Covalent Bonding in the Late Actinide Elements

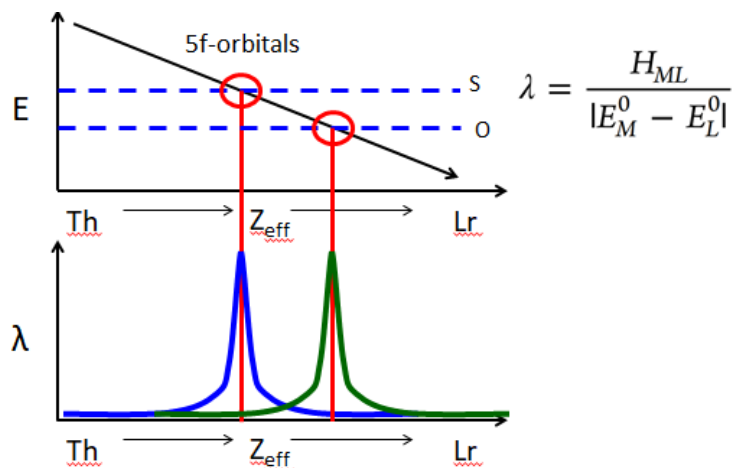Christopher Caroff   Literature Seminar   November 27th 2018

Much of the chemistry of the actinide series can be understood in terms of the decrease in f-orbital energies as these orbitals are contracted by an increasing effective nuclear charge. Early in the series (Th-Pu) the f and d orbitals remain relatively diffuse and high in energy, which allows these elements to mimic certain aspects of transition metal chemistry such as accessibility of higher oxidation states and the ability to form strong covalent bonds. Later in the series (beyond Pu) the f-orbital contraction causes the actinides to behave much more like the lanthanides, dominated by the trivalent oxidation state. The lanthanide-like behavior of the late actinides causes problems in nuclear fuel reprocessing. Both curium and americium are difficult to separate from the lanthanide elements because their ionic radii and preferred oxidation states are similar.[1] Developing a deeper understanding of the chemical behavior of the actinides could prove beneficial in nuclear waste reprocessing. The reality of actinide chemistry is that it is much more complex than can be understood with simple parallels to transition metals and lanthanides. Both the 5f and 6d orbitals are very similar in energy throughout the actinide series. Relativistic effects, spin-orbit coupling, and multiple orbitals with sufficient diffusivity to participate in bonding all serve to complicate matters further.[2-4]

Modern spectroscopic techniques now make it possible to probe directly the extent of covalency in actinide-ligand bonds. Chlorine K-edge X-ray absorption spectroscopy shows that there is significant 5f and 6d bonding character in several early actinide complexes such as UCl_6^{2-}.[5] To date, only one example of a direct probe of actinide covalency has been reported for any actinide heavier than plutonium: covalency was measured in $AmCl_6^{3-}$ through Cl K-edge XAS and compared with that in the analogous lanthanide complex $EuCl_6^{3-}$ (**Figure 1**).[6] These results demonstrate that there is more orbital mixing in americium-chlorine bonds than is seen the analogous europium complex. The authors attribute the increase in covalency to the more diffuse nature of americium atomic orbitals.
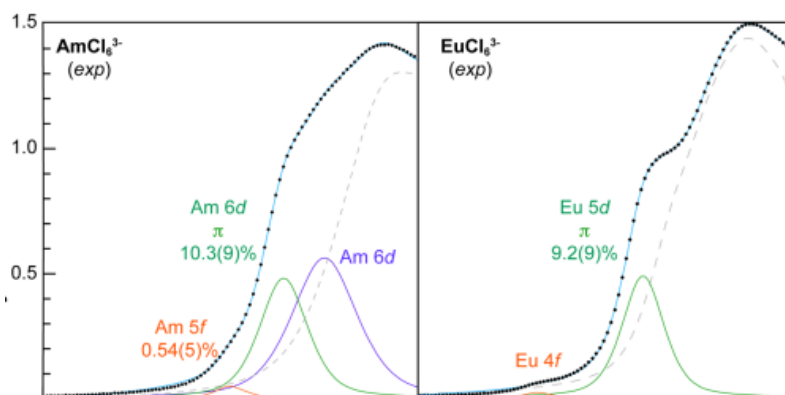
Figure 1. Cl K-edge XAS spectra demonstrating increased orbital mixing for the $AmCl_6^{3-}$ complex relative to the $EuCl_6^{3-}$ complex based on peak intensity. Am is the heaviest actinide for which a direct probe of covalency has been measured.[6]

