Reactions of Lanthanides and Actinides in Molten Alkali Metal/Polychalcogenide Fluxes at Intermediate Temperatures (250–600 °C)

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From the reaction of the elemental lanthanides and actinides in molten alkali metal/polychalcogenide salts, several new ternary compounds have been discovered. Specifically, these phases are K$_4$USe$_8$ (I) and AlNQ$_4$ (II), where A = K, Ln = Ce or Tb, and Q = Se or A = Rb, Ln = Ce, Q = Te; and NaLaSn$_3$ (III), where Ln = La, Ce. The K$_4$USe$_8$ crystallizes in the orthorhombic space group Fdd2 (No. 43) with a = 17.331(4) Å, b = 20.584(3) Å, c = 8.811(3) Å, Z = 8. The K CeSe$_3$ crystallizes in the tetragonal space group P4/nbm (No. 125) with a = 6.376(2) Å, c = 8.327(1) Å, Z = 2. The KTbSe$_4$ crystallizes in the tetragonal space group P4/nbm (No. 125) with a = 6.255(2) Å, c = 8.227(1) Å, Z = 2. The RbCeTe$_4$ crystallizes in the tetragonal space group P4/nbm (No. 125) with a = 6.952(3) Å, c = 9.084(4) Å, Z = 2. The NaCeSe$_4$ crystallizes in the orthorhombic space group Pmmm (No. 59) with a = 5.683(1) Å, b = 4.238(2) Å, c = 9.820(2) Å, Z = 2. The NaLaS$_3$ crystallizes in the orthorhombic space group Pmmm (No. 59) with a = 5.752(4) Å, b = 4.2796(6) Å, c = 9.841(2) Å, Z = 2. Compound I features discrete [U(Se$_2$)$_4$]$^{4-}$ anions, while (II) and (III) possess extended structures in which the lanthanide and chalcogenide atoms form infinite two-dimensional layers. In (II) the lanthanide cations are in square antiprismatic coordination environments, connected into layers by Q–Q bonds. In (III), the lanthanide bond to a mixture of mono- and disulfides in a bicapped trigonal prismatic geometry; these polyhedra subsequently connect in two dimensions, forming layers equivalent to those seen in the ZrSe$_2$ structure type. Details of the synthesis, structure, and properties of these compounds are discussed.

Introduction

The chemistry between metal cations and polychalcogenide ligands has been studied extensively over the years using a variety of solution-based techniques. This has led to a considerable amount of empirical knowledge concerning the complexes that have resulted, although the complex solution equilibria that polychalcogenides are prone to, based on their ability to undergo self-redox reactions, have made synthetic predictability difficult. In many systems the reaction of metals in molten polychalcogenide salts has been a valuable addendum to these studies. Because of the unique reaction characteristics of molten A$_2$Q$_x$ salts, these media have had value in accessing compounds previously unknown even in systems that had been well studied with conventional solution techniques. The new phases seen in molten salt reactions have also tended to be solid-state structures with extended covalent bonding in one or more dimensions through the lattice, a sharp contrast to the discrete ionic complexes commonly resulting from solution. For many elements, however, studying metal/polyvalent (Q$_x$)$^{2-}$ chemistry can be exceedingly difficult. Group 4 and 5 transition metals, lanthanides, and actinides can access very high oxidation states and hence become very hard Lewis acids. As such they are especially oxophilic species that, when given a choice, would rather coordinate to oxygen-containing (hard base) ligands rather than those with chalcogenide (soft base) binding sites. Therefore they enjoy a particularly rich oxide chemistry.

By using molten A$_2$Q$_x$ fluxes, the opportunity presents itself to study the reaction of highly oxophilic metals with polychalcogenide ligands directly, without the need for any sort of polar solvent medium. These fluxes were described by Schede to be excellent recrystallizing media for many chalcogenides. He also hinted that at lower temperatures new phases containing the alkali atom may form. Some of the earliest investigations into using A$_2$Q$_x$ fluxes as intermediate temperature media were performed on group 4 and 5 metals. From these studies, the phases K$_4$Ti$_3$S$_{14}$, Na$_2$Ti$_2$Se$_8$, and K$_3$NbNd$_2$Se$_7$ were identified.

In this work, U has been the only actinide whose reactivity with A$_2$Q$_x$ fluxes was studied. Several U/O binaries exist, but the only one to have discrete polychalcogenides is UO$_3$ (Q = S, Se, Te), which is isostructural to ZrSe$_2$. This structure type, to be discussed at length later, contains (Q$_2$)$_{2-}$ fragments which, through

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6 Abstract published in Advance ACS Abstracts, November 1, 1996.
A brief look at known ternary compounds containing alkali cations is warranted because working with $A_2Q_x$ fluxes naturally lead to the incorporation of $A^+$ into the resulting lattice. For alkali metals (and $T^+$) only one stoichiometry had been known for many years: $\text{ALnQ}_2$.\textsuperscript{10} This phase exists in two different structure types depending on the relative sizes of the $A^+$ and $\text{Ln}^3$ cations. Generally, for small alkali metal cations (Li$^+$ and some Na$^+$ analogues), the phase is simply a NaCl derivative with the two cations disordered throughout the lattice. As $A^+$ increases in size, the cations order themselves in the NaCl lattice such that every other layer of cations changes composition between $A^+$ and $\text{Ln}^3$. The recent characterization of $\text{RbDy}_2\text{Se}_8$ has added another structure type to the $A/\text{Ln}/Q$ family.\textsuperscript{11} This phase is a relative of the $\text{LnTe}_3$ structure type ($2+4$ coordination, forming the shortest sides of a trigonal prism around the $U$ atoms.

