Inorg. Chem. **2009**, *48*, 2729−2731

Inorganic Chemistry
Communication

$K_2Ln_2As_2Se_9$ (Ln = Sm, Gd): The First Quaternary Rare-Earth Selenoarsenate Compounds with a 3D Framework Containing Chairlike As_2Se_4 Units

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Received December 11, 2008

The new compounds $K_2Ln_2As_2Se_9$ (Ln = Sm, Gd) were obtained by applying the reactive flux method. The structure consists of a three-dimensional (3D) $[Ln_2As_2Se_9]^{2-}$ framework with K^+ ion-filling tunnels running along the *b* axis. The two unique Ln^{3+} cations are coordinated by two Se_2^{2-} dumbbells, two $AsSe_3^{3-}$ pyramids, and one chairlike $As_2Se_4^{2-}$ unit in a bicapped trigonal-prismatic geometry. The Ln^{3+}-centered trigonal prisms share triangular faces with neighboring prisms, forming one-dimensional chains along the *b* axis. These chains are linked to each other to form layers by sharing Se^{2-} anions on the capped sites of the trigonal prisms. The As_2Se_4 units connect these layers to form the 3D framework.

The reactivity of rare-earth (RE) elements in molten alkali-metal polythioarsenates has been investigated recently, and several novel compounds with interesting structures and physical properties have been prepared.[1−3] These fluxes are formed by the in situ fusion of A_2S_3 (A_2S)/As_2S_3 (As)/S (A = alkali metal) to produce various $[As_yS_z]$ units. The discrete species can vary in composition and structure and form the basis for producing a large number of ternary and quaternary compounds in a rational and systematic way. The results published until now demonstrate that Eu^{2+} seems to favor As^{3+} in a wide composition range. The considerable structural diversity in the Eu compounds is due to the stereochemically active lone-pair electrons of As^{III}. The trivalent Nd, Sm, and Gd, however, favor As^{5+} species. The large size and high coordination numbers of RE elements may lead to special metal−chalcogen bonding characteristics in these compounds.

The corresponding RE polyselenoarsenate system also merits investigation because of potential new compounds and information about similarities and differences between P, As, and Sb chemistry. Now the question is whether As forms compounds with structures reminiscent of those of selenophosphates like thioarsenates or As mimics the chemistry of selenoantimonates. When the properties of P, As, and Sb are compared, there seems to be a boundary at As in terms of the chemical and electronic behavior. The most stable oxidation states of P are 4+ and 5+, as evidenced by the frequent occurrence of $[P_2Se_6]^{4-}$ and $[PSe_4]^{3-}$ building units.[4−9] These oxidation states are not likely for Sb because of the greater stability of the 3+ oxidation state in the presence of Se,[10−12] and no $Sb^{IV}Se_x$ unit was reported so far. The ethane-like units $[As_2Se_6]^{4-}$ and $[Sb_2Se_6]^{4-}$ do not exist. Therefore, we anticipate a difference among the $[P_xSe_y]^{n-}$, $[As_xSe_y]^{n-}$, and $[Sb_xSe_y]^{n-}$ chemistry.

In this Communication, we report on the reactivity of Ln (Ln = Sm, Gd) metals in potassium selenoarsenate melts and the characterization of the two isostructural compounds $K_2LnAs_2Se_9$ (Ln = Sm, Gd), the first series of compounds with a three-dimensional (3D) anionic framework containing $[AsSe_3]^{3-}$pyramids and chairlike $[As_2Se_4]^{2-}$ units as building blocks, which is unknown in the corresponding P and Sb chemistry.

The compounds $K_2LnAs_2Se_9$ were obtained as black needles or platelets in potassium polyselenoarsenate fluxes of relatively low Lewis basicity or selenium-rich flux (formally "$K_2As_2Se_8$" or "$K_2As_3Se_{9.5}$").[13] These compounds are not formed in more basic fluxes, suggesting that relatively low basicity is important for stabilization of the compounds. The products obtained under more basic reaction conditions

