Inorganic Chemistry
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pubs.acs.org/IC

Synthesis of Terminal Monochalcogenide and Dichalcogenide Complexes of Uranium Using Polychalcogenides, $[E_n]^{2-}$ (E = Te, n = 2; E = Se, n = 4), as Chalcogen Atom Transfer Reagents

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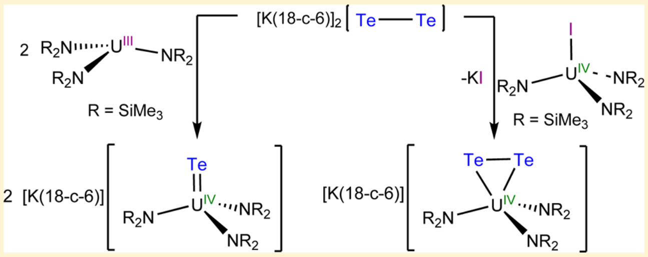
Supporting Information



ABSTRACT: Reaction of KH with elemental tellurium, in the presence of 18-crown-6, results in the formation of the ditelluride, $[K(18\text{-crown-}6)]_2[Te_2]$ (**1**), in good yield. Similarly, reaction of KH with elemental selenium, in the presence of 18-crown-6, results in the formation of $[K(18\text{-crown-}6)]_2[Se_4]$ (**4**). Both **1** and **4** are capable of chalcogen atom transfer to U(III). For example, addition of 0.5 equiv or 1 equiv of $[K(18\text{-crown-}6)]_2[Te_2]$ (**1**) to $[U(NR_2)_3]$ (R = $SiMe_3$) or $[U(I)(NR_2)_3]$, respectively, results in the formation of the new U(IV) tellurides, $[K(18\text{-crown-}6)][U(Te)(NR_2)_3]$ (**2**), and $[K(18\text{-crown-}6)][U(\eta^2\text{-}Te_2)(NR_2)_3]$ (**3**), in moderate yields, while addition of 0.5 equiv of $[K(18\text{-crown-}6)]_2[Se_4]$ (**4**) to $[U(NR_2)_3]$ results in the formation of the U(IV) diselenide, $[K(18\text{-crown-}6)][U(\eta^2\text{-}Se_2)(NR_2)_3]$ (**5**). Interestingly, **5** can be converted into the monoselenide $[K(18\text{-crown-}6)][U(Se)(NR_2)_3]$ (**6**) via reaction with Ph_3P.

INTRODUCTION

Metal chalcogenide complexes are found in a broad spectrum of fields, including catalysis,[1−3] nanomaterials,[4−9] and bioinorganic chemistry.[10−12] For example, the molybdenum disulfide complex, $[(PY5Me_2)Mo(\eta^2\text{-}S_2)]^{2+}$ ($PY5Me_2$ = 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine), is an effective catalyst for proton reduction,[3] while nanoparticles of the II−VI semiconductors are being employed in a wide variety of applications.[4,6,13,14] In addition, iron sulfur clusters are widely used by enzymes for electron delivery,[10−12] and metal sulfur interactions form the skeletons of the nitrogenase,[15] nitrous oxide reductase,[16,17] and carbon monoxide dehydrogenase active sites.[18]

In support of research in these fields, a variety of chalcogen transfer reagents have been developed, including $R_3P{=}E$,[19] thiirane,[20] and RSSSR.[21,22] However, it is apparent that in many cases the outcomes of chalcogen atom transfer are difficult to predict and/or a mixture of products are often generated. For example, Kubas and co-workers reported that reaction of Et_2S_3 with $[CpFe(CO)_2]_2$ generated a mixture of $Cp_2Fe_2(S_2)(SEt)_2$, $Cp_3Fe_3(S_2)(SEt)$, $Cp_4Fe_4S_4$, $Cp_4Fe_4S_5$, and $Cp_4Fe_4S_6$, all in low isolated yields.[22] Similarly, van der Berg and co-workers demonstrated that reaction of $Me_2Si(\eta^5\text{-}C_5H_4)_2Fe_2(CO)_4$ with S_8 under thermal conditions provided a mixture of $[Me_2Si(\eta^5\text{-}C_5H_4)_2]_2Fe_5S_{12}$ and $[Me_2Si(\eta^5\text{-}C_5H_4)_2]_2Fe_4S_6$, while under photolytic conditions $[Me_2Si(\eta^5\text{-}C_5H_4)_2]_2Fe_4S_6(CO)$ was formed instead.[23,24] In addition, our research group reported that oxidation of $[U(NR_2)_3]$ (R = $SiMe_3$) with S_8 resulted in formation of mixtures of $[U(NR_2)_3]_2(\mu\text{-}S)$ and $[U(NR_2)_3]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$.[25]

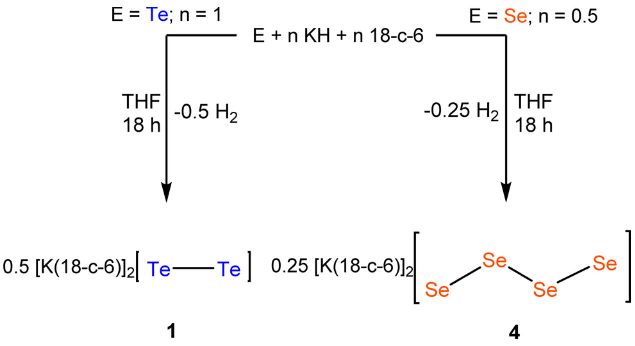
The lack of kinetic control observed upon reaction of these chalcogen sources with metal complexes demonstrates the need for new chalcogen reagents that can deliver chalcogen atoms in a more controlled fashion. Toward this end, we recently reported the ability of $KSCPh_3$ to act as a convenient sulfur atom source. In particular, reaction of $KSCPh_3$ with $[U(NR_2)_3]$ resulted in formation of a terminal sulfide, $[K(18\text{-crown-}6)][U(S)(NR_2)_3]$ (R = $SiMe_3$), via spontaneous release of the trityl radical.[26] Interestingly, $KSCPh_3$ is acting as a 1e$^-$ oxidant in this transformation, an observation that can be rationalized by assigning a formal −1 oxidation state to the sulfur atom. In contrast, other common sulfur sources, such as S_8 or $Ph_3P{=}S$, are 2e$^-$ oxidants. This is significant because uranium, like all f elements, is reluctant to undergo 2e$^-$ redox chemistry. As a result, there is a redox mismatch between $[U(NR_2)_3]$ and many chalcogen transfer reagents. With this in mind, we desired to extend the trityl release strategy to the synthesis of terminal selenides and tellurides of uranium; however, to our knowledge the analogous $KECPh_3$ (E = Se, Te) compounds are not known. This prompted a search for other chalcogen atom sources wherein each chalcogen atom formally possessed a −1 oxidation state, which should allow access to the desired E(−I/−II) redox couple. In this regard, the dichalcogenides, $[E_2]^{2-}$ (E = Se, Te), appear to be a viable choice.[27] These materials are poised to perform the desired 1e$^-$ redox chemistry, as formally, each chalcogen atom in $[E_2]^{2-}$ possesses the desired −1 oxidation state.[28−33]

