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Multi-electron reduction of sulfur and carbon disulfide using binuclear uranium(III) borohydride complexes†

Polly L. Arnold,*a Charlotte J. Stevens,a Nicola L. Bell,a Rianne M. Lord,a Jonathan M. Goldberg,b Gary S. Nichola and Jason B. Love*a

The first use of a dinuclear U(III)/U(III) complex in the activation of small molecules is reported. The octadentate Schiff-base pyrrole, anthracene-hinged ‘Pacman’ ligand L8 combines two strongly reducing U(III) centres and three borohydride ligands in [M(THF)4][U(BH4)2(µ-Ⅲ-Ⅲ)] 1-M, (M = Li, Na, K). The two borohydride ligands bound to uranium outside the macrocyclic cleft are readily substituted by aryloxide ligands, resulting in a single, weakly-bound, encapsulated endo group 1 metal borohydride bridging the two U(III) centres in [U(OAr)2(µ-Ⅲ-MBh4)(L8)(THF)2] 2-M (OAr = OC6H2(Bu3)2,2,4,6, M = Na, K). X-ray crystallographic analysis shows that, for 2-K, in addition to the endo-BH4 ligand the potassium counterion is also incorporated into the cleft through η2-interactions with the pyrrolides instead of extraneous donor solvent. As such, 2-K has a significantly higher solubility in non-polar solvents and a wider U–U separation compared to the ‘ate’ complex 1. The cooperative reducing capability of the two U(III) centres now enforced by the large and relatively flexible macrocycle is compared for the two complexes, recognising that the borohydrides can provide additional reducing capability, and that the aryloxide-capped 2-K is constrained to reactions within the cleft. The reaction between 1-Na and S8 affords an insoluble, presumably polymeric paramagnetic complex with bridging uranium sulfides, while that with CS2 results in oxidation of each U(III) to the notably high U(V) oxidation state, forming the unusual trithiocarbonate (CS3)2– as a ligand in [{U(CS3)}2(µ-Ⅲ-Ⅲ)] (4). The reaction between 2-K and S8 results in quantitative substitution of the endo-BH4 by a bridging persulfido (S)2– group and oxidation of each U(III) to U(V), yielding [{U(OAr)2(µ-Ⅲ-Ⅲ)-S2)(LA)(THF)2}] (5). The reaction of 2-K with CS2 affords a thermally unstable adduct which is tentatively assigned as containing a carbon disulfido (CS2)2– ligand bridging the two U centres (6a), but only the mono-bridged sulfido (S)2– complex [{U(OAr)2(µ-S)(L8)}] (6) is isolated. The persulfido complex (5) can also be synthesised from the mono-bridged sulfido complex (6) by the addition of another equivalent of sulfur.

Introduction

The U(III) oxidation state is strongly reducing and its molecular complexes are well known for their ability to activate small molecules1–3 such as arenes,4–6 N2,7–10 CO11–19 and CO2.20–26 The coordination of actinides with chalcogenide ligands has begun to attract increasing interest.27–31 Understanding and controlling the activation and functionalisation of chalcogen elements and their compounds is important in the petroleum industry and in functional polymer technologies, and is increasingly of interest for new methods in organic and biomimetic syntheses,32 both with d-block33–41 and rare earth metal42,43 complexes. The kinetically facile nature of the soft atom transfer reactions with the harder metal cations suggests opportunities in catalytic chalcogen atom-transfer processes, yet the binding mode and stoichiometry of the incorporated chalcogen atoms/fragments is as yet unpredictable and so far appears to be primarily dependent on subtle differences in steric accessibility of the reducing metal centre(s). Furthermore, complexes that exhibit different binding modes with polarisable atoms such as these can provide new insight into the role of f- and other valence orbitals in actinide-ligand bonding which is fundamentally important to improving the safe handling of nuclear waste materials.44–49

