Recent Advances in Thorium and Uranium Chemistry

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From actinium (atomic number 89) to lawrencium (atomic number 103), the actinide elements represent a series of elements in the periodic table known for their radioactivity. Although these elements have historically been understudied with respect to transition metals, the actinides are known to exhibit a variety of distinctive physical and chemical properties. A greater understanding of the fundamental chemistry of the actinides is of great interest for applications such as nuclear fuels, nuclear waste remediation, and small-molecule activation.

Two important factors that affect the chemistry of the actinide elements, besides their large radii, are the presence 5f-orbitals in the valence shell and relativistic effects. Because of their nodal character, the f-orbitals potentially enable the actinides to engage in φ-bonding, which is not possible for the transition metals, and can lead to unique bonding and chemistries.

The electronic structures of actinide elements are also affected by relativistic effects: as a mass accelerates to an appreciable fraction of the speed of light, the relativistic mass increases. Relativistic effects, which are trivial until the nuclear charge becomes very large, cause the inner electrons in the s- and p-orbitals to contract and become more core-like. Consequently, for the actinide elements the outer electrons in the d- and f-orbitals are more shielded from the nuclear charge and so undergo radial expansion (Figure 1).[1] The expansion of the 5f-orbitals allows for a wide range of accessible oxidation states, especially for the early actinides. In addition, the radial expansion of the valence orbitals allows for greater bonding (overlap) with ligands, so that early actinide elements such as thorium and uranium can participate in multiple bonding to π-acceptor ligands. For the later actinides, however, the 5f-orbitals become more core-like and the trivalent state becomes dominant, just as it is for lanthanide elements.

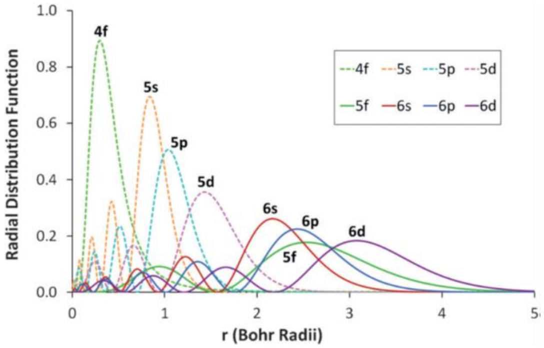

Figure 1. Radial distribution functions for 4f, 5s, 5p, 5d, 5f, 6s, 6p, and 6d orbitals

The early actinide elements thorium and uranium have isotopes with long half-lives, and their radioactivity is modest; as a result, of all the actinides these two elements have been the most intensively studied. Their electronic structure and chemical reactivity can be modulated by the ligand field the metals are subjected to, and these aspects can be modeled by advanced computational methods. Using experiment and theory in conjunction help to elucidate structure-activity relationships in actinide chemistry.

N-heterocyclic carbenes (NHC) are a commonly used class of ligand in transition metal chemistry because of the stability they impart to metal complexes as a result of their strong σdonating ability.[2] However, few actinide complexes of neutral NHCs are known.[3] Recently, macrocyclic NHCs able to accommodate the large atomic radii of thorium and uranium were used in the first successful synthesis and isolation of the first macrocyclic NHC-f-block complexes and the first octa-NHC complexes of any metal (Figure 2).[4] Computational modeling of these complexes shows that compounds **1** and **3** have similar orbital depictions despite the different geometries, square-antiprismatic and square-prismatic, respectively. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the uranium compounds **1** and **3** are metal-based with almost exclusive f-character, whereas for the thorium complex **2** these orbitals are more NHC-based. Density functional theory studies of the complexes shows a larger HOMO/LUMO energy gap with the NHC complexes than those in $An^{IV}(COT)_2$ (An = U, Th; COT = cycloctatetraenyl). This finding suggests that NHCs are stronger field ligands than COT toward actinides.