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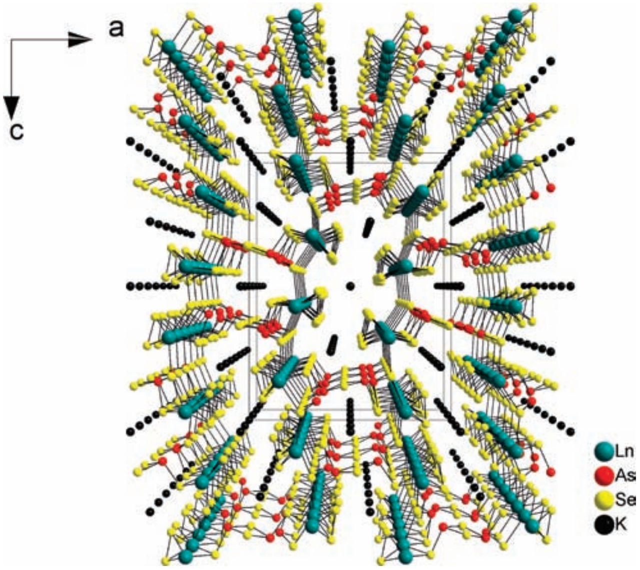

Figure 1. View of the structure of $K_2Ln_2As_2Se_9$ along [010] showing a $^{3}_{\infty}[Ln_2As_2Se_9]^{2-}$ framework containing K atoms.

were also investigated. When fluxes with molar ratios of 2:1:6 and 3:1:6 for $K_2Se_3/As_2Se_3/Se$ (formal composition of the melts: "$K_4As_2Se_{15}$" and "$K_4As_2Se_{18}$") were applied, the compounds were not formed and K_3AsSe_4 and $LnSe_2$ were identified as the main products. Attempts to prepare $K_2Ln_2As_2Se_9$ from the stoichiometric molar ratio of $K_2Se_3/Ln/As_2Se_3/Se$ were also unsuccessful.

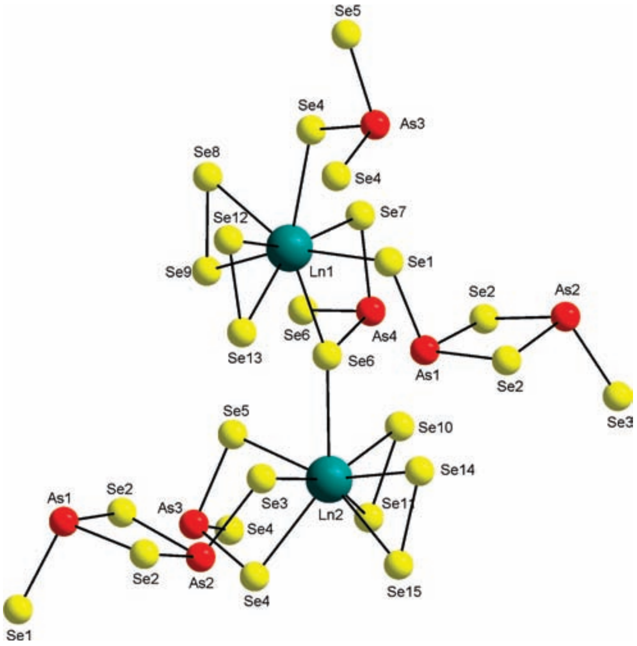

Figure 2. Coordination environment of the Ln (Ln = Sm, Gd) atoms and the As atoms with a labeling scheme. Selected bond lengths (in Å) for $K_2Sm_2As_2Se_9$: Sm1−Se12, 2.9379(8); Sm1−Se9, 2.9403(8); Sm1−Se13, 2.9597(9); Sm1−Se7, 2.9740(8); Sm1−Se8, 2.9762(9); Sm1−Se6, 2.9776(9); Sm1−Se1, 2.9977(8); Sm4−Se4, 3.0526(9); Sm2−Se14, 2.9530(8); Sm2−Se11, 2.9617(9); Sm2−Se5, 2.9926(8); Sm2−Se10, 2.9935(8); Sm2−Se15, 3.0043(8); Sm2−Se4, 3.0100(9); Sm2−Se3, 3.0282(8); Sm2−Se6, 3.0873(9); As1−Se1, 2.4303(15); As1−Se2, 2.4691(11); As2−Se3, 2.4263(15); As2−Se2, 2.4982(11); As3−Se4, 2.4173(10); As3−Se5, 2.4200(15); As4−Se6, 2.4022(10); As4−Se7, 2.4394(16); Se8−Se9, 2.3719(17); Se10−Se11, 2.3910(16); Se12−Se13, 2.3740(16); Se14−Se15, 2.3980(16). Selected bond lengths (in Å) for $K_2Gd_2As_2Se_9$: Gd1−Se12, 2.9153(10); Gd1−Se9, 2.9190(10); Gd1−Se13, 2.9366(9); Gd1−Se7, 2.9403(9); Gd1−Se8, 2.9567(10); Gd1−Se6, 2.9607(9); Gd1−Se1, 2.9685(10); Gd4−Se4, 3.0381(8); Gd2−Se14, 2.9302(9); Gd2−Se11, 2.9368(9); Gd2−Se5, 2.9611(9); Gd2−Se10, 2.9739(10); Gd2−Se15, 2.9777(9); Gd2−Se4, 2.9963(9); Gd2−Se3, 2.9979(9); Gd2−Se6, 3.0774(8); As1−Se1, 2.4286(16); As1−Se2, 2.4663(13); As2−Se3, 2.4207(17); As2−Se2, 2.4997(13); As3−Se4 2.4090(11); As3−Se5, 2.4141(16); As4−Se6, 2.3934(12); As4−Se7, 2.4373(16); Se8−Se9, 2.3676(18); Se10−Se11, 2.3808(17); Se12−Se13, 2.3667(16); Se14−Se15, 2.3885(17).

