Uranium complexes supported by an aryloxide functionalised triazacyclononane macrocycle: synthesis and characterisation of a six-coordinate U(III) species and insights into its reactivity†

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A reactive low-valent uranium(III) complex supported by an aryloxide functionalised triazacyclononane has been synthesised and provides a platform for enhanced uranium reactivity.

Coordiatively unsaturated, electron-rich transition metal complexes have proven to be powerful species for small molecule activation and functionalisation. The three-coordinate \( ([\text{1-AdArN})_3 \text{Mo}^{III}] \) and \([\text{L}^2\text{Fe}^2\text{Cl}] \) are important representatives of this class of complexes. These complexes have been shown that the sterically encumbering ligands provide the low-valent metal ions with a platform for activating and, in the case of the molybdenum tris-anilide complex, splitting the inert dinitrogen molecule.5 Cummins,5 Scott,5 and more recently, Cloke et al.2 have demonstrated that uranium complexes show transition metal-like behaviour and are similarly competent to bind and activate dinitrogen. In our efforts to synthesise uranium complexes with enhanced reactivity for small molecule activation, we are currently investigating low-valent, aryloxide-uranium complexes supported by macrocyclic polyamine ligands. Here we report the first uranium aryloxide complexes supported by a macrocyclic polyamine ligand. The macrocyclic polyamine ring serves as the anchor unit, shielding the trivalent uranium centre, and the tert-butyl groups of the aryloxide pendant arms form a protected pocket of reactivity.

Treatment of \([\text{U(N(SiMe}_3)_2)_3] \) with one equivalent of 1,4,7-tris(3,5-di-tert-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane (\( \text{ArOH} \)) in pentane at \(-40 \, ^\circ\text{C} \) yields the six-coordinate uranyl(III) complex \([(\text{ArOH})_3\text{U} \text{(NCH}_3)_2] \) (Scheme 1).† Complex 1 can be synthesised in analytically pure form on a multi-gram scale and was spectroscopically characterised by \( ^1\text{H} \) NMR, UV/vis/NIR, and IR spectroscopy as well as SQUID magnetisation measurements. The monomeric nature of 1 was established by molecular weight determination in pentane solution and elemental analysis.† The \( ^1\text{H} \) NMR spectrum of 1 recorded in benzene-\( d_6 \) at 20 \, ^\circ\text{C} \) displays 10 resonances between \(-22 \) and +13 ppm. Two relatively sharp and intense signals at 4.15 and 2.63 ppm are assigned to the tert-butyl groups on the aryloxide pendant arms. The assignment of an additional eight paramagnetically broadened and shifted signals remains equivocal; however, their presence is indicative of deviation from idealised \( C_3 \) symmetry. Single crystal X-ray diffraction analysis of the highly reactive, coordinatively unsaturated complex 1 remained elusive. Recrystallisation of 1 from acetonitrile, however, yielded a seven-coordinate uranium(III) complex \([(\text{ArO})(\text{tacn})\text{U(NCH}_3)_2] \) in which the open coordination site of 1 is occupied by an axial acetonitrile molecule. Detailed characterisation, including an X-ray diffraction study, of this compound will be reported elsewhere.

The magnetic moment of solid samples of 1 is strongly temperature dependent, varying from 1.77 \( \mu_\text{B} \) at 5 K to 2.92 \( \mu_\text{B} \) at 300 K. The experimentally determined effective magnetic moment \( \mu_{\text{eff}} \) at room temperature is considerably lower than that calculated for an \( ^3\text{I} \) uranium species with a \( ^3\text{I} \) ground state. However, the temperature dependence and magnitude of \( \mu_{\text{eff}} \) is identical to that of the crystallographically characterised \([(\text{ArO})(\text{tacn})\text{U(NCH}_3)_2] \). It also compares well to other trivalent uranyl macrocyclic complexes, such as \([\text{U(N(SiMe}_3)_2)] \) \( ( \mu_{\text{eff}} \text{ between 35 and 280 K} = 3.40 \mu_\text{B}) \).

Attempts to recrystallise 1 from pentane and solutions of Et\(_2\)O or THF at RT yielded mono- and dinuclear seven-coordinate uranyl(IV) complexes, namely \([(\text{ArO})(\text{tacn})\text{U}^\text{IV} \text{(OAr)}] \) (2, Fig. 1) and \([(\text{ArO})(\text{tacn})\text{U}^\text{IV} \text{(SMe)}] \) (3, Fig. 2).†

We suggest that 2 forms via an sp\(^2\)-sp\(^3\) bond cleavage of the coordinated ligand in complexes of 1.† This disintegration reaction is associated with formation of undefined by-products. Dinuclear 3 forms nearly quantitatively through C–O bond

† Electronic supplementary information (ESI) available: synthetic and analytical results, including elemental analysis, for all new complexes, crystallographic information for 2 and 3, and computational details for 1, figures and tables. See http://www.rsc.org/suppdata/chemcomm/b2/b208473h/

