

The riches of uranium

Uranium is best known, and feared, for its involvement in nuclear energy. **Marisa J. Monreal** and **Paula L. Diaconescu** take a look at how its unique combination of properties is now increasingly attracting the attention of chemists.

It is nearly impossible to find an uplifting, funny, or otherwise endearing quote on uranium — the following dark wisecrack¹ reflects people's sinister feelings about this element: "For years uranium cost only a few dollars a ton until scientists discovered you could kill people with it". But, in the spirit of rebranding, it is interesting to note that the main source of Earth's internal heat comes from the radioactive decay of uranium, thorium and potassium-40 that keeps the outer core liquid, induces mantle convection and, subsequently, drives plate tectonics.

Uranium is the naturally occurring element with the highest atomic number. Its discovery in 1789 in the mineral pitchblende (or uraninite) is credited to the German chemist Martin Heinrich Klaproth who named it after the planet Uranus, itself only discovered eight years earlier. Although at the time Klaproth thought that he had discovered uranium metal, its actual isolation was not achieved until 1841, by the French chemist Eugène-Melchior Péligot who reduced the anhydrous uranium tetrachloride present in the ore with potassium. Through the end of the nineteenth century and until the mid-twentieth century, uranium was widely used, for example, in the colouring of glass, giving it a greenish–yellow hue (from UO_2 ; 'Vaseline glass').

The discovery of radioactivity in 1896 by Henri Becquerel from a uranium sample, and subsequent research by Enrico Fermi and others from 1934 on, eventually showed that ^{235}U can undergo a chain reaction of nuclear fission. This made it attractive for the nuclear power industry but also for Little Boy, the first nuclear weapon used in a war. Uranium's use in nuclear weapons is, understandably, the source of the widespread phobia felt by most for uranium. However, it is only weakly radioactive — the half-life of ^{238}U is 4.468×10^9 years — and emits alpha particles. These have a low penetration depth

and can be arrested by the skin, making depleted uranium (composed mainly of ^{238}U) safe to work with as long as it is not inhaled or ingested.

Studying the fundamental chemistry of uranium is an exotic endeavour, but those who embrace it will reap its benefits. Haber and Bosch found that uranium was a better catalyst than iron for making ammonia². The isolation of an $\eta^1\text{-OCO}$ complex of uranium³ also showed that, even though it is not involved in natural processes, it can help shed light on their mechanism: similar complexes are proposed to be instrumental in the photosynthetic fixation of CO_2 , but transition-metal models have remained elusive.

Synthetic chemists are excited about uranium's properties. Uranium brings the best of many worlds to the table: like the lanthanides, it generates electrophilic complexes that show high reactivity towards normally inert substrates. Like the transition metals, it benefits from multiple oxidation states (III to VI), a property that has been greatly exploited in redox reactions. However, unlike the lanthanides, which generate mostly ionic compounds, and unlike the transition metals, which use their *d* orbitals for coordination bonds, uranium can use its *f* orbitals (pictured) to form covalent bonds⁴.

Furthermore, uranium's large radius makes unique coordination environments possible. One class of compounds in particular encompasses the many unusual properties of uranium: the inverted sandwiches of arene-bridged diuranium complexes, which showed that δ back-bonding with *f* orbitals is the equivalent of π back-bonding in transition metal organometallic chemistry⁵.

Although the use of uranium catalysts for drug synthesis seems unlikely, it is worth considering that what Haber and Bosch

found about uranium's superior catalytic activity may not be an isolated event. The organometallic chemistry of uranium was born during the 'Manhattan project' — code name of the development of the first nuclear weapon during the Second World War. This field truly began to attract interest in 1956 when Reynolds and Wilkinson reported the preparation of the first cyclopentadienyl derivatives⁶. The discovery of

uranocene electrified the field as much as that of ferrocene had pushed forward the organometallic chemistry of transition metals. Today, examples of processes catalysed by uranium complexes include the hydrogenation of alkenes and the oligomerization, dimerization, hydrosilation and hydroamination of terminal alkynes.

Reports of researchers taking advantage of the unique properties of uranium are appearing with increasing frequency, and it is only a matter of time until these processes are transformed from stoichiometric to catalytic. Uranium may still cost more than a few dollars a ton, but scientists are using it for a lot more than just weapons. □

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References

1. <http://www.todayinsci.com>
2. <http://go.nature.com/etvnrj>
3. Castro-Rodriguez, I., Nakai, H., Rheingold, A. & Meyer, K. *Science* **305**, 1757–1759 (2004).
4. Kozimor, S. A. *et al. J. Am. Chem. Soc.* **131**, 12125–12136 (2009).
5. Diaconescu, P. L., Arnold, P. L., Baker, T. A., Mindiola, D. J. & Cummins, C. C. *J. Am. Chem. Soc.* **122**, 6108–6109 (2000).
6. Reynolds, L. T. & Wilkinson, G. *J. Inorg. Nucl. Chem.* **2**, 246–253 (1956).