As in binary systems, examples of ternary $A$/activinide/Q phases are sparse. The unit cell has been reported for $\text{KUS}_3$,\textsuperscript{12} but the structure could not be successfully refined. Some of the known phases include $\text{Cu}_2\text{U}_2\text{O}_3$,\textsuperscript{13} $\text{CrU}_2\text{S}_7$,\textsuperscript{14} $\text{MgU}_2\text{S}_7$,\textsuperscript{15} $\text{ScU}_2\text{Se}_6$,\textsuperscript{16} $\text{Cu}_2\text{Se}_5$, and feature $U$ centers in high coordination environments. Generally, for small alkali metal cations (Li$^+$ and some Na$^+$ analogues), the phase is simply a NaCl derivative with the two cations disordered throughout the lattice. As $A^+$ increases in size, the cations order themselves in the NaCl lattice such that every other layer of cations changes composition between $A^+$ and $\text{Ln}^3$. The recent characterization of $\text{RbDy}_2\text{Se}_8$ has added another structure type to the $A/\text{Ln}/Q$ family.\textsuperscript{11} This phase is a relative of the $\text{LnTe}_3$ structure type ($2+4$ coordination, forming the shortest sides of a trigonal prism around the $U$ atoms.

As in binary systems, examples of ternary $A$/activinide/Q phases are sparse. The unit cell has been reported for $\text{KUS}_3$,\textsuperscript{12} but the structure could not be successfully refined. Some of the known phases include $\text{Cu}_2\text{U}_2\text{O}_3$,\textsuperscript{13} $\text{CrU}_2\text{S}_7$,\textsuperscript{14} $\text{MgU}_2\text{S}_7$,\textsuperscript{15} $\text{ScU}_2\text{Se}_6$,\textsuperscript{16} $\text{Cu}_2\text{Se}_5$, and feature $U$ centers in high coordination environments. Recently, the new phases $\text{CsUTe}_6$ and $\text{CsTiUTe}_6$ were reported to form from cesium alkali metal polychalcogenide melts.\textsuperscript{16} The compounds discussed have all resulted from high-temperature ($>600^\circ\text{C}$) solid-state reactions, except for $\text{RbDy}_2\text{Se}_8$ which was grown from a $\text{RbCl}/\text{LiCl}$ flux at $680^\circ\text{C}$. The solid-state chemistry between these elements has never been reported under any but high-temperature synthetic conditions. The binary lanthanide chalcogenide phases $\text{MTe}_3$ ($M = \text{La}, \text{Pr}$) were shown to form at $<600^\circ\text{C}$ in $A_2Q_x$ fluxes.\textsuperscript{17} Molten $A_2Q_x$ fluxes, however, allow for a changing of the conditions by varying $x$, and as we show here, can lead to ternary new phases.\textsuperscript{2} The first stage in the investigation of f-block metal reactivity in $A_2Q_x$ fluxes was to experiment on simple ternary systems. The considerable thermodynamic stability of the known binary and ternary compounds often led to their formation even under the relatively mild synthetic techniques employed here. Despite this, it was discovered that, with appropriate flux compositions, several new ternary chalcogenides can be accessed at intermediate temperatures. The reactivity of some lanthanides and actinides, in combination with $Cu$ containing $A_2Q_x$ fluxes was shown to result in the quaternary compounds $K_2\text{Cu}_2\text{Ce}_5\text{Se}_4$, $\text{KCuCe}_2\text{Se}_6$, $\text{KCuLa}_2\text{Se}_6$, $\text{CsCuCe}_2\text{Se}_6$, $\text{KCuCe}_2\text{Se}_5$, and $\text{KCuSe}_4$.\textsuperscript{18} In this paper the syntheses, structures, and properties of the new ternary phases $K_2\text{USe}_3$ (II), $\text{ALnQ}_4$ (II) ($A = \text{K, Ln = Ce or Tb}$, and $Q = \text{Se or } A = \text{Rb, Ln = Ce, Q = Te}$), and $\text{NaLnS}_3$ (III) ($\text{Ln = La, Ce}$) will be discussed. Preliminary reports on this work have been published previously.\textsuperscript{19}

### Experimental Section

#### Synthesis

Reagents. The following reagents were used as obtained: cerium, 40 mesh, Johnson M. Matthey Co., Ward Hill, MA; uranium metal, 60 mesh, Cerac, Milwaukee, WI; lanthanum, 40 mesh, Cerac, Milwaukee, WI; selenium powder, 100 mesh, Aldrich, Milwaukee, WI; tellurium powder, 200 mesh, Aldrich, Milwaukee, WI; sulfur powder, sublimed, J T Baker Co., Phillipsburg, NJ; rubidium metal, analytical reagent, Johnson Matthey, Ward Hill, MA; potassium metal, analytical reagent, Mallinckrodt Inc., Paris, KY; sodium metal, analytical reagent, Mallinckrodt Inc., Paris, KY; dimethylformamide, analytical reagent grade, EM Science, Inc., Gibbstown, NJ; K$_2$S, K$_2$Se, and K$_2$Te were prepared as described previously.\textsuperscript{20}

$\text{KUS}_3$. This compound was synthesized from a mixture of 0.126 g (0.80 mmol) of $\text{K}_2\text{Se}$, 0.095 g (0.40 mmol) of U, and 0.257 g (3.25 mmol) of Se. These reagents are theroughly mixed, sealed in an evacuated Pyrex ampule, and heated at 300 °C for 12 days (cooling 2 °C/h). Afterward, the tube is opened with a glass cutter, and the entire solid mass is placed in a 250 mL Erlenmeyer flask, which has a sidearm attachment, to allow for the purging of the flask contents with N$_2$. Excess polychalcogenide flux is removed by dissolving it in successive portions of degassed dimethylformamide (DMF). Approximately 50–100 mL of solvent is added to the flask resulting in a green/brown solution as the excess $\text{K}_2\text{Se}$ is dissolved. Nitrogen flow through the flask is maintained during the isolation to prevent oxidation of the solubilized polychalcogenide by ambient O$_2$ which would cause elemental Se to precipitate. When a portion of solvent (as evidenced by a very dark color to the solution), it is carefully decanted from the remaining solid, and a fresh portion is added. Since $\text{K}_2\text{USe}_3$ has proven to be slightly

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soluble in DMF, washing is continued only until the green/ brown color of an \( \text{Se}^{2-} \) solution is replaced by a slowly evolving brown/yellow color, indicating \( \text{KUCSe} \) as the primary component in solution. The sample is decanted one final time and then dried under vacuum. The remaining material is a black microcrystalline product. Homogeneity was confirmed by comparing the powder X-ray diffraction pattern of the product against the pattern calculated using X-ray single-crystal data (see Supporting Information). Solution UV/Vis spectroscopy showed enough yields as high as 53% have been achieved (based on uranium).

