variables = 55, $\mu = 20.372$ mm^{-1}, $D_c = 4.511$ g cm^{-3}, $R_{int} = 3.32\%$, GOF = 1.213, $R_1 = 2.38\%$, $R_w = 5.92$ for $I > 2\sigma$ (I).

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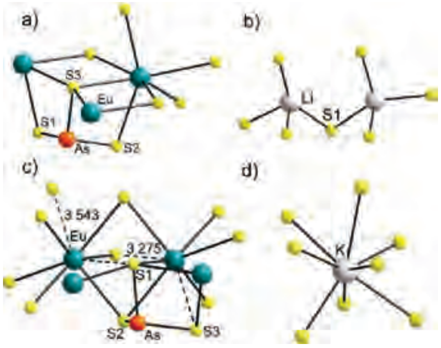

Figure 3. (a) Local coordination environment of Eu and As and the μ_4-S3 center in $LiEuAsS_3$. (b) Distorted tetrahedral Li center in **I**. (c) Coordination environment of μ_5-sulfide anion S1, trigonal-pyramidal As, and distorted bicapped trigonal-prismatic Eu in **IIa**−**c**. (d) Local environment of the alkali metal in the layered structures (**IIa**−**c**).

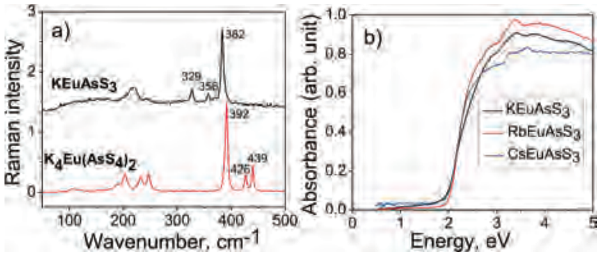

Figure 4. (a) Fourier transform Raman spectra for pyramidal $As^{III}S_3$ [$KEuAsS_3$] and tetrahedral $As^{IV}S_4$ [$K_4Eu(AsS_4)_2$] building units. (b) UV−vis absorption spectra for **IIa**−**c**.

or Cs (Figure 1b). The layers are parallel to the *bc* plane. Unlike **I**, here each $[AsS_3]^{3-}$ anion bridges to four Eu atoms (Figure 2b) and the coordination environment of S1 is very unusual. The μ_5-S1 is bonded to four Eu atoms and one As atom to form an unusual *umbrella-like* geometry ("tetra umbrella"), with all four Eu atoms nearly on the square plane and S1 located 0.26 Å above it (Figure 3c). The As−S1 bond defines the umbrella handle. To the best of our knowledge, this μ_5-sufide anion geometry is new.

The Eu atoms in **IIa**−**c** have a distorted bicapped trigonal-prismatic environment with six short Eu−S distances in the range of 2.941(2)−3.083(2) Å (solid line) and two other longer Eu−S distances at 3.256(2) and 3.480(2) Å (dotted line) (Figure 3c).[12] The EuS_8 polyhedra share-edges and rectangular faces to form a chain along the *b* axis, and the chains are linked into layers through edge sharing (Figure 2b). The rectangular face-sharing creates Eu−Eu distances of ~3.804(4) Å. All three As−S bond distances are normal and in the range of 2.221(1)−2.283(1) Å.[4,11]

The K, Rb, and Cs ions have eight-coordinated distorted bicapped trigonal-prismatic geometry. The A···S interactions are mostly ionic in nature. The layered structure with the relatively larger alkali metals (K, Rb, and Cs) and a 3-D framework with the smaller alkali-metal Li is in accordance with the predictions derived from the counterion effect on the dimensionality of the structure.[12]

The Raman spectra obtained on polycrystalline samples of **IIa**−**c** were similar and exhibit a very strong peak at 382 cm^{-1} together with some weak bands (Figure 4a). These are assigned to the stretching and deformation modes of the $[As^{III}S_3]^{3-}$ anion. These values are shifted to lower frequencies compared with those of the $[As^{V}S_4]^{3-}$ anion because of the stronger As^{V}−S interactions relative to As^{III}−S as follows from the longer As−S bonds in $[As^{III}S_3]^{3-}$ compared to those in $[As^{V}S_4]^{3-}$.[5a]

Temperature-dependent (2−400 K) magnetic susceptibility measurements of **IIa** (see the Supporting Information) show Curie law behavior, with an effective magnetic moment of 7.64 μ_B mol^{-1}. This is close to the calculated 7.9 μ_B mol^{-1} for Eu^{2+} ions. Therefore, the compounds are charge balanced based on the formalism $A^{+}Eu^{2+}(AsS_3)^{3-}$.

The solid-state UV−vis optical absorption spectra of **IIa**−**c** show a very strong absorption onset at ~2.0 eV (Figure 4b).[13] This is attributed to excitations within the $^{2}_{\infty}[Eu(AsS_3)^{-}]$ layer and believed to originate from transitions involving filled S-based p orbitals in the valence band and empty Eu d orbitals in the conduction band. The alkali metal does not seem to play a significant role in defining the electronic structure of the framework, consistent with the predominantly ionic character of the A···S interactions. The thermal behavior of **IIa**−**c** investigated by means of differential thermal analysis suggests that the compounds melt congruently (see the Supporting Information).

The use of the As-rich flux suppresses the formation of As^{5+} and leads to stabilization of the As^{3+} species. This is because the As-rich compositions have lower sulfur content and are less oxidizing. This reaction condition favors the new thioarsenates, $LiEuAsS_3$, $KEuAsS_3$, $RbEuAsS_3$, and $CsEuAsS_3$, which have no phosphorus analogues, and bypasses the formation of $A_4Eu(AsS_4)_2$, which do. Thus, controlling the As fraction could be a useful synthetic approach to discovering new varieties of chalcoarsenate building blocks with low-valent arsenic.

Acknowledgment. Financial support from the National Science Foundation (Grant DMR-0801855) is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic files (CIF) and experimental details for $LiEuAsS_3$, $KEuAsS_3$, $RbEuAsS_3$, and $CsEuAsS_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Selected bond lengths (in Å) for $LiEuAsS_3$: Eu−S1 2.987(2), 3.139(2); Eu−S2 2.949(2), 2.998(2); Eu−S3 2.929(2), 2.960(2), 3.092(2); As−S1 2.262(2); As−S2 2.225(2); As−S3 2.263(2). $KEuAsS_3$: Eu−S1 3.256(1), 3.083(1), 3.056(1), 3.034(1); Eu−S2 3.025(1), 3.027(1); Eu−S3 2.941(1), 3.479(2); As−S1 2.221(1); As−S2 2.225(1); As−S3 2.284(1). $RbEuAsS_3$: Eu−S1 3.046(1), 3.059(1), 3.086(1), 3.275(1); Eu−S2 3.013(1), 3.025(1); Eu−S3 2.943(1), 3.543(2); As−S1 2.278(1); As−S2 2.221(1); As−S3 2.219(1). $CsEuAsS_3$: Eu−S1 3.068(1), 3.069(1), 3.099(1), 3.342(1); Eu−S2 3.018(1), 3.003(1); Eu−S3 2.949(1); As−S1 2.268(1); As−S2 2.226(1); As−S3 2.223(1).

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