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

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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 L₄ combines two strongly reducing U(III) centres and three borohydride ligands in [M(THF)₂][U(BH₄)₂(L₄)(THF)]₂ (M = Li, Na, K). The two borohydride ligands bound to uranium outside the macroyclic cleft are readily substituted by arylxide ligands, resulting in a single, weakly-bound, encapsulated endo group 1 metal borohydride bridging the two U(III) centres in [U(OAr)₂(μ-MBH₄)(L₄)(THF)]₂ (OAr = OC₆H₄Bu₃-2,4,6, M = Na, K). X-ray crystallographic analysis shows that, for 2-K, in addition to the endo-BH₄ ligand the potassium counteranion is also incorporated into the cleft through η₁-interactions with the pyrroldes 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 arylxide-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-κ²,κ²-CS₃)(L₄)]⁻ (4). The reaction between 2-K and S₈ results in quantitative substitution of the endo-KBH₄ by a bridging persulfido (S₂)₂⁻ group and oxidation of each U(III) to U(V), yielding [{U(OAr)₂(μ-κ²,κ²,S₂)(L₄)}⁻ (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 (5S²⁻ complex [U(OAr)₂(μ-S-L₄)]⁻ (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 molecules such as arenes, N₂, CO₂, CO, N₂O, and C₂H₆. The coordination of actinides with chalcogenide ligands has begun to attract increasing interest. 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, both with d-block and rare earth metal 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.

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...
atoms of elemental sulfur, or an S atom from CS₂, providing two reducing electrons to form [U(VI)]₂ species, occasionally with further incorporation of CS₂. Products are often formed as a mixture of persulfidated (E₂)⁻⁻-bridged [U(VI)]₂ complexes such as (μ-η²:η²-S₂)[U(η⁵)]₂], where [U(η⁵)]₂ = [UC₆H₄Me₂]₄⁷ [U(η⁵)]₂ = N[SiMe₃]₅], [U[SiMe₃NPh]₃] and [U(AdArO)₃]¹¹, and sulfido (E₂)⁻⁻-bridged [U(VI)]₂ complexes such as (μ-S)[U(η⁵)]₂ and (μ-S)[U[(SiMe₂NPh)₃]¹₂]. The first terminal uranium persulfidated complex was U[(SiMe₂NPh)₃]¹¹, which can also be formed directly from the U(VI) precursor and CS₂. Finally, the ‘ate’ U(IV) siloxide complex [K₂(18-crown-6)][(μ-S₂)[U[(SiMe₂NPh)₃]¹¹] has been shown to react with CS₂ to form a variety of potassium-bound reduction products including [K₂(18-crown-6)][(μ-S₂)[U[(SiMe₂NPh)₃]¹¹] and [(μ-S₂)[U[(SiMe₂NPh)₃]¹¹]. One monosulfidated complex adds CS₂ to form the [U(VI)]₂ complex, which can also be formed directly from the U(VI) precursor and CS₂. The reaction of H₄LA with M(SiMe₃)₂ (M = K, Na and Ar = C₆H₄[2-Bu]) in THF shows a single stretch at 2280 cm⁻¹ which can be explained by the low coordination number of the metal cation. The reaction of H₄LA with M(SiMe₃)₂ in THF shows a single stretch at 2280 cm⁻¹ which can be explained by the low coordination number of the metal cation.

