Switchable π-coordination and C–H mettallation in small-cavity macrocyclic uranium and thorium complexes†‡

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New, conformationally restricted ThIV and UIV complexes, [ThCl2(L)] and [U2(L)], of the small-cavity, dipyrrolic, dianionic macrocycle trans-cali[2]benzene[2]pyrrolylido (L)2 are reported and are shown to have unusual κ5,x5 binding in a bent metallocene-type structure. Single-electron reduction of [U2(L)] affords [U][ThF4(L)] and results in a switch in ligand binding from κ5-pyrrolylido to η6-arene sandwich coordination, demonstrating the preference for arene binding by the electron-rich UIII ion. Facile loss of THF from [U][ThF4(L)] further increases the amount of U–arene back donation. [U][I] can incorporate a further UIII equivalent, U5, to form the very unusual dinuclear complex [U2I4(L)] in which the single macrocycle adopts both κ5,x5 and η6-κ6,x6 binding modes in the same complex. Hybrid density functional theory calculations carried out to compare the electronic structures and bonding of [U][II(L)] and [U][II4(L)] indicate increased contributions to the covalent bonding in [U2I4(L)] than in [U][II(L)], and similar U–arene interactions in both. MO analysis and QTAIM calculations find minimal U–U interaction in [U2I2(L)]. In contrast to the reducible U complex, treatment of [ThCl2(L)] with either a reductant or non-nucleophilic base results in metallation of the aryl rings of the macrocycle to form the (L–2H)4 tetraanion and two new and robust Th–C bonds in the π-ate complexes [K(THF)2ThIV(μ-CI)(L–2H)]2 and K[ThIV[N(SiMe3)2](L–2H)].

Introduction

The organometallic chemistry of the early actinides has seen rich growth in recent times.1–5 However, compared to the d-block, the study of arene complexes of the f-block is still in its infancy. We recently reported the spontaneous reduction of arenes mediated by the disproportionation of two UIII centres to yield the uranium–arene complexes [[X2U]([μ-C6H4R])](X = N[SiMe3]2 or OAr, R = H, Me, SiH3, Ph, BBN).6 In this type of arene compound, the actinide-to-ligand back donation from molecular orbitals with δ-symmetry is becoming recognised as a major component of the bonding.7–14 These ‘softer’ δ-interactions between the metal and ligand provide an important opportunity to probe covalency in actinide bonding, which has implications in the separation of the transuranics and lanthanides from the early actinides in nuclear waste.15–19 Organothorium complexes exhibiting arene interactions are even rarer, with only a few complexes reported, for example [Li(DME)]1[η6–1,3–{[2-C3H11N](CH2)2C6H4}2][ThCl4]1a and the cationic [{X2A1}Th(CH2SiMe3)1(n6-C6H6)][B(C6F5)4], (X2A1 = 4,5-bis(2,6-diisopropylanilino)-2,7-di-tert-butyl-9,9-dimethylxanthene).21

Pyrrolic macrocyclic ligands have been shown to support a diverse array of f-block chemistry,22 including dinitrogen cleavage,23,24 stable alkyl complexes,25 and the first f-block example of the reductive disproportionation of CO2 to carbonate and CO.26 Focusing on actinnide chemistry, we (Love and Arnold) used an octadentate, tetraanionic Pacman-shaped Schiff-base pyrrole macrocycle to make UIII and NpIII iodides ([AnIII]2(L))2, that showed magnetic coupling between the AnIII centres,27 and mononuclear [UIV(L)]2.28,29 Although pyrroline ligands can coordinate to the metal centre in a κ1 mode through the N atom or in a κ5 mode, similar to classical cyclopentadienyl coordination to a metal, the κ1 mode is by far the more common of the two.15,20–17 The trans-cali[2]benzene[2]pyrrolylido, (L)2, combines two pyrroline heterocycles with two aryl rings...
connected via dimethylmethane linkers. The lack of extended conjugation in this macrocycle, as compared to porphyrins, grants it a large degree of flexibility, allowing the possibility of either σ- or π-bonding of the ligand to the metal centre through either the pyrrolide or arene. Complexes of this ligand are limited to two examples of SmIII, [SmCl(L)] displays a η6-arene-κ5-pyrrolide binding mode to the SmIII cation (Scheme 1). Treatment of [SmCl(L)] with LiMe resulted in isolation and partial characterisation of products, including [SmIII(L-THF)] the product of single aryl-metalation of the ligand and [SmIII(L)] the ligand which incorporates a partially protonated and N-confused macrocycle. In the reaction of [SmCl(L)] with NaH, [Sm(L)(L-H)] the product of single aryl-metalation of the SmIII cation (Scheme 1). The molecular structures of 1 and 2 contrasts to that seen in the SmIII complex [SmCl(L)] (Scheme 1) which displays a 1,3-alternating conformer but with substantial flattening of the pyrrolide rings in a shallow double cone conformation, with an endo bound η6-κ5:κ5 SmIII cation in the arene cavity. The binding mode of the singly aryl metallated [Sm(THF)(L-H)] is nominally similar to 1 and 2 in that it has κ5:κ5 pyrrolide binding, but in the SmIII case it is a result of the cation being located deeper within the macrocyclic cavity; the contraction of the pyrrolide cone gives κ5:κ5 binding with a [κ5-C5N]cent-Sm-[κ5-C5N]cent angle of 136.25(5)° and concomitant splaying of the arene rings on metallation. This contrast in macrocycle binding between actinide(IV) and samarium(III) is notable given their similar ionic radii.

