

# NJC

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## The structure determination of uranocene and the first COT lanthanide complexes

Cite this: DOI: 10.1039/x0xx00000x

Kenneth N. Raymond<sup>a</sup>

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

**This paper results from my introductory talk at the symposium “Frontiers of Organo-f-Element Chemistry.” Although my active research in organoactinide and -lanthanide chemistry ended early in my career, it led to an interest in actinide coordination chemistry that continues to this day; I am a member of the actinide research group of the Chemical Sciences Division of the Lawrence Berkeley National Laboratory. My remarks will be somewhat personal and are intended to provide a perspective on the history of this field but I hope to connect it to what has become a new and very active area of research; this class of compounds is now associated with what are essentially quantum confined multiconfigurational molecules.**

The organometallic chemistry of the actinides and lanthanides goes back many years. The excellent review by Dietmar Seyferth,<sup>1</sup> then the editor of *Organometallics*, presents a thorough and scholarly review of the history of this field and its developments up to just over a decade ago. Largely subsequent to that time have come the new multiconfigurational analyses that will be the subject of my later comments.

As Seyferth described in his review: “The first organoactinide compounds were prepared 105 years after Frankland’s discovery of dimethylzinc, the first organometallic compound to be reported in the literature. However, once the first cyclopentadienyluranium compounds had been reported by Reynolds and Wilkinson, the pace of research in this new area of organometallic chemistry was fast and furious. Cyclopentadienyl derivatives of the other actinide elements, thorium, protoactinium, neptunium, plutonium, curium, berkelium, and californium, followed, but organouranium compounds and, to a somewhat lesser extent, those of thorium received most of the attention. Using depleted, i.e., <sup>238</sup>U free of <sup>235</sup>U, uranium and thorium, actinide chemistry could be investigated in the standard university chemistry laboratory using appropriate precautions, but study of the chemistry of the other actinides required specialized (and expensive) facilities. The discovery of uranocene in 1968 was a milestone in organouranium chemistry. Uranocene attracted much

attention in the general organometallic community, since it was the first representative of an entirely new class of  $\pi$ -bonded sandwich complexes.”

My involvement in this chemistry began in the first year or so of my appointment as an assistant professor. Although I did not yet have my own diffractometer, I had access to X-ray single crystal diffraction data in the Templeton Laboratory at the Berkeley Lab. I had made it something of a policy decision at the beginning of my career that I would not do other people’s structures since at the time crystallography had not yet been fully integrated into synthetic chemistry programs and I did not want to be regarded as a staff crystallographer. As Andy Streitwieser describes it in his autobiography:<sup>2</sup>

“Ken Raymond had just been appointed, beginning July 1968, as an Assistant Professor at Berkeley. Ken is an inorganic chemist and an expert X-ray crystallographer. He recalls my telling him about our new uranocene synthesis over lunch at the Faculty Club one day that Fall and asking about the feasibility of doing a structure determination. I was aware that uranium would dominate the X-ray diffraction and that the electron density about the much lighter carbon might be difficult to detect. Ken thought it might be feasible; however, at Berkeley he planned to downplay his crystal structure work and to emphasize other research interests. I thereupon took from my pocket a vial with some beautiful uranocene crystals and he was hooked. He determined the structure in collaboration with Allen Zalkin, a research chemist and X-ray structure expert at the Lawrence Berkeley Laboratory (LBL), and proved the  $D_{8h}$  structure with two planar octagonal rings having uranium at the center ....It is amusing that they had trouble publishing their result. A referee objected that the contribution of carbon to the diffraction compared to the much heavier uranium would be too small to determine, exactly the fear that prompted me to consult Ken in the first place. Only when Ken pointed out to the referee that the symmetry of uranocene was such that the uranium could not contribute to many of the reflections was the communication published.”



Figure 1: Kenneth Raymond and Andrew Streitwieser in 1978, at the celebration of the 10th anniversary of the discovery of uranocene (unknown photographer; reproduced by permission of Kenneth Raymond and Andrew Streitwieser).

My recollection of this interaction is substantially the same as Andy's. I made an exception to my policy and never regretted it. Remarkably, Andy Streitwieser encouraged me to publish the structure paper<sup>3</sup> without his name on it. This was a very generous thing for a famous and senior colleague to do for a junior, untenured faculty member. Andy continues to be a good friend (and nearby neighbor). Following the communication of the structure of uranocene as we were writing the full paper it became clear that although a number of organometallic compounds had been prepared in previous years,<sup>1</sup> little was known about their structures and bonding. I set up a dry box facility to deal with these very air sensitive materials and proceeded to make a number of compounds that had already been reported in the literature, often replacing cyclopentadienyl with methylcyclopentadienyl to avoid the spinning of these functional groups in the solid state. This was important at the time since low temperature X-ray diffraction was not yet a routine capability. After some years of doing this chemistry, I presented a simple ionic radius model that could accurately predict the coordination number and bond distances to reasonable approximations. This led to the publication of our review "Structural Criteria for the Mode of Bonding of Organoactinides and -lanthanides and Related Compounds" in 1980.<sup>4</sup> Discussing the structure of uranocene we stated "A dominant question concerning organometallic compounds of the f metals is the degree to which

