

## Dichalcogenide Bonding in Seven Alkali-Metal Actinide Chalcogenides of the $KTh_2Se_6$ Structure Type

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The solid-state compounds  $CsTh_2Se_6$ ,  $Rb_{0.85}U_{1.74}S_6$ ,  $RbU_2Se_6$ ,  $TiU_2Se_6$ ,  $Cs_{0.88}(La_{0.68}U_{1.32})Se_6$ ,  $KNp_2Se_6$ , and  $CsNp_2Se_6$  of the  $AAn_2Q_6$  family ( $A$  = alkali metal or TI;  $An$  = Th, U, Np;  $Q$  = S, Se, Te) have been synthesized by high-temperature techniques. All seven crystallize in space group  $Immm$  of the orthorhombic system in the  $KTh_2Se_6$  structure type. Evidence of long-range order and modulation were found in the X-ray diffraction patterns of  $TiU_2Se_6$  and  $CsNp_2Se_6$ . A  $4a \times 4b$  supercell was found for  $TiU_2Se_6$  whereas a  $5a \times 5b \times 5c$  supercell was found for  $CsNp_2Se_6$ . All seven compounds exhibit Q–Q interactions and, depending on the radius ratio  $R_{An}/R_A$ , disorder of the A cation over two sites. The electrical conductivity of  $RbU_2Se_6$ , measured along  $[100]$ , is  $6 \times 10^{-5} \text{ S cm}^{-1}$  at 298 K. The interatomic distances, including those in the modulated structure of  $TiU_2Se_6$ , and physical properties suggest the compounds may be formulated as containing tetravalent Th or U, but the formal oxidation state of Np in the modulated structure of  $CsNp_2Se_6$  is less certain. The actinide contraction from Th to U to Np is apparent in the interatomic distances.

### Introduction

Binary actinide chalcogenides,  $An_xQ_y$  ( $An$  = Th, U, Np;  $Q$  = S, Se, Te), display a variety of interesting electrical and magnetic properties.<sup>1–5</sup> The insertion of an alkali metal into these compounds allows for the subtle manipulation of the structures, and consequently their physical properties. For this reason, extensive investigations of the ternary  $A/An/Q$  ( $A$  = alkali metal or TI) system have been undertaken. The compounds known for the lighter alkali metals are  $A_2US_3$  ( $A$  = Li, Na),<sup>6</sup> which crystallize in space group  $C2/m$  of the monoclinic system. In these, as well in the isostructural  $A_2UTE_3$  ( $A$  = K, Rb) compounds,<sup>7</sup> there is no Q–Q bonding, so the compounds charge balance with  $U^{4+}$ . The compound  $KUS_2$ ,<sup>8</sup> isostructural

to  $UOS$ ,<sup>9,10</sup> crystallizes in the space group  $P4/nmm$  of the tetragonal system. The lack of S–S bonding as well as magnetic measurements<sup>11</sup> suggest that unlike  $UOS$  it is a compound of  $U^{3+}$ . The remainder of the  $A/An/Q$  compounds crystallize in orthorhombic space groups and feature some degree of Q–Q bonding.  $K_4USe_8$ <sup>12</sup> of the  $Fdd2$  space group is the only example of a molecular actinide species among the  $A/An/Q$  compounds. The U atom sits at the center of a distorted dodecahedron of four  $Se_2^{2-}$  ligands forming the  $[U(Se_2)_4]^{4-}$  complex anion that charge balances with four  $K^+$  cations. Once again, the U is assigned a formal oxidation state of +4. The compound  $CsUTE_6$ ,<sup>13</sup> belonging to the  $Pnma$  space group, has U atoms coordinated in tricapped trigonal-prismatic arrangements of Te atoms. If a Te–Te single-bond distance is arbitrarily taken to be less than 2.99 Å, then anionic chains in the  $[010]$  direction may be formulated as  $^\infty[U_2(Te_3)_3(Te_2)(Te)^{2-}]$ . This also results in a formal oxidation state of +4 for U.

There are few well-characterized Np chalcogenides beyond the  $Np_xQ_y$  binaries. The known compounds include  $NpTQ$

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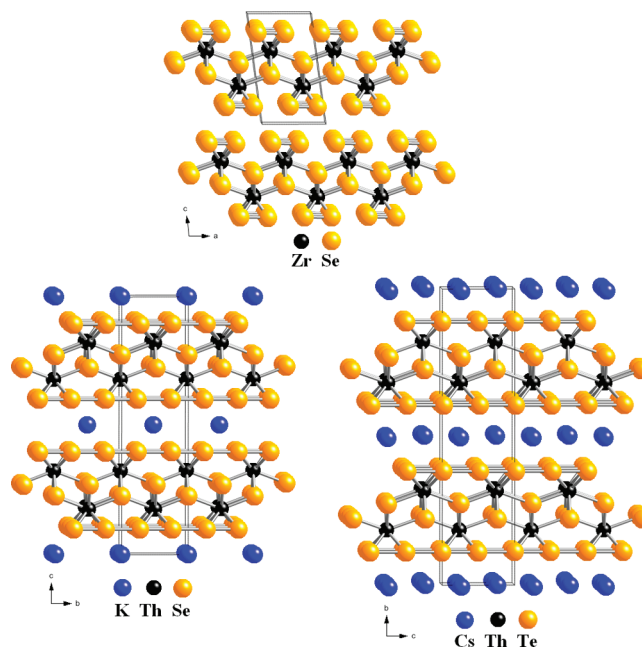
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( $T = O, As, Sb$ ;  $Q = S, Se, Te$ ),<sup>9,14–17</sup> the superconducting Chevrel phase  $Np_{1+x}Mo_6Se_8$ ,<sup>18,19</sup>  $NpCuSe_2$ ,<sup>20</sup> and the  $AMnPs_3$  ( $A = K, Rb, Cs$ ;  $M = Cu, Ag$ ) compounds.<sup>21</sup> On the basis of magnetic measurements the compounds  $NpTQ$  ( $T = As, Sb$ ;  $Q = S, Se, Te$ )<sup>14,16</sup> and  $Np_{1+x}Mo_6Se_8$ <sup>18,19</sup> contain  $Np^{3+}$ , but the compounds  $NpOQ$  ( $Q = S, Se$ ) contain  $Np^{4+}$ .<sup>22,23</sup> Interatomic distances and structural comparisons in  $NpCuSe_2$  indicate that the compound contains  $Np^{3+}$ ,<sup>20</sup> whereas those for the  $AMnPs_3$  compounds<sup>21</sup> indicate  $Np^{4+}$ . Although, insofar as we know, there are no previously characterized ternary  $A/Np/Q$  compounds, the Pu compound  $KPu_3Se_{8-x}$  is known.<sup>24</sup> This compound crystallizes in the  $Cmcm$  space group isostructural to  $RbDy_3Se_8$ <sup>25</sup> and presumably contains  $Pu^{3+}$ .