Almost all instances of the activation of sulfur or sulfur-containing small molecules by an actinide involve the assembly of two mononuclear U(III) centres around one or more inert atoms.
atoms of elemental sulfur, or an S atom from CS₂, providing two reducing electrons to form [U⁰]₂ products, occasionally with further incorporation of CS₂. Products are often formed as a mixture of the persulfido (E₂)²⁻-bridged [U⁰]₂ complexes such as (µ-η⁵⁺₂⁻⁴⁻S₆)[UX]₂ [where [UX] = [U(C₆H₄Me)]₄, ¹⁷ [U(N⁵⁺⁻)]₂ (N⁵⁺ = N[SiMe₃]₃), ²⁷ [U(SiMe₂NPh)₃]₃ and [U(UOAr)₂tacn]), ³¹, and sulfido (E₂)²⁻-bridged [U⁰]₂ complexes such as (µ-S)[U(N⁵⁺⁻)]₃ ²⁷ and (µ-S)[U([(SiMe₂NPh)₃tacn] ³⁰. The first terminal uranium persulfido complex was [U(SiMe₂NPh)₃tacn] (η²-C₈H₄-[S₉]), ³⁸ Incorporation of up to four S atoms has also been observed, e.g. in [K(18-crown-6)](η²-S₉)[U(N⁵⁺⁻)]₃ (n = 1–3), ³² and (µ-S₂)[U([(ArO)₃tacn] ³¹. One monosulfido complex adds CS₂ to form the [U⁰]₂CS₃ adduct ([µ-κ²⁺₂⁻⁴⁻CS₃]⁻[U(UOAr)₂tacn] ³², which can also be formed directly from the U⁰ precursor and CS₂. Finally, the ‘ate’ U⁻⁻ siloxide complex [K(18-crown-6)][U(µ-SiMe₃)₃] has been shown to react with CS₂ to form a variety of potassium-bound reduction products including [K₆(18-crown-6)][U(µ-SiMe₃)₃] and pyridine but sparingly soluble in toluene and hot benzene.

We reasoned that the preorganisation of two U⁻⁻ centres could enhance the rate and selectivity of small molecule activation reactions in the now two-body problem. In light of this we reported the first structurally characterised binuclear [U⁻⁻]₂ complex of a single ligand using the small cavity macrocycle trans-calix[2]benzene[2]pyrrole. ²⁹ We further showed that the reaction between [U(BH₄)]₂(THF)₂] and the anions of the ‘Pacman’-shaped Schiff-base polymeric macrocycles ⁵₅–⁵₇ afforded another two classes of molecule that combine two U⁻⁻ centres in a single ligand structure. ³⁸ The larger of the two ‘Pacman’ ligands, hinged by anthracenyl groups, forms the unusual ‘ate’ complex, [Na(THF)₄][U(BH₄)]₂([µ-BH₄(L)]²⁻[THF]₃) ¹⁸

Herein, we report reactivity studies of 1 and a new derivative in which the exo-coordination sites of both U⁻⁻ centres are protected by ‘capping’ aryloxide groups. We demonstrate the differences in reactivity between these compounds and their unique selectivity for the formation of (µ-S, (µ-S₂) or (µ-CS₃) in their reactions with S₈ and CS₂.

**Results and discussion**

The reaction of H₄L₄ with KN(SiMe₃)₂, followed by U(BH₄)₃(THF)₂ affords [K(THF)₄][[U(BH₄)₃]₂([µ-BH₄(L)]²⁻[THF]₃) ¹⁻K in good yield; ¹⁻K is the potassium analogue of our recently reported sodium complex ¹⁻Na. ⁵₆–⁵₉ Reactions of ¹⁻K to target exo-X ligand substitution with amide, alkoxide, aryloxide, cyclopentadienyl, allyl and allyl anions were investigated (see ESI).

The most successful reactions, as evidenced by $^¹$H NMR spectroscopy are those between ¹⁻K and two equivalents of the aryloxide MOAr where M = K, Na and Ar = C₆H₄(β-Bu)₂-2,4,6 (Scheme 1). A $^¹$H NMR spectra of both reaction mixtures are very similar and each display a new set of very broad, paramagnetically shifted resonances of low intensity, which nevertheless are consistent with a single, symmetric macrocyclic ligand environment. A large quantity of dark green crystals formed over 4 h in the ¹⁻Na/KOAr reaction mixture. Analysis of these by X-ray diffraction revealed their composition to be [[U(OAr)₄]([endo-µ-κ²⁻₄⁻BH₄]₂(L)]²⁻[THF]₃) ²⁻K in which the two exo BH₄⁻ ligands have been exchanged for aryloxides and the Na⁺ cation of ¹⁻Na has been exchanged for a K⁺ cation which notably now binds within the macrocyclic cleft (Fig. 1). Single crystals also formed in the ¹⁻Na/NaOAr reaction mixture, but only after standing for two weeks. These were characterised as the analogous Na⁺-containing product [[U(OAr)₄]([endo-µ-κ²⁻₄⁻NaBH₄]₂(L)]²⁻[THF]₃) ²⁻Na in which again the Na⁺ cation is also located within the macrocyclic cleft (Fig. 1). The in situ NMR scale reaction between ¹⁻K and NaOAr yielded resonances consistent with the formation of only ²⁻K. Interestingly, no reaction occurs between ¹⁻K and two equivalents of LiOAr. On a preparative scale, the reaction of ¹⁻Na with KOAr in THF allows crystalline ²⁻K to be isolated in 59% yield. Crystalline ²⁻K is insoluble in THF and pyridine but sparingly soluble in toluene and hot benzene. The $^{¹¹}$B NMR spectrum of ²⁻K in C₆D₆ is sharper than that of the crude product formed from an in situ synthesis in d₆-THF and contains paramagnetically shifted resonances corresponding to a symmetric macrocycle and two equivalent aryloxy ligands. One resonance that integrates to 18H is seen at 4.1 ppm for the meta protons of the aryl-

