Novel Uranium-Small Molecule Interactions, and X-ray Spectromicroscopy for Nuclear Forensics

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Introduction

Dihydrogen complexes are mainstays of transition metal chemistry
• Homogeneous hydrogenations
• Biocatalytic chemistry
• Hydrogen storage

Since discovery in 1984, dihydrogen complexes have been implicated in main group as well as lanthanide chemistry

No counterpart in the actinides

Experimental Results

\(^1\)H nuclear magnetic resonance (\(^1\)H NMR) spectroscopy very sensitive to paramagnetic ion interactions:

\[
\Delta \lambda = \Delta \omega / \omega_0 = \Delta \omega_{\text{FS}} + \Delta \omega_{\text{CS}} + \Delta \omega_{\text{PCS}}. 
\]

Titration experiment shows linear dependence of \(\Delta \omega_{\text{CS}}\) chemical shift on \([\text{Cp}_2\text{H}_{\text{SiMe}}_3\text{U}]\):

\[
\begin{align*}
\text{Fig. 3.} \quad \text{\(^1\)H NMR spectra (500 MHz, 296 K) of a ~3 mM solution of \(\text{H}_2\) in \(\text{C}_6\text{D}_6\) containing the indicated equivalents of \([\text{Cp}_2\text{H}_{\text{SiMe}}_3\text{U}]\). Concentrations calibrated to internal hexamethylbenzene.}
\end{align*}
\]

Temperature dependence deviates from Curie-Weiss behavior:

\[
\text{Fig. 4.} \quad \text{Plot of chemical shift vs. 1000/T for a methylcyclo-hexane-d14 solution of \(\text{H}_2\) \([\text{Cp}_2\text{H}_{\text{SiMe}}_3\text{U}]\) and hexamethylbenzene.}
\]

Theoretical Modeling

Density functional theory calculations:
• Geometry similar to \(\text{Cp}^*_3\text{Eu-H}_2\), but very close U-H contacts
• U-H\(_2\) bonding orbital shows 1-electron involvement

\[
\begin{align*}
\text{Fig. 5.} \quad \text{Optimized structure of complex 1.}
\end{align*}
\]

\[
\begin{align*}
\text{Fig. 6.} \quad \text{U-H\(_2\) bonding orbital in complex 1.}
\end{align*}
\]

Mission Relevance

The NNSA’s understanding of actinide chemistry informs its development of technologies capable of characterizing and analyzing nuclear materials. As such, continuing to study new actinide-based materials is critical to maintaining a current and effective detection and analysis protocol. This research expands the community’s knowledge base in fundamental actinide-element interactions, relevant to the structure and properties of materials such as actinide carbides, silicides, and post-transition-metal alloys.

The detection of trace elements in taggart samples greatly facilitates material accounting. Furthermore, the application of synchrotron X-ray techniques to actinide material analysis can yield information as to material origin and refinement method(s) for nuclear forensics purposes.

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References


Design and Synthesis

Target: electron-rich uranium complex with vacant coordination site

Start synthesis from uranium turnings:

\[
\begin{align*}
\text{U}^2 + 3/2 \text{I}_2 + \text{EtO} \text{sonication, 7 d} \rightarrow \text{U}^3
\end{align*}
\]

Separately, synthesize bulky, multihaptic “Cp” ligand:

\[
\begin{align*}
\text{Na}^+ \text{SiMe}_3 + \text{EtO} \text{sonication, 7 d} \rightarrow \text{K}^+ \text{SiMe}_3
\end{align*}
\]

Combine ligand and U(l) to yield uranium(III) complex with open coordination site:

\[
\begin{align*}
\text{U}^3 + 3 \text{(CpSiMe)K} \text{reflux, 1 d} \rightarrow \text{Me}_2\text{Si}
\end{align*}
\]

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