The most studied members of the  $A/An/Q$  ternary compounds belong to the  $AA_2Q_6$  family. These can be further subdivided into two structure types, namely,  $CsTh_2Te_6$ <sup>26</sup> and  $KTh_2Se_6$ <sup>27</sup> (shown with their parent structure  $ZrSe_3$ <sup>28</sup> in Figure 1). The  $CsTh_2Te_6$  structure type, which includes  $KTh_2Te_6$ <sup>29</sup> and  $Tl_{1.12}U_2Te_6$ ,<sup>30</sup> crystallizes in space group  $Cmcm$  of the orthorhombic system. The  $KTh_2Se_6$  structure type, which includes  $RbTh_2Se_6$ ,<sup>31</sup>  $K_{0.91}U_{1.79}S_6$ ,<sup>32</sup>  $KU_2Se_6$ ,<sup>24</sup> and  $CsU_2Se_6$ ,<sup>24</sup> crystallizes in space group  $Immm$  of the orthorhombic system. Both structure types have  $AnQ_3$  layers intercalated with  $A^+$  cations. The difference between the two is that each successive  $AnQ_3$  layer in the  $Cmcm$  structure type is shifted by  $1/2a$ , whereas each successive  $AnQ_3$  layer in the  $Immm$  structure type is shifted by  $1/2(a + b)$ .<sup>32</sup>

Even though previous UV/vis, Raman,<sup>27</sup> diffuse reflectance,<sup>32</sup> X-ray photoelectron spectroscopic,<sup>24</sup> electrical conductivity,<sup>32</sup> and magnetic measurements<sup>27,30,32</sup> suggest that the compounds in this family contain  $An^{4+}$ , the formula does not charge balance. Evidence of a  $4a \times 4b$  supercell was found from electron diffraction measurements on the  $ATh_2Se_6$  (K and Rb) compounds,<sup>27</sup> but the modulated structure was not solved. A



**Figure 1.** Comparison of the  $KTh_2Se_6$  and  $CsTh_2Te_6$  structure types along with their parent structure,  $ZrSe_3$ .

tentative model proposed is that one in every four  $Se_2^{2-}$  moieties is reduced to two  $Se^{2-}$  anions thus allowing for normal charge balance in the compound as  $(A^+)_2(Th^{4+})_4(Se^{2-})_6(Se_2^{2-})_3$ .<sup>27</sup>

Here we report the syntheses of  $CsTh_2Se_6$ ,  $Rb_{0.85}U_{1.74}S_6$ ,  $RbU_2Se_6$ ,  $TlU_2Se_6$ ,  $Cs_{0.88}(La_{0.68}U_{1.32})Se_6$ ,  $KNp_2Se_6$ , and  $CsNp_2Se_6$ , their average structures, the modulated structures of  $TlU_2Se_6$  and  $CsNp_2Se_6$ , and the electrical conductivity of  $RbU_2Se_6$ .

## Experimental Section

**Syntheses.** The following reagents were used as obtained from the manufacturers: K (Cerac, 98%), Rb (Strem, 99+%), Cs (Aldrich, 99.5%), La (Cerac, 99.9%), S (Mallinckrodt, 99.6%), Se (Cerac, 99.999%),  $Tl_2Se$  (Aldrich, 99.999%),  $CsCl$  (Strem, 99.999%), Sb (Aldrich, 99.5%),  $HgSe$  (Alfa Aesar, 99.9%), and Ag (Aldrich, 99.99+%).  $^{232}Th$  foil was kindly supplied by Prof. M. G. Kanatzidis. Finely divided U powder was prepared from  $^{238}U$  turnings (ORNL) by a modification<sup>33</sup> of the literature procedure.<sup>34</sup> Brittle  $^{237}Np$  chunks (ORNL) were used as provided and crushed. The alkali-metal chalcogenide reactive fluxes<sup>35</sup>  $K_2Se$ ,  $Rb_2S_3$ ,  $Rb_2Se_3$ , and  $Cs_2Se_3$  were prepared by the stoichiometric reactions of the alkali metals with S or Se in liquid  $NH_3$  at 194 K.

Reactions were carried out in carbon-coated fused-silica tubes. The tubes were charged with reaction mixtures under an Ar atmosphere in a glovebox. The tubes were evacuated to  $10^{-4}$  Torr and flame-sealed before being placed in a computer-controlled furnace. Selected single crystals from each reaction were examined by Energy Dispersive X-ray (EDX) analyses on a Hitachi S-3400 SEM. All the compounds are stable in air.

**Synthesis of  $CsTh_2Se_6$ .**  $CsTh_2Se_6$  was synthesized by the reaction of Th (0.14 mmol),  $Cs_2Se_3$  (0.14 mmol), and Se (0.39 mmol) in accordance with the literature procedure.<sup>29</sup>

**Synthesis of  $Rb_{0.85}U_{1.74}S_6$ .** The compound  $Rb_{0.85}U_{1.77}S_6$  was obtained from the reaction of U (0.5 mmol),  $Rb_2S_3$  (0.95 mmol), and S (3.9 mmol). The sample was heated to 973 K in 15 h, kept at 973 K for 120 h, cooled at  $3 K h^{-1}$  to 373 K, and then the

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furnace was turned off. The reaction mixture was washed free of flux with *N,N*-dimethylformamide and then dried with acetone. Black needles of  $\text{Rb}_{0.85}\text{U}_{1.77}\text{S}_6$  were obtained in about 10 wt % yield based on U. EDX analysis of the crystals showed the presence of Rb, U, and S.

**Synthesis of  $\text{RbU}_2\text{Se}_6$ .** The reaction mixture consisted of U (0.17 mmol),  $\text{Rb}_2\text{Se}_3$  (0.17 mmol), Se (1.5 mmol), and Sb (0.17 mmol). The reaction mixture was placed in a furnace where it was heated to 923 K in 25 h, kept at 923 K for 120 h, cooled at  $2\text{ K h}^{-1}$  to 423 K, and then quickly cooled to 298 K. The product was washed free of flux with *N,N*-dimethylformamide and then dried with acetone. It contained long golden black plates of  $\text{RbU}_2\text{Se}_6$  in about 40 wt % yield based on U. EDX analysis of selected crystals showed the presence of Rb, U, and Se, but not of Sb.

**Synthesis of  $\text{TIU}_2\text{Se}_6$ .** The reaction mixture consisted of U (0.17 mmol),  $\text{HgSe}$  (0.25 mmol),  $\text{TI}_2\text{Se}$  (0.13 mmol), and Se (0.25 mmol). The mixture was placed in a furnace where it was heated to 1073 K in 24 h, kept at 1073 K for 7 days, cooled at  $2\text{ K h}^{-1}$  to 479 K, and then the furnace was turned off. The product consisted of golden black plates of  $\text{TIU}_2\text{Se}_6$  in about 20 wt % yield based on U, as well as black prisms of recrystallized  $\text{HgSe}$ . EDX analysis of selected crystals of  $\text{TIU}_2\text{Se}_6$  showed the presence of TI, U, and Se, but not of Hg.

**Synthesis of  $\text{Cs}_{0.88}(\text{La}_{0.68}\text{U}_{1.32})\text{Se}_6$ .** The reaction mixture consisted of U (0.13 mmol), La (0.13 mmol), Se (0.50 mmol), and  $\text{CsCl}$  (1.2 mmol). The mixture was placed in a furnace where it was heated to 1123 K in 17 h, kept at 1123 K for 6 days, cooled at  $3\text{ K h}^{-1}$  to 673 K, and then the furnace was turned off. The product was washed free of salt with deionized water and then dried with acetone. It contained black plates of  $\text{Cs}_{0.88}(\text{La}_{0.68}\text{U}_{1.32})\text{Se}_6$  in about 25 wt % yield based on U. EDX analysis of selected crystals showed the presence of Cs, La, U, and Se, but not of Cl.

**Caution!**<sup>23,27</sup> *Np* and any ingrown daughter products are  $\alpha$ - and  $\gamma$ -emitting radioisotopes and as such are considered a health risk. Their use requires appropriate infrastructure and personnel trained in the handling of radioactive materials. Our procedures used for the syntheses of *Np* compounds have been described elsewhere.<sup>21</sup>

**Synthesis of  $\text{KNp}_2\text{Se}_6$ .** The reaction mixture consisted of *Np* (0.08 mmol),  $\text{K}_2\text{Se}$  (0.03 mmol), and Se (0.24 mmol). It was placed in a furnace where it was heated to 1173 K in 15 h, kept at 1173 K for 96 h, cooled at  $5.75\text{ K h}^{-1}$  to 603 K, and finally cooled at  $3\text{ K h}^{-1}$  to 298 K. The product consisted of small black rectangular plates of  $\text{KNp}_2\text{Se}_6$  in low yield. These were manually extracted from the product mixture.

