Recent Developments in Synthetic Americium Chemistry

Robert Joseph Lastowski　　Literature Seminar　　July 21, 2020

The synthetic chemistry of the actinides has historically been dominated by metals early in the series, notably uranium and thorium, as demonstrated by the fact that compounds of these two elements make up 95% of deposited actinide structures in the Cambridge Structural Database (CSD) (Table I). Consistent with this emphasis, the first organometallic actinide complex reported was the uranium cyclopentadienyl complex Cp_3UCl ($Cp = C_5H_5^-$), published in 1956 by Reynolds and Wilkinson.[1] In contrast, synthetic studies of the mid-actinides such as americium (Am) have been hindered by the scarcity of available starting materials.[2] In the United States, production of long-lived radioisotopes at Oak Ridge National Laboratories (ORNL) began in the 1950s and halted in 1998, largely due to competition from Russia.[3] The resulting inventory is continually managed by the Department of Energy (DOE).[4] In 2018, production resumed at ORNL and domestic purchase of ^{241}Am is once again possible.[5] Recently, there has been an increase in papers devoted to synthetic americium chemistry, and more than half of the 32 reported CSD entries have been reported in the last five years. This "influx" of new studies has started to provide experimental tests of computationally predicted aspects of americium compounds, such as the presence of significant spin-orbit coupling, the operation of an inverse trans influence, and the impact of relativistic core electron velocities on the electron energy level diagrams.

Table I. Actinide-containing entries in the CSD as of June 2020.

	Th	Pa	U	Nd	Pu	Am	Cm	Bk	Cf
Number of CSD entries	1,866	17	17,239	618	339	32	7	4	6

One of the difficulties in synthetic trans-plutonium chemistry has been the lack of convenient synthons. In the past, the only readily available starting material was $^{243}AmO_2$. Although this oxide can be converted into anhydrous $AmCl_3$ by high temperature routes, more commonly it was converted (without isolation or purification) into an aqueous solution of americium halides.[6, 7] Because anhydrous $AmCl_3$ is insoluble in organic solvents, and aqueous solutions are incompatible with many reactions of interest, there has been interest in expanding the repertoire of americium starting materials. In 2019, a convenient route to the isolation of anhydrous halides $[AmCl(\mu\text{-}Cl)_2(thf)_2]_n$ and $AmBr_3(thf)_4$ was described, and the products were characterized by single crystal X-ray diffraction (XRD) and electronic absorption spectroscopy (EAS).[8] These two Lewis base adducts (Figure 1) are readily soluble in organic solvents and have the potential to serve as convenient precursors for further exploration of nonaqueous americium chemistry.

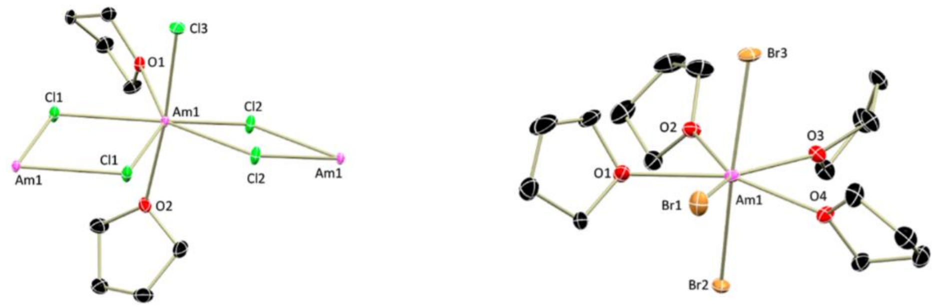

Figure 1. Molecular structures of $[\mathrm{AmCl(\mu\text{-}Cl)_2(thf)_2}]_n$ (left) and $\mathrm{AmBr_3(thf)_4}$ (right).

One recent landmark in the nonaqueous chemistry of americium is first crystal structure of a compound containing an Am–C bond: the tris-cyclopentadienyl complex $\mathrm{Am(Cp^{tet})_3}$ ($\mathrm{Cp^{tet}} = \mathrm{C_5Me_4H^-}$).[6] A single crystal XRD study reveals that crystals of $\mathrm{Am(Cp^{tet})_3}$ are isomorphous to other $\mathrm{M(Cp^{tet})_3}$ complexes (M = Th, U, La, Ce, Pr, Nd, Sm, Tb, Yb, Lu, Y): all of these compounds possess molecular C_{3h} symmetry (Figure 2). UV/vis/NIR spectroscopy coupled with spin-orbit (SO) CASSCF/NEVPT2 calculations reveal that $\mathrm{Am(Cp^{tet})_3}$ exhibits intense LMCTs and weak 5f-5f transitions, whose energies indicate that the ligand field splits the metal 5f orbitals even though they are largely non-bonding. Additional DFT/PBE calculations yielded a qualitative MO diagram for $\mathrm{Am(Cp^{tet})}$, suggesting that the bonding MOs of $\mathrm{Am(Cp^{tet})_3}$ stem from the symmetry-allowed mixing of metal d-orbitals with lower-lying ligand orbitals. This study is one of the first to involve air- and moisture-sensitive chemistry of a trans-plutonium actinide on a large (5 mg) scale.[6]

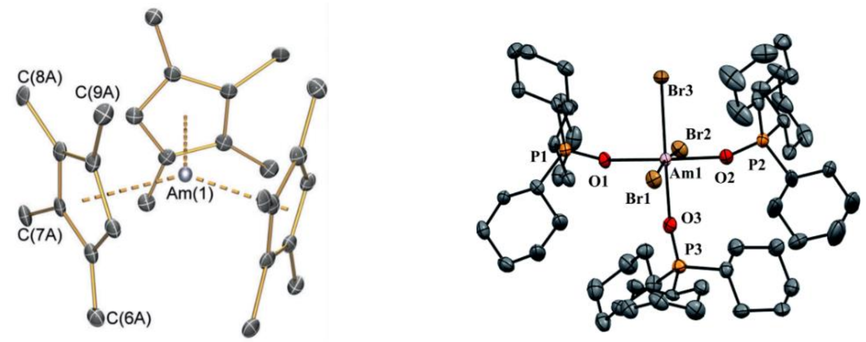

Figure 2. Molecular structures of $\mathrm{Am(Cp^{tet})_3}$ (left) and *mer*-$\mathrm{AmBr_3(OPcy_3)_3}$ (right).

