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Synthesis, structure, and reactivity of crystalline molecular complexes of the $\{[C_5H_3(SiMe_3)_2]_3Th\}^{1-}$ anion containing thorium in the formal +2 oxidation state†

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Reduction of the Th³⁺ complex Cp_3^r Th, **1** $[Cp'' = C_5H_3(SiMe_3)_2]$, with potassium graphite in THF in the presence of 2.2.2-cryptand generates $[K(2.2.2\text{-cryptand})][Cp_3^r$ Th], **2**, a complex containing thorium in the formal +2 oxidation state. Reaction of **1** with KC_8 in the presence of 18-crown-6 generates the analogous Th^{2+} compound, $[K(18\text{-crown-6})(THF)_2][Cp_3^r$ Th], **3**. Complexes **2** and **3** form dark green solutions in THF with $\varepsilon = 23\,000\,M^{-1}\,cm^{-1}$, but crystallize as dichroic dark blue/red crystals. X-ray crystallography revealed that the anions in **2** and **3** have trigonal planar coordination geometries, with 2.521 and 2.525 Å Th-(Cp'' ring centroid) distances, respectively, equivalent to the 2.520 Å distance measured in **1**. Density functional theory analysis of $(Cp_3^rTh)^{1-}$ is consistent with a $6d^2$ ground state, the first example of this transition metal electron configuration. Complex **3** reacts as a two-electron reductant with cyclooctatetraene to make $Cp_2^rTh(C_8H_B)$, **4**, and [K(18-crown-6)]Cp''.

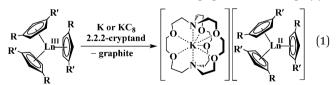
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One of the fundamental characteristics of any metal is the extent to which it loses electrons to form charged species in different formal oxidation states. This ionization can occur in the gas phase to form short-lived species in a wide range of oxidation states, but the number of oxidation states available in solution in molecular metal complexes for productive chemistry is smaller. Chemists have tested the limits of oxidation states of all the elements for over 100 years and the boundaries of oxidation states accessible in solution are well established.

Nevertheless, it was recently discovered that the +2 oxidation state is accessible in soluble molecular complexes for all the elements in the lanthanide series except promethium, eqn (1).



Ln = La, Ce (R = R'= SiMe₃) Ln = Pr, Gd, Tb, Y, Ho, Er, Lu (R = H, R'= SiMe₃)

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Previously, it was thought that only the traditional six Ln²⁺ ions of Eu, Yb, Sm, Tm, Dy, and Nd were obtainable in solution on the basis of calculated reduction potentials² and solid state chemistry.³

Extension of this reductive chemistry to uranium was not initially tried since it is well known that the redox chemistry of uranium, which includes multiple oxidation states, +3, +4, +5, and +6, is quite different from that of the rare earths. Although it was likely that uranium would be different, an analogous synthesis was eventually attempted and the first fully characterizable U^{2+} complex, $[K(2.2.2\text{-cryptand})][Cp'_3U]$ $(Cp' = C_5H_4SiMe_3)$, was isolated according to eqn (2).

$$Me_{3}Si \longrightarrow U_{0}^{SiMe_{3}} \times C_{8} \times C_{8} \times C_{8} \times C_{9} \times C_{9}$$

Synthesis of a Th^{2+} complex via eqn (1) or (2) seemed even more unlikely for several reasons. Complexes of Th^{3+} are already difficult to obtain. The $\mathrm{Th}^{4+}/\mathrm{Th}^{3+}$ redox potential is estimated to be -3.0 and -3.8 V vs. NHE 5 and a $\mathrm{Th}^{3+}/\mathrm{Th}^{2+}$ redox potential of -4.9 V vs. NHE is in the literature. Reduction to metallic thorium would be predicted to be favored before formation of a Th^{2+} species. Many studies have been reported to find oxidation states lower than +4 for thorium, but only five Th^{3+} complexes have ever been structurally characterized.

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analog of eqn (2) was not possible since Cp₃Th has not yet been synthesized. Despite these issues, thorium reduction chemistry was examined using $Cp_3''Th$ $[Cp'' = C_5H_3(SiMe_3)_2-1,3]^{7k}$ prepared by Lappert et al. in 1986, and the results are described here.

