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Homoleptic U(III) and U(IV) Amidate Complexes

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The syntheses of the first homoleptic U(III) and U(IV) amidate complexes are described. These can be interconverted by chemical reduction/oxidation, showing a unusual change in coordination number from four in the U(III) complex to eight in the U(IV) complex in the solid state structures.

Within the last few years, interest in improving control over the coordination chemistry of actinides has grown tremendously, leading to remarkable achievements in organometallics[1–5] and nanotechnology,[6–9] and to innovative developments in radioactive waste separation[10–13] and environmental remediation.[13–16] Uranium coordination complexes are of interest to chemists due to their wide array of accessible geometries and unusual reactivity.[17–31] Due to the electropositive nature and large atomic size of uranium, coordination chemists frequently employ sterically-encumbered ligands to stabilize uranium complexes in non-aqueous systems. Cyclopentadienyl (Cp) derivatives are often used to provide steric support around the uranium center, but a large amount of research has been directed towards developing actinide complexes using alternative ligand systems,[18,26,32] including carbenes,[33,34] carboxylates,[28,29,35] and amidinates.[36–40] Interestingly, amidates, which can be seen as hybrids of carboxylates to amidinates, have been only sparsely studied as ligands in actinide chemistry.[24,41] In contrast, amidate complexes of group IV metals have been investigated for a variety of applications. Ti(IV) and Zr(IV) amidate complexes are well-studied as catalysts for hydroamination,[42–45] and recently, homoleptic zirconium amidate complexes have demonstrated high efficacy as molecular precursors for chemical vapor deposition of ZrO_2 thin films.[46,47] Due to the presence of two distinct donor sites in the amidate backbone, amidate ligands typically bond in one of four primary modes, illustrated in *Figure 1*.

This variety in binding modes enables metal amidate complexes to adopt a number of different geometries and electron-donating abilities. Steric factors can affect the denticity of the binding, while electronic factors such as the hardness of the cation affect whether binding to N or O is electronically preferred.[44,48] Due to the high oxophilicity and the large ionic radii of U(III) and U(IV), we hypothesized that either chelating or O-bound coordination would be observed for amidate complexes of these metal centers. Here, we report the syntheses of the first homoleptic U(III) and U(IV) amidate complexes, which exhibit significant differences in their solid-state coordination geometries.

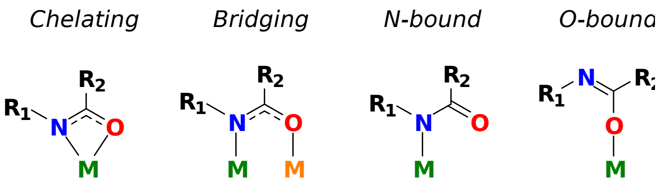

Figure 1: Binding modes of amidates to metal centers.

The amide proligand N-(2,6-diisopropylphenyl)pivalamide (H(TDA)) **(1)** was synthesized according to literature methods[49] and purified by sublimation. Deprotonation of **1** with $KN(SiMe_3)_2$ afforded the corresponding potassium amidate K(TDA) **(2)** as a colorless powder in 86% yield. Using **2** as a precursor for the metalation of uranium led to the formation of complicated mixtures of –ate complexes, resulting in poor yields of the desired uranium complexes. However, addition of 18-crown-6 to **2** gave the crowned potassium amidate K(TDA)(18c6) **(3)** in 96% yield, and this compound was substantially more effective as a starting material for metalation. The crystal structure of **3** can be found in the supporting information. *(Figure S17, Tables S1 and S2)*

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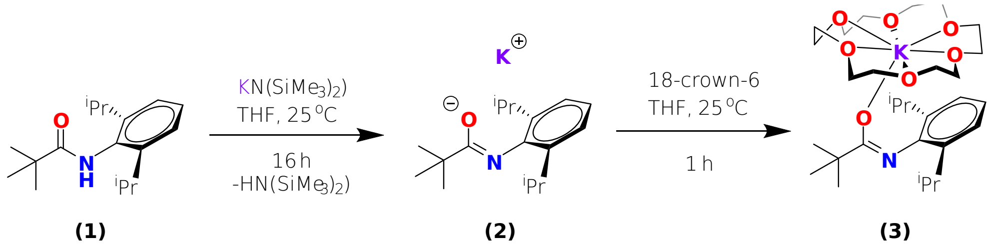
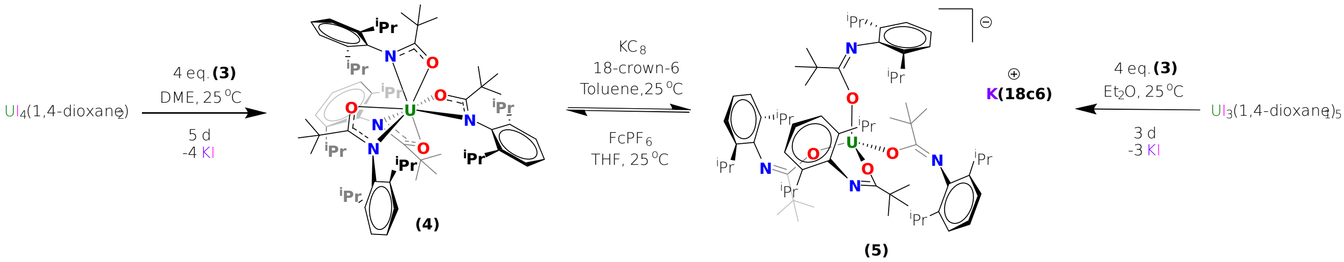