**Scheme 1** The reaction of H₄L₄ with M(SiMe₃)₂ (M = Li, Na, K) and U(BH₄)₃(THF)₂ to yield [Na(THF)₄][U(BH₄)₃([µ-BH₄(L)]²⁻[THF]₃) ¹⁻Na, previously reported) and the group 1 analogues ¹⁻Li and ¹⁻K, further reaction with MOAr yields [M(UOAr)(THF)₄[endo-µ-κ²⁻₄⁻BH₄(L)] (OAr = OC₆H₄β-Bu₂-2,4,6, M = K, ²⁻K; M = Na, ²⁻Na).
binding mode in solution, identical to that observed in the solid state for 1-Na.

The geometry of each U\textsuperscript{III} centre in 2-K (Fig. 1) is best described as a distorted pentagonal bipyramid. The coordination environment of the U\textsuperscript{III} centre shows five equatorial donor atoms, comprising the four nitrogen atoms of the macrocycle and one oxygen atom of THF solvent, which sits between the macrocyclic hinges, and the borohydride. The aryloxide ligand occupies the exo axial coordination site and the BH\textsubscript{4} ligand (hydrogens not located) sits within the macrocyclic cleft bridging the two U\textsuperscript{III} centres with long U–B distances of about 3.3 Å (Table 1).

The phenyl rings of the aryloxide ligands are perpendicular to the anthracenyl hinges of the macrocycle and the angle at the O atom (U1–O1–Cipso = 154.0(5)° (2-K), 153.3(6)° (2-Na)) orients the ortho\textsuperscript{2}Bu groups away from the THF donor. The U\textsuperscript{III} cations are considerably displaced out of the macrocycle N4 donor planes, away from the intermetallic cleft, by 0.70 Å in 2-K and 0.69 Å in 2-Na, and the sum of the four N–U–N angles in the two structures is 337.9(8)° and 338.1(8)° respectively. The separation of the bulky aryloxide ligand from the N4 plane of the macrocycle is imposed by steric demand. Therefore, the displacement of the U\textsuperscript{III} centres out of the N4 plane is a compromise between optimised U–OAr and U–N bond lengths. The resulting mean U–N(imine) distances of 2.65 Å in both complexes and the mean U–N(pyrrolide) distances of 2.50 Å (2-K) and 2.51 Å (2-Na) are lengthened compared to those observed in 1-Na (2.62 Å and 2.49 Å). The U1–O1 bond lengths in 2-K and 2-Na are 2.231(5) Å and 2.245(6) Å respectively (Table 1). These are longer than the U\textsuperscript{III} OAr distances in [U(OC\textsubscript{6}H\textsubscript{3}iPr\textsubscript{2}-2,6)\textsubscript{3}]\textsuperscript{54} and [U(OC\textsubscript{6}H\textsubscript{3}tBu\textsubscript{2}-2,6)\textsubscript{3}]\textsuperscript{59} which range from 2.149(4) to 2.214(7) Å but similar to the mean U–OAr distance of 2.22 Å observed in the constrained aryloxide TACN complexes U[\textsuperscript{2}ArO\textsubscript{3}(TACN)].\textsuperscript{60,61}

