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# U(IV) Chalcogenolates Synthesized via Oxidation of Uranium Metal by Dichalcogenides

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Treatment of uranium metal with dichalcogenides in the presence of a catalytic amount of iodine in pyridine affords molecular U(IV) chalcogenolates that do not require stabilizing ancillary ligands. Oxidation of $U^0$ by PhEEPh yields monomeric seven-coordinate $U(EPh)_4(py)_3$ (E = S(**1**), Se(**2**)). The dimeric eight-coordinate complexes $[U(EPh)_2(\mu_2\text{-EPh})_2(CH_3CN)_2]_2$ (E = S(**3**), Se(**4**)) are obtained by crystallization from solutions of **1** and **2** dissolved in acetonitrile. Oxidation of $U^0$ by pySSpy and crystallization from thf yields nine-coordinate $U(Spy)_4(thf)$ (**5**). Incorporation of elemental selenium into the oxidation of $U^0$ by PhSeSePh results in the isolation of $[U(py)_2(SePh)(\mu_3\text{-Se})(\mu_2\text{-SePh})]_4{\cdot}4py$ (**6**), a tetrameric cluster in which each U(IV) ion is eight-coordinate and the $U_4Se_4$ core forms a distorted cube. The compounds were analyzed spectroscopically and the single-crystal X-ray structures of **1** and **3**–**6** were determined. The isolation of **1**–**6** represents six new examples of actinide chalcogenolates and allows insight into the nature of “hard” actinide ion–”soft” chalcogen donor interactions.

## Introduction

Interest in 5f element chemistry with nontraditional donor atom ligands is necessary for fully comprehending the chemical-bonding possibilities and electronic interactions of these elements. Bonding in actinide complexes is dominated by ionic interactions with ligands containing “hard” donors such as oxygen. The degree to which covalency is a factor in bonding with “softer” donors such as sulfur and selenium is uncertain, largely because of a paucity of well-characterized molecular compounds. Actinide coordination complexes with thiolates and, in particular, selenolates have received scant attention compared to transition metal and lanthanide complexes. Historically, lanthanide−chalcogen bonds were generally supported by sterically demanding ancillary ligands.[1] Although such compounds are of interest, in order to move toward a more complete understanding of the nature of f metal ion−chalcogen bonds, it is desirable to prepare homoleptic complexes without the steric influences of bulky stabilizing substituents. Relatively recently, it has been shown that oxidation of elemental lanthanides is a viable synthetic route to unsupported complexes containing only chalcogenolate anions and solvent molecules bound to the lanthanide ion.[2] There are examples of molecular actinide chalcogenolates; however, many include sterically bulky, inert Cp* or other stabilizing ligands.[3] There is a clear scope for advancing actinide chalcogenolate chemistry, particularly by isolating complexes in which the chalcogenolate is the only coordinated anion. In this paper, we report the oxidation of uranium metal by dichalcogenides as a method for preparing tetravalent molecular uranium chalcogenolates without ancillary stabilizing ligands.

## Experimental Section

All reactions were performed in an MBraun Labmaster 130 helium atmosphere drybox. Diethyl ether and thf were dried using activated alumina columns (A2, 12 32, Purify). Other solvents were

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purchased in anhydrous grade from Aldrich and all solvents were stored over a 1:1 mixture of 3 and 4 Å molecular sieves before use. Oxide-free uranium metal foil was prepared in a manner previously described.[4] Infrared spectra were obtained as Nujol mulls between KBr plates on a Nicolet Magna-IR 560 spectrometer equipped with a DTGS detector. All $^1$H NMR spectra were referenced to residual protio resonances and obtained on samples in 4 mm Teflon NMR tube liners inserted into 5 mm NMR tubes in order to multiply contain the radioactive samples. NMR spectra were recorded at ambient temperature on a Bruker Avance 300 MHz spectrometer. Electronic absorption spectra were recorded on a Varian Cary 6000i UV−vis−nIR spectrophotometer. Elemental analyses were performed by the Micro-Mass facility at the University of California, Berkeley, CA. Some of the elemental analyses are slightly lower than expected. Similar findings for trivalent lanthanide complexes have been attributed to thermal dissociation of neutral donor atom ligands at ambient temperature.[2b]

**$U(SPh)_4(py)_3$ (1).** Uranium metal (0.1640 g, 0.689 mmol) suspended in pyridine (7 cm$^3$) was treated with diphenyl disulfide (0.1918, 0.878 mmol) and a catalytic amount of iodine (0.0093 g, 0.037 mmol). The mixture was heated at 60 °C for 36 h and then stirred at ambient temperature for 6 days. The brown solution was filtered through a glass fiber circle to remove unreacted uranium metal. The solvent was removed in vacuo to give a viscous residue that was washed with hexanes (7 cm$^3$) and dried in vacuo to give a brown powder that was washed with hexanes (5 cm$^3$) on a medium porosity frit and dried in vacuo again (0.3579 g, 89% yield based on PhSSPh). A single crystal suitable for X-ray diffraction was grown by crystallization from a pyridine solution layered with hexanes.

