The Role of f-orbitals in the Bonding and Reactivity of Thorium and Uranium Complexes

Joseph Nugent Literature Seminar 10/11/2016

When uranium or any other heavy, radioactive element is mentioned, people's minds tend to drift towards thoughts of either a clean energy future or, alternatively, mass destruction. There is a stigma associated with these elements that has hampered their use in many applications where they might otherwise have been suitable.[1,2] Increased use of nuclear fuel as an attractive, low-CO_2 energy option brings thorium and uranium more to the forefront of our society. Thorium, which is 3- to 4-times as abundant as uranium, can be used in breeder reactors, making it an excellent fuel for our future energy needs. Uranium, when used as a nuclear fuel, leads to large quantities of high purity depleted uranium (DU) as a waste product from enrichment programs. The DOE estimates the amount of DU stored around the eastern US in steel cylinders is on the order of 700,000 tons.[3]

Despite the relative availability of thorium and uranium, research in actinide chemistry remains highly underdeveloped. At the time of a review in 2013, there were around 4000 crystal structures of actinide complexes, a large percentage (~84%) of them being uranium.[4] The percentage breakdown can be seen in Figure 1.

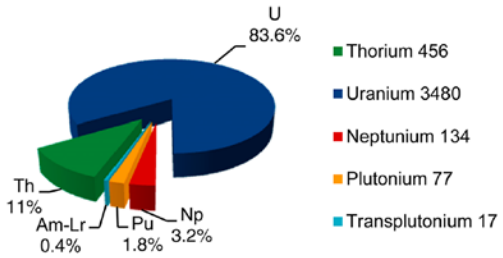

Figure 1. Pie-chart representing the percentage breakdown of actinide entries in the Cambridge Structural Database by element (2013).

This amount pales in comparison to the number of structures for even a single d-block transition metal; copper, for example, having 41,668 structures alone at the time.[4] This comparison emphasizes to what extent actinide chemistry still lags behind d-block transition metal chemistry, and helps explain the still nascent understanding of f-element chemistry.

The study of f-block metals presents a new set of challenges when compared to d-block transition metals. One of the less understood aspects of f-block metals is the role and extent of f-orbitals in their bonding. For the lanthanides, the 4f orbitals are considered more "core-like" and do not seem to be perturbed significantly by ligand fields.[5] However, for the actinides the 5f orbitals have much greater radial extension, leading to the involvement of the 5f orbitals in bonding (more so for the early actinides).[6] The f-orbitals have an extra nodal plane when compared to d-orbitals. This causes a disconnect between the extent of overlap that d- and f-orbitals can obtain in a given ligand field. Actinides also typically have larger atomic radii than d-block metals and are often capable of expanded electron counts (>18). These factors allow for binding schemes not possible for d-block transition metals. On top of f-orbital involvement, relativistic effects add further complication to modeling these systems.

Despite implicit complications, comparisons of Th and U with d-block transitions metals help to elucidate the role of f-orbitals in bonding. Researchers wanted to probe why U and Th can form a Cp^*_2 bis(hydrazonato) complex while the d-block transition metals Zr and Hf cannot.[7] After proving that sterics are likely not the critical factor at play, DFT was performed on U, Th, and Zr to probe f-orbital participation in the bonding. It was found that f-orbitals provided by both U and Th allowed for more effective stabilization of the bis(hydrazonato) ligand set. Computational evidence suggested that one of the preferentially stabilizing interactions is the overlap of U and Th f-orbitals with the antisymmetric combination of ligand orbitals, versus a Zr d-orbital. A visual representation of this can be seen in Figure 2.

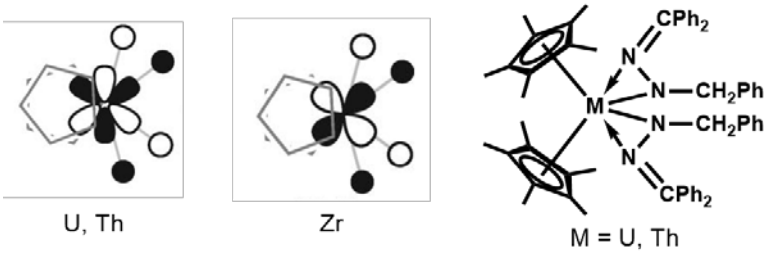

Figure 2. Illustration of f-orbital provided by U and Th (left) versus d-orbital provided by Zr (center) and bis(hydrazonato) complex of U and Th (right)

This interaction, along with f-orbital stabilization of π-interactions, makes bis(hydrazonato) complexes of U and Th more thermodynamically favorable than Zr. However, the formation of the bis(hydrazonato) U and Th complexes is more of a kinetic phenomenon where f-orbital contribution to transition states greatly lowers their energies below that of Zr, which cannot contribute f-orbitals. This illustrates the importance of f-orbitals in facilitating different ligand sets.

