Reactivity of uranium(IV) bridged chalcenido complexes U^{IV}–E–U^{IV} (E = S, Se) with elemental sulfur and selenium: synthesis of polychalcenido-bridged uranium complexes†

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We report the syntheses, electronic properties, and molecular structures of a series of polychalcenido-bridged dinuclear uranium species. These complexes are supported by the sterically encumbering but highly flexible, single N-anchored tris(aryloxide) chelator \( \text{AdArO}_3\text{N}^{3–} \). Reaction of an appropriate uranium precursor, either the U(III) starting material, \([(\text{AdArO})_3\text{N)}\text{U(DME)}]]\), or the dinuclear monochalcenido-bridged uranium(IV/IV) compounds, \([(\text{AdArO})_3\text{N)}\text{U(DME)}]_2[\mu-E]]\) (E = S, Se), with elemental sulfur or selenium, yields new complexes with a variety of bridging chalcogenide entities \( \mu-E_m^{n–} \) (E = S, m = 2, n = 1 or 2 and E = Se, m = 2, 4; n = 2). Activation of the heavy chalcogens typically requires either a coordinatively unsaturated, strongly-reducing metal complex or a compound with a metal–metal bond. Since uranium complexes in the +IV oxidation state, are generally considered rather unreactive, the observed reaction of the here employed uranium(IV/IV) species with elemental chalcogens is fairly remarkable.

In uranium coordination chemistry, chalcenido ligands tend to prefer bridging coordination modes.† However, by utilizing an ylide-masked U(III) starting material that slows the rate of comproportionation, and thus prevents the formation of bridging chalcogenide complexes, the monomeric, terminal chalcogenide species \([\text{H}_3\text{CPh}_2\text{][(R=E)}\text{U(E)]}}\) (E = S, Se, Te; R = SiMe₃) were synthesized recently by Hayton et al.8

Surprisingly, despite the propensity of the heavier chalcogenides to catenate to rings and chains of various sizes, there are only a few actinide complexes featuring polychalcenide ligands.

The few existing complexes include the thorium pentasulfido complex \([\text{Cp}^*\text{ThS}_5]\), that was obtained via salt metathesis reaction of \([\text{Cp}^*\text{ThCl}_2]\) with \( \text{Na}_2\text{S}_5 \) by Sattelberger et al., and the homoleptic diselenido complex \( \text{K}_4[\text{U(Se}_2\text{)}]\), synthesized by Kanatzidis et al. via molten salt synthetic techniques.9 Additionally, Boncella et al. were able to synthesize the two tetrachalcenido complexes \([\text{BU}_3\text{bpy}]\text{[U(NBu}_3\text{)[(I)]}_2[\mu-E_m^{n–}]}\) (E = S, Se; \( E_m^{n–} \)) by activating elemental sulfur and selenium, respectively, with a dinuclear uranium(IV/IV) halide complex that serves as a two-electron reductant.7

Herein, we report the syntheses, electronic properties, and molecular structures of a series of dinuclear uranium polychalcenido complexes of the type \([(\text{AdArO})_3\text{N)]\text{U(IV)]}_2[\mu-E_m^{n–}]]\) with \( \mu-E_m^{n–} = \text{S, m = 2, n = 1 or 2 and E = Se, m = 2, 4; n = 2.} \) These new compounds can be synthesized in a remarkably controlled manner just by the appropriate choice of uranium precursor and the stoichiometric addition of the elemental chalcogen.
Results and discussion

