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$Eu_3(AsS_4)_2$ and $A_xEu_{3-y}As_{5-z}S_{10}$ (A = Li, Na): Compounds with Simple and Complex Thioarsenate Building Blocks

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$Eu_3(AsS_4)_2$ and $A_xEu_{3-y}As_{5-z}S_{10}$ (A = Li, Na) are the members of a new thioarsenate family. They feature As^{5+} and As^{3+} centers, respectively. The rhombohedral $Eu_3(AsS_4)_2$ features a new structure type consisting of eight-coordinate Eu^{2+} centers and AsS_4^{3-} anions, whereas the monoclinic $A_xEu_{3-y}As_{5-z}S_{10}$ ($Li_{0.73}Eu_3As_{4.43}S_{10}$ and $Na_{0.66}Eu_{2.86}As_{4.54}S_{10}$) belong to the rathite sulfosalt family and are comprised of apparent $[As_{10}S_{20}]^{10-}$ segments linked with Eu^{2+} ions to give a three-dimensional network. They appear to be alkali-metal-stabilized derivatives of the putative parent phase "$Eu_3As_5S_{10}$".

Rare-earth chalcogenides exhibit rich structural chemistry arising in part because of the variable coordination environment of rare-earth ions that can range from six- to nine-coordinate. These compounds can exhibit broadly interesting properties. For example, Ce_2SiS_5, $Ce_6Si_4S_{17}$, and $Ce_4Si_3S_{12}$[1]are important as potential pigment materials. Eu_2GeS_4[2] displays ferroelectric behavior while Eu_2CuS_3[3] is a rare example with Eu atoms in two different valent states. In addition, rare-earth chalcogenide spinels exhibit geometric magnetic frustration.[4] Rare-earth sulfides have shown promise as optical and electronic materials,[5] and corresponding glasses[6] are being considered as fiber lasers and optical amplifiers.

The polychalcophosphate flux technique[7] has served to discover varieties of new chalcophosphate materials.[8] Recently, we have shown that the polychalcoarsenate flux has the potential to reveal novel compounds containing different building blocks; $[As^{III}Q_x]^{3-}$ (x = 3, 4, and 5) and $[As^{V}Q_4]^{3-}$ (Q = S, Se).[9]

Here we describe the reactivity of Eu metal with molten alkali metal polythioarsenate salts.[7] The structural chemistry of Eu−As−S appears to be related to that of lead arsenosulfide minerals, commonly known as the rathite groups,[10] where rathite-I is $(PbTl)_3As_4(AsAg)S_{10}$, rathite-Ia is $Pb_{3.5}As_{4.5}S_{10}$, rathite-III is $Pb_3As_5S_{10}$, and dufrenoysite is $Pb_4As_4S_{10}$. The reported structures of the rathite sulfosalts seem to be incomplete partly because of the disorder present and partly because of the lack of the advanced structural tools in the early 60's, when most of these studies were performed.[11] Among these, only $Pb_4As_4S_{10}$ preserves charge neutrality, whereas the others (e.g., $Pb_3As_5S_{10}$, $Pb_{3.5}As_{4.5}S_{10}$, $(PbTl)_3As_4(AsAg)S_{10}$, etc.) need some kind of partial or mixed occupancy and additional elements (heteroatoms) in certain sites to give a stable and realistic formula. Understanding sulfosalt chemistry is of major interest in mineralogy because the exact composition of these minerals can serve as a geological indicator.[12]

Since Pb and Eu can exhibit marked chemical similarities, we expected that the reaction of Eu in polythioarsenate fluxes could yield compounds analogous to rathite-I, rathite-Ia, etc. Here we describe the new compounds $Eu_3(AsS_4)_2$ (**I**), $Li_{0.73}Eu_3As_{4.43}S_{10}$ (**IIa**), and $Na_{0.66}Eu_{2.86}As_{4.54}S_{10}$ (**IIb**).[13] **I** is a basic salt involving the elementary $[AsS_4]^{3-}$ unit and presents

