Introduction

The U\textsuperscript{III} oxidation state is strongly reducing and its molecular complexes are well known for their ability to activate small molecules\textsuperscript{1-3} such as arenes,\textsuperscript{4-5} N\textsubscript{2},\textsuperscript{6-10} CO\textsubscript{2},\textsuperscript{11-19} and CO\textsubscript{2}.
\textsuperscript{20-26} The coordination of actinides with chalcogenide ligands has begun to attract increasing interest.\textsuperscript{27-31} Understanding and controlling the activation and functionalisation of chalcogen elements and their compounds is important in the petrochemical industry and in functional polymer technologies, and is increasingly of interest for new methods in organic and biomimetic syntheses,\textsuperscript{32} both with d-block\textsuperscript{33-41} and rare earth metal\textsuperscript{42,43} 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.\textsuperscript{46-49}

Almost all instances of the activation of sulfur or sulfur-containing small molecules by an actinide involve the assembly of two mononuclear U\textsuperscript{III} centres around one or more...
atoms of elemental sulfur, or an S atom from CS₂, providing two reducing electrons to form [UO₂]γ products, occasionally with further incorporation of CS₂. Products are often formed as a mixture of the persulfurid (E₂)γ-bridged [UO₂]γ complexes such as (µ-η²:η²-S₂)[U(O][X][, where [UX][ = [UC₂H₄Me]),47 [U(N²)](N² = N(siMe₃))],27 [U(siMe₂Nph)₃(tacn)]18 and [U(μ₄ArO)₄(tacn)]1,21, and sulfur (E₂)γ-bridged [UO₂]γ complexes such as (µ-S)[U(N²)](N² = N(siMe₂Nph)₃(tacn)].26 The first terminal uranium persulfurid complex was U([siMe₂Nph)₃(tacn)](η²-S₂).26 Incorporation of up to four S atoms has also been observed, e.g., in [K(18-crown-6)][(η²-S)[U(N²)](N² = N(siMe₂Nph)₃(tacn)](n = 1–3),22 and (µ-S)[U(μ₄ArO)₄(tacn)].23 One monosulfido complex adds CS₂ to form the [UO₂]CS₃ adduct (µ-κ²:κ²:κ²-CS₃)₄U([μ₄ArO)₄(tacn)], which can also be formed directly from the UO₂ precursor and CS₂. Finally, the ‘ate’ UO₂ siloxide complex [K(18-crown-6)U(OSi(ÔBu))₃] has been shown to react with CS₂ to form a variety of potassium-bound reduction products including [K(18-crown-6)U(OSi(ÔBu))₃] (µ-κ²:κ²:κ²-CS₃)₂,23

We reasoned that the preorganisation of two UO₂ 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 [UO₂]γ complex of a single ligand using the small cavity macrocycle trans-calix[2]benzen[e]pyrrole.24 We further showed that the reaction between [U(BH₄)₃(THF)] and the anions of the ‘Pacman’-shaped Schiff-base polymeric macrocycles55-57 afforded another two classes of molecule that combine two UO₂ centres in a single ligand structure.28 The larger of the two ‘Pacman’ ligands, ligated by anthracenyl groups, forms the unusual ‘ate’ complex, [Na(THF)]₄

\[\text{[U}^{2+}2\text{B}H_{3}]_{2}(\mu-\text{B}H_{3})(L)^{(3)}\text{THF}]_{2} \rightarrow \text{1-Na, Scheme 1.}\]

Herein, we report reactivity studies of 1 and a new derivative in which the exo-coordination sites of both UO₂ 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(isMe)₂, followed by U(BH₄)₃(THF) affords \([K(THF)]_{3}[U^{2+}2\text{BH}_{3}]_{2}(L)^{(3)}\text{THF}]_{2} \rightarrow \text{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 ¹H NMR spectroscopy are those between 1-K and two equivalents of the aryloxido MOAr where M = K, Na and Ar = C₆H₄(ÔBu)₂-2,4,6 (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(\text{OAr})]_{3}(\mu-\text{endo-μ-KBH}_3)_{2}(L)^{(3)}\text{THF}]_{2} \rightarrow \text{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(\text{OAr})]_{3}(\mu-\text{endo-μ-NaBH}_3)_{2}(L)^{(3)}\text{THF}]_{2} \rightarrow \text{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 ¹H NMR spectrum of 2-K in CD₆D₆ is sharper than that of the crude product formed from an in situ synthesis in d₅-THF and contains paramagnetically shifted resonances corresponding to a symmetric macrocycle and two equivalent aryloxide ligands. One resonance that integrates to 18H is seen at 4.1 ppm for the protons of the aryl-endo groups. The solution state IR shows a single stretch at 2280 cm⁻¹ corresponding to the symmetric U(µ₂-η²-S), (µ₂-η²-S₂)-H₂BH₃U ionic.