**Synthesis of  $\text{CsNp}_2\text{Se}_6$ .** The reaction mixture consisted of *Np* (0.09 mmol),  $\text{Cs}_2\text{Se}_3$  (0.10 mmol), Se (0.46 mmol), and Ag (0.04 mmol). It was placed in a furnace where it was heated to 373 K in 4 h, kept at 373 K for 20 h, heated to 873 K in 6 h, kept at 873 K for 96 h, cooled at  $4\text{ K h}^{-1}$  to 573, and then quickly cooled to room temperature. The product contained thick black rectangular plates of  $\text{CsNp}_2\text{Se}_6$  in low yield; these were manually extracted from the product mixture.

**Structure Determinations.** Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) on a Bruker SMART-1000 CCD diffractometer<sup>36</sup> for the two Rb compounds and on a Bruker APEX2 CCD diffractometer<sup>37</sup> for the remaining five compounds. The crystal-to-detector distance was 5.023 cm for the Th and U compounds, and 5.106 cm for the *Np* compounds. Crystal decay was monitored by recollecting 50 additional frames at the end of the data collection. Data were collected by a scan of  $0.3^\circ$  in  $\omega$  in groups of 606 frames at  $\varphi$  settings of  $0^\circ$ ,  $90^\circ$ ,  $180^\circ$ , and  $270^\circ$ . The collection

of intensity data was carried out with the program SMART<sup>36</sup> for the Rb compounds and with the APEX2<sup>37</sup> software for all other compounds. Cell refinement and data reduction were carried out with the use of the program SAINT v7.34a in APEX2.<sup>37</sup> Face-indexed absorption corrections were performed numerically with the use of the program SADABS.<sup>38</sup> Then that program was employed to make incident beam and decay corrections. The structures were solved with the direct-methods program SHELXS and refined with the least-squares program SHELXL.<sup>39</sup> Each final refinement included a secondary extinction correction. The program STRUCTURE TIDY<sup>40</sup> was used to standardize the positional parameters. Reciprocal lattice plots of data were investigated with the program RLATT,<sup>37</sup> and all modulated data were refined with the program JANA2006.<sup>41</sup>

With the use of reflections consistent with space group *Immm* the structures were solved in a routine fashion, taking into consideration nonstoichiometry, cation disorder, or both as required. The site occupancies for Rb and U in  $\text{Rb}_{0.85}\text{U}_{1.74}\text{S}_6$  were refined in the same manner as described previously for  $\text{K}_{0.91}\text{U}_{1.79}\text{S}_6$ .<sup>32</sup> Additionally, for  $\text{RbU}_2\text{Se}_6$  and the Cs compounds, the A cation was disordered over two sites, A(1) and A(2), as found for the Cs cation in the isostructural compound  $\text{CsU}_2\text{Se}_6$ .<sup>24</sup> Independent refinements of these occupancies confirmed full occupancy. Consequently, in the final refinements the site occupancies were constrained to  $\alpha$  for A(2) and  $1 - \alpha$  for A(1). The refined values of  $\alpha$  were found to be 0.135(7), 0.201(6), and 0.268(8) for  $\text{RbU}_2\text{Se}_6$ ,  $\text{CsTh}_2\text{Se}_6$ , and  $\text{CsNp}_2\text{Se}_6$ , respectively. The Cs was also disordered over two sites in  $\text{Cs}_{0.88}(\text{La}_{0.68}\text{U}_{1.32})\text{Se}_6$ . In addition, the La/U ratio was not known, as both La and U occupy the same crystallographic site. As a result that ratio along with independent site occupancies of Cs(1) and Cs(2) were refined. The occupancies of Cs(1) and Cs(2) refined to 0.703(9) and 0.176(8), respectively. Although the refinement of site occupancies from X-ray diffraction data to determine composition is often unreliable and is not a recommended procedure,<sup>42</sup> in this instance the result of  $\text{Cs}_{0.88(2)}\text{La}_{0.68(4)}\text{U}_{1.32(4)}\text{Se}_6$  makes chemical sense, corresponding as it does to an oxidation state of +3.9(1) for U if we assume an oxidation state of +3 for La.

Additional experimental details for conventional structure solutions are given in Table 1 and in the Supporting Information. Selected metrical details are presented in Table 2.

During the refinements of  $\text{TIU}_2\text{Se}_6$  and  $\text{CsNp}_2\text{Se}_6$  it became evident that a number of relatively weak observed reflections did not conform to space group *Immm*. Further examination of reciprocal lattice plots of these data revealed both the strong Bragg reflections used in the conventional refinement and weaker satellite reflections. Those satellite reflections occur at approximately  $0.25a$  and  $0.25b$  for  $\text{TIU}_2\text{Se}_6$  and  $0.4a$  and  $0.2b$  for  $\text{CsNp}_2\text{Se}_6$ . The modulated reflection data were integrated using initial  $\mathbf{q}$ -vectors of  $\mathbf{q} = 0.25\mathbf{a}^* + 0.25\mathbf{b}^*$  for  $\text{TIU}_2\text{Se}_6$  and  $\mathbf{q} = 0.4\mathbf{a}^* + 0.2\mathbf{b}^*$  for  $\text{CsNp}_2\text{Se}_6$ . No satellite reflections were observed in the diffraction patterns of the other five compounds. It may be that evidence of such satellite reflections could be found at lower temperatures.

The data for  $\text{TIU}_2\text{Se}_6$  were refined to a monoclinic unit cell  $a = 4.0391(5)$ ,  $b = 5.551(7)$ ,  $c = 21.655(3)$ ,  $\beta = 90.022(2)$ ,  $\mathbf{q} = 0.2433(2)\mathbf{a}^* + 1/4\mathbf{b}^*$  in the super space group  $P2_1/m(\alpha\beta)00$  to an overall  $R$  index of 0.096 ( $R_w = 0.229$ ) with 1221 main reflections (667 observed), 2402 first-order satellite reflections (258 observed), and 1720 second-order reflections (16 observed). During final refinement the modulation was constrained to a commensurate  $4a \times 4b \times c$  supercell ( $\mathbf{q} = 1/4\mathbf{a}^* + 1/4\mathbf{b}^*$ ) resulting in an overall  $R$  index of 0.096 ( $R_w = 0.218$ ) for 198 parameters and 5343 observed reflections.

