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# Analysis of synthesis and molecular structure

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**Abstract**
In this paper the in-depth crystallographic and spectroscopic characterization along with a computational study to investigate the electronic structure of this new class of uranium complexes is presented, herein.

**Keywords:** synthesis and molecular structure

## Introduction

The issue of covalency remains an important subject of debate [1-3]. To elucidate fundamental questions regarding trends in bonding and reactivity in uranium and other actinide metal compounds, the detailed investigation and discovery of unprecedented species is necessary. In our efforts to identify and isolate new uranium complexes with enhanced reactivity relevant to binding, ctivation, and functionalization of small molecules, we are currently investigating the coordination chemistry of uranium metal centers with classical Wernertype ligands. The stabilizing abilities of "classic" macrocyclic amines have made this class of chelators an indispensable tool for transition metal coordination chemistry. However, to the best of our knowledge, uranium complexes of macrocyclic polyamine ligands have not yet been reported in the literature.

Here we report uranium (III, IV, and V) tris-aryloxide derivatives supported by triazacyclononane to demonstrate that the coordinated ligand provides an unprecedented platform for enhanced uranium reactivity. The introduction of the functionalized triazacyclononane ligand, 1,4,7-tris(3,5-di-tent-butyl-2- hydroxybenzyl)-1,4,7-triazacyclononane [4], to a uranium(III) metal center results in the formation of stable core complexes with only one reactive coordination site. The ancillary ligand occupies six coordination sites, leaving the seventh, an axial position, available for ligand substitution reactions and redox events associated with small molecule or organic functional group activation. This coordination mode to uranium is distinctly different from that observed for binding to transition metals with which the ligand fouls exclusively coordinatively saturated octahedral complexes [5-11].

## Results and Discussion

Synthesis and Molecular Structure of lb. Treatment of [U(N(Si(CH3)3)2)3]12'13 with 1 equiv of 1,4,7-tris(3,5-di-tert-buty1-2-hydroxybenzy0-1,4,7-triazacyclononane4 ((ArOH)3tacn) in pentane yields a reactive uranium(III) species [((ArO)3tacn)U] (la) on amultigram scale (70% recrystallized yield) as a redbrown crystalline substance (Scheme 1) molecules are omitted for clarity.

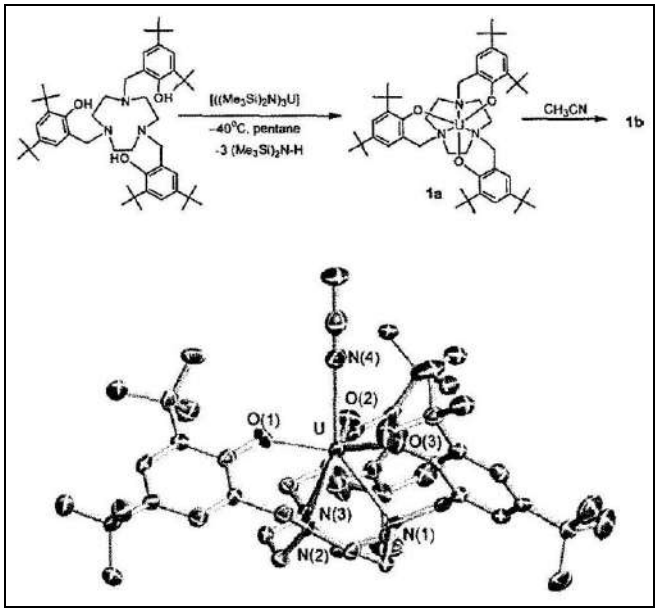


**Fig 1:** Molecular structure of [((ArO)3tacn)U(NCCH3)] in crystals of 1n·2CH3CN. Selected hydrogen atoms and cocrystallized solvent

Recrystallization of la from acetonitrile at -40 °C yields the purple crystalline compound [((ArO3)tacn)U(NCCH3)] (lb) in approximately 90% yield. An X-ray diffraction study on single crystals of lb reveals an axial acetonitrile molecule in the coordination sphere of the seven-coordinate uranium species (Figure 1).