*Scheme 1: Synthesis of the crowned amidate ligand K(TDA)(18c6) (**3**).*

The homoleptic uranium amidate complex U(TDA)$_4$ **(4)** was synthesized by reacting UI$_4$(1,4-dioxane)$_2$ with four equivalents of **3**. *(Scheme 2)*

Complex **4** was isolated as pale green crystals in 23% yield from a cooled solution of HMDSO. Its room temperature ^{1}H NMR spectrum showed only a set of four paramagnetically-broadened resonances between 0 and 7 ppm, corresponding to the aromatic, *iso*-propyl methine, *tert*-butyl, and *iso*-propyl methyl protons. Using a similar salt metathesis reaction procedure, the U(III) complex **5** was obtained from the reaction between **3** and UI$_3$(1,4-dioxane)$_{1.5}$ in diethyl ether, and isolated in 66% yield as large red blocks.

The room temperature ^{1}H NMR spectrum of **5** showed a set of seven resonances, comprising six broad peaks from the uranium-bound ligands and one sharp peak at 3.5 ppm from the crown ether. The two most upfield resonances at -3.3 and 0.5 ppm were assigned to the inequivalent isopropyl methyl protons.



*Scheme 2: Synthesis and redox interconversion of the homoleptic uranium amidate complexes **4** and **5**.*

Previous studies with Hf and Zr amidate complexes have shown amidate ligands to be hemilabile at elevated temperatures, allowing for rapid interconversion between isomers.[50] To determine whether the solid-state coordination geometries of **4** and **5** were preserved in solution, variable-temperature NMR spectra were collected in d^8-THF from -78 to +70 °C. At 70 °C, **4** and **5** both exhibited five broad and paramagnetically shifted peaks, consistent with four-coordinate geometries in which the amidate ligands were equivalent on the NMR timescale. Upon cooling below 0 °C, a complex new set of multiple resonances emerged, suggesting lower symmetries for both molecules; however, attempts to formulate ^{1}H NMR assignments were thwarted by large paramagnetic shifts and broadening of the ligand resonances arising from coupling to the uranium centers.[51] These observations provide only a qualitative indication that multiple structures are potentially accessible in solution for **4** and **5**.

Since the NMR data alone were insufficient to shed light on the structures of **4** and **5**, we turned to single crystal X-ray diffraction studies to probe bonding interactions in the solid-state; these showed **4** to be eight-coordinate, with all four amidate ligands chelated (κ_2-O,N) to the U(IV) center in a distorted dodecahedral geometry *(Figure 2)*. The U-N bonds in **4** were found to be longer than the U-O interactions by an average of 0.33 ± 0.11 Å. To our surprise, the molecular structure of **5** showed no U-N bonding interactions; instead, the uranium in **5** was four-coordinate, with four (κ_1-O) amidates arranged in a distorted tetrahedral geometry ($\tau_4' = 0.92$). In addition, the average C–O bond distances increased from 1.315(4) to 1.330(4) Å in **4** vs. **5**, while the average C–N bond distances decreased from 1.301(7) to 1.279(6) Å in **4** vs. **5**, respectively, consistent with the resonance structures shown in *Figure 1*.