It is important to note that this type of analysis becomes increasingly challenging later in the actinide series due to the short radioactive half-lives and the complications associated with high energy ionizing radiation. Historically, late actinide bonding has been described as mostly ionic, but it is important to determine whether this is actually the case. In the molecular orbitals formed by metal-ligand overlap, the degree of orbital mixing can be described by a mixing coefficient that is proportional to the spatial orbital overlap, and inversely proportional to the energy difference between the metal and the ligand. Because spatial overlap of orbitals is significantly reduced late in the actinide series due to the contraction of the valence f-orbitals, the degree of orbital mixing should become increasingly sensitive to the energy difference between the metal and the ligand.[2] A qualitative example of how the orbital mixing for an actinide can be influenced by energy when the overlap term is small can be seen in **Figure 2**. This phenomenon has been observed computationally but direct observation has been made difficult due to the lack of data on actinide compounds beyond plutonium.[7]

Recently, crystal structures for an isostructural series of late actinide complexes from plutonium to californium with 2,6-pyridinedicarboxylate (DPA) ligands were published.[8,9] This series presents a rare opportunity to investigate the chemical nature and

$$\lambda = \frac{H_{ML}}{|E_M^0 - E_L^0|}$$

Figure 2. Qualitative example of the sensitivity of covalency in the actinide series with changing ligand energy. λ is the mixing coefficient or degree of orbital mixing, H_{ML} is the spatial orbital overlap, E_M^0 is the metal based orbital energy, and E_L^0 is the ligand based orbital energy.

bonding late in the actinide series. The $Cf(HDPA)_3$ and $Bk(HDPA)_3$ complexes differ in both their magnetic and spectroscopic properties from that exhibited by $Am(HDPA)_3$ and $Cm(HDPA)_3$ but no satisfactory explanation for this difference was proposed.[8,9] A more recent publication showed that there is a significant change in the complexation thermodynamics between Cm and Bk, which supports the previously observed deviations in chemical behavior. DFT modeling of these complexes showed that the number of molecular orbitals with partial f-character increases significantly from Cm to Bk, coincident with the observed changes in chemical behavior. In addition, the valence orbitals for the actinide DPA complexes become nearly degenerate in energy with the frontier molecular orbitals for the DPA^{2-} ligand at Bk and remain similar in energy for the Cf complex (**Figure 3**).[10] The authors propose that the chemical changes observed in this series can be attributed to increased covalency for Bk and Cf due to energy degeneracy driven covalency late in the actinide series.

In the absence of a significant spatial orbital overlap term, covalent bonding in the late actinides is made possible through energy degeneracy driven covalency. This effect has been shown to be very sensitive to ligand energy due to the limited diffusivity of the valence orbitals. It may be possible to exploit energy degeneracy driven covalency late in the actinide series to develop useful methods to separate the minor actinides from the lanthanides in nuclear fuel

reprocessing. Additional data on the late actinides is necessary for continued exploration of energy degeneracy driven covalency and its effects on the chemistry of the late actinides, particularly how they deviate from predicted behavior.
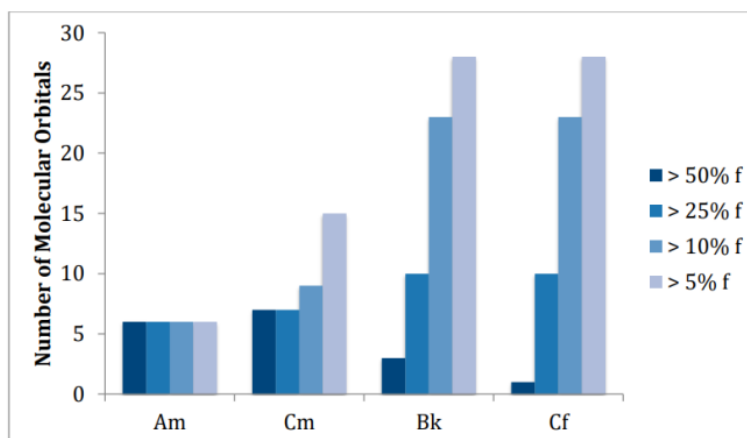
Figure 3. Increased mixing of f-orbitals with orbitals from the DPA^{2-} ligands coincident with energy near degeneracy of the actinide complexes with the free DPA^{2-} ligands.[10]

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