The main difference between the structures of 2-K and 2-Na is the binding of the K\textsuperscript{+} and Na\textsuperscript{+} cations within the cleft. The larger K\textsuperscript{+} ion is sandwiched symmetrically between all four pyrrolide rings (Fig. 1a) with K1–[pyr]centroid separations of 3.154(2) Å and 3.153(2) Å. By contrast, the smaller Na\textsuperscript{+} ion is disordered over two sites about the crystallographic C\textsubscript{2} axis, presumably because it cannot effectively bridge all four

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Comparison of selected distances (Å) and angles (°) in the structures of 2-K and 2-Na</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>2-K</td>
</tr>
<tr>
<td>U1–U1’</td>
<td>6.5881(3)</td>
</tr>
<tr>
<td>Mean U–N\textsubscript{im}</td>
<td>2.65</td>
</tr>
<tr>
<td>Mean U–N\textsubscript{pyr}</td>
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<tr>
<td>U1–N\textsubscript{c} plane</td>
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</tr>
<tr>
<td>U1–O1</td>
<td>2.231(5)</td>
</tr>
<tr>
<td>U1–B1</td>
<td>3.312(1)</td>
</tr>
<tr>
<td>U1–O2</td>
<td>2.554(5)</td>
</tr>
<tr>
<td>B1–M1</td>
<td>3.036(11)</td>
</tr>
<tr>
<td>M1–[pyr]centroid</td>
<td>3.154(2), 3.153(2)</td>
</tr>
<tr>
<td>U1–B1–U1’</td>
<td>168.2(4)</td>
</tr>
<tr>
<td>O1–U1–B1</td>
<td>178.3(2)</td>
</tr>
<tr>
<td>U1–O1–Cipso</td>
<td>154.0(5)</td>
</tr>
</tbody>
</table>

Fig. 1  Solid-state structure of 2-K showing side view (a) and front view (b), and solid-state structure of 2-Na, side view (c). For clarity, the major orientation of the disordered ‘Bu groups in 2-K is shown in (a) and the meso ethyl groups, aryloxide substituents, THF molecules, and tert-butyl groups are omitted from (b); all H atoms and lattice solvent are also omitted (displacement ellipsoids are drawn at 50% probability). Full details for 2-Na are in the ESI.†
pyrrolides. This results in three shorter Na1-[pyr]centroid distances of 2.85(4), 3.04(2) and 3.08(4) Å and one long, non-bonding separation of 3.61(2) Å (Fig. 1c). The larger and more polarisable K+ is clearly a better match for the Pacman macrocyclic cleft than Na+. Based on the M1--B1 separations, the U ions form a standard bonding interaction with the BH4− anion.35,36 Reported terminal K··BH4 separations range from 2.947(3) Å to 3.091(4) Å with a mean value of 3.00 Å, while terminal Na··BH4 separations range from 2.600(6) Å to 2.841(2) Å with a mean value of 2.68 Å. The K1–B1 (3.036(11) Å) and Na1–B1 (2.747(2) Å) separations in 2-K and 2-Na lie within these ranges, close to the mean values. The elongated K1–B1 distance means that the BH4− ligand sits further back into the molecular cleft in 2-K and the U1–B1–U1’ angle in 2-K (168.2(4)°) is more acute than that in 2-Na (173.0(6)°).

The effect of the out-of-cleft distortion of the U1111 centres is a marked lengthening of both the U···U and the U···(endo-BH4) separations. The U1··U1’ separation is 6.5881(3) Å in 2-K and 6.5265(7) Å in 2-Na compared to 5.9243(3) Å in 1-Na. U1–B1 is 3.312(1) Å in 2-K and 3.269(1) Å in 2-Na compared to 2.977(7) Å and 2.949(7) Å in 1-Na. The U–B distances in 2 are the longest observed for any uranium borohydride complex, with the next longest being complex 1-Na followed by 2.927(7) Å in [U(BH4)L′] (L′ = trans-calix[2]benzene[2]pyrrolidine).29 This raises the question of whether there is a bond between the U1111 ions and the endo BH4− group in 2-K and 2-Na or whether the BH4− group is held within the cleft by association with its M+ counter-ion. The observed 11B NMR shift of the endo BH4− group in 2-K (188 ppm) is significantly paramagnetically shifted from that of free KBH4 (−40 ppm) indicating that there is some electronic overlap between the U1111 centres and the BH4− group in solution. Therefore, it is likely that in-cleft cation binding in 2-K and 2-Na contributes to the stabilisation of a very weak and long U(BH4)−U interaction.

