Identification of Oxidation State +1 in a Molecular Uranium Complex

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ABSTRACT: The concept of oxidation state plays a fundamentally important role in defining the chemistry of the elements. In the f block of the periodic table, well-known oxidation states in compounds of the lanthanides include 0, +2, +3 and +4, and oxidation states for the actinides range from as high as +7 to +2. Oxidation state +1 is conspicuous by its absence from the f-block elements. Here we show that the uranium(II) metallocene \( [\eta^3-C_5\Pr_2]_2 \) and the uranium(III) metallocene \( [\eta^5-C_5\Pr_2]_2 \) can be reduced by potassium graphite in the presence of 2.2.2-cryptand to the uranium(I) metallocene \( [\eta^5-C_5\Pr_2]_2^- \) (1) \( (C_5\Pr_2 = \text{pentaisopropylcyclopentadienyl}) \) as the salt of \( [\text{K}(2.2.2-\text{crypt})]^- \). An X-ray crystallographic study revealed that 1 has a bent metalloocene structure, and theoretical studies and magnetic measurements confirmed that the electronic ground state of uranium(I) adopts a \( 5f^6(7s/6d)^2(6d_{22y}^2/6d_{xy})^1 \) configuration. The metal–ligand bonding in 1 consists of contributions from uranium 5f, 6d, and 7s orbitals, with the 6d orbitals engaging in weak but non-negligible covalent interactions. Identification of the oxidation state +1 for uranium expands the range of isolable oxidation states for the f-block elements and potentially signposts a synthetic route to this elusive species for other actinides and the lanthanides.

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consistent with the lower uranium oxidation state in the molecular orbitals (MOs) provided in Tables S2 and S3. The occupied 5f, 6d, and 7s orbitals form an energetically closely packed manifold. The three 5f orbitals occupied by three unpaired electrons all have more than 91% 5f character and show very little covalency. The 6d orbitals are weakly mixed with the nearly doubly degenerate highest-occupied MOs of the ligands. The 6d contribution in the main metal–ligand bonding orbitals varies from 0 to 14% depending on the orbital and is evidence of weak but non-negligible uranium–cyclopentadienyl covalency in I.

The molar magnetic susceptibility ($\chi_M$) of an unrestrained polycrystalline sample of [K(2.2.2-crypt)]I was measured from 2.5 to 200 K in a direct current (dc) field of 1 kOe (Figure 3, left). Above 90 K, $\chi_M T$ is strongly temperature-dependent, reaching a value 3.43 cm$^3$ K mol$^{-1}$ at 200 K, equivalent to an effective magnetic moment ($\mu_{\text{eff}}$) of 5.35$\mu_B$. This magnetic moment is much larger than any reported value for a molecular uranium complex even at 300 K, including those for [U($\eta^5$-C$_5$Pr$_5$)$_2$]$^{17}$ and [U($\eta^5$-C$_5$Pr$_5$)$_2$]$^{23}$. Between 90 and 10 K, $\chi_M T$ varies only slightly in the range of 0.98–1.17 cm$^3$ K mol$^{-1}$ or 2.80–2.90$\mu_B$ before decreasing sharply to 0.43 cm$^3$ K mol$^{-1}$ or 1.85$\mu_B$ at 2.5 K. The temperature-dependence of $\chi_M T$ is unusual and suggests gradual population of a thermally accessible excited electronic state at higher temperatures. At lower temperatures, the sharp drop in $\chi_M T$ is consistent with the onset of single-molecule magnet (SMM) behavior. Interpretation of the susceptibility is difficult because of the large number of low-lying states in the uranium(I) ion involving strong interactions of the 7s and 6d orbitals with the ligands. This leads to a densely packed manifold of thermally accessible states with largely varying magnetic properties. The low-temperature susceptibility can be interpreted in terms of a coupling model where the intershell exchange coupling is stronger than the intrashell LS coupling (where L and S are the orbital and spin angular momenta, respectively; Table S4). The increase in the susceptibility at higher temperatures most likely results from population of thermally accessible states where the spin and orbital momenta are not coupled fully antiparallel, leading to a larger total momentum.

Alternating current (ac) magnetic susceptibility measurements on unrestrained [K(2.2.2-crypt)]I in zero dc field revealed slow relaxation of the magnetization and SMM properties. The imaginary component of the ac susceptibility ($\chi''$) shows frequency ($\omega$)-dependent maxima at $T = 2.3–8$ K (Figure 3 center and Figures S12 and S13). The relaxation times ($\tau$) were extracted from these data, and the temperature dependence of $\tau$ was fitted using $\tau^{-1} = t_0^{-1} \exp(-E_u/k_BT)$ (i.e., only an Orbach term), which yielded an effective energy

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**Scheme 1. Synthesis of [K(2.2.2-crypt)]I and Its Oxidation with Copper Iodide or Azobenzene**

**Figure 1.** Molecular structure of [K(2.2.2-crypt)]I. For clarity, the carbon atoms in black are not numbered, and the hydrogen atoms are not shown.

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Orbitals with strong atomic-like 5f character. One electron occupies a quasi-σ-symmetric orbital that is an admixture of the 7s and 6d$_{xy}$ atomic orbitals. Based on decomposition of the orbital into a basis of uranium(I) orbitals, the orbital has 63% 7s character and 28% 6d character. The orbital has a toroidal shape that is typical for lanthanide(II) and uranium(II) metallocones.

