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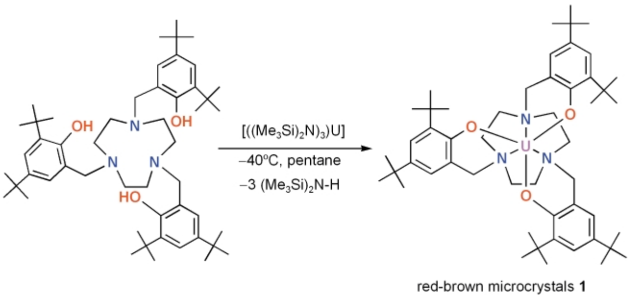
**A reactive low-valent uranium(III) complex supported by an aryloxide functionalised triazacyclononane has been synthesised and provides a platform for enhanced uranium reactivity.**

Coordinatively unsaturated, electron-rich transition metal complexes have proven to be powerful species for small molecule activation and functionalisation. The three-coordinate [(1-AdArN)$_3$Mo$^{III}$][1] and [L'Fe$^{II}$Cl][2] are important representatives of this class of complexes. For these complexes it was shown that the sterically encumbering ligands provide the low-valent metal ions with a platform for activating[3] and, in the case of the molybdenum tris-anilide complex, splitting the inert dinitrogen molecule.[4] Cummins,[5] Scott,[6] and more recently, Cloke *et al*.[7] 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 one side of the uranium centre, and the *tert*-butyl groups of the aryloxide pendent arms form a protected pocket of reactivity.

Treatment of [U(N(SiMe$_3$)$_2$)$_3$][8] with one equivalent of 1,4,7-tris(3,5-di-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane ((ArOH)$_3$tacn)[9] in pentane at −40 °C yields the six-coordinate uranium(III) complex [((ArO)$_3$tacn)U] (**1**, Scheme 1).†

Complex **1** can be synthesised in analytically pure form on multi-gram scale and was spectroscopically characterised by $^1$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 $^1$H NMR spectrum of **1** recorded in benzene-d$_6$ at 20 °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 [((ArO)$_3$tacn)U(NCCH$_3$)] 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.



**Scheme 1**

The magnetic moment of solid samples of **1** is strongly temperature dependent, varying from 1.77 $\mu_B$ at 5 K to 2.92 $\mu_B$ at 300 K. The experimentally determined effective magnetic moment $\mu_{eff}$ at room temperature is considerably lower than that calculated for an f$^3$ uranium species with a $^4I_{9/2}$ ground state. However, the temperature dependence and magnitude of $\mu_{eff}$ is identical to that of the crystallographically characterised [((ArO)$_3$tacn)U(NCCH$_3$)]. It also compares well to other trivalent monomeric uranium complexes, such as [U(N(SiMe$_3$)$_2$)$_3$] ($\mu_{eff}$ (35–280 K) = 3.40 $\mu_B$).[8]

Attempts to recrystallise **1** from pentane and solutions of Et$_2$O or THF at RT yielded mono- and dinuclear seven-coordinate uranium(IV) complexes, namely [((ArO)$_3$tacn)U$^{IV}$(OAr)] (**2**, Fig. 1) and [{((ArO)$_3$tacn)U$^{IV}$}$_2$(μ-O)] (**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

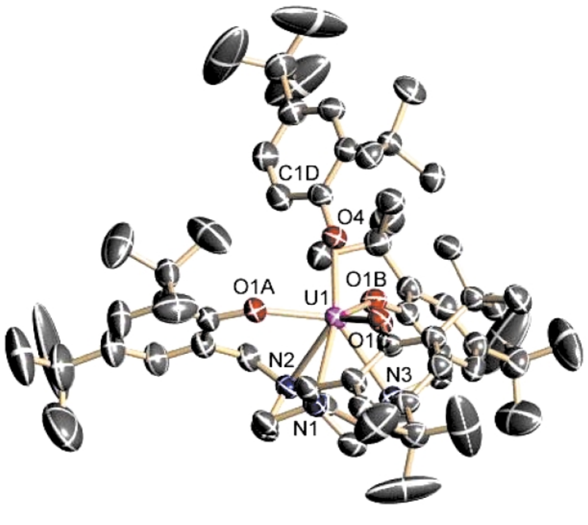


**Fig. 1** Solid-state molecular structure of [((ArO)$_3$tacn)U(OAr)] in crystals of **2**·C$_5$H$_{12}$. Hydrogen atoms and co-crystallised solvent molecules are omitted for clarity. ORTEP, 40% probability ellipsoids. Selected bond lengths (Å) and angles (°): U(1)–N(1) 2.691(4), U(1)–N(2) 2.719(4), U(1)–N(3) 2.698(4), U(1)–O(1A) 2.204(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(ArO-plane) 0.2, U(1)–O(4)–C(1D) 141.4(4).

