Metathesis of a U^{VI} imido complex: a route to a terminal U^{V} sulfide†

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Herein, we report the synthesis and characterisation of the first terminal uranium(v) sulfide and a related U^{VI} trithiocarbonate complex supported by sterically demanding tris(tert-butoxy)siloxide ligands. The reaction of the potassium-bound U^{VI} imido complex, [U(Im)]{OSi(OtBu)3}2K (4), with CS2 led to the isolation of perthiodicarbonate [K(18c6)]{C2S6}4 (6), with concomitant formation of the U^{IV} complex, [U(OSi(OtBu)3)2], and S=CSS=CCl=NaCl. In contrast, the reaction of the U^{VI} imido complex, [K(2.2.2-cryptand)][U(Ad)] {OSi(OtBu)3}2 (5), with one or two equivalents of CS2 afforded the trithiocarbonate complex, [K(2.2.2-cryptand)][U(CS)2(OSi(OtBu)3)2] (7), which was isolated in 57% yield, with concomitant elimination of the adamantyl thiocyanate product, S=CSS=N=Na. Complex 7 is likely formed by fast nucleophilic addition of a U^{V} terminal sulfide intermediate, resulting from the slow metathesis reaction of the imido complex with CS2, to a second CS2 molecule. The addition of a solution of H2S in thf (1.3 eq.) to 4 afforded the first isolable U^{V} terminal sulfide complex, [K(2.2.2-cryptand)][US(OSi(OtBu)3)2] (8), in 41% yield. Based on DFT calculations, triple-bond character with a strong covalent interaction is suggested for the U–S bond in complex 7.

Introduction

Interest in multiply-bonded uranium pnictogen and chalcogen compounds has grown considerably in recent years.1 The study of actinide–chalcogen bonds is in part motivated by the efficiency of chalcogen donors in the selective separation of actinides from lanthanides in spent nuclear fuel, a property that has been related to covalent contributions in actinide–chalcogen bonds.2 Early attempts to prepare terminal sulfido, selenido and tellurido complexes of uranium involved oxidation of a U^{III} precursor with a chalcogen-atom donor, and led exclusively to chalcogenide-bridged compounds.3e–f In recent years, a handful of terminal and alkali-capped mononuclear uranium chalcogenides have been prepared and characterised.4 All characterised terminal sulfido, selenido and tellurido complexes contain a tetravalent uranium ion.5e–g–i Only one U^{V} complex containing a linear O==U=S2 core has been characterised by Hayton and co-workers.6 Several terminal mono-oxo complexes of pentavalent uranium7–9 and a few capped10–13 and terminal U^{V} nitrides14,15 have been prepared in recent years, but terminal sulfido, selenido and tellurido complexes of U^{VI} remain undiscovered. Since the degree of covalency in the uranium–chalcogenide bond is expected to be higher in higher oxidation states,16 the isolation of a U^{VI} terminal sulfide is of great interest for elucidating the involvement of 5f orbitals in U–S bonding. In general, pentavalent uranium compounds are attractive candidates for the investigation of bonding and magnetic properties due to their simple 5f configuration,12 but the number of molecular uranium compounds containing a U^{VI}–S bond remain rare.5g,12b,19 The presence of stable U^{VI} cations in chalcogenide materials has also been reported.14

Different approaches have been used in order to prevent the formation of bridging species when preparing U^{IV} monochalcogenide complexes by oxidation of U^{III} compounds.4h–k Recently, our group used sterically demanding tris(tert-butoxy)siloxide ligands to prevent the formation of a bridging chalcogenide complex. The reaction of the ate complex, [U(OSi(OtBu)3)2]4K, with the two-electron oxidising agent, Ph3P=, in the presence of 2.2.2-cryptand, led to the isolation of the terminal uranium(v) monosulfide complex, [K(2.2.2-cryptand)][US(OSi(OtBu)3)2]4K.6e We note that all of the examples mentioned above resulted in the formation of a U^{IV} monochalcogenide complex in spite of the fact that a two-electron oxidising agent was used in the sulfur–transfer reactions to U^{III}. This suggests that the isolation of terminal sulfides of U^{V} or U^{VI} from U^{III} might not be possible. A monosulfido complex of

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UIV was also prepared by deprotonation of a hydrosulfido analogue, [[(Ad,MeArO)₃tacn]U(NAd)SH] supported by a tripodal hexadentate aminophenolate ligand. The reported electrochemical studies indicated that this complex could be electrochemically oxidised, most likely to the UIV=V species, but preliminary attempts to chemically oxidise and isolate a UIV sulfido complex were not successful.

Here we investigate new possible routes to isolate a UIV terminal sulfide using tris(tert-butoxy)siloxide as the supporting ligands. This ligand previously allowed for the isolation of a tetrahedral coordination geometry formed by four monodentate tris(tert-butoxy)siloxide imido complexes with CS₂ and H₂S affinity for the first UIV terminal sulfide and trithiocarbonate complexes.

Results and discussion

Syntheses and molecular structures

Attempts to isolate a UIV terminal sulfide from the chemical oxidation of the uranium(IV) siloxide complex, [K₂[2.2.2-cryptand]][U(OSi(OrBu)₃)₄]K, only led to decomposition products.