Results and discussion

Synthesis of [AnIVX2(L)]

The trans-calix[2]benzene[2]pyrrole (H2L), was synthesised according to the literature procedure, and was deprotonated in situ with KH to yield the potassium salt K2L. The reaction between K2L and equimolar AnX4(solvent)2 (An = Th, X = Cl, solvent = DME; An = U, X = I, solvent = Et2O) in THF at 80 °C for up to 3 days, followed by work-up to remove KX yielded the new compounds [ThCl2(L)] as a yellow solid in 66% yield and [U1I2(L)] as a red solid in 53% yield (Scheme 2). The synthesis of 2 proceeds cleanly irrespective of alkali metal salt or solvent (THF or arene) employed; for example, 2 is also readily accessible from U2I2 in toluene (see ESIT). The 1H NMR spectra of both 1 and 2 show the macrocyclic ligand to have C2v symmetry. In 2, the resonances are broadened and contact shifted (110 to −16 ppm) due to presence of the paramagnetic UIV f2 ion and the aryl protons closest to the metal centre are not observed. The methyl groups of 1 and 2 are observed as two singlets of equal intensity due to the magnetic inequivalence of the endo and exo faces of the ligand upon metallation. Single crystals suitable for X-ray diffraction were grown from a THF solution of 1 layered with n-hexane and allowed to stand at ambient temperature for 3 days. For 2, single crystals were grown at −30 °C from a saturated toluene solution.

The molecular structures of 1 and 2 (Fig. 1 and ESIT respectively), are isomorphous and show a new binding mode for (L)2 – with a 1,3-alternating double cone macrocycle conformation with endo metallocene-type binding of the An(IV) cation κ5:κ5 between the two pyrrolide rings and an empty arene cavity. The average An-[C5N]centroid distances and the metallocene angles [κ5-C5N]cent-An-[κ5-C5N]cent are similar to those seen in the cyclopentadienyl AnIV complexes [CP*3AnX2].

The distances to the ipso-carbons of the rings (Th1–C9, 3.024(2) Å, Th1–C29, 3.017(2) Å; U1–C9, 3.045(5) Å and U1–C29, 3.022(5) Å) are too long to suggest an agostic interaction. The ligand binding in 1 and 2 contrasts to that seen in the SmIII complex [SmCl(L)] (Scheme 1) which displays a 1,3-alternating conformation but with substantial flattening of the pyrrolide rings in a shallow double cone conformation, with an endo bound η6-κ5:κ5 SmIII cation in the arene cavity. The binding mode of the singly aryl metallated [Sm(THF)(L-H)] is nominally similar to 1 and 2 in that it has κ5:κ5 pyrrolide binding, but in the SmIII case it is a result of the cation being located deeper within the macrocyclic cavity; the contraction of the pyrrolide cone gives κ5:κ5 binding with a [κ5-C5N]cent-Sm-[κ5-C5N]cent angle of 136.25(5)° and concomitant splaying of the arene rings on metallation. This contrast in macrocycle binding between actinide(IV) and samarium(III) is notable given their similar ionic radii.
Reduction of [$\text{UI}^{IV}_{2}(L)$] to [$\text{UI}^{III}(\text{THF})(L)$]

