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Inorganic chemistry

Californium–carbon bond captured in a complex

Julie E. Niklas & Henry S. La Pierre

The scarcity and high radioactivity of the heaviest actinide elements, such as californium, make their study a formidable challenge. A landmark report describes the first structural characterization of a californium–carbon bond. **See p.421**

The detailed study of a class of organometallic compounds known as the metallocenes has driven crucial developments in areas such as catalysis, electrochemistry and nanotechnology. On page 421, Goodwin *et al.*[1] report the synthesis and characterization of a metallocene complex of californium, a member of the actinide series of elements (Fig. 1a). Substantial technical challenges had to be overcome to handle this air-sensitive complex of a highly radioactive element — just two milligrams of californium were used in the work. Remarkably, the authors report the first crystallographic measurement of a californium–carbon bond. Organometallic complexes of actinide ions have emerged as a frontier of research that challenges accepted models of bonding in coordination complexes (compounds consisting of a central atom or ion bound to ligands). Goodwin and colleagues' findings will help to map periodic trends of physico-chemical properties across the heavy actinides.

Californium (Cf) is not found in nature, and was first produced in 1950, enabling the identification of a range of its chemical and nuclear properties[2]. The advent of programmes to produce elements heavier than plutonium (the transplutonium elements) subsequently allowed larger quantities of californium to be prepared. Currently, californium is the heaviest element for which greater than microgram quantities are available, enabling measurement of its bulk properties in compounds. Nevertheless, in contrast to the rapidly developing chemistry of the naturally occurring early actinide elements thorium and uranium, the chemistry of californium (and of the other transplutonium elements) remains severely constrained by the element's high radioactivity, low abundance and high cost. The field has therefore received limited attention since the 1970s.

Goodwin *et al.* address this knowledge gap by preparing and characterizing a californium metallocene complex (Fig. 1b). They chose to use the californium-249 isotope, because it has a longer half-life (351 years)[2] than other isotopes of this element. To put the radioactivity of this isotope into perspective, its specific activity is roughly 12 million times that of depleted uranium (uranium-238, which itself requires special handling protocols).

In addition to the challenges involved in handling the isotope on the requisite small scale of available isotope, there were concerns that radiolytic decay of californium might damage the samples. The authors therefore tuned the synthesis of the metallocene so that the crystalline complex could be produced in a day. They also optimized the synthesis in model reactions using ions of the lanthanide series of elements. Lanthanides are cheaper and easier to handle than is californium, and their ions have a similar radius to the californium ion, which makes them useful substitutes in model reactions.

Goodwin and colleagues also prepared a metallocene using americium-241, an actinide that is close to californium in the periodic table, with a similar radioactive decay rate, and which emits α-particles that have similar energies to those emitted by californium-249. They used this metallocene to investigate the potential of radiolysis to affect which products formed in their reactions, and the products' crystal stability. Armed with all the information from the model studies, the authors went on to successfully isolate and characterize the target californium metallocene, which turned out to have a 'bent' structure (the two organic ligands in the complex are not parallel; Fig. 1b).

The first actinide metallocene[3] was a uranium compound isolated in 1968, and its characterization redefined our understanding of metal–ligand bonding in the actinide elements[4]. In the past few years, metallocene frameworks have also afforded the first structural characterization of actinide–carbon bonds beyond uranium in the periodic table (plutonium[5,6] and americium[7]). Goodwin and colleagues' work extends structurally characterized actinide–carbon bonds to californium, and enables the bonding and electronic

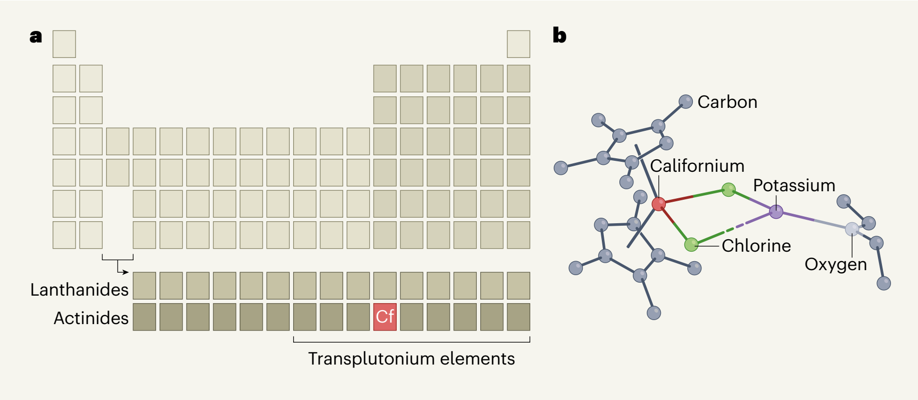

Figure 1 | An organometallic complex of californium. a, The lanthanides and actinides are two series of elements in the periodic table, and the transplutonium elements are actinides that are heavier than plutonium. The actinide californium (Cf) is highly radioactive and very scarce, and its compounds are therefore extremely difficult to prepare and analyse. **b**, Goodwin *et al.*[1] have synthesized the organocalifornium complex $[Cf(Cp^{tet})_2Cl_2K(OEt_2)]_n$ and obtained its crystal structure (shown). The complex adopts a 'bent metallocene' configuration in which the two ligands twist away from a parallel configuration to accommodate the Cf^{3+} ion as it binds to (coordinates) two chloride ions. The chloride ions are stabilized by a potassium ion (K^+), which coordinates the oxygen atom of a solvent molecule. Cp^{tet} is an organic ligand (tetramethyl-cyclopentadienyl); Et, ethyl group (C_2H_5). Hydrogen atoms are not shown.

structure of the transplutonium elements to be compared in detail with those of the lanthanides and early actinides.