Thus, in our search for a UIV terminal sulfide, we anticipated that UIV terminal imido complexes would be the ideal starting materials. Notably, several examples of reactions of transition metal imido compounds with CS₂ have been reported and they usually lead to the formation of sulfide and isothiocyanate products via a cycloaddition pathway. The formation of a UIV terminal oxo complex from the reaction of a UIV imido complex with CO₂ has been reported, but a similar strategy using CS₂ has never been used to prepare terminal uranium sulfides. Hydrosulfidolysis of imido compounds also represents a successful route to terminal or bridging sulfide complexes of d-block transition metals, but it has never been applied for f-elements.

We have previously shown that [K(18c6)][U(OSi(OrBu)₃)₄] can be used to effect a two-electron reduction of adamantyl azide, affording the UIV monoimido complex [K(18c6)][U(NAd)_{OSi(OrBu)₃}₄] (1). With regard to the important effect of alkali cations and crown-ether-bound alkali cations on the reactivity of uranium compounds supported by tris(tert-butoxy)siloxide ligands, we have now prepared the analogous complexes, [U(NAd)_{OSi(OrBu)₃}₄] (4), and [K(2.2.2-cryptand)][U(NAd)_{OSi(OrBu)₃}₂] (5), by reduction of adamantyl azide with [K₂[2.2.2-cryptand]][U(OSi(OrBu)₃)₄] (2) and [K(2.2.2-cryptand)][U(OSi(OrBu)₃)₄] (3), respectively.

The charge-separated UIV tetrasiloxide precursor, [K₂[2.2.2-cryptand]][U(OSi(OrBu)₃)₄] (3), is conveniently prepared in high yield by stirring the reported complex, [U(OSi(OrBu)₃)₄]K (2), with 2.2-cryptand in toluene. Complex 3 crystallised from a mixture of thf and hexane as two crystallographically unique pairs of [K₂[2.2.2-cryptand]]⁻ and [U(OSi(OrBu)₃)₄]⁺ ions in the orthorhombic space group, P2₁2₁2₁. The molecular structure is shown in Fig. 2. The four-coordinate uranium ions feature a tetrahedral coordination geometry formed by four monodentate tris(tert-butoxy)siloxide ligands. The structure is very similar to that of [K(18c6)][U(OSi(OrBu)₃)₄] and the U-O bond lengths of the two complexes are comparable (U-O_{ave} = 2.228 Å in [K(18c6)][U(OSi(OrBu)₃)₄]; U-O_{ave} = 2.21 Å in 3).

Treating complexes 2 and 3 with adamantyl azide in toluene yielded the UIV imido complexes, [U(NAd)_{OSi(OrBu)₃}₄]K (4), and [K(2.2.2-cryptand)][U(OSi(OrBu)₃)₄] (5), respectively (Scheme 1). Complex 4 is highly soluble in hexane, toluene and thf, whereas 5 is sparingly soluble in toluene but highly soluble in thf. The ¹H NMR spectra of 4 and 5 in d₅-toluene are similar to that of the reported complex 1, and show four paramagnetically shifted resonances attributable to the adamantyl protons, and one peak corresponding to the tert-butyl protons of the siloxide ligands. However, in the case of 5 the siloxide peak is sharp, while in the case of 4 a broad peak is observed, suggesting fluxional binding of the potassium ion in toluene solution for complex 4. Complex 5 shows three additional imido resonances in the ¹H NMR spectrum.

Dark brown crystals of the heterobimetallic complex 4-tol crystallised from toluene in the orthorhombic space group, Fdd2. The molecular structure is shown in Fig. 3. The central uranium ion is five coordinate and it is ligated by four negatively charged oxygen atoms of the tris(tert-butoxy)siloxide ligands, and one nitrogen atom of the imido group. The U-N bond

Fig. 1 Molecular structures of the UIV terminal oxo complex, [UO_{OSi(OrBu)₃}₄]K (left), and the UIV terminal imido complex, [K(18c6)][U(NAd)_{OSi(OrBu)₃}₄] (1) (right).

Fig. 2 Molecular structure of one of the crystallographically unique pairs of [K₂[2.2.2-cryptand]][U(OSi(OrBu)₃)₄] in crystals of 3 shown with 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): U₁–O₁ = 2.223(4), U₁–O₂₁ = 2.193(4), U₁–O₄₁ = 2.211(4), U₁–O₆₁ = 2.220(4).
ion is highly distorted due to the coordination of three siloxide ligands to the six-coordinate potassium ion, which fits into a pocket formed by three \( \kappa^2-O \)-siloxide ligands.