The reduction of [$\text{UI}^{IV}_{2}(L)$], 2 by KC$_8$ in THF at low temperature resulted in a colour change from red to dark green. Filtration to remove KI and washing to remove trace H$_2$L allowed the isolation of the U$^{III}$ complex [$\text{UI}(\text{THF})(L)$] 3 as a dark brown solid in a moderate, 30% yield (Scheme 3). In coordinating solvents, 3 exists as the thermally stable solvate [$\text{UI}(S)(L)$] ($S =$ THF, pyridine, dioxane). Single crystals suitable for X-ray diffraction were grown from a saturated THF solution at $-30^\circ$C and the solid state structure of 3 is shown in Fig. 2. In the absence of coordinated solvent, 3 shows very limited solubility in hydrocarbon solvents and decomposes in diethyl ether. Coordinated solvent is removed under vacuum to yield [$\text{UI}(L)$] 3a, as supported by the EI mass spectrum and combustion analysis. We were also able to obtain single crystals of the unsolvated complex 3a by layering a THF solution with $n$-hexane at ambient temperature (Fig. 2b).

As in 2, the $^1$H NMR spectrum of 3 shows resonances that are consistent with an approximately $C_{2v}$ symmetric macrocyclic environment, with the methyl groups observed as two magnetically inequivalent singlets of equal intensity; in contrast to 2, all of the aryl protons are observed. The ligand resonances for 3 are contact shifted and broadened, as expected for a U$^{III}$ complex, in a spectral window (19 to $-35$ ppm) narrower than for 2. In 3, resonances for coordinated solvent were not observed, indicative perhaps of a fluxional process at ambient temperature on the $^1$H NMR timescale, in keeping with the lability of the coordinated solvent.

In contrast to the Sm$^{III}$ chemistry, reduction of 2 to 3 proceeds cleanly and results in a dramatic change in macrocycle conformation. With the change in oxidation state from U$^{IV}$ to U$^{III}$, ligand binding switches from the unusual $\kappa^2:\kappa^3$ metalloocene binding in 1 and 2 to the $\eta^1:\kappa^2:\eta^1$ bis(arene) binding seen in [SmCl($L$)], showing a clear preference for arene binding in uranium(n). This bis(arene) sandwiched structural motif is reminiscent of that seen in the bis(arene) complexes of the zero oxidation state lanthanides and early transition metals [M(η-Bz$_2$)$_2$] [Bz$^+$ = 1,3,5-(Bu$_3$)C$_6$H$_2$], uniquely accessible by metal vapour synthesis. 44 Complex 3 also represents a rare example of a monomeric uranium(n) cation stabilised by a single dianionic ligand and with a single halide site for subsequent metathesis chemistry.

The U–N, U–O, and U–I distances in 3 are unremarkable. The [aryl]$_{\text{cent}}$-U-[aryl]$_{\text{cent}}$ angles, 172$^\circ$ in 3 and 174$^\circ$ in 3a are almost linear and similar to that found in [SmCl($L$)] (176$^\circ$). The U1–C$_{\text{avg}}$ distances in both 3 (3.001 Å) and 3a (2.970 and 2.950 Å) are longer than those of the inverse $\mu$-arene sandwich complexes of uranium$^9$ and are comparable to the U$^{III}$ aryloxoide complex, [U(O-2,6-Pr$_3$C$_6$H$_3$)$_2$]$_2$, $^7$ U1–C$_{\text{avg}}$ of 2.92(2) Å, which exists as a $\pi$-arene bridged dimer in the solid state, and to the two U$^{III}$ adducts of hexamethylbenzene.$^{98,99}$ The C–(aryl) distances (range 1.360(11)–1.413(10) Å in 3) are unchanged from 2 or benzene (average 1.40 Å).$^{100,101}$

Interestingly, the loss of coordinated THF from 3 to form 3a results in a significant shortening of U–L bonds, for example U1–N1 contracts from 2.530(6) to 2.468(10) Å and the lengthening of some of the arene C–C bonds in 3a (C–C 1.382(19)–1.444(2) Å) is now notable, and suggests a greater stabilising back donation from the U$^{III}$ centre into the arene groups. The change of $\pi$-binding and incorporation of U$^{III}$ into the arene cavity on reduction of 2 to 3 causes the interplanar angle of the arene cavity to decrease significantly from 21.88$^\circ$ to 18.05$^\circ$. An even smaller value of 15.55$^\circ$ is observed for 3a and thus this metric can be used as a measure of the uranium–arene interaction.

