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and Richard A. Andersen

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Hydrido[Tris(hexamethyldisilylamido)]-Thorium(IV) and -Uranium(IV)

By Howard W. Turner, Stephen J. Simpson, and Richard A. Andersen*

Abstract: Reaction of chlorotris(hexamethyldisilylamido)-thorium(IV) or uranium(IV) and sodium hexamethyldisilylamide in refluxing tetrahydrofuran or perdeuterotetrahydrofuran yields monomeric hydrido-[tris(hexamethyldisilylamido)]-thorium(IV) or -uranium(IV), or its deuteride, respectively. The hydrides react with carbon tetrachloride yielding chloroform and $\text{ClM}[\text{N}(\text{SiMe}_3)_2]_3$ where M is thorium or uranium. Further, the hydrides with n-butyllithium followed by methylbromide or deuterio-trifluoroacetic acid afford $\text{MeM}[\text{N}(\text{SiMe}_3)_2]_3$ or $\text{DM}[\text{N}(\text{SiMe}_3)_2]_3$, respectively, M = Th or U.

Sir: Metal hydrides are known for most of the metals. The 4f- and 5f-block metals, except those of the man-made ones, form rather stable metallic, binary hydrides of the type MH_2 and MH_3^1 . In contrast, only one molecular hydride of the f-block metals has been described, viz., $(\text{Me}_5\text{C}_5)_4\text{M}_2\text{H}_4$ where M is thorium or uranium.² We wish to describe the first monomeric, mono-hydride derivatives of these metals, viz., $\text{HTh}[\text{N}(\text{SiMe}_3)_2]_3$ and $\text{HU}[\text{N}(\text{SiMe}_3)_2]_3$.

Reaction of chlorotris(hexamethyldisilylamido)thorium(IV)³ with one molar equivalent of sodium hexamethyldisilylamide in refluxing tetrahydrofuran yields hydridotris(hexamethyldisilylamido)thorium as white needles from pentane,⁴ mp 145-147°C, $\nu_{\text{ThH}} = 1480 \text{ cm}^{-1}$,

^1H NMR (PhH) δ 0.90 and 0.40 due to the hydride and trimethylsilyl resonances, respectively. The deuteride, $\text{DTh}[\text{N}(\text{SiMe}_3)_2]$, $\nu_{\text{ThD}} = 1060 \text{ cm}^{-1}$ can be prepared by refluxing $\text{ClTh}[\text{N}(\text{SiMe}_3)_2]_3$ and $\text{NaN}(\text{SiMe}_3)_2$ in perdeutero-tetrahydrofuran. The uranium hydride and deuteride were prepared similarly. Hydridotris(hexamethyldisilylamido)uranium was crystallized from pentane as brown-yellow needles⁴, mp 97-98°C, $\nu_{\text{UH}} = 1430 \text{ cm}^{-1}$, $\nu_{\text{UD}} = 1020 \text{ cm}^{-1}$. We have been unable to locate the hydride signal in the ^1H NMR spectrum of this paramagnetic ($\mu_B = 2.6$ B.M. in benzene solution) substance, though the trimethylsilyl groups resonate at δ -19.5. The hydrides can also be prepared from $\text{ClM}[\text{N}(\text{SiMe}_3)_2]_3$ and tert-butyllithium or lithium triethylhydridoborate in pentane.

The metal-bound hydrides were further characterized by their reaction chemistry, see scheme. The hydrides react with carbon tetrachloride yielding chloroform (identified by its NMR spectrum) and $\text{ClM}[\text{N}(\text{SiMe}_3)_2]_3$, M is thorium or uranium. The latter were identified by mp, mixed mp, ir, and NMR spectra. Further, addition of n-butyllithium to a pentane solution of the hydrides followed by methylbromide yields $\text{MeM}[\text{N}(\text{SiMe}_3)]_3^3$, M = Th or U quantitatively. The product from reaction of n-butyllithium with the hydride derivatives affords $\text{SHM}[\text{N}(\text{SiMe}_3)_2]_3$ or $\text{DM}[\text{N}(\text{SiMe}_3)_2]_3$ (M is Th or U) upon addition of trifluoroacetic acid or deuterio-trifluoroacetic acid, respectively.

The uranium and thorium hydrides have also been characterized by a single crystal X-ray analysis, though the hydrogen atom was not located.⁵

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4. All new compounds gave satisfactory elemental analysis for C, H, and N and molecular ions (M-2) in the mass spectrometer.
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M = Th, U

Scheme

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