Employing the tacn (tacn = 1,4,7-triazaacyclonane) and a single N-anchored tris(aryl oxide) ligands, we recently reported a series of chalcogen-bridged compounds containing purely inorganic chalcogenido ligands, \[ \left[ \left( \text{AdArO} \right)_3 \text{N} \right] \text{UIV(DME)}_2 \mu-E \] and \[ \left[ \left( \text{AdArO} \right)_3 \text{N} \right] \text{UIV(DME)}_2 \mu-E \] (E = S, Se), that can be synthesized from the uranium(III) starting materials \[ \left( \text{Bu}_{3} \text{BuArO}_3 \right) \text{tacl} \] and \[ \left( \text{AdArO} \right)_3 \text{N} \] with stoichiometric amounts of elemental sulfur or selenium, respectively.\(^{14}\) The sterically shielded but potentially reactive \( \mu-E \) bridging selenido- and telluro-bridged complexes can be obtained by reacting \( \left[ \left( \text{AdArO} \right)_3 \text{N} \right] \text{UIV(DME)}_2 \mu-E \] (E = S, Se) do not undergo any further reactions with the elemental chalcogens or, e.g., \( \text{CO}_2 \). Likewise, the complex of the bridging oxygen analogue \[ \left[ \left( \text{AdArO} \right)_3 \text{N} \right] \text{UIV(DME)}_2 \mu-O \] does not exhibit such reactivity.

In contrast, we could show that complexes of the N-anchored ligand system, \[ \left[ \left( \text{AdArO} \right)_3 \text{N} \right] \text{UIV(DME)}_2 \mu-O \] (E = O, S, Se), easily react with \( \text{CO}_2 \) and even the heterocumulene analogues \( \text{CS}_2 \) and \( \text{COS} \) to form dinuclear \( \text{U(IV-IV)} \) mixed-carbonate complexes.\(^{28,31,40}\) This observation is attributed to the higher flexibility of the tetradaentate \( \left( \text{AdArO} \right)_3 \text{N} \) ligand compared to the hexadentate \( \left( \text{Bu}_{3} \text{BuArO}_3 \right) \text{tacl} \) chelate. To further probe the reactivity of \[ \left[ \left( \text{AdArO} \right)_3 \text{N} \right] \text{UIV(DME)}_2 \mu-Se \] (E = O, S, Se), we thoroughly investigated its propensity to react with chalcogens by applying precise stoichiometric amounts of elemental sulfur and selenium. Tellurium did not show any reactivity; nor is the corresponding Te-bridged precursor \[ \left[ \left( \text{AdArO} \right)_3 \text{N} \right] \text{UIV(DME)}_2 \mu-Te \] accessible. However, applying this method to the \( \text{U(III)} \) precursor and mono \( \text{S}- \) and \( \text{Se}- \) bridged \( \text{U(IV)} \) species, we were able to synthesize compounds \[ \left[ \left( \text{AdArO} \right)_3 \text{N} \right] \text{UIV(DME)}_2 \mu-Se \] (E = O, S, Se), \( \left[ \left( \text{AdArO} \right)_3 \text{N} \right] \text{UIV(THF)}_2 \mu-Se \] (E = O, S, Se), and \( \left[ \left( \text{AdArO} \right)_3 \text{N} \right] \text{UIV(DME)}_2 \mu-Se \) (E = O, S, Se), that feature a variety of different di- and tetra-chalcogenido bridging ligands (Chart 1). These bridging polychalcogenido uranium complexes are a rare species with only a few examples in actinide chemistry.\(^{37,39}\)

Interestingly, Ph\(_2\)P=E (E = S, Se), known to be a potent chalcogen atom transfer reagent, did not react with the bridging chalcogenido ligands of complexes 2 and 6.\(^{41}\) A series of mixed-chalcogenido bridged complexes can be obtained by reacting selenium bridged complex 2, or sulfur bridged complex 6, with precisely one equiv. of elemental sulfur or selenium, respectively. Due to the expected strong disorder in the resulting single crystals we did not further pursue the isolation of these compounds.