**Synthesis of [$\text{UI}^{III}_{2}(L)$]***

Given the stability of 3 it was obvious to question whether it could be synthesised directly from a U$^{III}$ precursor. While reactions between K$_4$L or Li$_4$L and UI$_3$ in THF result in the formation of 3, a major by-product, identified as the very unusual dinuclear complex [$\text{UI}^{III}_{2}(L)$], 4 is observed. Moreover, the reaction of base-free UI$_3$ (two equivalents) with Li$_2$L in

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**Scheme 3** Reduction of [$\text{UI}^{IV}_{2}(L)$] 2 to [$\text{UI}^{III}(\text{THF})(L)$] 3.
toluene afforded 4 as the sole ligand-containing product which was isolated as an analytically pure material in a 22% yield (Scheme 4). The $^1$H NMR spectrum of 4 displays resonances that are consistent with a single ligand environment of $C_{2v}$ symmetry. These resonances are contact shifted and broadened, with the width of the spectral window (60 to $–35$ ppm) intermediate between those of 2 and 3, and, as in 2, the aryl protons closest to the $\kappa^2$:$\kappa^2$ uranium cation are not observed. Single crystals of dinuclear UIII 4 were grown from hot benzene (Fig. 3); these data show that the macrocycle bridges the two [$U^{III}_2$]$^+$ units with both $\kappa^2$:$\kappa^2$ and $\eta^1$:$\kappa^2$:$\kappa^2$ binding modes. The stabilisation of not one but two uranium(III) centres by this single dianionic ligand was unexpected and is remarkable.

The $\kappa^3$:$\kappa^3$ pyridyl binding of U2 in 4 is similar to that seen in 2, although the U2–[$\kappa^2$:$\kappa^2$N]cent(ave) distance of 2.583 Å is longer (2.480 Å in 2) and the metallocene angle is much smaller, [$\kappa^3$:$\kappa^3$N]cent–U2–[$\kappa^2$:$\kappa^2$N]cent of 139° (cf. 163° in 2) resulting in a more classical, bent-sandwich geometry. Likewise, the $\eta^1$:$\kappa^2$:$\eta^1$:$\kappa^2$ bis-arene bonding of U1 in 4 is very similar to that seen in 3 and 3a; the interplanar arene angle is 16.41° in 4, intermediate between 3 (18.05°) and 3a (15.55°). The U1–[aryl]cent(ave) distances are also longer (2.799 and 2.748 Å) than in 3 (2.669 and 2.612 Å) and the [aryl]cent–U1–[aryl2]cent angle narrower (164.99° cf. 172° in 3). The U1…U2 separation of 3.8639(5) Å in 4 is dictated by the macrocycle geometry and is significantly longer than the shortest reported example, the amidobridged [$U^{III}$]complex, [$U(C_6H_6)_2$]$_2$ [$\eta^1$:$\eta^1$:$\eta^1$,$\eta^1$],HN(CH$_2$)$_2$N(CH$_2$)$_2$N(CH$_2$)$_2$NH (3.3057(9) Å).

The use of toluene as a solvent for UI$_3$ reaction chemistry can result in decreased product yields due to the formation of insoluble aggregates. However, it is necessary in our case to prevent a solvent-dependent equilibrium between 3 and UI$_3$ and 4 (Scheme 5). Dissolution of crystals of 4 in $d_8$-thf results in an immediate colour change from brown to purple and a 1 : 0.05 ratio of 3 : 4 was determined by $^1$H NMR spectroscopy. Complex 3 is stable in hydrocarbons, even after loss of coordinated solvent, but the mixing of 3 with an equimolar amount of UI$_3$ in $d_8$-toluene results in the slow formation of 4 (3 : 4, 1 : 0.02 after 1 h, 1 : 0.13 after 15 h). We have not been able to determine the resting position of the equilibrium because of poor solubility and the solution behaviour of 3 and 4 necessarily limits the choice of reaction and work-up solvents for this chemistry.

Complexes 3 and 4 are thermally robust and isolable, albeit in moderate yields, free from metallation or oxidation products, and represent an important synthetic entry into UIII chemistry in a new and versatile macrocyclic ligand environment.

