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## Homoleptic Aryl Complexes of Uranium (IV)

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**Abstract:** The synthesis and characterization of sterically unencumbered homoleptic organouranium aryl complexes containing U-C  $\sigma$ -bonds has been of interest to the chemical community for over 70 years. Reported herein are the first structurally characterized, sterically unencumbered homoleptic uranium (IV) aryl-ate species of the form  $[U(Ar)_{6l}]^{2^{-}}$  (Ar = Ph, p-tolyl, p-Cl-Ph). Magnetic circular dichroism (MCD) spectroscopy and computational studies provide insight into electronic structure and bonding interactions in the U-C  $\sigma$ bond across this series of complexes. Overall, these studies solve a decades long challenge in synthetic uranium chemistry, enabling new insight into electronic structure and bonding in organouranium complexes.

Originally proposed for applications in isotope separation and enrichment over 70 years ago,<sup>[1-2]</sup> homoleptic organometallic complexes of uranium with simple alkyl or aryl ligands are of significant research interest for insight into electronic structure and bonding in uranium organometallic chemistry. Despite the significant challenges inherent in their isolation and characterization due to their severe air and thermal sensitivities,<sup>[3]</sup> the past 30 years have seen seminal contributions in the synthesis and characterization of homoleptic uranium-alkyl complexes from Sattelberger, Hayton, and Bart.<sup>[4-11]</sup> Unfortunately, corresponding advances in the isolation and characterization of homoleptic uranium-aryl complexes have been exceedingly more rare despite decades of research.

Early attempts to isolate homoleptic uranium aryl complexes were first reported in 1977 by Sigurdson and Wilkinson.<sup>[12]</sup> In these studies, the reaction of uranium tetrachloride (UCl<sub>4</sub>) with lithium nucleophiles resulted in the formation of anionic, thermally unstable uranate (IV) species which could not be isolated and readily decomposed at or below room temperature. However, using techniques including NMR and alcoholysis, the general formula [Li(solvent)]<sub>2</sub>[UR<sub>6</sub>] was assigned to the insitu formed species. In 2016, the first structurally characterized, homoleptic uranium-aryl complex was reported by Arnold and co-workers - a homoleptic uranium(III)-aryl species (Figure 1) that takes advantage of steric protection provided by the bulky Terph<sup>-</sup> ligand.<sup>[13]</sup> Despite this important advance, homoleptic uraniumaryl complexes beyond the +3 oxidation state and containing nonsterically encumbering substituents remain an unsolved synthetic problem. It is of interest to note, however, that Hayton and coworkers have recently reported two homoleptic thorium aryl-ate complexes, each with unique geometries about the actinide metal center (Figure 1).<sup>[14]</sup>

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Figure 1. Previously reported homoleptic actinide-aryl complexes.

We were motivated to re-explore this longstanding challenge in the preparation of homoleptic uranium-aryl complexes with nonsterically encumbered aryl ligands utilizing our low temperature synthetic capabilities previously successfully applied to similar synthetic challenges in homoleptic iron-aryl chemistry.<sup>[15]</sup> Herein, we report the first homoleptic six-coordinate uranate (IV) complexes containing only uranium-carbon σ-bonds between a uranium center and phenyl, *p*-tolyl and *p*-CI-phenyl ligands and, combined with spectroscopic and theoretical studies, develop insight into electronic structure and bonding in these unique complexes.

Our initial synthetic studies targeted the isolation of the uranium(IV) complex,  $[UPh_6]^{2^-}$ . Drop-wise addition of 6 equiv. of phenyllithium (PhLi) to UCl<sub>4</sub> at -80 °C in a Et<sub>2</sub>O/THF mixture resulted in an immediate color change from pale green to dark red. Note that analogous reactivity can be achieved using the adduct  $[UCl_4(1,4-dioxane)]_2$  under otherwise identical reaction conditions.<sup>[16]</sup> Addition of hexane and subsequent crystallization at -80 °C afforded highly air and thermally sensitive red needles suitable for single-crystal X-ray diffraction studies, identified as  $[Li(THF)_4][(THF)LiU(Ph)_6]\cdot 1.5THF$  (1) (Figure 2A) (<sup>1</sup>H NMR, see SI). Isolated yields up to 60% have been achieved for crystalline material of 1. Magnetic susceptibility studies using the Evans method resulted in an average magnetic moment of 2.2(2) B.M. at -80 °C consistent with previous measurements of other six-coordinate U(IV) complexes.<sup>[4, 17]</sup>