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**Table 1.** Crystal Data and Conventional Structure Refinements for  $\text{AAn}_2\text{Q}_6$  Compounds<sup>a</sup>

	$\text{CsTh}_2\text{Se}_6$	$\text{Rb}_{0.85}\text{U}_{1.74}\text{S}_6$	$\text{RbU}_2\text{Se}_6$	$\text{TlU}_2\text{Se}_6$	$\text{Cs}_{0.88}(\text{La}_{0.68}\text{U}_{1.32})\text{Se}_6$	$\text{KNp}_2\text{Se}_6$	$\text{CsNp}_2\text{Se}_6$
fw	1070.75	686.32	1035.29	1154.19	999.38	986.86	1080.67
<i>a</i> (Å)	4.1777(4)	4.034(4)	4.066(3)	4.0387(5)	4.1540(5)	4.0377(7)	4.011(1)
<i>b</i> (Å)	5.6221(5)	5.427(5)	5.552(5)	5.5524(7)	5.6575(7)	5.525(1)	5.519(1)
<i>c</i> (Å)	24.015(2)	21.21(2)	22.44(2)	21.646(3)	23.721(3)	21.558(4)	24.060(6)
<i>V</i> (Å <sup>3</sup> )	564.05(9)	464.2(7)	506.6(7)	485.4(1)	557.5(1)	480.9(2)	532.5(2)
<i>T</i> (K)	100(2)	153(2)	153(2)	100(2)	100(2)	296(2)	100(2)
$\rho_c$ (g cm <sup>-3</sup> )	6.305	4.910	6.786	7.897	5.954	6.815	6.739
$\mu$ (mm <sup>-1</sup> )	48.804	36.536	58.172	72.252	44.07	44.544	43.205
<i>R</i> ( <i>F</i> ) <sup>b</sup>	0.029	0.026	0.029	0.034	0.042	0.029	0.044
<i>R</i> <sub>w</sub> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) <sup>c</sup>	0.065	0.060	0.081	0.109	0.103	0.063	0.104
<i>q</i> <sup>c</sup>	0.0361	0.03	0.04	0.04	0.03	0.0197	0.0299

<sup>a</sup> For all structures, *Z* = 2, space group is *Immm*, and  $\lambda = 0.71073 \text{ \AA}$ . <sup>b</sup>  $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$  for  $F_o^2 > 2\sigma(F_o^2)$ . <sup>c</sup>  $R_w(F_o^2) = \{ \sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4 \}^{1/2}$ . For  $F_o^2 < 0$ ,  $w^{-1} = \sigma^2(F_o^2)$ ; for  $F_o^2 \geq 0$ ,  $w^{-1} = \sigma^2(F_o^2) + (qF_o^2)^2$ .

**Table 2.** Selected Interatomic Distances (Å) for  $\text{AAn}_2\text{Q}_6$  Compounds<sup>a</sup>

	$\text{CsTh}_2\text{Se}_6$	$\text{Rb}_{0.85}\text{U}_{1.74}\text{S}_6$	$\text{RbU}_2\text{Se}_6$	$\text{TlU}_2\text{Se}_6$	$\text{Cs}_{0.88}(\text{La}_{0.68}\text{U}_{1.32})\text{Se}_6$	$\text{KNp}_2\text{Se}_6$	$\text{CsNp}_2\text{Se}_6$
A(1)–Q(2) × 8	3.767(1)	3.446(3)	3.490(2)	3.343(1)	3.780(1)	3.3478(7)	3.781(1)
A(2)–Q(2) × 8	3.725(1)		3.459(2)		3.624(1)		3.739(1)
An–Q(1) × 2	2.959(1)	2.775(3)	2.891(2)	2.884(1)	2.908(1)	2.8673(9)	2.869(2)
An–Q(1) × 2	3.0061(7)	2.823(2)	2.961(2)	2.9570(7)	2.9645(7)	2.9443(6)	2.9367(9)
An–Q(2) × 4	2.985(1)	2.847(2)	2.927(2)	2.922(1)	2.978(1)	2.9048(7)	2.898(1)
Q(2)···Q(2)	2.698(3)	2.106(5)	2.698(3)	2.704(3)	2.422(3)	2.681(2)	2.647(3)
	2.924(3)	3.321(4)	2.854(3)	2.849(2)	3.236(2)	2.844(2)	2.872(3)

<sup>a</sup> The An and Q(1) atoms have crystallographic symmetry *mm*2, the Q(2) atom has crystallographic symmetry *m*..., and the A(1) and A(2) atoms have crystallographic symmetry *mmm*.

All refinements became unstable upon removal of the isotropic displacement parameter constraints. The weakness of the satellite reflections seriously degraded the refinements. Attempts to collect a more intense data set with the use of Cu radiation proved impossible because no suitable crystals could be found.

The modulated data for  $\text{CsNp}_2\text{Se}_6$  were refined to an orthorhombic unit cell  $a = 4.0098(9) \text{ \AA}$ ,  $b = 5.519(1) \text{ \AA}$ ,  $c = 24.064(5) \text{ \AA}$ ,  $\mathbf{q} = 0.396(3) \mathbf{a}^* + 0.1980(5) \mathbf{b}^* - 0.034(2) \mathbf{c}^*$ . When the orthorhombic cell was transformed to the reduced triclinic cell the refinement improved and the triclinic unit cell  $a = 4.0146(9) \text{ \AA}$ ,  $b = 5.525(1) \text{ \AA}$ ,  $c = 12.520(3) \text{ \AA}$ ,  $\alpha = 102.785(3)^\circ$ ,  $\beta = 99.228(3)^\circ$ ,  $\gamma = 89.977(3)^\circ$ ,  $\mathbf{q} = 0.3958(2) \mathbf{a}^* + 0.1966(3) \mathbf{b}^* + 0.2088(6) \mathbf{c}^*$  resulted. The incommensurate structure was solved in the triclinic superspace group  $P1(\alpha\beta\gamma)0$  to an *R* index of 0.053 from 3565 main reflections (2865 observed) and 7240 first-order satellite reflections (982 observed) with all displacement parameters of like atoms constrained to be equivalent. In the final refinement the data were constrained to a commensurate  $5a \times 5b \times 5c$  supercell with  $\mathbf{q} = 0.4\mathbf{a}^* + 0.2\mathbf{b}^* + 0.2\mathbf{c}^*$ , constraints on the displacement parameters were removed, the instability factor was increased to 0.055, and the Cs(2) occupancy factor was varied. This led to an overall *R* index of 0.0491 for 274 parameters and 3847 observed reflections. Even though refinement of the modulated structure improved with constraint of the *q*-vector indices to rational fractions, the temperature dependence of the *q*-vector was not investigated. This would be necessary to establish the true nature of the modulation.

Additional experimental details are given in Table 3 and in the Supporting Information. Selected metrical details are presented in Table 4.

**Electrical Conductivity Measurement.** The electrical resistivity of a single crystal of  $\text{RbU}_2\text{Se}_6$  was measured along [100] between 235 and 325 K utilizing a Fluke 73 Series II multimeter while the sample was submerged inside a Quantum Design PPMS instrument where the sample temperature was controlled. The crystal, approximately 2 mm in length, was mounted with two leads constructed of 15  $\mu\text{m}$  diameter Cu wire and 8  $\mu\text{m}$  diameter graphite fibers, and attached with Dow 4929N silver paint. Below 235 K the total resistance of the sample was beyond the limit (32 M $\Omega$ ) of the multimeter.

