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Reversible Chalcogen-Atom Transfer to a Terminal Uranium Sulfide

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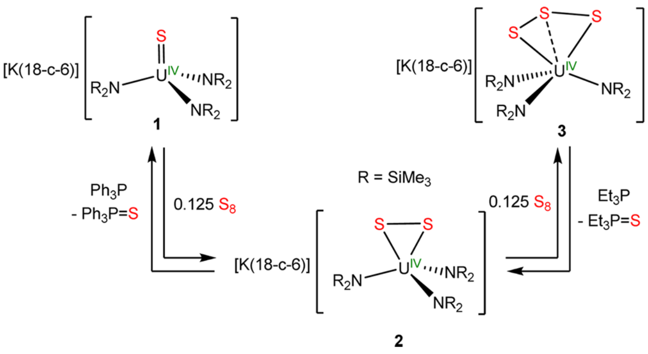
Supporting Information

ABSTRACT: The reaction of elemental S or Se with [K(18-crown-6)][U(S)(NR_2)$_3$] (**1**) results in the formation of the new uranium(IV) dichalcogenides [K(18-crown-6)][U(η^2-S_2)(NR_2)$_3$] (**2**) and [K(18-crown-6)][U(η^2-SSe)(NR_2)$_3$] (**5**). The further addition of elemental S to **2** results in the formation of [K(18-crown-6)][U(η^3-S_3)(NR_2)$_3$] (**3**). Complexes **2**, **3**, and **5** can be reconverted into **1** via the addition of R_3P (R = Et, Ph), concomitant with the formation of $R_3P{=}E$ (E = S, Se).

The addition of sulfur to an organic substrate provides convenient access to a variety of useful products, such as thiiranes, which serve as attractive starting materials for a diverse array of sulfur-containing compounds.[1−6] The use of S_8 as the sulfur source in these reactions is particularly attractive because it is both cheap and atom economical. However, catalysts that can perform S-atom transfer using S_8 are rare,[4,5] and those that are known have limited scope.[6−11] For example, [(EtO)$_2$PS_2)$_2$Mo═O] can catalyze S-atom transfer from S_8 to a small selection of activated olefins,[9,10] but other substrates have proven more challenging. Interestingly, in this example, the active S donor is likely [(EtO)$_2$PS_2)$_2$Mo═O(η^2-S_2)]. This complex transfers an S atom to the olefin, forming a thiirane and [(EtO)$_2$PS_2)$_2$Mo═O(S)]; the latter then reacts with S_8 to regenerate [(EtO)$_2$PS_2)$_2$Mo═O(η^2-S_2)]. Similarly, Bergman and co-workers demonstrated that [Cp*$_2$Ti(η^2-S_2)] could transfer an S atom to PR_3 (R = Me, Ph), forming the monosulfide [Cp*$_2$Ti(S)]. This complex could be converted back to the disulfide via the addition of S_8. Interestingly, [Cp*$_2$Ti(η^2-S_2)] reacts with another equiv of sulfur to give a trisulfide complex, [Cp*$_2$Ti(κ^2-S_3)].[12,13] Several other metal complexes are also competent for catalytic S-atom transfer; however, they invariably use thiiranes as the S-atom source.[4,5,14] These aforementioned limitations point to the need for further exploration of chalcogen-atom reactivity with metal complexes. Herein, we demonstrate reversible chalcogen-atom transfer to a terminal uranium sulfide using elemental S and Se as the chalcogen sources. This represents the first reported reactivity study for a terminal chalcogenide of uranium.

Recently, we reported the synthesis of a terminal uranium(IV) monosulfide complex, [K(18-crown-6)][U(S)(NR_2)$_3$] (**1**; R = $SiMe_3$), via oxidation of [U(NR_2)$_3$] with KSCPh_3.[15] We have subsequently endeavored to study the reactivity of this complex with chalcogens and chalcogen sources. Thus, the reaction of 0.125 equiv of S_8 with **1**, in tetrahydrofuran (THF), results in the formation of a red-orange solution. Crystallization from Et_2O/pentane affords the new uranium(IV) disulfide, [K(18-crown-6)][U(η^2-S_2)(NR_2)$_3$] (**2**), as red-orange crystals in 59% yield (Scheme 1).