The unique coordination model of this ligand to the large uranium ion makes this ligand an attractive chelator for the stabilization of coordinatively unsaturated, reactive species. The tert-butyl substituents of the aryloxide ligands form a protective cavity around the $CH_3CN$, which is the reactive site of this system as evidenced by the reactivity studies described below. Undesired side reactions trans to the reactive site are eliminated due to shielding by the triazacyclononane fragment.

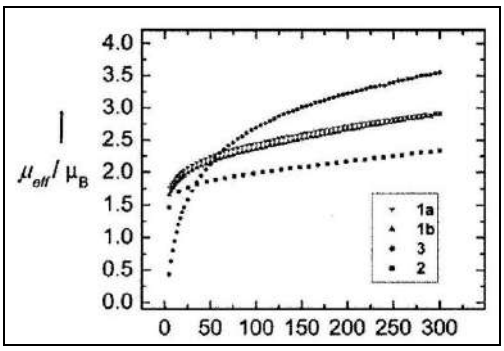


**Fig 2:** Temperature dependence of the effective magnetic moment μeff of solid samples of la, lb, 2, and 3.

The $^1H$ NMR spectra of la and lb recorded in $C_6D_6$ are very similar: In the spectrum of lb, two resonances at 2.28 and 4.11 ppm can be readily assigned to the tert-butyl groups but are high-field shifted as compared to la (2.63 and 4.15 ppm). Eight more resonances between -25 and 20 ppm integrate properly. Although the assignment remains largely equivocal, their position is diagnostic in determining the purity and stability of la and lb in solution. The protons of the coordinated acetonitrile molecule in lb cannot be detected. This likely is due to signalbroadening resulting from their close proximi and relatively strong binding to the paramagnetic uranium center (vide infra).

Magnetism of lb. SQUID magnetization measurements were carried out to study the temperature behavior of the trivalent uranium species la and lb. The temperature behaviors as well as the magnetic moments of lb are remarkably similar to those of the analogous six-coordinate precursor molecule la (Figure 2).

Complex lb displays a strong temperature-dependent magnetic moment, varying from 1.66μB at 4 K to 2.90 μB at room temperature. This magnetic moment of 2.90 μB at room temperature, however, is significantly smaller than the expected moment of pμ (calcd)) 3.62 μB for an f-element species with three unpaired electrons and full spin-orbit coupling (Russel- Saunders term: $^4I_{9/2}$). Accordingly, measurements were carried out in the temperature range between 5 and 350 K, to study whether samples of lb reach saturation magnetization at elevated temperatures corresponding to the expected value for an $f^3$ ion. It was found that the magnetic moment continuously increases to 3.40 μB at 350 K and does not reach a plateau at this temperature.[14] The observed reduced magnetic moment is likely due to a significant degree of covalency in the uranium(III) species, quenching spin-orbit coupling and thus reducing the magnetic moment (vide infra).

**Table 1:** Mulliken Populations for [((ArO)3tacn)U(NCCH3)]a

| atom | charge | spin-density | spin | S | P | D | F |
|---|---|---|---|---|---|---|---|
| U | 1.6775 | 2.8753 | α<br>β | 1.1356<br>1.0529 | 2.9571<br>2.9133 | 0.7366<br>0.4637 | 2.7696<br>0.2937 |
| $O_{av}$ | –0.7050 | –0.0429 | α<br>β | 0.9362<br>0.9374 | 2.3697<br>2.4107 | 0.0252<br>0.2334 | 0.0000<br>0.0000 |
| $N_{tacn,av}$ | –0.5021 | –0.0130 | α<br>β | 0.7979<br>0.8005 | 1.9063<br>1.9176 | 0.0402<br>0.0394 | 0.0000<br>0.0000 |
| $N_{CH3CN}$ | –0.2081 | 0.0006 | α<br>β | 0.8184<br>0.8316 | 1.7535<br>1.7491 | 0.0324<br>0.0231 | 0.0000<br>0.0000 |
| $C_{H3CN}$ | 0.1539 | 0.2535 | α<br>β | 0.2535<br>0.6342 | 1.3580<br>1.1250 | 0.0374<br>0.0371 | 0.0000<br>0.0000 |

α For electronically equivalent atoms, mean values are given.