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a new structure type. The structure of compounds **IIa** and **IIb** are related to that of $Pb_3As_5S_{10}$[10] and $Ba_3Sb_{4.66}S_{10}$.[14]

The structure of **I** was solved[15] in the space group $R\bar{3}c$. It is a dense packing of tetrahedral $[AsS_4]^{3-}$ ligands and Eu^{2+} centers. An interesting feature is the arrangement of $[AsS_4]^{3-}$ down the *c* axis where packing configuration of the anions is rotationally staggered, Figure 1a. Figure 1b shows the centrosymmetric arrangement of the $[AsS_4]^{3-}$ anions. The first two tetrahedra, labeled T1 and T2 are staggered by an angle of ∼17°. The next two tetrahedra, labeled T3 and T4, are also staggered by ∼17° with respect to each other, but the T2 and T3 tetrahedra are staggered by 60°.

The Eu atom binds to eight S atoms in a distorted bicapped trigonal prismatic geometry, Figure 1c. The Eu−S bonds range from 2.9549(13) to 3.144(1) Å and compare well with those found in $KEuPS_4$.[16] The As−S bond distances are in the normal range.[9] The S−As−S angles are almost ideal tetrahedral angles with values of 109.97(4)° and 108.97(4)°. Cubic $Pb_3(PS_4)_2$[17] is the closest chemical analogue of $Eu_3(AsS_4)_2$, but it has a different structure.

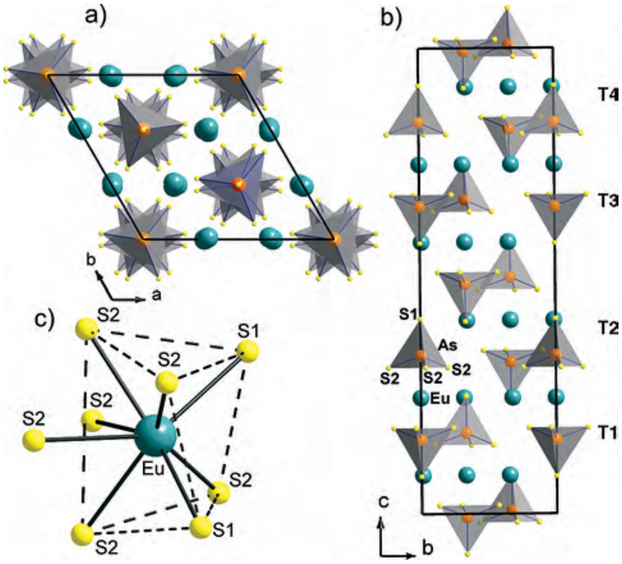

Figure 1. (a) Unit cell of $Eu_3(AsS_4)_2$ viewed down the *c* axis, showing the hexagonal arrangement of Eu atoms around the staggered $[AsS_4]^{3-}$ tetrahedra. (b) Unit cell view of $Eu_3(AsS_4)_2$ down the *a* axis showing the orientation of $[AsS_4]^{3-}$ tetrahedra along the *c* axis. (c) Extended coordination sphere of the Eu center. Eu−S(1), 3.1438(10) Å; Eu−S(2), 2.9549(13), 3.0519(16), 3.0522(16), 3.4309(14) Å; As−S(1), 2.187(2) Å; As−S(2), 2.1630(12) Å.

The compounds **IIa** and **IIb** derive from the general formula $A_xEu_{3-y}As_{5-z}S_{10}$ [where, $z = (1 + x - 2y)/3$], with $(x, y, z) = (0.73, 0, 0.57)$ for Li and $(x, y, z) = (0.66, 0.14, 0.46)$ for Na. The presence of Li and Na in these compounds was independently confirmed by elemental analysis conducted with inductively couple plasma mass spectrometry (ICP-MS). The structures of **IIa** and **IIb** were solved with a monoclinic space group $P2_1/c$.[15] They are isostructural to each other and do not contain $[AsS_4]^{3-}$. They are closely related to the structures of $Pb_3As_5S_{10}$[18] and $Ba_3Sb_{4.66}S_{10}$.[14] The overall structure is composed of thick slabs linked together by nine-coordinate Eu^{2+} ions [(Eu(2) and Eu(3)]. Figure 2a shows the orientation of the slabs along the *c* axis. Adjacent slabs are related to each other by a 2_1 screw axis. The slabs themselves are created by "stitching" of ribbons through Eu(1) and As(5) atoms. In turn, the ribbons are constructed from apparent $[As_{10}S_{20}]^{10-}$ segments, which are linked by Eu(1) atoms along the *a* axis, Figure 2b.