Addition of potassium graphite to a dark blue solution of Cp₃Th, 1, and 2.2.2-cryptand in THF immediately forms a green solution from which dichroic dark blue/red crystals of $[K(2.2.2\text{-cryptand})][Cp_3''Th]$, 2, can be isolated and crystallographically characterized, Fig. 1, eqn (3). The analogous reaction with 18-crown-6 instead of 2.2.2-cryptand as the potassium chelator provides [K(18-crown-6)(THF)₂][Cp₃"Th], 3, which was also crystallographically characterized [see (ESI†)], eqn (3). Elemental analysis was consistent with the structures determined crystallographically. The ¹H and ¹³C NMR spectra of 2 and 3 gave resonances in the diamagnetic region with a Me₃Si ¹H NMR resonance shifted about 0.4 ppm from that of KCp". A resonance was observed in the 29Si NMR spectrum of 3 at -6 ppm in the region close to the -8 and -15.5 ppm signals of diamagnetic Cp₃ThBr and KCp", respectively. Evans method measurements8 on both 2 and 3 and SQUID analysis9 at low temperature suggest the [Cp₃"Th]¹⁻ anion is diamagnetic. No EPR spectra were observed for 2 and 3. Decomposed samples showed the EPR spectrum of Cp₃"Th.^{7m}

$$\begin{array}{c|c} SiMe_3 & 2.2.2\text{-cryptand} \\ KC_8 & SiMe_3 \\ Me_3Si & KC_8 \\ Me_3Si & KC_8 \\ Me_3Si & KC_8 \\ SiMe_3 & -graphite \\ SiMe_3 & -graphite \\ \hline \\ SiMe_3 & -graphite \\ \hline \\ SiMe_3 & -graphite \\ \hline \\ SiMe_3 & SiMe_3 \\ \hline \\$$

The structures of the anions in 2 and 3 are very similar to the structure of Cp₃Th. All three structures have a trigonal planar arrangement of the three Cp" rings around thorium with a sum of (ring centroid)-Th-(ring centroid) angles of 360°. The

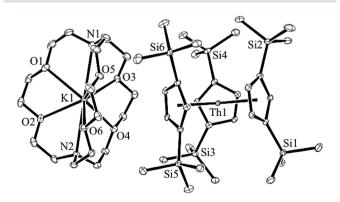


Fig. 1 Molecular structure of $[K(2.2.2-cryptand)][Cp_3''Th]$, 2. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

structure of 2, however, is not isomorphous with the lanthanum complex of the same formula, [K(2.2.2-cryptand)][Cp₃'La].^{1a} The average Th-(Cp" ring centroid) distances of 2.521 Å in 2 and 2.525 Å in 3 are equivalent to the 2.520 Å distance in $Cp_3^{"}$ Th. The negligible differences in the Th-(ring centroid) distances between the Th³⁺ precursor and the formally Th²⁺ complexes 2 and 3 are similar to the small differences between the Cp₃Ln and $Cp_3^{"}Ln Ln^{3+}$ complexes and the $(Cp_3^{'}Ln)^{1-}$ and $(Cp_3^{"}Ln)^{1-}$ complexes, respectively, of all the new Ln²⁺ ions that have 4fⁿ5d¹ ground states¹ instead of the 4fⁿ⁺¹ configurations expected by reduction of a 4fⁿ Ln³⁺ ion. Similarly, the 2.521 Å U-(ring centroid) distance in the U^{2+} complex, $[K(2.2.2-cryptand)][Cp'_3U]$, which appears to have a 5f³6d¹ ground state, is only slightly larger than the 2.508 Å value in the U3+ analog, Cp3'U.4 These small changes in M-(ring centroid) distances match the small changes in radial size commonly seen in transition metal complexes, 10 but contrast with the 0.10-0.20 Å differences generally seen for complexes of 4fⁿ⁺¹ Ln²⁺ complexes compared to their 4fⁿ Ln³⁺ counterparts.¹¹

The UV-Vis spectra of 2 and 3 in THF, Fig. 2, contain absorptions at 650 nm with extinction coefficients of 23 000 M⁻¹ cm⁻¹, that are significantly larger than those of Cp₃"Th, 5000 M⁻¹ cm⁻¹. This is similar to the larger intensities observed for the +2 complexes, [K(2.2.2-cryptand)][Cp₃'Ln]^{1c,d} and [K(2.2.2-cryptand)][Cp₃'U], compared to their +3 analogs, Cp₃'Ln and Cp₃'U, respectively. However, the absorptions of the Th²⁺ complexes are even more intense and the solutions look like ink.