Chemical Science

Scheme 1. The reaction of H₄L₄ with M(SiMe)₂ (M = Li, Na, K) and U(BH₄)₃(THF) to yield Na[UO₂][([UO₂][μ-BH₄][L]THF)] (1-Na, previously reported) and the group 1 analogues 1-Li and 1-K; further reaction with MOAr yields [M[UO₂](THF)]₂(endo-μ-BH₄)[L] (OAr = OC₆H₄Bu₂-2,4,6, M = K, 2-K; M = Na, 2-Na).
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-t-Bu groups away from the THF donor. The U^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^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(pyrolide) 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 2.23(1) Å and 2.24(5) Å respectively (Table 1). These are longer than the U^III^–OAr distances in [U(OC₆H₃₅Pr₂-2,6)₃]₃²⁺ and [U(OC₆H₃₅Bu₂-2,6)]₃⁹ 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)]₃⁶⁻²¹.

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 pyrolide 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

![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 t-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.†](Image)

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

|       | 2-K          | 2-Na         |
|-------|--------------|--------------|
| U1⋯U1’ | 6.5881(3)    | 6.5265(7)    |
| Mean U–Nim | 2.65        | 2.65        |
| Mean U–Npyr | 2.50        | 2.51        |
| U1–N₄ plane | 0.70       | 0.69        |
| U1–O1  | 2.231(5)    | 2.245(6)    |
| U1⋯B1  | 3.312(1)    | 3.269(1)    |
| U1–O2  | 2.554(5)    | 2.592(6)    |
| B1–M1  | 3.036(11)   | 2.747(2)    |
| M1–[pyr]centroid | 3.154(2), 3.153(2) | 2.85(4), 3.04(2), 3.08(4), 3.61(2) |
| U1–B1–U1’ | 168.2(4) | 173.0(6) |
| O1–U1–B1 | 178.3(2) | 177.6(1) |
| U1–O1–Cipso | 154.0(5) | 153.3(6) |

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

The geometry of each U^III^ centre in 2-K (Fig. 1) is best described as a distorted pentagonal bipyramid. The coordination environment of the U^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 BH₄ ligand (hydrogens not located) sits within the macrocyclic cleft bridging the two U^III^ centres with long U–B distances of about 3.3 Å (Table 1).
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 M11--B1 separations, the U ions form a standard bonding interaction with the BH4 anion.\textsuperscript{66,67} Reported terminal K--BH4 separations range from 2.947(3)\textdegree to 3.091(4)\textdegree Å with a mean value of 3.00 Å, while terminal Na--BH4 separations range from 2.600(6)\textdegree to 2.841(2)\textdegree 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\textdegree 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 UIII 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[B(\text{pyr})]L”] ([“L” = trans-calix[2]benzenelene][pyrrolylido]).\textsuperscript{29} This raises the question of whether there is a bond between the UIII ions and the endo BH4\textdegree group in 2-K and 2-Na or whether the BH4\textdegree group is held within the cleft by association with its M+ counter-ion. The observed 11B NMR shift of the endo BH4\textdegree group in 2-K (188 ppm) is significantly paramagnetically shifted from that of free KH4\textdegree (−40 ppm) indicating that there is some electronic overlap between the UIII centres and the BH4\textdegree 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 [U4S8(L4)]\textsubscript{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 Na[B(\text{H2})3S4], the caesium analogue of which has previously been made from the reaction between CsBH4, BH3 and H2S (eqn (1)).\textsuperscript{68} 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 binds as a terminal multiply bonded ligand led us to assign a polymeric structure for 3 as drawn in Scheme 2.