Recent examples have also implicated f-orbital participation in divergent reactivity between analogous Th and U complexes.[8] A specific example with isostructural U and Th complexes proceeded in a fashion exactly opposite what would have been predicted a priori.[9] An overall scheme can be found in Figure 3.

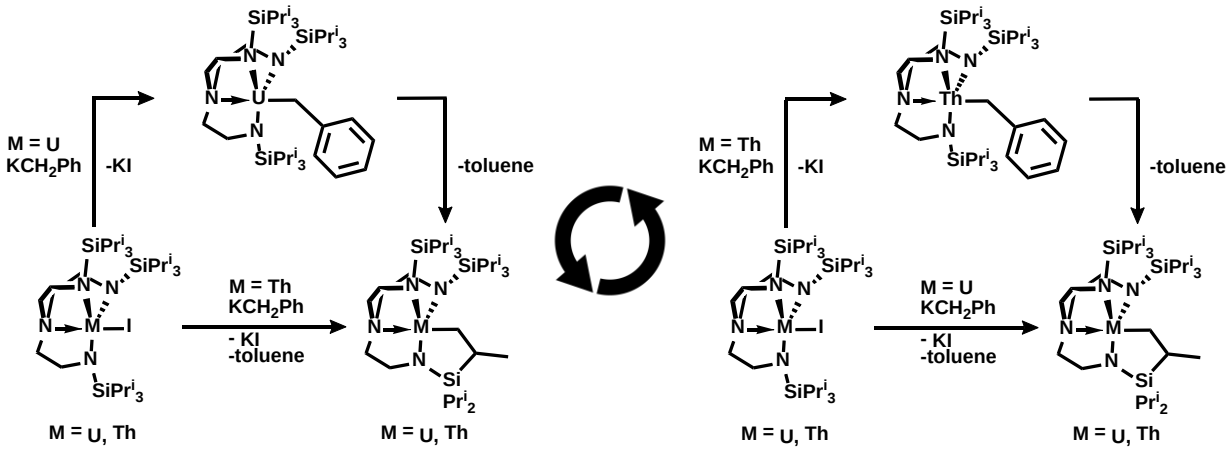

Figure 3. Predicted reaction scheme (left) vs. observed reaction scheme (right)

This report reacted benzyl potassium (KCH_2Ph) with the isostructural [U($Tren^{TIPS}$)I] and [Th($Tren^{TIPS}$)I] ($Tren^{TIPS}$ = $N(CH_2CH_2NSiPr^i_3)_3^{3-}$) complexes. The $Tren^{TIPS}$ ligand framework, with $SiPr^i$ groups appended to the anionic nitrogen arms, has been shown to undergo facile cyclometallation with U and Th alkyls. Because Th is more ionic in its bonding than U, this led researchers to predict that the [Th($Tren^{TIPS}$)I] complex would be more reactive to cyclometallation in the presence of KCH_2Ph than the [U($Tren^{TIPS}$)I] complex. The exact opposite trend was found, with the Th benzyl complex being isolated and the U benzyl complex being too transient to isolate. The explanation for this phenomenon was that U was able to stabilize the cyclometallation intermediate with more f-orbital participation leading to reactivity that is divergent from what would be expected.

The lack of predictive ability in these Th- and U-systems is indicative that the exact role of f-orbitals remains poorly understood. Very subtle differences in transition state and product stabilities brought about by f-orbital participation can result in reactivity and bonding that would not be predicted otherwise. Aside from the quest for fundamental knowledge, a noble goal in and of itself, understanding the role of f-orbitals in the binding of Th, U, and the other actinides could carry with it huge practical benefits. A deeper understanding of these subtle phenomena has implications in catalysis, separation of lanthanides and actinides from nuclear waste streams, and a myriad of other industrial applications. The chemistry of U, Th, and the other f-block elements is an area still primed for discovery.

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