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Identification of Oxidation State +1 in a Molecular Uranium Complex

Luciano Barluzzi, Sean R. Giblin, Akseli Mansikkamäki,* and Richard A. Layfield*

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 state +1 has been isolated. Lanthanum monoiodide (LaI) is the only known molecular compound of an f-block element in the oxidation state +1. Recently, a cyclic voltammetry study of this uranium(I) compound revealed two electrochemical events, assigned to the uranium(II)/uranium(III) and uranium(III)/uranium(IV) couples. Unexpectedly, further reduction to an unstable species uranium(II)/uranium(III) and uranium(III)/uranium(IV) and 7s orbitals, with the 6d orbitals engaging in weak but non-negligible covalent interactions. Identification of the oxidation state +1 has been isolated. Lanthanum monoiodide (LaI) is the only known molecular compound of an f-block element in the oxidation state +1. Recently, a cyclic voltammetry study of this uranium(I) compound revealed two electrochemical events, assigned to the uranium(II)/uranium(III) and uranium(III)/uranium(IV) couples. Unexpectedly, further reduction to an unstable species.

The oxidation state of an element strongly influences the stability, reactivity, and physical properties of the compounds it forms. There is considerable motivation for isolating elements in new oxidation states since this can lead to new chemistry while also providing a deeper fundamental understanding of bonding and electronic structure. In the lanthanide series, the oxidation state +3 is thermodynamically the most stable species by far. Recent reports of molecular compounds containing praseodymium and terbium in the oxidation state +4 are therefore notable advances. Similarly, the synthesis and isolation of compounds containing the full series of lanthanides (except promethium) in the oxidation state +4 are therefore notable advances. The lanthanide series, the oxidation state +3 is thermodynamically the most stable species by far. Recent reports of molecular compounds containing praseodymium and terbium in the oxidation state +4 are therefore notable advances. Similarly, the synthesis and isolation of compounds containing the full series of lanthanides (except promethium) in the oxidation state +4 are therefore notable advances.

The molecular structure of [K(2.2.2-crypt)][U(η⁵-C⁵Pr₃)s] under the same conditions. Isolated yields of crystalline material were 55–60%. Reduction of [U(η⁵-C⁵Pr₃)s] and [U(η⁵-C⁵Pr₃)s] does not occur in the absence of cryptand. The molecular structure of [K(2.2.2-crypt)][I] features two disordered units of I. The major component of I adopts a bent metallocene geometry with a Cp°–U–Cp° angle of 163.4(3)° and U–Cp° distances of 2.564(8) and 2.585(7) Å (Cp° denotes the center of the pentafluoro cyclopentadienyl ligands) (Figures 1 and S1 and Table S1). Compared to the linear uranium(II) metallocene [U(η⁵-C⁵Pr₃)s], appreciably different from the linear uranium(II) metallocene [U(η⁵-C⁵Pr₃)s].

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able distortion of the structure occurs upon one-electron reduction to 1. The U–C\(_{\text{ptz}}\) distances in 1 are also significantly longer than the analogous distances of 2.504(1) Å in [U(\(\eta^5\)-C\(_2\)H\(_5\))\(_2\)] and 2.496(3) Å in the uranium(III) complex [U(\(\eta^5\)-C\(_2\)H\(_5\))\(_2\)]\(_2\), consistent with the lower uranium oxidation state in 1.

Compound [K(2,2,2-crypt)]\(_2\) can be stored as a solid at –40 °C seemingly indefinitely without decomposition. In contrast, gradual decomposition to a light-brown solid occurs within a few hours at room temperature. Brown solutions of [K(2,2,2-crypt)]\(_2\) in benzene-\(d_6\) decompose over 5 days to give a green solution that 1H NMR spectroscopy revealed to consist of [K(\(\eta^5\)-C\(_2\)H\(_5\))\(_2\)]\(_2\), [K(2,2,2-crypt)]\(_2\)\([\text{C}_{2}\text{Ph}]\), and a gray precipitate, presumed to be metallic uranium. These observations suggest that the uranium(I) metalloocene disproportionate in solution (Figures S3–S5). In THF, [K(2,2,2-crypt)]\(_2\) decomposes immediately to give an intractable mixture (Figures S6 and S7). To discount the possibility of hydride ligands bound to uranium, carbon tetrachloride was added to [K(2,2,2-crypt)]\(_2\). The formation of chloroform or dichloromethane was not observed by \(^1\)H and \(^13\)C NMR spectroscopy (Figures S8 and S9). Chemical reversibility of the reactions that form [K(2,2,2-crypt)]\(_2\) was confirmed by the addition of 1 or 2 equiv of the mild oxidant copper(I) iodide, which led to the formation of [U(\(\eta^5\)-C\(_2\)H\(_5\))\(_2\)]\(_2\) and [U(\(\eta^5\)-C\(_2\)H\(_5\))\(_2\)]\(_2\) respectively (Scheme 1 and Figures S10 and S11).