**Table 3.** Crystal Data and Modulated Structure Refinements for  $\text{TlU}_2\text{Se}_6$  and  $\text{CsNp}_2\text{Se}_6$ <sup>a</sup>

	$\text{TlU}_2\text{Se}_6$	$\text{CsNp}_2\text{Se}_6$
superspace group	$P2/m(\alpha\beta)00$	$P1(\alpha\beta\gamma)0$
fw	1154.2	1080.8
<i>a</i> (Å)	4.0391(5)	4.0146(9)
<i>b</i> (Å)	5.5510(7)	5.525(1)
<i>c</i> (Å)	21.654(3)	12.520(3)
$\alpha$ (deg)	90	102.785(3)
$\beta$ (deg)	90	99.228(3)
$\gamma$ (deg)	90.022(2)	89.977(3)
<i>q</i> -vector	$1/4\mathbf{a}^* + 1/4\mathbf{b}^*$	$2/5\mathbf{a}^* + 1/5\mathbf{b}^* + 1/5\mathbf{c}^*$
<i>V</i> (Å <sup>3</sup> )	485.5(1)	267.1(1)
<i>Z</i>	2	1
$\rho_c$ (g cm <sup>-3</sup> )	7.8925	6.717
$\mu$ (mm <sup>-1</sup> )	72.202	43.07
overall <i>R</i> ( <i>F</i> ) <sup>b</sup> / <i>R</i> <sub>w</sub> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) <sup>c</sup>	0.096/0.218	0.049/0.130
main reflections <i>R</i> ( <i>F</i> )/ <i>R</i> <sub>w</sub> ( <i>F</i> <sub>o</sub> <sup>2</sup> )	0.091/0.214	0.044/0.118
1st order reflections <i>R</i> ( <i>F</i> )/ <i>R</i> <sub>w</sub> ( <i>F</i> <sub>o</sub> <sup>2</sup> )	0.119/0.303	0.097/0.197
<i>S</i> (obs)/ <i>S</i> (all)	6.25/2.49	0.96/0.83
number of refined parameters	198	274
constraints	18	5

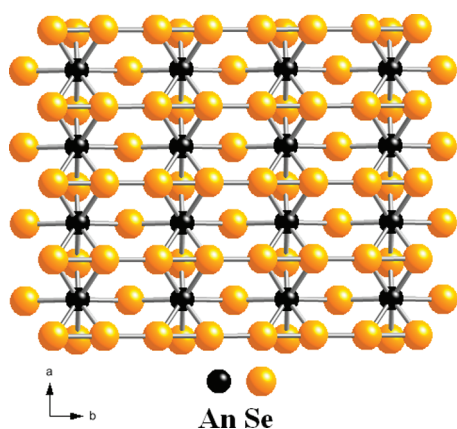
<sup>a</sup> For both structures, *T* = 100(2) K and  $\lambda = 0.71073 \text{ \AA}$ . <sup>b</sup>  $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$  for  $F_o^2 > 3\sigma(F_o^2)$ . <sup>c</sup>  $R_w(F_o^2) = \{ \sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4 \}^{1/2}$ .  $w^{-1} = \sigma^2(F_o^2) + qF_o^2$ ; *q* = 0.012 for Cs and 0.0004 for Tl.

## Results and Discussion

**Syntheses.**  $\text{CsTh}_2\text{Se}_6$ ,  $\text{Rb}_{0.85}\text{U}_{1.74}\text{S}_6$ , and  $\text{KNp}_2\text{Se}_6$  were prepared by the reactive flux method.<sup>35</sup>  $\text{RbU}_2\text{Se}_6$  was synthesized inadvertently while attempting to obtain a quaternary compound in the Rb/U/Sb/Se system. Its synthesis proceeded from the reaction of U, Sb,  $\text{Rb}_2\text{Se}_3$ , and Se at 923 K with a 40 wt % yield. Attempts to produce  $\text{RbU}_2\text{Se}_6$  rationally without Sb present were unsuccessful. It is possible that Sb reacted to form  $\text{RbSb}_x\text{Se}_y$ , in situ, to promote crystal growth, as was observed in the synthesis of  $\text{RbTh}_2\text{Se}_6$ .<sup>27</sup>  $\text{TlU}_2\text{Se}_6$  was prepared in 20 wt % yield as the unintentional

**Table 4.** Selected Interatomic Distances (Å) from the Modulated Structures of  $\text{ThU}_2\text{Se}_6$  and  $\text{CsNp}_2\text{Se}_6$ 

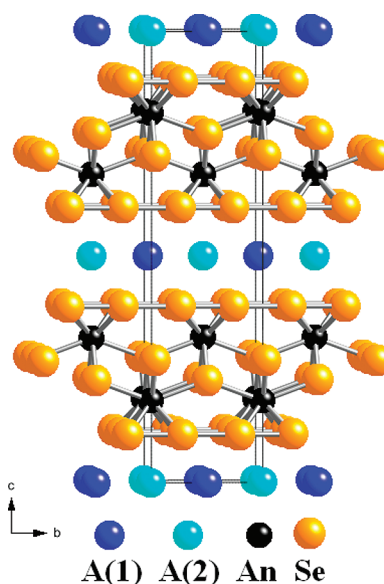
	$\text{ThU}_2\text{Se}_6$			$\text{CsNp}_2\text{Se}_6$		
	average	minimum	maximum	average	minimum	maximum
A(1)–Q(2)	3.34	3.21	3.45	3.79	3.57	4.02
A(2)–Q(2)	3.34	3.22	3.47	3.69	3.52	3.80
An–Q(1)	2.93	2.84	3.08	2.91	2.85	2.96
An–Q(2)	2.93	2.89	2.97	2.90	2.86	2.95
Q(2)–Q(2)	2.78	2.50	3.01	2.76	2.46	3.10

**Figure 2.** One-half of the  ${}^2_2[\text{An}_2\text{Se}_6]^-$  layer in the  $\text{AAn}_2\text{Se}_6$  structure, as viewed down [001].

product from the reaction of U, HgSe,  $\text{Th}_2\text{Se}_6$ , and Se at 1073 K. Attempts to produce  $\text{ThU}_2\text{Se}_6$  rationally without HgSe were unsuccessful.  $\text{Cs}_{0.88}\text{La}_{0.68}\text{U}_{1.32}\text{Se}_6$  was prepared from the reaction of U, La, Se, and CsCl at 1123 K. Interestingly, it is the first compound of the  $\text{KTh}_2\text{Se}_6$  structure type<sup>27</sup> to be synthesized with an excess of an alkali-metal halide salt rather than with an alkali-metal polychalcogenide reactive flux.  $\text{CsNp}_2\text{Se}_6$  was synthesized inadvertently while trying to obtain the Se analogue of  $\text{CsAgNpS}_3$ .<sup>21</sup> Owing to the scarcity of Np metal, a rational synthesis of the compound was not attempted.

**Structures.** The average structures of all seven compounds belong to the  $\text{KTh}_2\text{Se}_6$  structure type<sup>27</sup> in space group *Immm* of the orthorhombic system. These structures can be visualized by insertion of A atoms into the corresponding  $\text{AnQ}_3$  structure (Figure 1). ( $\text{Cs}_{0.88}\text{La}_{0.68}\text{U}_{1.32}\text{Se}_6$  is analogous to the previously reported  $\text{CsU}_2\text{Se}_6$ ,<sup>24</sup> with both La and U disordered over the same site.) In all the compounds, each An atom is coordinated by eight Q atoms in a distorted bicapped trigonal-prismatic geometry. The  $\text{AnQ}_8$  trigonal prisms share faces in the [100] direction and edges in the [010] direction, resulting in  ${}^2_2[\text{An}_2\text{Q}_6]^-$  layers (Figure 2). The  $\text{A}^+$  cations are intercalated between layers in either one or both of the two square-prismatic sites (Figure 3). Part of the coordination at these sites involves either four short or four long Q–Q interactions.