Syntheses and molecular structures of di- and tetrachalcogenido bridged uranium complexes

The reaction of a yellow solution of the dinuclear, tetravalent complex \[ \left[ \left( \text{AdArO} \right)_3 \text{N} \right] \text{UIV(DME)}_2 \mu-Se \] (2) in benzene with precisely 1 equiv. of elemental selenium powder results in the formation of a brown solution after several hours. Filtration of the reaction solution and subsequent removal of the volatiles yields the complex \[ \left[ \left( \text{AdArO} \right)_3 \text{N} \right] \text{UIV(DME)}_2 \mu-Se \] (3) in 85% yield (Scheme 1, right). This reactivity is remarkable since the uranium(IV) oxidation state, as well as the heavy chalcogenos, are considered to be rather unreactive, and the requirements for elemental chalcogen activation usually are either a coordinatively unsaturated, strongly-reducing metal complex or a compound with a metal–metal bond.\(^{38}\) Nonetheless, Hayton et al. were able to perform the remarkable two-electron oxidation of the terminal monooxo uranyl(nv) complex \[ \text{Cp}^+\text{Co}[\text{R}^2\text{N}]_2\text{U(O)} \] (R = SiMe\(_3\)) with the elemental chalcogens to form sulfur and selenium substituted uranyl analogues \( \text{O}=\text{U}=\text{E}\)\(^{37}\) (E = S, Se).\(^{22}\) Also, the choice of an appropriate ligand appears to play a key role, since even iodine can oxidize \( \text{U(n)} \) to \( \text{U(v)} \) under the right conditions.\(^{41}\) The bridging \( \text{Se}_2^2- \) ligand in the uranium(IV) starting complex \[ \left[ \left( \text{AdArO} \right)_3 \text{N} \right] \text{UIV(DME)}_2 \mu-Se \] (2) apparently is very electron-rich and thus capable of reducing another selenium atom without involving the two uranium(nv) centers in any further redox chemistry. Alternatively, 3 can be synthesized directly from the uranium(III) starting material \[ \left[ \left( \text{AdArO} \right)_3 \text{N} \right] \text{UIV(DME)}_2 \mu-Se \] and precisely 2 equiv. of selenium powder (Scheme 1). Recrystallization of 3 in a concentrated DME solution yields brown crystals suitable for X-ray diffraction. The solid state structure reveals the dinuclear, tetravalent uranium complex \[ \left[ \left( \text{AdArO} \right)_3 \text{N} \right] \text{UIV(DME)}_2 \mu-Se \] that features the bridging \( \mu-\eta^2:\eta^2:\text{Se}_2^2- \) unit as well as a bridging DME molecule (Fig. 1, top). The coordination geometry of both seven-coordinate uranium centers can be best described as distorted mono-capped trigonal prismatic. The \( \eta^2- \)bridging \( \text{Se}_2^2- \) unit is located in the axial position and is trans to the nitrogen anchor. This geometry is in contrast to complex 2, where the bridging \( \mu-Se \) unit is located in the equatorial position cis to the nitrogen anchor.\(^{14}\)

The U-Se bonds are slightly asymmetric (U1-Se1,
2.962(1) Å; U1–Se2, 3.060(1) Å; U2–Se1, 3.078(1) Å; U2–Se2, 2.942(1) Å) and are slightly longer compared to typical U–Se–U bond distances (Table 1).14,19,37,43 The Se1–Se2 bond distance of 2.377(1) Å is comparable to the respective bond lengths in transition metal32,33,44,45 and lanthanide complexes22,46–49 as well as uranium perselenide complexes (2.293(2)–2.401(4) Å).39,50 Additionally, the U(IV)–Se2−–U(IV) entity adopts a M2L2-butterfly structural motif, with a torsion angle of 125.02° and is strongly bent compared to the structurally similar bis-methylselenido complex [Na(DME)]2[((AdArO)3N)UIV]2(μ–Se)2] that has a torsion angle of 160.8° between the two uranium centers and the two Se2− ligands.14 The average U–OAr bond distances of 2.149 Å are slightly shorter than those observed in 2 (2.178, 2.179 Å) but are still within the range of U–OAr bond distances in other complexes supported by the (AdArO)3N3 ligand.14,20,21