The structure of $K_2Ln_2As_2Se_9$ (Ln = Sm, Gd) is characterized by the occurrence of a 3D tunnel $^{3}_{\infty}[LnAs_2Se_9]^{2-}$ framework (Figure 1).[14] The coordination geometry around both Ln^{3+} cations is a bicapped trigonal prism of Se^{2-} anions (Figure 2). Four Se^{2-} ions from two diselenide dumbbells form the two short parallel edges of the trigonal prism. The Se−Se bond lengths are normal, ranging from 2.3719(17) to 2.3980(16) Å for $K_2Sm_2As_2Se_9$ and from 2.3667(16) to 2.3885(17) Å for $K_2Gd_2As_2Se_9$. The other four Se^{2-} ions are located at two apexes and two capping sites of the prism. The (Ln1 and Ln2) centered trigonal prisms share two trigonal faces with neighboring prisms along the *b* axis, forming one-dimensional (1D) chains. These chains are arranged side by side and linked into a layer by sharing the capping Se^{2-} of the trigonal prisms. The layer is similar to that found in $K_2Gd_2Sb_2Se_9$.[11] The difference from $K_2Gd_2Sb_2Se_9$ lies in the connection of pyramidal $AsSe_3$ and chairlike As_2Se_4 units. In $K_2Gd_2Sb_2Se_9$, Sb^{3+} ions are in distorted octahedral environments, sharing edges to form double chains. In contrast to $K_2Gd_2Sb_2Se_9$, the $[AsSe_3]$ and $[As_2Se_4]$ units in the title compounds are not connected with each other. Each $[AsSe_3]^{3-}$ unit joins four neighboring Ln^{3+} centers, employing one Se^{2-} for each Ln^{3+} and the other two Se atoms as bridges to different $[LnSe_8]$ polyhedra. Neutral 1D compounds $Ln(dien)_2[AsSe_4]$ (Ln = Nd, Sm) were synthesized under solvothermal conditions.[15] In contrast to the title compounds, a selenoarsenate(V) species is

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(13) **$K_2Sm_2As_2Se_9$.** A mixture of K_2Se_3 (0.093 g, 0.30 mmol), Sm (0.045 g, 0.30 mmol), As_2Se_3 (0.115 g, 0.30 mmol), and Se (0.047 g, 0.60 mmol) was loaded into a fused-silica tube in a nitrogen-filled glovebox. It was flame-sealed under vacuum ($\sim 10^{-3}$ mbar) and then heated to 973 K within 24 h. After 5 days at 973 K, it was cooled down to 373 K at a rate of 3 K/h followed by rapid cooling to room temperature. A mixture containing black platelets (~50% yield based on Sm) was obtained after dissolution of the excess flux in *N*,*N′*-dimethylformamide. Attemps to prepare pure $K_2Sm_2As_2Se_9$ have failed so far. **$K_2Gd_2As_2Se_9$.** Black platelets were isolated in ~30% yield from the mixture of K_2Se_3 (0.078 g, 0.25 mmol), Gd (0.039 g, 0.25 mmol), As_2Se_3 (0.1437 g, 0.372 mmol), and Se (0.039 g, 0.50 mmol) using a procedure similar to that above. Semiquantitative energy-dispersive X-ray analysis gave an average composition of $K_{1.0}Gd_{1.1}As_{1.3}Se_{4.6}$.