Reactions of 1 and 2

Reactions to compare the small molecule activation chemistry of 1-Na and 2-K were carried out, noting both the high number of potential reducing equivalents in 1 and the weak binding of the central, and unsolvated MBH4 in 2.

Complex 1-Na was dissolved in THF and 0.75 equivalents of S8 was added, immediately forming a red solution of a product we assign as [u2S8(u4)]3− from elemental analysis, and analysis of the boron–sulfur containing by-products of the reaction, Scheme 2. The 1H NMR spectrum of a freshly made solution shows paramagnetically shifted resonances between +34 and −23 ppm that correspond to a symmetrical macrorcycle environment; some H2S is also seen in solution. The 11B NMR spectrum contains two triplets in a 4 : 1 ratio at −6.2 and −16.5 ppm, the latter of which can be assigned to Na2[(BH3)2S4], the caesium analogue of which has previously been made from the reaction between CsBH4, BH3 and H2S (eqn (1)).66 The initially-soluble reaction product precipitates from the reaction mixture over a 12 h period and remains insoluble in common polar aprotic solvents. This observation and the rarity with which S bonds as a terminal multiply bonded ligand led us to assign a polymeric structure for 3 as drawn in Scheme 2.

$$\text{CsBH}_4 + 2\text{THF} : \text{BH}_3 + 2\text{H}_2\text{S} \rightarrow [\text{Cs}_2(\text{BH}_3)_2\text{S}_4] + 4\text{H}_2$$ (1)

A THF solution of 1-Na was treated with an excess (>9 equivalents) of S8, upon which the reaction mixture immediately turned bright orange, and quantitative deposition of the product characterised as \([\text{U}([\text{CS}_3])_2(\mu-\text{k}^2:\text{k}^2-\text{CS}_3)L^4])\) A as an orange solid is observed after ca. 15 min. The 1H NMR spectrum of the reaction mixture before precipitation shows a single symmetrical paramagnetically shifted macrorcycle environment with resonances between +25 and −44 ppm. The IR spectrum of solid 4 shows no absorptions in the region 2500–2000 cm−1 confirming that no borohydride ligands remain. The 11B NMR spectrum of the supernatant shows two sharp singlets at 0.29 and 0.5 ppm, attributed to boron-sulfide-containing by-products, and shows that the BH4 ligands have provided additional reducing capability to the U1111 centres in 1. Related borohydride reduction reactions from simple group 1 salts are shown in eqn (2)–(5). Both resonances appear at a higher frequency than known reaction products of NaBH4 and BH3 with CS2, namely \([\text{CH}_2(\text{BH}_2)_2\text{S}_2]^- (−13.7/15.8 \text{ ppm})\) and \([(\text{BH}_3)(\text{SCH}_2\text{S})_3]^- (−17.0 \text{ ppm})\).70 The 11B NMR resonance at 0.5 ppm is attributed to the known anion \([\text{B}[(\text{SCH}_2\text{S})_2]_3]^- (\text{eqn (4)})\) which is formed from the sub-stoichiometric reaction of NaBH4 with CS2. The corresponding CH2 group is observed as a quartet at 3.97 ppm in the 1H NMR spectrum.71 The second species in the 11B NMR appears closer to the polymeric species, formulated as \([\text{B}[(\text{SCH}_2\text{S})_2]_3]^- (0.0 \text{ ppm}, \text{eqn (5)})\) suggesting a similar formulation for the resonance at 0.29 ppm possibly with an intermediate charge \((e.g. \text{B}[(\text{SCH}_2\text{S})_2]_3^{3-})\).73

$$\text{NaBH}_4 + 2\text{BH}_3 + 2\text{CS}_2 \rightarrow \text{Na}[(\text{BH}_2)_2\text{S}_2(\text{SCH}_2\text{S})_4] + 3\text{H}_2$$ (2)

$$2\text{BH}_3 + \text{CS}_2 \rightarrow [\text{BH}*(\text{SCH}_2\text{S})_2]$$ (3)

$$5\text{NaBH}_4 + 4\text{CS}_2 \rightarrow \text{Na}_4[(\text{SCH}_2\text{S})_3]+2\text{B}_2\text{H}_6$$ (4)

$$\text{NaBH}_4 + 2\text{CS}_2 \rightarrow \{\text{Na}[(\text{SCH}_2\text{S})_3]\}_n$$ (5)