At first, we investigated the reaction of \([\text{U(NAd)}\{\text{OSi(O}2\text{Bu})3\}]_4\{\text{K}\} \) with \( ^{13}\text{CS}_2 \). An analogous approach has been used to prepare a uranium terminal oxo complex by reaction of a \( \text{U}^\text{V} \) imido complex with \( \text{CO}_2 \). The proposed mechanism for the formation of the terminal oxo involves a \( [2+2] \) cycloaddition reaction followed by extrusion of isocyanate to afford the terminal oxo complex.\(^{12}\)

In the present case, reactions between 4 and one or two equivalents of \( ^{13}\text{CS}_2 \) were slow. Monitoring the reactions by \(^1\text{H}\) NMR spectroscopy showed that in both cases consumption of the starting material took place over two to three days, and it proceeded with the concomitant formation of \([\text{U}\{\text{OSi(O}2\text{Bu})3\}]_4\) \(^4\) (in 35% yield) and additional unidentified uranium product(s). None of these products could be identified as a terminal sulfide, even when the 4 : \( \text{CS}_2 \) ratio was 1 : 1. The \(^{13}\text{C}\) NMR spectra of the crude reaction mixtures in \( d_8\)-toluene show the presence of the metathesis by-product, the isothiocyanate \( \text{S}=\text{C}=\text{NAd} \), in both cases, as well as an additional signal at 132 ppm assigned to the perthiodicarbonate \( \text{C}_2\text{S}_6^{2-} \). The formation of an insoluble compound is also observed. The \(^{13}\text{C}\) NMR spectrum in \( d_6\)-dmsso of the residue obtained after removal of toluene form the reaction mixture shows the presence of peaks at 267 ppm and 129 ppm assigned to the \( \text{C}_2\text{S}_6^{2-} \) and to the \( \text{C}_2\text{S}_6^{2-} \) species in a ratio of 1 : 1.2. Adding \( 18\text{c6} \) to a 1 : 2 toluene reaction mixture of 4 and \( \text{CS}_2 \) allowed for the crystallisation of the unusual \( \text{C}_2\text{S}_6^{2-} \) coupling product, \([\text{K}(18\text{c6})]_2[\text{C}_2\text{S}_6] \) (Scheme 2). The molecular structure of 6 was determined by X-ray crystallography (see ESI†). Perthiodicarbonate species are rare but some examples are known, \( \text{e.g.} [\text{PPh}_4]\_2[\text{C}_2\text{S}_6] \), which formed from aerial oxidation of a reaction mixture of \( \text{PPh}_3\) and \( \text{K}_2(\text{C}_2\text{S}_4) \).\(^{19}\)

Complex 6 plausibly arises from uranium(\( \text{V} \))-mediated oxidation of the trithiocarbonate in a putative \([\text{U}^\text{V}(\text{CS}_3)]\) \( \{\text{OSi(O}2\text{Bu})3\}\) intermediate. Such an intermediate is likely to be formed from the reaction of a \( \text{U}^\text{V} \) terminal sulfide, formed from the metathesis of the imido group with a \( \text{CS}_2 \) molecule, with a second \( \text{CS}_2 \) molecule.

The presence of bound potassium ions incorporated into the structure of uranium siloxide complexes has been shown to have an important effect on the reactivity of \( \text{U}^\text{III} \) complexes with \( \text{CS}_2 \), and on the stability of the resulting products with respect

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**Scheme 1** Syntheses of \([\text{U(NAd)}\{\text{OSi(O}2\text{Bu})3\}]_4\{\text{K}\} \) (4) and \([\text{K}(2.2.2\text{-cryptand})][\text{U(NAd)}\{\text{OSi(O}2\text{Bu})3\}]_4\{\text{K}\} \) (5).

**Scheme 2** Reaction of 4 with \( ^{13}\text{CS}_2 \): isolation of 6.
to trithiocarbonate or tetrathiooxalate ligand loss.\textsuperscript{13w} Thus, we anticipated that the analogous reactions carried out with the U\textsuperscript{v} imido complex 5, where the presence of 2.2.2-cryptand prevents cation binding to the siloxides, might enable us to stabilise the U\textsuperscript{v} terminal sulfide and terminal trithiocarbonate intermediates.

Indeed, the reaction of 5 with two to five equivalents of CS\textsubscript{2} in toluene afforded the trithiocarbonate complex [K(2.2.2-cryptand)][U(CS\textsubscript{3}){OSi(O\textsubscript{2}toluene}]\textsubscript{5} (7) in 57% yield (Scheme 3). The \textsuperscript{1}H NMR spectrum of 7 in \textsubscript{d}\textsubscript{6}-toluene exhibits two signals with equal integration ratios at 1.77 ppm and 1.51 ppm, respectively, corresponding to the tert-butoxy protons of the siloxide ligands, indicating a C\textsubscript{2} symmetric species in solution. The \textsuperscript{13}C NMR spectrum of 7 in toluene shows a broad signal at 180 ppm that is assigned to the bound trithiocarbonate ligand. In addition to this signal, the \textsuperscript{13}C NMR spectrum of the crude reaction mixture in \textsubscript{d}\textsubscript{6}-toluene showed the presence of the thiocyanate product, S=O=Na\textsubscript{3}, a resonance at 132 ppm assigned to C\textsubscript{2}S\textsubscript{6} and a signal at 247 ppm (free CS\textsubscript{2}). The \textsuperscript{1}H NMR spectrum of the reaction mixture also shows the presence of a signal assigned to [U(OSi(OBu\textsubscript{3}))\textsubscript{5}]\textsuperscript{+}, but in a much smaller amount (8\%) compared to what was found in the reaction of 4 with CS\textsubscript{2}.