'covalency' is important in the bonding." It is remarkable to me that, 36 years after these words were written, this continues to be an object of controversy and cutting edge research. This is because, with new physical characterization techniques and with great advances in theory, the bonding aspects can be examined in much finer detail. As we stated in our review "We seek here to address the question: 'How covalent is the bonding in these compounds?' This in turn hinges on what is meant by 'covalent'. Within a careful limited structural definition of covalent and ionic bonding, this question can be examined in some detail." As we concluded in our review "We have developed a formalism, based only on structure, within which to address the question of predominant mode of bonding in organometallic complexes of the lanthanide and actinide elements. The formalism considers the general structural features and the metal coordination number for a series of structurally related compounds. We have shown that an ionic model can explain these features as observed in organoactinides and -lanthanides well, while the same model does not work well in the d-metal  $MCp_2$  metallocenes, where covalent bonding often dominates." We went on to say "While we caution that structural variations are not usually very sensitive to small changes in bonding and alternative definitions of 'ionic and 'covalent' based on other physical methods may well lead to different conclusions within such formalisms, we conclude that within the limits of our structural criteria the bonding in organoactinides and -lanthanides is ionic." This very broad statement is as true today as it was then but it ignores much of what is most interesting about the bonding as subsequent decades of research have shown.

A major reason for the impetus behind organoactinides and lanthanide chemistry in recent decades has been their use in chemical catalysis. The review "Recent advances in organothorium and organouranium catalysis" by Andrea and Eisen<sup>5</sup> describes applications in hydroamination, hydrosilylation of terminal alkynes, coupling of terminal alkynes with isonitriles, catalytic reduction of azides and hydrazines, ring opening polymerization of cyclic esters and polymerization of  $\alpha$ -olefins. While I will not further describe this area of chemistry, it remains a huge part of the research in this field. A recent and very complete review of organoactinide chemistry, focused on cyclopentadienyl compounds, is presented by one of the major researchers in this field, Michel Ephritikhine in his organometallics paper in 2013.<sup>6</sup>

Recent physical phenomena of the organoactinides and -lanthanides have shown a new variation of the Kondo effect, in which a local magnetic moment spin polarizes local conduction electrons to form a magnetic singlet.<sup>7</sup> While the coupling of f and conduction electrons is a common feature in f-electron intermetallics (and called "Kondo coupling") it was proposed that similar effects should occur should occur in carbon ring systems where electrons are delocalized in the aromatic ring and f-electrons can be localized on the central metal. The preparation of very pure cerocene enabled magnetic and X-ray absorption experiments to characterize the ground states of this molecule. In the paper "Cerocone revisited: the electronic structure and interconversion between  $Ce_2(C_8H_8)_3$  and  $Ce(C_8H_8)_2$ " a new synthetic procedure for preparation of cerocene and related compounds was presented.<sup>8</sup> The solid state magnetic susceptibility of cerocene showed that it behaves as a temperature independent paramagnet over a temperature range of 5-300 degrees. This and the  $L_{III}$  XANES,<sup>7</sup> are consistent with a mixed electronic state consisting of two configurations. While the atomic structure of cerocene is essentially the same as uranocene the electronic structure is very different. "The electronic structure of cerocene having a multiconfiguration ground-state that is an admixture of the two

configurations  $\text{Ce(III, } 4f^1)(\text{cot}^{1.5})_2$  and  $\text{Ce(IV, } 4f^0)(\text{cot}^2)_2$ ; the multiconfigurational ground-state has profound effects on the magnetic properties...<sup>8</sup> More recently this phenomenon has been observed in other types of materials, in particular substituted bipyridine complexes of bis(pentamethylcyclopentadienyl) ytterbium have shown that there are multiconfigurational, intermediate valence ground states. The nature of both the ground and first excited states were found to change depending on the position of methyl or dimethyl substitution in the bipyridine rings. "This article describes experimental and calculational results that strongly bolster previous assertions about intermediate valence (IV) behavior and the importance of configuration interactions (CI) in determining most of the important properties in certain classes of molecules, including bonding, magnetic, and spectroscopic behavior. The intertwining of IV and tautomeric effects, together with their magnetic and structural implications and the small enthalpy and entropy changes involved, indicates that the near-degeneracies that occur in these lanthanide organometallics and their transition-metal cousins create a situation where small perturbations will create large changes in properties."<sup>9</sup>