Results and discussion

The reaction of H₄LA with KN(SiMe₃)₂, followed by U(BH₄)₃(THF)₂ affords [K₂(THF)₃][[U(BH₄)₃]₂][U-BH₄(THF)₂][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, alkyl and allyl anions were investigated (see ESI). The most successful reactions, as evidenced by ¹H NMR spectroscopy are those between 1-K and two equivalents of the aryloxido MOAr where M = K, Na and Ar = C₆H₄[2-Bu] in good yield (Scheme 1). The ¹H 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))₃[endo-μ-κ₂-BH₄]₂(1-Na)] 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/KOAr reaction mixture, but only after standing for two weeks. These were characterised as the analogous Na⁺-containing product [(U(OAr))₃[endo-μ-κ₂-BH₄]₂ L₂[1-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 ¹H NMR spectrum of 2-K in CD₂Cl₂ is sharper than that of the crude product formed from an in situ synthesis in d₂-THF and contains paramagnetically shifted resonances corresponding to a symmetric macrocyclic and two equivalent aryloxide ligands. One resonance that integrates to 18H is seen at 4.1 ppm for the two para-Bu groups and one of integral 36H at ~0.1 ppm for the four ortho-Bu groups of the two aryloxides. The resonance corresponding to the four equivalent meta protons of the aryloxides cannot be distinguished from the macrocycle resonances of equal integral. A single broad resonance appears in the ¹¹B NMR spectrum at 188 ppm, attributed to the endo-KBH₄, in comparison to the two resonances seen at 212 ppm (1B, endo-BH₄) and 207 (2B, exo-BH₄) for 1-K. The solution state IR for complex 2-K in THF shows a single stretch at 2280 cm⁻¹ corresponding to a symmetric U(μ²-η₅-S₄), U(μ²-η₅-S₄)U₁⁺⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻˓—

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binding mode in solution, identical to that observed in the solid state for 1-Na.

The geometry of each UIII centre in 2-K (Fig. 1) is best described as a distorted pentagonal bipyramid. The coordination environment of the UIII 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 BH4 ligand (hydrogens not located) sits within the macrocyclic cleft bridging the two UIII centres with long U-B distances of about 3.3 Å (Table 1).

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Table 1 Comparison of selected distances (Å) and angles (°) in the structures of 2-K and 2-Na

<table>
<thead>
<tr>
<th>2-K</th>
<th>2-Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1⋯U1′</td>
<td>6.5881(3)</td>
</tr>
<tr>
<td>Mean U–N0</td>
<td>2.65</td>
</tr>
<tr>
<td>Mean U–Npyr</td>
<td>2.50</td>
</tr>
<tr>
<td>U1–N0 plane</td>
<td>0.70</td>
</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>

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’Bu groups away from the THF donor. The UIII 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 UIII 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 UIII–OAr distances in [U(OC6H3iPr2-2,6)3]54 and [U(OC6H3tBu2-2,6)3]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[(RArO)3(TACN)]60,61.

The main difference between the structures of 2-K and 2-Na is the binding of the K+ and Na+ cations within the cleft. The larger K+ 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+ ion is disordered over two sites about the crystallographic C2 axis, presumably because it cannot effectively bridge all four
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 [U3S8(2)]n.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 macrocycle environment; some H2 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 Na5[B(SCH2S)4]+2 B2H6, 5Na[B(SCH2S)4]+2 B2H6

5NaBH4 + 4CS2 → Na5[B(SCH2S)4]+2 B2H6

Small orange crystals of [([U(CS3)2][μ-κ2:κ2-CS3][L5])]4 were obtained from the concentrated THF solution. X-ray crystallographic analysis of 4 shows the incorporation of the rare trithiocarbonate (CS3)2− 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 U5+/U6+ (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 (CS3)2− 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 Na5 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 \([\text{U(OAr)}_2(\mu-S_2)\text{LA}](\text{5})\) in 41% yield (Scheme 2). In the solid-state structure (Fig. 3) the intermetallic cleft is occupied by a bridging persulphido ion, \((S_2)^{2-}\), 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 \(^1\text{H}\) 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 \(^1\text{H}\) 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 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 characterized on the basis of NMR spectroscopy as [(U(OAr))₂(μ-CS₂)(L₄)] (6a) and [(U(OAr))₂(μ-S)(L₄)] (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 and four of intensity 1H 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 meta proton. It is proposed from this that both aryloxide ligands are rigidly bound with the aryl rings coplanar with the anthracenyl groups of the macrocycle hinge. As no resonances are seen in the ¹³B 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 compounds and exo aryloxides inequivalent. Complex 6a is not stable in solution, and converts quantitatively to a new, C₉₂-symmetric complex either on standing at room temperature for five days or heating in benzene for 2.5 h; the resulting complex was characterized as the orange sulfido-bridged compound [(U(OAr))₂(μ-S)(L₄)] (6) (see below). No further reactivity 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 sulfido-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.⁸

