JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
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Identification of the +2 Oxidation State for Uranium in a Crystalline Molecular Complex, [K(2.2.2-Cryptand)][$(C_5H_4SiMe_3)_3U$]

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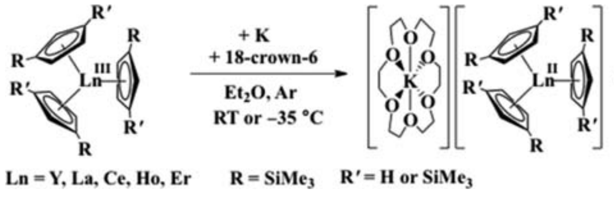
Supporting Information

ABSTRACT: Flash reduction of Cp'_3U ($Cp' = C_5H_4SiMe_3$) in a column of potassium graphite in the presence of 2.2.2-cryptand generates crystalline [K(2.2.2-cryptand)][Cp'_3U], the first isolable molecular U^{2+} complex. To ensure that this was not the U^{3+} hydride, [K(2.2.2-cryptand)][Cp'_3UH], which could be crystallographically similar, the hydride complex was synthesized by addition of KH to Cp'_3U and by reduction of H_2 by the U^{2+} complex and was confirmed to be a different compound. Density functional theory calculations indicate a $5f^36d^1$ quintet ground state for the $[Cp'_3U]^-$ anion and match the observed strong transitions in its optical spectrum.

Since uranium is a metal of critical global importance both as a source of nuclear energy and an environmental concern, it has been extensively studied to fully define its chemistry. One fundamental characteristic of any metal is the extent to which it loses electrons to form charged species in different oxidation states. Metals can be ionized in the gas phase to form short-lived species in a wide range of oxidation states, but the number of oxidation states available to any metal for productive chemistry in molecules in solution is smaller. This central aspect of metal chemistry has been constantly probed for over 100 years and the boundaries of accessible oxidation states are well established. The identification of new oxidation states is rare.

Nevertheless, new oxidation states recently have been discovered for the rare earth metals in soluble molecular species by examining reductions of Ln^{3+} ions (Ln = yttrium and the lanthanides) with potassium. The first molecular Ln^{2+} complexes for Ln = La,[1] Ce,[1] Y,[2] Ho,[3] and Er[3] were discovered by reduction of the tris(cyclopentadienyl) complexes, $[C_5H_3(SiMe_3)_2]_3Ln$ and $(C_5H_4SiMe_3)_3Ln$, eq 1. Since the rare earth metals have been less studied than other elements, it may be understandable that their full range of oxidation states is just being defined. However, another factor was the experimental difficulty in isolating the Y^{2+}, Ho^{2+}, and Er^{2+} complexes: the syntheses required short reaction times, temperatures below −35 °C, and argon as an inert atmosphere since the compounds react with dinitrogen. Further studies have shown that 2.2.2-cryptand is a superior encapsulating ligand to stabilize the K^+ countercation in these complexes and this has allowed the +2 oxidation state to be obtained for Pr^{2+}, Gd^{2+}, Tb^{2+}, and Lu^{2+} in the [K(2.2.2-cryptand)][$(C_5H_4SiMe_3)_3Ln$] complexes.[4] As a result, the +2 oxidation state is now known for all the rare earth metals except radioactive promethium.



(1)

It was of interest to determine if this approach to new M^{2+} ions for the rare earth metals would apply to uranium. Although similarities are often cited in the oxidation state chemistry of the rare earth metals and the later actinides from berkelium on,[5] there is no reason to expect that uranium, with its diverse oxidation state chemistry involving +3, +4, +5, and +6 ions, would necessarily mimic the rare earths in this regard. In fact, since the search for the existence of a U^{2+} ion in molecular species had been active for over 30 years, it might be expected that uranium would not behave analogously.

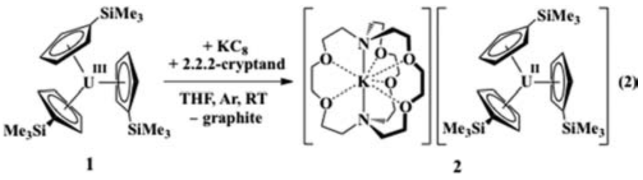
Attempts to synthesize molecules containing U^{2+} were published as early as 1980.[6] During this time period, species such as "$(C_5Me_5)_2U$" were discussed as possible transient intermediates in U^{3+} reduction reactions,[7] although it was concluded that "there is no evidence that any uranium(II) species is ever produced".[8] U^{2+} has also been discussed in complexes where the oxidation states of the ligands are ambiguous.[9] For example, the $[(anion)_2U]_2(C_6H_6)$ complexes could contain U^{4+} and $(C_6H_6)^{4-}$, U^{3+} and $(C_6H_6)^{2-}$, or U^{2+} and neutral benzene, C_6H_6.[9a−c] Since the C_6H_6 moiety in these complexes is not planar and is not displaced by strong neutral donor ligands, the U^{2+} hypothesis is unlikely. Solid state structures formally containing U^{2+}, e.g., the sulfide US,[10] have been known since the 1950s, but these have properties consistent with U^{3+} or U^{4+} with delocalized electrons in the solid state lattice.[11] U^{2+} has also been reported in the gas phase,[12] as a transient ion formed radiolytically,[13] and as OUCO in a neon matrix,[14] but molecular U^{2+} species isolable in solution have been unknown up to this point.