\( \text{KCeSe}_4 \). This compound was synthesized from a reaction of 0.078 g of \( \text{K}_2\text{Se} \) (0.5 mmol), 0.035 g of Ce (0.25 mmol), and 0.158 g of Se (2 mmol). These starting materials are thoroughly mixed in a nitrogen atmosphere glovebox and loaded into a Pyrex tube, which is subsequently evacuated to approximately \( 2 \times 10^{-3} \text{ mbar} \) and flame sealed. The mixture is heated at 300 °C for 6 days and cooled at 2 °C/h to 100 °C followed by cooling to 50 °C in 1 h. The product is isolated in the manner described for the isolation of \( \text{KUCSe} \) above. The remaining material is deep blue-to-black square chunks of \( \text{KCeSe}_4 \). The product is insoluble in DMF and is inert in both air and water for extended periods, although some manner of surface degradation appears to be evident in the magnetic air and water for extended periods, although some manner of brown/yellow color, indicating \( \text{KUCSe}_8 \) as the primary component in solution.

\( \text{NaCeS}_3 \). Either of the following combinations of starting materials may be used to form \( \text{NaLaS}_5 \): 0.060 g (0.77 mmol) of \( \text{Na}_2\text{S} \), 0.105 g (0.75 mmol) of La, and 0.096 g (3.0 mmol) of S or 0.040 g (0.5 mmol) of \( \text{Na}_2\text{S} \), 0.105 g (0.75 mmol) of La, and 0.154 g (4.5 mmol) of S. The former resulted in crystals suitable for single-crystal X-ray diffraction studies, while the latter is typically microcrystalline. The starting materials are mixed and sealed into Pyrex tubes as described previously. The samples are placed in a computer-controlled furnace and heated to 370 °C over 12 h. They remain at this temperature for 2 days after which the furnace is cooled to 160 °C over 50 h and then allowed to cool naturally to 50 °C. The excess flux is dissolved by washing the sample with degassed DMF as described previously. The isolated product is pale yellow when microcrystalline but orange as the size of the crystals increases. Purity of the sample was confirmed by comparing its X-ray powder diffraction pattern to one calculated from the single-crystal diffraction data. \( \text{NaLaS}_5 \) is highly stable in air and common organic solvents and remains intact in \( \text{H}_2\text{O} \) over short periods of time (<8 h). After sufficient contact with water, the phase converts to an amorphous oxide with the scent of \( \text{H}_2\text{S} \) present.

**Physical Measurements.** Powder X-ray Diffraction. Analyses were performed using a calibrated Rigaku Rotaflex rotating anode powder diffractometer controlled by an IBM computer and operating at 45 kV/100 mA, employing Ni-filtered Cu radiation. The samples are ground to a fine powder and mounted by spreading the sample onto a piece of double-sided sticky tape affixed to a glass slide. For air-sensitive compounds, samples were prepared in an \( \text{N}_2 \)-filled glovebox and coated with mineral oil before analysis. Powder patterns were calculated by using the CERIUS molecular modeling program developed by Molecular Simulations, St. John’s Innovation Centre, Cambridge, England.

**Infrared Spectroscopy.** Infrared spectra of the \( 600–50 \text{ cm}^{-1} \), were recorded on a computer-controlled Nicolet-740 Fourier transform infrared spectrophotometer in 4 cm\(^{-1}\) resolution. Analyses were performed on finely ground solid samples using CsI as the pressed pellet matrix. For air-sensitive compounds, samples were prepared in an \( \text{N}_2 \)-filled glovebox and pressed into a pellet immediately upon removal.

**Solid-State UV/Vis Spectroscopy.** Spectra were recorded using a Hitachi U-2000 spectrophotometer. Samples were dissolved and loaded into UV/vis cells inside an \( \text{N}_2 \)-filled glovebox.

Rational synthesis of pure \( \text{NaCeS}_5 \) was achieved from two different ratios of starting materials. Either a mixture of 0.078 g (1.0 mmol) of Na\(_2\)S, 0.070 g (0.5 mmol) of Ce, and 0.096 g (3.0 mmol) of S or 0.040 g (0.5 mmol) of Na\(_2\)S, 0.070 g (0.5 mmol) of Ce, and 0.064 g (2.0 mmol) of S can be used. Both have in common that the resulting fluxes (Na\(_2\)S and Na\(_2\)Se) are fairly Lewis basic and are present in only a moderate excess to the Ce metal. After being mixed and sealed into Pyrex tubes as described earlier, the reactants are heated to 370 °C over 12 h, held at that temperature for 2 days, and then cooled to 160 °C over 50 h followed by quenching to room temperature. The excess flux is removed using degassed DMF as described above. The resulting brick red powder was confirmed as \( \text{NaCeS}_5 \) by X-ray powder diffraction. The material is insoluble in DMF and appears to be stable in dry air. However, \( \text{NaCeS}_5 \) is extremely moisture sensitive and any contact with water turns the entire sample black, which is seen by powder X-ray diffraction to contain CeO\(_2\). Even ambient air has sufficient humidity to form a black surface coating over a short period of time, although the coating seems to be protective of the internal compound as its relative amount does not increase with longer exposure to the atmosphere.
Table 1. Crystallographic Data for K₄USe₈, K₁₃Ce₄, KTbSe₄, RbCeTe₄, NaCeS₃, and NaLa₃S₃

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<th></th>
<th>K₄USe₈</th>
<th>K₁₃Ce₄</th>
<th>KTbSe₄</th>
<th>RbCeTe₄</th>
<th>NaCeS₃</th>
<th>NaLa₃S₃</th>
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<td>513.86</td>
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<td>0.02 × 0.08 × 0.08</td>
<td>0.04 × 0.42 × 0.46</td>
<td>0.01 × 0.07 × 0.08</td>
<td>0.01 × 0.04 × 0.44</td>
<td>0.02 × 0.26 × 0.40</td>
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<td>1.18</td>
<td>2.0</td>
<td>1.69</td>
<td>0.61</td>
<td>1.47</td>
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a R = Σ(|F₀| - |F₁|)/Σ|F₀|. R = Σ|F₀|/Σ|F₁| where the reflections were weighted according to w = 1/[σ(F₁)² + (0.03F₁)²]² (where w = weight of a given F₁).