Small orange crystals of \([\text{U}([\text{CS}_3])_2(\mu-\text{k}^2:\text{k}^2-\text{CS}_3)L^4]\) were obtained from the concentrated THF solution. X-ray crystallographic analysis of 4 shows the incorporation of the rare trithiocarbonate \((\text{CS}_3)_2^{3-}\) motif in the endo and both of the exo uranium coordination sites from which charge balancing arguments assign the notably high formal oxidation state of UV/3 (Fig. 2). While the crystallographic data are poor and prevent a full discussion of structural parameters, the U···U separation is 5.85 Å (from an average of the three structures in the unit cell). This is the first case in which two uranium centres have been shown to provide a total of four reducing electrons (rather than just one each) in the rare formation of the \((\text{CS}_3)_2^{3-}\) ligand, and the first time that more than one thiocarbonate ligand has been formed through reductive activation by a single molecule.

The reactivity of the more soluble complex 2-K provides an interesting comparison with that of 1-M. Reactions of 2-K were carried out with both S8 and CS2 in the anticipation of displacing the single, weakly bound endo-KBH4 molecule.
Addition of an excess of S₈ to a slurry of 2-K in toluene resulted in the immediate formation of a pale orange solution and a pale yellow precipitate of KBH₄. Addition of hexanes to the filtrate results in the deposition of orange crystals of the thermally stable product \([\text{U(OAr)}_2(m\text{-S}_2\text{-k}_2-S_2)(\text{LA})]\) (5) in 41% yield (Scheme 2). In the solid-state structure (Fig. 3) the intermetallic cleft is occupied by a bridging persulphido ion, \((\text{S}_2)_2^{2-}\), suggesting that both uranium centres have been oxidised to UIV. This is reinforced by the reduction of the U–L bond lengths (cf. 2-K), in keeping with the values for known U⁴⁺ complexes (see below). The \(^1\text{H}\text{NMR} \) spectrum of a solution of 5 displays paramagnetically shifted resonances corresponding to a single \(C_2\)-symmetric macrocycle environment and two equivalent aryloxide ligands, as was observed in the \(^1\text{H}\text{NMR} \) spectrum of 2-K. However, in contrast to 2-K, the aryloxide rings appear to be rotating freely in solution as only three resonances in a 36:18:4 ratio are seen. No resonances are seen in the \(^{11}\text{B}\) NMR spectrum of 5.

Scheme 2  Contrasting reactions of \([\text{Na}(\text{THF})_4][\text{U}(\text{BH}_4)_2]\{\mu-\text{BH}_4\}[(\text{LA})(\text{THF})_2]\) (1-Na) and \([\text{U(OAr)(THF)}_2\text{[endo-}\mu-\text{KBH}_4](\text{LA})]\) (2-K) and the synthesis of complexes 3–6 (OAR = OC₆H₂₃Bu₃-2,4,6).

Addition of an excess of S₈ to a slurry of 2-K in toluene resulted in the immediate formation of a pale orange solution and a pale yellow precipitate of KBH₄. Addition of hexanes to the filtrate results in the deposition of orange crystals of the thermally stable product \([\text{U(OAr)}_2(m\text{-S}_2\text{-k}_2-S_2)(\text{LA})]\) (5) in 41% yield (Scheme 2). In the solid-state structure (Fig. 3) the intermetallic cleft is occupied by a bridging persulphido ion, \((\text{S}_2)_2^{2-}\), suggesting that both uranium centres have been oxidised to UIV. This is reinforced by the reduction of the U–L bond lengths (cf. 2-K), in keeping with the values for known U⁴⁺ complexes (see below). The \(^1\text{H}\text{NMR} \) spectrum of a solution of 5 displays paramagnetically shifted resonances corresponding to a single \(C_2\)-symmetric macrocycle environment and two equivalent aryloxide ligands, as was observed in the \(^1\text{H}\text{NMR} \) spectrum of 2-K. However, in contrast to 2-K, the aryloxide rings appear to be rotating freely in solution as only three resonances in a 36:18:4 ratio are seen. No resonances are seen in the \(^{11}\text{B}\) NMR spectrum of 5.