The location of As(5) and As(4) in the $[As_{10}S_{20}]^{10-}$ segment gives the impression that it is a real polythioarsenatate anion. Both the As(4) and As(5) sites are partially occupied. When this fact is considered, it becomes evident that $[As_{10}S_{20}]^{10-}$ is actually composed of two shorter segments of $[As_3S_7]^{5-}$ and a disordered polythioarsenate anion in between, Figure 2c.

The Li atoms in **IIa** are disordered with As(4) atoms, whereas the Na atoms in **IIb** are found both in the As(4) and Eu(1) sites. The alkali metal ions adopt a much distorted octahedral geometry.

The presence of Li and Na reflects the corresponding fluxes in which the compounds **IIa** and **IIb** were synthesized. Attempts to prepare the alkali-metal-free analogue, i.e., $Eu_3As_{4.33}S_{10}$ or $Eu_{3.5}As_{4.5}S_{10}$, did not succeed and led to different phases including $Eu_{4.5}As_9S_{18}$. Only when Li and Na were present during synthesis could we prepare **IIa** and **IIb**, which

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(13) **$Eu_3(AsS_4)_2$:** It was prepared by combining Eu (0.091g, 0.6mmol), As (0.03g, 0.4mmol), and S (0.051g, 1.6mmol). The starting materials were loaded in a fused-silica tube in a nitrogen-filled glove box. The tube was evacuated (<10−4 Torr) and sealed, put in a computer-controlled furnace, and heated to 650 °C in 10 h. It was maintained at this temperature for 60 h, followed by cooling at the rate of 5 °C/h to room temperature. The product consisted of dark-red chunks. Semi-quantitative microprobe analysis using energy dispersive spectroscopy (EDS) on the dark-red chunks gave "$Eu_{3.4}As_2S_{7.2}$". **$Li_{0.73}Eu_3As_{4.43}S_{10}$:** This compound was isolated from the reaction mixture of Li_2S (0.015g, 0.33mmol), Eu (0.101g, 0.67mmol), As (0.125g, 1.67mmol), and S (0.075g, 2.33mmol) using a similar procedure as above. The product was isolated by washing with dimethylformamide. **$Na_{0.66}Eu_{2.86}As_{4.54}S_{10}$:** It was isolated from the reaction of Na_2S(0.039g, 0.05mmol), Eu (0.15g, 0.1mmol), As (0.074g, 0.1mmol), and S (0.111g, 0.35mmol) similarly as above. EDS analysis on the black crystal gave "$Eu_{3.4}As_{5.1}S_{10.4}$".