IR (KBr, Nujol; cm$^{-1}$): 1578(m), 1467(s), 1378(s), 1308(m), 1218(w), 1171(w), 1154(m), 1080(m), 1065(m), 1038(m), 1024(m), 1003(m), 975(w), 941(w), 920(w), 898(w), 849(w), 770(m), 737(s), 722(s), 688(s), 626(m), 475(m). UV−vis−nIR (solution of **1** in pyridine; $\lambda_{max}$, nm): 609, 643, 686, 1165, 1245, 1353, 1483. $^1$H NMR ($CD_2Cl_2$): Three broad resonances for pyridine at 8.61, 7.68, and 7.26 ppm. Anal. Calcd for $C_{39}H_{35}N_3S_4U$: C, 51.63; H, 3.87; N, 4.61. Found: C, 47.35; H, 3.32; N, 2.36.

**$U(SePh)_4(py)_3$ (2).** Uranium metal (0.1797 g, 0.755 mmol) suspended in pyridine (7 cm$^3$) was treated with diphenyl diselenide (0.3005 g, 0.963 mmol) and a catalytic amount of iodine (0.0103 g, 0.041 mmol). The mixture was heated at 60 °C for 36 h and then stirred at ambient temperature for 6 days. The red-brown solution was filtered through a glass fiber circle to remove unreacted uranium metal. The solvent was removed in vacuo to give a viscous residue that was washed with hexanes (10 cm$^3$) and dried in vacuo to give a red-brown powder that was washed with hexanes (5 cm$^3$) on a medium porosity frit and dried in vacuo again (0.4781 g, 90% yield based on PhSeSePh).

IR (KBr, Nujol; cm$^{-1}$): 1576(m), 1465(s), 1378(s), 1308(m), 1218(m), 1171(w), 1155(m), 1065(m), 1038(m), 1020(m), 1003(m), 977(w), 939(w), 921(w), 897(w), 846(w), 775(w), 765(w), 752(m), 733(s), 725(s), 691(s), 663(m), 622(m), 460(m). UV−vis−nIR (solution of **2** in pyridine; $\lambda_{max}$, nm): 687, 842, 894, 1170, 1266, 1368, 1492. $^1$H NMR ($CD_2Cl_2$): Three broad resonances for pyridine at 8.62, 7.69, and 7.30 ppm. Anal. Calcd for $C_{39}H_{35}N_3Se_4U$: C, 42.60; H, 3.21; N, 3.82. Found: C, 41.71; H, 3.01; N, 3.90.

**$[U(SPh)_2(\mu_2\text{-}SPh)_2(CH_3CN)_2]_2$ (3).** Compound **1** (0.1033 g, 0.1133 mmol) was dissolved in actonitrile (3 cm$^3$) and filtered to remove a significant amount of undissolved material; the volume of the filtrate was reduced in vacuo to 1.5 cm$^3$, and diethyl ether was allowed to vapor diffuse into the filtrate to give dark brown blocks suitable for X-ray diffraction (0.0206 g, 24% yield based on U).

IR (KBr, Nujol; cm$^{-1}$): 1559(w), 1540(w), 1466(s), 1377(s), 1304(m), 1170(m), 1156(m), 1079(m), 1065(w), 1038(w), 1023(m), 975(m), 938(w), 920(w), 893(w), 849(w), 734(s, sh), 723(s), 688(w). UV−vis−nIR (prepared in situ by dissolving **1** in $CH_3CN$; $\lambda_{max}$, nm): 687, 1125, 1449. Anal. Calcd for $C_{56}H_{52}N_4S_8U_2$: C, 44.44; H, 3.46; N, 3.70. Found: C, 43.43; H, 3.32; N, 3.58.

**$[U(SePh)_2(\mu_2\text{-}SePh)_2(CH_3CN)_2]_2$ (4).** An X-ray diffraction quality single crystal of **4** was grown by vapor diffusion of hexanes into an acetonitrile solution of **2**.

**$U(Spy)_4(thf)$ (5).** Uranium metal (0.1615 g, 0.679 mmol) suspended in pyridine (5 cm$^3$) was treated with dipyridyl disulfide (0.2243 g, 1.018 mmol) and a catalytic amount of iodine (0.0078 g, 0.031 mmol). The mixture was heated at 70 °C for 30 min and then stirred at ambient temperature for 10 days. The solvent was removed in vacuo to give a viscous dark brown residue that was washed with hexanes (2 × 10 cm$^3$) and dried in vacuo to give a yellow powder (0.3574 g). The powder was dissolved in thf (15 cm$^3$) and filtered; the volume of the filtrate was reduced to 2.5 cm$^3$ in vacuo, and diethyl ether was allowed to vapor diffuse into the filtrate to give yellow-brown crystals over a few days. The crystals were dried in vacuo to give a yellow-brown powder (0.2404 g, 65% yield based on pySSpy and a product formula of $U(Spy)_4$). The crystals that formed from vapor diffusion of diethyl ether into the thf solution were of suitable quality for analysis by single-crystal X-ray diffraction.

IR (KBr, Nujol; cm$^{-1}$): 1586(m), 1547(m), 1465(s), 1412(m), 1378(s), 1311(w), 1262(m), 1257(m), 1241(w), 1221(w), 1182(w), 1139(m), 1133(m), 1085(m), 1075(w), 1067(w), 1037(m), 1016(w), 1002(m), 967(w), 923(w), 860(m), 754(s), 738(m), 727(s), 697(m), 639(m), 624(w), 484(m), 451(m). UV−vis−nIR (solution of **5** in benzene; $\lambda_{max}$, nm): 606, 699, 893, 1130, 1215, 1568. $^1$H NMR ($CD_2Cl_2$): Four broad resonances at 12.14, 8.34, 7.78, and 4.35 ppm and two less-intense broad resonances at 5.62 and 3.51 ppm. Two signals for thf at 3.12 and 1.58 ppm. Anal. Calcd for $C_{24}H_{20}N_4S_4U$ (excluding the thf molecule): C, 39.45; H, 2.76; N, 7.67. Found: C, 37.84; H, 2.86; N, 7.87.

