

Bonding with actinides

Suzanne Bart from Purdue University talks to *Nature Chemistry* about her investigations into the chemistry of actinides, and why she finds them both challenging and rewarding.

■ What are the main experimental challenges that come with working with the actinides?

All of the actinides are radioactive, so their handling requires the utmost care as well as specialized personal protective and laboratory equipment, though to various degrees depending on the element. Early actinides such as thorium and uranium are relatively abundant and have radioactive decay rates and products with manageable half-lives for typical laboratory settings. Our uranium compounds are very sensitive to temperature, oxygen and water, so we handle them all in inert-atmosphere dryboxes and store them in freezers at $-35\text{ }^{\circ}\text{C}$. On the other hand, the transuranics are much trickier to handle, they are only available in small quantities and are highly radioactive — specialized facilities and protective equipment are required, along with constant monitoring and extremely careful preparation of experiments, which even involves carrying out rehearsals with non-radioactive analogues.

In addition, compound analysis also comes with challenges. It can be hard to find facilities for routine characterization staffed with people who are willing and able to handle such compounds. For instance, in the US only a few companies will perform elemental analysis on uranium and thorium. Similarly, electron paramagnetic resonance spectroscopy — quite routine for *d*-block metals — is more challenging for uranium compounds as it often requires liquid-helium temperatures to enable the observation of uranium-based electrons. Furthermore, in comparison to the transition metals, there is far less literature to rely on for data interpretation.

■ Why is synthesizing new types of actinide compounds, and isolating new oxidation states, significant?

In my opinion, the synthesis of new materials based on *f*-block elements is always exciting. In contrast to the chemistry of the *d*-block metals, which is now well-established, current hot topics in actinide chemistry involve the elucidation and manipulation of metal–element multiple-bond interactions, the establishment of new oxidation states and the comprehension



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of how to manipulate redox properties, as well as the generation of transuranic organometallics. Pursuing these studies will lead to a greater understanding of bonding regimes and discovery of new chemical transformations.

■ Why is it important to determine in such great detail the bonding interactions between actinides (and lanthanides) and other elements — bond order, degree of covalency, π back-bonding?

Understanding the interaction of the *f*-block elements with organic ligands is essential to determining their basic bonding properties. Because the lanthanides and actinides have little variation in terms of their individual properties (which notoriously caused difficulties in first separating and identifying them), a way to distinguish them from each other is by leveraging their unique interactions with main-group elements. The ability of actinides to engage in covalent bonding is thus a key exploitable property that sets them apart from lanthanides.

■ You mostly work with uranium — are applications related to nuclear energy and waste remediation a main motivation in uranium chemistry?

Nuclear energy and waste remediation are important motivators, and are driving some funding in the US right now. However, my group is also interested in the fundamental redox properties of these elements, looking towards how to accomplish multi-electron reactions related to organometallic

transformations. *f*-Block elements have great potential in small-molecule activation because they are much more electron-rich than their *d*-block counterparts, and are highly reducing. Their much larger size also gives more flexibility in terms of the types of organic ligands that can be used as a support.

■ Why did you get into this particular area of chemistry?

As a graduate student I became intrigued by organouranium species, and pursued a postdoctoral appointment in Karsten Meyer's group to learn more about their syntheses, means of characterization and importance in inorganic chemistry. My favourite aspect of uranium chemistry is that oftentimes the products obtained and reactivity observed are unexpected. Although routine characterization methods such as NMR spectroscopy and X-ray crystallography are useful for molecule identification, the paramagnetic nature of low- and mid-valent uranium compounds make them amenable to other analytical techniques, including superconducting quantum interference device (SQUID) magnetometry and electron paramagnetic resonance spectroscopy. When combined with computational methods, all of the data gives us a complete picture of how a molecule is put together, and of its electronic structure. In the end, figuring out how all of the details fit together is very rewarding!

■ What are the challenges that lie ahead in actinide chemistry?

There are, of course, important scientific challenges to consider, such as handling and recycling nuclear materials, increasing the availability of new isotopes to study and developing analytical tools to fully understand these new compounds. Others include educating the current student pool, and maintaining and expanding the current workforce. In the US, a majority of actinide chemistry occurs at national laboratories, so an important hurdle to overcome is how to facilitate, increase and maintain communication between these organizations and the students and faculty in academia.

INTERVIEW BY ANNE PICHON