The anion of 1 consists of a six-coordinate U(IV) center bonded to six phenyl rings with a high degree of distortion from octahedral geometry. One of the lithium cations interacts with the  $\pi$ -systems of three of the ligands, which appears to further augment the distortion. The three C-U-C angles for the lithium-coordinating phenyl ligands range from 76.77(2)° to 79.33(2)°, whereas those for the three independent phenyl rings range from 92.74(19)° to 101.76(2)° (Table 1). A similar distortion with lithium atom interaction has previously been reported for a hexaphenyl hafnium complex, [Li(THF)\_4][(THF)LiHf(Ph)\_6].<sup>[18]</sup>

With a successful method identified for the synthesis and isolation of 1, the para-substituents of the aryl ring were varied in order to evaluate the effect of the electronic contribution of the ligands on the nature of the U-C bond. As a starting point, ptolyllithium was selected in order to incorporate a more electronrich aryl ligand. Drop-wise addition of 6 equiv. of p-tolyllithium to [UCl<sub>4</sub>(1,4-dioxane)]<sub>2</sub> in a Et<sub>2</sub>O/THF mixture at -80 °C resulted in an immediate color change from yellow/orange to red. Subsequent crystallization at -80 °C afforded air and temperature sensitive red/orange plates suitable for single-crystal X-ray diffraction studies and identified as [(THF)<sub>3</sub>LiXLi(THF)<sub>3</sub>][(THF)LiU(p-tolyl)<sub>6</sub>]·Et<sub>2</sub>O·0.62THF (2) (Figure 2B) (<sup>1</sup>H NMR, see SI). Isolated yields of 45% have been achieved

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Figure 2. X-ray crystal structures of the homoleptic uranium-aryl complexes (A)  $[Li(THF)_{4}][(THF)LiU(Ph)_{6}] \cdot 1.5THF$  (1) and  $[(THF)_{3}LiXLi(THF)_{3}][(THF)LiU(p-tolyl)_{6}] \cdot Et_2O \cdot 0.62THF$  (2), X = 0.64Br, 0.36Cl (B). Independent cations and hydrogens atoms omitted for clarity. Thermal ellipsoids are shown at 50% probability.

for crystalline material of **2**. Magnetic susceptibility studies using the Evans method resulted in an average magnetic moment of 2.3(2) at -80 °C.

Complex 2 exhibits an analogous distortion away from pure octahedral symmetry as observed for 1, with one lithium-THF counterion interacting with the aryl ring system. The average U-C bond lengths of the two complexes are nearly identical, 2.525(11) for 1 and 2.518(11) Å for 2. In both uranium aryl complexes, the aryl rings feature asymmetric U-Cipso-Cortho angles, suggestive of an agostic interaction. For example, the U-C1-C2 bond angle in the uranium hexaphenyl complex has a bond angle of 142.8(4) degrees while the U-C1-C6 bond angle is 100.7(3) degrees, a difference of greater than 42 degrees. In the hexatolyl complex, this sample pair of angles differs by nearly 41 degrees (Table S1). Natural bond orbital (NBO) second-order perturbation theory analyses of 1 and 2 suggest that agostic interactions contribute to the structure stabilization by 6.47 and 6.56 kcal/mol, respectively (Figure S1). This type of agostic interaction has also been observed by Hayton et al. in the previously reported distorted sixcoordinate thorium phenyl-ate species.<sup>[1</sup>

Noting the structural similarities of complexes **1** and **2**, isolation of an analogous  $[U(Ar)_6]^2$  complex containing an electron-poor aryl ring system, *p*-chlorophenyl, was also targeted. Drop-wise addition of 6 equiv. of *p*-chlorophenyllithium (*p*-Cl-PhLi) to  $[UCl_4(1,4-dioxane)]_2$  in Et<sub>2</sub>O/THF at -80 °C resulted in an immediate color change from yellow/orange to very dark red, nearing black. Subsequent crystallization at -80 °C afforded dark red/black hexagonal blocks, suitable for single-crystal X-ray diffraction studies and identified as  $[Li(THF)_4]_2[U($ *p* $-Cl-Ph)_6]$  (**3**)

Table 1. Selected metrics of 1, 2, and 3.



**Figure 3.** (A) X-ray crystal structure of the uranium hexaaryl complex,  $[\text{Li}(\text{THF})_4]_2[U(\rho\text{-Cl-Ph})_6]$ , **3**, in the distorted octahedral geometry obtained at 193 K. Cations and hydrogen atoms omitted for clarity. Thermal ellipsoids are shown at 50% probability. (B) Crystal structure of the uranium hexaaryl complex,  $[\text{Li}(\text{THF})_4]_2[U(\rho\text{-Cl-Ph})_6]$ , **3**, in the nearly octahedral geometry obtained at 243 K. Cations and hydrogen atoms omitted for clarity. Thermal ellipsoids are shown at 50% probability.