**$[U(py)_2(SePh)(\mu_3\text{-}Se)(\mu_2\text{-}SePh)]_4{\cdot}4py$ (6)** Uranium metal (0.1756 g, 0.738 mmol) suspended in pyridine (7 cm$^3$) was treated with PhSeSePh (0.3453 g, 1.106 mmol) and a catalytic amount of iodine

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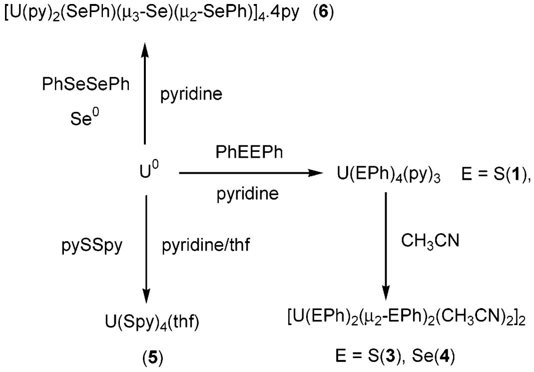
**Scheme 1.** Outline of the Syntheses of **1**−**6** through Oxidation of Uranium Metal by Dichalcogenides. A Catalytic Amount of Iodine was Included in All of the Oxidations.



(0.0101 g, 0.040 mmol). The mixture was heated at 50 °C for 36 h and then stirred at ambient temperature for 7 days. Elemental selenium (0.0437 g, 0.553 mmol) was added to the reaction mixture, and stirring continued at ambient temperature for 5 days. The red-brown solution was filtered and the filtrate volume was reduced in vacuo to 4 $cm^3$; the filtrate was layered with hexanes (10 $cm^3$) and stored at −35 °C. After 3 weeks, the deep red powder that had precipitated was collected and dried in vacuo (0.3497 g, 36% yield based on PhSeSePh). X-ray diffraction quality crystals were obtained by layering a concentrated pyridine solution with hexanes and storing at −35 °C, resulting in some dark red-brown needles after 1 day.

IR (KBr, Nujol; $cm^{-1}$): 1599(m), 1576(w), 1570(w), 1559(w) 1464(s), 1378(s), 1308(m), 1218(m), 1172(w), 1155(m), 1065(m), 1038(m), 1020(m), 1003(m), 976(w), 936(w), 922(w), 896(w), 845(w), 772(w), 765(w), 751(w), 740(s, sh), 732(s), 723(s, sh), 691(s), 663(w), 622(w), 461(w). UV−vis−nIR (solution of **6** in pyridine; $\lambda_{max}$, nm): 685, 1170, 1364, 1491. $^1H$ NMR ($CD_2Cl_2$): Multiple unresolved resonances between 6.5 and 9.0 ppm. Anal. Calcd for $C_{108}H_{100}N_{12}Se_{12}U_4$: C, 37.43; H, 2.91; N, 4.85. Found: C, 37.35; H, 2.77; N, 3.72.

## Results

Oxidation of uranium metal by ca. 1.5 equiv of dichalcogenide in the presence of a catalytic amount of iodine and the coordinating solvent pyridine proceeds, with initial heating, over the course of several days to yield U(IV) thiolates and selenolates (Scheme 1). There were no observable reactions when thf or acetonitrile was used as a solvent instead of pyridine. In our work, we used a small quantity of iodine to aid oxidation, whereas in the majority of related lanthanide research, mercury is used to amalgamate the $Ln^0$ metal. Radiological waste disposition options preclude us from using mercury with uranium. Although there are examples of lanthanide tellurolates reported in the literature,[1a,b,e,5] our attempts to oxidize uranium metal with diphenyl ditelluride failed or resulted in intractable products. The single-crystal structures of **1** and **3**−**6** were determined (Table 1). Unfortunately, EA values are frequently determined to be lower than the calculated values for these types of compounds. We have sent some of the samples for duplicate analyses, and the analyses are consistently found to be lower than the calculated values. Similar results were found by other researchers for lanthanide complexes;[2a,10e] that is, lower than expected EA values because of the thermal dissociation of solvent molecules. Unfortunately, we do not have the capability to measure powder X-ray diffraction patterns on air-sensitive samples to be able to establish with certainty that the bulk powdered samples are identical to the single crystals.

**$U(EPh)_4(py)_3$, (E = S(1), Se(2)).** Oxidation of $U^0$ with diphenyl disulfide and diphenyl diselenide results in isolation, after workup, of **1** as a brown powder and **2** as a red-brown powder, in 89 and 90% yields, respectively. Compound **1** is crystallized by layering a pyridine solution with hexanes, and its X-ray structure has been determined. Complex **1** is a U(IV) monomer bonded to four $PhS^-$ anions and three coordinated pyridine molecules (Figure 1). The geometry about the seven-coordinate uranium center is best described as distorted pentagonal bipyramidal with the S atoms of two thiolate ligands in the apical positions and the two remaining thiolate S atoms and three N atoms of the pyridine molecules in the equatorial plane. The average U−S distance is 2.734(3) Å, and the average U−N distance is 2.597(9) Å (Table 2), which is normal for a pyridine molecule coordinated to U(IV). The thiolate anions coordinate in a bent fashion with an average U−S−C angle of 115.9(4)°. Single crystals suitable for X-ray diffraction could not be grown for the selenolate complex **2**, but spectroscopic analysis suggests that a formulation analogous to **1** is correct.