Received: May 30, 2014
Published: September 9, 2014

RESULTS AND DISCUSSION

Di- and polychalcogenides are most commonly synthesized by reduction of the elemental chalcogens with the alkali metals under solventothermal conditions or in liquid ammonia.[27,32−45] The polychalcogenide crystals generated by these routes often feature the inclusion of solvents that are incompatible with the highly air- and water-sensitive U(III) tris(amide), [U(NR_2)$_3$], a common U(III) starting material used in our laboratory. Thus, we endeavored to develop a procedure for the synthesis of polychalcogenides that only employed anhydrous reagents. Accordingly, addition of 1 equiv of KH to Te powder, in the presence of 1 equiv of 18-crown-6, in tetrahydrofuran results in the production of a violet-blue suspension, concomitant with gas evolution, over the course of 18 h. The violet-blue powder, [K(18-crown-6)]$_2$[Te_2] (**1**), can be isolated in 72% yield by collection on a glass frit (Scheme 1).

Scheme 1. Syntheses of Polychalcogenide Complexes 1 and 4



Violet-blue crystals suitable for X-ray diffraction were grown from a dilute MeCN solution layered with Et_2O. Complex **1** crystallizes in the monoclinic space group *C*2/*c*, and its solid state molecular structure is shown in Figure 1. Complex **1** is situated on a crystallographically imposed C_2 axis. As a result, half of the molecule is generated by symmetry. In the solid state, **1** features a [μ-η^2:η^2-Te_2]$^{2-}$ anion coordinated by two [K(18-crown-6)]$^+$ moieties. Its Te−Te distance (2.7877(6) Å) is similar to the Te−Te distances (av 2.78 Å) in other structurally characterized complexes containing the [Te_2]$^{2-}$ anion.[32,46−49] In addition, the Te−K distances are 3.483(1) and 3.6327(9) Å, and are similar to those observed in the Zintl phase, K_2Te_2 (av K−Te = 3.57 Å).[32] Also, of note, several other crown ether solvates of the polychaclogenides have been previously structurally characterized, including [Na(15-crown-5)]$_2$[Se_5], [K(18-crown-6)]$_2$[S_6], and [Na(15-crown-5)]$_2$[S_6].[43−45]

Complex **1** is insoluble in nonpolar or ethereal solvents, but is soluble in acetonitrile or pyridine. Its violet-blue color in the solid state is indicative of the presence of the [Te_2]$^{2-}$ anion.[41,46,50−52] However, upon dissolution of **1** in MeCN, a red-violet solution is generated, which is consistent with the presence of both the [Te_2]$^{2-}$ and [Te_3]$^{2-}$ anions. In fact, all attempts to recrystallize **1** result in the coprecipitation of both violet-blue crystals, indicative of the presence of **1**, and violet-red crystals, which we suggest are [K(18-crown-6)]$_2$[Te_3].[41,46,50−52] This hypothesis is further supported by the UV−vis spectrum of **1** in MeCN, which exhibits a broad peak centered at 550 nm and a peak at 298 nm (Figure S24, Supporting Information), consistent with the presence of both [Te_2]$^{2-}$ and [Te_3]$^{2-}$ anions.[41,51] The formation of [Te_3]$^{2-}$ can be rationalized by invoking the disproportionation of [Te_2]$^{2-}$, a process that is known to occur for the [Te_2]$^{2-}$ anion in a variety of solvents.[41,46,50−52] The formation of polytellurides, such as [Te_3]$^{2-}$, upon dissolution of **1** is not ideal from a synthetic perspective, as they contain at least one Te atom with a formal 0 oxidation state. Nonetheless, this does not appear to adversely affect its use as a Te transfer reagent (see below), possibly because the average oxidation state of the tellurium does not change upon disproportionation.

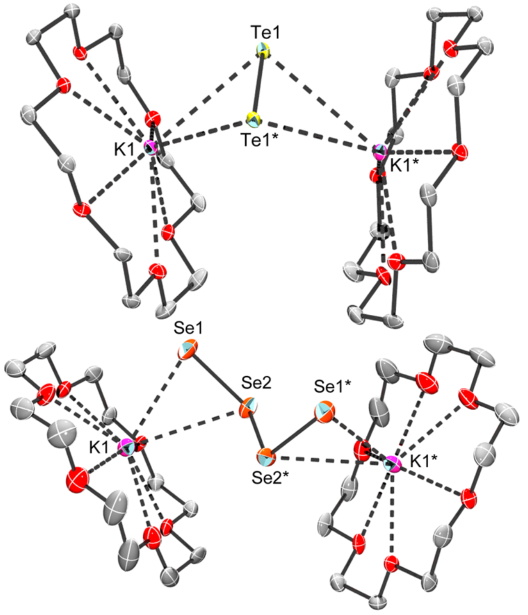
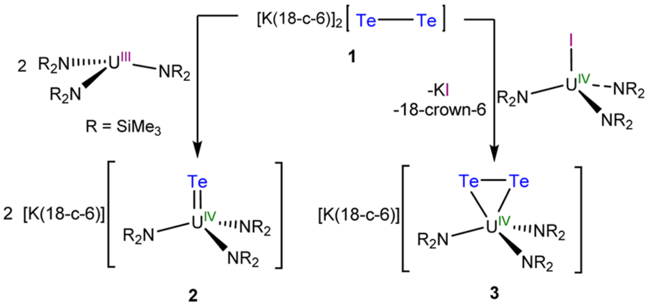


Figure 1. Solid state molecular structures of **1** (top) and **4**·2MeCN (bottom), with 50% probability ellipsoids. Two molecules of acetonitrile in **4** and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å): **1**, Te1−Te1* = 2.7877(6), K1−Te1 = 3.483(1), K1−Te1* = 3.6327(9); **4**, Se1−Se2 = 2.333(1), Se2−Se2* = 2.332(2), K1−Se1 = 3.208(2), K1−Se2 = 3.486(2).