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

A THF solution of 1-Na was treated with an excess (>9 equivalents) of CS2, upon which the reaction mixture immediately turned bright orange, and quantitative deposition of the product characterised as [\{U(CS3)2\}m+:μ-x:κ-x:κ-x-CS3\}L\textsuperscript{4−}] \textsuperscript{4} 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 macrocycle environment with resonances between +25 and −44 ppm. The IR spectrum of solid 4 shows no absorptions in the region 2500−2000 cm\textsuperscript{−1} confirming that no borohydride ligands remain. The 13B 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 UIII 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}_3(\text{BH}_2)\text{S}_2]\text{−} (−13.7/15.8 ppm)\textsuperscript{71} and [\text{BH}_2(\text{SCH}_2\text{S})_2]\text{−} (−17.0 ppm).\textsuperscript{72} The 11B NMR resonance at 0.5 ppm is attributed to the known anion [B(\text{SCH}_2\text{S})_2\text{−}] (eqn (4)) which is formed from the sub-stoichiometric reaction of NaBH4 with CS2. The corresponding CH3 group is observed as a quartet at 3.97 ppm in the 1H NMR spectrum.\textsuperscript{73} The second species in the 11B NMR appears closer to the polymeric species, formulated as {[B(\text{SCH}_2\text{S})_3\text{−}]}\textsubscript{n} (0.0 ppm, eqn (5) suggesting a similar formulation for the resonance at 0.29 ppm possibly with an intermediate charge (e.g. [B(\text{SCH}_2\text{S})_3\text{−}])\textsuperscript{74}.

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

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

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

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

Small orange crystals of [\{U(CS3)2\}m+:μ-x:κ-x:κ-x-CS3\}L\textsuperscript{4−}] (4) were obtained from the concentrated THF solution. X-ray crystallographic analysis of 4 shows the incorporation of the rare trithiocarbonate (CS3)\textsuperscript{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 U\textsuperscript{V}/U\textsuperscript{VI} (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)\textsuperscript{2−} ligand, and the first time that more than one thiocarbamate 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 $S_8$ to a slurry of 2-K in toluene resulted in the immediate formation of a pale orange solution and a pale yellow precipitate of KBH$_4$. Addition of hexanes to the filtrate results in the deposition of orange crystals of the thermally stable product $\left\{U(OAr)\right\}_2(\mu-\text{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, $(\text{S}_2)^{2-}$, suggesting that both uranium centres have been oxidised to U$^{IV}$. This is reinforced by the reduction of the U–L bond lengths (cf. 2-K), in keeping with the values for known U$^{IV}$ complexes (see below). The $^1$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 $^1$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 $^{11}$B

Scheme 2  Contrasting reactions of $[\text{Na}(\text{THF})_4]\{\text{U(BH}_4\right\}_2(\mu-\text{BH}_4)(\text{LA})(\text{THF})_2\]$ (1-Na) and $[\text{U(OAr)}(\text{THF})_2(\text{endo-μ-KBH}_4)(\text{LA})]$ (2-K) and the synthesis of complexes 3-6 (OAR = OC$_6$H$_2$Bu$_3$-2,4,6).

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 $^t$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 [\([U(OAr)]_2(\mu-CS_2)(L^*)\)] (6a) and [\([U(OAr)]_2(\mu-S)(L^*)\)] (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 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 ¹ⁱB 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 sulfido-bridged compound [\([U(OAr)]_2(\mu-S)(L^*)\)] (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 3, 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.

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 macrocyle, 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 macrocycyle 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 2.23(3) 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–C₁_pso = 169.0(3))’ is less acute than that observed in 2-K (154.0(5)). The mean U₁–N(pyrrrolide) 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).

Table 2 Selected structural parameters of complexes 5 and 6

|     | 5          | 6          |
|-----|------------|------------|
| U₁–U’ | 5.157(5)   | 5.189(5)   |
| Mean U–N_im | 2.63 | 2.59 |
| Mean U–N_pyr | 2.41 | 2.42 |
| U–N 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) |
| S₁–S₂ | 2.707(3) | 2.118(3) |
| O₁–U₁–S₁ | 125.7(1) | 140.1(2)/143.2(2) |
| O₁–U₁–S₂ | 166.6(1) | 131.98(7) |
| U₁–S₁–U’ | 135.0(1) | 170.2(1) |
| S₁–U₂ | 70.40(8) | 64.62(8) |
| U₁–S₁ | 169.0(3) | 170.6(3)/167.8(6) |

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). 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, U’, S₁ and S₂ are not coplanar but instead the \([U_2S_4]^{-}\) 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 uranium bridging symmetrically between two U⁴⁺ centres in \([U(N[SiMe₃]₃)_2]_2(\mu-k^2-x^2-S₂)\] and \([U([SiMe₃]NPH)₅]TACN)]_2(\mu-k^2-x^2-S₂)\] respectively.