To examine the possibility that U^{2+} could be isolated like the Ln^{2+} ions,[2−4] Cp'_3U, **1**[15] ($Cp' = C_5H_4SiMe_3$), under argon was treated with potassium in THF/Et_2O in the presence of 2.2.2-cryptand. The reaction forms dichroic dark maroon/green

Received: July 11, 2013
Published: August 28, 2013

dx.doi.org/10.1021/ja406791t | *J. Am. Chem. Soc.* 2013, 135, 13310−13313

crystals identified by single crystal X-ray diffraction as the U^{2+} complex $[(2.2.2\text{-cryptand})K][Cp'_3U]$, **2**, eq 2, Figure 1a. To avoid the decomposition of **2** as it forms in solution, the reaction was carried out by quickly passing a concentrated solution of **1** and 2.2.2-cryptand in THF/Et_2O through a fritted glass tube packed with potassium graphite (KC_8). As the solution moves down this flash reduction column, **2** is formed, the graphite byproduct remains on the column, and a dark black/green filtrate emanates from the tube. If this filtrate is subsequently cooled to −35 °C, layered with Et_2O, and allowed to crystallize at −35 °C, crystalline **2** can be isolated in >60% yield.[16] Complex **2** is stable at room temperature in the solid state for several days, but has a half-life of only 1.5 h in THF. It can be converted back to **1** and $[K(2.2.2\text{-cryptand})][BPh_4]$ by oxidation with $AgBPh_4$.



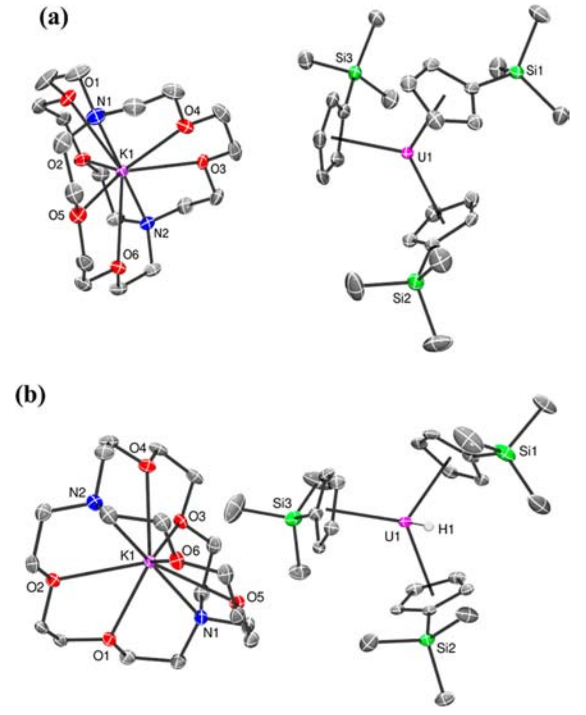
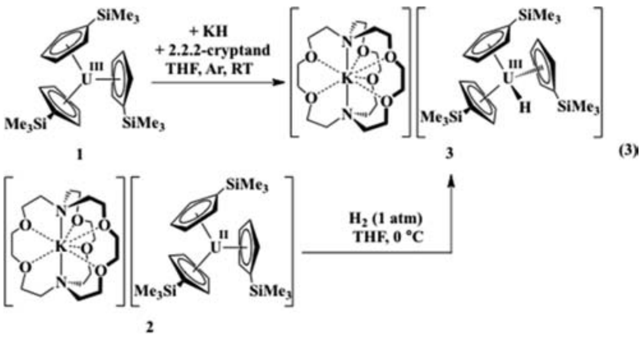


Figure 1. X-ray crystal structures of (a) $[K(2.2.2\text{-cryptand})][Cp'_3U]$, **2**, and (b) $[K(2.2.2\text{-cryptand})][Cp'_3UH]$, **4**. Thermal ellipsoids are drawn at the 50% probability level and all hydrogen atoms (except for the hydride ligand in **4**) have been omitted for clarity.