We next tested the ability of **1** to act as a chalcogen atom transfer source for U(III). Addition of 0.5 equiv of **1** with [U(NR_2)$_3$] affords [K(18-crown-6)][U(Te)(NR_2)$_3$] (**2**) as black plates in 51% yield, after crystallization from Et_2O (Scheme 2). During the transformation, two U(III) centers reduce the [Te_2]$^{2-}$ anion, breaking the Te−Te bond, resulting in the formation of two U(IV) terminal tellurides. It should be noted that the [U(Te)(NR_2)$_3$]$^-$ anion has been previously synthesized,[53] but in much lower isolated yield.

The connectivity of complex **2** was verified by X-ray crystallography, and its solid state molecular structure is

Scheme 2. Syntheses of Complexes 2 and 3



shown in Figure 2. Selected metrical parameters are collected in Table 1. Complex **2** crystallizes in the triclinic space group $P\bar{1}$ as a diethyl ether solvate, **2**·0.5Et$_2$O. In addition, there are four independent molecules in the asymmetric unit. The [U(Te)(NR$_2$)$_3$]$^-$ anion in **2** features a pseudotetrahedral geometry similar to that previously observed for this moiety.[53] The U−Te bond lengths (av 2.90 Å) are significantly shorter than those reported for complexes with U(IV)−Te single bonds (av 3.12 Å),[25,54,55] and are suggestive of multiple bond character within the U−Te interaction. Furthermore, the U−Te bond distances of **2** are comparable to that previously reported for [Ph$_3$PCH$_3$][U(Te)(NR$_2$)$_3$] (2.866(2) Å).[25] The telluride ligand in complex **2** is also coordinated to the K$^+$ ion of the [K(18-crown-6)]$^+$ moiety. The K−Te bond distances (av 3.51 Å) are longer than the previously reported K−E distances (K−O = 2.640(5), av K−S = 3.112 Å) of the structurally identical oxo and sulfido complexes, consistent with the increase in ionic radii of Te^{2-} versus O^{2-} and S^{2-}.[26]

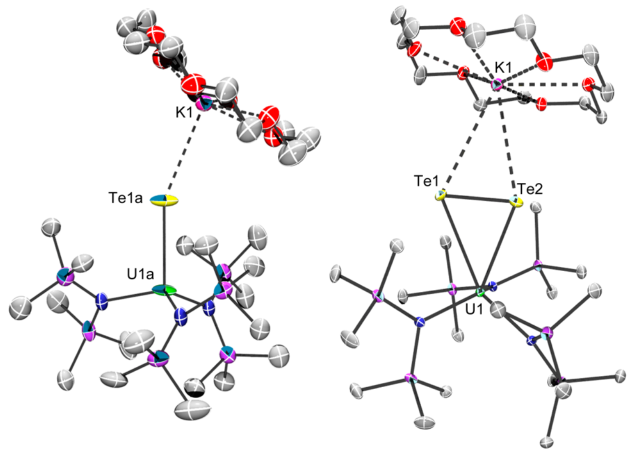


Figure 2. Solid state molecular structures of **2**·0.5Et$_2$O (left) and **3**·0.5Et$_2$O (right), with 50% probability ellipsoids. Three molecules of **2**, diethyl ether solvates, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): **2**, U1a−Te1a = 2.917(3), U1b−Te1b = 2.88(2), U2−Te2 = 2.879(2), U3−Te3 = 2.881(2), U4a−Te4a = 2.885(2), U4b−Te4b = 2.94(2), Te1a−K1 = 3.507(9), Te1b−K1 = 3.48(2), Te2−K2 = 3.467(2), Te3−K3 = 3.598(5), Te4a−K4 = 3.508(5); **3**, U1−Te1 = 3.1650(3), U1−Te2 = 3.0506(3), Te1−K1 = 3.7635(7), Te2−K1 = 3.6344(7), Te1−Te2 = 2.7456(4), N1−U1−N2 = 99.60(8), N1−U1−N3 = 107.78(8), N2−U1−N3 = 127.19(8).

Table 1. Selected Bond Distances (Å) and Angles (deg) for [K(18-crown-6)][U(E)(NR$_2$)$_3$] (E = O, S, Se, Te)

	O[a]	S[a]	Se (**6**)	Te (**2**)
U−E (av)	1.890(5)	2.449	2.590	2.898
E−K (av)	2.640(5)	3.112	3.192	3.511
U−N (av)	2.36	2.30	2.29	2.33
N−U−N (av)	117.0	116.8	116.8	112.2

[a] Taken from ref 26.

The ^{1}H NMR spectrum of **2** in pyridine-d_5 exhibits two broad resonances at −1.48 and 3.23 ppm, in a 54:24 ratio, assignable to the methyl groups of the silylamide ligands and the methylene groups of the 18-crown-6 moiety, respectively (Figure S3, Supporting Information), while its NIR spectrum is consistent with the presence of a U(IV) center (Figure S25, Supporting Information).[25,26,53,56−58]

We also explored the reactivity of **1** with the known U(IV) iodide, [U(I)(NR$_2$)$_3$],[56] on the assumption that **1** could also function as a [Te$_2$]$^{2-}$ synthon. Thus, addition of 1 equiv of **1** to a cold (−25 °C) stirring mixture of [U(I)(NR$_2$)$_3$] in pyridine results in the formation of a black solution. Crystallization of the resulting solid from Et$_2$O affords [K(18-crown-6)][U(η^2-Te$_2$)(NR$_2$)$_3$] (**3**) as a black crystalline solid in 38% yield (Scheme 2).