(Figure 3) (<sup>1</sup>H NMR, see SI). Isolated yields of 70% have been achieved for crystalline material of **3**. Magnetic susceptibility studies using the Evans method resulted in an average magnetic moment of 2.5(2) B.M. for **3** at -20 °C.

Compared to complexes 1 and 2, complex 3 is significantly less distorted from octahedral symmetry as it lacks lithium counterion interaction with any of the aryl rings. Low temperature X-ray experiments resulted in a disorder over two positions of the one crystallographically unique aryl ring. Unfortunately, due to the limitation of the crystallographic -3 (S<sub>6</sub>) symmetry and having just one unique ligand, the exact distortion from octahedral of the sixcoordinate complex is difficult to define. Using the distorted thorium hexaphenyl complex reported by Hayton and coworkers<sup>[14]</sup>, the geometry was assigned as that observed in Figure 3A. The increased thermal stability of 3 (stable at 0 °C for several hours) enabled X-ray experiments at elevated temperatures (243 K) to be performed to evaluate the effects of temperature on the structural distortion of the complex. A decrease in distortion was observed at elevated experimental temperatures where the dianion is ordered with respect to the crystallographic -3 (S<sub>6</sub>) position and a nearly octahedral geometry is observed (Figure 3B). While it is of interest whether this same flexibility also exists in 1 and 2, the thermal instability of these complexes does not allow for elevated temperature experiments to be performed.

To gain further insight into potential electronic structure effects of the aryl ligand variations in these homoleptic  $[U(Ar)_{6}]^{2}$ complexes, magnetic circular dichroism (MCD) spectroscopic measurements were utilized. Note that the near-infrared (NIR) region contains the formally Laporte forbidden f→f transitions, but gains some dipole-allowed character due to low symmetry and metal-ligand covalency. These transitions are much more intense in C-term MCD due to the spin-orbit coupling (SOC) acting more efficiently in the uranium-centered states than in the ligand-based charge transfer states.<sup>[19]</sup> All three complexes have very similar UV-vis MCD spectra (Figure S2). The energy region of 5000-12000 cm<sup>-1</sup> (Figure 4) contains a series of  $f \rightarrow f$  transitions which, unlike those in the symmetric [UCI6] complex, are split due to the decent of symmetry in the distorted six-coordinate complexes. Complexes 1 and 2 have nearly identical 5 K, 7 T NIR MCD spectra with three groupings of transitions in the 5000-7000 cm<sup>-1</sup> (features I), 8000-9500 cm<sup>-1</sup> (features II), and 10,700 cm<sup>-1</sup> (features III) energy regions. While the spectrum of complex 3

Complex	C1-M-C7 (°)	C7-M-C13 (°)	C13-M-C1 (°)	C19-M-C25 (°)	C25-M-C31 (°)	C31-M-C19 (°)	Avg. M-C (Å)
U(Ph) <sub>6</sub> 2-	79.3 (2)	78.8 (2)	76.8 (2)	92.7 (2)	100.2 (2)	101.8 (2)	2.53 (11)
U(Tolyl) <sub>6</sub> 2-	78.9 (1)	77.8 (1)	75.9 (1)	98.1 (1)	102.3 (1)	96.2 (1)	2.52 (11)
U(4-CI-Ph) <sub>6</sub> <sup>2-</sup>	95.7 (2)	84.4 (2)	95.7 (2)	77.1 (2)	101.2 (2)	84.4 (2)	2.53 (11)

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Figure 4. 5 K, 7 T NIR MCD spectra of 1 (top, red), 2 (center, blue), and 3 (bottom, green).

exhibits slight variations in energy and overall number of f-f transitions (attributed to the reduced distortion from  $O_h$  symmetry in this complex), overall, these are minimal and support very similar overall electronic structures for all three complexes.