X-ray diffraction data showed that **2** is isomorphous with the Ln^{2+} rare earth complexes, $[K(2.2.2\text{-cryptand})][Cp'_3Ln]$ (Ln = Y, Pr, Gd, Tb, Ho, Er, Lu), **3**.[4] The $[K(2.2.2\text{-cryptand})]^+$ cation in **2** is well separated from the anion and has normal structural parameters.[4] The bond distances of the three Cp′ rings in **2** are equivalent within the error limits, e.g., the C−C average distances in the three rings are 2.414(13), 2.418(10), and 2.413(14) Å. The U−C(Cp′ ring) distances fall in a narrow range, 2.762(3)-2.822(3) Å with average U−C(Cp′ ring) distances of 2.801(16), 2.789(17), and 2.792(17) Å for the three rings.

The average U−(Cp′ ring centroid) distance in **2** (2.521 Å) is 0.013 Å longer than that in **1** (2.508 Å).[15b] This small difference is similar to the 0.02−0.03 Å difference between the $4f^n$ Ln^{3+} Cp'_3Ln complexes and the Ln^{2+} complexes **3** that appear to have $4f^n5d^1$ rather than $4f^{n+1}$ electron configurations.[4] The small difference in distances between **2** and **1** is consistent with 6d character in **2** as discussed below. It should be noted that if **2** contained U^{3+} and a $(Cp'_3)^{4-}$ ligand set, a *decrease* in metal−ligand bond distances would be expected due to stronger electrostatic interaction between the more highly charged components.

To rule out the possibility that **2** was a U^{3+} hydride complex, i.e., $[K(2.2.2\text{-cryptand})][Cp'_3UH]$, **4**, containing a crystallographically undetected hydride ligand, the direct synthesis of **4** was attempted. The $[Cp'_3UH]^-$ anion was previously observed spectroscopically,[17] but not as the potassium cryptand salt that would allow direct comparison. Addition of KH to **1** in the presence of 2.2.2-cryptand produces **4** as a dark red, room-temperature stable compound, eq 3. More remarkably, **4** can be made by direct reaction of **2** with H_2, eq 3, indicating that the U^{2+} ion can reduce hydrogen. The ^1H NMR spectrum of **4** contains a broad resonance at 560 ppm that is assignable to the hydride ligand since it is also present in the ^2H NMR spectrum of the deuterium analog, $[K(2.2.2\text{-cryptand})][Cp'_3UD]$. No hydride resonances are observed in this region in the ^1H NMR spectrum of **2**.



Complex **4** was also differentiated from **2** by X-ray crystallography, Figure 1b. The high quality data allowed for the location and refinement of a single hydride ligand bound to uranium with a U−H distance of 2.14(4) Å. The average (Cp′ ring centroid)−U−(Cp′ ring centroid) angle of 118.9° in **4** is smaller than the 120.0° average in **2** and the displacement of uranium out of the plane defined by the three Cp′ ring centroids is greater in **4** (0.269 Å) than that in **2** (0.032 Å). These are clearly two different complexes.[18]

Density functional theory (DFT)[19] was used to examine the energies of the possible electron configurations for the U^{2+} ion in **2**. Small core quasi-relativistic effective core potentials and basis sets were used for uranium.[20] The gas-phase U^{2+} ion is known to have a $5f^4$ configuration (see Supporting Information), but the DFT calculations indicate a $5f^36d^1$ quintet ground state for the $[Cp'_3U]^-$ anion. The highest occupied molecular orbital (HOMO) has mainly $6d^1$ character and resembles a d_{z^2} orbital, Figure 2. This is similar to the HOMOs of the $4f^n5d^1$ Ln^{2+} complexes **3**.[4] The stabilization of the $6d_{z^2}$ orbital with respect to the 5f orbitals has previously been noted in studies on trivalent tris(cyclopentadienyl) actinide complexes.[5d,21] Further computational validation of

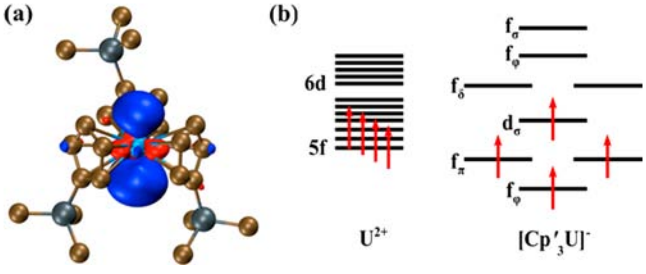


Figure 2. Density functional theory calculations. (a) Contour plot of the HOMO of the $[Cp'_3U]^-$ anion in **2**. Contour value is 0.05. (b) Qualitative 5f and 6d splitting of the different electronic configurations found in gas-phase and molecular U^{2+} ions.

the reported ground states is given in the Supporting Information.