In attempts to further investigate the synthesis of complex 3, we added increasingly more than 2 equiv. of Se, ultimately leading to the formation of yet another, olive-green product. An X-ray diffraction analysis of single crystals obtained by slow diffusion of hexane into a saturated toluene solution revealed a dinuclear tetravalent uranium complex, namely [[[(AdArO)3N]UIV]2(μ–η1:η1–Se4)](4); now bridged by four selenium atoms with a formal oxidation state of Se4− (Fig. 1, bottom). Hence, we adjusted the reaction conditions appropriately and added exactly 4 equiv. of selenium powder to [[[(AdArO)3N]UIII(DME)]2] and stirred the reaction solution for 3 days after which olive-green 4 forms (Scheme 1, bottom). Complex 4 was obtained after filtration and drying of the solids in vacuo in 90% yield. Alternatively, [[[(AdArO)3N]UIV(DME)]2(μ–Se)] (2) can be treated with just 3 equiv. of selenium powder to obtain 4 with a similar yield. Evidently, 3 is still reactive towards elemental selenium powder and is able to insert two more selenium atoms into the bridging Se2− unit of 3 to form the Se4− ligand found in 4. This reactivity clearly shows the proclivity of selenium to catenate to chains as there is no redox chemistry involving the uranium centers and their oxidation state of +IV is retained (vide infra).

The molecular structure of 4 shows two tetravalent uranium centers in a distorted mono-capped trigonal prismatic geometry. Two Se atoms of the Se4− moiety are located trans and one Se atom is situated cis to the nitrogen anchor. In contrast to 3, the uranium centers in 4 are not coordinated by additional solvent molecules. The bridging Se4− moiety features alternating Se–Se bond distances with two very similar bond lengths with Se1–Se2 at 2.316(2) Å as well as a slightly larger bond distance of 2.438(1) Å for Se2–Se3 (Table 1). Thus, the bridging Se4− unit is reminiscent to complexes of the 1,3-butadiene ligand.51–53 Similar bond properties are known for polysulfide ligands and can be attributed to charge localization at the first and last selenium atoms of the chain.33,54,55 Only three selenium atoms of the Se4− ligand are coordinated to each uranium center in a μ–η3:η3 fashion. The U–Se bonds are all slightly asymmetric and range from 3.052(2) to 3.125(1) Å, which is marginally longer than the bond distances in 3 and other reported U–Se distances.8,14,19 The average U–OAr bond distances of 2.123 and 2.126 Å in 4 are even shorter than those observed in 3 (2.149, 2.164 Å), which indicates a stronger
aryl oxide-to-uranium binding and lower electron density at the uranium centers with an increasing number of coordinated Se atoms. It should be noted that the crystal structure of the investigated crystal of 4 revealed the presence of a minor fraction (less than 7%) of the corresponding bis-μ-selenido complex \[\text{[(AdArO)}_2 \text{N})_2 \text{U(μ-Se)}_2\] leading to some disorder in the central U-Se₂=U moity.³⁶