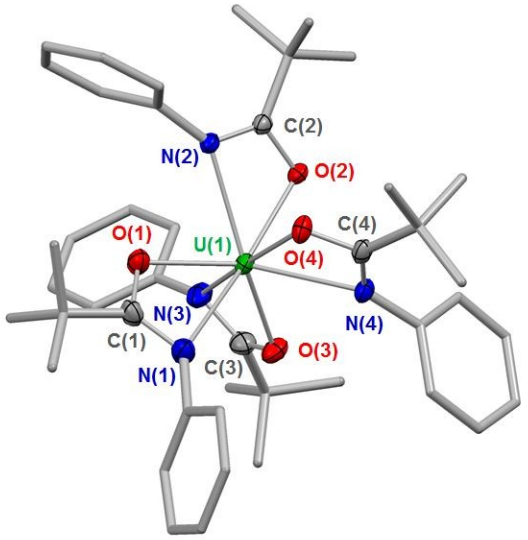


*Figure 2: X-ray crystal structure of **4** with 50% probability thermal ellipsoids. Hydrogen atoms and isopropyl groups are omitted for clarity.*

Considering the larger ionic radius of U(III) (1.03 Å vs 0.89 Å in U(III) and U(IV), respectively),[52] the observation of a four-coordinate geometry in the U(III) complex **5** and an eight-coordinate geometry in the U(IV) compound was unexpected. Several factors could be considered as influencing this behavior: i) the higher covalent character of U(IV)[53] could favor stronger U-N interations in **4**; ii) the effect of electrostatic repulsion in U-L interactions in anionic **5** relative to neutral **4** may result in a lower coordination number; iii) in situations where the energy differences are small, crystal packing effects cannot be ruled out.[54] Notably, **5** was the main product of the reaction between **3** and $UI_3(1,4\text{-dioxane})_{1.5}$ regardless of the stoichiometry used; no U(III) products with increased coordination numbers were isolated.

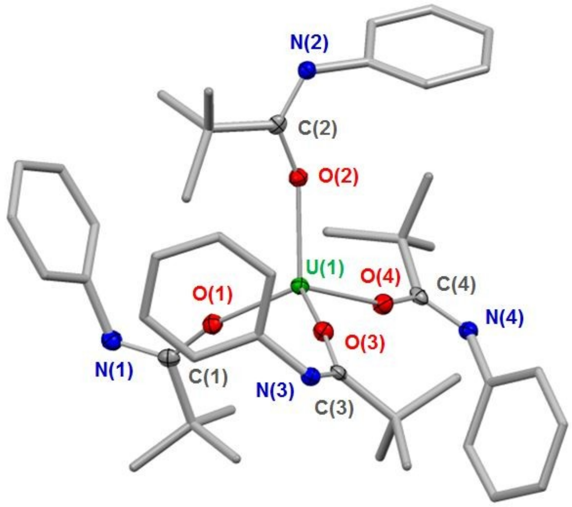


*Figure 3: X-ray crystal structure of **5** with 50% probability thermal ellipsoids. Hydrogen atoms, isopropyl groups, solvents and counter-ions are omitted for clarity.*

We were next interested to determine if **4** and **5** could be interconverted by chemical reduction/oxidation reactions. Since both complexes were chemically accessible from the corresponding U(IV) and U(III) precursors, chemical reduction/oxidation reactions to interconvert between the two species were pursued. While weak reducing agents such as cobaltocene showed no reaction with **4**, addition of KC_8 to a diethyl ether solution of **4** and 18-crown-6 caused the solution to darken from pale green to deep red, and we isolated **5** from the reaction mixture after a short reaction time (2 min); prolonged reaction times led to decomposition. Furthermore, **5** was readily oxidized by ferrocenium hexafluorophosphate in THF to give **4**.

We examined the cyclic voltammograms of **4** and **5** using $^nBu_4NPF_6$ as the electrolyte in THF or acetonitrile. No redox processes were observable within this solvent window; solvents with a larger reductive window, such as nitromethane, were not suitable for use with these complexes.

In summary, we have prepared the first homoleptic U(IV) and U(III) amidate complexes **4** and **5**, using the sterically-hindered N-(2,6-diisopropylphenyl)pivalamido (TDA) ligand. Complexes **4** and **5** were interconverted through reduction of **4** with KC_8 or oxidation of **5** with $FcPF_6$. The solid-state geometry of ligands around the uranium center was seen to be highly dependent upon the oxidation state of uranium for these complexes: counterintuitively, the larger U(III) center adopted a four-coordinate tetrahedral structure, and the smaller U(IV) center adopted an eight-coordinate distorted dodecahedral structure. This unusual finding for U(IV) in comparison to U(III) further serves to highlight the delicate interplay between steric and electronic effects in these molecular systems.

Table 1: Selected atomic distances (Å) and angles (deg) for 4 and 5.

Atoms	4	5
U1 – O1	2.270(2)	2.234(2)
U1 – O2	2.321(2)	2.235(2)
U1 – O3	2.316(2)	2.236(2)
U1 – O4	2.276(2)	2.253(2)
U1 – N1	2.721(3)	-
U1 – N2	2.535(2)	-
U1 – N3	2.535(2)	-
U1 – N4	2.713(2)	-
C – O avg	1.315(2)	1.330(5)
C – N avg	1.301(7)	1.279(6)
O – C – N avg	114.2(6)	125.5(7)

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