Structures and Bonding in K$_{0.91}$U$_{1.79}$S$_6$ and KU$_2$Se$_6$

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The compounds K$_{0.91}$U$_{1.79}$S$_6$ and KU$_2$Se$_6$, members of the AAn$_2$Q$_6$ actinide family (A = alkali metal or Tl; An = Th or U; Q = S, Se, or Te), have been synthesized from US$_2$, K$_2$S, and S at 1273 K and U, K$_2$Se, and Se at 1173 K, respectively. KU$_2$Se$_6$ shows Curie–Weiss behavior above 30 K and no magnetic ordering down to 5 K. The value of $\mu_{\text{eff}}$ is 2.95(1) $\mu_B$/U. Its electronic spectrum shows the peaks characteristic of 5f–5f transitions. It is a semiconductor with an activation energy of 0.27 eV for electrical conduction. Both K$_{0.91}$U$_{1.79}$S$_6$ and KU$_2$Se$_6$ crystallize in space group Immm of the orthorhombic system and are of the KTh$_2$Se$_6$ structure type. Both contain infinite one-dimensional linear Q–Q chains characteristic of the AAn$_2$Q$_6$ family. Typical of the known AAn$_2$Q$_6$ compounds, in KU$_2$Se$_6$, there are two alternating Se–Se distances of 2.703(2) and 2.855(2) Å, both much longer than an Se–Se single bond. In contrast, in K$_{0.91}$U$_{1.79}$S$_6$, the first sulfide of this family to be characterized structurally, there are alternating normal S$_2$ 2− pairs 2.097(5) Å in length. In K$_{0.91}$U$_{1.79}$S$_6$, the formal oxidation state of U is 4+.

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Introduction

The actinide compounds of formula AAn$_2$Q$_6$ (A = alkali metal or Tl; An = Th or U; Q = S, Se, or Te) present interesting problems in chemical bonding. When Q = Te, the known compounds CsTh$_2$Te$_6$, Th$_{1.12}$U$_2$Te$_6$, and KTh$_2$Te$_6$ crystallize in space group Cmcm of the orthorhombic system. These compounds are isostructural; the layered structure features not only isolated Te$_2$− species but linear, infinite, one-dimensional Te chains with Te−Te distances approximately 0.35 Å longer than that of a typical Te−Te single bond. When Q = Se, the known compounds KTh$_2$Se$_6$, RbTh$_2$Se$_6$, and CsU$_2$Se$_6$ crystallize in space group Immm of the orthorhombic system. These compounds, which are isostructural, have a layered structure that differs in its stacking pattern from that of the Cmcm structure. The Immm structure contains discrete Se$_2$ 2− species and infinite one-dimensional Se chains with Se−Se distances about 0.35 Å longer than a typical Se−Se single bond.

Efforts have been made to understand the bonding in these compounds when Q = Se. Thus, it has been postulated that in the ATh$_2$Se$_6$ (A = K, Rb) compounds the Se atoms in the [Th$_2$Se$_6$] layers accept the extra electrons from the A atoms, thereby breaking one out of four Se$_2$ 2− bonds. This picture is supported by a variety of physical measurements on these compounds. This formulation leaves Th with the expected formal oxidation state of 4+. On the basis of XPS measurements, a formal oxidation state of 4+ was assigned to U in KU$_2$Se$_6$. In an effort to clarify further the bonding in the AAn$_2$Q$_6$ compounds, we report here the syntheses, structure, and some physical properties of K$_{0.91}$U$_{1.79}$S$_6$ and KU$_2$Se$_6$.

Experimental Section

Synthesis of K$_{0.91}$U$_{1.79}$S$_6$. The compound was prepared by the reactive flux method. K$_2$S was prepared by the stoichiometric reaction of K (Cerac, 98%) and S (Mallinckrodt, 99.6%) in liquid NH$_3$ at 194 K. $\beta$-US$_2$ was prepared by the stoichiometric reaction of U turnings (depleted, ORNL) with S in a carbon-coated fused-silica ampule. The heating profile was 673 K for 20 h, followed by slow cooling to 298 K.

