Divalent Lanthanides and Uranium

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All the Lanthanides Do It and Even Uranium Does Oxidation State +2

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The rare-earth elements include the elements scandium, yttrium, and the lanthanides (lanthanum through lutetium). In compounds, they are all trivalent subject to their valence electron configurations $(n)d^1(n+1)s^2$; the $4f^n$ $(n=1–14)$ electrons of the lanthanoids (cerium through lutetium) act as core-like electrons. About a century ago it was first recognized that some of them can also be divalent (samarium, europium, and ytterbium).[1] The elements neodymium, dysprosium, and thulium were added to this list in the last half of the twentieth century.[2] All of these oxidation states were first discovered as dihalides MX_2 in the solid state. It took a while for solution (coordination and organometallic) chemists to produce stable compounds with these elements.[3] The rare-earth elements in all of these compounds have an electronic configuration of $[Xe]4f^{n+1}5d^06s^0$, and thus allow the ionic formulation M^{2+}.

A configuration crossover to $[Xe]4f^n\mathbf{5d^1}6s^0$ occurs for lanthanum, cerium, praseodymium, and gadolinium in the solid diiodides MI_2.[4] These iodides then are two-dimensional metals, the 5d electrons delocalize into a conduction band. Trapping the d^1 electron in a localized state appears to be possible only at low temperatures, as in $Sc_{0.89}I_2$ and maybe for PrI_2-IV.[5] It was thus a great surprise when it was reported in 2008 that the $5d^1$ configuration could be preserved in an organometallic coordination compound. Three of the "super-bulky" ligands $(Cp'')^- = (1,3\text{-}(SiMe_3)_2C_5H_3)^-$ encapsulate completely a La^{2+} or Ce^{2+} ion in the anion $[M(Cp'')_3]^-$ with a K^+ ion trapped in [2.2.2]crypt.[6]

This concept, namely to trap the $5d^1$ electron in a spacious anion and get it as far away as possible from an active cation in an equally spacious complex cation utilizing excellently coordinating cryptands or crowns, has been applied to complete the series of divalent lanthanides as well as yttrium in coordination chemistry[7] (Figure 1). For the synthesis, the bulky neutral complexes $[M(Cp')_3]$ $(R=Y, Ho, Er; Cp'=(C_5H_4SiMe_3))$ were reduced with potassium in the presence of 18-crown-6.[7a,b] As an alternative to 18-crown-6, the cryptand crypt[2.2.2] was used to trap the K^+ ions even more efficiently. The salts $[K(crypt[2.2.2])]^+[M(Cp')_3]^-$ have higher stability against decomposition with temperature. Reactions were possible at room temperature in THF, provided that the reaction time was short. Thereby the remainder M^{2+} with M = Pr, Gd, Tb, Lu were added and the list of divalent lanthanides in molecular anionic complexes completed.[7c]

Sc						
Y						
La	Ce	Pr	Nd	Pm	Sm	Eu
Gd	Tb	Dy	Ho	Er	Tm	Yb
Lu						
Ac	Th	Pa	U	Np	Pu	Am

Figure 1. The divalent lanthanides M^{2+} (M = La–Lu) as well as yttrium and uranium as they appear in molecular complexes with M^{2+} in the electronic configurations $[Xe]4f^{n+1}5d^06s^0$ (blue) and $[Xe]4f^n5d^16s^0$ ($[Rn]5f^36d^17s^0$ for U^{2+}) (red).

The next target in this race for new and low oxidation states was that for an actinide, and especially uranium. Although many attempts had been undertaken to isolate compounds with divalent uranium with the electronic configuration $[Rn]5f^46d^07s^0$ or $[Rn]5f^36d^17s^0$, the only one that comes close in the solid state is $Na_{0.5}UCl_3$, a chloride with metallic luster and Na^+ cations in the channels along [001] in the hexagonal UCl_3-type structure.[8] By flash reduction of $[U(Cp')_3]$ in a column filled with KC_8 in the presence of crypt[2.2.2], $[K(crypt[2.2.2])][U(Cp')_3]$ has now been isolated as black/green crystals at −35 °C.[9]

In the crystal structures of the isomorphous compounds $[K(crypt[2.2.2])][M(Cp')_3]$ with M = Y, Pr, Gd, Tb, Ho, Er, Lu, U as well as in the similar $[K(crypt[2.2.2])][M(Cp'')_3]$ with M = La, Ce, cations and anions are well separated with K^+ and M^{2+} both in the center of the bulky ligands. The mean distances M–Cp′(centroid) for the series M = Pr, Gd, Tb, Y, Ho, Er, Lu, ranging from 2.54 to 2.39 Å, nicely reflect the lanthanide contraction with Y^{2+} between Tb^{2+} and Ho^{2+}. The averaged U–Cp′(centroid) distance is 2.52 Å, which is close to that for Pr–Cp′(centroid) (Figure 2).