An organocalifornium complex[8] was first prepared in 1970, and was partially characterized using a technique called powder X-ray diffraction. Surprisingly, the complex was ruby red in colour, in stark contrast to the mint green of other californium compounds. This observation fuelled speculation about whether the formation of californium–carbon bonds drives changes in the electronic structure and absorption spectra of californium compounds. In their reactions, Goodwin *et al.* observed a change in colour from mint green to red–orange as the californium starting material was converted into the metallocene complex. Crystals of the isolated metallocene were dark orange, reminiscent of the organocalifornium complex described in 1970.

The authors' spectroscopic measurement confirmed that the californium ion was in the +3 oxidation state, and suggested that the metal–ligand bonds are largely ionic, with limited covalent character. Crucially, it also revealed a broad, colour-determining feature in the ultraviolet–visible–near-infrared spectrum, due to charge transfer from the ligand to the metal. State-of-the-art theoretical modelling of the complex's electronic structure, grounded by the experimentally determined structure of the californium metallocene and its lanthanide analogues, confirmed that the metal–ligand bonds are largely polarized and ionic, as indicated by the spectroscopic data. Notably, the models also showed that the energy gap between the metal and ligand orbitals of the californium complex is smaller than that in the lanthanide analogues. This causes the charge-transfer feature to occur in the visible region of the spectrum, giving the complex its striking red–orange colour. By contrast, the colourless dysprosium metallocene (dysprosium is a lanthanide) has a comparable charge-transfer feature in the ultraviolet region of the complex's spectrum.

The discovery of the reason for the divergent spectroscopic features of the californium and dysprosium metallocenes is a subtle, but important, finding that opens up questions about the electronic structure of the transplutonium elements. In particular, the small difference in the covalency of metal–ligand bonds between the dysprosium and californium complexes points to other phenomena that drive the unique properties of the transplutonium elements. A study of another californium compound[9] indicated that crystal field splitting is substantially greater in trivalent californium (Cf^{3+} ions) than in trivalent early actinides. (Crystal field splitting is a phenomenon in which valence orbitals in an ion that are of equal energy are split by ligand binding into higher- and lower-energy groups of orbitals.) As a result, crystal field splitting in trivalent californium competes with spin–orbit coupling (another phenomenon that alters the energies of valence orbitals).

Moreover, the observation that the energy gap between the ligand and metal valence orbitals in the californium metallocene is smaller than that in the dysprosium metallocene can be explained by the fact that the energies of metal valence orbitals in the transplutonium elements are lower than are those in the lanthanides. This observation supports previously reported spectroscopic evidence[10] suggesting that complexes of divalent californium (Cf^{2+} ions) could potentially be prepared — lower-energy metal valence orbitals help to stabilize complexes of elements in their lower oxidation states.

Goodwin and colleagues' preparation and analysis of a californium metallocene, currently the heaviest element for which such feats are feasible, allows us to dream that the open questions about the transplutonium elements' electronic structures can be resolved experimentally. In this regard, the logistical complexity of the current experiments should be noted: the study required the talents of researchers from four institutions, and the isotopes were produced at a fifth laboratory. The work has therefore established a substantial physical and scientific infrastructure that will enable scientists to address how valence, spin–orbit coupling and crystal-field effects entwine to govern magnetism, spectral properties and metal–ligand bonding in the transplutonium elements.

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Microbiology

A centenarian entourage of bile acids and gut bacteria

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A study in humans indicates that certain bile acids that are produced by bacteria and commonly found in people over 100 boost gut health and protect against infection. These findings shed light on the contributors to healthy ageing. **See p.458**

As we age, we are more likely to develop ageing-related illnesses such as cardiovascular disease, cancer and type 2 diabetes. Yet centenarians — people who are more than 100 years old — are less susceptible to such conditions than are ageing individuals who do not live as long[1,2] (see go.nature.com/3csogm6). For some centenarians, answers to this conundrum might lie in the gut. On page 458, Sato *et al.*[3] identify a previously unknown connection between healthy ageing in humans over the age of 100, and gut bacteria and bile acids (Fig. 1).

The study of bile acids began in earnest in the early 1900s, with the characterization of the primary bile acids: cholic acid and chenodeoxycholic acid[4]. Primary bile acids are synthesized from cholesterol in the liver. They are then transported to the small intestine, where they undergo extensive modifications through the process of metabolism by gut bacteria and, as a result, form what are called secondary bile acids. Bile acids have long been recognized for their detergent properties, such as their ability to dissolve fat and fat-soluble vitamins. It has also emerged that they can act as potent hormones that control metabolic processes in the intestine, liver, pancreas and brain.

Over the past several years, the number of bile acids identified in the body has grown greatly, aided by advances in