Inorg. Chem. **2006**, *45*, 3307–3311

Inorganic Chemistry
Article

Structures and Bonding in $K_{0.91}U_{1.79}S_6$ and KU_2Se_6

Hiroshi Mizoguchi,[†] Danielle Gray,[†] Fu Qiang Huang,[†,#] and James A. Ibers*,[†]

Department of Chemistry, Northwestern University, Evanston, Illinois 60208, and Shanghai Institute of Ceramics, Shanghai 200050, PRC

Received December 14, 2005

The compounds $K_{0.91}U_{1.79}S_6$ and KU_2Se_6, members of the AAn_2Q_6 actinide family (A = alkali metal or Tl; An = Th or U; Q = S, Se, or Te), have been synthesized from US_2, K_2S, and S at 1273 K and U, K_2Se, and Se at 1173 K, respectively. KU_2Se_6 shows Curie–Weiss behavior above 30 K and no magnetic ordering down to 5 K. The value of μ_{eff} is 2.95(1) μ_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_2Se_6 crystallize in space group *Immm* of the orthorhombic system and are of the KTh_2Se_6 structure type. Both contain infinite one-dimensional linear Q–Q chains characteristic of the AAn_2Q_6 family. Typical of the known AAn_2Q_6 compounds, in KU_2Se_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+.

Introduction

The actinide compounds of formula AAn_2Q_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 $CsTh_2Te_6$,[1] $Tl_{1.12}U_2Te_6$,[2] and KTh_2Te_6[3] 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_2Se_6,[4] $RbTh_2Se_6$,[4] and CsU_2Se_6[5] 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-} 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_2Se_6 (A = K, Rb) compounds the Se atoms in the $[Th_2Se_6]$ layers accept the extra electrons from the A atoms, thereby breaking one out of four Se_2^{2-} bonds.[4] This picture is supported by a variety of physical measurements on these compounds.[4] 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_2Se_6.[5] In an effort to clarify further the bonding in the AAn_2Q_6 compounds, we report here the syntheses, structure, and some physical properties of $K_{0.91}U_{1.79}S_6$ and KU_2Se_6.

Experimental Section

Synthesis of $K_{0.91}U_{1.79}S_6$. The compound was prepared by the reactive flux method.[6] K_2S was prepared by the stoichiometric reaction of K (Cerac, 98%) and S (Mallinckrodt, 99.6%) in liquid NH_3 at 194 K. β-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, then 873 K for 20 h, followed by slow cooling to 298 K.

A reaction mixture of K_2S (0.5 mmol), β-US_2 (0.5 mmol), and S (0.5 mmol) was loaded into a fused-silica ampule in an Ar-filled

---

[*] To whom correspondence should be addressed. E-mail: ibers@chem.northwestern.edu.
[†] Northwestern University.
[#] Shanghai Institute of Ceramics.

(1) Cody, J. A.; Ibers, J. A. *Inorg. Chem.* **1996**, *35*, 3836−3838.
(2) Tougait, O.; Daoudi, A.; Potel, M.; Noël, H. *Mater. Res. Bull.* **1997**, *32*, 1239−1245.
(3) Wu, E. J.; Pell, M. A.; Ibers, J. A. *J. Alloys Compd.* **1997**, *255*, 106−109.
(4) Choi, K.-S.; Patschke, R.; Billinge, S. J. L.; Waner, M. J.; Dantus, M.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1998**, *120*, 10706−10714.
(5) Chan, B. C.; Hulvey, Z.; Abney, K. D.; Dorhout, P. K. *Inorg. Chem.* **2004**, *43*, 2453−2455.
(6) Sunshine, S. A.; Kang, D.; Ibers, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 6202−6204.

10.1021/ic052140l CCC: $33.50

glovebox. The ampule was evacuated to 10^{-4} Torr and sealed. 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[5] 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 USe_3 and US_3. USe_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 ω in four groups of 606 frames at φ 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] and face-indexed absorption corrections were performed numerically with the use of the program XPREP.[10] Because the crystals were so 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 SHELXS 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 resultant formulas were $K_{1.01(2)}U_2S_{6.69(6)}$ 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 $K_{0.91(2)}U_{1.79(2)}S_6$, 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.