Crystallization of 4 from coordinating solvent induces a geometry change of the coordinated Se₄²⁻ ligand. X-ray diffraction analysis of olive-green/brown single crystals, obtained from slow hexane diffusion into a THF solution of the complex reveal the molecular structure of 5 (Fig. 2, Scheme 2). The dinuclear tetravalent uranium complex \[\text{[(AdArO)}_2 \text{N})_2 \text{U(μ-Se)}_2\] exhibits a bridging Se₄⁻ ligand (as opposed to the open-square-like Se₄⁻ unit in 4). Additionally, both uranium centers are now coordinated by one additional THF solvent molecule. In contrast to 4, the bridging Se₄⁻ unit of 5 is coordinated in a μ-η²-η²-fasion and is structurally very similar to the bridging tetrarselenido complex \[\text{[(Bu}_3\text{bpy})\text{U(N(Bu)}_2\text{)]_2(μ-η²-η²-Se)}_2\] synthesized by Boncella et al.²⁷ The dinuclear complex is situated on a crystallographic inversion center and exhibits C₁ molecular symmetry. Each uranium center in 5 adopts a distorted mono-capped trigonal prismatic coordination geometry. The U–Se bond lengths of 2.913(1) Å and 3.178(1) Å are indicative of a strong anionic U–Se₁ bond and a weaker dative interaction U–Se₂, respectively, an observation that is identical to that reported by Boncella and coworkers.²⁷ Furthermore, similar to 4, compound 5 exhibits two shorter Se–Se bonds at 2.288(1) Å and one longer bond at 2.420(0) Å between Se₂–Se₃; the average U–OAr bond distances of 2.135 Å are comparable with those observed for compound 4 (Table 1). Complexes 4 and 5 are unambiguously distinguishable by ¹H NMR spectroscopy. The signals of 4 are very sharp compared to the broadened signals of 5, which is likely due to the fluxional nature of the coordinated THF solvent molecules. It should be noted that a second minor species (5.5%) in the investigated crystal of 5 was identified as \[\text{[(AdArO)}_2 \text{N})_2 \text{U(μ-Se)}_2\] with a bridging Se₄⁻ ligand (see ESI²⁸). Unfortunately, this compound could not be synthesized reproducibly nor isolated in pure form. Attempts to isolate different products by adding even more equivalents of elemental selenium to compounds 4 and 5 have not been successful. This observation might be attributed to the decreasing solubility of complexes 4 and 5.

### Table 1

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<th>Structural parameter</th>
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<td>2.962(1), 3.060(1)</td>
<td>3.076(1), 3.121(1), 3.052(2)</td>
<td>2.913(1), 3.178(1)</td>
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<td>3.079(1), 2.942(1)</td>
<td>3.056(1), 3.125(1), 3.077(2)</td>
<td>3.178(1), 2.913(1)</td>
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<td>Se₁–Se₂, Se₃–Se₄</td>
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<td>2.377(1)</td>
<td>2.316(2), 2.310(2)</td>
<td>2.288(1)</td>
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<tr>
<td>Se₂–Se₃</td>
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<td>—</td>
<td>2.438(1)</td>
<td>2.420(2)</td>
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<tr>
<td>U–OAr</td>
<td>2.178, 2.179</td>
<td>2.149, 2.164</td>
<td>2.123, 2.126</td>
<td>2.135</td>
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<td>U₁–N₁₂, N₁₂</td>
<td>2.556(6), 2.551(6)</td>
<td>2.595(2), 2.601(2)</td>
<td>2.545(3), 2.551(3)</td>
<td>2.591(4)</td>
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to yield complex 7 analytically pure in 88% yield. An X-ray diffraction analysis of crystals grown by diffusing DME into a saturated THF solution revealed two crystallographically independent but chemically equivalent molecules in the asymmetric unit (Z = 2), namely two dinuclear uranium complexes [([(AdArO)3N]U{μ-η²:η²-S2})2] (7A) (Fig. 3, top) and [([(AdArO)3N]-U{μ-η²:η²-S2}[μ-η¹:η²-S2]) (7B) (Fig. 3, bottom) that contain four bridging sulfur atoms. However, in contrast to 4, the bridging unit in both complexes 7A and 7B is not comprised of a S₄²⁻ chain-type ligand but of two independent S₂ moieties. In contrast to complexes 3–5, and within the scope of the present study, the oxidation state of the uranium centers (and chalcogenide ligands) in 7A and 7B cannot be unambiguously identified (vide infra). Complexes 7A and 7B could be formulated either as two U(IV) centers with two bridging supersulfido S₂⁻ units or as two U(V) centers bridged by two persulfido S₂⁻⁻⁻ ligands. Each of the eight-coordinate uranium centers in 7A adopts a distorted square-antiprismatic coordination geometry. The bridging S₂ fragments in 7A both feature an η¹⁻:η²-binding mode and show two almost identical S₁–S₂ and S₃–S₄ bond distances of 2.050(2) Å and 2.053(2) Å, respectively (Table 2). These bond distances are at the shorter end of known S–S bond lengths observed in other uranium₁,₁⁹,₅⁰,₅⁷–₆¹ and transition metal complexes,₆²–₆₆ featuring the persulfido ligand S₂⁻⁻⁻. However, the very rare supersulfido complexes of the transition metals have shown a wider range for the S–S bond length, ranging from 1.944–2.023 Å, depending on the metal center, the supporting ligand, and the coordination mode.₆₇–₇₀ Accordingly, based on the bond metric of the S₂ moiety, an exact assignment (persulfide vs. supersulfide) remains impossible. Both ligands