In high-valent early actinides such as compounds of the uranyl ion ($\mathrm{UO_2^{2+}}$), a phenomenon called the inverse trans influence (ITI) has been observed, in which hard, polarizing, strongly bound ligands tend to reside trans to one another and mutually strengthen interactions with the metal center.[9] This phenomenon has been hypothesized to be a result of a polarization of semi-core p-orbital electron density towards vacant f-orbitals creating a hole trans to tightly bound ligands.[9, 10] In an effort to determine the presence of the ITI in low valent trans-plutonium actinides, Windorff and coworkers isolated and characterized the americium complex *mer*-$\mathrm{AmBr_3(OPcy_3)_3}$ (cy = cyclohexanyl) (Figure 2).[10] The contraction of homo-trans metal-ligand bonds (i.e., Br trans to Br, or O trans to O, vs. Br trans to O) observed by XRD is vanishingly small, despite the expectations of frozen core, semi core electron repulsion, and natural localized molecular orbital calculations. One conclusion is that the ITI in Am^{III} does not significantly involve the Am 6p orbitals, as described for high valent early actinides.[10] This species adds to the one previously known compound containing Am–Br bonds[8] and to the three previously known compounds containing an americium–halogen bond.[7, 8]

The ability to synthesize and isolate americium compounds on scales suitable for rigorous characterization will aid in the thorough determination of the reactivity of the mid-actinides. The recently described synthetic routes to $[AmCl(\mu\text{-}Cl)_2(thf)_2]_n$ and $AmBr_3(thf)_4$ provide organic-soluble synthons of anhydrous Am^{III} well-suited to air- and moisture-sensitive chemistry. The characterizations of $Am(Cp^{tet})_3$ and $AmBr_3(OPcy_3)_3$ serve as examples of the synthetic scales now possible, as well as the ability to experimentally investigate computationally predicted phenomena. The coming isolation of a wide range of americium compounds will aid in extending the boundaries of modern synthetic inorganic chemistry.

References

1. Reynolds, L. T.; Wilkinson, G., π-Cyclopentadienyl Compounds of Uranium-IV and Thorium-IV. *Journal of Inorganic and Nuclear Chemistry* **1956,** *2*, 246-253.
2. Jones, M. B.; Gaunt, A. J., Recent Developments in Synthesis and Structural Chemistry of Nonaqueous Actinide Complexes. *Chemical Reviews* **2013,** *113*, 1137-1198.
3. Krouse, C. ORNL's Enriching Isotopes Again. https://www.oakridger.com/news/20190312/ornls-enriching-isotopes-again.
4. Patton, B. D.; Robinson, S. M., Minor Actinide Production at Oak Ridge National Laboratory. *United States: N. p.* **2019**.
5. FY 2020 Congressional Budget Justification; Isotope Production and Distribution Program Fund. https://www.energy.gov/sites/prod/files/2019/05/f62/fy-2020-doe-sc-isotope-production-congressional-budget-request.pdf.
6. Goodwin, C. A. P.; Su, J.; Albrecht-Schmitt, T. E.; Blake, A. V.; Batista, E. R.; Daly, S. R.; Dehnen, S.; Evans, W. J.; Gaunt, A. J.; Kozimor, S. A.; Lichtenberger, N.; Scott, B. L.; Yang, P., $[Am(C_5Me_4H)_3]$: An Organometallic Americium Complex. *Angewandte Chemie International Edition* **2019,** *58*, 11695-11699.
7. Cross, J. N.; Su, J.; Batista, E. R.; Cary, S. K.; Evans, W. J.; Kozimor, S. A.; Mocko, V.; Scott, B. L.; Stein, B. W.; Windorff, C. J.; Yang, P., Covalency in Americium(III) Hexachloride. *Journal of the American Chemical Society* **2017,** *139*, 8667-8677.
8. Galley, S. S.; Sperling, J. M.; Windorff, C. J.; Zeller, M.; Albrecht-Schmitt, T. E.; Bart, S. C., Conversion of Americia to Anhydrous Trivalent Americium Halides. *Organometallics* **2019,** *38*, 606-609.
9. Gregson, M.; Lu, E.; Mills, D. P.; Tuna, F.; McInnes, E. J. L.; Hennig, C.; Scheinost, A. C.; McMaster, J.; Lewis, W.; Blake, A. J.; Kerridge, A.; Liddle, S. T., The Inverse-trans-influence in Tetravalent Lanthanide and Actinide Bis(carbene) Complexes. *Nature Communications* **2017,** *8*, 14137.
10. Windorff, C. J.; Celis-Barros, C.; Sperling, J. M.; McKinnon, N. C.; Albrecht-Schmitt, T. E., Probing a Variation of the Inverse-Trans-Influence in Americium and Lanthanide Tribromide Tris(tricyclohexylphosphine Oxide) Complexes. *Chemical Science* **2020,** *11*, 2770-2782.