### 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 U⁰ centres to U⁴⁺. The angle at the O atom of the aryloxides (U₁–O₁–Cipso = 169.0(3)°) is less acute than that observed in 2-K (154.0(5)°). The mean U₁–N(pyrrrole) 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 (S₂)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) Å. S₂ is disordered over two sites related by rotation about the C₁ 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)₂(μ-κ²-x²–x²-S₂)] and [(U[SiMe₃]₂(NPH)₂(TACN)]₂(μ-κ²-x²–x²-S₂)].⁹

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

| U₁–U₁’ | 5.1571(5) | 5.1899(5) |
| Mean U–Nim | 2.63 | 2.59 |
| Mean U–Npyr | 2.41 | 2.42 |
| U–N₅ plane | −0.07 | −0.10/−0.03 |
| U–O | 2.091(3) | 2.081(6)/2.099(6) |
| U₁–S₁ | 2.8229(8) | 2.608(2)/2.594(2) |
| U₁–S₂ | 2.707(3) | |
| S₁–S₂ | 2.118(3) | |
| O₁–U₁–S₁ | 125.7(1) | 140.1(2)/143.2(2) |
| O₁–U₁–S₂ | 166.6(1) | |
| U₁–S₁–U₁’ | 131.9(7) | |
| U₁–S₂–U₁’ | 135.0(1) | 172.0(1) |
| S₁–U₁–S₂ | 70.4(8) | |
| S₂–S₁–U₁ | 64.6(8) | |
| U₁–S₁–U₁’ | 165.4 | |
| U₁–O₁–Cipso | 169.0(3) | 170.4(5)/167.8(6) |

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**Fig. 4** Solid-state structure of 6 showing side view (left) and front view (right). For clarity, all H atoms and lattice solvent are omitted along with the meso ethyl groups and aryloxide ortho-‘Bu groups from the right-hand drawing (displacement ellipsoids are drawn at 50% probability).
U\textsuperscript{IV} 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 aryloxides are tilted back toward the hinges of the macrocycle to avoid unfavourable steric interactions between their ortho\textsuperscript{-}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 \textit{ca}. 0.16 Å compared to the mean U–S distance observed in the persulfoxido 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 U···U separation is 5.1899(5) Å. Other mono-sulphido bridged complexes prepared to date include \{[U[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{2}(μ-S)]\}\textsuperscript{2+} [5,1899(5) Å] and \{[U[AdArO]\textsubscript{2}(μ-DMEM)]\} [5.14 Å]. In these compounds the U–S bond lengths range from 2.588(1) Å to 2.736(2) Å, the U···U separations vary from 5.176(3) Å to 5.4407(6) Å and the U–S–U angles range from 165.2(2)° to 180°. The structural parameters of the \{U-(μ-S)-U\} unit in 6 lie within these limits and so the rigid environment of the Pacman macrocycle does not appear to cause an excessive distortion.

We attribute the formation of complex 6 to the slow reduction of the bound CS\textsubscript{2} molecule in 6a to form S\textsuperscript{2−} and release CS\textsubscript{2}. This is an unusual transformation since CS\textsubscript{2} is not expected to be stable, and so not prone to eliminate, in contrast to reactions of CO with reducing metal complexes that often eliminate CO and form an oxo bridge.\textsuperscript{72,73} Despite this, CS\textsubscript{2} formed from reductive disproportionation of CS\textsubscript{2} has been trapped previously.\textsuperscript{74–77} To probe whether this transformation is accelerated by heating, a solution of 6a in C\textsubscript{6}D\textsubscript{6} was boiled for 2.5 hours forming an orange solution and a brown precipitate. The subsequent \textsuperscript{1}H NMR spectrum displayed one major set of paramagnetically shifted resonances assignable to a single, symmetric Pacman product consistent with the transformation of 6a into 6. The \textsuperscript{1}H NMR spectrum of 6 exhibits just five aryloxide resonances in the ratio 18 : 18 : 18 : 2 : 2, as was seen for the similarly persulfoxido complex 5.