Scheme 2 Synthesis of THF-coordinated tetraselenido complex 5 from different starting materials 1–4.

Synthesis and molecular structure of polysulfido-bridged uranium complexes

The μ-sulfido complex [([(AdArO)₃N]U{μ-η²:η²-(DME)}₂{μ-S})] (6) exhibits similar reactivity to the μ-selenido bridged complex [([(AdArO)₃N]U{μ-η²:η²-(DME)}₂{μ-Se})] (2) if treated with 0.375 equiv. of elemental sulfur in benzene (Scheme 3). Immediate colour change of the reaction mixture to dark brown was observed and, within 5 minutes of further stirring, a dark brown solid precipitated. After 2 hours of stirring, the solution was filtered and the precipitate was washed with benzene and dried in vacuo.

Scheme 3 Syntheses of sulfur-bridged complexes 6 (top) and 7 (bottom) via different pathways using precise stoichiometric amounts of elemental sulfur. A disulfido complex (right) is proposed as an intermediate during the formation of 7.
are slightly skewed, pointing toward each other, and the distances between S1–S3 (3.836 Å) and S2–S4 (3.366 Å) rule out the formation of a conceivable S₄⁻ unit. The U–S bond distances are slightly different from each other and range from 2.741(2) to 3.020(2) Å, which is slightly longer than the bond lengths observed in [(AdArO),N]U⁴⁺(DME)₂[μ-S₄]¹⁴⁻ (6) and other bridging sulfido complexes reported in the literature.¹⁴,¹⁹,³⁷

The average U–OAr bond distances of 2.104 Å and 2.106 Å, respectively, are significantly shorter than those observed in 6, which is an observation that was also made for complexes 4 and 5. Complex 7B is slightly different from 7A as only one S₂ unit features the η²:η²-binding mode that was already observed in 7A. The second S₂ moiety exhibits a μ-η¹:η² binding mode, which results in both uranium centers being situated in a different coordination environment. The U₁ ion has a coordination number of eight and features a distorted square-antiprismatic coordination geometry, while U₂ is only seven-coordinate and adopts a distorted monodapped octahedral coordination environment. The U–S bond lengths (2.684(2)–2.860(2) Å) and S–S bond distances (2.051(2), 2.044(2) Å) are all in the same range as observed in 7A (Table 2). Finally, the average U–OAr bond distances of 2.110 Å and 2.087 Å can be compared to the observations made in complexes 4, 5, and 7A.

We investigated if the persulfido complex [(AdArO),N]U⁴⁺(DME)₂[μ-S₃] (μ-S₂), which might be a possible intermediate in the formation of 7, could be synthesized similarly to 3. However, all attempts to form a persulfido complex lead to the precipitation of 7. This selective formation of 7 likely is due to the S₈ ring structure of elemental sulfur as well as the low solubility of complex 7, which leads to an excess of sulfur atoms in the coordination vicinity of the uranium center and subsequent precipitation of 7. Likewise, trying to form the persulfido complex by reacting 7 with stoichiometric amounts of 1 in a comproportionation reaction only lead to intractable mixtures of different products, from which no pure compound could be isolated.