**Electronic structure and bonding of [UIII(L)] and [U$_2^{III}$L$_4$(L)]**

In order to probe the electronic structure and bonding in 3a and 4 we turned to quantum chemistry in the form of hybrid density functional theory (PBE0). Geometry optimisations proceeded smoothly to yield structures in excellent agreement with those found by X-ray crystallography: e.g. for 3a ($C_3$ symmetry) U1–I = 3.150 Å, U–N(av) = 2.455 Å and U–C(av) = 2.926 Å; for 4 ($C_{2v}$ symmetry) U1–I = 3.119 Å, U2–I = 3.025 Å, U1–N = 2.644 Å, U2–N = 2.718 Å, U1–C(av) = 3.126 Å, U2–C(av) = 2.870 Å and U1–U2 = 3.768 Å (see ESI† for tabular comparison).

The calculated interplanar arene angles in 3a and 4 are 13.61° and 14.68° respectively, very similar to the experimental values of 15.55° and 16.41°, respectively. The average C–C(arene) bond lengths are also very similar for 3a and 4 at 1.395 Å and 1.392 Å respectively.

A valence molecular orbital (MO) energy level diagram for 3a is presented in Fig. 4. The highest three orbitals (140–142) have predominantly uranium 5f character (84, 91 and 94% respectively), as anticipated for a UIII system. The highest occupied pyridyl $\pi$-based levels separate into two pairs (138–139 and 136–137) with very little metal contribution. Below these orbitals come the iodide $p$-based levels; 134 and 135 ($p_x$) and 133 ($p_y$). Finally, a block of six orbitals (127–132) are seen, which feature U–N $\sigma$ bonding (MOs 127 and 129) and four arene $\pi$-based levels, the most stable of which (MOs 128 and 130) clearly display uranium–arene $\delta$ bonding.

**Fig. 3** Solid state structure of 4 (displacement ellipsoids are drawn at 50% probability). For clarity, H atoms are omitted. Selected bond distances (Å) and angles (°) for 4: U1–I1 3.1096(6), U1–N1 2.669(5), U1–[aryl]cent 2.799, U1–[aryl2]cent 2.748, U1–C$_{ave}$ 3.105, C–C 1.383(9)–1.410(8), U2–C$_{ave}$ 2.699, [aryl]cent–U1–[aryl2]cent 164.99°, U2–I2 3.043(8), U2–I3 3.025(6), U2–[k$^2$-$\kappa^2$N]cent 2.583, [k$^3$-$\kappa^3$N]cent–U2–[k$^3$-$\kappa^3$N]cent 139.03°, U1–U2 3.8639(5).

**Scheme 3** Synthesis of [U$_2$L$_4$(L)] 4.

**Scheme 5** Equilibrium behaviour of 3 and 4 in solution.
The valence molecular orbital structure of 4 is presented in Fig. 5. The increased number of metal and halogen atoms yields a more crowded valence region, but the character of the orbitals can once again be discerned. The principal difference between Fig. 4 and Fig. 5 is the energy of the pyrrolide π orbitals; in 3a they are less stable than the iodide p-based MOs whereas in 4 the opposite is true; the energies of the iodide p-based levels are approximately the same in the two systems, whereas the pyrrolide π orbitals are ca. 2 eV more stable in 4 than 3a.

Table 1 contains the average uranium atomic orbital contribution to the I p-based and U–arene δ bonding orbitals of 3a and 4. Although arguably a rather crude measure, these data indicate slightly larger metal contributions to the orbitals of 4 vs. their 3a analogues, suggestive of enhanced covalency in the former.

Single point calculations on (L)²⁻ in its geometry in 3a and 4 reveal that it is 58.8 kJ mol⁻¹ more stable in the former (at the SCF level). In both cases the four highest occupied MOs are the pyrrolide π levels which contribute to Fig. 4 and 5, and these are slightly more stable in (L)²⁻ in its 3a geometry than in that of 4 (e.g. the HOMO of (L)²⁻/3a is 35.2 kJ mol⁻¹ more stable than the HOMO of (L)²⁻/4). Clearly, however, this situation is reversed when the macrocycle incorporates uranium – as noted above, the pyrrolide π-based orbitals are about 2 eV (ca. 200 kJ mol⁻¹) more stable in 4 than 3a. The explanation almost certainly lies in the extent to which the uranium atomic orbitals are mixed into the pyrrolide levels. A good comparison is MO 139 of 3a (Fig. 4) with MO 151 of 4 (Fig. 5); the former has a very minor (4%) non-bonding 5f contribution whereas the latter features 15% uranium 6d character in what is clearly a metal–pyrrolide δ bonding interaction. We can therefore conclude that at least part of the driving force for the macrocycle to adopt the more constrained geometry in 4 than in 3a is the covalent bonding it gains with U2 in the former.