Scheme 1

Fig. 1 Solid-state molecular structure of \([(\text{ArO})(\text{tacn})\text{U(OAr)}] \) in crystals of 2-C\(_8\)H\(_8\). Hydrogen atoms and co-crystallised solvent molecules are omitted for clarity. ORTEP, 40% probability ellipsoids. Selected bond lengths (\( \text{Å} \)) and angles (\( ^\circ \)); U(1)–N(1) 2.693(4), U(1)–N(2) 2.719(4), U(1)–N(3) 2.698(3), U(1)–O(1A) 2.040(4), U(1)–O(1B) 2.195(3), U(1)–O(1C) 2.185(4), U(1)–O(4) 2.165(4), U(1)–O(2)(ArO-plane) 0.2, U(1)–O(4)–C(1D) 141.4(4).
activation and oxygen atom abstraction of I in Et₂O and THF. The X-ray diffraction analyses of single-crystals of 2 and 3 give insight into the unique coordination mode of the tris-aryloxide [N₃O₃]⁻ ligand to the large uranium ion. While (ArO)₃-tacn forms exclusively coordinatively saturated octahedral complexes with the seventh, axial position available for ligand substitution and redox events.

The axial position is occupied in complexes 2 and 3, resulting in an [N₃O₃]⁻ ligand environment, with the fourth oxygen atom provided either by a terminal aryloxide (2) or a bridging oxo ligand (3). The average U–N(tacn) bond distance was determined at 2.703 Å in 2 and 2.746 Å in 3. The uranium–aryloxide interaction is strong, resulting in U–O(ArO) bond lengths of 2.195 Å ((OAr₃)₃uacn) and 2.165 Å (p-OAr₃) in 2 and 2.235 Å in 3. While in 2 the uranium ion is placed 0.2 Å below the trigonal plane of the three aryloxide oxygen atoms, the displacement of the U(iv) ion in dinuclear 3 is only 0.08 Å, thus allowing for a slightly more efficient bonding interaction to the bridging O²⁻ ligand. The uranium–nitrogen bond distances in 2 and 3 compare well to those found in the tetramethylethylenediamine uranium(iv) complex: [tmeda]U(Cl)₄ (d(U–Nav) = 2.79 Å).\(^1\)

The uranium(iv) \(U^{IV}\) ions in 2 and 3 possess a \(^1\)H\(_4\) electronic ground state. The effective magnetic moments of 2 and 3 were determined to be strongly temperature-dependent, varying from \(\mu_{eff} = 2.85 \mu_B\) (2) and 4.55 \(\mu_B\) (3) at 300 K to approx. 1 \(\mu_B\) at 5 K. It is noteworthy that 2 and 3 are almost colorless in solution and only slightly green and pale blue in crystalline form. This observation is in agreement with the complexes' electronic absorption spectra, which show a large number of sharp, weak absorption bands between 400 and 2500 nm, typically assigned to partly parity forbidden \(f\rightarrow f\) transitions.\(^2\)

The formation of 2 and 3 underlines the enhanced reactivity of monomeric 1. DFT quantum mechanical methods\(^3\) were applied to rationalise the reactivity and to elucidate the electronic structure of 1. The geometry optimisation results in a core structure similar to those found in the solid-state structures of 2 and 3, the only difference being the increased in-plane shift of the U(m) ion towards the tacn chelator. Electrons 1–3, the three most energetic electrons of system 1, were found to be uranium based (see Fig. 3). The energy differences, \(\delta\), between SOMO-1/SOMO-2 and SOMO-2/SOMO-3 are small (\(\delta \sim 3.6\) eV).

Fig. 2: Solid-state molecular structure of \([(\text{ArO})₃\text{tacn})\text{U}]^{2+}\) in crystals of 3 and 2. Hydrogen atoms and co-crystallised solvent molecule are omitted for clarity. ORTEP, 40% probability ellipsoids. Selected bond lengths (Å): U(1)–N(1) 2.744(6), U(1)–N(2) 2.768(6), U(1)–N(3) 2.727(6), U(1)–O(1A) 2.230(4), U(1)–O(1B) 2.222(4), U(1)–O(1) 2.2095(4), U(1)–(ArO)₃ plane 0.08.

Fig. 3: Molecular orbitals depicted for the three most energetic electrons in the system of 1. From top to bottom: SOMO-1, SOMO-2, SOMO-3 (left: side view, right: top view).

\(\delta\) mol\(^{-1}\) and thus almost degenerate. SOMO-3 is largely \(f\) in character. Its electron density is within the plane of the three aryloxide atoms. In contrast, SOMO-2 and -1 possess unpaired spin density that is perpendicular to this plane, shielded by the triazacyclononane backbone on one side but pointing out into the open reactivity cavity. Accordingly, complex 1 behaves like a di-radical and is very reactive towards small molecules. In our ongoing investigations we found that 1 reacts with organic azides to yield uranium(v) imido complexes.\(^4\)

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Notes and references