Electronic structure of polychalcogenido bridged U(IV/IV) complexes

In order to probe the formal oxidation state of the uranium ions and their electronic structures, we performed variable temperature (2–300 K) dc magnetization measurements on compounds 3, 4, and 5. SQUID measurements reveal magnetic moments of μₑff = 3.81 (3), 3.25 (4) and 3.99 (5) μB at 300 K, which decrease with decreasing temperature to μₑff = 0.43 (3), 0.55 (4), and 0.46 (5) μB at 2 K (Fig. 4). Accordingly, the observed magnetic moments and their temperature-dependency is characteristic of uranium(IV) complexes with an f⁶ electron configuration and a 3H₄ ground state.¹⁴,²¹,⁷¹

An investigation of the temperature-dependent behaviour of disulfido bridged complex 7 revealed a magnetic moment of μₑff = 2.33 μB at 300 K (per formula unit) that decreases to 0.37 μB at 2 K upon decreasing temperature (Fig. 5, top). While a low-temperature magnetic moment of ~0.4–0.5 μB is typically observed in uranium(IV) compounds, the unusually low magnetic moment of 2.33 μB at room temperature is more indicative of a uranium(III) species.⁷² Antiferromagnetic exchange coupling between two uranium centers can significantly decrease the overall magnetic moment and is typically observed as a maximum in the plot of χM vs. T.¹⁴,⁷¹ The magnetic susceptibility of 7, however, does not show a maximum (Fig. 5, bottom); and hence, antiferromagnetic exchange coupling is not evident for this compound but cannot be ruled out entirely.

### Table 2  Selected bond distances (in Å) for complexes 6, 7A, and 7B

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<th>Structural parameter</th>
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<th>7A</th>
<th>7B</th>
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<tr>
<td>U₁–S</td>
<td>2.736(2)</td>
<td>2.741(2), 3.020(2), 2.809(2), 2.767(2)</td>
<td>2.684(2), 2.860(2), 2.842(2), 2.859(2)</td>
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<td>U₂–S</td>
<td>2.713(2)</td>
<td>2.858(2), 2.763(2), 2.766(2), 2.924(2)</td>
<td>2.724(2), 2.783(2), 2.757(2)</td>
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<td>S₁–S₂, S₃–S₄</td>
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<td>2.050(2), 2.053(2)</td>
<td>2.051(2), 2.044(2)</td>
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<td>U–OAr</td>
<td>2.185, 2.180</td>
<td>2.104, 2.106</td>
<td>2.110, 2.087</td>
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<tr>
<td>U₁–NZ₁</td>
<td>2.558(6), 2.565(6)</td>
<td>2.550(4), 2.529(4)</td>
<td>2.566(4), 2.554(4)</td>
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Furthermore, increased covalency of the U–Se bonds in 3–5 and the U–S bonds in 7, respectively, can also reduce the overall magnetic moment.\textsuperscript{24} The observed non-magnetic ground state of 7 at low temperature ($\mu_{\text{eff}} = 0.37$ B.M. at 2 K) allows for different interpretations, arising from several possible electronic configurations and magnetic exchange interactions within the [U(S\textsubscript{2})\textsubscript{2}U] unit: the ground state could result from non-interacting U(IV) f\textsuperscript{2} ions (singlet $\Gamma\textsubscript{1}$; ground state within the $^3H_4$ ground manifold) with through-space, antiferromagnetically coupled supersulfide (S$\textsubscript{2}^-$) ligands or an entirely antiferromagnetically coupled system of U(IV) and bridging radical anions. Alternatively, and assuming that the bridging S\textsubscript{2} ligands are further reduced to diamagnetic persulfides, S\textsubscript{2}$^2-$, the U(IV) f\textsuperscript{1} ions could be strongly antiferromagnetically coupled to yield the observed non-magnetic ground state at 2 K. Closer inspection of the $\chi_M$ vs. $T$ plot (Fig. 5, bottom) indeed reveals a plateau at approx. 50 K with increasing $\chi_M$ below 30 K. While the increased susceptibility at lower temperatures might arise from minor paramagnetic impurities, the saddle point could – in principle – be qualitatively interpreted as the onset of an ordering phenomenon in an antiferromagnetically coupled system.\textsuperscript{73,75–77} However, the current magnetization study does not allow for an unambiguous assignment of the U ions’ and bridging S\textsubscript{2} ligands’ oxidation states.