Table 1. Crystal Data and Structure Refinements for KU_2Q_6[a]

	$K_{0.91}U_{1.79}S_6$	KU_2Se_6
a, Å	4.0321(4)	4.0586(6)
b, Å	5.3929(5)	5.5578(8)
c, Å	20.556(2)	21.683(3)
V, Å ^{3}	446.99(7)	489.1(1)
ρ_c, g/cm^3	4.856	6.715
μ, cm^{-1}	341.3	557.4
$R(F)$[b]	0.0248	0.0204
$R_w(F_o^2)$[c]	0.0582	0.0564

[a] For both structures, $Z = 2$, space group = *Immm*, $T = 153$ K, and $\lambda = 0.71073$ Å. [b] $R(F) = \sum||F_o| - |F_c||/|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. [c] $R_w(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4\}^{1/2}$ for all data. $w^{-1} = \sigma^2(F_o^2) + (q_1P)^2 + q_2P$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$. $q_1 = 0.0156$, $q_2 = 22.25$ for KU_2S_6; 0.0280, 0 for KU_2Se_6.

The unit cell parameters for KU_2Se_6 of 4.0586(6), 5.5578(8), and 21.683(3) Å (a, b, c) at 153 K in Table 1 may be compared with those reported earlier[5] 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 MPMS-5 SQUID magnetometer was used. All measurements were corrected for core diamagnetism.[13]

Diffuse Reflectance Measurements. Diffuse reflectance data for KU_2Se_6, USe_3, and US_3 were collected over the spectral 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

---

(7) Ben Salem, A.; Meerschaut, A.; Rouxel, J. *C. R. Acad. Sci., Sér. 2* **1984**, *299*, 617−619.

(8) Flahaut, J.; Picon, M. *Bull. Soc. Chim. Fr.* **1958**, *6*, 772−780.

(9) *SMART Version 5.054 Data Collection and SAINT-Plus Version 6.45a Data Processing Software for the SMART System*; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2003.

(10) Sheldrick, G. M. *SHELXTL Version 6.14*; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2003.

(11) Gelato, L. M.; Parthé, E. *J. Appl. Crystallogr.* **1987**, *20*, 139−143.

(12) Mironov, Y. V.; Cody, J. A.; Albrecht-Schmitt, T. E.; Ibers, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 493−498.

(13) Mulay, L. N.; Boudreaux, E. A., Eds. *Theory and Applications of Molecular Diamagnetism*; Wiley-Interscience: New York, 1976.

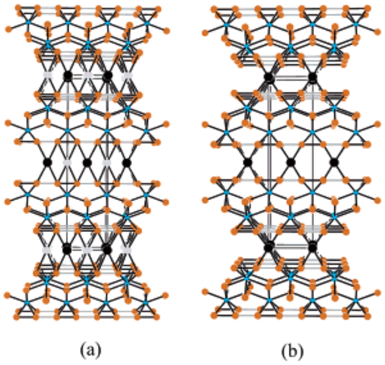

Figure 1. Structures of (a) CsU_2Se_6 and (b) KU_2Se_6 as viewed down the *a* axis. Color code: orange = Se; blue = U; black = A; gray = disordered position of A; black bond = shorter distance in the Se−Se chain; gray bond = longer distance.

other hand, the synthesis of KU_2Se_6 from K_2Se, 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_2Q_6 structures are those of $CsTh_2Te_6$ (space group *Cmcm*)[1] and the closely related KTh_2Se_6 (space group *Immm*).[4] 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 the layers. In the *Cmcm* structure, each succeeding UQ_3 layer is shifted by 1/2*a*. In the *Immm* structure, each succeeding UQ_3 layer is shifted by 1/2*a* and 1/2*b*.