Scheme 1. Reversible S-Atom Transfer between Uranium Sulfides



Complex **2** crystallizes in the monoclinic space group $P2_1/n$, and its solid-state molecular structure is shown in Figure 1.

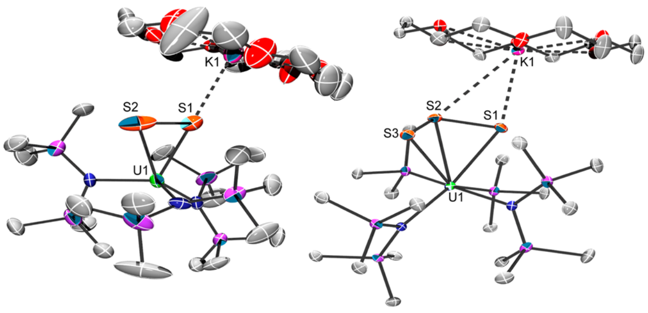


Figure 1. Solid-state molecular structures of complexes **2** (left) and **3**·Et_2O (right), with 50% probability ellipsoids. Et_2O solvate and H atoms are omitted for clarity.

Complex **2** features a distorted tetrahedral geometry about uranium [N1−U1−N2 = 102.4(3)°, N2−U1−N3 = 108.1(3)°, and N1−U1−N3 = 128.4(3)°], and the U−S bond distances are quite different [U1−S1 = 2.589(4) Å and U1−S2 = 2.747(3) Å], both attributable to steric crowding between the [η^2-S_2]$^{2-}$ moiety and the bulky silylamide coligands.[16] The S−S bond distance in 2 [2.160(7) Å] is longer than those of other uranium disulfides,[17−22] possibly because of the coordination of the [K(18-crown-6)]+ moiety to the [S2]2- ligand. The K1−S1 bond distance in **2** [3.176(5) Å] is similar to that of **1** (ave K−S

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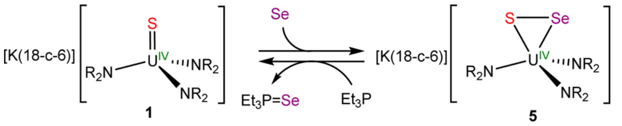
= 3.112 Å) and shorter than the K−E bond distances of the structurally identical diselenide, [K(18-crown-6)][U(η^2-Se_2)(NR_2)$_3$] (ave K−Se = 3.260 Å), and ditelluride, [K(18-crown-6)][U(η^2-Te_2)(NR_2)$_3$] (ave K−Te = 3.704 Å),[16] consistent with the smaller ionic radii of S^{2-} versus Se^{2-} and Te^{2-}. We do not believe that the K^+ cation plays a role in stabilizing the [η^2-S_2]$^{2-}$ moiety. As evidence, [K(2,2,2-cryptand)][U(S)(NR_2)$_3$], which we have previously prepared,[15] appears to feature reactivity identical with that of its 18-crown-6 analogue, **1**.