A reaction mixture of K$_2$S (0.5 mmol), $\beta$-US$_2$ (0.5 mmol), and S (0.5 mmol) was loaded into a fused-silica ampule in an Ar-filled...
The sample was heated to 1273 K in 23 h, kept at 1273 K for 48 h, cooled at 10 K/h to 773 K, and then cooled at 120 K/h to 298 K. Black plates of the desired product $K_{0.91}U_{1.79}S_6$ were obtained in about 5% yield, based on U. These plates were manually extracted from the melt.

Synthesis of $KU_2Se_6$. An earlier preparation of $KU_2Se_6$ involved the reaction of $K_2Se$, U, and Se at 773 K. Here the reaction mixture consisted of $K_2Se$ (0.17 mmol) (prepared by the stoichiometric reaction of K and Se (Cerac, 99.99%) in liquid NH$_3$ at 194 K), U (0.5 mmol), and Se (1.4 mmol). The sample was heated to 1173 K in 15 h, held at 1173 K for 96 h, cooled at 5.75 K/h to 603 K, and then cooled at 3 K/h to 298 K. The yield of golden-black needles of $KU_2Se_6$ was approximately 25%, based on U.

Selected single crystals of each of the above compounds were examined with an EDX-equipped Hitachi S-3500 SEM. The presence of the stated elements in approximately 1:2:6 ratios was confirmed.

Syntheses of $US_3$ and $USe_3$. $US_3$ was prepared from the elements.$^7$ Its X-ray powder pattern was consistent with that calculated from single-crystal data.$^7$ $US_3$ was also prepared from the elements. Its powder pattern agreed with one given previously.$^8$

Structure Determinations. Single-crystal X-ray diffraction data were collected by the use of graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 153 K on a Bruker SMART-1000 CCD diffractometer.$^9$ The crystal-to-detector distance was 5.023 cm. Data were collected by scans of 0.3° in $\omega$ in four groups of 606 frames at $\varphi$ settings of 0°, 90°, 180°, and 270° at exposure times of 15 s/frame. The collection of the intensity data was carried out with the program SMART.$^9$ Crystal decay was monitored by re-collecting 50 initial frames at the end of each data collection. Cell refinement and data reduction were carried out with the use of the program SAINT.$^9$ Face-indexed absorption corrections were performed numerically with the use of the program XPREP.$^9$ Because the crystals were too thin, a Leitz microscope with a calibrated traveling micrometer eyepiece was employed to measure accurately the dimensions of the crystal faces for the face-indexed absorption corrections. Then, the program SADABS$^{10}$ was used to make incident beam and decay corrections.

Each crystal structure was solved with the direct methods program SHELXL and refined with the full-matrix least-squares program SHELXL.$^{10}$ The program STRUCTURE TIDY$^{11}$ was used to standardize the positional parameters. After refinement of the standard anisotropic model including extinction, the occupancy of the U site was fixed but the occupancies of the alkali metal A and the chalcogen Q sites were varied in an ensuing refinement. The resulting formulas were $K_{1.01(2)}U_2Se_{6.06(6)}$ and $K_{0.98(2)}U_2Se_{6.06(2)}$. The $Q = Se$ formula does not differ significantly from the stoichiometric formula $KU_2Se_6$, and in the final refinement, the site occupancies were fixed at this composition. On the other hand, the $Q = S$ compound is clearly nonstoichiometric, the above formula being equivalent to $K_{0.97(2)}U_{1.79(2)}Se_6$, indicative of K and U vacancies. Accordingly, in a final refinement, the occupancies of the two S sites were fixed but the occupancies of the U and K sites were varied. This refinement converged to give the same formula, namely