Results and Discussion

K₄USe₈ Structure. A single [USe₈]₄⁻ anion is shown in Figure 1, with selected bond distances and angles in

![Figure 1](image_url)
Table 2. Fractional Atomic Coordinates and $B_{eq}$ Values for K$_4$USe$_8$ with Estimated Standard Deviations in Parentheses

<table>
<thead>
<tr>
<th>atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$B_{eq}$</th>
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<tr>
<td>U</td>
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<td>0</td>
<td>0</td>
<td>0.0217</td>
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<tr>
<td>Se(1)</td>
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<td>Se(2)</td>
<td>1.1100(2)</td>
<td>0.0303(1)</td>
<td>-0.2165(4)</td>
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<td>Se(3)</td>
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<td>0.0244(1)</td>
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<tr>
<td>Se(4)</td>
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<tr>
<td>K(1)</td>
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<td>2.3(3)</td>
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<td>1.2211(4)</td>
<td>0.1662(3)</td>
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<td>2.1(3)</td>
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$B$ values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameters defined as $B_{eq} = \frac{1}{3}\sum_{j=1}^{3}(a_{ij}^2B_{j} + b_{ij}^2B_{j} + c_{ij}^2B_{j})$. 

Table 3. Fractional Atomic Coordinates and $B_{eq}$ Values for KCeS$_8$, KTBSe$_8$, and RbCeS$_8$ with Estimated Standard Deviations in Parentheses

<table>
<thead>
<tr>
<th>atom</th>
<th>x</th>
<th>y</th>
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<th>$B_{eq}$</th>
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<tr>
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<td>Tb</td>
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<td>1/2</td>
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<tr>
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<td>0.2911(1)</td>
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<tr>
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</tbody>
</table>

$B$ values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameters defined as $B_{eq} = \frac{1}{3}\sum_{j=1}^{3}(a_{ij}^2B_{j} + b_{ij}^2B_{j} + c_{ij}^2B_{j})$. 

Table 4. Fractional Atomic Coordinates and $B_{eq}$ Values for NaLaS$_3$ with Estimated Standard Deviations in Parentheses

<table>
<thead>
<tr>
<th>atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$B_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>1/4</td>
<td>1/4</td>
<td>0.12835(3)</td>
<td>0.83(2)</td>
</tr>
<tr>
<td>S(1)</td>
<td>-3/4</td>
<td>1/4</td>
<td>0.0658(2)</td>
<td>0.94(5)</td>
</tr>
<tr>
<td>S(2)</td>
<td>0.4332(2)</td>
<td>-1/4</td>
<td>0.3199(1)</td>
<td>1.56(5)</td>
</tr>
<tr>
<td>Na</td>
<td>-3/4</td>
<td>1/4</td>
<td>0.3963(4)</td>
<td>2.1(1)</td>
</tr>
<tr>
<td>Ce</td>
<td>3/4</td>
<td>1/4</td>
<td>0.3718(7)</td>
<td>0.49(2)</td>
</tr>
<tr>
<td>S(1)</td>
<td>1/4</td>
<td>1/4</td>
<td>0.4595(2)</td>
<td>0.63(6)</td>
</tr>
<tr>
<td>S(2)</td>
<td>0.5648(2)</td>
<td>-1/4</td>
<td>0.1821(1)</td>
<td>1.02(4)</td>
</tr>
<tr>
<td>Na</td>
<td>3/4</td>
<td>1/4</td>
<td>0.1015(3)</td>
<td>1.3(1)</td>
</tr>
</tbody>
</table>

$B$ values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameters defined as $B_{eq} = \frac{1}{3}\sum_{j=1}^{3}(a_{ij}^2B_{j} + b_{ij}^2B_{j} + c_{ij}^2B_{j})$. 

Table 5. Selected Bond Distances (Å) and Angles (deg) for K$_4$USe$_8$ with Standard Deviations in Parentheses

<table>
<thead>
<tr>
<th>bond</th>
<th>distance (Å)</th>
<th>angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-Se(1)</td>
<td>2.840(3)</td>
<td>79.95(9)</td>
</tr>
<tr>
<td>U-Se(2)</td>
<td>2.903(3)</td>
<td>129.00(8)</td>
</tr>
<tr>
<td>U-Se(3)</td>
<td>2.923(3)</td>
<td>131.91(9)</td>
</tr>
<tr>
<td>U-Se(4)</td>
<td>2.920(3)</td>
<td>133.93(9)</td>
</tr>
<tr>
<td>Se(1)-Se(2)</td>
<td>2.385(4)</td>
<td>119.91(8)</td>
</tr>
<tr>
<td>Se(1)-Se(3)</td>
<td>127.9(1)</td>
<td>129.00(8)</td>
</tr>
<tr>
<td>Se(1)-Se(4)</td>
<td>129.1(1)</td>
<td>131.91(9)</td>
</tr>
<tr>
<td>Se(2)-Se(3)</td>
<td>129.00(8)</td>
<td>131.91(9)</td>
</tr>
<tr>
<td>Se(2)-Se(4)</td>
<td>130.91(9)</td>
<td>119.91(8)</td>
</tr>
</tbody>
</table>

at the U center, leaving the four basal selenium atoms in a nearly square-planar arrangement; in an ideal dodecahedron the trapezoids slice further into each other. Second, the presence of the Se–Se bonds, although slightly elongated (2.38 and 2.40 Å), necessitates the corresponding Se–U–Se angle be smaller than in an ideal dodecahedron. 

Figure 2. Ortep drawings of the coordination environments of the atoms K(1) (A) and K(2) (B) in the structure of K$_4$USe$_8$. 