CsU_2Se_6,[5] $K_{0.91}U_{1.79}S_6$, and KU_2Se_6 crystallize with the KTh_2Se_6 structure type in space group *Immm*. However, the Cs atom is disordered over two positions in the structure of CsU_2Se_6,[5] whereas the K atoms are ordered in the structures of $K_{0.91}U_{1.79}S_6$ and KU_2Se_6. This is a steric effect. The structures of CsU_2Se_6[5] and KU_2Se_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_2Q_6 family and related compounds bear on the question of chemical bonding, and these are summarized in Table 2. In the structure of CsU_2Se_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_2Se_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_2Se_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.

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

compound	d_{short} (Å)	d_{long} (Å)	d_{short}/d_{long}	ref
$K_{0.91}U_{1.79}S_6$[a]	2.097(5)	3.295(5)	0.636	this work
KU_2Se_6[a]	2.703(2)	2.855(2)	0.947	this work
CsU_2Se_6[a]	2.665(6)	2.894(6)[d]	0.921	5
$Tl_{1.12}U_2Te_6$[b,c]	3.037(3)	3.054(3)	0.994	2
KTh_2Se_6[a]	2.727(2)	2.907(2)	0.938	4
$RbTh_2Se_6$[a]	2.728(3)	2.906(3)	0.939	4
KTh_2Te_6[b]	3.057(3)	3.085(3)	0.991	3
$CsTh_2Te_6$[b]	3.052(3)	3.088(3)	0.988	1
US_3	2.086(4)	3.290(4)	0.634	17
USe_3	2.363(1)	3.294(5)[d]	0.717	7
α-UTe_3	2.751(1)	3.350(1)	0.821	29
ZrS_3	2.090(5)	3.035(5)	0.689	30
$ZrSe_3$	2.34	3.07	0.76	31
$ZrTe_3$	2.794(1)	3.105(1)	0.900	32

[a] Space group *Immm*. [b] Space group *Cmcm*. [c] A more extensive tabulation of Te−Te linear chain geometries is given in ref 33. [d] Distance not given in the reference but calculated from data therein.

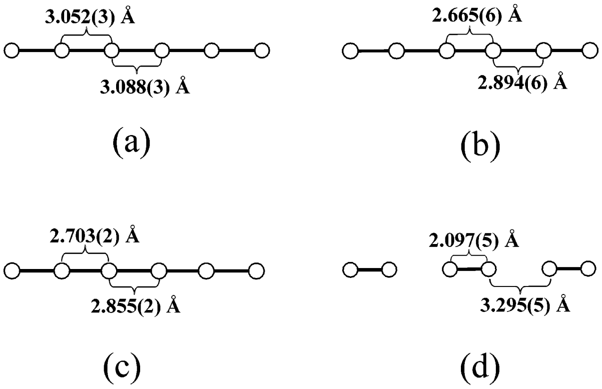

Figure 2. Q−Q chains in (a) $CsTh_2Te_6$, (b) CsU_2Se_6, (c) KU_2Se_6, and (d) $K_{0.91}U_{1.79}S_6$.

Table 3. Selected Distances (Å) for $K_{0.91}U_{1.79}S_6$ and KU_2Se_6

	$K_{0.91}U_{1.79}S_6$	KU_2Se_6
K−Q(2) × 8	3.339(2)	3.3574(6)
U−Q(1) × 2	2.761(2)	2.8884(7)
U−Q(1) × 2	2.8082(8)	2.9648(5)
U−Q(2) × 4	2.846(2)	2.9241(6)
Q(2)−Q(2)	2.097(5)	2.703(2)

Selected distances for $K_{0.91}U_{1.79}S_6$ and KU_2Se_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 2.8884(7) to 2.9648(5) Å for KU_2Se_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 3.3574(6) Å may be compared with those of 3.255(2)−3.530(2) Å for $KCuZrSe_3$.[16]

The structure of KU_2Se_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_2Se_6 established from the refinement of the X-ray data does not distinguish these two

---

(14) Noël, H.; Padiou, J. *Acta Crystallogr. Sect. B: Struct. Sci.* **1976**, *32*, 1593−1595.

(15) Ijjaali, I.; Mitchell, K.; Huang, F. Q.; Ibers, J. A. *J. Solid State Chem.* **2004**, *177*, 257−261.

(16) Mansuetto, M. F.; Keane, P. M.; Ibers, J. A. *J. Solid State Chem.* **1992**, *101*, 257−264.