The An ionic radii decrease from Th to Np. The reduction in an An coordination sphere decreases the An–Se interatomic distances and consequently the Se–Se interactions. These reductions accordingly cause the  ${}^2_2[\text{An}_2\text{Se}_6]^-$  layer to contract. This contraction determines whether the A cation can occupy only one square-prismatic site or disorder over both of the square-prismatic sites. The occurrence of disorder depends on the radius ratio between the eight-coordinate actinide ( $R_{\text{An}}$ ) and the alkali-metal ( $R_{\text{A}}$ ) ions. A similar trend of the cation radius ratio determines whether members of the

**Figure 3.** Crystal structure of an  $\text{AAn}_2\text{Se}_6$  compound showing the disorder over the A(1) and A(2) sites. View is down [100].**Table 5.** Radius Ratio versus A Site Occupancy in the  $\text{AAn}_2\text{Se}_6$  Compounds

compound	$R_{\text{An}}$	$R_{\text{A}}$	$R_{\text{An}}/R_{\text{A}}$	ordered	A(2)	reference
					occupancy	
$\text{Rb}_{0.86}\text{Zr}_2\text{Se}_6$	0.84	1.61	0.52	N	0.36	44
$\text{K}_{1.10}\text{Zr}_2\text{Se}_6$	0.84	1.51	0.56	N	0.46	44
$\text{CsNp}_2\text{Se}_6$	0.98	1.74	0.56	N	0.268(8)	this work
$\text{CsU}_2\text{Se}_6$	1.00	1.74	0.57	N	0.30	24
$\text{CsTh}_2\text{Se}_6$	1.05	1.74	0.60	N	0.201(6)	this work
$\text{Cs}_{0.88}(\text{La}_{0.68}\text{U}_{1.32})\text{Se}_6$	1.05	1.74	0.60	N	0.176(8)	this work
$\text{RbU}_2\text{Se}_6$	1.00	1.61	0.62	N	0.135(7)	this work
$\text{ThU}_2\text{Se}_6$	1.00	1.59	0.63	Y		this work
$\text{KNp}_2\text{Se}_6$	0.98	1.51	0.65	Y		this work
$\text{RbTh}_2\text{Se}_6$	1.05	1.61	0.65	Y		27
$\text{KU}_2\text{Se}_6$	1.00	1.51	0.66	Y		24
$\text{KTh}_2\text{Se}_6$	1.05	1.51	0.70	Y		27

$\text{ALnS}_2$  ( $\text{Ln} = \text{La}–\text{Lu}$ ) family of compounds adopt the  $\text{NaCl}$  or the  $\alpha\text{-NaFeO}_2$  structure type.<sup>43</sup> As shown in Table 5, which also includes the only nonactinide members of the  $\text{KTh}_2\text{Se}_6$  structure type ( $\text{K}_{1.10}\text{Zr}_2\text{Se}_6$  and  $\text{Rb}_{0.86}\text{Zr}_2\text{Se}_6$ ),<sup>44</sup> compounds with smaller values of  $R_{\text{An}}/R_{\text{A}}$  exhibit disorder. The present compounds,  $\text{RbU}_2\text{Se}_6$  and  $\text{ThU}_2\text{Se}_6$ , are at the borderline between ordered and disordered structures. Note that the disorder is only found in the Se compounds and neither  $\text{K}_{0.91}\text{U}_{1.79}\text{S}_6$ <sup>32</sup> nor  $\text{Rb}_{0.85}\text{U}_{1.75}\text{S}_6$  exhibits disorder of the A cation.

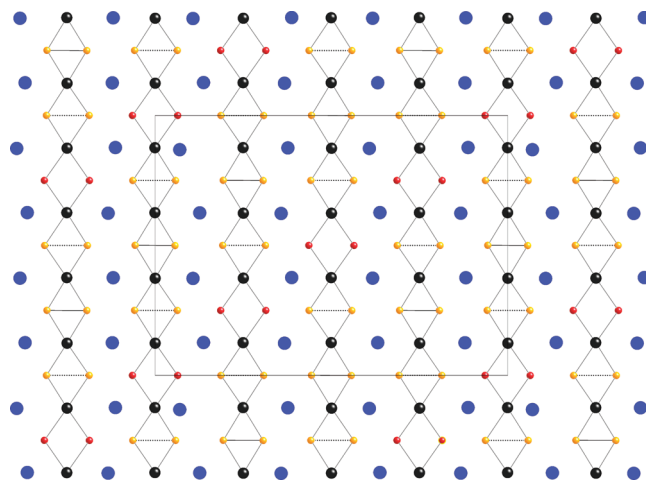
(43) Bronger, W. In *Crystallography and Crystal Chemistry of Materials with Layered Structures*; Lévy, F., Ed.; D. Reidel Publishing Company: Dordrecht-Holland, 1976; pp 93–125.

(44) Klepp, K. O.; Harringer, N. A.; Kolb, A. *Z. Naturforsch. B: Chem. Sci.* **2002**, *57*, 1265–1269.

All general cation–anion interatomic distances are normal. Thus: U–S, 2.775(3)–2.847(2) Å vs 2.645(2)–3.099(3) Å in  $\text{Cu}_2\text{U}_3\text{S}_7$ ;<sup>45</sup> Th–Se, 2.959(1)–3.0061(7) Å vs 2.9309(7)–3.1611(7) Å in  $\text{MnThSe}_3$ ;<sup>46</sup> U–Se, 2.884(1)–2.961(2) Å vs 2.850(2)–3.126(3) Å in  $\text{MnUSe}_3$ ;<sup>46</sup> Rb–S, 3.446(3) Å vs 3.312(1)–3.483(1) Å in  $\text{RbInS}_2$ ;<sup>47</sup> K–Se, 3.3478(7) Å vs 3.190(7)–3.694(8) Å in  $\text{K}_4\text{USe}_8$ ;<sup>12</sup> Rb–Se, 3.459(2) and 3.490(2) Å vs 3.402(1)–3.600(2) Å in  $\text{RbInSe}_2$ ;<sup>47</sup> Tl–Se, 3.343(1) Å vs 3.344(4)–3.403(4) Å in  $\text{TlV}_5\text{Se}_8$ ;<sup>48</sup> and Cs–Se, 3.624(1)–3.781(1) Å vs 3.586(2)–3.825(1) Å in  $\text{CsCuUSe}_3$ .<sup>49</sup> The U(La)–Se distances of 2.908(1)–2.978(1) Å in  $\text{Cs}_{0.88}\text{(La}_{0.68}\text{U}_{1.32})\text{Se}_6$  may also be compared to those of 3.0295(6) Å in  $\text{RbLaSe}_2$ .<sup>50</sup> Because of the disorder on the (La,U) site in  $\text{Cs}_{0.88}\text{La}_{0.68}\text{U}_{1.32}\text{Se}_6$ , the (La,U)–Se average interatomic distances are longer than a typical U–Se interatomic distance, but shorter than a typical La–Se interatomic distance. The Np–Se interatomic distances for  $\text{KNp}_2\text{Se}_6$  and  $\text{CsNp}_2\text{Se}_6$ , which are in the range of 2.8673(9) to 2.9443(6) Å, are shorter than those found for  $\text{Np}^{3+}$  in  $\text{NpCuSe}_2$  (2.9330(6) to 3.1419(6) Å).<sup>20</sup> Even though Nd (the 4f analogue of Np) does not form an isostructural compound, the Np–Se bonds here are much shorter than those found for 8-coordinate Nd in  $\text{CsNd}_5\text{Se}_8$  (2.994(1) to 3.1616(5) Å)<sup>51</sup> or 6-coordinate Nd in  $\text{RbNdSe}_2$  (2.9591(6) to 3.4320(8) Å).<sup>50</sup> The  $\text{Np}^{3+}$ –Se distance in  $\text{NpCuSe}_2$ <sup>20</sup> differs from that in  $\text{NdCuSe}_2$ <sup>52</sup> by less than 0.021 Å. Clearly, the Np–Se distances in the present compounds are consistent with Np in the formal oxidation state +4, rather than +3.