(14) Single-crystal X-ray diffraction data were collected at 170 K (Sm) and 293 K (Gd) using STOE imaging-plate diffraction systems (IPDS-1 for $K_2Sm_2As_2Se_9$ and IPDS-2 for $K_2Gd_2As_2Se_9$) with graphite-monochromatized Mo Kα radiation. Numerical absorption corrections were applied. Direct methods and full-matrix least-squares refinements against F^2 were carried out with the *SHELXTL* package. Crystal data for $K_2Sm_2As_2Se_9$: orthorhombic *Pnma*, $Z = 4$, $a = 17.1739(11)$ Å, $b = 8.4628(5)$ Å, $c = 22.6963(15)$ Å, $V = 3298.7(4)$ Å^3, λ_{max}(Mo Kα) = 28.05°, total reflections = 4090, unique reflections $[F_o^2 > 2\sigma(F_o^2)] = 3095$, numbers of variables = 164, $\mu = 31.365$ mm^{-1}, $D_c = 4.991$ g cm^{-3}, $R_{int} = 7.12\%$, GOF = 0.992, R1 = 3.48% for $I > 2\sigma(I)$, wR2 = 8.84% for all data. Crystal data for $K_2Gd_2As_2Se_9$: orhthorhombic *Pnma*, $Z = 4$, $a = 17.1836(4)$ Å, $b = 8.3743(2)$ Å, $c = 22.6192(5)$ Å, $V = 3254.9(1)$ Å^3, λ_{max}(Mo Kα) = 29.27°, total reflections = 4696, unique reflections $[F_o^2 > 2\sigma(F_o^2)] = 3632$, numbers of variables = 164, $\mu = 32.721$ mm^{-1}, $D_c = 5.115$ g cm^{-3}, $R_{int} = 5.80\%$, GOF = 1.005, R1 = 3.93% for $I > 2\sigma(I)$, wR2 = 9.64 for all data.

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observed. The $[AsSe_4]^{3-}$ units act as μ_3-bridging ligands. As expected, the As−Se bond length in the $[AsSe_4]^{3-}$ tetrahedron is obviously shorter than those in both title compounds. The $[As_2Se_4]$ moieties link Ln−Se layers, forming a 3D framework. A similar structural $[As_2Se_4]$ building group has been observed in $Ba_2As_2Se_5$.[16] The As−Se bond lengths range from 2.4263(15) to 2.4982(11) Å in $[As_2Se_4]$ for $K_2Sm_2As_2Se_9$ and from 2.4207(13) to 2.4997(13) Å for $K_2Gd_2As_2Se_9$, with the terminal Se^{2-} the shorter distances, while those in $[AsSe_3]$ are between 2.4173(10) and 2.4394(16) Å for $K_2Sm_2As_2Se_9$ [2.3934(12)−2.4373(16) Å for $K_2Gd_2As_2Se_9$]. The three unique K^+ ions are coordinated by six to eight Se^{2-} anions [K1−Se, 3.216(2)−3.433(2) Å; K2−Se, 3.2596(9)−3.3272(8) Å; K3−Se, 3.3163(8)−3.5700(9) Å for $K_2Sm_2As_2Se_9$; K1−Se, 3.208(2)−3.434(2) Å; K2−Se, 3.2597(9)−3.3376(9) Å; K3−Se, 3.3054(10)−3.5692(10) Å for $K_2Gd_2As_2Se_9$].

Among these compounds, solid-state UV/vis/near-IR spectroscopy[17] shows that $K_2Sm_2As_2Se_9$ has a relatively steep absorption edge that corresponds to an energy band gap E_g of ~1.7 eV, comparable to the band gaps observed for lanthanoide(III) sesquiselenides Ln_2Se_3 (Ln = La, Ce, Pr, Nd, Tb).[18] The electronic absorption responsible for the gap is likely an electronic charge-transfer excitation from the top of the valence band (VB) to the bottom of the conduction band (CB), where the uppermost part of the VB can be presumably attributed to Se 4p states and the bottom of the CB results most likely from empty Sm 5d orbitals. Besides the band edge, there are several absorptions characteristic of the f → f transitions of Sm^{3+} ($^6H_{5/2} \rightarrow {}^{2S+1}L_J$) observed between 5000 and 11 000 cm^{-1} below the interband transition (Figure 3). The transitions can be tentatively assigned with the help of previous reports.[19−23] The Raman spectra[24] obtained on powders of $K_2Ln_2As_2Se_9$ exhibit very strong peaks at 225 cm^{-1} (Sm) and 221 cm^{-1} (Gd) together with some weak bands that are assigned to the stretching and deformation modes of the As−Se vibration, which causes an overtone at 443 cm^{-1}. These values are shifted to lower energies compared with those of thioarsenates because of the larger mass of Se.