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(15) **$Eu_3(AsS_4)_2$:** A full sphere of data was collected on a red crystal using a Bruker AXS SMART diffractometer. An empirical absorption correction was applied using SADABS. The structure was solved with direct methods using the SHELXTL package. Hexagonal $R\bar{3}c$, a = 9.254(3) Å, b = 9.254(3) Å, c = 27.698(12) Å, D_c = 4.182 g/cm^3, crystal dimensions: 0.15 × 0.10 × 0.03 mm^3, θ = 2.94−28.26°, μ = 19.540 mm^{-1}, 1834 total reflections, 541 unique reflections with R_{int} = 0.027, GOF = 1.008, R1 = 2.38%, wR2 = 5.80% for $I > 2\sigma(I)$. **$Li_{0.73}Eu_3As_{4.43}S_{10}$ (IIa):** Single-crystal X-ray diffraction data were collected using a STOE imaging plate diffraction system (IPDS-2) with graphite-monochromatized Mo Kα radiation. A numerical absorption correction was applied using X-area suite program. Direct methods and full-matrix least squares refinement against F^2 for 169 variables was performed with SHELXTL package. Monoclinic $P2_1/c$, a = 8.4565(3) Å, b = 7.8249(3) Å, c = 24.617(1) Å, α = 99.78(3)°, D_c = 4.607 g/cm^3, crystal dimensions: 0.20 × 0.08 × 0.05 mm^3, θ = 1.68−29.41°, μ = 21.912 mm^{-1}, 10 849 total reflections, 4320 unique reflections with R_{int} = 0.0726, GOF = 1.074, R1 = 3.66%, wR2 = 9.38 for $I > 2\sigma(I)$. **$Na_{0.66}Eu_{2.86}As_{4.54}S_{10}$ (IIb):** Data collection and refinement was same as that of **IIa** except it had ∼7% pseudo-merohedral twining. Twin law $R = (-1\ 0\ 0, 0\ -1\ 0, 1\ 0\ 1)$. Monoclinic $P2_1/c$, a = 8.4300(6) Å, b = 7.8040(4) Å, c = 25.139(2) Å, α = 100.226(6)°, D_c = 4.530 g/cm^3. Crystal dimensions: 0.20 × 0.08 × 0.05 mm^3, θ = 1.68−29.41°, μ = 21.313 mm^{-1}, 14 682 total reflections, 4512 unique reflections with R_{int} = 0.0730, GOF = 1.088, R1 = 4.49%, wR2 = 9.81% for $I > 2\sigma(I)$.

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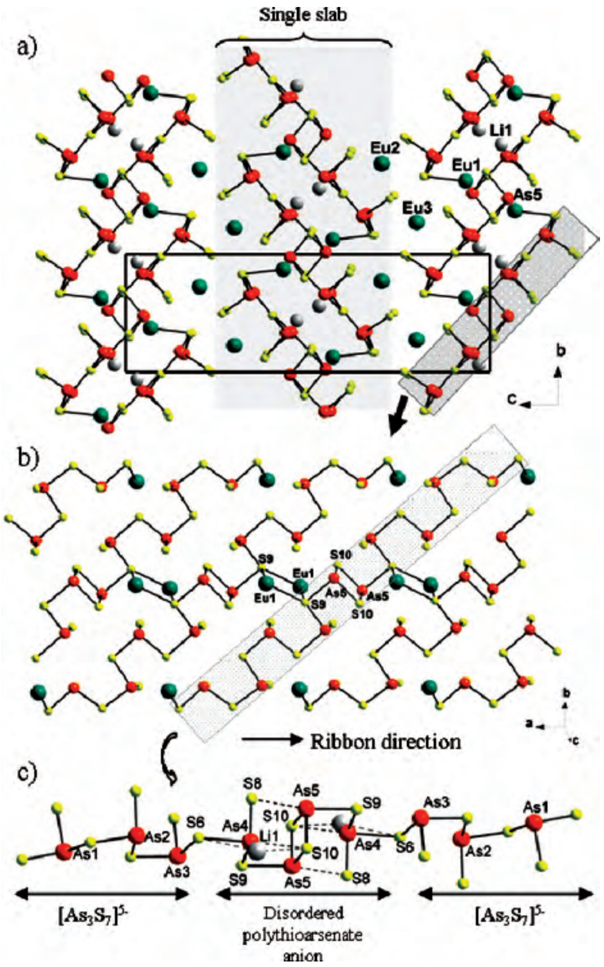

Figure 2. (a) Extended unit cell view of the $Li_{0.73}Eu_3As_{4.43}S_{10}$ structure, showing the packing of slabs (shaded region in the middle). (b) Detail view of the ribbon, showing stitching among $[As_{10}S_{20}]^{10-}$ segments parallel to the *a* axis. The Li atom is removed for clarity. (c) View of the $[As_{10}S_{20}]^{10-}$ segment with the atomic labeling scheme; it shows the relative position of the short segment $[As_3S_7]^{5-}$ and the disordered polythioarsenate anion. The Li−S interactions are shown by dotted lines.