$$ K_{0.91(2)}U_{1.79(2)}S_6. $$

Although the determination of composition from the refinement of X-ray occupancies is not without its pitfalls,$^{12}$ there are two features that lead us to believe that the present calculations are reliable. The first is that the structure is a simple one that involves only one U, one K, and two Q positions in the asymmetric unit. Whether one varied the occupancies of K and U while keeping the occupancies of Q1 and Q2 fixed or whether one varied the occupancies of K, Q1, and Q2 while keeping the occupancy of U fixed, the same results were obtained. Thus, the refinement is stable and convergence to a false minimum is highly unlikely. The second is that in each refinement the ratio Q1:Q2, which is 1:2 for the stoichiometric structure, remained at 1:2 within statistical error. Additional crystallographic details and selected metrical data are given in Table 1 and in the Supporting Information.

The unit cell parameters for $KU_2Se_6$, of 4.0586(6), 5.5578(8), and 21.683(3) Å at 153 K in Table 1 may be compared with those reported earlier of 4.058(3), 5.556(4), and 21.710(17) Å at 298 K. (No structure determination was carried out in the earlier investigation.)

Magnetic Susceptibility Measurement. The magnetic susceptibility data were collected for a 22 mg sample of $KU_2Se_6$, in the temperature range 5−390 K with a measuring field of 500 G, after cooling in either a zero field or at 10 kG. The crushed sample was contained in a gelatine capsule. A Quantum Design PPMS-5 SQUID magnetometer was used. All measurements were corrected for core diamagnetism.$^{13}$

Diffuse Reflectance Spectra. Diffuse reflectance data for $KU_2Se_6$, $US_3$, and $USe_3$ were collected over the wavelength range 500−2600 nm with a Varian Cary 5000 double-beam spectrometer. MgO was used as a reference. The Kubelka−Munk function was used to transform the data into absorbance.

Electrical Conductivity Measurements. Standard four-probe electrical conductivity measurements were made over the temperature range 200−300 K on a plate-shaped single crystal of $KU_2Se_6$. Electrical contacts were applied with the use of silver paste. A Quantum Design PPMS instrument was used.

Results and Discussion

Syntheses. The synthesis of $K_{0.91}U_{1.79}S_6$ proceeded from the reaction of $K_2S$, $US_2$, and S at 1273 K. It is an inefficient synthesis, affording only about a 5% yield of black plates of the desired product. Attempts to increase the yield and the size of the crystals obtained were unsuccessful. On the
other hand, the synthesis of KU$_2$Se$_6$ from K$_2$Se, U, and Se at 1173 K afforded high-quality golden-black needles in about 25% yield. The compounds are stable in air for a few hours.

Structures. The two structure types comprising the known AAn$_2$Q$_6$ structures are those of CsTh$_2$Te$_6$ (space group Cmcm) and the closely related KTh$_2$Se$_6$ (space group Immm). Both are layered structures. The difference between the Cmcm and Immm structure types lies in the stacking of the UQ$_3$ layers and the positioning of the A atom between these structures. In the Cmcm structure, each succeeding UQ$_3$ layer is shifted by 1/2a. In the Immm structure, each succeeding UQ$_3$ layer is shifted by 1/2a and 1/2b.

CsU$_2$Se$_6$,\(^5\) K$_{0.91}$U$_{1.79}$S$_6$, and KU$_2$Se$_6$ crystallize with the KTh$_2$Se$_6$ structure type in space group Immm. However, the Cs atom is disordered over two positions in the structure of CsU$_2$Se$_6$,\(^5\) whereas the K atoms are ordered in the structures of K$_{0.91}$U$_{1.79}$S$_6$ and KU$_2$Se$_6$. This is a steric effect. The structures of CsU$_2$Se$_6$ and KU$_2$Se$_6$ are shown in Figure 1. In addition to isolated Q atoms in the UQ$_3$ layers, linear chains of Q atoms with alternating Q–Q distances are found in these structures. The details of the linear Q chains characteristic of the AAn$_2$Q$_6$ family and related compounds bear on the question of chemical bonding, and these are summarized in Table 2. In the structure of CsU$_2$Se$_6$,\(^5\) disorder occurs because the Cs atom can either occupy the space between four short Se–Se pairs or the space between four long Se–Se pairs. In each of the K$_{0.91}$U$_{1.79}$S$_6$ and KU$_2$Se$_6$ structures, the K atom only occupies the position between the four long Q–Q pairs because it will not physically fit in the space between the short Q–Q pairs.

