Experimental report

17/04/2019

Proposal: 5-12-332 **Council:** 4/2017

Title: Organoactinide C-H agostic interactions

Research area: Chemistry

This proposal is a resubmission of 5-12-328

Main proposer: Polly ARNOLD

Experimental team: Connor HALLIDAY
Tatsumi OCHIAI

Local contacts: Laura CANADILLAS DELGADO

Samples: U[N(SiMe3)2]3
C90H138N2O6U2
C63H92O4U2

Instrument	Requested days	Allocated days	From	To
D19	18	10	09/04/2018	19/04/2018

Abstract:

Recently at the ILL we were able to collect neutron diffraction data on uranium tris(aryloxide) 1. The data which was collected in September 2016 is currently being processed however, short contacts between C-H bonds and the uranium centre are expected to be found.
Following this very recent success, we propose to investigate weak C-H agostic interactions of simple organouranium complexes [{(DtbpO)2U}2(C6H6)] 2, U[ODbtp]3 3, U[N(SiMe3)2]3 4 and U[CH(SiMe3)2]3 5 which are in the lower oxidations states (+3/+4). In addition to neutron diffraction studies, we are also investigating the behaviour of these single crystalline solids at varying pressures at the University of Edinburgh in collaboration with Prof. Simon Parsons. Single crystal neutron diffraction of these compounds would allow the exact positions of the hydrogen atoms to be determined and thus identify potential C-H agostic interactions with the uranium centres.

Abstract

A neutron diffraction analysis was carried out at 295 K on a single crystal of $U[ODtbp]_3$ in order to accurately locate the U· · · H distances. The measurement has been combined with lab based X-ray diffraction measurement of the same material at the same temperature. Several additional parameters were refined in order to account for systematic differences in the C-H bond lengths and thermal parameters determined by X-ray and neutron methods (Blessing 1995 Acta B51, 816-823). A single set of coordinates were refined for atoms other than H. A total of 29616 neutron and 42635 X-ray reflections were collected and merged to yield 4176 and 6802 independent reflections with $I>2(\sigma I)$ and R_{int} of 0.08 and 0.04, respectively. A final agreement factor of $R_1 = 6.9$ was observed. Distances involving the hydride ligands are: U1…H(1A) = 2.431 Å, U1…H(2A) = 2.489 Å, U2…H(1B) = 2.431 Å, U2…H(2B) = 2.507 Å, U2…H(3B) = 2.785 Å.

Experimental Report

Organouranium metal complexes that have weak interaction between the central uranium metal and the H-C moiety of the substituents are intriguing because of their potential roles in stabilizing low-coordinate uranium centers. Besides, a structural study of low coordinate uranium cations can provide insights into the intricacies of covalent and ionic binding of 5f elements which are poorly understood. Therefore, the structural characterization of low-coordinated complexes of uranium (+III, +IV) constitutes an important field of research. The most reliable way to get accurate geometric information about hydrogen positions in these types of complexes is by carrying out neutron structure determinations. $[\{(DtbpO)_2U\}_2(C_6H_6)]$, $U[ODtbp]_3$, $U[N(SiMe_3)_2]_3$ were three of the target compounds proposed for this study. Prior to this experiment, to our knowledge, as of yet, no U-H-C bonds have been precisely analyzed by neutron diffraction. It was our hope that results from this experiment would further enhance our understanding of the interaction of C-H with organouranium metal complexes. Neutron-sized crystalsof the complexes were available. These crystals were extremely air sensitive and only $U[ODbtp]_3$ survived the mounting procedure, which was carried out in an N_2 filled glove box. Data were subsequently collected on $U[ODbtp]_3$ with the new very-intense vertical axis Laue diffractometer (VIVALDI), which irradiates the sample with a broad wave band of neutrons. TOPAS academic was used for structural refinements. Experiment N°5-12-332

Figure 1 represents an ORTEP plot of $U[ODbtp]_3$.

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The results from this experiment provided accurate locations of the hydrogen positions and geometric information concerning U-H-C bonds, of which there are no other examples. We plan to extend this study to other low-valent uranium complexes in hopes of gaining a more complete understanding of these types of interactions

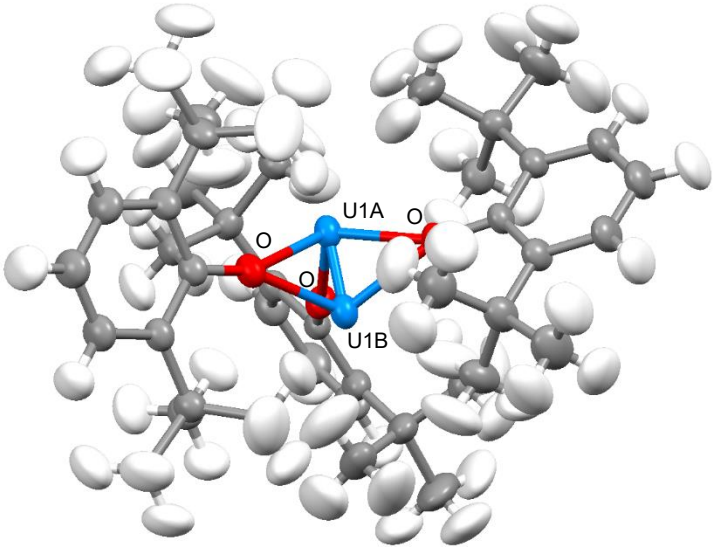

Figure 1: ORTEP plot of U[ODbtp]$_3$ showing the hydride positions