Complex **3** was characterized by X-ray crystallography, and its solid state molecular structure is shown in Figure 2. Complex **3** crystallizes in the triclinic space group $P\bar{1}$ as a diethyl ether solvate **3**·0.5Et$_2$O. Complex **3** features a highly distorted pseudotetrahedral geometry about the uranium center. In particular, the N—U—N angles (127.19(8)°, 107.78(8)°, and 99.60(8)°) are significantly distorted from those expected for an idealized tetrahedron, the geometry that is typically observed for [UX(NR$_2$)$_3$]$^{0/-}$-type complexes.[26,53] This deformation is likely due to the presence of three sterically demanding N(SiMe$_3$)$_2$ ligands, which cannot easily accommodate the [η^2-Te$_2$]$^{2-}$ ligand. As a result, the two U—Te bond distances in **3** are notably different (U1—Te1 = 3.1650(3), U1—Te2 = 3.0506(3) Å), which we attribute to the steric crowding of the [η^2-Te$_2$]$^{2-}$ ligand in the C_3 symmetric pocket of the tris(amide) ligand scaffold. The U—Te bond distances are comparable to those previously reported for U—Te single bonds.[54,59,60] These distances are also significantly longer than those of **2**, further supporting the multiple bond character in the U═Te interaction of the latter complex. The Te—Te distance in **3** (2.7456(4) Å) is similar to that of complex **1**, but slightly longer than the known range of Te—Te bond distances (2.665(2)−2.703(2) Å) in other structurally characterized terminal [η^2-Te$_2$]$^{2-}$ complexes.[61−71] The [Te$_2$]$^{2-}$ ligand in **3** also features weak dative interactions to the K$^+$ ion of the [K(18-crown-6)]$^+$ moiety, resulting in an overall [μ-η^2:η^2] coordination mode, similar to observed in complex **1**. The Te—K distances (Te1—K1 = 3.7635(7) and Te2—K1 = 3.6344(7) Å) are longer than those observed in complex **1**, but are comparable to those observed in K$_2$Te$_2$.[32]

To our knowledge, complex **3** is the first example of a uranium complex containing a terminal [η^2-Te$_2$]$^{2-}$ ligand. Only a few other terminal uranium dichalcogenides are known, including [K]$_4$[U(Se$_2$)$_4$], reported by Kanatzidis and co-workers in 1991.[72] More recently, Bart and co-workers reported the synthesis of [Tp*$_2$U(η^2-E$_2$)] (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate, E = S, Se),[73] while Mazzanti and co-workers reported the synthesis of the first U(V) terminal disulfide, [U((SiMe$_2$NPh)$_3$-tacn)(η^2-S$_2$)] (tacn =1,4,7-triazacyclononane).[74] Several bridging [η^2-E$_2$]$^{2-}$ complexes of uranium are also known, including [(R$_2$N)$_3$U]$_2$(μ-η^2:η^2-S$_2$),[25] and [((^{Ad}ArO)$_3$N)U]$_2$(μ-η^2:η^2-Se$_2$)(μ-DME) ((^{Ad}ArO)N) = tris(2-hydroxy-3-adamantyl-5-methyl-benzyl)amine).[75] More importantly, the rational synthesis of **3**, via a salt metathesis protocol, stands in stark contrast to most other routes to the [η^2-Te$_2$]$^{2-}$ ligand, which typically utilize elemental tellurium and whose outcomes are a challenge to predict. Accordingly, we suggest that complex **1** could be used for the rational installation of the terminal [η^2-Te$_2$]$^{2-}$ ligand in other systems.

The ^{1}H NMR spectrum of **3** in benzene-d_6 exhibits an extremely broad resonance at −4.98 ppm, assignable to the methyl groups of the silylamide ligands, and a broad resonance at 2.35 ppm, assignable to the methylene groups of the 18-

crown-6 moiety (Figure S4, Supporting Information). This latter resonance is shifted significantly upfield from that anticipated for free 18-crown-6 (3.39 ppm in benzene-d_6), suggestive of the presence of a paramagnetic shift due to formation of a close contact ion pair between [K(18-crown-6)]$^+$ and [U(η^2-Te$_2$)(NR$_2$)$_3$]$^-$ in solution. A similar shift was observed in the ^{1}H NMR spectrum of [K(18-crown-6)][U(S)(NR$_2$)$_3$] in benzene-d_6.[26] Upon dissolution of **3** in a more polar solvent, such as pyridine-d_5, the resonance assignable to the [K(18-crown-6)]$^+$ moiety shifts to 3.45 ppm, suggestive of the formation of better separated cation/anion pairs in this solvent (Figure S5, Supporting Information).

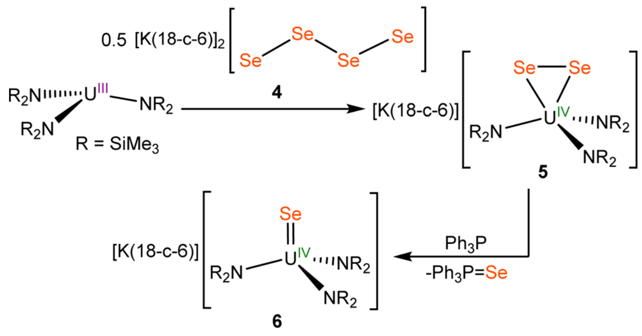
Given the demonstrated synthetic utility of complex **1**, we endeavored to synthesize its selenium analogue. Thus, addition of 0.5 equiv of KH to selenium powder, in the presence of 0.5 equiv of 18-crown-6, in tetrahydrofuran, results in the production of a deep brown suspension, concomitant with gas evolution, over the course of 18 h. The brown powder, [K(18-crown-6)]$_2$[Se$_4$] (**4**), can be isolated in 72% yield by collection on a glass frit (Scheme 1).

Orange-brown crystals of **4** suitable for X-ray crystallographic analysis were grown from a MeCN solution layered with Et$_2$O. Complex **4** crystallizes in the orthorhombic space group *Pbcn* as an acetonitrile solvate, **4**·2MeCN. In the solid state, complex **4** features an [Se$_4$]$^{2-}$ anion bridging two [K(18-crown-6)]$^+$ moieties via two independent η^2 interactions. Complex **4** features asymmetric K−Se bond lengths (K1−Se1 = 3.208(2), K1−Se2 = 3.486(2) Å), which is indicative of a weak dative interaction between K1 and Se2. Finally, **4** exhibits Se−Se bond lengths (Se1−Se2 = 2.333(1), Se2−Se2* = 2.332(2), Å) comparable to other structurally characterized [Se$_4$]$^{2-}$ complexes.[76−80]

Similar to complex **1**, complex **4** is insoluble in nonpolar solvents, but is soluble in acetonitrile or pyridine. Dissolution of **4** in acetonitrile generates a deep green solution, indicative of the presence of the [Se$_3$]$^{2-}$ anion.[38,52,81] As is observed for the polytelluride anions, [Se$_4$]$^{2-}$ readily undergoes disproportionation, forming a complex mixture of polyselenides, including [Se$_3$]$^{2-}$.[40,46,81−85] This hypothesis is further supported by the UV−vis spectrum of **4** in MeCN, which exhibits two bands at 434 and 598 nm, and a shoulder around 390 nm (Figure S26, Supporting Information), consistent with the presence of both [Se$_3$]$^{2-}$ and [Se$_4$]$^{2-}$ anions.[81,86] Interestingly, all attempts to generate the [Se$_2$]$^{2-}$ anion by reduction of elemental Se with KH were unsuccessful. For example, reaction of KH with Se and 18-crown-6 in a 1:1:1 molar ratio, in THF, provided a brown powder consistent with the formation of [Se$_4$]$^{2-}$, and not a red material that would be indicative of the presence of the [Se$_2$]$^{2-}$ anion.[81] This suggests that KH is not capable of reducing elemental Se to [Se$_2$]$^{2-}$ under these conditions.[42,46,52,87−89]