**Electronic Structure of lb.**

The electronic structure of lb was studied using force-field methods and density functional theory calculations. Because of the low symmetry in lb, the coordinates of the diffraction analysis were taken as a starting point for the geometry optimization. The calculation converged in straightforward fashion, resulting in structural parameters within 3o. of the experimentally determined structure. Electrons 1-3, the three most energetic electrons of the system, were found to be uranium based (2.88 of the total spin density, see Table 1 (Mulliken population)). Analysis of these frontier orbitals (Figure 3) reveals the origin of the relatively short U-N($CH_3CN$) bond. SOMO-1 is almost a pure f-orbital. Its shape resembles those of the $x(x^2 - y^2)$ and $x(3x^2 - y^2)$ orbitals in a general set of f-orbitals and is antibonding with respect to the phenolate oxygen ligands. With respect to SOMO-1, SOMO-2 and SOMO-3 are slightly more stabilized (by 7.2 kJ/mol) via a π-back-bonding interaction with the apical acetonitrile ligand and almost doubly degenerate (Δ(SOMO-2 - SOMO-3) 1.14 kJ/mol). Interestingly, close examination of the total electron density in lb also shows that one of the three amine nitrogen donor atoms possesses a higher degree of U-N interaction than the

remaining two, resulting in one U-N(tacn) bond distance (2.665(6) Å) that is significantly shorter than the other two (2.715(6) and 2.721(5) Å). Uranium(III) species la and lb, with an open or masked coordination site at a reactive, low-valent uranium center, represent important precursor molecules to explore new modes of uranium reactivity. Few uranium complexes involving U-N multiple bonds have been described in the literature; however, isolation of a molecular uranium nitrido species remains elusive. Given the paucity of structural and reactivity studies of complexes with uranium nitrogen multiple bonds, synthesis, isolation, and characterization of novel potent uranium nitrido precursor compounds are important objectives of this research and are describe in following sections.

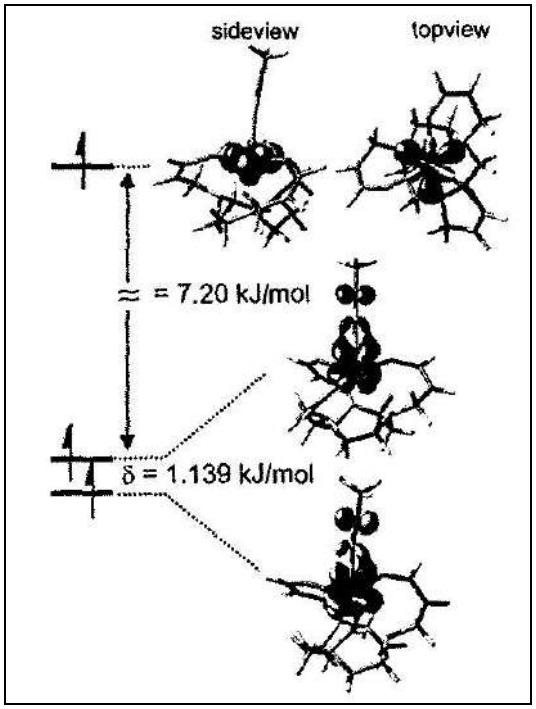


**Fig 3:** Molecular orbitals depicted for the three most energetic electrons in the system of 1b: SOMO-1 (top), SOMO-2/3 (middle and bottom)

## Conclusion

This observation is also manifested in the complexes electronic absorption spectra. Additional features in spectra of lb and 3 include weak and sharp absorptions bands in the visible and near-infrared region between 500 and 2200 nm (ε 20-100 $M^{-1}$ $cm^{-1}$), characteristic for f-f transitions typically found in actinide and especially lanthanide complexes.

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