In KU$_2$Se$_6$, the two alternating Se–Se distances of 2.703(2) and 2.855(2) Å are both considerably longer than a Se–Se single bond distance, for example, that of 2.363(1) Å in USe$_3$;\(^7\) in K$_{0.91}$U$_{1.79}$S$_6$, the S–S distances are 2.097(5) (a single bond distance) and 3.295(5) Å (a nonbonding distance). The Q–Q chains in these and related compounds are compared in Figure 2.

Selected distances for K$_{0.91}$U$_{1.79}$S$_6$ and KU$_2$Se$_6$ are presented in Table 3. These are normal. The U–Q distances, which range from 2.761(2) to 2.846(2) Å for K$_{0.91}$U$_{1.79}$S$_6$, may be compared with those of 2.76–2.99 Å for UFeS$_3$;\(^{14}\) the U–Se distances, which range from 2.884(7) to 2.9648(5) Å for KU$_2$Se$_6$, may be compared with those of 2.850(2), 2.935(2), and 3.126(3) Å for UMnSe$_3$.\(^{15}\) The K–Q distance of 3.339(2) Å for K$_{0.91}$U$_{1.79}$S$_6$ is in the range of 3.127(2)–3.382(2) Å found for KCuZrS$_3$;\(^{16}\) the K–Se distance of 3.357(4) Å may be compared with those of 3.255(2)–3.530(2) Å for KCuZrS$_3$.

The structure of KU$_2$Se$_6$ may be thought of as resulting from the insertion of K atoms into the USe$_3$ structure.\(^7\) Such insertion weakens the Se–Se bonds, either by formal oxidation of the K atom or by reduction of the U atom. The stoichiometric formula KU$_2$Se$_6$ established from the refinement of the X-ray data does not distinguish these two

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**Table 2. Q–Q Distances in the Infinite Linear Q–Q Chains of Selected Compounds**

<table>
<thead>
<tr>
<th>compound</th>
<th>d$_{short}$ (Å)</th>
<th>d$_{long}$ (Å)</th>
<th>d$<em>{short}$/d$</em>{long}$</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$<em>{0.91}$U$</em>{1.79}$S$_6$</td>
<td>2.097(5)</td>
<td>3.295(5)</td>
<td>0.636</td>
<td>this work</td>
</tr>
<tr>
<td>KU$_2$Se$_6$</td>
<td>2.703(2)</td>
<td>2.855(2)</td>
<td>0.947</td>
<td>this work</td>
</tr>
<tr>
<td>Tl$_{1.12}$U$_2$Te$_3$</td>
<td>2.665(6)</td>
<td>2.894(6)</td>
<td>0.921</td>
<td>5</td>
</tr>
<tr>
<td>KTh$_2$Se$_6$</td>
<td>2.727(2)</td>
<td>2.907(2)</td>
<td>0.938</td>
<td>4</td>
</tr>
<tr>
<td>RbTh$_2$Se$_6$</td>
<td>2.728(3)</td>
<td>2.906(3)</td>
<td>0.939</td>
<td>4</td>
</tr>
<tr>
<td>CsTh$_2$Te$_6$</td>
<td>3.057(3)</td>
<td>3.085(3)</td>
<td>0.991</td>
<td>3</td>
</tr>
<tr>
<td>CsTh$_2$Te$_6$</td>
<td>3.052(3)</td>
<td>3.088(3)</td>
<td>0.988</td>
<td>1</td>
</tr>
<tr>
<td>US$_3$</td>
<td>2.086(4)</td>
<td>3.290(4)</td>
<td>0.634</td>
<td>17</td>
</tr>
<tr>
<td>USe$_3$</td>
<td>2.363(1)</td>
<td>3.294(5)</td>
<td>0.717</td>
<td>7</td>
</tr>
<tr>
<td>α-USe$_3$</td>
<td>2.751(1)</td>
<td>3.350(1)</td>
<td>0.821</td>
<td>29</td>
</tr>
<tr>
<td>ZrS$_3$</td>
<td>2.090(5)</td>
<td>3.035(5)</td>
<td>0.689</td>
<td>30</td>
</tr>
<tr>
<td>ZrSe$_3$</td>
<td>2.34</td>
<td>3.07</td>
<td>0.76</td>
<td>31</td>
</tr>
<tr>
<td>ZrTe$_3$</td>
<td>2.794(1)</td>
<td>3.105(1)</td>
<td>0.900</td>
<td>32</td>
</tr>
</tbody>
</table>