**$[U(EPh)_2(\mu_2\text{-}EPh)_2(CH_3CN)_2]_2$, (E = S(3), Se(4)).** Compounds **1** and **2** are moderately soluble in acetonitrile, and crystallization by vapor diffusion with diethyl ether and hexanes gives **3** and **4**, respectively, in which uranium dimers have formed and the pyridine molecules have been displaced. The X-ray crystal structures of **3** and **4** are isostructural (Figures 2 and 3). Both U(IV) centers are eight-coordinate, best described as having triangular dodecahedral geometry,[6] and are bound to the N atoms of two terminal acetonitrile molecules, the E atoms of two terminal chalcogenolate anions, and the E atoms of four bridging chalcogenolate anions. In **3**, the $U{-}S_{terminal}$ distance is 2.813(2) Å, the average $U{-}S_{bridging}$ distances are longer at 2.9378(19) and 2.8667(19) Å, and the U−N distance is 2.478(6) Å (Table 3). The acetonitrile molecule is bent slightly away from uranium, with a U−N−C angle of 171.5(8)°. In **4**, the $U{-}Se_{terminal}$ distance is 2.8491(12) Å, the $U{-}Se_{bridging}$ distances are longer at 3.0564(10) and 2.9935(11) Å, and the U−N distance is 2.479(8) Å (Table 4). The angle between the bridging anions and the two uranium atoms, U−E−U, is 82.88(5)° for **3** and 81.55(3)° for **4**. The terminal chalcogenolate anions are bent away from the uranium atoms, with a U−S−C angle of 116.8(4)° in **3** and 113.9(3)° in **4**.

**$U(Spy)_4(thf)$ (5).** In addition to diphenyl disulfide and diphenyl diselenide, $U^0$ can also be oxidized with dipyridyl disulfide in pyridine. Crystallization from thf affords **5**, which is a nine-coordinate uranium monomer bonded to four bi-

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**Table 1.** Selected Crystallographic Data for **1** and **3**−**6**

| | **1** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|
| empirical formula | $C_{39}H_{35}N_3S_4U$ | $C_{56}H_{52}N_4S_8U_2$ | $C_{56}H_{52}N_4Se_8U_2$ | $C_{24}H_{24}N_4OS_4U$ | $C_{108}H_{100}N_{12}Se_{12}U_4$ |
| fw | 911.97 | 1513.56 | 1888.76 | 750.74 | 3465.64 |
| space group | $P2_1/c$ | $I4_1/a$ | $I4_1/a$ | $P2_12_12_1$ | $C2/c$ |
| $a$ (Å) | 11.6836(10) | 20.0352(19) | 20.203(3) | 9.4765(7) | 29.362(2) |
| $b$ (Å) | 16.1000(14) | 20.0352(19) | 20.203(3) | 15.3112(12) | 12.5300(9) |
| $c$ (Å) | 19.6157(17) | 13.988(3) | 13.990(4) | 18.3780(14) | 31.388(2) |
| $\beta$ (deg) | 93.162(2) | 90.00 | 90.00 | 90.00 | 111.5500(10) |
| $V$ (Å$^3$) | 3684.2(6) | 5615.0(13) | 5709.8(18) | 2666.6(4) | 10740.8(13) |
| $Z$ | 4 | 4 | 4 | 4 | 4 |
| $T$ (K) | 141(2) | 203(1) | 141(2) | 141(2) | 141(2) |
| $\lambda$ (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| $\mu$ (mm$^{-1}$) | 4.664 | 6.099 | 10.805 | 6.425 | 10.132 |
| $D_{\text{calcd}}$ (g/cm$^3$) | 1.644 | 1.790 | 2.197 | 1.870 | 2.143 |
| $R_1$ | 0.0453 | 0.0394 | 0.0415 | 0.0136 | 0.0325 |
| $wR_2$ | 0.0755 | 0.0548 | 0.0958 | 0.0141 | 0.0557 |

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for $U(SPh)_4(py)_3$ (**1**)

| | | | |
|---|---|---|---|
| U(1)−S(1) | 2.7298(17) | U(1)−N(1) | 2.563(5) |
| U(1)−S(2) | 2.7169(17) | U(1)−N(2) | 2.598(5) |
| U(1)−S(3) | 2.7298(16) | U(1)−N(3) | 2.629(5) |
| U(1)−S(4) | 2.7639(17) | | |
| U(1)−S(1)−C(1) | 114.4(2) | U(1)−S(3)−C(13) | 114.5(2) |
| U(1)−S(2)−C(7) | 115.7(2) | U(1)−S(4)−C(19) | 119.0(2) |