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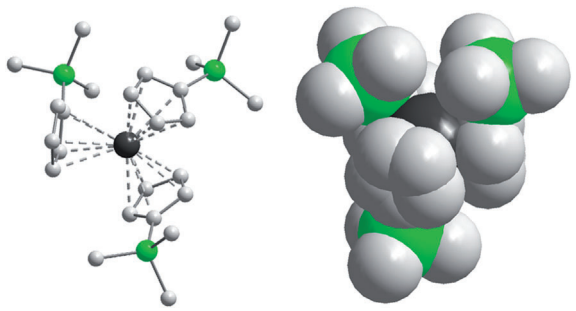

Figure 2. Ball-and-stick and space-filling representations of the anions as they appear in the crystal structures of [K(crypt[2.2.2])][M(Cp′)$_3$] with M = Y, Pr, Gd, Tb, Ho, Er, Lu, U. C gray, Si green, M black.

[K(crypt[2.2.2])][U(Cp′)$_3$], in THF at 0 °C, reduces dihydrogen to hydride, which is incorporated in the dark red U^{III} compound [K(crypt[2.2.2])][UH(Cp′)$_3$], ruling out that [K(crypt[2.2.2])][U(Cp′)$_3$] was actually a U^{III} compound with undetected hydride bound to the central uranium atom.

DFT calculations on a number of these compounds clearly show that the SOMO is always a d orbital, 5d^1 in the case of the divalent lanthanides and 6d^1 in case of U^{2+}. Thus, in contrast to the 5f^4 configuration of U^{2+} in the gas phase, in the complex anion [U(Cp′)$_3$]$^-$, U^{2+} has the electronic configuration 5f^{3}6d^1. A representation of the 6d^1 SOMO is shown in Figure 3.

The d^1 ground states of M^{2+} in the salts [K(crypt[2.2.2])][M(Cp′)$_3$] are consistent with their colors (UV/Vis absorption spectra) as well as EPR spectra and magnetic susceptibility. Aside from their physical properties, it is expected that they will exhibit a rich one-electron reductive chemistry. Small homo- and heteroatomic gas molecules such as H_2, N_2, CO, CO_2 are obvious targets, especially in view of work that has already been done in the group of Evans. For example, reduction of Y(N(SiMe$_3$)$_2$)$_3$ with potassium in the presence of 18-crown-6 and carbon monoxide produces the radical anion (CO)$^-$, which is then incorporated in the colorless coordination polymer salt [K$_2$(18-crown-6)$_2$][Y(N(SiMe$_3$)$_2$)$_3$(μ-CO)$_2$].[10] Byproducts exhibiting ynediolate formation or CO insertion show that there is indeed rich and novel chemistry out there to explore.

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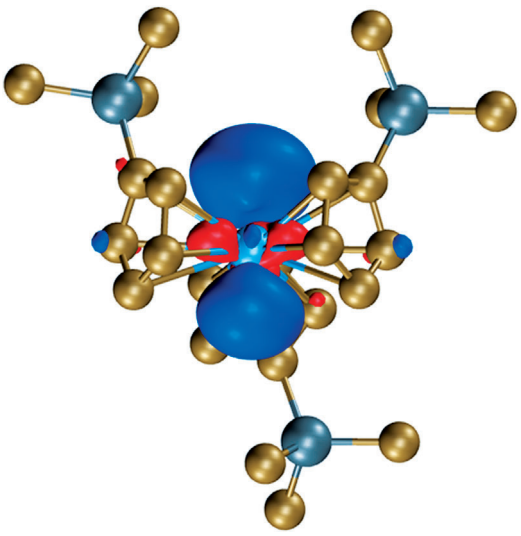

Figure 3. Molecular orbital plot of the anion [U(Cp′)$_3$]$^-$ showing that the 6d^1 SOMO has z^2 character. Reprinted with permission from Ref. [9]; Copyright 2013 American Chemical Society. C gold, Si silver/blue.