The potassium cations are located in two different sites. The first is coordinated by seven Se atoms in an irregular polyhedron (Figure 2a; range of K(1)—Se distances 3.475(7) Å — 3.190(7) Å; ave 3.357 Å) while the second is in a site coordinated by nine Se atoms, again in an irregular polyhedron (Figure 2b; range of K(2)—Se distances 3.694(8) Å — 3.253(7) Å; ave 3.470 Å). Examples of molecular uranium/chalcogenide complexes are sparse. A fully characterized homoleptic uranium thiolate has been recently reported. Prior to this, most work has dealt with complexes of uranyl with various sulfur containing ligands, including a complex containing a single $\eta^2$-S$_2$-.
Magnetic Properties. The magnetic susceptibility of K₄USe₈ was measured as a function of temperature (5–250 K) at a constant field of 5000 G. A plot of the data as $1/\chi_M$ vs $T$ is shown in Figure 3. Strong paramagnetic behavior, conforming to Curie-Weiss law, is observed from approximately 120 K on up. Below this region, a transition is observed at approximately 90 K and is then followed by antiferromagnetic ordering which has a critical temperature of 65 K at the midpoint of a broad and shallow transition. The $\mu_{\text{eff}}$ at 300 K is 3.82 $\mu_B$, consistent with an $f^2$ configuration where $L = 0$. The exhibited paramagnetic behavior of the compound at high temperatures renders difficult any $^{77}$Se NMR study of this compound. Antiferromagnetic transitions of various degrees have been reported for the uranium compounds $\text{MU}_8Q_17$ ($M = \text{Cr, V, Fe, Ni}$) by Noel and Troc, although their data are complicated by the presence of $M^{2+}$. Neither K⁺ nor Se²⁻ would contribute to any magnetic phenomenon, and so barring any impurity, we are observing behavior based solely on $\text{U}^{4+}$.

Spectroscopy. The solid-state far-IR spectrum of K₄USe₈ shows three peaks: 261 cm⁻¹, which can be tentatively assigned to Se–Se stretching in the diselenide groups, 168 and 153 cm⁻¹ which are presumably due to U–Se vibrations.

As mentioned before K₄USe₈ is slowly soluble in DMF, and similar behavior has been found with ethylenediamine. The compound was insoluble in neat acetonitrile, even with the addition of [Bu₄N]⁺; however, it was successfully dissolved in solutions of either CH₃CN (15C5) or (CH₂CH₂O)₆ (18C6) crown ethers, or 2,2,2-cryptand in CH₃CN.

In all solvents the solutions of K₄USe₈ gave brown/yellow colors of various hues which were stable, by UV/vis, out to 3 days. The DMF and CH₃CN/complexant solutions gave similar UV/vis spectra: one broad plateau at 400–430 nm for DMF and at 390–430 nm for CH₃CN/complexant. After decomposition the solutions revert to brown/green in color, and their UV/vis spectra show the features of a polyselenide solution (peaks at 440 and 640 nm for DMF, 417 and 560 nm for CH₃CN). Such a decomposition takes place in all solvents tested upon exposure to air, and simply upon standing, due to the high oxophilicity of U(IV), making distilled and degassed solvents a requirement. In ethylenediamine solutions of K₄USe₈, UV/vis shows peaks at 346, 404, 492, and 807 nm, while a polyselenide/ethylene diamine solution shows peaks at 408, 560, and 805 nm. Although clearly not a simple Se²⁻ solution, the presence of several peaks in the ethylenediamine solution indicates a significantly stronger solvent interaction with the anion than in either DMF or CH₃CN.

$\text{ALn}_4$ ($A = K$; Ln = Ce, Tb; Q = Se or A = Rb; Ln = Ce; Q = Te). Structure. In the $\text{ALn}_4$ structure, Ln and Q form two-dimensional anionic layers with $A^+$ in the interlayer gallery. The anionic layers themselves are further partitioned into two layers of $(Q_2)^{-2}$ units sandwiching a layer of $\text{Ln}^{3+}$ cations. The $\text{Ln}^{3+}$ cations are in a square antiprismatic environment, coordinated to the ends of eight dichalcogenides, four above the Ln plane and four below. A view of this arrangement is shown in Figure 4. Selected bond distances and angles are given in Table 6. It can be seen that the $(\text{Se}_2)^{2-}$ units point in a uniform direction within their layer and invert that direction in the layer below. Each $(\text{Se}_2)^{2-}$, in turn, bridges four $\text{Ln}^{3+}$ cations in a symmetrical $\mu_2\mu_2$ fashion. The expanded anionic layer is shown in Figure 5. Except for the expected changes in bond distances, the RbCeTe₄ analogue is almost perfectly isostructural, with the respective bond angles being comparable to those in the selenides. Table 6 lists the bond distances and angles of the telluride.

Figure 3. Inverse molar magnetic susceptibility ($1/\chi_M$) plotted against temperature (K) for K₄USe₈ (5000 G).
RbCeTe$_4$, 4.92 and 4.25 Å. Hence the y layers present too small a radius of Tb$^{3+}$ being smaller than that of Ce$^{3+}$. The cell volume of the Tb analogue is the smaller of the two (321.9(2) Å$^3$ vs 338.6(2) Å$^3$ for KCeSe$_4$), and the Ln–Se distances exhibit the expected changes as well (Tb–Se 2.980(1) Å; Ce–Se 3.075(1) Å). Both Ln–Se distances are consistent with the average values for the respective eight-coordinate Ln$^{3+}$ cations in the A$^+$, Ln$^{3+}$ units, analogous to the $T$2– units in ALnQ$_4$.

The change in structural dimensions when comparing the two KLSe$_4$ analogues is consistent with the ionic radius of Tb$^{3+}$ being smaller than that of Ce$^{3+}$. The cell volume of the Tb analogue is the smaller of the two (321.9(2) Å$^3$ vs 338.6(2) Å$^3$ for KCeSe$_4$), and the Ln–Se distances exhibit the expected changes as well (Tb–Se 2.980(1) Å; Ce–Se 3.075(1) Å). Both Ln–Se distances are consistent with the average values for the respective eight-coordinate Ln$^{3+}$ cations in the A$^+$, Ln$^{3+}$ units, analogous to the $T$2– units in ALnQ$_4$.

The repeating unit, shown in Figure 4, is the same for KCeSe$_4$, KTbSe$_4$, and RbCeTe$_4$, with standard deviations in parentheses.