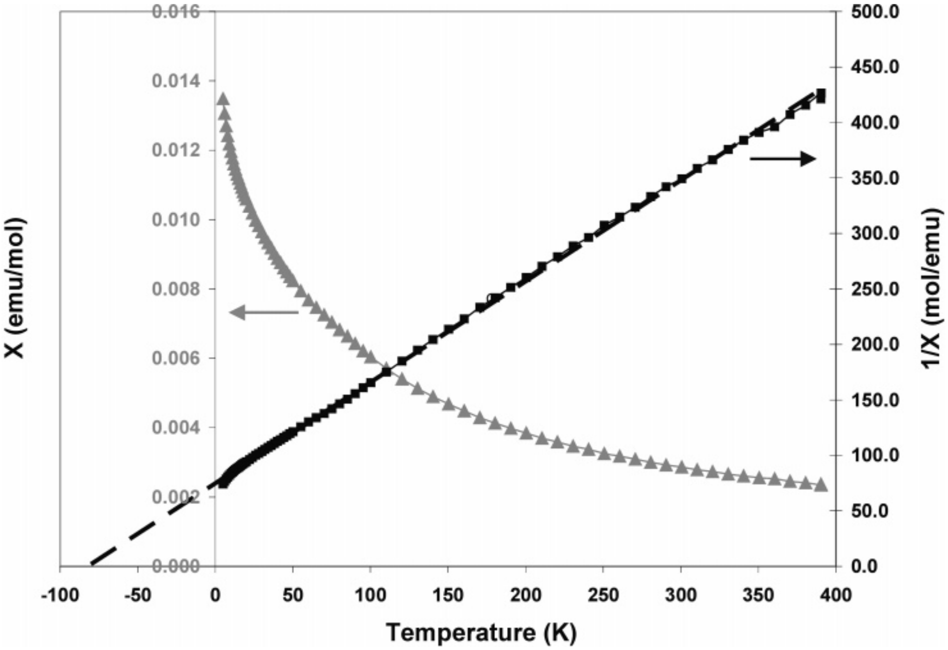

Figure 3. Magnetic susceptibility, χ, and χ^{-1} vs T for KU_2Se_6.

possibilities. The formal oxidation state of U in KU_2Se_6 was determined to be 4+ from XPS measurements,[5] 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 contamination. As opposed to KU_2Se_6, in $K_{0.91}U_{1.79}S_6$, the S−S single bonds are not weakened. Given the composition $K_{0.91(2)}U_{1.79(2)}S_6$, as established from the refinement of the X-ray data, the stoichiometric formulation $KU_2(S)_2(S_2)_2$ as indicated from the structure, and charge balance, the formal oxidation state of U in this compound is 3.96(5)+, hence 4+. From single-crystal diffraction studies, both US_3[17] and USe_3[7] are of the $ZrSe_3$ structure type. If we think of $K_{0.91(2)}U_{1.79(2)}S_6$ as resulting from the insertion of K into the US_3 structure with no change in the U^{4+} oxidation state, then we can envision the series $K_xU_{2-x/4}S_6$, $1 \geq x \geq 0$, as we progress from $KU_{1.75}S_6$ to U_2S_6 (US_3). In this series, the number of metal vacancies is $1 - 0.75x$, so clearly at some point as x decreases the $KU_{1.75}S_6$ structure will collapse. In the present instance of $x = 0.91$, the structure is stable, but undoubtedly other values of x are possible and may depend on reaction conditions.

