# Actinide-Based Endohedral Metallofullerenes

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In 1985, Smalley, Curl, and Kroto synthesized a new allotrope of carbon, $C_{60}$, by laser vaporization methods under a helium atmosphere.[1] The discovery of the structure that formed, deemed buckminsterfullerene by the authors, along with the discovery of fullerenes of other sizes with $C_n$ configurations, won them the Nobel Prize in Chemistry in 1996. Two weeks after their discovery, the same authors published the first example of a metal ion encapsulated within the cavity of a fullerene, La-$C_n$ (n = 44 – 76), where the lower carbon count $C_n$ configurations appeared to exhibit an increase in stability with the metal ion inclusion.[2] This discovery sparked interest in chemical research focused on using these so-named endohedral metallofullerenes (EMFs) as a new approach to the construction of superconductors (for alkali metal EMFs),[3] and as isolated environments to study fundamental principles of poorly understood f-block elements.

The first actinide-containing EMF was discovered in 1992, when the authors hypothesized an appropriately sized tetravalent ion would be able to stabilize $C_{28}$, a fullerene that had been previously detected by TOF-MS, but not isolated due to poor stability.[4] The low stability of this cluster was attributed to the presence of highly reactive sites centralized on fused pentagon rings, systems that violated the isolated pentagon rule (IPR), which states that fullerenes containing fused pentagon rings are destabilized due to high geometric strain.[5] It was believed, and subsequently supported by DFT calculations, that non-IPR cages can be stabilized through an ionic model in which electrons are transferred from the metal atom to the cage itself, localizing negative charge on the reactive carbon center, resulting in stabilization of these sites.[6,7]
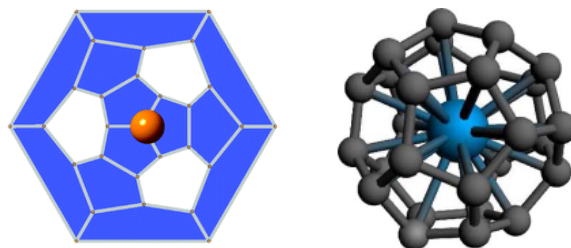


**Figure 1.** Schlegel representation for M@$C_{28}$ (left), and representative structure for M@$C_{28}$ (right, M = Hf, Th, U).[6,7]

Currently, research in the field of actinide EMFs can be divided into two main areas. One focuses on the encapsulation of small clusters as a means to study fundamental modes of binding for f-block elements,[8,9] while the other focuses on the host-guest interactions between the actinide ion and the fullerene cage itself, allowing for the isolation of new fullerene isomers with unique spectroscopic and electrochemical properties not found in native fullerenes.[10–12]

Actinide elements can access a wide variety of oxidation states. For example, uranium can exist in oxidation states ranging from $2^+$ to $6^+$.[13] In 2017, the first crystallographically characterized uranium EMFs, U@$D_{3h}$-$C_{74}$, U@$C_2$(5)-$C_{82}$ and U@$C_{2v}$(9)-$C_{82}$, were produced by Echegoyen and coworkers. These EMFs appeared to demonstrate cage isomer-dependent charge transfer, showing

that the formal oxidation state of the central metal ion is dependent on the orbital overlap of the f-orbitals of the metal with specific regions of the fullerene cage.[11]

One distinct advantage to using a fullerene environment to study bonding is that the system of interest is not perturbed or supported by any ancillary ligands beyond the interaction between the metal ion and the cage.[13] Within the last two years, two long sought-after actinide clusters were isolated within fullerene cages: diuranium ($U_2$) and diuranium carbide ($U_2C$).[8,9] Previously, diuranium had only been observed transiently as a mass spectrometry phenomenon, and computational studies on $U_2$ were inconsistent on whether or not diuranium could form a bonding interaction, and if it did form, what bond order would be observed.[8] X-ray absorption spectroscopy (XAS) along with crystallography showed evidence for a formal oxidation state assignment of 3+ on each uranium and a weak U-U bond with a distance between 3.793−3.460 Å, significantly shorter than the previously theorized 3.9 Å.[14] The bond distance also correlated with oxidation state, as reduction and oxidation of the system resulted in a shortening and lengthening of the U-U distance, respectively.[9]
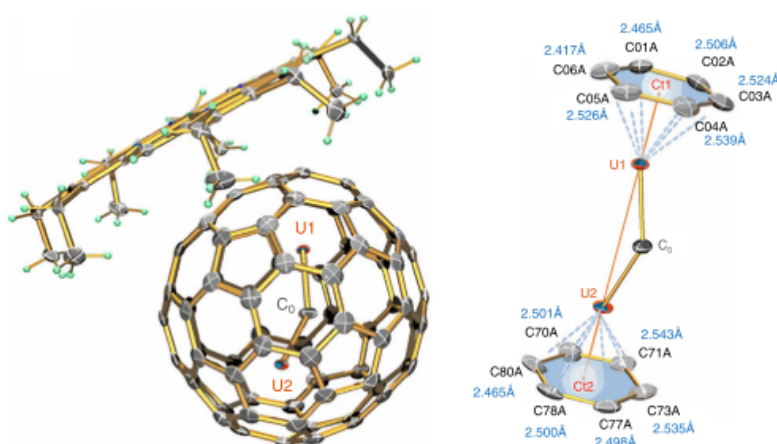


**Figure 2.** ORTEP representation of UCU@$I_h$(7)-$C_{80}$ at 40% probability, (left), and UCU cluster with nearby aromatic ring fragments, (right). Adapted from reference 8.

The diuranium carbide structure shown in Figure 2 was of special interest to the community, as information on uranium carbon double bonds were fundamentally lacking. Until these studies, most U=C structures contained supported carbene-like structures or uranyl halides supported by noble gas matrices.[15,16] In 2018, Chen and coworkers, isolated and characterized a $C_{80}$ EMF containing a unique U=C=U cluster. Crystal structures in conjunction with XPS and computational studies of the UCU cluster suggested a formal 5+ oxidation state on each of the uranium ions, with an unusually short U-C bond distance, indicative of a highly covalent double bond. Additionally, the UCU moiety exhibited a unique bent U=C=U bond angle of 142.8°, an angle that agreed with previous computational studies but had yet to be observed. This bond angle was attributed to localized negative charge on the carbide, generating electron lone-pair density akin to an intermediate hybridization between sp and $sp^2$ hybridized orbitals.[8]

Advancements in actinide chemistry have been held back because of the inherent radioactivity and associated health risks of working with 5f complexes.[11] Actinide EMFs provide a unique platform to study these elements, as small actinide clusters can be stabilized through

charge transfer processes inside the fullerene cage without solvent effects or additional ligand frameworks. Actinide elements also imbue unique properties to fullerenes that are not observed in lanthanide-containing EMFs as actinides can adopt a wide range of oxidation states, unlike lanthanides which are often limited to the II/III redox couple.[13] Future work should focus on more spectroscopic characterization of isolated compounds and the interplay between the endohedral clusters and their fullerene cages.

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