Dark brown crystals of complex 7-tol crystallised from toluene in the monoclinic space group, \textit{P}2\textsubscript{1}2\textsubscript{1}2\textsubscript{1}. The molecular structure is shown in Fig. 4 and selected bond lengths are summarised in Table 1. The six-coordinate uranium atom is coordinated by four siloxide oxygen atoms and two sulfur atoms of a terminally-bound \(\text{C}_2\text{S}–\text{trithiocarbonate} \) moiety, affording a distorted octahedral coordination geometry. The structure bears similarities to the recently reported terminal U\textsuperscript{v} trithiocarbonate [U(Tren\textsubscript{HPS})(\text{C}_2\text{S}–\text{thiocarbonate})][K(B15C5)]\textsubscript{5}\textsuperscript{+} and the related \textsuperscript{iv} trithiocarbonate complex, \([\text{K}(18\text{c}6)\textsubscript{2}][\text{U}(\text{C}_2\text{S}–\text{thiocarbonate})][\text{U}(\text{OSi(O\text{Bu}\textsubscript{3}))\textsubscript{5}])_{1}\textsuperscript{+}.\) However, in the latter U\textsuperscript{iv} complex, the 186-bond potassium cation is still able to bind two sulfur atoms of the trithiocarbonate group. The average U–O bond length (2.10(3) \(\text{Å}\)) is noticeably shorter than the corresponding average bond lengths in the U\textsuperscript{v} imido complexes, [K(18\text{c}6)][U(\text{NSiMe\textsubscript{3}O})\textsubscript{5}].

Fig. 4 Molecular structure of [U(CS\textsubscript{3}){OSi(O\text{Bu}\textsubscript{3}))\textsubscript{5}]- in crystals of 7-tol shown with 50\% probability thermal ellipsoids. [K(2.2.2-cryptand)]\textsuperscript{+}, hydrogen atoms and lattice solvent have been omitted for clarity.

Table 1 Selected bond lengths (\(\text{Å}\)) for complexes 7-tol and 8-1.5tol

<table>
<thead>
<tr>
<th>Structural parameters</th>
<th>7-tol</th>
<th>8-1.5tol</th>
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</thead>
<tbody>
<tr>
<td>U1–S1</td>
<td>2.772\textsubscript{(3)}</td>
<td>2.376\textsubscript{(5)}</td>
</tr>
<tr>
<td>U1–S2</td>
<td>2.747\textsubscript{(3)}</td>
<td>—</td>
</tr>
<tr>
<td>U1–O\textsubscript{ave}</td>
<td>2.14\textsubscript{(3)}</td>
<td>2.10\textsubscript{(3)}</td>
</tr>
<tr>
<td>C73–S\textsubscript{range}</td>
<td>1.68\textsubscript{(1)}–1.75\textsubscript{(1)}</td>
<td>—</td>
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\{OSi(OBu\textsubscript{3}))\textsubscript{5}\} and [K(18\text{c}6)][U(NAd)(OSi(OBu\textsubscript{3}))\textsubscript{5}] (2.16(2) \(\text{Å}\) and 2.20(2) \(\text{Å}\), respectively), and this is presumably a result of greater steric congestion in the two imido complexes, although electronic effects cannot be ruled out. The U–S bond lengths (2.747(3) \(\text{Å}\) and 2.772(3) \(\text{Å}\) are shorter than those in the aforementioned terminal (2.8415(8) and 2.8520(10) \(\text{Å}\)) and K(18\text{c}6)\textsuperscript{+}-capped U\textsuperscript{v} trithiocarbonate complex (2.9488(19) \(\text{Å}\) and 2.951(2) \(\text{Å}\)).\textsuperscript{17c} In the case of the capped complex, the difference is greater than would be expected given the difference in ionic radii between U\textsuperscript{iv} and U\textsuperscript{v} (0.13 \(\text{Å}\) for six-coordinate ions),\textsuperscript{21} probably due to the electron-withdrawing effect of the two coordinated \{K(18\text{c}6)\}\textsuperscript{+} units in the U\textsuperscript{iv} complex. The C–S bond lengths (1.679(13) \(\text{Å}\), 1.696(12) \(\text{Å}\) and 1.749(14) \(\text{Å}\) show similar values (within error) as previously observed for the related U\textsuperscript{v} trithiocarbonate complex, \([\text{K}(18\text{c}6)\textsubscript{2}][\text{C}_2\text{S}–\text{CS}3][\text{U}(\text{OSi(OBu\textsubscript{3}))\textsubscript{5}]] (1.723(8), 1.711(10) and 1.704(8) \(\text{Å}\)),\textsuperscript{18c} in agreement with charge delocalisation over the C\textsubscript{2}S\textsubscript{6} unit.