Tables containing the principal character and orbital contributions to the frontier MOs in 3a and 4 are included in the ESI,‡ alongside enlarged pictures of the MOs from Fig. 4 and 5.

The charges on the uranium atoms in 3a and 4 have been calculated in several different ways, and the results are collected in Table 2. It is typically the case that there are rather large differences between the absolute values of partial atomic charges calculated in different ways, though often the trends are similar and this is the case here. For all three charge analysis schemes, the uranium atom is most positive in 3a, while in 4, the arene-coordinated U1 is more positive than the π-pyrrolide coordinated U2. These data support the MO composition analysis described above; a higher partial charge is associated with less covalency, and hence we conclude that the bonding in 4 is more covalent than in 3a. Within 4 the lower charge on U2 suggests this atom is, overall, more covalently bonded than U1.

A less traditional approach, certainly within f element systems, to assessing the relative extent of ionicity and covalency is the Quantum Theory of Atoms-in-Molecules (QTAIM) which we have recently applied to a variety of uranium compounds.⁵⁴–⁶⁰ We have found the properties of bond critical points (BCPs) to be valuable additions to discussions of f element–ligand bonding, in particular the electron and energy densities. These are collated for selected BCPs of 3a and 4 in Table 3.¶
As with most BCP data for actinide compounds, the absolute values of both metrics are small, suggesting the uranium–ligand bonds are largely ionic. That said, we can use these data to assess relative covalency, and can relate them to the MO and partial charge arguments developed above. This is best done for the U–I bonds (which are obviously free of the complicating effects of macrocycle rearrangement) and comparison of the U–I data in 3a with 4 suggests that the U1–I bond in 4 is very similar to that in 3a. The slightly larger (absolute) values of ρ and H for U2–I indicate slightly greater covalency, in agreement with the charge data in Table 2. The κ1 U–N interaction is clearly significantly weaker in 4 (U1–N), as the bond distance is ≈0.2 Å longer than in 3a. This is reflected in ρ and H, which are both (absolutely) smaller in 4. At the QTAIM level the differences between the κ1 and κ2 U–N interactions in 4 are comparable with the differences between U1–I and U2–I, although now U2 has the smaller BCP metrics.

Also given in Table 3 are the delocalisation indices δ(A,B) for the selected bonds. δ(A,B) is the average number of electrons shared between atoms A and B, and is the bond order when atoms A and B are connected by a bond path, as is the case here. These data very much support the conclusions from the BCP

Table 1  Average uranium atomic orbital contribution (%) Mulliken analysis) to selected molecular orbitals of 3a and 4

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<tr>
<th>MO type</th>
<th>3a</th>
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<tr>
<td>Ip ‖</td>
<td>12 (10d, 2s)</td>
<td>14 (7d, 3s, 2f, 2p)</td>
</tr>
<tr>
<td>Ip ‖</td>
<td>7 (6f, 1d)</td>
<td>10 (8f, 2d)</td>
</tr>
<tr>
<td>U–arene δ</td>
<td>7 (d)</td>
<td>8.5 (d)</td>
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Table 2  Uranium partial atomic charges in 3a and 4

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<th>Hirshfeld</th>
<th>Mulliken</th>
<th>QTAIM</th>
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<td>3a</td>
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<td>+0.78</td>
<td>+2.04</td>
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<tr>
<td>4 U1</td>
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<td>+1.99</td>
</tr>
<tr>
<td>4 U2</td>
<td>+0.43</td>
<td>+0.48</td>
<td>+1.86</td>
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</table>

As with most BCP data for actinide compounds, the absolute values of both metrics are small, suggesting the uranium–ligand bonds are largely ionic. That said, we can use these data to assess relative covalency, and can relate them to the MO and partial charge arguments developed above. This is best done for the U–I bonds (which are obviously free of the complicating effects of macrocycle rearrangement) and comparison of the U–I data in 3a with 4 suggests that the U1–I bond in 4 is very similar to that in 3a. The slightly larger (absolute) values of ρ and H for U2–I indicate slightly greater covalency, in agreement with the charge data in Table 2. The κ1 U–N interaction is clearly significantly weaker in 4 (U1–N), as the bond distance is ≈0.2 Å longer than in 3a. This is reflected in ρ and H, which are both (absolutely) smaller in 4. At the QTAIM level the differences between the κ1 and κ2 U–N interactions in 4 are comparable with the differences between U1–I and U2–I, although now U2 has the smaller BCP metrics.