Complex **4** has proven to be a potent selenium transfer reagent for U(III). For example, addition of 0.5 equiv of **4** to a solution of [U(NR$_2$)$_3$] in a 2:1 mixture of THF and pyridine results in a rapid color change from dark green to orange-red. Crystallization of the resulting orange-red material from Et$_2$O affords [K(18-crown-6)][U(η^2-Se$_2$)(NR$_2$)$_3$] (**5**) as orange-red plates in 74% yield (Scheme 3). Formally, [Se$_4$]$^{2-}$ is acting as a 2e$^-$ oxidant during the transformation: two U(III) centers reduce the [Se$_4$]$^{2-}$ anion, breaking the central Se−Se bond, resulting in the formation of two U(IV) η^2-diselenide complexes. The ^{1}H NMR spectrum of **5** in pyridine-d_5 consists of two broad resonances at −7.65 and 3.47 ppm, assignable to the methyl groups of the silylamide ligands and the methylene groups of the 18-crown-6 moiety, respectively (Figure S9, Supporting Information), while the NIR spectrum of **5** is consistent with the presence of a U(IV) metal center (Figure S28, Supporting Information).[25,26,53,56−58]

Scheme 3. Syntheses of Complexes 5 and 6



Complex **5** crystallizes in the monoclinic space group *P*2$_1$, and its solid state molecular structure is shown in Figure 3. It features two molecules in the asymmetric unit that are nearly identical, so only one will be discussed in detail. Complex **5** is structurally similar to complex **3**; the only notable difference is that the dichalcogenide ligand is bound in an η^1 fashion to the K$^+$ cation in **5**, while in **3** it is coordinated in an η^2 fashion. As was observed for complex **3**, complex **5** features a highly distorted pseudotetrahedral geometry about the uranium center (N3−U1−N2 = 129.4(2), N3−U1−N1 = 106.6(2), N2−U1−N1 = 100.7(2)°), which we suggest is due to the steric crowding of the [η^2-Se$_2$]$^{2-}$ ligand by the tris(amide) ligand scaffold. As a consequence of this crowding, the U−Se bond distances of **5** (e.g, U1−Se1 = 2.7897(7), U1−Se2 = 2.8597(8) Å) feature a notable asymmetry. Nonetheless, the U−Se bond lengths in **5** are comparable to those observed for [Tp*$_2$U(η^2-Se$_2$)] (U−Se = 2.8147(5) and 2.7745(5) Å)[73] and [K]$_4$[U(Se$_2$)$_4$] (U−Se = 2.840(3), 2.903(3), 2.923(3), and 2.920(3) Å).[72] Finally, the Se−Se bond distances in **5** (Se1−Se2 = 2.368(1), Se3−Se4 = 2.366(1)Å) are similar to those observed

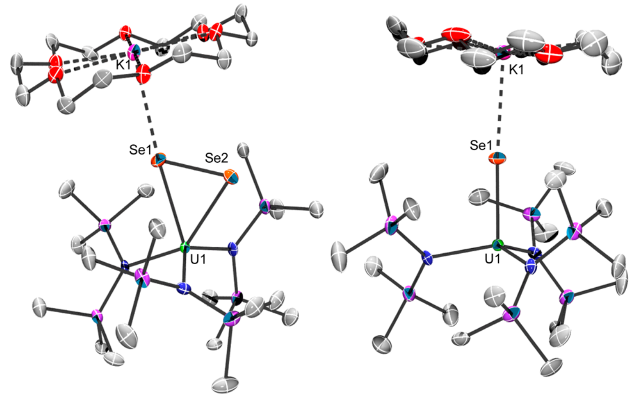


Figure 3. Solid state molecular structures of **5** (left) and **6** (right), with 50% probability ellipsoids. One molecule of **5**, one molecule of **6**, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): **5**, U1−Se1 = 2.7897(7), U1−Se2 = 2.8597(8), U2−Se3 = 2.7833(7), U2−Se4 = 2.8614(8), Se1−Se2 = 2.368(1), Se3−Se4 = 2.366(1), N1−U1−N2 = 100.7(2), N1−U1−N3 = 106.6(2), N2−U1−N3 = 129.4(2), N4−U2−N5 = 131.3(2), N4−U2−N6 = 100.3(2), N5−U2−N6 = 106.1(2); **6**, U1−Se1 = 2.585(1), U1−Se2 = 2.595(1), Se1−K1 = 3.150(3), Se2−K2 = 3.234(3).

in complex **4**, as well as to other structurally characterized complexes containing a terminal $[\eta^2\text{-Se}_2]^{2-}$ ligand (av 2.375 Å).[65,87,90−108]

We also explored the chalcogen atom transfer reactivity of complex **5**, as we hypothesized that **5** could be a viable precursor to a terminal monoselenide complex. Monitoring the reaction of **5** with 1 equiv of Ph_3P in pyridine-d_5 by ^1H NMR spectroscopy reveals the consumption of the starting material, and growth of a new broad resonance at −1.76 ppm, assignable to the methyl groups of the U(IV) monoselenide, $[K(18\text{-crown-6})][U(Se)(NR_2)_3]$ (**6**). In addition, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture reveals the formation of new resonance at 34.31 ppm, which is assignable to Ph_3PSe.[109,110] On a preparative scale, reaction of **1** equiv of PPh_3 with **5** in Et_2O affords $[K(18\text{-crown-6})][U(Se)(NR_2)_3]$ (**6**) as orange-red crystalline solid in 70% yield after workup (Scheme 3). The ^1H NMR spectrum of **6** in pyridine-d_5 consists of two broad resonances at −1.76 and 3.07 ppm, assignable to the methyl groups of the silylamide ligands and the methylene groups of the 18-crown-6 moiety, respectively (Figure S10, Supporting Information). Finally, the NIR spectrum of **6** is consistent with the proposed U(IV) oxidation state assignment, demonstrating that no change in uranium oxidation state occurs upon reaction of **5** with Ph_3P (Figure S29, Supporting Information).[25,26,53,56−58]