Accordingly, CW X-band EPR spectroscopic studies were performed on samples of 7 in liquid and frozen toluene solution at room temperature and 7 K, respectively. However, samples of 7 are EPR silent under these conditions. This is not unusual and – in principle – not in contrast with the formulation of 7 as U(IV/IV) with two bridging, radical anionic, supersulfido ligands, nor as paramagnetic U(IV/IV) with bridging, diamagnetic persulfido ligands. Previous studies have shown that both U(IV) species (e.g., U(IV) imidos)$^{78}$ and complexes of U(IV) with coordinated radical anions, such as carbon dioxide,$^{79}$ diphenyldiazomethane,$^{80}$ or benzophenone$^{81}$ are EPR inactive. These observations render attempts to assign the exact oxidation state of the uranium ions as well as the bridging ligands in complexes 7A and 7B difficult. Full understanding of the magnetic behavior of this compound and comparison to 1–6 requires collaborative XAS spectroscopic and DFT theoretical studies that are currently being planned and will be reported in due time.

\section*{Conclusion}
Polychalcogenido complexes of actinides – especially those featuring the heavier group 16 elements S, Se, and Te – are an exceedingly rare class of compounds. Generally, low-valent, strongly-reducing metals are essential for the activation of elemental chalcogen. Herein we demonstrated, however, that by carefully choosing the reaction conditions, even relatively unreactive uranium(IV) complexes can be employed for controlled and stoichiometric elemental chalcogen activation; given the chelating ligand at the U(IV) ion provides sufficient stability and flexibility. Thus, employing the sterically highly accommodating ($^{14}\text{AdArO})_3\text{N}^{3-}$ chelate, polyselenido complexes 3, 4, and 5 were synthesized \textit{via} different pathways, starting from either the U(IV) complex (2 and 6) or the U(III) complex (1), respectively. These complexes feature $\mu$-Se$_2$$^2-$, $\mu$-$\eta^1$-$\eta^1$-Se$_4$$^2-$, and $\mu$-$\eta^1$-$\eta^1$-Se$_4$$^2-$ bridging ligands. Selectivity of compound formation is achieved by using precise stoichiometric amounts of elemental chalcogen and appropriate solvents. The resulting complexes showed magnetic behavior that is characteristic of the uranium(IV) starting compounds; thus, demonstrating the unchanged redox state of the uranium centers. Hence, the reactivity likely stems from the Se$^2-$ and Se$_2$$^2-$ moieties.
themselves and is independent from the metal centers that are basically serving as a stage for chalcogenide transformation. The reactivity of elemental sulfur with the respective U(III) and U(V) complexes is distinctly different from that of selenium. The resulting complex \([([\text{Ar}]\text{O})_2\text{U}][\mu-\text{S}_2\text{O}_4]\) [7] features two bridging \(\text{S}_2\) units instead of a single \(\text{S}_2^{2-}\) ligand as observed with selenium. These novel uranium polychalcogenido complexes are currently being investigated with respect to chalcogen atom transfer chemistry.

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Notes and references

56 The impurities observed and refined in multiple single crystal X-ray diffraction studies of complexes 4 and 5 cannot be identified in the $^1$H NMR spectra of freshly prepared samples of these compounds; hence, concomitant formation can be ruled out. It is likely that the impurities are formed when complexes 4 and 5 are in solution for a prolonged period of time, such as during crystallization.
72 With the exception of one absorption band observed at approximately 1500 nm (6670 cm$^{-1}$, $\varepsilon = 10–100$ M$^{-1}$ cm$^{-1}$), the UV/vis-NIR spectra of all chalcogenide complexes reported here exhibit broad, featureless absorptions between 400 and 1400 nm (see ESI†). Thus, an absorption feature between 5000 and 6000 cm$^{-1}$, often indicative of the pentavalent state in uranium complexes, is present in all complexes reported here; even for those in which the U(IV) oxidation state is unambiguous.