leads us to speculate that the compounds may be stabilized by these cations. Given that the structure type is based on a ternary Eu/As/S composition, the Li and Na are regarded as "heteroatoms" and likely play a role in forming the title compounds. This is reminiscent of the heteroatom role that Tl and Ag play in stabilizing Pb−As−S minerals in nature.[10] The mixed A/As and partial As occupancy explains the relatively high anisotropic thermal parameters for As(4) and As(5) atoms. There are several long interactions (in the range of 2.7−2.9 Å), as indicated by the As(4)−S(10) and As(5)−S(8) contacts (dotted lines) in Figure 2c. This kind of bonding may be responsible for stabilizing the apparent $[As_{10}S_{20}]^{10-}$ segment and in combination with the alkali metals probably the whole structure itself. Our X-ray diffraction studies did not reveal any obvious supercell or modulation, as in some sartorite minerals.[19] The Eu(1) center

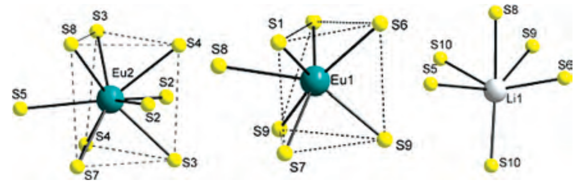

Figure 3. Coordination environment of Eu(1), Eu(2), and Li.

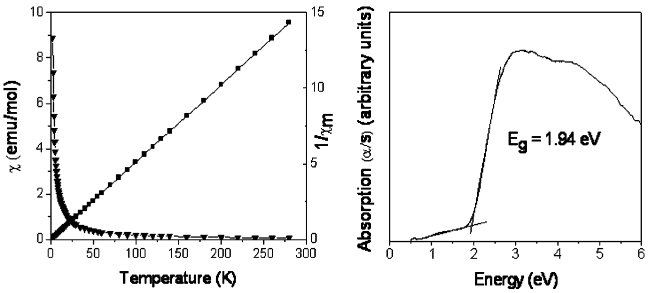

Figure 4. (a) Plots of the magnetic susceptibility and inverse magnetic susceptibility and (b) optical absorption spectrum of $Eu_3(AsS_4)_2$.

has a monocapped trigonal prismatic environment of S atoms, whereas Eu(2) and Eu(3) have tricapped distorted trigonal prismatic geometry, Figure 3. Magnetic susceptibility measurements on $Eu_3(AsS_4)_2$ are consistent with Eu^{2+}. The data follow Curie law from 2−300 K, with an effective magnetic moment of 12.53 μ_B/mol, Figure 4a. This is close to the calculated 13.68 μ_B for 3 Eu^{2+} ions. The optical absorption spectrum of $Eu_3(AsS_4)_2$ showed a very strong absorption onset at 1.9 eV, Figure 4b. This is attributed to a band gap excitation believed to originate from transitions involving filled primarily sulfur-based p orbitals in the valence band and empty Eu d orbitals in the conduction band.

The reactivity of Eu in polythioarsenate fluxes appears to be diverse and promises to uncover a potentially large homologous series of the type $Eu_nAs_{2m}S_{n+3m}$, as well as heteroatom stabilized ones. The scope of such series is broad and could parallel the wealth of natural sulfosalt compounds, as well as contribute to our understanding of the wider sulfosalt chemistry. For example, we have preliminary evidence for the existence of $Eu_{4.5}As_9S_{18}$ ($n,m = 4.5$) and $EuAs_2S_4$ ($n,m = 1$).[20] Homologies can be of great value in the design and prediction of compounds.[21]

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Supporting Information Available: Experimental details for characterization and X-ray crystallographic files in CIF format for $Eu_3(AsS_4)_2$, $Li_{0.73}Eu_3As_{4.43}S_{10}$, and $Na_{0.66}Eu_{2.86}As_{4.54}S_{10}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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