Complex **6** crystallizes in the triclinic space group $P\overline{1}$ and features two molecules in the asymmetric unit (Figure 3). Selected metrical parameters for **6** are collected in Table 1. Complex **6** is structurally identical with complex **2**.[26] The $[U(Se)(NR_2)_3]^-$ anion in **6** exhibits a pseudotetrahedral geometry about the uranium center, as evidenced by the N—U—N (av N—U—N = 116.8°) and Se—U—N angles (av Se—U—N = 100.5°).[26,53] The U—Se bond lengths in **6** (2.585(1) and 2.595(1) Å) are shorter than those observed in complex **5**, and are suggestive of multiple bond character in the U═Se interaction. They are also slightly shorter than the U—Se bond length in the only other reported U(IV) terminal selenide, $[Ph_3PCH_3][U(Se)(NR_2)_3]$ (2.6463(7) Å).[53] Finally, The E—K distances in **6** (3.150(3) and 3.234(3) Å) are shorter than those observed for complex **2** and longer than those of the analogous oxide and sulfide complexes (Table 1), consistent with the trend of increasing ionic radii as one moves down the group.

Interestingly, reaction of $[U(NR_2)_3]$ with 0.25 equiv of **4** in Et_2O results in the formation of complexes **5** and **6**, and the previously characterized bridging selenide complex, $[U(N(SiMe_3)_2)_3]_2(\mu\text{-Se})$,[25] in an approximate 1:1:1 ratio (see the Supporting Information). The formation of $[U(N(SiMe_3)_2)_3]_2(\mu\text{-Se})$ in this example can be rationalized by invoking Se atom transfer from complex **5** to unreacted $[U(NR_2)_3]$, which is present in excess under these conditions. Its presence further underscores our argument about the importance of matching the oxidation state of the chalcogen transfer reagent with the U(III/IV) redox couple.

CONCLUSION

In summary, we have demonstrated that the polychalcogenides, $[E_n]^{2-}$ (E = Te, n = 2; E = Se; n = 4), are effective chalcogen atom transfer reagents for the uranium tris(silylamide), $[U(NR_2)_3]$. Importantly, these reagents appear to be better matched to the U(III/IV) redox couple than traditional chalcogen atom transfer reagents, such as Ph_3PE or the elemental chalcogens. We suggest that $[K(18\text{-crown-6})]_2[Te_2]$ and $[K(18\text{-crown-6})]_2[Se_4]$ will be useful for installing the E^{2-} and $[E_2]^{2-}$ ligands in other complexes, especially those that are reluctant to undergo $2e^-$ redox chemistry, such as those of the first row transition metals and lanthanides. In this regard, we are exploring the utility of $[K(18\text{-crown-6})]_2[Te_2]$ and $[K(18\text{-crown-6})]_2[Se_4]$ to effect chalcogen atom transfer in other chemical systems. We are also exploring the ability of the polysulfide anions to perform analogous sulfur atom transfer reaction with $[U(NR_2)_3]$.

EXPERIMENTAL SECTION

General. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions under an atmosphere of nitrogen. Hexanes, diethyl ether (Et_2O), and toluene were dried using a Vacuum Atmospheres DRI-SOLV Solvent Purification system and stored over 3 Å sieves for 24 h prior to use. Tetrahydrofuran (THF) was distilled twice, first from calcium hydride and then from sodium benzophenone ketyl, and stored over 3 Å molecular sieves for 24 h prior to use. Dimethoxyethane (DME) was distilled from sodium benzophenone ketyl and stored over 3 Å molecular sieves for 24 h prior to use. Pyridine, benzene-d_6, pyridine-d_5, and tetrahydrofuran-d_8 were dried over 3 Å molecular sieves for 24 h prior to use. $[U(NR_2)_3]$[111] and $[U(I)(NR_2)_3]$,[56] were synthesized according to the previously reported procedures. All other reagents were purchased from commercial suppliers and used as received.

NMR spectra were recorded on a Varian UNITY INOVA 400 spectrometer, a Varian UNITY INOVA 500 spectrometer, or a Varian UNITY INOVA 600 MHz spectrometer. ^1H NMR spectra were referenced to external $SiMe_4$ using the residual protio solvent resonances as internal standards. $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4 in D_2O. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer with a NXR FT Raman Module. UV−vis−NIR experiments were performed on a UV-3600 Shimadzu spectrophotometer. Elemental analyses were performed by the Micro-Mass Facility at the University of California, Berkeley.

Synthesis of $[K(18\text{-crown-6})]_2[Te_2]$ (1). To a mixture of Te powder (200.8 mg, 1.57 mmol) and 18-crown-6 (422.0 mg, 1.60 mmol) in tetrahydrofuran (4 mL) was added KH (63.8 mg, 1.59 mmol). This mixture was allowed to stir for 18 h, during which time gas evolution was observed, concomitant with the deposition of a violet-blue powder. This material was collected by filtration through a glass frit, and subsequently rinsed with Et_2O (5 mL) to provide a violet-blue powder (488.5 mg, 72% yield). This material was used in subsequent reactions without further purification. Anal. Calcd for $C_{24}H_{48}K_2O_{12}Te_2$: C, 33.44; H, 5.61. Found: C, 26.27; H, 4.39. The low carbon % is attributed to the incomplete solvation of the K^+ cations by 18-crown-6. ^1H NMR (600 MHz, 25 °C, CD_3CN): δ 3.58 (s, 18-crown-6). IR (KBr Pellet, cm^{-1}): 529 (w), 614 (w), 730 (w), 839 (m), 965 (s), 1106 (s), 1251 (m), 1283 (m), 1351 (s), 1433 (w), 1452 (m), 1473 (m), 2744 (w), 2822 (m), 2882 (s). UV−vis−NIR (CH_3CN, 0.174 mM, 25 °C, L mol^{-1} cm^{-1}): 298 (ε = 10 661), 550 (ε = 3140). Crystals of **1** suitable for X-ray crystallography were grown from a dilute acetonitrile solution layered with diethyl ether.