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for $[U(SPh)_2(\mu_2\text{-}SPh)_2(CH_3CN)_2]_2$ (**3**)

| | | | |
|---|---|---|---|
| U(1)−S(1) | 2.8667(19) | U(1)−S(2) | 2.813(2) |
| U(1)−S(1A) | 2.9378(19) | U(1)−N(1) | 2.478(6) |
| U(1)−S(1)−U(1A) | 82.88(5) | U(1)−N(1)−C(13) | 171.5(8) |
| U(1)−S(2)−C(7) | 116.8(4) | | |

**Table 4.** Selected Bond Lengths (Å) and Angles (deg) for $[U(SePh)_2(\mu_2\text{-}SePh)_2(CH_3CN)_2]_2$ (**4**)

| | | | |
|---|---|---|---|
| U(1)−Se(1) | 2.9935(11) | U(1)−Se(2) | 2.8491(12) |
| U(1)−Se(1A) | 3.0564(10) | U(1)−N(1) | 2.479(8) |
| U(1)−Se(1)−U(1A) | 81.55(3) | U(1)−N(1)−C(13) | 171.3(8) |
| U(1)−Se(2)−C(7) | 113.9(3) | | |

dentate (through the S and N atoms) pyridyl sulfide anions and the O atom of a thf molecule (Figure 4), in 65% yield. The geometry about the U(IV) center is best described as distorted tricapped trigonal prismatic, with two S atoms of two pyridyl sulfide anions and one N atom of another pyridyl sulfide anion occupying the capping positions of the trigonal prism. One trigonal face of the prism is defined by one S atom of a pyridyl sulfide anion, one N atom of another pyridyl sulfide anion, and the O atom of the coordinated thf molecule. The other trigonal face of the prism is defined by the S and N atoms of one pyridyl sulfide anion and the N atom of another pyridyl sulfide anion. The average U−S distance is 2.8299(16) Å, the average U−N distance is 2.540(4) Å, and the U−O distance is 2.548(2) Å (Table 5). The average S−U−N bite angle is 58.09(12)°.

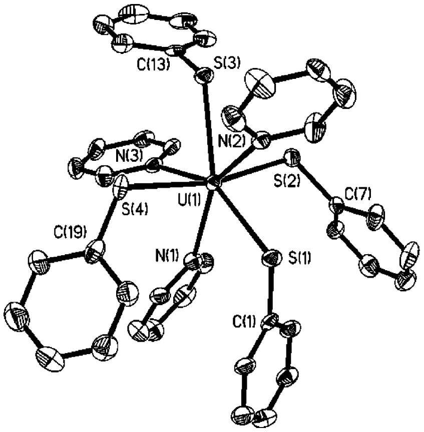

**Figure 1.** Thermal ellipsoid plot (50% probability level) of the structure of **1**; H atoms have been omitted for clarity.

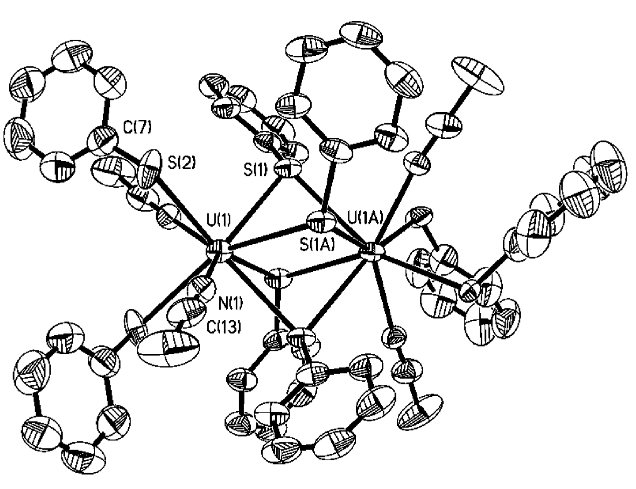

**Figure 2.** Thermal ellipsoid plot (50% probability level) plot of the structure of **3**; H atoms have been omitted for clarity.

**$[U(py)_2(SePh)(\mu_3\text{-}Se)(\mu_2\text{-}SePh)]_4\cdot 4py$ (6).** The addition of 0.75 equiv of $Se^0$ with 1.5 equiv of diphenyl diselenide to

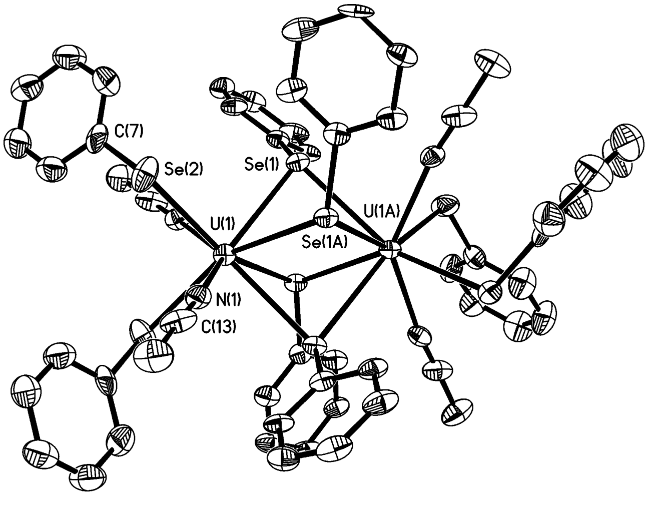

**Figure 3.** Thermal ellipsoid plot (50% probability level) plot of the structure of **4**; H atoms have been omitted for clarity.