The one remaining electron occupies a quasi-δ-symmetric 6d$_{z^2-\text{r}^2}$ and 6d$_{xy}$ set of orbitals with significant delocalization into the ligands. Several calculations were carried out to see whether a low-lying lower-spin electronic configuration existed, but all lower-spin states discovered lie at higher energy than the highest-spin state.

The bonding in 1 is shown in Figure 2, with quantitative contributions of the uranium and cyclopentadienyl orbitals to the molecular orbitals (MOs) provided in Tables S2 and S3. The occupied 5f, 6d, and 7s orbitals form an energetically closely packed manifold. The three 5f orbitals occupied by three unpaired electrons all have more than 91% 5f character and show very little covalency. The 6d orbitals are weakly mixed with the nearly doubly degenerate highest-occupied MOs of the ligands. The 6d contribution in the main metal–ligand bonding orbitals varies from 0 to 14% depending on the orbital and is evidence of weak but non-negligible uranium–cyclopentadienyl covalency in 1.

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barrier ($U_{el}$) of 14(1) cm$^{-1}$ and a pre-exponential term ($\tau_0$) of $1.1(3) \times 10^{-7}$ s (Figure S14).

The field dependence of the magnetization was measured for [K(2.2.2-crypt)][1] at 2 K on both the unrestrained material and the material restrained in glass wool. In fields below approximately 20 kOe, the two data sets are similar, with magnetic torque effects becoming evident only at higher fields. For the unrestrained sample, magnetic memory effects and

Figure 2. Qualitative molecular orbital diagram for 1. The numbers given are percentage contributions of the nonorthogonal fragment orbitals to the molecular orbitals. Only contributions larger than 5% are shown.

Figure 3. (left) Temperature dependences of $\chi M_T$ and $\mu_{eff}$ at $T = 2.5-200$ K in a field of 1 kOe. (center) Frequency dependence of $\chi''$ at the temperatures indicated in zero dc field. (right) Hysteresis at 2 K for the unrestrained (red) and restrained (blue) materials using an average sweep rate of 20 Oe s$^{-1}$. 
very narrow hysteresis loops were observed (Figure 3, right). This behavior is reminiscent of the neptunium(IV) compound neptunocene or [Np(η⁶-COT)]₂⁺ (COT = cyclooctatetraen-yl).²⁸

The 5f²(7s/6d)¹⁴(6d₂⁻,₃⁻/6d₃⁻) configuration of uranium(I) in [K(2,2,2-crypt)][¹] produced a rhombic powder X-band EPR spectrum at 10 K with g factors of 4.7, 1.6, and 1.2 (Figure S15). In contrast, the non-Kramers uranium(II) center in [U(η⁶-C₅H₅Pr₂)]²⁻ is EPR-silent (Figure S16). The UV/vis/NIR spectrum of [K(2,2,2-crypt)][¹] in benzene is essentially featureless except for intense charge transfer absorptions in the UV region and weak absorptions from 800 to 1450 nm (Figures S17 and S18).

Since complexes of uranium in low oxidation states can be multielectron donors toward small molecules,²⁹ we were interested to see how [K(2,2,2-crypt)][¹] would behave toward azobenzene, N₂Ph₂. Adding 1 equiv of azobenzene to [K(2,2,2-crypt)][¹] in benzene caused a color change from brown to green and precipitation of a dark-brown solid (Scheme 1). ²H NMR spectroscopy revealed the formation of [U(η⁶-C₅H₅Pr₂)]²⁻ (Figures S19 and S20), suggesting that a one-electron transfer process had occurred. The precipitate was identified by X-ray crystallography and IR and EPR spectroscopies to be the azobenzene radical anion [N₂Ph₂]⁻ as the salt of [K(2,2,2-crypt)]⁺ (Table S1 and Figures S21–S24). This one-electron reduction process contrasts to that shown by the uranium(II) complex [U(N(SiMe₅)₂)]₃⁺ toward azobenzene, which initiates a four-electron reduction and cleavage of the nitrogen–nitrogen double bond in the substrate.³⁰ This reactivity, combined with the disproportionation of [K(2,2,2-crypt)][¹] into its uranium(II) precursor and uranium metal, points to unexpected stability of [U(η⁶-C₅H₅Pr₂)]²⁻, most likely due to the stabilizing effect of the bulky ligands.

In conclusion, we have shown that a metallocene of uranium in the oxidation state +1 can be synthesized by reduction of uranium(II) and uranium(III) precursors. Reactivity studies, magnetic and spectroscopic measurements, and a DFT study are consistent with the presence of uranium(I) with a 5f²(7s/6d)¹⁴(6d₂⁻,₃⁻/6d₃⁻) ground-state electron configuration. The broader significance of [K(2,2,2-crypt)][¹] is that soluble molecular compounds of other actinides and some lanthanides in the oxidation state +1 should also be viable targets. The synthesis of a much larger family of compounds containing lanthanide(I) and actinide(I) centers introduces new possibilities for designing molecular magnets and luminescent materials and for developing new f-element reactivity.

ASSOCIATED CONTENT

Data Availability Statement
Additional research data supporting this publication are available at 10.25377/sussex.21184705.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c06519.

Synthesis, spectroscopic characterization, crystallographic details, magnetic property measurements, and computational details (PDF)

Accession Codes

CCDC 2169273 and 2170255 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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