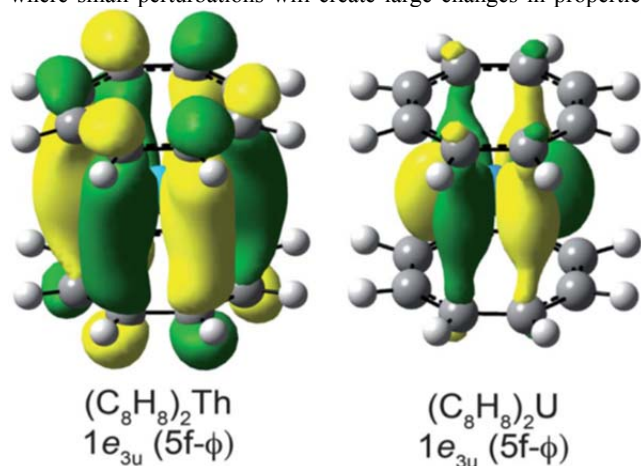


Figure 2: Representations of the antibonding  $1e_{3u}$  Kohn-Sham molecular orbitals for  $(\text{C}_8\text{H}_8)_2\text{Th}$  (left)  $(\text{C}_8\text{H}_8)_2\text{U}$  (right).

Reproduced from Ref. 10 with permission from The Royal Society of Chemistry

With regard to uranocene and thorocene, history has now come full circle. As described by Streitwieser<sup>2</sup> the inspiration behind the synthesis of uranocene was based on the  $\pi$  bonding (one nodal plane coincident with the bond axis) of the  $\pi$  orbitals of ligands such as cyclopentadienyl with metal d orbitals. The extension of this idea to f orbitals and the  $\delta$  symmetry  $\pi$  orbitals of cyclooctatetraene dianion suggested a new type of bonding – a  $\delta$  bond with two nodal planes coincident with the bond axis. After many years and studies this has now been extended by Minasian et al.<sup>10</sup> from DFT calculations and carbon K-edge X-ray absorption spectra (XAS) collected with a scanning transmission X-ray microscope (STXM). Both the experimental and computational results showed that the 5f orbitals engage in significant mixing with the  $\text{C}_8\text{H}_8^{2-}$  ligands for the lowest unoccupied molecular orbital which has  $\phi$  symmetry due to three nodal planes coincident with the bond axis, which **decrease** as the 5f orbitals drop in energy on moving from  $\text{Th}^{4+}$  to  $\text{U}^{4+}$  (see Figure 2). The experimental evidence for extensive f-orbital interactions in thorocene was provided by the C K-edge XAS analysis; however, f-type covalency in uranocene was found to be negligible. The results highlight two contrasting trends in orbital mixing from one pair of highly symmetric molecules, and show that covalency does not increase uniformly for different molecular orbital interactions with later actinides.

With this brief introduction I hope to have provided a full circle perspective on the early history of organoactinides and –lanthanide sandwich complexes from the beginning of simple structure analysis to the remarkable magnetic and electronic structures that have been characterized in recent years.

## Acknowledgement

I thank Drs. Corwin Booth and Stefan Minasian for assistance with references. This research is supported by the Director, Office of Science, Office of Basic Energy Sciences, and the Division of Chemical Sciences, Geosciences, and Biosciences of the U.S. Department of Energy at LBNL under Contract No. DE-AC02-05CH11231. I dedicate this paper to Andrew Streitwieser.

## References

- 1 D. Seyferth, *Organometallics*, 2004, **23**, 3562.
- 2 A. Streitwieser, *Andrew Streitwieser, Jr.: A Lifetime of Synergy with Theory and Experiment (Profiles, Pathways, and Dreams)*, American Chemical Society, Washington, DC, 1996.
- 3 A. Zalkin and K. N. Raymond, *J. Am. Chem. Soc.* 1969, **91**, 5667.
- 4 K. N. Raymond and J. Charles W. Eigenbrot, *Accounts of Chemical Research*, 1980, **13**, 276.
- 5 T. Andrea and M. S. Eisen, *Chemical Society Reviews*, 2008, **37**, 550.
- 6 M. Ephritikhine, *Organometallics*, 2013, **32**, 2464.
- 7 C. H. Booth, M. D. Walter, M. Daniel, W. W. Lukens and R. A. Andersen, *Physical Review Letters*, 2005, **95**, 267202.
- 8 M. D. Walter, C. H. Booth, W. W. Lukens and R. A. Andersen, *Organometallics*, 2009, **28**, 698.
- 9 C. H. Booth, D. Kazhdan, E. L. Werkema, M. D. Walter, W. W. Lukens, E. D. Bauer, Y.-J. Hu, L. Maron, O. Eisenstein, M. Head-Gordon and R. A. Andersen, *Journal of the American Chemical Society*, 2010, **132**, 17537.
- 10 S. G. Minasian, J. M. Keith, E. R. Batista, K. S. Boland, D. L. Clark, S. A. Kozimor, R. L. Martin, D. K. Shuh and T. Tyliszczaka, *Chemical Science*, 2014, **5**, 351.

<sup>a</sup> University of California, Berkeley, and Lawrence Berkeley National Laboratory, Berkeley, CA 94720