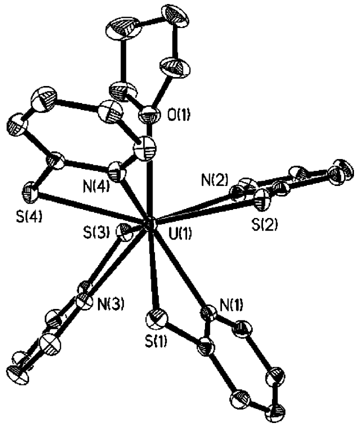

**Figure 4.** Thermal ellipsoid plot (50% probability level) plot of the structure of **5**; H atoms have been omitted for clarity.

**Table 5.** Selected Bond Lengths (Å) and Angles (deg) for U(Spy)$_4$(thf) (**5**)

| | | | |
|---|---|---|---|
| U(1)−S(1) | 2.8222(8) | U(1)−N(1) | 2.504(2) |
| U(1)−S(2) | 2.8322(8) | U(1)−N(2) | 2.575(2) |
| U(1)−S(3) | 2.8380(8) | U(1)−N(3) | 2.550(2) |
| U(1)−S(4) | 2.8273(8) | U(1)−N(4) | 2.531(2) |
| U(1)−O(1) | 2.548(2) | | |
| S(1)−U(1)−N(1) | 58.81(6) | S(3)−U(1)−N(3) | 57.78(6) |
| S(2)−U(1)−N(2) | 57.60(6) | S(4)−U(1)−N(4) | 58.15(6) |

uranium metal in pyridine oxidizes the metal, and crystallization from pyridine results in the formation of a U(IV) tetramer (Figure 5). Each U(IV) center is eight-coordinate, with a distorted bicapped trigonal prismatic geometry,[6] and bonded to three $\mu_3$-Se$^{2-}$ anions, the Se atom of one terminal PhSe$^-$ anion, the Se atoms of two $\mu_2$-PhSe$^-$ anions, and the N atoms of two terminal pyridine molecules. The crystal lattice also contains four pyridine solvent molecules of crystallization per uranium tetramer. Complex **6** can be viewed as being a distorted cubane type cluster (Figure 5), with the four U(IV) atoms and four Se$^{2-}$ anions occupying alternate vertices of the cube. The average U−SePh$_{\text{terminal}}$ distance is 2.9267(10) Å, the average U−SePh$_{\text{bridging}}$ distance is 3.0614(14) Å, the average U−Se$^{2-}$ distance is 2.8681(15) Å, and the average U−N distance is 2.619(10) Å (Table 6). The U$_4$Se$_4$ cube is heavily distorted, with the 12 internal angles at the vertices ranging from 71.63(2)° for Se(2)−U(1)−Se(2A) to 106.48(2)° for U(1)−Se(2)−U(1A). The terminal phenyl selenolate anions are bent away from the uranium atoms by an average U−Se−U angle of 114.06(25)°. The average U−Se−U angle between the uranium atoms and bridging phenyl selenolate anions is 82.965(23)°.

## Discussion

The use of 1.5 equiv of dichalcogenide in the reaction mixtures was intended to result in oxidation of uranium metal to U(III) chalcogenolate complexes, similar to the way in which uranium metal can be oxidized by 1.5 equiv of iodine in pyridine to form UI$_3$(py)$_4$.[4b] However, we found in all cases that uranium metal was oxidized to U(IV) by dichalcogenides. We have isolated six U(IV) thiolate or selenolate complexes that contain only chalcogen atoms (and nitrogen in **5**) and solvent molecules in the coordination sphere of uranium. There is only one mention in the literature of an attempt to use uranium metal as a precursor in the syntheses of U(IV) thiolates.[3f] U(SPh)$_4$ was isolated as an insoluble red powder in low yield (10%) by ultrasonication of U$^0$ turnings and excess PhSSPh in toluene. Sonication of U$^0$ in pure disulfide gave small amounts of U(SEt)$_4$ and U(S$^i$Pr)$_4$.

Many U(IV) thiolate compounds reported in the literature contain supporting ligands such as Cp and Tp type groups.[3b,c,l,m] There are a few examples in the Cambridge Structural Database of homoleptic uranium(IV) thiolates that were prepared from U(IV) precursors. The complex [NEt$_2$H$_2$][U(SPh)$_6$][3i] has U−S bond lengths ranging from 2.705(3) to 2.759(3) Å, consistent with those in **1**. The U−S bond lengths in [(thf)$_3$Na($\mu$-SPh)$_3$U($\mu$-SPh)$_3$Na(thf)$_3$] are 2.717(3) Å.[3j] The homoleptic dithiolate complex [Li(dme)]$_4$[U(SCH$_2$CH$_2$S)$_4$] has U−S bond lengths ranging from 2.789(4) to 2.900(4) Å.[3n] To the best of our knowledge, the only reported U(IV) selenolate complex is [U(C$_5$H$_4$SiMe$_3$)$_3$(SeMe)],[3e] which was not structurally characterized. Indeed, more generally, there are only three examples of structurally characterized molecular U−Se bonds, which are those in UO$_2$[Et$_2$NCSe$_2$]$_2$Ph$_3$AsO,[7] [U(Se$_2$)],$^{4-}$ [8] and U[N(SePPh$_2$)$_2$]$_3$·C$_6$D$_6$.[9]