Table 6. Selected Bond Distances (Å) and Angles (deg) for KCeSe$_4$, KTbSe$_4$, and RbCeTe$_4$ with Standard Deviations in Parentheses

<table>
<thead>
<tr>
<th>AMQ$_4$</th>
<th>KCeSe$_4$</th>
<th>KTbSe$_4$</th>
<th>RbCeTe$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M−Q</td>
<td>3.075(1)</td>
<td>2.980(1)</td>
<td>3.285(1)</td>
</tr>
<tr>
<td>M−A</td>
<td>4.164(7)</td>
<td>4.114(1)</td>
<td>4.542(2)</td>
</tr>
<tr>
<td>Se−Se$^a$</td>
<td>2.393(2)</td>
<td>2.393(2)</td>
<td>2.385(1)</td>
</tr>
<tr>
<td>Se−A</td>
<td>3.434(2)</td>
<td>3.414(2)</td>
<td>3.765(1)</td>
</tr>
<tr>
<td>A−A$^a$</td>
<td>4.509(1)</td>
<td>4.423(2)</td>
<td>4.916(2)</td>
</tr>
<tr>
<td>Q−M−Q$^b$</td>
<td>69.92(3)</td>
<td>70.55(4)</td>
<td>70.50(2)</td>
</tr>
<tr>
<td>Q−M−Q$^c$</td>
<td>108.27(7)</td>
<td>109.51(6)</td>
<td>109.40(5)</td>
</tr>
<tr>
<td>Q−M−Q$^d$</td>
<td>69.92(3)</td>
<td>70.55(3)</td>
<td>70.50(2)</td>
</tr>
<tr>
<td>Q−M−Q$^e$</td>
<td>80.61(7)</td>
<td>80.06(6)</td>
<td>81.16(4)</td>
</tr>
<tr>
<td>Q−M−Q$^f$</td>
<td>85.70(7)</td>
<td>84.15(6)</td>
<td>83.1(4)</td>
</tr>
<tr>
<td>Q−M−Q$^g$</td>
<td>110.20(3)</td>
<td>109.92(5)</td>
<td>109.01(1)</td>
</tr>
<tr>
<td>Q−M−Q$^h$</td>
<td>94.30(1)</td>
<td>94.85(5)</td>
<td>96.89(4)</td>
</tr>
</tbody>
</table>

A further feature of this structure is that in the direction parallel to (110), channels are formed, bounded on the opposite sides by Ln$^{3+}$ and on the top and bottom by (Q$_2$)$_2$$^2$ (Figure 6). Their dimensions are 4.16 Å (Ce to Ce) by 3.61 Å (Se to Se) in KCeSe$_4$, with the analogous dimensions in KTbSe$_4$ being 4.11 and 3.64 Å and in RbCeTe$_4$ 4.92 and 4.25 Å. Hence they present too small a volume for intercalation of most species, although Li$_2$ intercalation may be a possibility via reduction of (Q$_2$)$_2$$^2$ to 2Q$^2$$^2$.

The A$^+$ cations of the structure are collinear with the Ln$^{3+}$, being displaced from the Ln$^{3+}$ by only half the length of the c-axis. Except for their distances from the (Q$_2$)$_2$$^2$ layers, Ln$^{3+}$ and A$^+$ have the same coordination environment. This gives the ALnQ$_4$ phases a similarity to the known ALnQ$_2$ compounds which possess the α-NaFeO$_2$ structure type. In these ALnQ$_2$ phases, A$^+$ and Ln$^{3+}$ also share the same coordination environment (octahedral in this case) and, like ALnQ$_4$, are segmented such that every alternate cation layer is exclusively A$^+$ or Ln$^{3+}$.

The known chemical similarities between all members of the lanthanide group would tend to indicate that other elements in this family could also be accommodated in the ALnQ$_4$ structure type. Such possibilities were, in fact, investigated. When Ln = La and Q = Se,  

reactions analogous to those described resulted only in LaSe₂. Phases with powder X-ray diffraction patterns similar to Al₈O₃ were isolated from reactions where A = K, Ln = Nd or Eu, and Q = Se, but these were consistently contaminated with large amounts of amorphous powder of a binary phase.

Magnetic Properties. The magnetic susceptibility of KCeSe₄ was measured from 2 to 300 K at 300 G, and a plot of 1/\(\chi\) vs T is shown in Figure 7. The material appears to be paramagnetic although several anomalies in the data are present. At temperatures below 100 K, the curve is seen to deviate negatively from a straight line extrapolated from the higher temperature data. Such deviation has been reported for several Ce³⁺ compounds and has been attributed to crystal field splitting of the cation's \(^{2}F_{5/2}\) ground state.\(^{30}\) At temperatures above 100 K, Curie-Weiss law is not strictly adhered to, and a slight curvature remains in the data. In this temperature range an average \(\mu_{\text{eff}}\) of 2.3 ± 0.2 \(\mu_B\) has been calculated. This value is in accordance with the usual range for Ce³⁺ compounds (2.3–2.5 \(\mu_B\)) and is close to that of the free ion (2.54 \(\mu_B\)). This magnitude of \(\mu_{\text{eff}}\) is due to the shielding effect the outer electron cloud has on the embedded f-orbitals.\(^{31}\) It was found that the measurements on KCeSe₄ must be done on freshly isolated sample, as a probable phase change in aged samples gives artificially high values for the \(\mu_{\text{eff}}\). This phase change probably occurs to a small extent on the sample surface because the bulk of the sample remains intact by X-ray powder diffraction.

The temperature-dependent magnetic susceptibility of KTbSe₄ proved to be of nearly ideal Curie-Weiss behavior with only a slight deviation from linearity beginning below 50 K (Figure 8). Above this temperature, a \(\mu_{\text{eff}}\) of 9.25 ± 0.04 \(\mu_B\) was estimated by applying a straight-line curve fit to the data from several trials.

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The calculated $\mu_{\text{eff}}$ of a Tb$^{3+}$ cation (based on the $^7F_6$ ground state) is $9.72 \mu_B$ with typically observed experimental values being $9.5$–$9.8 \mu_B$. Also the small value of $\theta$ (ca. $-6$ K) indicates that the cation is much less prone to crystal field effects in this environment than is Ce$^{3+}$.