* Space group Immm.  
  ** Space group Cmcm.  
  A more extensive tabulation of Te–Te linear chain geometries is given in ref 33.  
  Distance not given in the reference but calculated from data therein.

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**Figure 2. Q–Q chains in (a) CsTh$_2$Te$_6$, (b) CsU$_2$Se$_6$, (c) KU$_2$Se$_6$, and (d) K$_{0.91}$U$_{1.79}$S$_6$.**

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**Table 3. Selected Distances (Å) for K$_{0.91}$U$_{1.79}$S$_6$ and KU$_2$Se$_6$**

<table>
<thead>
<tr>
<th>bond</th>
<th>K$<em>{0.91}$U$</em>{1.79}$S$_6$</th>
<th>KU$_2$Se$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K–Q(2)</td>
<td>3.339(2)</td>
<td>3.357(4)</td>
</tr>
<tr>
<td>U–Q(1) × 2</td>
<td>2.761(2)</td>
<td>2.884(7)</td>
</tr>
<tr>
<td>U–Q(1) × 2</td>
<td>2.8082(8)</td>
<td>2.9648(5)</td>
</tr>
<tr>
<td>U–Q(2) × 4</td>
<td>2.846(2)</td>
<td>2.9241(6)</td>
</tr>
<tr>
<td>Q(2)–Q(2)</td>
<td>2.097(5)</td>
<td>2.703(2)</td>
</tr>
</tbody>
</table>

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possibilities. The formal oxidation state of U in KU₂Se₆ was
determined to be 4+ from XPS measurements, although it
is not clear if the method is sufficiently sensitive to eliminate
other possible oxidation states in view of the breadth of the
binding energy signal and the possibility of surface con-
tamination. As opposed to KU₂Se₆, in K₀.₉₁U₁.₇₉S₆, the S–S
single bonds are not weakened. Given the composition
K₀.₉₁U₁.₇₉S₆, as established from the refinement of the
X-ray data, the stoichiometric formulation KU₂(S₆)₂(S₄)₂ as
indicated from the structure, and charge balance, the formal
oxidation state of U in this compound is 3.96(5),18 indicated from the structure, and charge balance, the formal
oxidation state of U in this compound is 3.96(5) +.