Density functional theory (DFT) using the TPSSh functional¹² was used to examine the $(Cp_3''Th)^{1-}$ anion in 2 and 3. Calculations using scalar-relativistic effective core potentials13 and triple-zeta valence basis sets, def-TZVP, for thorium14 predicted trigonal planar structures for Cp_3^r Th and $(Cp_3^r$ Th)¹⁻ that match the crystallographic data. The calculated Th-Cp"(centroid) lengths of 2.538 Å for Cp_3^r Th and 2.526 Å for $(Cp_3^r$ Th)¹⁻ are similar to the experimentally determined distances of 2.52 Å. It

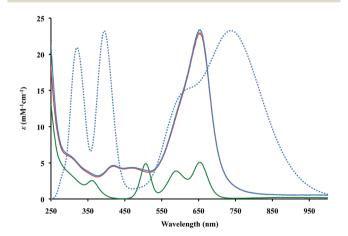


Fig. 2 Experimental (solid lines) UV-Vis spectra in THF at 298 K Cp_3^r Th, 1 (green), [K(2.2.2-cryptand)][Cp_3^r Th], 2 (red), and [K(18-crown-6)(THF)₂][Cp₃["]Th], **3** (blue) and calculated (dotted) UV-Vis spectra of $(Cp_3^{''}Th)^{1-}$ (blue) with theoretical extinction coefficients scaled down by a factor of 1.4.

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is interesting to note that the calculations for the Th^{3+} complex show a slightly longer metal ligand distance than for the Th^{2+} complex. The calculations indicate a spin-paired ground state of $6d^2$ for $(Cp_3''Th)^{1-}$ and a $6d^1$ ground state for $Cp_3''Th$; the latter is consistent with previous analyses of $Cp_3''Th$, 7g,m $(C_5Me_5)_2[^iPrNC(Me)N^iPr]Th^{7n}$ and $[K(DME)_2]\{[C_8H_6(Si^iBuMe_2)_2]_2Th\}$. 7l Gas-phase studies of Th^{2+} indicate a ground state of $5f^16d^1$, but the $6d^2$ configuration is just 63 cm^{-1} higher and the $5f^17s^1$ is 2527 cm^{-1} higher than the ground state. 15 For $(Cp_3Th)^{1-}$ the triplet $5f^16d^1$ state is computed to be 9–14 kcal mol^{-1} higher in energy than the singlet $6d^2$ ground state.

The 6d² singlet ground state can arise in this case due to stabilization of a d_{z^2} orbital by the trigonal ligand environment as found in DFT calculations on $(Cp_3'Ln)^{1-}$ and $(Cp_3'U)^{1-}$ complexes^{1c,d,4} and noted earlier in the literature for tris(cyclopentadienyl) metal complexes.^{7g,m,16} Indeed, both the lowest unoccupied molecular orbital (LUMO) of $Cp_3''Th$ and the highest occupied molecular orbital (HOMO) of $(Cp_3''Th)^{1-}$ have d_{z^2} character, Fig. 3. Complexes 2 and 3 provide the first examples of the 6d² configuration since stable transition metal ions are only known with the 5dⁿ configurations of the third row transition metals. The 6d² configuration is that predicted for ions like Rf^{2^+} and Db^{3^+} .¹⁷

Time-dependent density functional theory was used to simulate the UV-Vis spectra for the $(Cp_3^{''}Th)^{1-}$ anion as shown in Fig. 2 (see ESI† for a description of the predicted excitations). The maxima in the calculated spectra are lower in energy than those observed experimentally, but this is often the case with such calculations. Analysis of the calculated low energy peak shows that it arises from metal-to-metal transitions that have $d \to f$ and $d \to p$ character. The high energy peaks arise from metal-to-ligand charge transfer transitions similar to those found in the spectral analysis of $(Cp_3^{'}Ln)^{1-}$ and $(Cp_3^{'}U)^{1-}$. However, the $d \to f$ transitions found for $(Cp_3^{''}Th)^{1-}$ were not apparent in the analysis of the spectra of $(Cp_3^{'}Ln)^{1b-d}$ and $(Cp_3^{'}U)^{1-}$.

The rate of decomposition of [K(18-crown-6)(THF)₂][Cp₃⁻Th], 3, at room temperature was studied by ¹H NMR spectroscopy since monitoring by UV-Vis spectroscopy is complicated by the formation of highly colored Cp₃⁻Th, as identified by X-ray crystallography.^{7k} The rate of decomposition of 3 is much slower

Fig. 3 Contour plots of (a) the LUMO of $Cp_3^{\prime\prime}Th$ and (b) the HOMO of the $(Cp_3^{\prime\prime}Th)^{1-}$ anion in 3. Contour value is 0.05.