Complexes **1** and **2** are similar to the trivalent lanthanide complexes Yb(SPh)$_3$(py)$_3$, M(SePh)$_3$(py)$_3$ (M = Ho or Tm), Yb(SC$_6$H$_2$$^i$Pr$_3$)$_3$(py)$_3$, Sm(SAr)$_3$(py)$_3$, and Yb(SAr)$_3$(py)$_3$ (Ar = 2, 4, 6-triisopropylphenyl).[2d,e] **1** and **2** are monomeric, soluble in pyridine, and moderately soluble in acetonitrile and dichloromethane. Dissolution of **1** and **2** in acetonitrile followed by crystallization results in the formation of **3** and **4**, respectively, in which the coordination number of uranium has increased from seven to eight upon formation of the dimers, with the uranium atoms bridged by four PhE$^-$ anions. The U−Se bond lengths in **4** are all slightly longer than the corresponding U−S bond lengths in isostructural **3**, reflecting the difference in ionic radii of S and Se. The solubility of **3** is less than that of **1** and **2**, which hindered the acquisition of NMR and electronic absorption spectra. The formation of dimers has also been observed in Ln(III) complexes such as [Ln(SPh)$_3$(py)$_3$]$_2$ (Ln = Ho or Tm),[2b] which contain only two bridging anions, as compared with four bridging anions in **3** and **4**, because of the lower charge of Ln(III) compared to U(IV). There is an example of U(IV) bridged by four thiolate anions in [U(cot)$_2$(S$^i$Pr)$_2$]$_2$,[3h] in which the U−S$_{\text{bridging}}$ distances range from 2.806(3) to 2.895(3) Å, slightly shorter than the U−S$_{\text{bridging}}$ distances of 2.8667(19) and 2.9378(19) Å in **3**.

Oxidation with dipyridyl disulfide resulted in isolation of the first example of a U(IV) complex with pyridyl sulfide anions. Examples of U(VI) uranyl complexes with pyridyl and pyrimidyl thiolate ligands are [Me$_4$N][UO$_2$(NO$_3$)$_2$(C$_5$H$_4$NS)], [C$_{16}$H$_{25}$N$_2$S$_2$Si$_2$][UO$_2$(NO$_3$)$_2$(C$_8$H$_{12}$NSSi)], [HNEt$_3$]$_2$[(UO$_2$)$_2$(O$_2$)(SC$_4$N$_2$H$_3$)$_4$], [HNEt$_3$][H(UO$_2$)$_2$(O$_2$)(SC$_4$N$_2$H$_2$Me)$_4$], and [HNEt$_3$]$_2$[(UO$_2$)$_4$(O)$_2$(SC$_5$NH$_4$)$_6$].[3d,g] Ln(III) pyridyl thiolates have been prepared by the oxidation of elemental

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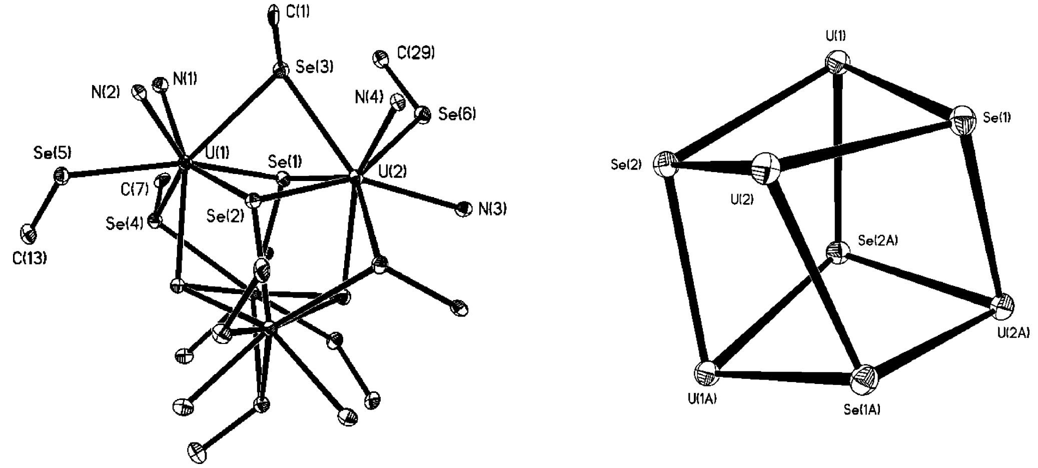

**Figure 5.** Thermal ellipsoid plots of **6**. The molecular structure is shown on the left, omitting, for clarity, H atoms and C atoms except for those directly bonded to the Se atoms of $PhSe^-$ anions. The $U_4Se_4$ distorted cubane core is shown on the right.

