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Uranium(III) and thorium(IV) alkyl complexes as potential starting materials†

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The synthesis and characterisation of a rare U(III) alkyl complex, U[4-Me2NC(H)C6H5]3, using the dimethylbenzylamine (DMBA) ligand has been accomplished. While attempting to prepare the U(IV) compound, reduction to the U(III) complex occurred. In the analogous Th(IV) system, C–H bond activation of a methyl group of one dimethylamine was observed yielding Th[4-Me2NC(H)C6H5][5-(CH2)MeNC(H)C6H5] with a dianionic DMBA ligand. The utility of these complexes as starting materials has been analyzed using a bulky dithiocarboxylate ligand to yield tetravalent actinide species.

During the Manhattan project, actinide alkyl complexes were desirable for their potential as volatile compounds for separations, especially uranium enrichment.1 More recently, organoactinide chemistry has experienced increased attention as exemplified by the Hayton and Bart groups. For example, Hayton has reported homoleptic U(IV),2 U(V), and U(VI) alkyl3 complexes as well as Th(IV) alkyl4 complexes while Bart has produced a series of U(IV) benzyl compounds.5,6 Nevertheless, Th(IV) and U(III) alkyl complexes7–11 remain scarce.

Recently, the Hayton group has used the lithium salt of dimethylbenzylamine (DMBA) to synthesize Th(IV) and U(IV) complexes.12,13 The lithiation of dimethylbenzylamine produces an ortho-metalated phenyl anion. This salt may be converted to the benzyl anion by reaction with potassium tert-butoxide,14,15 which is accompanied by a proton migration from the alpha-position of the benzyl methylene to the ortho-position of the phenyl. The only known complexes using this ligand transfer agent as starting material are a zirconium complex16 as well as most of the lanthanide series.15 Since the Ln(III) complexes are stabilized by this ligand, we surmised that U(III) would be stabilized in a similar fashion.

Reaction of UI3(THF)4 with three equivalents of K[4-Me2NC(H)C6H5] in Et2O for 3 h at −25 °C, eqn (1), results in a dark coloured solution. X-ray quality crystals were grown from a saturated toluene solution at −25 °C, and diffraction revealed the U(III) complex, U[4-Me2NC(H)C6H5]3, Fig. 1. Reaction with UCl4 also produced 1 along with half an equivalent of 1,2-bis(dimethylamino)-1,2-diphenylethane. The 1H NMR spectrum of 1 is fluxional at room temperature, but cooling to −78 °C made the spectrum assignable. The 1H NMR spectrum is paramagnetically shifted, and the amine methyl resonances are inequivalent at 47 ppm and −71 ppm. The methine proton is located at −94 ppm. Complex 1 is thermally unstable above room temperature but stable when stored cold in the solid-state. As mentioned previously, this compound represents a rare U(III) alkyl complex.