Synthesis of $[K(18\text{-crown-6})]U(Te)(NR_2)_3]$ (2). To a deep purple, cold (−25 °C), stirring solution of $[U(N(SiMe_3)_2)_3]$ (120.2 mg, 0.17 mmol) in THF (2 mL) was added dropwise a cold (−25 °C), red-violet solution of **1** (72.1 mg, 0.083 mmol) in pyridine (2 mL). This solution was allowed to stir for 30 min, whereupon the solvent was removed in vacuo and the resulting black solid was triturated with hexanes (5 mL). The resulting black powder was extracted with diethyl ether (6 mL) and filtered through a Celite column supported on glass wool (0.5 cm × 3 cm). The volume of the filtrate was reduced to 1 mL in vacuo. Storage of this solution at −25 °C for 24 h resulted in the deposition of black crystals, which were isolated by decanting off the supernatant (98.0 mg, 51%). It should be noted that complex **1** likely undergoes disproportionation to the higher polychalcogenides upon dissolution in pyridine, as indicated by the violet-red solution that it forms in this solvent. Anal. Calcd for $C_{30}H_{78}KN_3O_6Si_6TeU\cdot$

$0.5C_4H_{10}O$: C, 32.37; H, 7.05; N, 3.54. Found: C, 32.37; H, 6.58; N, 3.48. ^{1}H NMR (400 MHz, 25 °C, pyridine-d_5): δ −1.48 (br s, 54H, NSiCH_3), 3.23 (br s, 24H, 18-crown-6). IR (KBr Pellet, cm^{-1}): 609 (m), 662 (m), 688 (m), 723 (m), 841 (s), 883 (m), 934 (m), 964 (m), 1109 (s), 1183 (w), 1251 (m), 1284 (w), 1352 (m), 1454 (w), 1473 (w), 2894 (m), 2953 (m). UV−vis−NIR (C_4H_8O, 5.17 mM, 25 °C, L mol^{-1} cm^{-1}): 1016 (ε = 16.3), 1098 (ε = 31.9), 1198 (ε = 26.5), 1500 (ε = 12.8), 1650 (ε = 14.7), 1794 (ε = 13.5), 2060 (ε = 23.8), 2166 (ε = 29.2).

Synthesis of [K(18-crown-6)][U(Te_2)(NR_2)$_3$] (3). To a cold (−25 °C), stirring mixture of [U(I)(N($SiMe_3$)$_2$)$_3$] (61.5 mg, 0.073 mmol) in pyridine (3 mL) was added dropwise a cold (−25 °C) solution of **1** (64.0 mg, 0.074 mmol) in pyridine (3 mL). This mixture was allowed to stir for 20 min, whereupon the solvent was removed in vacuo and resulting black solid was triturated with hexanes (3 × 5 mL). The black powder was then extracted with diethyl ether (8 mL) and filtered through a Celite column supported on glass wool (0.5 cm × 3 cm). The volume of the filtrate was reduced to 1 mL in vacuo. Storage of this solution at −25 °C for 24 h resulted in the deposition of black crystals, which were isolated by decanting off the supernatant (34.9 mg, 38%). Anal. Calcd for $C_{30}H_{78}KN_3O_6Si_6Te_2U$: C, 28.20; H, 6.15; N, 3.29. Found: C, 28.49; H, 6.29; N, 3.04. ^{1}H NMR (400 MHz, 25 °C, benzene-d_6): δ −4.98 (br s, 54H, NSiCH_3), 2.35 (br s, 24H, 18-crown-6). ^{1}H NMR (400 MHz, 25 °C, pyridine-d_5): δ −6.40 (br s, 54H, NSiCH_3), 3.45 (br s, 24H, 18-crown-6). IR (KBr mull, cm^{-1}): 610 (w), 662 (w), 688 (w), 773 (w), 842 (s), 885 (m), 934 (m), 936 (m), 1108 (s), 1182 (w), 1251 (m), 1284 (w), 1352 (w), 1454 (w), 1473 (w), 2894 (m), 2954 (m). UV−vis−NIR (C_4H_8O, 4.41 mM, 25 °C, L mol^{-1} cm^{-1}): 1020 (ε = 33.3), 1078 (ε = 40.5), 1136 (ε = 34.0), 1318 (ε = 17.9), 1440 (ε = 10.4), 1500 (ε = 13.8), 1658 (ε = 11.3), 1804 (ε = 18.6), 2054 (ε = 63.4), 2180 (ε = 76.8).

Synthesis of [K(18-crown-6)]$_2$[Se_4] (4). To a mixture of Se powder (34.2 mg, 0.43 mmol) and 18-crown-6 (57.2 mg, 0.22 mmol) in tetrahydrofuran (4 mL) was added KH (8.7 mg, 0.22 mmol). This mixture was allowed to stir for 18 h, during which time gas evolution was observed, concomitant with the deposition of a brown powder. This material was collected by filtration through a glass frit, and subsequently rinsed with Et_2O (5 mL) to provide a brown powder (78.6 mg, 72% yield). This material was used in subsequent reactions without further purification. Anal. Calcd for $C_{24}H_{48}K_2O_{12}Se_4$: C, 31.24; H, 5.24; N, 0.0. Found: C, 29.76; H, 4.73; N, 0.29. The low carbon % is attributed to the incomplete solvation of the K^+ cations by 18-crown-6. ^{1}H NMR (500 MHz, 25 °C, CD_3CN): δ 3.58 (s, 18-crown-6). IR (KBr mull, cm^{-1}): 530 (w), 838 (m), 964 (s), 1106 (s), 1250 (m), 1285 (m), 1351 (m), 1454 (m), 1473 (m), 2824 (m), 2894 (s). UV−vis−NIR (CH_3CN, 0.323 mM, 25 °C, L mol^{-1} cm^{-1}): 390 (sh) (ε = 5280), 434 (ε = 6721), 598 (ε = 1401). Crystals of **4** suitable for X-ray crystallography were grown from a dilute acetonitrile solution layered with diethyl ether.