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† 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/cc/b2/b208473b/

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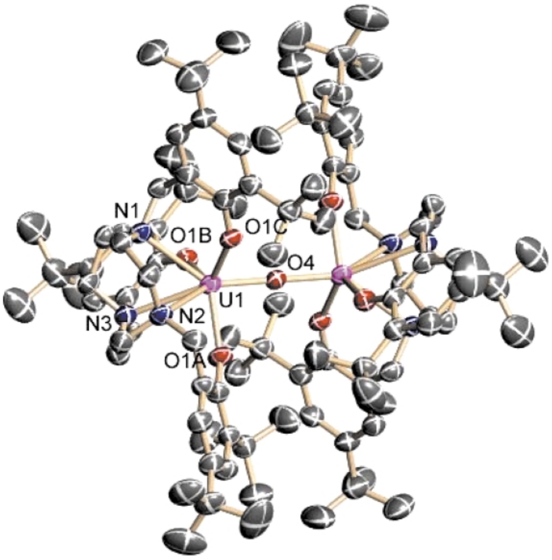

**Fig. 2** Solid-state molecular structure of $[\{((ArO)_3tacn)U\}_2(\mu\text{-}O)]$ in crystals of **3**$\cdot Et_2O$. Hydrogen atoms and co-crystallised solvent molecule are omitted for clarity. ORTEP, 40% probability ellipsoids. Selected bond lengths (Å): U(1)–N(1) 2.744(6), U(1)–N(2) 2.768(6), U(1)–N(3) 2.727(6), U(1)–O(1A) 2.230(4), U(1)–O(1B) 2.222(4), U(1)–O(1C) 2.222(4), U(1)–O(4) 2.1095(4), U(1)–$(ArO)_3$ plane 0.08.

activation and oxygen atom abstraction of **1** in $Et_2O$ and THF.† The X-ray diffraction analyses of single-crystals of **2** and **3** give insight into the unique coordination mode of the tris-anionic [N3O3]-ligand to the large uranium ion. While $(ArO)_3$tacn forms exclusively coordinatively saturated octahedral complexes with early first-row transition metals, such as V, Cr, Mn, and Fe,[9] it yields six-coordinate, coordinatively unsaturated uranium 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 [N3O4]-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 ($(OAr)_3$tacn) and 2.165 Å ($\eta^1$-OAr) in **2** and 2.225 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 $O^{2-}$ 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–$N_{av}$) = 2.79 Å).[10]

The uranium(IV) $f^2$ ions in **2** and **3** possess a $^3H_4$ 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–f transitions.†

The formation of **2** and **3** underlines the enhanced reactivity of monomeric **1**. DFT quantum mechanical methods† 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(III) 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 ($\delta \sim 3.6$ kJ $mol^{-1}$) 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.§

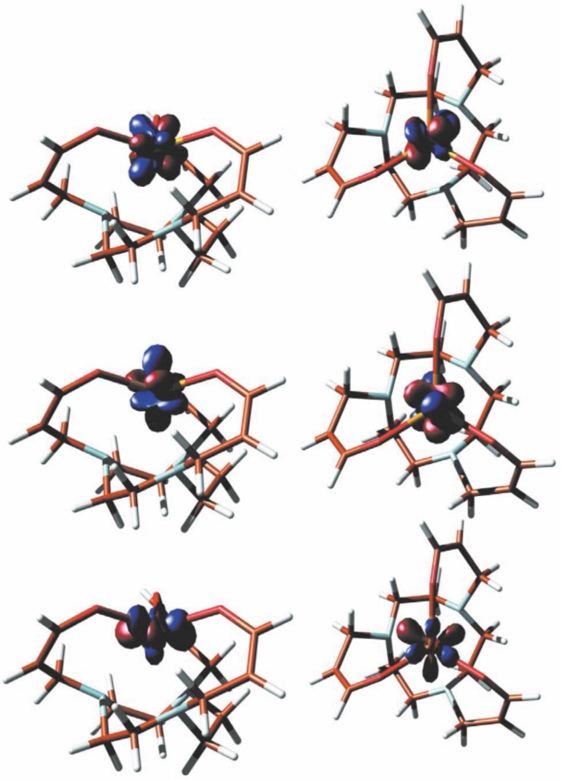

**Fig. 3** Molecular orbitals depicted for the three most energetic electrons in the system of **1**. From top to bottom: SOMO-1, SOMO-2, SOMO-3 (left: side view, right: top view).

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## Notes and references

‡ CCDC 195351 and 195352. See http://www.rsc.org/suppdata/cc/b2/b208473b/ for crystallographic data in CIF or other electronic format.

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