\textbf{Conclusions}

The reactions of [Na(THF)]\textsubscript{2}[\{U(BH\textsubscript{4})\textsubscript{2}(μ-BH\textsubscript{4})(L\textsubscript{A})(THF)\textsubscript{2}] (1-Na) with two equivalents of MOAr (where M = K or Na and OAr = OC\textsubscript{6}H\textsubscript{4}Bu\textsubscript{2}-2,4,6), result in the exclusive substitution of the exo-BH\textsubscript{4} for an arylxide, yielding \{[U(OAr)]\textsubscript{2}(endo-BH\textsubscript{4}M)(L\textsubscript{A})(THF)\textsubscript{2}] (K = 2-K and Na = 2-Na). An unusual bonding mode for MBH\textsubscript{4} is seen in which the M\textsuperscript{+} counter-ion sits adjacent to the BH\textsubscript{4} ligand in a cavity formed by the π-systems of four pyrrolide rings of the macrocycle. The U···U separation is increased by over 0.6 Å, presumably due to this additional \textit{endo-bound} ion pair.

The reaction of [Na(THF)]\textsubscript{2}[\{U(BH\textsubscript{4})\textsubscript{2}(μ-BH\textsubscript{4})(L\textsubscript{A})(THF)\textsubscript{2}] (1-Na) with excess S\textsubscript{8} formed an insoluble paramagnetic species 3, with a molecular formula suggesting the formation of a bridging uranium(s) sulfido coordination polymer. In addition, treatment of 1-Na with CS\textsubscript{2} results in the formation of [[U(CS\textsubscript{2})\textsubscript{2}(μ-η\textsuperscript{1}:η\textsuperscript{3}-CS\textsubscript{2})(L\textsubscript{A})] (4) in which unusual trithiocarbonate (CS\textsubscript{3})\textsuperscript{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(\textit{iv}) centres have been able to provide a total of four reducing electrons rather than just one each in the rare incorporation of the (CS\textsubscript{3})\textsuperscript{2−} ligand, and the first time that more than one thiocarbonate has been formed through reductive activation by a single molecule.

The larger cleft size and more loosely-bound \textit{endo}-BH\textsubscript{4} in 2 also provides a good site for the activation of S\textsubscript{8} and CS\textsubscript{2}, affording the \textit{endo}-(S\textsubscript{6})\textsuperscript{2−} \{[U(OAr)]\textsubscript{2}(μ-η\textsuperscript{1}:η\textsuperscript{3}-S\textsubscript{6})(L\textsubscript{A})\} (5) and \textit{endo}-(S\textsubscript{4})\textsuperscript{2−} \{[U(OAr)]\textsubscript{2}(μ-η\textsuperscript{2}-S\textsubscript{4})(L\textsubscript{A})\} (6) complexes, respectively. It is clear that the addition of the arylxide ligand in 2-K promotes the activation of the CS\textsubscript{2} exclusively between the two U\textsuperscript{IV} centres. In contrast, when the aryloxides are not present \textit{i.e}. in 1, the BH\textsubscript{4} groups are easily replaced and activation of CS\textsubscript{2} occurs in both the \textit{exo} and \textit{endo} positions. Therefore, to control and localise the activation of CS\textsubscript{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\textsuperscript{IV} centres effectively in 6 but in-cleft formation of the bulky thio carbonate ion is disfavoured. Similarly to related U\textsuperscript{IV} systems,\textsuperscript{59} sulfido 6 can be converted into persulfido 5 by the addition of elemental sulfur, suggesting the optimum cavity size between the two U\textsuperscript{IV} centres that fits this polarisable anion has been found. These first small molecule activations within the di-uranium(\textit{iv}) 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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\textbf{Notes and references}