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The U–Cipso distances are 2.766(3), 2.784(3), and 2.804(3) Å while the U–Cortho distances are 2.818(3), 2.813(3), and 2.816(3) Å. These distances are far shorter than the closest U–C interactions in U[CH(SiMe3)]3, but are similar to those found in [U(dddt)]2−, dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate.17 Therefore, the best description of the coordination of the DMBA ligand to U(Ph2BPz2)3 (10.8 Å), which does display SMM behaviour. 20 moment of exhibit single molecule magnet (SMM) behaviour, 18 that of the lithium salt. The uranium-methine carbon bond distances of 2.979(6) Å in (C5Me5)2Th(CH2C6H5)2, but are similar to the 2.700(8)– 2.842(4) Å observed for U–Cipso interactions in U(CH2C6H4R)4,R=H , 2p-Pr; 2p- Bu; 2-m- OMe; 2-o-picolyl, complexes,6 when the difference in T vs. T 1 above the ground state as 25 25 1.11 μB, which is in excellent agreement with the 1.09 μB. Assignment of this ground state to 1 is supported by a failure to observe an EPR spectrum at 2 K as the m1 = 3/2 substate is not EPR active. The first excited state of 1 is ~100 cm−1 above the ground state as determined from the temperature at which the plot of J/T vs. T deviates from linearity. Although U(m) complexes frequently exhibit single molecule magnet (SMM) behaviour,18 1 does not display a hysteresis in the magnetization vs. field measurements at 2 K. The lack of SSM behaviour is surprising given the uranium is a feature of complexes An[S2C(2,6-(Mes)2C6H3)]4(THF), An = U, Th, eqn (3). Both 3 and 4 were characterized by X-ray crystallography and were found to be structurally analogous (3 is shown in Fig. 3). Both are nine-coordinate with eight sulfur atoms and one THF molecule completing the coordination sphere in a monocapped square antiprismatic geometry. It is surprising that both thorium(n) and uranium(n) are large enough to accommodate four ligands as well as a THF molecule since dithiocarbamate,25 dithiophosphate,26 and dithiolene17 actinide(IV) complexes are typically eight-coordinate. Our rationale for the presence of the THF molecule is that it may be bound to the metal center prior to or during the addition of the [S2C(2,6-(Mes)2C6H3)]1− ligands, and upon coordination of the dithiocarbamate ligands, the THF is captured in the inner coordination sphere. The THF molecule cannot be removed by heat or vacuum. The space filling model of the compound is consistent with this explanation as is the observation that both complexes precipitate from the reaction mixture when the reaction is performed in THF. Another interesting feature of complexes 3 and 4 is that typically homolectic sulfur-based complexes are not produced by protonation reactions. For example, reaction of [(Me3Si)2N]2U(CH2SiMe3NSiMe3) with one equivalent of 2,6-Me2C6H4SH yields [(Me3Si)2N]2U[S2(2,6-Me2C6H4)]2, but using four equivalents results in intractable products.27 In our case, reaction of 1 or 2 with four equivalents of H2C=CH2 produced isolable compounds. Both compounds

\[ \text{ThCl}_3(\text{DME})_2 + 4 \text{K} \rightarrow \text{THF}, \text{THF} \]
are viable starting materials which may be useful alternatives to the widely used $\text{U}\,[\text{N(SiMe}_3\text{)}_2\text{]}_3$.\textsuperscript{28,29} 

The average U–S bond distances in 3 of 2.877(17) Å are longer than those seen in $\text{U}\,[\text{dddt}]_3$, which range from 2.717–2.760 Å. This increase is attributed to the greater steric properties of the terphenyl-based ligand. The average Th–S bond distances in 4 of 2.934(3) Å is similar to the 2.932(2) Å distance in the sterically demanding dithiophosphine complex $\text{Th}\,[\text{S}_2\text{PPr}_2]_3$. These distances are significantly longer than the 2.9075(5) Å and 2.911(4) Å distances in the less crowded complexes $\text{Th}\,[\text{S}_2\text{P(THF)}_2]_{10}$ and $\text{Th}\,[\text{S}_2\text{P(C}_6\text{H}_{11})_2]_{19}$,\textsuperscript{11} respectively. The difference in bond distances of 3 and 4 (≈ 0.057 Å) is consistent with the Shannon radii of nine-coordinate $\text{U}^+$ (1.19 Å) vs. $\text{Th}^+$ (1.23 Å).\textsuperscript{12}

In summary, using the potassium salt of dimethylbenzylamine, we have synthesized and characterized a rare $\text{U[nn]}$ alkyl complex. When the analogous reaction is attempted with a uranium(u) starting material, ligand coupling is observed along with reduction to $\text{U(n)}$. The thorium complex featured C–H bond activation of one of the methyls on the dimethylamine group. The synthetic utility of these complexes was evaluated using a sterically demanding dithiocarbamoyl ligand, $\text{HS}_2\text{C(}6\text{H}_3\text{Me}_2\text{)}_2$, which produced analogous products, $\text{An[S}_2\text{C(}2\text{,6-} \text{Mes}_2\text{C}_6\text{H}_3\text{)]}_6\text{(THF)}, \text{An} = \text{U; Th. Further reactivity is currently under investigation.}

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