**Table 6.** Selected Bond Lengths (Å) and Angles (deg) for $[U(py)_2(SePh)(\mu_3\text{-}Se)_2(\mu\text{-}SePh)]_4{\cdot}4py$ (**6**)

| | | | |
|---|---|---|---|
| U(1)−Se(1) | 2.7928(6) | U(2)−Se(1) | 2.8601(6) |
| U(1)−Se(2) | 2.9252(6) | U(2)−Se(2) | 2.8124(6) |
| U(1)−Se(2A) | 2.8704(7) | U(2)−Se(1A) | 2.9482(6) |
| U(1)−Se(3) | 3.1225(7) | U(2)−Se(3) | 3.0184(7) |
| U(1)−Se(4) | 3.0355(7) | U(2)−Se(4A) | 3.0691(6) |
| U(1)−Se(5) | 2.9185(7) | U(2)−Se(6) | 2.9349(7) |
| U(1)−N(1) | 2.640(5) | U(2)−N(3) | 2.590(5) |
| U(1)−N(2) | 2.611(5) | U(2)−N(4) | 2.636(5) |
| U(1)−Se(1)−U(2) | 91.491(18) | U(2)−Se(1)−U(2A) | 106.38(2) |
| U(1)−Se(2)−U(2) | 89.754(17) | U(1)−Se(3)−U(2) | 82.486(16) |
| U(1)−Se(1)−U(2A) | 90.050(18) | U(1)−Se(4)−U(2A) | 83.443(16) |
| U(1)−Se(2)−U(1A) | 106.48(2) | Se(1)−U(1)−Se(2) | 86.191(18) |
| U(1A)−Se(2)−U(2) | 91.268(18) | Se(1)−U(2)−Se(2) | 87.083(18) |
| Se(1)−U(1)−Se(2A) | 87.544(18) | Se(1)−U(2)−Se(1A) | 71.92(2) |
| Se(1A)−U(2)−Se(2) | 85.678(17) | Se(2)−U(1)−Se(2A) | 71.63(2) |
| U(1)−Se(5)−C(13) | 114.55(18) | U(2)−Se(6)−C(29) | 113.57(17) |

lanthanide with dipyridyl disulfide to form both anionic, $[PEt_4][Ln(Spy)_4]$, and neutral, $Ln(Spy)_3(py)_2$, complexes.[2c]

Finally, incorporation of 0.75 equiv of elemental Se into the uranium metal oxidation by diphenyl diselenide yields the novel tetrameric cubane-like U(IV) cluster, comprising both $PhSe^-$ and $Se^{2-}$ anions. The occurrence of a cluster such as **6** is likely through oxidation of $U^0$ to form $U(SePh)_4(py)_3$ (as for **2**), followed by reduction of $Se^0$ to $Se^{2-}$ with concomitant oxidative elimination of PhSeSePh. The most comparable uranium cluster containing $E^{2-}$ is the trinuclear complex $U_3(\mu_3\text{-}S)(\mu_3\text{-}S^tBu)(\mu_2\text{-}S^tBu)_3(S^tBu)_6$, prepared by protonation of $[Na(thf)_3]_2[U(S^tBu)_6]$ with $NEt_3HBPh_4$ in diethyl ether.[3k] A range of molecular lanthanide clusters have been reported,[10] and the closest comparison to **6** is the cubane type complex $Yb_4Se_4(SePh)_4(py)_8$,[10g] in which the major difference from **6** is that it does not contain any bridging $PhSe^-$ anions because of the +3 charge on ytterbium compared to +4 for uranium. It was noted that the $Yb-Se^{2-}$ bonds trans to the terminal $PhSe^-$ anion were longer than either of the two $Yb-Se^{2-}$ bonds trans to the pyridine ligand; this was attributed to a possible trans influence, indicative of covalency in the bonding. In **6**, the $U-Se^{2-}$ bond lengths are different (ranging from 2.7928(6) to 2.9482(6) Å); however, the geometry of the cube is heavily distorted, and the differences in bond lengths may well arise from steric influences of the bridging $PhSe^-$ anions.

The proton NMR spectra of **1**, **2**, **5**, and **6** are difficult to interpret, and not all the expected signals are observed, largely because of the paramagnetism of U(IV). The proton NMR of **3** was not recorded because of its low solubility in $CD_3CN$ and noncoordinating deuterated solvents. Similarly uninformative proton NMR spectra, offering very little structural information about the integrity of the complexes in solution, have been reported for paramagnetic Ln(III) chalcogenolates.[2b]

The electronic absorption spectra of **1**, **2**, **5**, and **6** display bands arising from f−f and f−d transitions.[11] There are distinctive bands in the spectra of **1**, **2**, and **6** in pyridine between 685 and 687 nm and 1165 and 1170 nm, which have previously been observed to be characteristic of U(IV) in the solution UV−vis−nIR spectra of complexes such as $UI_4(PhCN)_4$.[4a] The UV−vis−nIR spectrum of **5** in benzene has distinctive absorptions at 699, 1130, and 1215 nm. Compound **3** has poor solubility, but a UV−vis−nIR spectrum of **3**, presumed to form in situ, was recorded by dissolving **1** in acetonitrile and has characteristic absorbance bands at 687 and 1125 nm. There are also intense charge-transfer transitions below 500 nm in the electronic spectra of **1**−**3**, **5**, and **6**. We have not reported the extinction coefficients for the absorbances in the electronic spectra because the NMR spectra do not conclusively demonstrate that the structural integrity of the complexes are maintained in solution.

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In summary, we have shown that oxidation of uranium metal by dichalcogenides is a useful synthetic approach for isolating molecular uranium(IV) thiolates and selenolates without the need for stabilizing ancillary ligands. Although U(III) complexes were targeted, the oxidations proceed to the tetravalent state in all cases, resulting in the characterization of six new U(IV) chalcogenolate compounds. We are currently investigating the oxidation of plutonium metal by dichalcogenides in an effort to prepare trivalent actinide chalcogenolates by this route.

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**Supporting Information Available:** CIF files, IR, UV−vis−nIR, and $^1$H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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