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Synthesis and Characterization of AU_2Se_6 (A = K, Cs)

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Two new ternary uranium selenides, AU_2Se_6 (A = K, Cs), were prepared using the reactive flux method. Single crystal X-ray diffraction was performed on single crystals. The compounds crystallize in the orthorhombic *Immm* space group, $Z = 2$. CsU_2Se_6 has cell parameters of $a = 4.046(2)$ Å, $b = 5.559(3)$ Å, and $c = 24.237(12)$ Å. KU_2Se_6 has cell parameters of $a = 4.058(3)$ Å, $b = 5.556(4)$ Å, and $c = 21.710(17)$ Å. The compounds are isostructural to the previously reported KTh_2Se_6. The two-dimensional layered structure is related to $ZrSe_3$ with the alkali metals residing in the interlayer space. The oxidation states of uranium and selenium were evaluated using X-ray photoelectron spectroscopy (XPS). Uranium was found to be tetravalent, while selenium was found to be in two oxidation states, one of which is –2. The other oxidation state is similar to that found in a polyselenide network. While this structure is known, our work examines how the structure changes through the transactinide series.

Actinide elements in materials have access to multiple oxidation states, which may produce interesting structural or magnetic properties.[1] A series of ternary chalcogenide ternary compounds have been reported, including KTh_2Q_6 (Q = Se, Te), $CsTh_2Se_6$, and $CuTh_2Se_6$.[2] These compounds consist of layers of thorium selenide polyhedra that contain an elongated Q−Q bond, which has also been seen in $RbDy_3Se_8$ and $CsCe_3Te_8$.[3] The formal oxidation state for thorium is most likely tetravalent while the rare earth is most likely trivalent. The oxidation state for the chalcogenide atoms in these phases is difficult to assign, but a model of mixed oxidation state selenium has been proposed.[4] Our group has recently synthesized a plutonium analogue, KPu_3Se_{8-x}, which is isostructural to $RbDy_3Se_8$ but with one partially occupied selenium site.[5] Plutonium apparently prefers a structure where it behaves more like a rare earth element, while thorium prefers a structure more like a transition metal as found in $ZrSe_3$.[6] Our work examines which element in the actinide series changes from transition-metal-like to rare-earth-like. In this Communication, we report the preparation of the uranium analogues of these compounds and elucidate the oxidation states using X-ray photoelectron spectroscopy (XPS).

The salts, A_2Se_2 (A = K, Cs), were prepared from a stoichiometric ratio of the elements in liquid ammonia as described elsewhere.[7] ^{238}U ribbon was obtained from Los Alamos National Laboratory.[8] For KU_2Se_6, K_2Se_2 (0.1885 g, 0.7983 mmol), ^{238}U (0.0423 g, 0.178 mmol), and Se (0.1881 g, 2.382 mmol) were loaded into a fused silica ampule. For CsU_2Se_6, Cs_2Se_2 (0.0824 g, 0.1945 mmol), ^{238}U (0.0228 g, 0.0958 mmol), Si (0.0061 g, 0.2172 mmol), and Se (0.0493 g, 0.6244 mmol) were loaded into a fused silica ampule. The ampules were flame sealed under vacuum (~0.1 mTorr) and placed into a programmable furnace. The reaction was heated to 500 °C at 30 °C/h. After 200 h, the sample was cooled to room temperature at a rate of 3 °C/h. The ampules were opened in air and washed immediately with *N*,*N*-dimethylformamide (DMF) to reveal crystals. Black needlelike plates were isolated for KU_2Se_6. For CsU_2Se_6, washing the product revealed yellow blocks of $Cs_4Si_2Se_8$[9] and red/black plates of CsU_2Se_6. The unit cell for CsU_2Se_6 was also observed with reactions loaded without silicon (0.1540 mg Cs_2Se_2, 0.1512 mg Se, and 0.0742 g U). The silicon originally may have aided the growth of larger crystals.

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(2) (a) Wu, E. J.; Pell, M. A.; Ibers, J. A. *J. Alloys Compd.* **1997**, *255*, 106. (b) Cody, J. A.; Ibers, J. A. *Inorg. Chem.* **1996**, *35*, 3836. (c) Narducci, A. A.; Ibers, J. A. *Inorg. Chem.* **1998**, *37*, 3798.