Synthesis of [K(18-crown-6)][U(Se_2)(NR_2)$_3$] (5). To a deep green, cold (−25 °C), stirring mixture of **4** (89.9 mg, 0.097 mmol) dissolved in a 2:1 mixture of tetrahydrofuran and pyridine (4 mL) was added a deep purple, cold (−25 °C) solution of [U(N($SiMe_3$)$_2$)$_3$] (132.9 mg, 0.18 mmol) in tetrahydrofuran (2 mL). This solution was allowed to stir for 20 min, whereupon the solvent was removed in vacuo and the resulting orange-red solid was triturated with Et_2O (5 mL) and hexanes (2 × 5 mL). The orange-red powder was then extracted with diethyl ether (10 mL) and filtered through a Celite column supported on glass wool (0.5 cm × 2 cm). The volume of the orange-red filtrate was reduced in vacuo to 1 mL. This solution was then transferred to a 4 mL scintillation vial that was placed inside a 20 mL scintillation vial. Toluene (6 mL) was then added to the outer vial. Storage of this two vial system for 72 h resulted in the deposition of orange-red crystalline solid, which was isolated by decanting the supernatant (161.0 mg, 74%). Anal. Calcd for $C_{30}H_{78}KN_3O_6Se_2Si_6U$: C, 30.52; H, 6.66; N, 3.56. Found: C, 30.60; H, 6.86; N, 3.62. ^{1}H NMR (600 MHz, 25 °C, pyridine-d_5): δ −7.65 (br s, 54H, NSiCH_3), 3.47 (br s, 24H, 18-crown-6). IR (KBr mull, cm^{-1}): 610 (m), 663 (m), 772 (m), 845 (s), 897 (m), 921 (s), 964 (m), 1111 (s), 1182 (w), 1249 (s), 1284 (w), 1352 (m), 1454 (w), 1473 (w), 2826 (w), 2894 (s), 2951 (s). UV−vis−NIR (C_4H_8O, 3.92 mM, 25 °C, L mol^{-1} cm^{-1}): 1020 (ε = 45.6), 1080 (ε = 51.0), 1134 (ε = 43.1), 1322 (ε = 25.7), 1450 (ε = 16.8), 1508 (ε =18.9), 1626 (ε =15.8), 1806 (ε = 17.6), 2062 (ε = 60.7), 2160 (ε = 68.8).

Synthesis of [K(18-crown-6)][U(Se)(NR_2)$_3$] (6). To a deep orange-red, cold (−25 °C), stirring solution of **5** (102.5 mg, 0.087 mmol), in diethyl ether (3 mL) was added a cold (−25 °C) solution of Ph_3P (22.2 mg, 0.085 mmol) in diethyl ether (2 mL). The solution was allowed to stir for 15 min, during which time a white precipitate was deposited in the reaction vial. The reaction mixture was filtered through a Celite column supported on glass wool (0.5 cm × 2 cm). The volume of the orange-red filtrate was reduced in vacuo to 3 mL. Storage of this solution at −25 °C for 24 h resulted in the further deposition of colorless crystals, subsequently identified as $Ph_3P{=}Se$ by ^{31}P{^{1}H} NMR spectroscopy. These were isolated by decanting the supernatant. The volume of the supernatant was reduced in vacuo to 2 mL. This solution was then transferred to a 4 mL scintillation vial that was place inside a 20 mL scintillation vial. Toluene (6 mL) was then added to the outer vial. Storage of this two vial system for 48 h resulted in the deposition of an orange-red crystalline solid, which was isolated by decanting the supernatant (67.0 mg, 70%). Anal. Calcd for $C_{30}H_{78}KN_3O_6SeSi_6U$: C, 32.71; H, 7.14; N, 3.81. Found: C, 32.93; H, 6.87; N, 3.75. ^{1}H NMR (600 MHz, 25 °C, pyridine-d_5): δ −1.77 (br s, 54H, NSiCH_3), 3.12 (br s, 24H, 18-crown-6). IR (KBr pellet, cm^{-1}): 689 (w), 756 (w), 844 (s), 886 (m), 935 (s), 1046 (w), 1105 (s), 1182 (m), 1252 (s), 1285 (w), 1352 (m), 2896 (s), 2955 (s). UV−vis−NIR (C_4H_8O, 4.77 mM, 25 °C, L mol^{-1} cm^{-1}): 700 (ε = 33.9), 720 (ε = 32.0), 928 (ε = 6.9), 1112 (ε = 26.0), 1208 (ε = 32.5).

X-ray Crystallography. Data for **1**−**6** were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromator with a Mo Kα X-ray source (α = 0.710 73 Å). The crystals were mounted on a cryoloop under Paratone-N oil, and all data were collected at 100(2) K using an Oxford nitrogen gas cryostream. Data were collected using ω scans with 0.5° frame widths. Frame exposures of 10 s (low angle) and 15 s (high angle) were used for **1**. Frame exposures of 10 s were used for **2** and **6**. Frame exposures of 2 s were used for **3**. Frame exposures of 60 s were used for **4**. Frame exposures of 5 s (low angle) and 10 s (high angle) were used for **5**. Data collection and cell parameter determination were conducted using the SMART program.[112] Integration of the data frames and final cell parameter refinement were performed using SAINT software.[113] For complexes **1**−**4** and **6**, the absorption correction was performed using SADABS,[114] while for complex **5**, which crystallized as a racemic twin in a ratio of 46:54, the absorption correction was performed with TWINABS.[115] Subsequent calculations were carried out using SHELXTL.[116] Structure determination was done using direct or Patterson methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[116]

Complex **2** crystallizes in the triclinic space group $P\overline{1}$ with four independent molecules in the asymmetric unit, which raises the concern that the incorrect space group was chosen for this crystal. Inspection of the asymmetric unit reveals that the four molecules of **2** differ significantly in their U−Te−K angles (e.g., U1a−Te1a−K1 = 155.4(1)°, U1b−Te1b−K1 = 133.8(8)°, U2−Te2−K2 = 162.1(1)°, U3−Te3−K3 = 132.96(9)°, U4a−Te4a−K4 = 149.2(1)°), which disrupts any possible symmetry operations that could interrelate the four molecules, and results in the observed low symmetry space group. For this structure, U1, Te1, U4, and Te4 exhibited positional disorder, wherein each atom was modeled over two sites in a 90:10 ratio. In addition, the anisotropic displacement parameters of the K, Si, N, O, and C atoms among four molecules in the asymmetric unit were constrained with the EADP command, while for the U and Te atoms, only the thermal parameters of the disordered pairs were constrained. Finally, one of the diethyl ether solvate molecules in **2** exhibited positional disorder; one carbon of this molecule was modeled over two positions in a 50:50 ratio. The C−C and C−O bond distances of all the diethyl ether solvate molecules were constrained to 1.54 and 1.45

Å, respectively, using the DFIX command. Hydrogen atoms were not assigned to disordered carbon atoms. The diethyl ether solvate molecule in **3** exhibited positional disorder. One carbon atom was modeled over two positions in a 50:50 ratio. The C−C and C−O bond distances of the diethyl ether solvate were constrained to 1.54 and 1.45 Å, respectively, using the DFIX command. The C−C and C−N bond distances of the acetonitrile solvate molecule of **4** were constrained to 1.45 and 1.1 Å, respectively, using the DFIX command. A summary of the relevant crystallographic data for **1**−**6** is presented in Supporting Information Tables S1 and S2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic details (as CIF files) and spectral data for complexes **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences, Biosciences, and Geosciences Division under Contract DE-FG02-09ER16067.

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