Fig. 2  Solid-state structure of 4 showing side view (left) and front view (right). Due to poor quality data, the structure could not be refined adequately so only connectivity is described. All atoms were refined isotropically except the uranium atoms and those in the \(\text{CS}_3^2\) units. For the anisotropic atoms, displacement ellipsoids are drawn at 50% probability. For clarity, H-atoms are omitted and isotropic atoms are shown as wireframe. Colour code: green = uranium, yellow = sulfur, blue = nitrogen, grey = carbon.

Fig. 3  Solid-state structure of 5 showing side-on view (left) and front view (right). The alternative, symmetry generated S2 position, S2′ (dashed bonds), is only shown in the right hand structure. For clarity, all H atoms and lattice solvent are omitted, along with the macrocycle meso ethyl groups and aryloxide ortho Bu groups from the right-hand view (displacement ellipsoids are drawn at 50% probability).
NMR spectrum confirming the loss of KBH₄ from the cleft and its subsequent precipitation.

Addition of an excess of CS₂ to a suspension of 2-K in d₆-toluene results in a slow colour change from dark green to orange-brown over the course of 10 min and formation of an orange precipitate (Scheme 2). The solution species were characterised on the basis of NMR spectroscopy as [(U(OAr))₂(μ-CS₂)(L^4)] (6a) and [(U(OAr))₂(μ-S)(L^4)] (6). The resonances of the major species 6a indicate the presence of a single asymmetric macrocyclic compound in which the two compartments of the macrocycle are inequivalent. The two aryloxide ligands are also inequivalent; nine resonances are observed, five of intensity 9H corresponding to five of the six ‘Bu groups (the resonance of the sixth group is assumed to be concealed by the solvent resonances) and four of intensity 1H corresponding to each trans proton. It is proposed from this that both aryloxide ligands are rigidly bound with the ary rings coplanar with the anthracenyl groups of the macrocycle hinge. As no resonances are seen in the ¹¹B NMR spectrum, it is probable that displacement of KBH₄ by CS₂ has occurred, and that a bent (CS₂)₂⁻ unit binds asymmetrically between the two U⁴⁺ centres, rendering the macrocyclic compartments and exo aryloxides inequivalent. Complex 6a is not stable in solution, and converts quantitatively to a new, C₂-symmetric complex either on standing at room temperature for five days or heating in benzene for 2.5 h; the resulting complex was characterised as the orange sulfdido-bridged compound [(U(OAr))₂(μ-S)(L^4)] (6) (see below). No further reaction of 6 with CS₂ was observed, but boiling a benzene solution of 6 and excess S₈ resulted in the formation of an orange solution which showed resonances in the ¹H NMR spectrum corresponding to complex 5, Scheme 2.

By comparing the reactions of 1 and 2-K with excess CS₂, it is seen that the exo-aryloxide groups direct the uranium centres to activate only one molecule of CS₂ within the cleft, forming 6a initially and eventually the sulfdido-bridged 6. However, without the aryloxide capping ligands, 1 is able to activate CS₂ in both the exo and endo positions, with poor overall control, resulting in the formation of poorly soluble products.⁶⁶

**X-ray crystal structures of the endo-chalcogenido complexes 5 and 6**

Orange single crystals of 5 suitable for X-ray structural analysis were obtained from a C₆D₆/hexane solution. In the solid-state, the U⁴⁺ cations in 5 are seven coordinate, binding to the four N donors of the macrocycle, the exo-aryloxide ligand and both S atoms of the endo-bridging persulfido ion (Fig. 4). The solid-state structure of 5 confirms that, in contrast to 2, the aryloxide rings are indeed approximately coplanar with the anthracene hinges of the macrocycle with one ortho⁻‘Bu group on each ring sitting between the hinges. Also, the two THF molecules which were bound to the U centres in the equatorial sites in 2-K have dissociated during formation of 5. The U₁–O₁ bond length in 5 is 2.091(3) Å, which is reduced from 2.231(5) Å in 2-K and supports the oxidation of the U⁴⁺ centres to U⁵⁺. The angle at the O atom of the aryloxides (U₁–O₁–C_psp₂ = 169.0(3)°) is less acute than that observed in 2-K (154.0(5)°). The mean U₁–N(pyridine) distance has contracted from 2.50 Å in 2-K to 2.41 Å in 5, though the difference in the mean U₁–N(imine) distances is less marked (Table 2).