Spectroscopy. A solid-state far-IR spectrum of KCeSe$_4$ shows no peaks, the only feature being a broad absorption beginning at 250 cm$^{-1}$. The presence of this sort of feature is common in metallic materials, and so a four-probe conductivity measurement on a pressed pellet was performed at 300 K. A value of $5.1 \times 10^{-6}$ S/cm was found, however, indicating a semiconducting material.

The solid-state far-IR spectrum of KTbSe$_4$ was somewhat more informative. A strong peak is clearly present at 151 cm$^{-1}$, which because of its low energy can be safely assigned as a Tb–Se vibration. Two broad peaks are evident at 370 and 515 cm$^{-1}$ with a weak peak at 436 and a series of shoulders on the 370 peak at 325, 268, 227, and 201 cm$^{-1}$. Although tending to have a broad absorbance similar to that of KCeSe$_4$, the weak shoulders are all in a region where one would expect either Se–Se vibration energy (325 and 268 cm$^{-1}$) or slightly higher energy modes from the Tb–Se bonds (227 and 201 cm$^{-1}$).

The solid-state diffuse reflectance spectra of both compounds are shown in Figure 9. The sharp changes in $a/S$ vs energy (eV) in the spectra of these materials correspond to estimates of the their bandgaps at 1.54 eV for KCeSe$_4$ and 1.65 eV for KTbSe$_4$. This helps to confirm that both are valence precise semiconductors. Simply on the basis of color one would expect the respective bandgaps parallel to the c-axis. Layers are formed when neighboring chains share monosulfides; this is done such that the monosulfides of the trigonal prisms in one chain are the capping monosulfides of the neighboring chains (Figure 11). This results in the (LnS$_3$)$_n$– portion of the structure being analogous to the known phase, ZrSe$_3$; however, ZrSe$_3$ exhibits elongated Zr–Se bonds between the chains (Zr–Se = 2.72–2.74 Å within the chain, Zr–Se = 2.87 Å between the chains). The larger coordination spheres of the Ln cations easily accommodate the eight sulfur atoms, and in fact, the capping bonds are no longer than any of the other Ln–S bonds present (see Tables 7 and 8).

The Ce–S distances for NaCeS$_3$ range from 2.838(1) to 3.010(1) Å and are comparable with those in previously reported compounds (2.878 Å in KCeS$_2$, 2.88–3.26 Å in CeS$_3$). The disulfide bond of 2.105(3) Å is also reasonable. In NaLaS$_3$, the corresponding range

\[ \text{NaLnS}_3 \ (\text{Ln} = \text{La, Ce}). \]

Structure. As in the structure of KLnSe$_4$, NaLnS$_3$ possesses anionic Ln/Q layers charge balanced with $\text{A}^+$ in the interlayer gallery.

\[ \text{NaLnS}_3 \ (\text{Ln} = \text{La, Ce}). \]
binary compounds possess the alternating bilayer/disulfide units in both cases, albeit with different
The \( \text{Ln}^3 \) atoms are to sulfur atoms from two separate disulfide units.
the cation makes four bonds to three disulfides; two bonds are to both atoms of a disulfide while two more are to sulfur atoms from two separate disulfide units. The \( \text{Ln}^3/Q^2 \) bilayer is sandwiched between layers of disulfide units in both cases, albeit with different coordination patterns to the lanthanides. While the binary compounds possess the alternating bilayer/

Figure 12. Extended structure of NaLnS\(_3\) as seen parallel to the b-axis (circles with nonshaded octants: Na; open circles: Ln; circles with shaded octants: S).

Table 7. Selected Bond Distances (Å) and Angles (deg) for NaLaS\(_3\) with Standard Deviations in Parentheses

<table>
<thead>
<tr>
<th>Bond Distances (Å)</th>
<th>Na–S</th>
<th>S(2)–S(2)′</th>
<th>S(2)–S(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La–S(1)</td>
<td>2.869(1)</td>
<td>3.039(1)</td>
<td></td>
</tr>
<tr>
<td>La–S(1)′</td>
<td>2.941(2)</td>
<td>2.107(3)</td>
<td></td>
</tr>
</tbody>
</table>

Table 8. Selected Bond Distances (Å) and Angles (deg) for NaCeS\(_3\) with Standard Deviations in Parentheses

<table>
<thead>
<tr>
<th>Bond Distances (Å)</th>
<th>Na–S</th>
<th>S(2)–S(2)′</th>
<th>S(2)–S(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce–S(1)</td>
<td>2.803(3)</td>
<td>3.012(1)</td>
<td></td>
</tr>
<tr>
<td>Ce–S(1)′</td>
<td>2.909(1)</td>
<td>2.105(3)</td>
<td></td>
</tr>
</tbody>
</table>

Disulfide motif, the new ternary materials have both an extra layer of disulfides (reminiscent of the pattern in the \( \text{LnTe}_3 \) phases) and an extra layer of Na cations (Figure 13). In the \( \text{LnTe}_3 \) phases there is a flat square net of tellurium atoms sandwiched between distorted rock-salt layers of \( [\text{LnTe}]^{1+}\). In Na\( \text{LnS}_3 \) the corresponding square chalcogen net is strongly distorted into discrete \( \text{S}_2^2 \) units, and their bonding interaction with the distorted rock-salt layers of \( [\text{LnS}]^{1+}\) is enhanced.

Recently, it has been reported that the Ln/Q framework of the Na\( \text{LnS}_3 \) structure type can also be stabilized by a mixture of K\(^+\) and Cu\(^{2+}\) in the phase KCuCe\( \text{Se}_6 \). This quaternary phase features a monolayer of alkali cations between the anionic layers and Cu\(^{2+}\) ions residing in tetrahedral sites between the stacks of trigonal prisms. KCuCe\( \text{Se}_6 \) has the further interesting feature that only one full Cu\(^{2+}\) atom is disordered over two separate crystallographic sites that alternate down the intralayer "groove". This disorder implied both Cu\(^{2+}\) mobility in the quaternary phase and that the related phases K\( \text{CeS}_3 \) and Cu\( \text{CeS}_3 \) may be possible. The isolation of the Na\( \text{LnS}_3 \) phases lends credence to both these speculations by demonstrating the stability of the Ln/S framework. Further comparisons between the ternary and quaternary compounds will be made in a subsequent report detailing the synthesis and properties of three more members of this class of compounds: K\( \text{CuLaS}_6 \), Cs\( \text{CuCeS}_6 \), and K\( \text{CuCeSe}_6 \).