Magnetic Susceptibility. The magnetic susceptibility, , and its inverse, , as a function of temperature for KU₂-
Se₆ are shown in Figure 3. The field-cooled and zero-field-
cooled data are essentially superimposable. Above 30 K, the
Curie–Weiss law, , is obeyed. The Curie constant and the Weiss temperature obtained from parameter
fitting are 2.17(1) emu mol −1 K and −81.2(6) K, respectively. The effective magnetic moment, , calculated from the
Curie constant is 2.95(1) μB U. The values of for the
free ions U³⁺ (6d⁰5f³), U⁴⁺ (6d⁰5f⁴), and U⁵⁺ (6d⁰5f⁵)19 calculated using L–S coupling are 3.62, 3.58, and 2.54 μB/ U, respectively. The observed value of 2.95(1) μB/U in KU₂-Se₆ is consistent with values previously observed in solid-
state chalcogenides in which U has a formal oxidation state of 4+. For example, a value of 2.50 μB/U has been
reported for the compound Cu₂U₃S₇ in which the absence of S–S bonds and the propensity of Cu to be 1+ in chalcogenides implies U⁴+. Comparably comparisons are lacking for solid-state chalcogenides in which U has a formal oxidation state of 3+.

Magnetic ordering was not observed in KU₂Se₆ until 5 K. The negative Weiss constant implies antiferromagnetic
interactions among U ions. The related compound USe₃
(USe(Se₂)) exhibits antiferromagnetic-like behavior at 40 K.21
The U–U distances in KU₂Se₆ are 4.059(6) (ab plane) and
7.7531 Å (interplane), whereas they are 4.061(1) (ab plane) and 7.021 Å (interplane) in USe₃.7 The experimental
observation that magnetic ordering is less facile as the
interplane U–U distance increases is consistent with the Hill
plot.22

Diffuse Reflectance Spectra. Figure 4 shows the optical
spectra for KU₂Se₆, USe₃, and US₃. The characteristic peaks
from f–f transitions observed for USe₃ and US₃ are also
observed for RbU₂SbS₈ and KU₂SbSe₈ at nearly the same
positions. All four compounds formally contain U⁴+. Because of the interference of these characteristic peaks, the
band gaps of these materials can only be estimated to be in
the region 0.4–0.8 eV. The absorptions originating from 5f–

Figure 3. Magnetic susceptibility, , and its inverse, , vs T for KU₂Se₆.

(22) Miner, W. N., Ed. Plutonium 1970 and Other Actinides; AIME: Santa
Fe, 1970; Vol. 17.
Structures and Bonding in K\textsubscript{0.91}U\textsubscript{1.79}S\textsubscript{6} and KU\textsubscript{2}Se\textsubscript{6}

Electrical Conductivity. The value of the electrical conductivity along the a axis of a KU\textsubscript{2}Se\textsubscript{6} single crystal is 1 \times 10\textsuperscript{-3} S/cm at 300 K. The material is a semiconductor with conductivity decreasing with decreasing temperature in a simple Arrhenius-type thermally activated behavior. The derived activation energy of 0.27 eV for electrical conductivity is consistent with a band gap larger than 0.54 eV and hence consistent with the diffuse reflectance spectrum.

Electronic Structure. Why do the Q\ldots Q chains in K\textsubscript{0.91}U\textsubscript{1.79}S\textsubscript{6} and KU\textsubscript{2}Se\textsubscript{6} differ so markedly (Figure 2)? Ideally, band structure calculations for these compounds would be helpful in answering this question. However, such calculations for U compounds are complicated by a number of factors, including large spin–orbit interactions and electron repulsion for contracted U 5f orbitals, which is Mott Hubbard splitting. Therefore, we offer a qualitative argument. The binding energies for the single-bonded species are 226 kJ/mol\textsuperscript{24} for S\textsubscript{2} and 1.79 S\textsuperscript{6} and KU\textsubscript{2}Se\textsubscript{6} differ so markedly (Figure 2)? Therefore, we offer a qualitative argument.