Summarizing shortly the main results, we presented the first RE selenoarsenate compounds. When the composition or the Lewis basicity of the flux is changed, the reactivity of the RE element and the outcome of the reaction can be controlled. Namely, the compounds $K_2Ln_2As_2Se_9$ were successfully synthesized in a selenium-rich potassium polyarsenate flux with a relatively low Lewis basicity. These conditions seem to be essential for stabilization of the compounds because increasing the flux basicity results in the breakdown of the structures and the formation of simpler compounds.

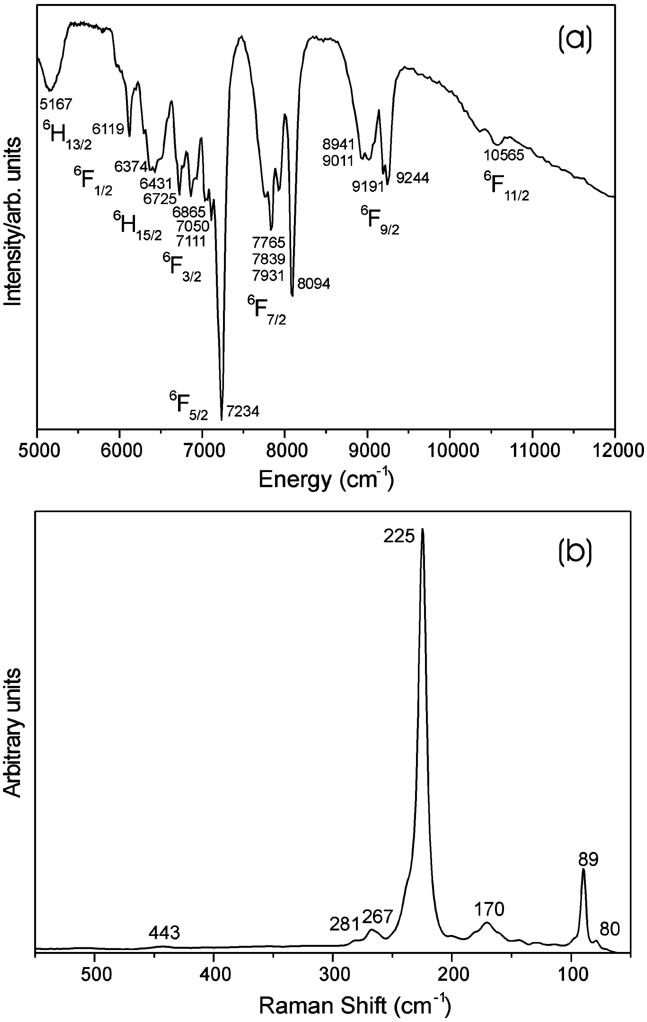

Figure 3. (a) Diffuse-reflectance and (b) Fourier transform Raman spectra of $K_2Sm_2As_2Se_9$.

Acknowledgment. Financial support by the State of Schleswig-Holstein and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic files in CIF format and powder diffraction patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) UV/vis/near-IR diffuse-reflectance spectra were recorded on a Cary 5 spectrometer (Varian Techtron Pty.). The spectrometer was equipped with an Ulbricht sphere (diffuse-reflectance accessory; Varian Techtron Pty.). The samples were ground together with $BaSO_4$ and prepared as a flat specimen of ~2 mm thickness. The resolution was 1 nm for the UV/vis range and 2 nm for the near-IR range. The measuring range was 250−2000 nm. $BaSO_4$ was used as a standard for 100% reflectance.

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(24) The Fourier transform Raman spectrum was recorded on an ISF-66 spectrometer (Bruker) with an additional FRA 106 Raman module. A Nd:YAG laser was used as the source of excitation (λ = 1064 nm). The samples were ground and prepared on Al sample holders. The measuring range was −1000 to +3500 cm^{-1} with a resolution of 2 cm^{-1}.