Complex 7 is the first example of a U\textsuperscript{v} uranium trithiocarbonate complex and is only the second example of a terminal trithiocarbonate complex in f element chemistry.\textsuperscript{28} Complex 7 shows higher stability than a putative trithiocarbonate intermediate formed in the reaction of the K\textsuperscript{+} (4) U\textsuperscript{v} imido complex with CS\textsubscript{2}. This is probably explained by the fact that in the absence of K\textsuperscript{+} cations binding the trithiocarbonate group, oxidation of the trithiocarbonate by U\textsuperscript{v} is not a favoured pathway. Complex 7 is likely formed by the nucleophilic
addition of a U\textsuperscript{V} terminal sulfide intermediate to a CS\textsubscript{2} molecule (Scheme 4). Fast addition of terminal and bridging U\textsuperscript{IV} sulfide to CS\textsubscript{2} to afford terminal or bridging U\textsuperscript{IV} thiacarbonyl complexes has been previously reported.\textsuperscript{4,22}

Monitoring the reaction between equimolar amounts of complex 5 and 13CS\textsubscript{2} by \textsuperscript{1}H NMR spectroscopy showed a very slow reaction, due in part to the very low solubility of 5 in toluene, and after ten days, complex 7 and unreacted complex 4 were present in equimolar quantities. There is no evidence of the formation of the U\textsuperscript{V} terminal sulfide intermediate under these conditions, probably due to its fast reaction with an additional CS\textsubscript{2} molecule.

We reasoned that using a less bulky imido complex might increase the rate of the first step of the reaction, thereby allowing for the isolation of a terminal sulfide complex, but NMR-scale reactions between [K(2.2.2-cryptand)][USiMe\textsubscript{3}]\{OSi(O\textsubscript{t}Bu\textsubscript{3})\textsubscript{4}\} and two equivalents of 13CS\textsubscript{2} showed that this strategy was unsuitable (see ESI\textsuperscript{f}). The reaction was slow, and although multiple products were formed, it was possible to identify complex 7 in the reaction mixture by \textsuperscript{1}H NMR spectroscopy. The presence of a terminal sulfide complex, but not a terminal U\textsuperscript{V} terminal sulfide intermediate was detected.

These results show that although the metathesis reaction of the U\textsuperscript{V} imido complex with CS\textsubscript{2} leads to a terminal U\textsuperscript{V} sulfido complex, the reaction is rather slow and the plausible U\textsuperscript{V} terminal sulfide intermediate cannot be isolated due to its rapid reaction with another molecule of CS\textsubscript{2} to afford the thiacarbonyl complex. In an analogous approach, we anticipated that the high basicity of the imido group could be exploited in an acid/base metathesis reaction with H\textsubscript{2}S to afford a terminal sulfide product. Indeed, treating a pre-chilled (−40 °C) suspension of [K(2.2.2-cryptand)][U(NAd){OSi(O\textsubscript{t}Bu\textsubscript{3})\textsubscript{4}]} (4) in toluene with a fresh, commercially available 0.8 M solution of H\textsubscript{2}S in třfluore (1.3 eq.) afforded the first isolable U\textsuperscript{V} terminal sulfide complex, [K(2.2.2-cryptand)][USi(O\textsubscript{t}Bu\textsubscript{3})\textsubscript{4}]} (8) (Scheme 3) in 41% yield. Some unidentified side products also formed in the reaction, but a \textsuperscript{1}H NMR spectroscopy experiment using naphthalene as an internal standard showed that the conversion rate to the terminal sulfide product was 76%. The \textsuperscript{1}H NMR spectrum of 8 in \textsubscript{d}\textsubscript{6}-toluene only shows one broad resonance at 1.20 ppm that corresponds to the tert-butyl protons of the siloxide ligands, along with three signals for the cryptand protons. The fact that only one signal is observed for the siloxide protons suggests that the structure of 8 is fluxional in solution. Complex 8 is reasonably thermally stable and it only showed minor decomposition in solution over the course of a week at room temperature. The formation of the terminal sulfide is likely to involve a double H-atom transfer from the H\textsubscript{2}S to the imido nitrogen. No intermediate reaction product was observed by NMR spectroscopy, suggesting that if the plausible uranium amide/hydrosulfide intermediate is formed (as previously proposed in the hydrosulfidolysis of titanium imido complexes), then the H-transfer from the bound SH to the resulting amido group is fast.\textsuperscript{19b}

Dark brown crystals of complex 8-1.5tol crystallised from toluene as two crystallographically independent units. The molecular structure is shown in Fig. 5 and selected bond lengths are listed in Table 1. The uranium atoms in each molecule are ligated by one terminally bound sulfide atom and the negatively charged oxygen atoms of four siloxide ligands, resulting in a distorted trigonal bipyramidal coordination geometry. The U–S bond lengths of the two independent molecules are 2.376(5) Å and 2.396(5) Å, respectively, which are considerably shorter than the corresponding bond length in the U\textsuperscript{IV} analogue, [K(2.2.2-cryptand)][USi(O\textsubscript{t}Bu\textsubscript{3})\textsubscript{4}]} (2.5220(14) Å).\textsuperscript{24} However, this difference is about what would be expected after accounting for the difference in ionic radii between U\textsuperscript{IV} and U\textsuperscript{V} (0.13 Å).\textsuperscript{24} The predicted values for the U–S double and triple bonds according to Pyykkö are significantly shorter (respectively 2.28 Å and 2.13 Å).\textsuperscript{23} A similar discrepancy between the Pyykkö values and experimental values was also observed for a triply bonded terminal U\textsubscript{VI} sulfide (U≡S = 2.39 Å in the O≡U≡S\textsuperscript{2+} fragment).\textsuperscript{6} The average U–O bond lengths (2.14(3) Å for molecule 1 and 2.13(4) Å for molecule 2, respectively) are longer than the corresponding average bond length in complex 7. Given that a sulfide ligand is considerably less bulky than a trithiocarbonate moiety, this difference can probably be attributed primarily to electronic effects. The Vis/NIR spectrum of
The NBO analysis indicates the same bonding situation, with HOMO and HOMO-1 in Fig. 6) are found in the MO spectrum. HOMO-3 and HOMO-4 in Fig. 6) and a C\(g\)\(_4\) multiple bond character was found. Rather, two bonds in previous studies.