Table 3  Electron (ρ) and energy (H) densities (au) at selected bond critical points in 3a and 4, and delocalisation indices (δ(A,B))

<table>
<thead>
<tr>
<th>Complex</th>
<th>Parameter</th>
<th>ρ</th>
<th>H</th>
<th>δ(A,B)</th>
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<tr>
<td>3a</td>
<td>U–I</td>
<td>0.039</td>
<td>−0.007</td>
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<td>U–N(avg)</td>
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<td>4</td>
<td>U1–I</td>
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<td>−0.007</td>
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<tr>
<td></td>
<td>U2–I</td>
<td>0.047</td>
<td>−0.009</td>
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<td></td>
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<td>−0.003</td>
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<tr>
<td></td>
<td>U2–N</td>
<td>0.037</td>
<td>−0.001</td>
<td>0.264</td>
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</table>

Fig. 5  Valence MO energy level diagram for 4. a spin MOs numbers 145–170 (highest occupied MO) are shown, with an isosurface cutoff of 0.035 au. The principal character of each orbital is also indicated.
analysis, as $\delta$ (A, B) for U-I in 3a and U1-I in 4 are very similar, whereas U2-I has a slightly larger $\delta$ (A, B), and the U-N bond order in 3a is larger than in 4.

It is noteworthy that QTAIM analysis does not locate a U-U bond path in 4 and hence, by the theory’s rigorous definition of chemical bonding, 4 does not contain a U-U bond. This is certainly in keeping with analysis of the valence orbital structure, which finds little evidence of MOs with contributions from both uranium atoms. To a large extent, Fig. 5 suggests that the two uranium centres have independent electronic structures.

**Reactivity of [ThCl$_2$(L)]**

The $\pi$-$\delta$-acceptor capabilities and flexibility of this macrocycle led us to study the reduction chemistry of 1. Treatment of a THF solution of 1 with two equivalents of K/naphthalenide at room temperature over 16 h resulted in a change from yellow to red-brown and the precipitation of KCl (Scheme 6). Prompt filtration, followed by diffusion of n-hexane into the filtrate allowed analytically pure crystals of the new colourless complex (L$^{-2\text{th}}$ = CMe$_2$(NC$_4$H$_2$)CMe$_2$)$_2$ (C$_6$H$_3$-1,3)$_2$) to be isolated in 31% yield. The $^1$H NMR spectrum of 5 showed a resonance at 211.7 ppm, which is shifted to higher frequency from 121.6 ppm in 1, and is assigned as the Th-bound ipso-aryl carbon. This resonance is comparable to those reported for [Cp$^*$$_2$Th(η-MeC$_6$H$_5$)$_2$]Cl at 224.8 ppm,$^{44}$ and [Th([2-CH$_2$NM$_2$C$_6$H$_4$])$_2$] at 230.8 ppm (ref. 62) but at a higher frequency to other metalated- or alkyl-ThIV complexes.$^{63,64}$

The molecular structures of 5 and 6 show a $\kappa^5$-η: $\kappa^5$-η ligand bonding mode, but with two new Th-C bonds to C9 and C29, from the double metallation of the macrocycle. The potassium counter-ion occupies the cavity subtended by the two aryl rings in both cases. Complex 5 is a chlorido-bridged dimer in the solid state, whereas complex 6 exists as a K-bridged linear polymer (Fig. 7). There is no significant change to pyrrolide binding on metallation, but the arene cavity has undergone double arylation of the macrocycle formed as a result of double arylation of the macrocycle.$^{65,66}$

The constrained geometry of the macrocycle is reflected in the long Th-C distances in 5 (Th1-C9 2.659(8) Å, Th1-C29 2.669(9) Å) and 6 (Th1-C9 2.691(16) Å, Th1-C29 2.693(12) Å), longer than those found in the similarly metallated complex [Li(DME)$_3$]$_2$[ThCl$_2$(η$^5$-C$_6$H$_5$)$_2$(1,3-CMe$_2$)$_2$] (2.612(8) Å).$^{28}$