The binding energies of the single-bonded species are 226 kJ/mol\textsuperscript{24} for S\textsubscript{2} and 209 kJ/mol\textsuperscript{24} for Se\textsubscript{2}. Although no value for Te\textsubscript{2} is known, it should be less than that for Se\textsubscript{2}. From the molecular orbital diagram for Q\textsubscript{2}, it is known that near the HOMO–LUMO gap the states are Q np Q np \sigma, \pi, \pi*, and \sigma*. The \pi and \pi* states are doubly degenerate. These four states are modified by Q ns Q ns \sigma bonding. At the HOMO, the \pi* states are fully occupied by electrons, indicating the existence of a Q–Q single bond. The LUMO is Q np Q np \sigma*. Because of their binding energies, the position of the LUMO of S\textsubscript{2} is higher relative to that of Se\textsubscript{2}.

We consider solids constructed from such Q\textsubscript{2}– species. The compound USe\textsubscript{3} contains two different Se\ldots Se distances, 2.361(5) and 3.294(5) Å. The average Se–Se bond length in \alpha-Se\textsubscript{3} at 299 K is 2.336(7) Å; it is known that near the HOMO–LUMO gap the states are Q np Q np \sigma, \pi, \pi*, and \sigma*. The \pi and \pi* states are doubly degenerate. These four states are modified by Q ns Q ns \sigma bonding. At the HOMO, the \pi* states are fully occupied by electrons, indicating the existence of a Q–Q single bond. The LUMO is Q np Q np \sigma*. Because of their binding energies, the position of the LUMO of S\textsubscript{2} is higher relative to that of Se\textsubscript{2}.

\textsuperscript{5f} transitions are much weaker in KU\textsubscript{2}Se\textsubscript{6} than in the other compounds.

Next, we consider KU\textsubscript{2}Se\textsubscript{6} where the Se–Se bonds are longer than in USe\textsubscript{3} and discrete Se–Se single-bonded pairs are no longer present (Table 2). The Se\textsuperscript{2}– species has been reduced, presumably by an electron from the K atom that is inserted into the Se 4p \sigma* orbital. From charge balance, this compound is represented as KU\textsuperscript{1.25}(Se\textsuperscript{2}–)\textsubscript{2}(Se\textsuperscript{1.25–})\textsubscript{4} with one-fourth of the Se 4p \sigma* band occupied by the inserted electron. The Se\textsuperscript{1–} chain in USe\textsubscript{3} and the Se\textsuperscript{1.25–} chain in KU\textsubscript{2}Se\textsubscript{6} can be derived by adding extra electrons to a linear chain of equally spaced neutral Se atoms. The linear Se chain is distorted by the intrinsic charge density waves and the cation (K\textsuperscript{+}, U\textsuperscript{4+}) distribution. Thus, we would expect semiconducting behavior in these compounds, consistent with experiment.

Finally, we consider K\textsubscript{0.91}U\textsubscript{1.79}S\textsubscript{6}. The electron responsible for the reduction of the Se–Se single bond in the Se\textsuperscript{2}– species in KU\textsubscript{2}Se\textsubscript{6} cannot reduce the stronger S–S single bond in the S\textsuperscript{2}– species because of the relatively higher position of the S 3p \sigma* orbital compared to the Se 4p \sigma* orbital. Electron insertion into the S\textsuperscript{2}– dimer chain leading to a delocalized S chain with S–S distances longer than a normal single bond does not lower the total energy of the system as effectively as the formation of cationic vacancies. The structural difference between the sulfide and the selenide arises because the S valence states are more localized (anionic) than are the Se and Te states. Therefore, a compensation takes place via the formation of cationic vacancies that results in the observed formulation K\textsubscript{0.91}U\textsubscript{1.79}S\textsubscript{6}. Apparently, the formation of cationic vacancies is also more facile than reduction of the U\textsuperscript{4+} ion.

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Supporting Information Available: Crystallographic data in CIF format for K\textsubscript{0.91}U\textsubscript{1.79}S\textsubscript{6} and KU\textsubscript{2}Se\textsubscript{6}. This material is available free of charge via the Internet at http://pubs.acs.org.

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