Magnetic Susceptibility. The magnetic susceptibility, χ, and its inverse, χ^{-1}, as a function of temperature for KU_2Se_6 are shown in Figure 3. The field-cooled and zero-field-cooled data are essentially superimposable. Above 30 K, the Curie−Weiss law, $\chi = C/(T - \theta)$, is obeyed. The Curie constant and the Weiss temperature obtained from parameter fitting are 2.17(1) emu·K/mol and −81.2(6) K, respectively. The effective magnetic moment, μ_{eff}, calculated from the Curie constant is 2.95(1) μ_B/U. The values of μ_{eff} for the free ions U^{3+} ($6d^05f^3$), U^{4+} ($6d^05f^2$), and U^{5+} ($6d^05f^1$) calculated using L−S coupling are 3.62, 3.58, and 2.54 μ_B/U, respectively. The observed value of 2.95(1) μ_B/U in KU_2Se_6 is consistent with values previously observed in solid-state chalcogenides in which U has a formal oxidation state of 4+.[18−20] For example, a value of 2.50 μ_B/U has been reported for the compound $Cu_2U_3S_7$ in which the absence of S−S bonds and the propensity of Cu to be 1+ in chalcogenides implies U^{4+}.[18] Comparable comparisons are lacking for solid-state chalcogenides in which U has a formal oxidation state of 3+.

Magnetic ordering was not observed in KU_2Se_6 until 5 K. The negative Weiss constant implies antiferromagnetic interactions among U ions. The related compound USe_3 ($USe(Se_2)$) exhibits antiferromagnetic-like behavior at 40 K.[21] The U···U distances in KU_2Se_6 are 4.059(6) (*ab* plane) and 7.753(1) Å (interplane), whereas they are 4.06(1) (*ab* plane) and 7.02(1) Å (interplane) in USe_3.[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 KU_2Se_6, USe_3, and US_3. The characteristic peaks from f−f transitions observed for USe_3 and US_3 are also observed for RbU_2SbS_8 and KU_2SbSe_8[23] at nearly the same positions. All four compounds formally contain U^{4+}.[23] 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−

---

(17) Kwak, J.; Gray, D. L.; Yun. H.; Ibers, J. A. *Acta Crystallogr., Sect. E* **2006**, *62*, i86−i87.

(18) Daoudi, A.; Lamire, M.; Levet, J. C.; Noël, H. *J. Solid State Chem.* **1996**, *123*, 331−336.

(19) Tougait, O.; Potel, M.; Padiou, J.; Noël, H. *J. Alloys Compd.* **1997**, *262−263*, 320−324.

(20) Tougait, O.; Potel, M.; Noël, H. *J. Solid State Chem.* **2002**, *168*, 217−223.

(21) Noël, H. *J. Less-Common Met.* **1986**, *121*, 265−270.

(22) Miner, W. N., Ed. *Plutonium 1970 and Other Actinides*; AIME: Santa Fe, 1970; Vol. 17.

(23) Choi, K.-S.; Kanatzidis, M. G. *Chem. Mater.* **1999**, *11*, 2613−2618.

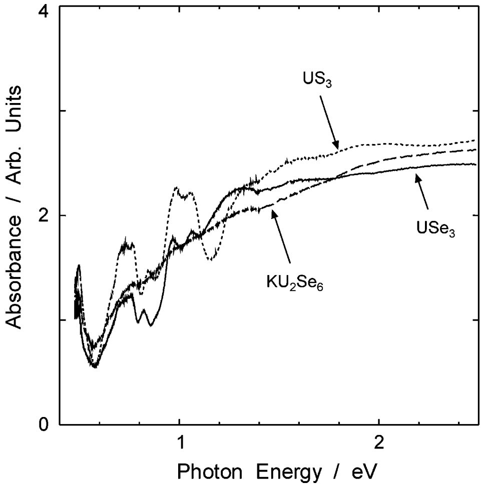

Figure 4. Photon energy vs absorbance for KU_2Se_6, US_3, and USe_3.

5f transitions are much weaker in KU_2Se_6 than in the other compounds.

Electrical Conductivity. The value of the electrical conductivity along the *a* axis of a KU_2Se_6 single crystal is 1 10^{-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⋯Q chains in $K_{0.91}U_{1.79}S_6$ and KU_2Se_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[24] for S_2^{2-} and 209 kJ/mol[24] for Se_2^{2-}. Although no value for Te_2^{2-} appears to be known, it should be less than that for Se_2^{2-}. From the molecular orbital diagram for Q_2^{2-},[25] it is known that near the HOMO−LUMO gap the states are Q np Q np σ, π, π*, and σ*. The π and π* states are doubly degenerate. These four states are modified by Q ns Q ns σ bonding. At the HOMO, the π* states are fully occupied by electrons, indicating the existence of a Q−Q single bond. The LUMO is Q np Q np σ*. Because of their binding energies, the position of the LUMO of S_2^{2-} is higher relative to that of Se_2^{2-}.