UV complexes. intermediate in the formation of 8 as an intermediate in the formation of 8 from 5.

The X-band EPR spectra of 7 and 8 were measured in a toluene/acetonitrile glass (see ESI†). While no signal was detected at room temperature, an EPR signal, featuring broad linewidths (600 to 800 mT), that unambiguously originates from a metal-centred unpaired electron was observed at 10 K for both complexes. In both cases, the EPR signal was fitted with a rhombic set of \(g\)-values \(g_1 = 1.25; g_2 = 1.03; g_3 = 0.72\) for 7 and \(g_1 = 1.38; g_2 = 1.24; g_3 < 0.6\) for 8) that are comparable to those reported for the octahedral uranium\((\nu)\) complex, \([\text{UO(O{i}Si(Or\text{Bu})_3)_4K}]\) \(g_1 = 1.248; g_2 = 0.856; g_3 = 0.485\).\(^{44}\)

Computational bonding analysis

In order to investigate the nature of the U–S bond in complexes 7 and 8, we performed calculations at the B3PW91 level, as this method was successfully applied to describe the U–chalcogen bonds in previous studies.\(^{26,27}\) Firstly, the bonding situation was analysed in the U\(^{IV}\) trithiocarbonate complex (7). No clear U–S multiple bond character was found. Rather, two \(\sigma\) U–S bonds (HOMO-4 and HOMO-5 in Fig. 6) and a C\(\equiv\)S double bond (HOMO and HOMO-1 in Fig. 6) are found in the MO spectrum. The NBO analysis indicates the same bonding situation, with 77–78\% S and 23–22\% U, and involve a hybrid 6d/5f orbital at the uranium centre. Finally, the WBI of the U–S bonds are 0.94 and 1.02, in line with a \(\sigma\) bond with highly covalent character. The bonding in the U\(^{IV}\) dipotassium trithiocarbonate is quite similar to the one found in 7. Indeed, two \(\sigma\) U–S bonds are found but these bonds are even more polarised than in 7, with a contribution of 90\% from sulfur. This is reflected in the WBI (only 0.47/0.50), indicating a less covalent bond. However, since the U\(^{IV}\) trithiocarbonate complex involves the coordination of two potassium atoms, its putative U\(^{IV}\) equivalent was computed to check the influence of the two potassium ions on the bonding. In the latter U\(^{IV}\) complex, the bonding is also consistent with two U–S \(\sigma\) bonds. These bonds appear to be as polarised as in 7, with a 77/80\% contribution from sulfur to the bonding.

On the other hand, the WBI are 0.72/0.75, intermediate between the values found for 7 and the U\(^{IV}\) compound, in line with an influence of the potassium on the covalency. Indeed, the presence of the interaction between the potassium and the trithiocarbonate decreases the covalency in the U–S bond, mainly because the atomic orbitals of sulfur need to overlap with both U and K. Using similar methods, we analysed the bonding in complex 8 and compared it with the bonding found in its U\(^{IV}\) analogue.\(^{44}\) Molecular orbital analysis (Fig. 7) clearly indicates a triple bond that is similar to that observed for the U\(^{IV}\) analogue. The HOMO-3 is the \(\sigma\) bond, whereas HOMO-1 and HOMO are the two \(\pi\) orbitals. Natural Bonding Orbital (NBO) analysis is in line with this bonding description. Indeed, at the first order, three bonding orbitals \(1\sigma, 2\sigma, \text{and } 2\pi\) are found and they are strongly polarised towards S (77\%, 80\% and 81\%)}
for the $\sigma$ orbital and the two $\pi$ orbitals, respectively). Finally, the Wiberg Bond Index (WBI) is 2.2, in line with a triple bond with very strong covalent character. This is very close to the value of 2.25 that was found for the $^{195}$U analogue, indicating that oxidation of the $^{197}$U complex does not affect the bonding but only removes an electron from one of the 5f orbitals that becomes the LUMO of the $^{197}$U system (Fig. 7).

**Experimental**

**General procedures**

Unless otherwise noted, all manipulations were carried out at ambient temperature under an argon atmosphere using Schlenk techniques and an MBraun glovebox equipped with a purifier unit. The water and oxygen level were always kept at less than 1 ppm. Glassware was dried overnight at 150 °C prior to use.