Similar to **1**, complex **2** also reacts with elemental S. The addition of 0.125 equiv of S_8 to complex **2** results in the clean formation of uranium(IV) trisulfide, [K(18-crown-6)][U(η^3-S_3)(NR_2)$_3$] (**3**; Scheme 1). Crystallization from Et_2O affords **3** as vibrant orange crystals in 34% yield. Complex **3** crystallizes in the triclinic space group $P\overline{1}$ as an Et_2O solvate, **3**·Et_2O (Figure 1). Complex **3** is the first reported uranium trisulfide and features the unprecedented [η^3-S_3]$^{2-}$ ligand. This contrasts with other structurally characterized complexes containing the terminal [S_3]$^{2-}$ ligand, which feature a κ^2-coordination mode.[23−28] As was observed for **2**, complex **3** exhibits unequal U−S bond distances [U1−S1 2.835(1) Å, U1−S2 = 2.819(1) Å, and U1−S3 = 2.760(1) Å], a consequence of the steric clash between the [η^3-S_3]$^{2-}$ ligand and the bulky silylamide ligand. The S−S bond distances in **3** [S1−S2 = 2.059(2) Å and S2−S3 = 2.066(1) Å] are shorter than those of **2** but similar to those of other terminal uranium disulfides (ave 2.08 Å).[17−21]

We also explored the scope of chalcogen-atom transfer to the terminal sulfide ligand in **1**. Thus, the addition of 1 equiv of Se to a solution of complex **1**, in a 2:1 mixture of Et_2O/THF, results in a color change to dark orange-red over the course of 2 h. Crystallization from Et_2O affords the selenosulfide complex [K(18-crown-6)][U(η^2-SSe)(NR_2)$_3$] (**5**) as a dark orange-red crystalline solid in 52% yield (eq 1). Complex **5** crystallizes in the monoclinic space group $P2_1$ with two independent molecules in the asymmetric unit (Figure 2). Complex **5** represents the first structurally characterized complex with a terminal [SSe]$^{2-}$ ligand; other selenosulfide complexes feature the bridging [μ-η^2:η^2] binding mode.[29−36] Complex **5** is isostructural to **2**, and, not surprisingly, its S−Se bond distances [Se1−S1 = 2.242(3) and Se2−S2 = 2.240(3) Å] are longer than the S−S distance in **2** but shorter than the Se−Se distances in [K(18-crown-6)][U(η^2-Se_2)(NR_2)$_3$] (ave 2.367 Å).[16] In addition, the U−S [2.664(2) and 2.653(2) Å] and U−Se [2.845(1) and 2.851(1) Å] bond distances in **5** are comparable to the U−S distances in **2** (ave 2.668 Å) and the U−Se distances in [K(18-crown-6)][U(η^2-Se_2)(NR_2)$_3$] (ave 2.824 Å), respectively.[16] Attempts to synthesize the analogous tellurosulfide complex were unsuccessful. Addition of elemental Te to complex **1**, in pyridine-d_5, results in no reaction after 60 h, as determined by ^{1}H NMR spectroscopy (Figure S8 in the SI). The inability of elemental Te to oxidize the S^{2-} ligand of **1** is consistent with the lower oxidation potential of Te versus S and Se.[37]



(1)

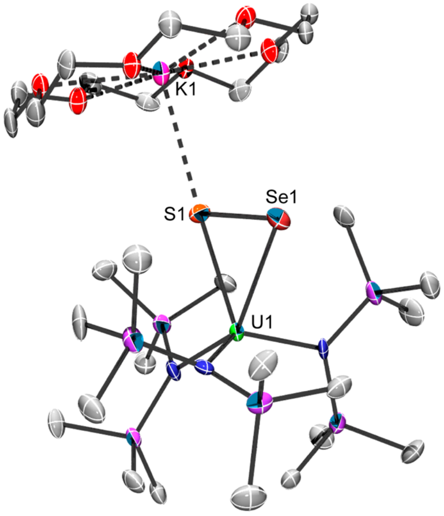


Figure 2. Solid-state molecular structure of **5** with 50% probability ellipsoids. H atoms omitted for clarity.