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
U^IV 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 sterical 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 = 172.0(1)^°) and the U1...U2 separation is 5.1899(5) Å. Other mono-sulfido bridged complexes prepared to date include \{[U[N(SiMe$_2$)$_2$]]$_2$(μ-S)]$_2$[U(OAr)$_2$(μ-S)] (Ar = 2,6-\textit{C}_6\textit{H}_3(\textit{Bu})$_2$) and \{[U(AdArO)$_2$(μ-S)]$_2$(μ-S)]$_2$\}. In these compounds the U–S bond lengths range from 2.588(1) Å to 2.736(2) Å, the U1...U2 separations vary from 5.176(3) Å to 5.4407(6) Å and the U–S–U angles range from 125.2(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 reductive cleavage of the bound CS$_2$ molecule in 6a to form S$^2^-$ and release CS. This is an unusual transformation since CS is not expected to be stable, and so not prone to eliminate, in contrast to reactions of CO$_2$ with reducing metal complexes that often eliminate CO and form an oxo bridge.\textsuperscript{72,73} Despite this, CS$^2^-$ formed from reductive disproportionation of CS$_2$ has been trapped previously.\textsuperscript{41,42} To probe whether this transformation is accelerated by heating, a solution of 6a in C$_6$D$_6$ was boiled for 2.5 hours forming an orange solution and a brown precipitate. The subsequent $^1$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 $^1$H NMR spectrum of 6 exhibits just five arylxide resonances in the ratio 18 : 18 : 18 : 2 : 2, as was seen for the similarly symmetric persulfido complex 5.

**Conclusions**

The reactions of [Na(THF)$_2$][{(U(BH$_4$)$_2$(μ-BH$_4$))(L$^A$(THF))}$_2$] (1-Na) with two equivalents of MOAr (where M = K or Na and OAr = OC$_6$H$_4$(\textit{Bu})$_2$-2,4,6), result in the exclusive substitution of the exo-BH$_4$ for an arylxide, yielding [U(OAr)$_2$(endo-BH$_4$M)(L$^A$(THF))$_2$] (K = 2-K and Na = 2-Na). An unusual binding mode for MBH$_4$ is seen in which the M$^+$ counter-ion sits adjacent to the BH$_4$ ligand in a cavity formed by the π-systems of four pyrroline rings of the macrocycle. The U...U separation is increased by over 0.6 Å, presumably due to this additional endo-bound ion pair.

The reaction of [Na(THF)$_2$][(U(BH$_4$)$_2$(μ-BH$_4$))(L$^A$(THF))] (1-Na) with excess S$_8$ formed an insoluble paramagnetic species 3, with a molecular formula suggesting the formation of a bridging uranium(v) sulfido coordination polymer. In addition, treatment of 1-Na with CS$_2$ results in the formation of \{[(U(CS$_2$)$_2$(μ-η$^1$:η$^1$:η$^2$:CS$_2$)]$(L^A)$\} (4) in which unusual triothiocarbonate (CS$_2$)$_2^-$ motifs are seen in both the \textit{endo} and \textit{exo} positions. To our knowledge, this is the first case in which two uranium(II) centres have been able to provide a total of four reducing electrons rather than just one each in the rare incorporation of the (CS$_2$)$_2^-$ 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 endo-BH$_4$ in 2 also provides a good site for the activation of S$_8$ and CS$_2$, affording the endo-(S$_2$)$_2^-$ \{[U(OAr)$_2$(μ-η$^1$:η$^1$:η$^2$:S$_2$)]$(L^A)$\} (5) and endo-(S$_2$)$_2^-$ \{[U(OAr)$_2$(μ-S)]$(L^A)$\} (6) complexes, respectively. It is clear that the addition of the arylxide ligand in 2-K promotes the activation of the CS$_2$ exclusively between the two U$^{III}$ centres. In contrast, when the arylxides are not present i.e. in 1, the BH$_4$ groups are easily replaced and activation of the CS$_2$ occurs in both the \textit{exo} and \textit{endo} positions. Therefore, to control and localise the activation of 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$^{IV}$ centres effectively in 6 but in-sift formation of the bulky thiocarbonate ion is disfavoured. Similarly to related U$^{IV}$ systems,\textsuperscript{39} sulfido 6 can be converted into persulfido 5 by the addition of elemental sulfur, suggesting the optimum cavity size between the two U$^{IV}$ centres that fits this polarisable anion has been found. These first small molecule activations within the di-uranium(II) Pacman cleft exemplify the flexibility of the anthracylen-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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