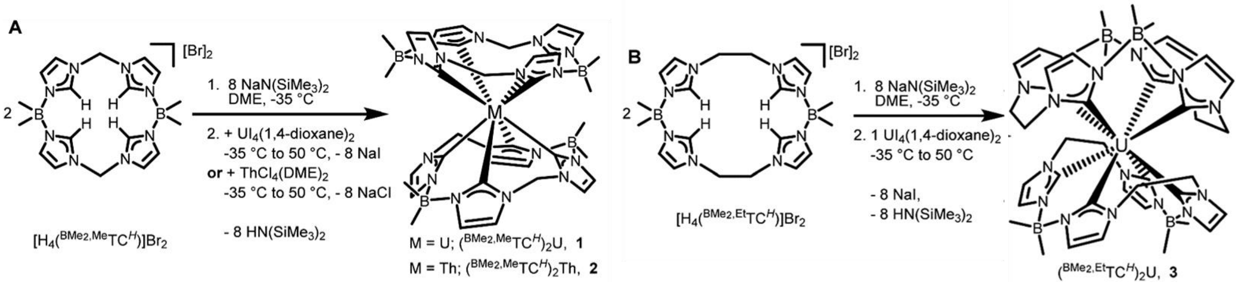

Figure 2. Synthesis of actinide NHC 'sandwich' complexes

The Walter group has synthesized the first stable actinide metallacyclopropene complex, $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th^{IV}(\eta^2\text{-}C_2Ph_2)$.[5] They explored its reactivity and found that its reactivity differs from that of related d-block metallacyclopropenes. In subsequent work, they synthesized the uranium counterpart, $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U^{IV}(\eta^2\text{-}C_2Ph_2)$, and studied its structure and reactivity.[6] Despite their similarities in structure, the two complexes exhibit different chemistries. For example, the reaction of the uranium complex with Me_3SiCHN_2 yields an imido cyanido product, $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U^{IV}(=NN=CHSiMe_3)(CN)$. However, the thorium complex reacts with a different diazo ligand, 9-$N_2C(C_{12}H_8)$, to form $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2][\eta^5,\sigma\text{-}1,2\text{-}(Me_3C)_2\text{-}4\text{-}(CH_2CMe_2)C_5H_2]Th[NC(C_{12}H_8)CH(Ph)C(Ph)=N]$. Using density functional theory to model the complexes, they found that uranium engages in stronger σ- and π-bonding than thorium with the metallacyclopropene group, $An^{IV}(\eta^2\text{-}C_2Ph_2)$. This conclusion is supported by natural localized molecular orbital analysis, which determines the percent contribution to a bond from an atom. The contribution of the f-orbitals to the bonding is greater in uranium than in thorium. This difference can help explain the observed differences in the chemistries between the two complexes.

In the original Haber-Bosch patent, uranium was reported to be a better catalyst for dinitrogen reduction than iron. However, it is difficult to ligate dinitrogen to f-block elements. Arnold and co-workers reported stable, dinuclear actinide complexes bearing aryloxide ligands that can catalyze the reduction and functionalization of molecular dinitrogen, including the catalytic conversion of molecular dinitrogen to a secondary silylamine (Figure 3).[7] Their results show that ammonia and silylamine can be produced from both **1** and **2**, implicating **1** as a pre-catalyst. It has been previously reported that potassium is a necessary component for dinitrogen reduction in these dinuclear metal complexes.[8] Here, the group similarly observes that the addition of crown ethers, which can bind potassium, turns off dinitrogen reduction. They discovered that the substitution of potassium with sodium does likewise. One possibility is that potassium binds stronger to the arene rings, the presence of these positive charges changes the electronic structure of the uranium atom. The strong actinide–aryloxide bonds and stable +4 oxidation state mean that the products can be released without decomposing the complex, enabling the catalysis to proceed at ambient temperatures and pressures. Work is in progress to identify the kinetic regime in which improved turnovers of dinitrogen to ammonia or secondary silylamines can be achieved, and whether group 4 analogues of **1** can be active catalysts.

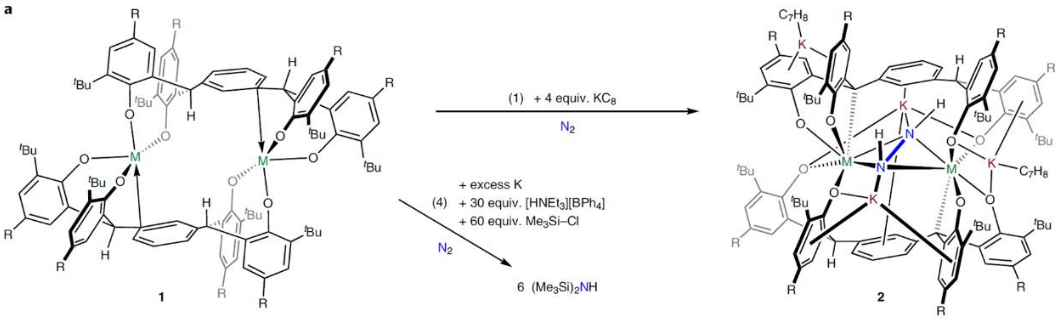

Figure 3. The activation, protonation and silylation of N_2 by complexes 1 and 2

The results above not only exemplify the rich and varied chemistries exhibited by the actinide elements, but they also provide insight to the electronic structure of the early actinide elements. Further progress will be enabled by a greater understanding of actinide structure-activity relationships and how these relationships can be modulated by the ligand field.

References

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