Utilizing the calculated NIR MCD spectra (Figure 5, Figure S3), the transitions in the experimental NIR MCD spectra can be assigned. The free ion U(IV) has a <sup>3</sup>H spin-free ground state and low lying <sup>3</sup>F and <sup>1</sup>G levels (Table S2). The added ligand field of the aryl ligands of complexes 1, 2, and 3 removes the degeneracy of the free-ion states, but all three complexes retain a spin-free ground state derived from the free ion <sup>3</sup>H term. Likewise, the SOC ground state is derived from the free-ion <sup>3</sup>H<sub>4</sub> ground state (i.e. is of dominant <sup>3</sup>H free-ion parentage), which is split on average by 2500 cm<sup>-1</sup> by the ligand field. The excited states that are responsible for the first group of MCD bands derive mainly from the free ion <sup>3</sup>H<sub>5</sub> term, the second group of MCD bands derive mainly from the free ion  ${}^{3}F_{3}$  and  ${}^{3}F_{4}/{}^{1}G_{4}$  terms, and the third group of MCD bands derive mainly from the free-ion <sup>3</sup>H<sub>6</sub> term. Due to the combined influence of ligand field and SOC, the ion levels with different S, L and J quantum numbers are mixed and therefore we only report the dominant ion spin-state contributions in Figures 5 and S3. The analysis of the calculated electronic states confirms that the similarity of the measured MCD spectra of the different complexes reflects the similarity of their ground and low-energy excited electronic states, and the similarity of the ligand field effects across the series.



Figure 5. PT2+SO calculated (blue) and experimental (black) MCD spectra of 1 in the NIR region. Spin-orbit states describing main MCD features are labeled according to the expansion in terms of spin-free states of the U<sup>4+</sup> free ion (see Table S2).

To further probe the metal-ligand bonding interactions in this series of uranium (IV) aryl complexes, additional computational studies were performed to analyze the metal-ligand orbital interactions. Structures for the three complexes were optimized (see SI) starting from the crystal structure coordinates for complexes 1 and 2, and from a symmetric structure complying with the  $S_6$  symmetry for complex 3. For comparison, the analogous thorium hexaphenyl complex, [Th(Ph)<sub>6</sub>]<sup>2-</sup>, was also optimized from the previously reported C3 structure (Figure S4, Table S3). The calculated average M-C bond lengths of complexes 1-3 agree with the measurements. Averaged Wiberg Bond Index (WBI) calculations predict similar bonding interactions for the uranium complexes, with slightly less covalency in 3, likely due to the electron withdrawing nature of the aryl rings. It is of interest to note that the WBI values for complexes 1-3 are larger than that of [Th(Ph)<sub>6</sub>]<sup>2-</sup>, suggesting an increase of metal-ligand covalency for U(IV). Indeed, [Th(Ph)<sub>6</sub>]<sup>2</sup> has less total metal orbital character (%M) (16%) in the metal-carbon bonding orbitals than 1-3 (20-23%) (Figure 6, Table S4). The contributing metal orbitals of [Th(Ph)6]<sup>2-</sup> are primarily 6d in nature (70% 6d, 20% 5f). For



**Figure 6.** M-C bonding NLMOs (M = Th or U) for  $Th(Ph)_6^{2*}$  and  $U(aryl)_6^{2*}$  complexes **1**, **2**, and **3** with their respective % metal character and 6d/5f orbital contributions to the metal character M-C bonding NLMOs. Hydrogen atoms removed for clarity.

complexes **1** and **2** the 5f character is increased (38%, 40%) compared to the Th complex, while for complex **3** the 5f (47%) and 6d (43%) contributions are evenly split. The increase of 5f bonding character in complex **3** can be attributed to a better directionality of the 5f metal orbitals toward the ligand orbitals, enhancing metal-ligand orbital overlap, facilitated by the molecular geometry approaching  $O_h$ .

The synthesis and structural characterization of homoleptic aryl uranium complexes has been a longstanding goal in f-element chemistry which, to date, has been limited to a single homoleptic uranium(III) complex with sterically encumbered aryl ligands. In this study we have reported the first isolated and structurally characterized organouranium complexes containing simple aryl ligands of the form  $[U(Ar)_6]^{2-}$  (Ar = Ph, *p*-tolyl, *p*-Cl-Ph), and gained

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insight into electronic structure and bonding through a combination of advanced MCD and theoretical studies. The theoretical MCD studies allowed for quantitative analysis of the similarities in the electronic structure and ligand field splitting across the series of homoleptic uranium (IV) species. This work serves as a critical advancement towards the synthesis and characterization of non-stabilized homoleptic organouranium aryl species. Moving forward, the effect of oxidation state on the electronic structure and bonding of these homoleptic uranium aryl species as well as insight into the decomposition pathways of these highly sensitive complexes will continue to provide unique insight into structure and bonding in organouranium chemistry.

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Keywords: uranium • organometallic • homoleptic • MCD

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Reported herein are the first structurally characterized and sterically unencumbered uranium (IV) homoleptic aryl-ate species. MCD spectroscopy and computational studies provide insight into electronic structure and bonding interactions across this series of complexes providing insight into organouranium complexes with exclusively U-C σ-bonds.



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