In the reactions between 1 and either K or KN$^\text{IV}$, potassium cation incorporation occurs readily in the arene cavity of the macrocycle, and allows clean substitution chemistry of the halide ligands, although it also facilitates double C-H metallation of the ligand aryl groups by the Th$^{IV}$ centre. There is no evidence to suggest that these reactions proceed through a Th$^{III}$ oxidation state.$^{65}$ The inaccessibility of the Th$^{IV}$ oxidation state ($\sim$3.0 eV vs. SHE)$^{65,67}$ is doubtless a factor in the different reactivity of complexes 1 and 2 with reductants.
Hybrid DFT studies of 3a and 4 suggest very similar U–arene interactions in these complexes. These computational data indicate slightly larger covalency contributions to the bonding in the U\(^{III}\)(L) complex 4 than in the U\(^{IV}\)(L) complex 3a with the pyrrolide \(\pi\)-orbitals significantly stabilised (ca. 200 kJ mol\(^{-1}\) lower in energy) by forming a metal–pyrrolide \(\delta\) bonding interaction that contains ca. 15\% uranium 6d character. Therefore, at least part of the driving force for the macrocycle to adopt the more constrained geometry in 4 than in 3a is the gain in covalent bonding in the former. Analysis of the calculated charges on the uranium atoms by a number of methods support the greater covalency in the \(\pi\)-pyrrolide-bound U atom, which has a lower positive charge than the \(\pi\)-arene bound U atom.

Further computational analysis by the QTAIM method suggests that in 4, the two U\(^{III}\) centres have approximately independent electronic structures, and the degree of covalency in the U–L bonds is greater in the pyrrolide-bound U than the arene-bound U.

In contrast, the Th chemistry of (L)\(^{2-}\) is dominated by ligand metatation processes due to the inaccessibility of Th(III) and the proximity of the aryl C–H bonds to the Th metal centre. Rare new Th–aryl bonds are formed in [K(THF)\(_2\)Th(μ-Cl)(L\(^{2-}\))], \(^5\) and K[Th(N\(^5\))]/(L\(^{2-}\)) \(^6\) in which the macrocycle has retained the \(\kappa^5:\kappa^1\) binding mode to Th\(^{IV}\) whilst a potassium cation resides in the arene cavity occupied by U\(^{III}\) in complexes 3 and 4. It is likely that alkali metal cation complexation into the \(\pi\)-framework of the macrocycle facilitates this new reaction chemistry.

This small-cavity macrocycle has enabled access to two different metal – 6\(\pi\)-electron binding modes in homobimetallic (U\(^{III}\)) and heterobimetallic (K\(^+\)Th\(^{IV}\)) actinide complexes for the first time. The ability of the macrocycle to adopt different binding modes and switch between them, should facilitate new low oxidation state U chemistry. Further work is in progress to explore the cooperative bimetallic reactivity of 4 and the new hydrocarbyl reaction chemistry that (L\(^{2-}\)) can support.

Conclusions

We have shown that the small-cavity macrocycle (L)\(^{2-}\) is capable of binding an actinide cation in either a \(\kappa^5:\kappa^3\) pyrrolide–metal-loocene or \(\eta^6:\kappa^1:\eta^6:\kappa^1\) bis(arene) manner. This is unusual as the normal binding mode of a pyrrolide ligand is \(\kappa^1\) through the N atom, a feature that has been exploited by us and others in \(\kappa^1\)-pyrrole-based macrocycles (e.g. Pacman and expanded porphyrins) for supporting new actinide chemistry. As such, the switchable coordination of (L)\(^{2-}\) provides a unique and well-defined molecular environment in which to interrogate the \(\pi\) and \(\delta\) bonding interactions between these ligands and actinide metal cations. This feature is best exemplified in the preference for \(\pi\)-arene bonding in the lower oxidation state U\(^{III}\) complexes [UI(THF)(L)] \(^3\) and desolvated [UI(L)] \(^3\) a which clearly display covalent uranium–arene \(\delta\)-bonding.

The use of base-free conditions allows the isolation of the very unusual dinuclear complex [U\(_2\)I\(_4\)(L)] \(^4\) in which the macrocycle bridges two [U\(^{III}\)I\(_2\)]\(^+\) units and adopts both \(\kappa^5:\kappa^3\) and \(\eta^6:\kappa^1:\eta^6:\kappa^1\) binding modes.

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Notes and references

§ Although one of us (NK) has recently argued that orbital mixing and covalency (in the generally accepted chemical sense at least, if not the Heitler-London definition) should be separated in compounds of elements toward the middle of the actinide series, it is more likely that they are synonymous in uranium chemistry.

¶ The satisfactory location of all the metal–carbon BCPs in carboyclic sandwich molecules is notoriously difficult, and so it proved with 3a and 4. Hence these data are considered unreliable and are not included here.