Complexes **2**, **3**, and **5** were also characterized by ^{1}H NMR spectroscopy. In pyridine-d_5, complex **2** exhibits two broad resonances at −8.20 and 3.52 ppm, assignable to the methyl groups of the silylamide ligands and the 18-crown-6 moiety, respectively (Figure S4 in the SI). Complexes **3** and **5** feature nearly identical chemical shifts, but the silylamide resonance for **3** is extremely broad (full width at half-maximum = 2150 Hz; Figure S5 in the SI), possibly reflecting the slow rotation about the U−N bond due to the presence of the bulky [η^3-S_3]$^{2-}$ ligand. The near-IR spectra of **2**, **3**, and **5** are all consistent with the presence of the U^{IV} metal ion (Figures S19−S21 in the SI),[15,22] which is significant because it confirms that no metal-based redox chemistry is occurring; all redox chemistry is localized on the chalcogenide ligand.

Previously, we demonstrated that the reaction of [K(18-crown-6)][U(η^2-Se_2)(NR_2)$_3$] with Ph_3P afforded [K(18-crown-6)][U(Se)(NR_2)$_3$] and $Ph_3P{=}Se$.[16] This result encouraged us to explore the reactions of complexes **2** and **3** with phosphines. Gratifyingly, the addition of 1 equiv of Et_3P to a cold (−25 °C) solution of **3**, in Et_2O, results in a color change from orange to red-orange over the course of 1 h. Crystallization from Et_2O affords **2** as a red-orange crystalline solid in 59% yield (Scheme 1). Also formed in this reaction is $Et_3P{=}S$, as confirmed by the in situ ^{31}P{^{1}H} NMR spectrum of the reaction mixture (Figure S3 in the SI).[38,39] Similarly, the addition of PPh_3 to a solution of complex **2** in pyridine-d_5 results in the formation of **1** and $Ph_3P{=}S$ (Scheme 1), as evidenced by in situ ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, respectively (Figures S9 and S10 in the SI).[15,38] The reactivity of complex **5** with phosphines was also probed. The reaction of **5** with 1 equiv of Et_3P results in the rapid formation of $Et_3P{=}Se$ and complex **1**, as determined by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies (eq 1 and Figures S11 and S12 in the SI).[15,40] No evidence for the formation of [K(18-crown-6)][U(Se)(NR_2)$_3$] or $Et_3P{=}S$ is observed in the reaction mixture, which is surprising considering that the P−S bond dissociation enthalpy is greater than that of P−Se.[41] That said, the longer U−Se bond versus the U−S bond in **5** suggests that the barrier for Se transfer is lower than that for S transfer, which provides a possible kinetic explanation for the observed chemoselectivity.

The reactivity of complex **1** closely parallels that of several transition-metal systems, such as [Cp*$_2$Ti(S)].[12,13] However, **1** is the first actinide chalcogenide that undergoes demonstrated reversible chalcogen-atom transfer. Previous chalcogen reactivity with the actinides has been restricted to either atom addition or atom abstraction. For example, Meyer and co-workers reported that $[((^{Ad}ArO)_3N)U(DME)]_2(\mu\text{-Se})$ reacts with elemental Se to form $[((^{Ad}ArO)_3N)U]_2(\mu\text{-}\eta^2{:}\eta^2\text{-Se}_2)(\mu\text{-DME})$,[42] but the Se atom abstraction reaction was not described. Similarly, Mazzanti and co-workers reported that the uranium(V) disulfide $[U((SiMe_2NPh)_3\text{-tacn})(\eta^2\text{-S}_2)]$ reacts with Ph_3P to give $Ph_3P{=}S$, but the metal-containing component of the reaction mixture proved to be intractable.[17]

In summary, we have demonstrated that elemental S and Se react with the terminal sulfide complex **1** to generate new terminal uranium(IV) dichalcogenide complexes, **2** and **5**. Importantly, this addition is reversible, and the reaction of the dichalcogenides with a phosphine regenerates complex **1**, concomitant with the formation of $R_3P{=}E$ (E = S, Se). This reversibility suggests that **1** could be developed as a catalyst for chalcogen-atom transfer, and we are currently exploring this possibility.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, crystallographic details (as a CIF file), and spectral data for complexes **2**–**5**. 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.

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