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(5) Space group *Cmcm*, $a = 4.1257$ Å, $b = 25.4642$ Å, $c = 3.99$ Å. Manuscript in preparation.

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(7) Liao, J.-H.; Kanatzidis, M. G. *Inorg. Chem.* **1992**, *31*, 431−439.

(8) *Warning: ^{238}U is radioactive with a half-live of 4.5×10^9 years. Although its own activity is low, the daughter products of decay can cause samples to become highly radioactive over time (γ).*

(9) Space group *C*2/*m*, a = 15.148(3) Å, $b = 7.5988(14)$ Å, $c = 10.0568(18)$ Å, $\beta = 121.833(2)°$. Manuscript in preparation.

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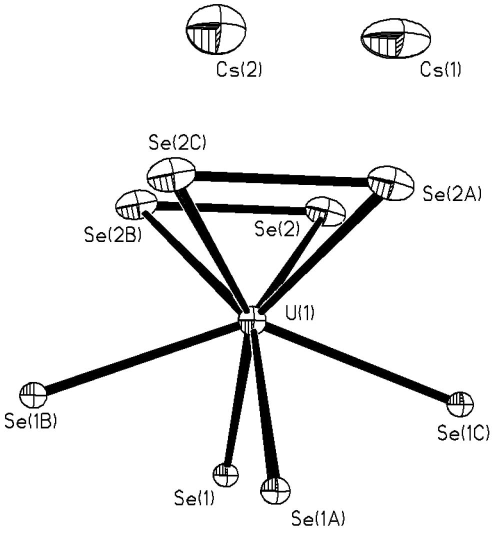

Figure 1. Thermal ellipsoid at 50% of CsU_2Se_6 showing the bicapped trigonal prism.

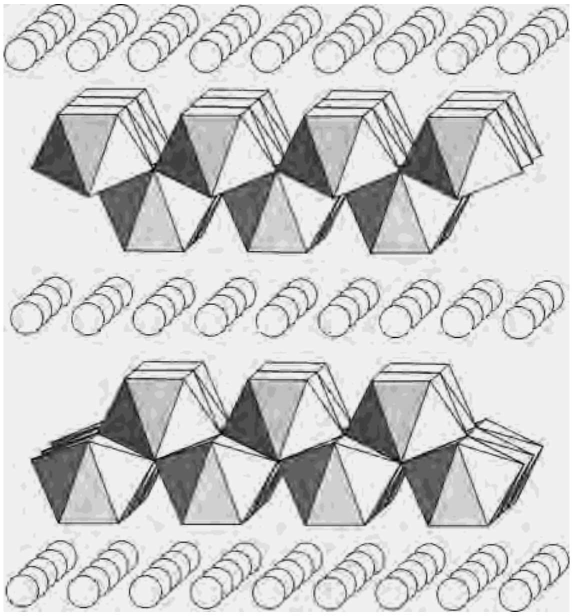

Figure 2. Polyhedral view of CsU_2Se_6 (Cs atoms open circles) showing the zigzag edge shared bicapped trigonal prisms separated by layers of cesium atoms.

A single crystal of CsU_2Se_6 was selected for analysis by X-ray diffraction.[13] Intensity data sets were collected using a Bruker Smart CCD diffractometer. These data were integrated using SAINT,[10] a SADABS correction was applied,[11] and the structures were solved by direct methods using SHELXTL.[12] There were 1489 (262 independent) reflections collected, and an absorption correction was applied. Data were collected within a θ range of 3.36−23.19° to a completeness of 99.2% with a data index range of $-4 \leq h \leq 4$, $-6 \leq k \leq 6$, $-25 \leq l \leq 25$. The structure was solved in *Immm* ($R_{\mathrm{int}} = 0.0910$) by direct methods with final electron density residuals of 4.329 and −2.871 e Å^{-3}, and all atoms were refined anisotropically on F^2 for 22 variables. Selected crystallographic data and atomic positions are reported.[13] A single crystal of KU_2Se_6 was selected for X-ray diffraction, and the unit cell was obtained,[13] but a full structural analysis was not performed. Powder XRD showed the product appeared to be a single phase.[13]