**Starting materials**

The solvents were purchased, in their anhydrous form, from Aldrich or Cortecne (deuterated solvents), conditioned under argon and vacuum distilled from K/benzophenone (toluene, THF) or sodium dispersion (hexane) or dried over 4 Å molecular sieves for one week (DMSO). All reagents were dried under high vacuum for 5 days prior to use. HOSi(OrBu)$_3$ was purified by sublimation prior to use. Depleted uranium turnings were purchased from the “Société Industrielle du Combustible Nucléaire” of Annecy (France), [U(OSi(OrBu)$_3$)$_2$]$_2$K [2,46] [K(18c6)] [U(OSi(OrBu)$_3$)$_2$]$_4$ [15] and [K(18c6)][U(NAd)](OSi(OrBu)$_3$)$_4$ [1]$_{15}$ were prepared according to the published procedures. The complex [K(2.2.2-cryptand)][U(NSiMe)$_3$](OSi(OrBu)$_3$)$_4$ was prepared from 3 following a procedure analogous to that reported for [K(18c6)][U(NSiMe)$_3$](OSi(OrBu)$_3$)$_4$ [15].

Synthetic details for the preparation of [K(2.2.2-cryptand)][U(OSi(OrBu)$_3$)$_2$] [3], [U(NAd)](OSi(OrBu)$_3$)$_4$K [4], and [K(2.2.2-cryptand)][U(NAd)](OSi(OrBu)$_3$)$_4$ [5] are given in the ESL.†

**NMR, IR, Vis/NIR and EPR spectroscopy**

NMR spectra were performed in J. Young NMR tubes. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker 400 MHz spectrometer. NMR chemical shifts are reported in ppm and were referenced to the residual $^1$H and $^{13}$C signals of the deuterated solvents. IR analyses were performed with a Perkin-Elmer Spectrum One FT-IR Spectrometer. The sample was placed into the Harrick High Temperature Chamber DRIFT cell under an argon atmosphere. Scans were performed in a range between 400 and 4000 cm$^{-1}$ at a resolution of 4 cm$^{-1}$. Vis/NIR spectra were recorded on a Perkin Elmer Lambda 950 instrument. Data were collected in 10 mm path length cuvettes equipped with a J. Young valve. The samples were loaded under argon in the glovebox and were run in toluene. EPR spectra of 7 and 8 were measured with a Bruker Elexys E500 spectrometer working at 9.4 GHz frequency with an Oxford ESR900 cryostat for 4–300 K operation. Baseline correction of the raw EPR spectrum was performed with cubic spline (Kep 2.4b.12, Bruker). Simulations were performed with the Easyspin 5.1.3 program.‡

**Elemental analyses**

Samples were analysed under nitrogen by the elemental analyses department of the EPFL using a Thermo Scientific Flash 2000 Organic Elemental Analyzer.

**X-ray analyses**

Crystallographic data for X-ray analyses of all complexes are given in Table S1.† Figure graphics were generated using MERCURY 3.9: Cambridge, U.K., 2001–2016. CCDC-1535285 [7], CCDC-1535286 [6], CCDC-1535287 [8] CCDC-1535288 [4] and CCDC-1535289 [3] contain the supplementary crystallographic data for this paper.†

Bragg-intensities of 3, 4, 6, 7 and 8 were measured at low temperature [100 K and 140 K (compound 8)], respectively using Cu Kα radiation ($\lambda = 1.54184$ Å) on a Rigaku SuperNova dual system diffractometer equipped with an Atlas CCD detector for compound 4 and 7 and equipped with an Atlas S2 CCD detector for compound 4, 6 and 8. The datasets were reduced and then corrected for absorption with CrysAlisPro.‡

The solutions and refinements for the structures were performed by SHELXT† and SHELXL-2016 (release 6),‡ respectively. In the case of 7, the solution and refinement for the structure were performed by SHELX-97.‡‡ The crystal structures were refined using full-matrix least-squares based on $F^2$ with all non-hydrogen atoms anisotropically defined. The hydrogen atoms were placed in calculated positions by means of the “riding” model.

In the case of 4, the structure contained half of a toluene molecule in the asymmetric unit and it was disordered along a two-fold axis. The atoms were refined anisotropically and in order to have a convergent least-squares refinement, distance and similarity restraints (SADI, SIMU, ISOR and FLAT) were applied.

In the case of 6, the structure was refined as a two-component twin with HKLF 5 file obtained by treating the data with CrysAlisPro‡‡ yielding to the value of 0.432(2) for the BAF parameter. One 18c6 is disordered over two positions. The atoms of each orientation were located in difference Fourier map. The major and minor parts were refined anisotropically, but distance and similarity restraints (DFIX, SADI, ISOR and FLAT) were used for a convergent least-squares refinement, yielding to site occupancy ratios of 0.511(5)/0.489(5). The second 18c6 was just partially disordered over two positions but treated in the same way yielding to site occupancy ratios of 0.64(1)/0.36(1).

In compound 7, light atoms (C and O) showed unstable anisotropic behaviour and restraints (SIMU 0.02 card) were necessary to handle them.