We consider solids constructed from such Q_2^{2-} species. The compound USe_3 contains two different Se⋯Se distances, 2.361(5) and 3.294(5) Å. The average Se−Se bond length in α-Se_8 at 299 K is 2.336(7) Å;[26] a typical nonbonding Se⋯Se distance is around 3.3 Å, for example, 3.269(2) Å in Gd_2Se_3.[27] Therefore, for USe_3, the valence description $U^{4+}(Se^{2-})(Se_2^{2-})$ is plausible. The electronic structure around the Fermi energy is dominated by the interaction among the U^{4+} 6d5f, Se 4p π/π* (occupied states), and Se 4p σ* (unoccupied state) for Se_2^{2-}. This black compound is semiconductive.[28]

Next, we consider KU_2Se_6 where the Se−Se bonds are longer than in USe_3 and discrete Se−Se single-bonded pairs are no longer present (Table 2). The Se_2^{2-}species has been reduced, presumably by an electron from the K atom that is inserted into the Se 4p σ* orbital. From charge balance, this compound is represented as $KU^{4+}{}_2(Se^{2-})_2(Se^{1.25-})_4$ with one-fourth of the Se 4p σ* band occupied by the inserted electron. The Se^{1-} chain in USe_3 and the $Se^{1.25-}$ chain in KU_2Se_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^+, U^{4+}) distribution. Thus, we would expect semiconducting behavior in these compounds, consistent with experiment.

Finally, we consider $K_{0.91}U_{1.79}S_6$. The electron responsible for the reduction of the Se−Se single bond in the Se_2^{2-} species in KU_2Se_6 cannot reduce the stronger S−S single bond in the S_2^{2-}species because of the relatively higher position of the S 3p σ* orbital compared to the Se 4p σ* orbital. Electron insertion into the S_2^{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 $K_{0.91}U_{1.79}S_6$. Apparently, the formation of cationic vacancies is also more facile than reduction of the U^{4+} ion.

Acknowledgment. We thank J. Millstone and Dr. C. A. Mirkin for help with the use of their UV/vis spectrophotometer. Funding for this work was kindly provided by the U.S. Department of Energy Grant ER-15522.

Supporting Information Available: Crystallographic data in CIF format for $K_{0.91}U_{1.79}S_6$ and KU_2Se_6. This material is available free of charge via the Internet at http://pubs.acs.org.

IC052140L

---

(24) Klotz, I. M.; Rosenberg, R. M. *Chemical Thermodynamics: Basic Theory and Methods*, 6th ed.; John Wiley and Sons: New York, 2000.

(25) Flomer, J. C. W.; Jellinek, F.; Calis, G. H. M. *J. Solid State Chem.* **1988**, *72*, 137−144.

(26) Maaninen, A.; Konu, J.; Laitinen, R. S.; Chivers, T.; Schatte, G.; Pietikäinen, J.; Ahlgrén, M. *Inorg. Chem.* **2001**, *40*, 3539−3543.

(27) Folchnandt, M.; Schneck, C.; Schleid, T. *Z. Anorg. Allg. Chem.* **2004**, *630*, 149−155.

(28) Shlyk, L.; Troc, R.; Kaczorowski, D. *J. Magn. Magn. Mater.* **1995**, *140−144*, 1435−1436.

(29) Stöwe, K. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1419−1422.

(30) Furuseth, S.; Brattås, L.; Kjekshus, A. *Acta Chem. Scand. Ser. A* **1975**, *29*, 623−631.

(31) Krönert, W.; Plieth, K. *Z. Anorg. Allg. Chem.* **1965**, *336*, 207−218.

(32) Stöwe, K.; Wagner, F. R. *J. Solid State Chem.* **1998**, *138*, 160−168.

(33) Huang, F. Q.; Ibers, J. A. *J. Solid State Chem.* **2001**, *159*, 186−190.