AU_2Se_6 (A = Cs, K) is isostructural to the thorium compounds ATh_2Q_6 (A = K, Cs; Q=Se, Te).[4] The uranium is coordinated by 8 selenium atoms in a bicapped trigonal prism, Figure 1. The U−Se bond distances range from 2.895(3) to 2.9601(19) Å. The uranium selenide layers comprise one-dimensional chains of faced-shared polyhedra, Figure 2, that stack in a zigzag formation through edge sharing of the polyhedra to form layers. The cesium atoms separate the uranium selenide layers and are disordered; Cs(1) is 29.6% occupied while Cs(2) is 70.4% occupied. The compound also contains an elongated selenium bond distance as seen in the thorium analogues. The closest Se−Se distance within the polyhedron is 2.665(6) Å between adjacent Se(2) atoms, Figure 1.

Quality single crystals were difficult to obtain for KU_2Se_6. The unit cell was calculated from a data set of 1800 frames. We concluded that KU_2Se_6 crystallizes in the *Immm* (No. 71) space group and is isostructural to CsU_2Se_6.[13] As expected, the length of the *c*-axis is shorter than the *c*-axis of CsU_2Se_6 due to the smaller radius of potassium.

The $[U_2Se_6]^-$ layers are similar to the $ZrSe_3$[6] and $ThSe_3$[14] structure types. For AU_2Se_6 and the thorium analogues, the alkali metal resides within the interlayer spaces of the compound. For KPu_3Se_{8-x}, the structure is isostructural to $RbDy_3Se_8$.[5] The $[Pu_3Se_{8-x}]^-$ layer is related to $NdTe_2$,[15] $NdTe_3$,[16] and $PuSe_2$[17] structure types, and the alkali metal resides within the interlayer spacing of the $[Pu_3Se_{8-x}]^-$ layers. The uranium and thorium structures are related to a transition metal structure, while the plutonium analogue is related to a rare earth structure, suggesting a more rare-earth-like chemistry for plutonium chalcogenides.

XPS spectra were collected for KU_2Se_6 to elucidate the oxidation states of uranium and selenium. XPS analyses were performed on a Physical Electronics PE5800 ESCA/AES system. Spectra were collected using a hemispherical analyzer, a multichannel detector, and a 7 mm monochromatic Al Kα X-ray source (1486.6 eV). A low energy (~1 eV) electron neutralizer was used for charge neutralization. The sample was attached using conductive carbon tape and then sputtered with an argon plasma for 60 s to remove any oxide

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(10) *SAINT; Data processing software for the SMART system*; Bruker Analytical X-ray Instruments, Inc.; Madison, WI, 1995.

(11) Sheldrick, G. M. *SADABS*; University of Gottingten: Germany, 1997.

(12) *SHELXTL 6.1*; Bruker AXS Inc.: Madison, WI, 2000.

(13) Selected crystallographic data for CsU_2Se_6: space group, *Immm* (No. 71); fw = 1082.73; $a = 4.046(2)$ Å; $b = 5.559(3)$ Å; $c = 24.237(12)$ Å; $Z = 2$; $V = 545.1$ Å^3; $\rho_{\mathrm{calcd}} = 6.596$ g/cm^3; $\lambda = 0.71073$ Å; collection temperature = 298 K; linear abs coeff = 52.919 mm^{-1}; R1 ($I > 2\sigma$) = 0.0500; wR2 ($I > 2\sigma$) = 0.1298. $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. Selected crystallographic data for KU_2Se_6: space group, *Immm* (No. 71); fw = 988.92; $a = 4.058(3)$ Å; $b = 5.556(4)$ Å; $c = 21.710(17)$ Å; $Z = 2$; $V = 489.3$ Å^3; $\rho_{\mathrm{calcd}} = 6.709$ g/cm^3; $\lambda = 0.71073$ Å; collection temperature = 298 K. An indexed powder XRD pattern can be found in the Supporting Information.