The (S₈)₂⁻ unit in 5 is symmetry defined to be equidistant from the two U⁴⁺ centres but the U₁–S₁ bond length of 2.8229(8) Å is longer than the U₁–S₂ length of 2.707(3). S₂ is disordered over two sites related by rotation about the C₂ axis and the occupancy of each site was fixed at 0.5. U₁, U₁’, S₁ and S₂ are not coplanar but instead the U₂S₂ unit forms a bent diamond with a dihedral angle of 165.4°. Bridging persulfido uranium complexes are rare, with the only two examples having been reported very recently, and both featuring a persulfido ion bridging symmetrically between two U⁴⁺ centres in [(U[N(SiMe₃)₂]₂)(μ-κ²-x⁵-S₂)]⁷⁻ and [(U[(SiMe₃)₃NPH]₂(TACN)]₂(μ-x⁵-x⁵-S₂)].⁸⁸

Orange block-shaped crystals of 6 suitable for X-ray crystallography were obtained by addition of hexanes to a toluene solution (Fig. 4). The coordination environment about the two...
UⅣ ions in 6 is distorted octahedral and the four N donors of the macrocycle occupy the equatorial plane with the \textit{exo} arylxide and \textit{endo} bridging sulfido ligands axial. There is, however, a large deviation from idealised octahedral geometry; the angles between the \textit{trans} axial ligands O1–U1–S1 and O2–U2–S2 are 143.2(2)° and 140.1(2)°, respectively. As with 5, the arylxides are tilted back toward the hinges of the macrocycle to avoid unfavourable steric interactions between their \textit{ortho}-Bu groups and the \textit{exo meso} ethyl groups of the macrocycle. At 2.594(2) Å and 2.608(2) Å, the U–S bond lengths in 6 are reduced by ca. 0.16 Å compared to the mean U–S distance observed in the persulfido complex 5 (Table 2).

The geometry of the \{U\+\((μ-S)\)-U\} core in 6 is approaching linear (U1–S1–U2 is 172.0(1)°) and the U1⋯U2 separation is 5.1899(5) Å. Other mono-sulfido bridged complexes prepared to date include \{[U(N[SiMe3]2)3]2(μ-S)\}2+ [U(OAr)]2(μ-η1:η2-S:O)\}2+ and \{[U(AdArO)\+N(DME)]\}2+ (4) in which unusual persulfido \(\text{CS}_2\) motifs are seen in both the \textit{endo} and \textit{exo} positions. To our knowledge, this is the first case in which two uranium(\text{II}) centres have been able to provide a total of four reducing electrons rather than just one each in the rare incorporation of the \(\text{CS}_2\)\(^{2-}\) ligand, and the first time that more than one thiocarbonato has been formed through reductive activation by a single molecule.

The larger cleft size and more loosely-bound endo-BH\(_4\) in 2 also provides a good site for the activation of \textit{S}8 and \(\text{CS}_2\), affording the endo-(S)\(^{2-}\) \{[U(OAr)]2(μ-η1:η2-S:O)\}2+ (5) and endo-(S)\(^{2-}\) \{[U(OAr)]2(μ-S)\}2+ (6) complexes, respectively. It is clear that the addition of the arylxide ligand in 2-K promotes the activation of the \(\text{CS}_2\), exclusively between the two U\+ centres. In contrast, when the arylxides are not present \(\text{i.e.}\) in 1, the BH\(_4\) groups are easily replaced and activation of \(\text{CS}_2\) occurs in both the \textit{exo} and \textit{endo} positions. Therefore, to control and localise the activation of \(\text{CS}_2\), the \textit{exo} arylxide ligands are essential.

The unusual reactivity of 2-K is attributed to the unique environment imposed by the Pacman macrocycle. It is concluded that the \textit{endo} persulfido ion may be comfortably incorporated in 5 but further incorporation of sulfur is restricted. Similarly, the sulfido ion bridges the U\+ centres effectively in 6 but in-cleavage of the bulky thiocarbonato is disfavoured. Similarly to related UV\+ systems,\(^{39}\) sulfido 6 can be converted into persulfido 5 by the addition of elemental sulfur, suggesting the optimum cavity size between the two U\+ centres that fits this polarisable anion has been found. These first small molecule activations within the di-uranium(\text{II}) Pacman cleft exemplify the flexibility of the anthracenyl-hinged macrocycle, with U⋯U separations ranging from 4.1927(3) Å to 6.5881(3) Å, and that the use of different \textit{endo} ligands and bridging modes could lead to a wider application of these systems towards other less readily reducible molecules.

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### Notes and references