The Q–Q interactions are of the utmost importance in understanding the  $\text{KTh}_2\text{Se}_6$  structure type. Q(1) atoms are bonded only to the An atoms in the layers, but Q(2) atoms form infinite chains with alternating short and long Q–Q interactions. In  $\text{Rb}_{0.85}\text{U}_{1.75}\text{Se}_6$ , the short and long S–S interactions are 2.106(5) and 3.321(4) Å, respectively. The short interaction is indicative of an S–S single bond, whereas the long interaction is a non-bonding distance. Similarly, for  $\text{Cs}_{0.88}\text{La}_{0.68}\text{U}_{1.32}\text{Se}_6$ , the Se–Se interactions are 2.422(3) and 3.236(2) Å, a Se–Se single bond and a non-bonding distance, respectively. This may be contrasted with the similarly determined Se–Se interactions in the other five compounds where both the short and the long Se–Se interactions are significantly longer than Se–Se single bonds such as those observed in  $\text{K}_4\text{USe}_8$  (2.385(4) and 2.401(4) Å).<sup>12</sup>

**Modulated Structures.** The data collected for  $\text{TlU}_2\text{Se}_6$  display a two-dimensional  $4a \times 4b$  supercell like that found previously in  $\text{KTh}_2\text{Se}_6$  and  $\text{RbTh}_2\text{Se}_6$ .<sup>27</sup> The Se–Se interatomic distances found here suggest the presence of  $\text{Se}_2^{2-}$  and  $\text{Se}^{2-}$  moieties and a range of Se–Se bond lengths from 2.50 to 3.01 Å. Even though a Se–Se bond length of 2.50 Å is long for a single bond, it is only



**Figure 4.**  $4a \times 4b$  Tl/U/Se layer from the supercell of  $\text{TlU}_2\text{Se}_6$ , as viewed down [001]. Red Se atoms are discrete  $\text{Se}_2^{2-}$  anions; orange Se atoms participate in Se–Se bonding. For Se–Se bonds: solid  $\leq 2.5$  Å, 2.5 < dashed  $\leq 2.6$  Å, and 2.6 < dotted  $\leq 2.7$  Å.

0.08 Å longer than those found in  $\text{Cs}_{0.88}\text{La}_{0.68}\text{U}_{1.32}\text{Se}_6$ . As with any structure solution, bond distance comparisons like those detailed above can allow for the formulation of an oxidation state model. Figure 4 displays a view down the [001] axis of the diselenide chains with neighboring Tl and U layers. A number of Se–Se interactions arbitrarily distinguished by their length are shown. The pattern of Se interactions seems to fit well with the suggested breaking of one out of four Se–Se bonds. The interatomic distances would likely change with a better refinement but the pattern of electron density should be maintained. As previously described,<sup>27</sup> this one-out-of-four model allows for an oxidation state description in this compound as  $(\text{Tl}^+)_2(\text{U}^{4+})_4(\text{Se}_2^{2-})_4(\text{Se}^{2-})_6(\text{Se}_2^{2-})_3$  if Se–Se interatomic distances longer than 2.7 Å are considered  $\text{Se}_2^{2-}$  anions.

In contrast to the  $4a \times 4b$  supercell found in the Th and U compounds, the present solution to the modulated structure of  $\text{CsNp}_2\text{Se}_6$ , solved in the reduced crystallographic triclinic unit cell, reflects a  $5a \times 5b \times 5c$  supercell, but solutions in the orthorhombic cell suggest the supercell is also two-dimensional but  $5a \times 5b$ . The reflection conditions of the data suggest the symmetry is higher, possibly  $I2/m$ , but an accurate solution of a higher symmetry structure has not been found. The modulated structure of  $\text{CsNp}_2\text{Se}_6$  also displays diselenide bonds shorter than those of the conventional solution with the shortest at 2.46 Å (Table 4). Because the  $\text{Cs}^+$  cations are also disordered over two positions, the modulated solution contains both charge density and site occupancy waves and Figure 5 displays a view down the [001] axis of  $\text{CsNp}_2\text{Se}_6$  similar to Figure 4 for  $\text{TlU}_2\text{Se}_6$ . As may be expected from the electronic structure arguments presented below, the figure clearly shows the coupling between diselenide bond breaking and Cs occupancy.

Instead of the one-out-of-four model of diselenide bond breaking, the structure can be understood as the breaking of two out of every five diselenide bonds from the parent  $\text{NpSe}_3$  structure and the formation of a “new” diselenide from two neighboring Se atoms. The result is two isolated  $\text{Se}_2^{2-}$  anions with Se–Se interatomic distances between 2.86 and 3.10 Å and essentially a one-in-five model. No simple description of the bonding in  $\text{CsNp}_2\text{Se}_6$  results from  $5a \times 5b \times 5c$  supercell, as displayed in Figure 5 and Table 4. The larger supercell

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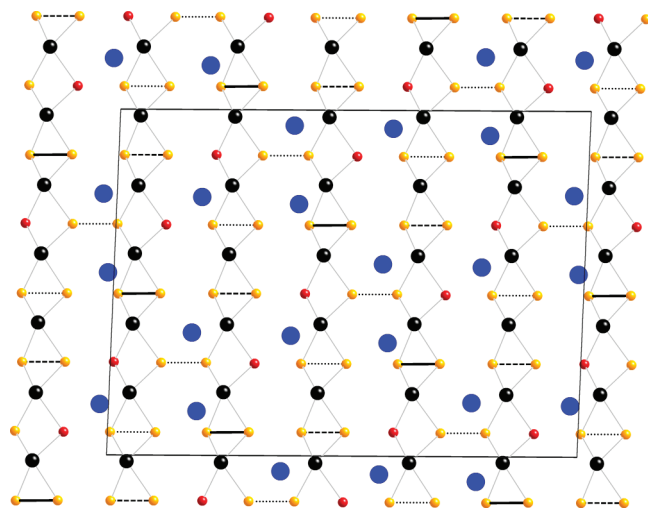
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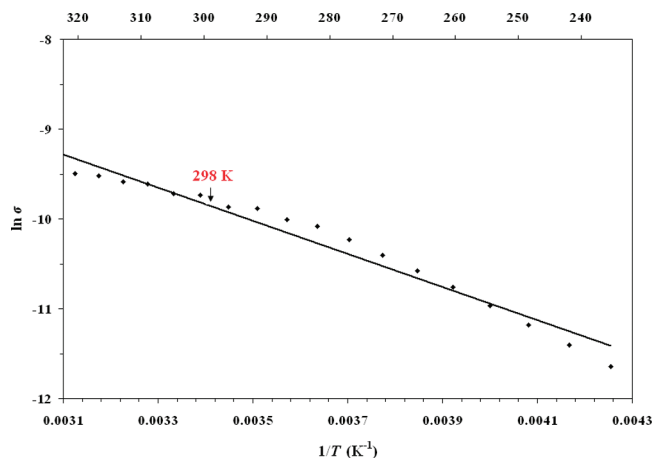


**Figure 5.**  $5a \times 5b \times 5c$  Cs/Np/Se layer from the supercell of  $\text{CsNp}_2\text{Se}_6$ , as viewed down [001]. Cs atoms are displayed on positions greater than 65% occupied. Red Se atoms are discrete  $\text{Se}_2^{2-}$  anions; orange Se atoms participate in Se–Se bonding. For Se–Se bonds: solid  $\leq 2.5$  Å, 2.5 < dashed  $\leq 2.6$  Å, and 2.6 < dotted  $\leq 2.7$  Å.

found in  $\text{CsNp}_2\text{Se}_6$  compared to that of Th and U could be an indication of the presence of  $\text{Np}^{3+}$ . If Se–Se bonds below 2.7 Å are considered to be  $\text{Se}_2^{2-}$  then the formula can be written  $\text{Cs}_5\text{Np}_{10}(\text{Se})_{14}(\text{Se}_2)_8$  and can be charge balanced with a one-to-ten  $\text{Np}^{3+}/\text{Np}^{4+}$  ratio. If this were the case then localization of the  $\text{Se}_2^{2-}$  units might be expected, as was found with the trivalent La doping of  $\text{CsU}_2\text{Se}_6$  to form  $\text{Cs}_{0.88}\text{La}_{0.68}\text{U}_{1.32}\text{Se}_6$ . The Np–Se interatomic distances in the modulated structure change very little from the conventional structure ranging from 2.85 to 2.96 Å and still suggest  $\text{Np}^{4+}$ . A fully realized solution to the charge-balance problem may require quantification of the Cs vacancies by ICP measurements. If the Cs/Np ratio is reduced then the model also charge balances with  $\text{Np}^{4+}$ .