Figure 3. shows a comparison of the electronic absorption spectra of **1**, **2**, and **4** in THF. Complexes **1** and **4** display the low extinction coefficients typical of f → f/π* transitions for the $5f^3$ U^{3+} ion. Here, f → f/π* denotes a mixture of f → f and f → π* transitions with considerable ligand character, see Supporting Information. Complex **2** on the other hand, absorbs much more strongly in the UV−vis due to transitions of predominantly 6d → 6d/π* character. This behavior is reminiscent of the Ln^{2+} complexes **3** which exhibit strong 5d → 5d/π* transitions in the UV−vis.[4] Time dependent DFT calculations of the UV−vis spectra of **1**, **2**, and **4** qualitatively match the experimental results. The calculations on **2** predict strong absorptions due to 6d → π*/5f and π → 6d/5f transitions that match the experimentally observed peaks. In contrast, the calculated excitations of **1** and **4** (see Supporting Information) lack strong absorptions in the 350−900 nm range. This is consistent with the $6d^1$ character of the ground state of **2** vs the $5f^3$ configurations of the U^{3+} complexes **1** and **4**.

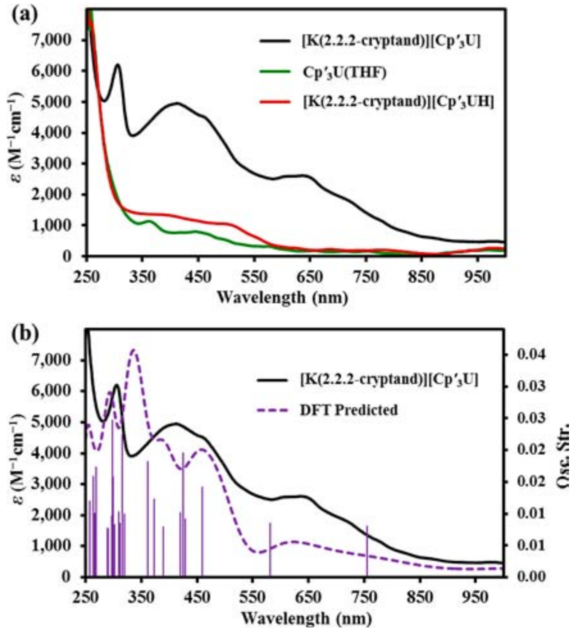


Figure 3. (a) Experimental UV−vis spectra of **1**, **2**, and **4** in THF at 298 K. (b) Experimental (solid) and calculated (dotted) UV−vis spectra of **2** in THF at 298 K, with pertinent theoretical excitations shown as vertical lines and extinction coefficients scaled down by a factor of 1.5.

In summary, soluble, crystalline molecular species containing uranium in the +2 oxidation state can be synthesized and isolated. This provides new options for exploration of the reactivity and physical properties of uranium compounds and demonstrates that the fundamental properties of this important metal are not yet fully defined.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental and computational details; crystallographic data collection, structure solution, and refinement; and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences of the Department of Energy (DE-SC0004739, W.J.E.) for support of the experimental studies and the U.S. National Science Foundation (CHE-1213382, F.F.) for support of the theoretical studies. We thank Prof. Andrew S. Borovik for spectroscopic assistance.

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(16) Synthesis of **2**: In an argon-filled glovebox, a 1 cm × 10 cm glass column equipped with a medium frit and a 14/20 vacuum filtration adapter was packed tightly with excess KC_8 (~700 mg). A dark red-brown solution of Cp'_3U, **1** (0.488 g, 0.751 mmol), and 2.2.2-cryptand (0.283 g, 0.751 mmol) in 6 mL of 1:1 THF/Et_2O was passed through the KC_8 column and immediately filtered into a precooled 30 mL collection flask held in a 100 mL beaker containing chilled hexane (−35 °C). The column was rinsed with 2 mL of 1:1 THF/Et_2O and the effluent combined with the initial filtrate. The dark black/green solution was placed at −35 °C for 1 h and 20 mL of Et_2O was layered on top. After 24 h, the mother liquor was decanted and the black crystalline solids were rinsed with 5 mL of Et_2O and dried under vacuum (5 min) to yield **2** (0.585 g, 68%). Larger crystals suitable for X-ray diffraction were obtained by dissolving **2** in minimal 1:1 THF/Et_2O and cooling to −35 °C.

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