To obtain further insight into the electron configuration and bonding in 1, density functional theory (DFT) calculations were carried out. The electron configuration was determined to be \(5\delta^0(7s/6d_z^2)^1(6d_{x^2−y^2}/6d_{xy})^3\). Three electrons occupy orbitals with strong atomic-like 5f character. One electron occupies a quasi-\(\sigma\)-symmetric orbital that is an admixture of the 7s and 6d\(_{x^2−y^2}\) 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) metalloenes.\(^{17,24}\) The one remaining electron occupies a quasi-\(\delta\)-symmetric 6d\(_{x^2−y^2}\) 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.

The molar magnetic susceptibility (\(\chi_M\)) of an unrestrained polycrystalline sample of [K(2,2,2-crypt)]\(_2\) 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,\(^{26}\) including those for [U(\(\eta^5\)-C\(_2\)H\(_5\))\(_2\)]\(_2\)\(_2\) and [U(\(\eta^5\)-C\(_2\)H\(_5\))\(_2\)]\(_2\).\(^{23}\) 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.\(^{25}\) 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 \(L S\) 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)]\(_2\) in zero dc field revealed slow relaxation of the magnetization and SMM properties. The imaginary component of the ac susceptibility (\(\chi''\)) showed frequency (\(f\))-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 the equation \(\tau^{-1} = \tau_0^{-1} \exp(−U_{\text{eff}}/k_BT)\) (i.e., only an Orbach term), which yielded an effective energy
barrier ($U_{\text{eff}}$) of 14(1) cm$^{-1}$ and a pre-exponential term ($\tau_0$) of 1.1(3) × 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](image1.png)

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](image2.png)

Figure 3. (left) Temperature dependences of $\chi_M T$ and $\mu_{\text{eff}}$ 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 \([\text{Np}(\eta^5\text{-COT})_2]\)  \((\text{COT} = \text{cyclooctatetraenyl})\).\(^{28}\)

The \(5f^6(7s/6d, 2)^{(6d^{2}_{xy} / 6d_{xy})}^{1}\) configuration of uranium- \((\text{I})\) in \([\text{K}(2.2.2\text{-crypt})][\text{I}]\) 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 \([\text{U}(\eta^2\text{-C}\text{Pr}_2)\text{]}\) is EPR-silent (Figure S16). The UV/vis/NIR spectrum of \([\text{K}(2.2.2\text{-crypt})][\text{I}]\) 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 synthesized by reduction of uranium(II) and uranium(III) precursors. Reactivity studies, combined with the disproportionation of \([\text{K}(2.2.2\text{-crypt})]\) toward azobenzene, 

- \(\text{N}^+\text{Ph}−\text{S}^-\text{Ph}^+\) as the salt of \([\text{K}(2.2.2\text{-crypt})]\) (Table S1 and Figures S21–S24). This one-electron reduction process contrasts to that shown by the uranium(II) complex \([\text{U}(\text{SiMe}_3)_2\text{]}\) 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 \([\text{K}(2.2.2\text{-crypt})]\) into its uranium(II) precursor and uranium metal, points to unexpected stability of \([\text{U}(\eta^2\text{-C}\text{Pr}_2)\text{]}\), 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(II) with a \(5f^6(7s/6d, 2)^{(6d^{2}_{xy} / 6d_{xy})}^{1}\) ground-state electron configuration. The broader significance of \([\text{K}(2.2.2\text{-crypt})][\text{I}]\) is that soluble molecular compounds of other actinides and some lanthanides are consistent with the presence of uranium(I) with a 5f magnetic and spectroscopic measurements, and a DFT study.

### 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.

### AUTHOR INFORMATION

**Corresponding Authors**

Akseli Mansikkamäki — NMR Research Group, University of Oulu, FI-90014 Oulu, Finland; Email: akseli.mansikkamaki@oulu.fi

Richard A. Layfield — Department of Chemistry, School of Life Sciences, University of Sussex, Brighton BN1 9QJ, U.K.; orcid.org/0000-0002-6020-0309; Email: r.layfield@sussex.ac.uk

**Authors**

Luciano Barluuzzi — Department of Chemistry, School of Life Sciences, University of Sussex, Brighton BN1 9QJ, U.K.; orcid.org/0000-0001-6682-342X

Sean R. Giblin — School of Physics and Astronomy, Cardiff University, Cardiff CF24 3AA, U.K.

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/jacs.2c06519

**Notes**

The authors declare no competing financial interest.

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