In the case of 8, the structure was refined as a two-component twin crystal and data (in HKLF 5 format) were obtained by treating the data with CrysAlisPro‡‡ yielding to the value of 0.448(1) for the BAF parameter. The structure included one molecule of toluene in the asymmetric unit, it was disordered over an inversion centre and refined in a ‘PART-1’ environment. The atoms were refined anisotropically, but distance
and similarity restraints (DFIX and SIMU) were employed for a stable least-squares refinement.

**Synthesis of [K(2.2.2-cryptand)][U{OSi(OtBu)}₄] (7)**

[2.2.2-cryptand][U{OSi(OtBu)}₄] (46 mg, 0.025 mmol) was suspended in toluene (0.5 mL) and then ¹³C₅₂ (7.4 µL, 0.12 mmol) was added by syringe. The mixture was monitored periodically by ¹H NMR spectroscopy until there was no more consumption of the starting material and the reaction is sensitive to the quality of the ¹H NMR spectroscopy. A conversion experiment using naphthalene as an internal standard determined the conversion of 4 into [U{OSi(OtBu)}₄] to be 35% by ¹H NMR spectroscopy.

**Reaction of 8 with CS₂ to afford 7**

A 0.59 M solution of ¹³CS₂ in d₈-toluene (5.0 µL, 0.0030 mmol) was added to a brown solution of [2.2.2-cryptand][USi(OtBu)₃] (46 mg, 0.025 mmol) in d₈-toluene (1.5 mL), and then the resulting solid was recrystallised from toluene at −40 °C and then for two hours at room temperature the following morning. The solvent was then removed under vacuum, leaving a dark brown oil. Hexane (3 × 1 mL) and then the resulting solid was recrystallised from toluene several times at −40 °C, affording analytically pure dark brown crystals of 8 (36 mg, 41%). Single crystals suitable for X-ray crystallography were grown from toluene at −40 °C and then for two hours at room temperature the following morning. The solvent was then removed under vacuum, leaving a dark brown oil. Hexane (0.5 mL) was added to the oil and then the mixture was dried under vacuum giving a brown solid. The solid was washed with hexane (3 × 1 mL), and then the resulting solid was recrystallised from toluene several times at −40 °C, affording analytically pure dark brown crystals of 8 (36 mg, 41%). Single crystals suitable for X-ray crystallography were grown from toluene at −40 °C. Anal. calcd for Cₜ₉H₁₅₄K₆Na₄O₈SSi₄U (815.30): C, 33.94; H, 4.38; N, 0.79. Found C, 33.73; H, 4.36; N, 0.73. ¹H NMR (400 MHz, d₈-toluene, 298 K): δ [ppm] 4.08 (s, 12H, 2.2.2-cryptand), 3.05 (t, 12H, 2.2.2-cryptand), 1.20 (brs, 12H, OSi(OtBu)₃). ¹³C NMR (100.6 MHz, d₈-toluene, 298 K): δ [ppm] 180.88 (CS₂), 73.76 (OSiOC(CH₃)), 71.05 (OSiOC(CH₃)), 56.38 (2.2.2-cryptand), 32.44 (OSiOC(CH₃)). IR (DRIFT, cm⁻¹): 2967s, 2924m, 2898m, 2818m, 1477w, 1459w, 1447w, 1385m, 1360s, 1297w, 1261m, 1239s, 1222m, 1196s, 1133m, 1108s, 1077s, 1050s, 1024s, 975s, 957s, 917s, 825m, 801s, 765w, 755s, 710m.

A conversion experiment using naphthalene as an internal standard determined the conversion of 4 to 8 to be 76% by ¹H NMR spectroscopy.

**Conclusions**

To summarise, we have prepared and fully characterised the first examples of stable terminal U⁺₄ sulfide and thiocarbonate complexes using bulky siloxides as supporting ligands.

DFT calculations were performed to investigate the nature of the U–S bond in complexes 7 and 8, and the results were compared with the analyses of the analogous U⁴⁺ complexes. Based on this analysis, triple-bond character with strong covalent character is suggested for the U–S bond in the terminal uranium(v) sulfide 8, in line with previous studies on terminal U⁴⁺ sulfides. Single-bond character was found for the U–S bond in complex 7, which turned out to be more covalent than in the U⁴⁺ analogue.
In conclusion, we have shown that the metathesis of U(VI) imido complexes with CS$_2$ or H$_2$S provides a convenient route to terminal sulfides. However, the metathesis reaction with CS$_2$ was very slow and resulted in nucleophilic addition of the putative intermediate to CS$_2$. Moreover, the presence of siloxide-bound cations in the U(VI) imido precursor resulted in the isolation of a side-reaction product, the perthiodicarbonate, salt [K(18c6)][C$_2$S$_4$O$_4$], resulting from the oxidation of CS$_3^{2-}$ by U(VI).

In contrast, the metathesis of U(VI) with H$_2$S readily forms a stable terminal U(VI) sulfide. The hydrosulfidolysis of uranium imides reported here provide a versatile route to uranium terminal chalcogenides that should be easily extended to other uranium oxidation states and to other chalcogenides. Work in this direction is in progress.

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Notes and references