Magnetic Susceptibility. The temperature-dependent magnetic susceptibility response of NaCe\( \text{S}_3 \) at 2000 G is shown in Figure 14. Despite the change in chalcogenide environment, the magnetic behavior of the Ce\(^{3+}\) remains similar to that seen in K\( \text{CeSe}_4 \): a Curie–Weiss paramagnet at high temperatures with deviations caused by crystal field splitting ensuing as the temperature drops. Above the onset of deviation, an \( \mu_{\text{eff}} \) of 2.3 \( \pm \) 0.2 \( \mu_\text{B} \) and a \( \Theta \) of \(-71 \pm 1 \) K were estimated by fitting a straight line to the data. Again the \( \mu_{\text{eff}} \) is close to that calculated for the free ion, consistent with the known insensitivity of f-orbitals to chemical environments. The magnetic response of Na\( \text{LaS}_3 \) was not investigated as La\(^{3+}\) is an \( \text{F}^0 \) cation and so is expected to be diamagnetic.

Spectroscopy. As would be expected from their isostuctural nature, the solid-state far-IR spectra of NaCe\( \text{S}_3 \) and Na\( \text{LaS}_3 \) are very similar, with only the frequencies of the peaks shifting in response to the slight mass difference between the two lanthanides. Both materials show a strong peak in the region corresponding to \( S–S \) vibrations (493 cm\(^{-1}\) for NaCe\( \text{S}_3 \) and 490 cm\(^{-1}\) for Na\( \text{LaS}_3 \)). A manifold of strong overlapping peaks is seen at lower energies which have been assigned as the Ln–S vibrations of their respective compounds. In Na\( \text{CeS}_3 \) these peaks are at 277, 243, 193, and 177 cm\(^{-1}\) and a final, and much weaker peak exists at 137 cm\(^{-1}\). The peaks of the corresponding manifold in Na\( \text{LaS}_3 \) are at 276, 241, 209, 188, 174, and 137 cm\(^{-1}\).

The solid-state diffuse reflectance spectra of NaCe\( \text{S}_3 \) and Na\( \text{LaS}_3 \) are shown in Figure 15. The difference in color of the two phases is clearly evident in the change in band gap between the two. The red NaCe\( \text{S}_3 \) exhibits a band gap of 2.15 eV while the yellow La analogue one of 2.61 eV. NaCe\( \text{S}_3 \) has a considerable tailing below the initial absorption edge, which suggests either sample

impurity or indirect character in the material's bandgap. The difference in bandgap between the two suggests that it may be possible to produce solid solutions of the formula NaLa$_{1-x}$Ce$_x$S$_3$ in which the bandgap of the material would be tunable based on the lanthanide ratio. Preliminary synthetic investigation of such phases were made by reacting various ratios of La/Ce in the previously described flux reaction for the ternary phase. Although evidence for solid solution behavior was observed, the final products were not of uniform homogeneity.

**Figure 13.** Schematic comparative drawings highlight the relationship between the (A) CeS$_2$, (B) NaLnS$_3$ and (C) LnTe$_3$ structures. The edge sharing rhombi represent distorted bilayers of the rock-salt [LnQ]$^{2+}$; the solid lines, sheets of (Q$_n$)$^{n-}$; and the open circles, Na$^{+}$ cations.

**Figure 14.** Inverse molar magnetic susceptibility ($1/\chi_M$) plotted against temperature (2–300 K) for NaCeS$_3$ (2000 G). (B) shows an expanded view of the region 2–25 K.

**Figure 15.** Solid-state diffuse reflectance spectra of NaCeS$_3$ (solid line) and NaLaS$_3$ (dashed line) plotted as absorption coefficient ($\alpha$/S) vs energy (eV).

**Conclusions**

Although the conditions of the molten A$_2$Q$_x$ flux have given rise to new phases in these systems, much of what has been described has some similarity to previously known f-block/chalcogenide chemistry. The most similarities were found in the NaLnS$_3$ structure type, which possesses several features closely related to those seen in the known polychalcogenide containing binaries. From a compositional standpoint, this is not too surprising because NaLnS$_3$ has only one equivalent of S more than LnQ$_2$, and it has exactly the same Ln/Q stoichiometry as the LnTe$_3$ phases. Because of the unique ability of Te to form infinite covalently bonded nets, the LnTe$_3$ phase had not been seen in either S or Se systems but distorted variants of it should be possible. The formation of a phase with increased amounts of S or Se becomes possible if some cationic species is available to balance the charge. With some help from Na, the Ln/S framework in NaLnS$_3$ merely expands along known structural themes.

The ALnQ$_4$ phases move slightly further from the known base of Ln/Q$_x$ binaries while still retaining some similarities. There is no Ln/Q$^{2-}$ bilayer here as there was in NaLnS$_3$; instead the Ln$^{3+}$ cations are coordinated...
directly and exclusively to \((Q_2)^2^−\). Since both the ALnQ₄ and NaLnS₃ structure types have such strong relationships to the known binary compounds, it is likely that any further phases isolated from these systems will possess variations on the discussed structural themes.

The most chalcogenide-rich phase presented is, of course, K₄USe₈. Rather than forming an extended structure, the \([USe₈]^4^−\) dodecahedron is stabilized. Actinides have a slightly greater covalent character to their bonding and higher charge than do the lanthanides. This may give an increased tendency to form discrete complexes, but it certainly does not preclude extended networks.

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**Supporting Information Available:** Calculated and observed X-ray powder diffraction patterns, and anisotropic thermal parameters (13 pages); listings of calculated and observed structure factors for K₄USe₈, KCeSe₄, KTbSe₄, RbCeTe₄, NaCeS₃, and NaLaS₃ (10 pages). Ordering information is given on any current masthead page.

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