**Electronic Structure.** The electronic structure of the  $\text{KTh}_2\text{Se}_6$  structure type has been explained by the insertion of an electron from the alkali metal into the S 3p  $\sigma^*$  or Se 4p  $\sigma^*$  orbital, respectively. For  $\text{K}_{0.91}\text{U}_{1.79}\text{S}_6$ <sup>32</sup> it has been postulated that the formation of an infinite S–S chain with longer than normal bonding distances (3.295(5) Å) is less effective at decreasing the total energy of the system than is the formation of cationic vacancies. This rationalizes the non-stoichiometric A/U ratios for  $\text{K}_{0.91}\text{U}_{1.79}\text{S}_6$  and  $\text{Rb}_{0.85}\text{U}_{1.75}\text{S}_6$ . From charge balance, these sulfur compounds can be formulated as  $(\text{K}^+)_{0.91}(\text{U}^{3.96+})_{1.79}(\text{S}^{2-})_2(\text{S}_2^{2-})_2$  and  $(\text{Rb}^+)_{0.85}(\text{U}^{4.09+})_{1.75}(\text{S}^{2-})_2(\text{S}_2^{2-})_2$  and hence as compounds of  $\text{U}^{4+}$ .

For the selenide compounds in the  $\text{KTh}_2\text{Se}_6$  structure type, two alternative explanations of the electron distribution have been proposed. The first is that the electron from the alkali metal occupies one-fourth of the Se 4p  $\sigma^*$  orbitals.<sup>32</sup> The second is that the donation of an electron from the alkali metal to the selenide chain breaks one of the diselenide bonds; this fits well with the modulated structures discussed above. The first explanation allows the formula of the selenides to be represented as  $(\text{A}^+)(\text{An}^{4+})_2(\text{Se}^{1.25-})_4(\text{Se}_2^{2-})_2$  whereas the simplified model for the modulated Th and U structures can be written as  $(\text{A}^+)_2(\text{An}^{4+})_4(\text{Se}^{2-})_6(\text{Se}_2^{2-})_3$ . As described above, the  $5a \times 5b \times 5c$  superstructure in  $\text{CsNp}_2\text{Se}_6$  does not conform to this simplified model but the long-range order still displays shorter Se–Se bonds than are found in the



**Figure 6.** Plot of  $\ln \sigma$  versus  $1/T$  for  $\text{RbU}_2\text{Se}_6$ , showing a linear Arrhenius fit to the data.

conventional structures. Currently the only Se exception is the disordered  $\text{Cs}_{0.88}(\text{La}_{0.68}\text{U}_{1.32})\text{Se}_6$  compound where the extra electron from the alkali metal resides on the  $\text{La}^{3+}$  cation and the structure displays normal  $\text{Se}_2^{2-}$  bond distances. The formula for this doped compound can be represented as  $(\text{Cs}^+)_{0.88}(\text{La}^{3+})_{0.68}(\text{U}^{3.85+})_{1.32}(\text{Se}_2^{2-})_2(\text{Se}_2^{2-})_2$ . There seems to be a delicate balance between the oxidation/reduction potentials of the An and  $\text{Se}_2$  moieties during the formation of these compounds. If the Np compounds could be synthesized from alkali halide salts rather than polyselenide fluxes, it might be possible to obtain Np compounds similar to the disordered lanthanide/actinide compound. It is unfortunate that the understanding of these potentials in solid-state environments remains rudimentary.

**Electrical Conductivity of  $\text{RbU}_2\text{Se}_6$ .** Figure 6 displays the temperature dependence of the electrical conductivity of  $\text{RbU}_2\text{Se}_6$  along [100]. At 298 K the conductivity  $\sigma$  is  $6 \times 10^{-5} \text{ S cm}^{-1}$ . Below 235 K, the sample resistance increased beyond the detection limits of the secondary multimeter (32 M $\Omega$ ). This semiconductor shows a simple Arrhenius-type thermal activation  $\sigma = \sigma_0 \exp(-E_a/(k_B T))$ , where  $k_B$  is the Boltzmann constant. The calculated thermal activation energy,  $E_a$ , is 0.159(1) eV. To compare, the conductivity of  $\text{KU}_2\text{Se}_6$  is  $1 \times 10^{-3} \text{ S cm}^{-1}$ , with a calculated activation energy of 0.27 eV.<sup>32</sup> Other members of the  $\text{AAn}_2\text{Q}_6$  family, including  $\text{ATH}_2\text{Se}_6$  and  $\text{ATH}_2\text{Te}_6$  (A = K, Cs), have electrical conductivities below  $1 \times 10^{-5} \text{ S cm}^{-1}$ .<sup>26,29</sup>

**Final Remarks.** The structural and physical property data collected here provide further support for an oxidation state of +4 for Th and U compounds in the  $\text{KTh}_2\text{Se}_6$  structure type, but in the Np compounds the oxidation state is less clear. The Np–Se interatomic distances determined by the conventional refinement along with refinements of the modulated structures point toward  $\text{Np}^{4+}$ , but the  $5a \times 5b \times 5c$  supercell for  $\text{CsNp}_2\text{Se}_6$  cannot be charge balanced without mixed valent Np or reduced Cs occupancy. By setting an arbitrary limit on what can be described as an Se–Se single bond it is possible to present a simplified interpretation of the complex superstructures. It is interesting that the superspace refinements of the modulated structures of some  $\text{LnTe}_3$  compounds<sup>53</sup> still lead to Te–Te distances far longer than

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the expected single-bond distance. With respect to the  $AAn_2Q_6$  compounds, it is unfortunate that no previous attempts were made to solve and refine their modulated structures. In fact, to date few of the  $AAn_2Q_6$  compounds have displayed measurable satellite data indicative of modulation. Further physical property measurements need to be made on the Np compounds to substantiate the +4 oxidation state as these would be the first examples insofar as we know of  $Np^{4+}$  in a selenide environment. Previous attempts to synthesize the Se analogues to  $Np^{4+}$  sulfides proved unsuccessful,<sup>21</sup> and the other non-oxide selenides are considered  $Np^{3+}$  compounds.<sup>9,14–20</sup> It is interesting that the Np compounds crystallize here in the  $AAn_2Q_6$  structure that is stable for  $Th^{4+}$  and  $U^{4+}$  rather than in the  $RbDy_3Se_8$  structure<sup>25</sup> known to be stable for  $Pu^{3+}$ .<sup>24</sup>

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**Supporting Information Available:** The crystallographic file in CIF format for the conventional refinements of  $CsTh_2Se_6$ ,  $Rb_{0.85}U_{1.74}S_6$ ,  $RbU_2Se_6$ ,  $TiU_2Se_6$ ,  $Cs_{0.88}(La_{0.68}U_{1.32})Se_6$ ,  $KNp_2Se_6$ , and  $CsNp_2Se_6$  and a pdf file for the refinements of the modulated structures of  $TiU_2Se_6$  and  $CsNp_2Se_6$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.