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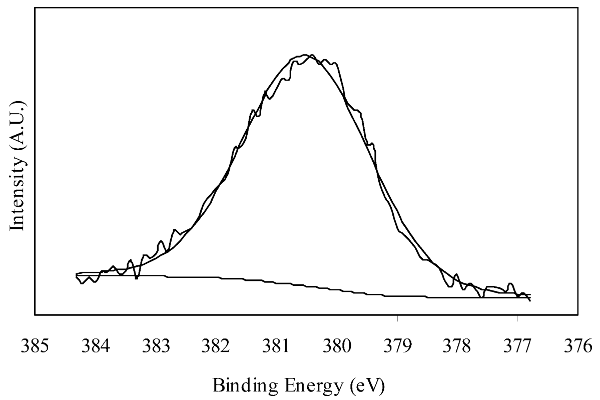

Figure 3. XPS of 4f7/2 peak of U. Solid smooth lines are the fitted peaks.

layer from the crystals. Spectra were normalized to C1s peak,[18] and curves were fitted using Gaussian functions and confirmed the stoichiometry.

The binding energy for the 4f7/2 peak of uranium is at 380.5 eV, Figure 3. This binding energy is close to the $+4$ uranium in UO_2 at 380.6 eV;[19] uranium (VI) (UO_2MoO_4) was reported at 381 eV.[20] We conclude that uranium oxidation states in KU_2Se_6 and CsU_2Se_6, by their isostructural nature, are tetravalent. The 0.1 eV shift of the binding energies between KU_2Se_6 and UO_2 may be due to different local environments and different electron withdrawing properties between oxygen and selenium.

Two distinct oxidation states were observed for the 3d5/2 peak of selenium at 55.3 and 53.4 eV, Figure 4. The peak at 55.3 eV can be correlated to USe, also at 55.3 eV, which contains a polyselenide network of selenium.[21] The oxidation state for the network is difficult to assign. The peak at 53.4 eV is correlated to PbSe, also at 53.4 eV.[22] The oxidation state of selenium can be assigned to -2 and is mostly likely due to the crystallographic Se(1). XPS results demonstrated that two oxidation states existed but cannot distinguish whether the crystallographically unique Se(2) is in a mixed oxidation state as proposed by Kanatzidis.[4] Although the ratio of the crystallographically unique Se(1) and Se(2) indicates that the amounts are empirically the same, the XPS showed higher peak intensity for Se(2) at 55.3 eV. This is due to the surface sensitive nature of XPS. The crystals fracture along the interplanar surfaces leaving the Se(2) layer the most exposed. The peak intensity for Se(1) at 53.4 eV was perhaps lower due the longer path for the electrons. The estimated ratio of the integrated peak areas does not reasonably balance the charge of this compound.

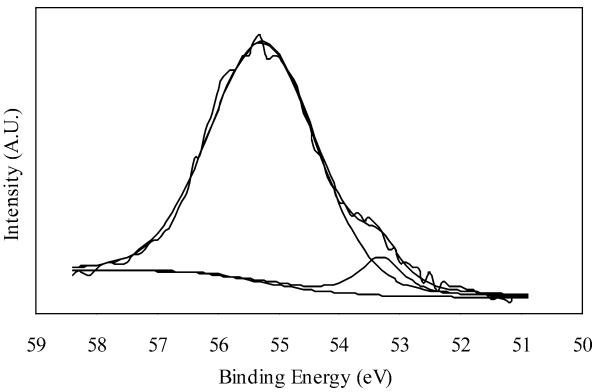

Figure 4. XPS of 3d5/2 peak of Se. Solid smooth lines are the fitted peaks.

In summary, we have prepared two uranium ternaries that are isostructural to KTh_2Q_6. The compounds are structurally related to $ZrSe_3$ with the $[U_2Se_6]^-$ layers separated by Cs^+ ions. Our work demonstrates that uranium, like thorium, behaves more like a transition metal than a rare earth metal. The next logical step is to test whether a neptunium analogue behaves similarly or more like plutonium. By performing XPS, the oxidation state of uranium was determined to be $+4$. Two distinct XPS peaks exist for selenium that confirm a polyselenide layer of selenium and a -2 of selenium. The polyselenide layer may be in a mixed oxidation state, which could manifest as interesting properties. This series of compounds may have interesting magnetic properties, which are currently being studied.

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Supporting Information Available: Additional crystallographic details, tables of atom positions and all bond distances and angles, anisotropic thermal parameters, and powder XRD. This information is free of charge via the Internet at http://pubs.acs.org.

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