than that of the U^{2+} complex, [K(2.2.2-cryptand)][Cp'_3U], which has a half-life of 1.5 h in THF at room temperature. Complex 3 decomposed only 8% after 8 days at 298 K and a sample kept in the dark showed even less decomposition. This suggests that the formally Th^{2+} species are significantly more stable than the other newly discovered +2 ions. 1d,4

Complexes 2 and 3 were treated with H_2 to determine if a Th^{3+} hydride complex such as "[K(2.2.2-cryptand)][Cp₃"ThH]" would form in analogy to the complex formed by reaction of [K(2.2.2-cryptand)][Cp₃'U] with H_2 .⁴ Analogous chemistry is not observed with either H_2 or KH. Complexes 2 and 3 react in solution within minutes with 1 atm of H_2 and also over several hours at 60 psi in the solid state¹⁹ to make EPR active new crystalline complexes that appear to be bimetallic, but suitable models for the crystallographic data on the products have not been obtainable. The reactivity of 2 and 3 with H_2 contrasts with that of the Th^{3+} complex, Cp_3 "Th, which does not react under analogous conditions.

The $(Cp_3^"Th)^{1-}$ anion displays net two-electron reduction chemistry in its reaction with 1,3,5,7-cyclooctatetraene (C_8H_8) . The Th^{4+} complex $Cp_2^"Th(C_8H_8)$, 4, is formed as shown in eqn (4) and was characterized by X-ray crystallography, Fig. 4. The $(C_8H_8)^{2-}$ ring in 4, like that of $(C_5Me_4H)_2U(C_8H_8)^{20}$ displays considerable distortion from the normal planar geometry with several atoms 0.095 Å out of the best plane of the eight carbon atoms. This is reflected by a large range of $Th-C(C_8H_8)$ distances: 2.736(4) to 2.841(4) Å. This 0.105 Å range is similar to the 0.123 Å range in $(C_5Me_4H)_2U(C_8H_8)^{20}$

$$|Cp''_{3}Th||K(18-crown-6)(THF)_{2}| \xrightarrow{C_{8}H_{8}} -|K(18-crown-6)||Cp''|| = 0$$

$$3$$

$$(4)$$

$$SiMe_{3}$$

$$SiMe_{3}$$

$$SiMe_{3}$$

The isolation of the formally Th^{2+} ion in $(Cp_3''Th)^{1-}$ is likely aided by the stabilization of the potassium counter-cation by the 18-crown-6 and 2.2.2-cryptand ligands. This was also observed with U^{2+} in the $(Cp_3'U)^{1-}$ anion⁴ and in the $(Cp_3'Ln)^{1-}$ complexes of the new Ln^{2+} ions.¹ In the absence of these

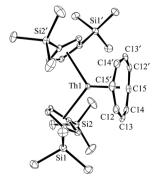


Fig. 4 Molecular structure of $Cp_2^{\prime\prime}Th(C_8H_8)$, 4. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity. $Th-C(C_8H_8)$ distances (Å): Th-C12, 2.815(4); Th-C13, 2.841(4); Th-C14, 2.769(3); Th-C15, 2.736(4).

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potassium-stabilizing chelates, isolation of Th²⁺ appears to be more difficult as described in a 2001 paper by Lappert and coworkers on the formation of Cp₃"Th by Na-K reduction of Cp₃ThCl.^{7m} In that paper, Lappert reports that treatment of Cp₃ThCl with excess Na-K alloy caused the initially blue solution (presumably Cp₃["]Th) to change to dark green. They isolated a diamagnetic green compound they postulated to be "[K(THF)_r][ThCp₃] and/or ThCp₂(THF)_r" but they could not characterize it or obtain reproducible analytical results. Hence, the $(Cp_3''Th)^{1-}$ anion was probably generated over 10 years ago, but could not be isolated in pure form as a simple $[K(THF)_r]^{1+}$ salt.

In summary, although it is difficult to obtain Th³⁺ complexes, further reduction is still possible with thorium: the +2 formal oxidation state of this metal is accessible in soluble molecular complexes. The Th²⁺ complexes provide the first examples of an isolable ion with a 6d² electron configuration, the configuration possible for fourth row transition metal congeners of Hf²⁺ or Ta³⁺. The synthesis of these complexes demonstrates the power of specific ligand fields to generate new ground states with actinides. The identification of Th²⁺ is more evidence that the oxidation state diversity for the f elements is still increasing. Stabilization of higher-lying d orbitals by the ligand field appears to be a key factor in isolating these new ions and provides a new option in expanding the oxidation state chemistry of these elements. This approach should be pursued further as attempts are made to synthesize soluble molecular complexes of +1 ions of these metals.

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