[1] a) C. Matignon, E. C. Cazes, *Ann. Chim. Phys.* **1906**, *8*, 417; b) G. Jantsch, N. Skalla, *Z. Anorg. Allg. Chem.* **1929**, *185*, 49; c) W. Klemm, H. Bommer, *Z. Anorg. Allg. Chem.* **1937**, *231*, 138.

[2] a) J. D. Corbett, *Rev. Chim. Miner.* **1972**, *10*, 289; b) G. Meyer, *Chem. Rev.* **1988**, *88*, 93; c) G. Meyer, *Z. Anorg. Allg. Chem.* **2007**, *633*, 2537.

[3] a) M. N. Bochkarev, I. L. Fedushkin, A. A. Fagin, T. V. Petrovskaya, J. W. Ziller, R. N. R. Broomhall-Dillard, W. J. Evans, *Angew. Chem.* **1997**, *109*, 123; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 133; b) W. J. Evans, *Coord. Chem. Rev.* **2000**, *206*, 263; c) W. J. Evans, N. T. Allen, J. W. Ziller, *J. Am. Chem. Soc.* **2000**, *122*, 1749; d) M. N. Bochkarev, I. L. Fedushkin, S. Dechert, A. A. Fagin, H. Schumann, *Angew. Chem.* **2001**, *113*, 3268; *Angew. Chem. Int. Ed.* **2001**, *40*, 3176; e) M. N. Bokharev, *Coord. Chem. Rev.* **2004**, *248*, 835; f) W. J. Evans, *Inorg. Chem.* **2007**, *46*, 3245; g) F. Jaroschik, F. Nief, L. Richard, X.-F. Le Goff, *Organometallics* **2007**, *26*, 1123; h) F. Jaroschik, A. Momin, F. Nief, X.-F. Le Goff, G. B. Deacon, *Angew. Chem.* **2009**, *121*, 1137; *Angew. Chem. Int. Ed.* **2009**, *48*, 1117; i) F. Nief, *Dalton Trans.* **2010**, *39*, 6589.

[4] a) J. D. Corbett, L. F. Druding, W. J. Burkhard, C. B. Lindahl, *Discuss. Faraday Soc.* **1961**, *32*, 79; b) L. F. Druding, J. D. Corbett, *J. Am. Chem. Soc.* **1961**, *83*, 2462; c) C. Felser, K. Ahn, R. K. Kremer, R. Seshadri, A. Simon, *J. Solid State Chem.* **1999**, *147*, 19.

[5] a) G. Meyer, L. Jongen, A.-V. Mudring, A. Möller in *Inorganic Chemistry In Focus*, *Vol. 2* (Eds.: G. Meyer, D. Naumann, L. Wesemann), Wiley-VCH, Weinheim, **2005**, pp. 105–120; b) G. Meyer in *Inorganic Chemistry In Focus*, *Vol. 3* (Eds.: G. Meyer, D. Naumann, L. Wesemann), Wiley-VCH, Weinheim, **2006**, pp. 45–60.

[6] a) P. Hitchcock, M. F. Lappert, L. Maron, A. V. Protchenko, *Angew. Chem.* **2008**, *120*, 1510; *Angew. Chem. Int. Ed.* **2008**, *47*, 1488; b) G. Meyer, *Angew. Chem.* **2008**, *120*, 5040; *Angew. Chem. Int. Ed.* **2008**, *47*, 4962.

[7] a) R = Y; M. R. MacDonald, J. W. Ziller, W. J. Evans, *J. Am. Chem. Soc.* **2011**, *133*, 15914; b) R = Ho, Er: M. R. MacDonald, J. E. Bates, M. E. Fieser, J. W. Ziller, F. Furche, W. J. Evans, *J. Am. Chem. Soc.* **2012**, *134*, 8420; c) R = Pr, Gd, Tb, Lu: M. R. MacDonald, J. E. Bates, J. W. Ziller, F. Furche, W. J. Evans, *J. Am. Chem. Soc.* **2013**, *135*, 9857.

[8] T. Schleid, G. Meyer, *Naturwissenschaften* **1989**, *76*, 118.

[9] M. R. MacDonald, M. E. Fieser, J. E. Bates, J. W. Ziller, F. Furche, W. J. Evans, *J. Am. Chem. Soc.* **2013**, *135*, 13310.

[10] M. Fang, J. H. Farnaby, J. W. Ziller, J. E. Bates, F. Furche, W. J. Evans, *J. Am. Chem. Soc.* **2012**, *134*, 6064.