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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 Th^{3+} complex Cp_3Th , **1** [$Cp'' = C_5H_3(SiMe_3)_2$], with potassium graphite in THF in the presence of 2.2.2-cryptand generates $[K(2.2.2-cryptand)][Cp_3Th]$, **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, $[K(18-crown-6)(THF)_2][Cp_3Th]$, **3**. Complexes **2** and **3** form dark green solutions in THF with $\epsilon = 23\,000\ M^{-1}\ cm^{-1}$, 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 $(Cp_3Th)^{1-}$ 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 $Cp_2Th(C_8H_8)$, **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).¹

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

Previously, it was thought that only the traditional six Ln^{2+} 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, $[K(2.2.2-cryptand)][Cp'_3U]$ ($Cp' = C_5H_4SiMe_3$), was isolated according to eqn (2).⁴



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 Th^{4+}/Th^{3+} redox potential is estimated to be −3.0 and −3.8 V *vs.* NHE⁵ and a Th^{3+}/Th^{2+} redox potential of −4.9 V *vs.* NHE is in the literature.⁶ Reduction to metallic thorium would be predicted to be favored before formation of a Th^{2+} species.⁶ Many studies have been reported to find oxidation states lower than +4 for thorium,⁷ but only five Th^{3+} complexes have ever been structurally characterized.^{7k-o} An

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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 $(\text{Cp}_3\text{Th})^{1-}$ and a $6d^1$ ground state for Cp_3Th ; the latter is consistent with previous analyses of Cp_3Th ,^{7g,m} $(\text{C}_5\text{Me}_5)_2[\text{PrNC}(\text{Me})\text{N}^+\text{Pr}]\text{Th}^{7n}$ and $[\text{K}(\text{DME})_2][[\text{C}_8\text{H}_6(\text{Si}^i\text{BuMe}_2)_2\text{Th}]^{7l}$. 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 $(\text{Cp}_3\text{Th})^{1-}$ the triplet $5f^16d^1$ state is computed to be $9\text{--}14\text{ kcal mol}^{-1}$ higher in energy than the singlet $6d^2$ ground state.

The $6d^2$ 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 $(\text{Cp}_3\text{Ln})^{1-}$ and $(\text{Cp}_3\text{U})^{1-}$ 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_3Th and the highest occupied molecular orbital (HOMO) of $(\text{Cp}_3\text{Th})^{1-}$ have d_{z^2} character, Fig. 3. Complexes 2 and 3 provide the first examples of the $6d^2$ configuration since stable transition metal ions are only known with the $5d^n$ configurations of the third row transition metals. The $6d^2$ configuration is that predicted for ions like Rf^{2+} and Db^{3+} .¹⁷

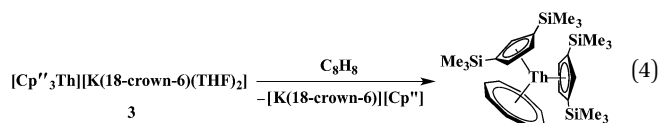
Time-dependent density functional theory was used to simulate the UV-Vis spectra for the $(\text{Cp}_3\text{Th})^{1-}$ anion as shown in Fig. 2 (see ESI† for a description of the predicted excitations). The maxima in the calculated spectra are lower in energy than those observed experimentally, but this is often the case with such calculations.¹⁸ Analysis of the calculated low energy peak shows that it arises from metal-to-metal transitions that have $d \rightarrow f$ and $d \rightarrow p$ character. The high energy peaks arise from metal-to-ligand charge transfer transitions similar to those found in the spectral analysis of $(\text{Cp}_3\text{Ln})^{1-}$ ^{1b-d} and $(\text{Cp}_3\text{U})^{1-}$.⁴ However, the $d \rightarrow f$ transitions found for $(\text{Cp}_3\text{Th})^{1-}$ were not apparent in the analysis of the spectra of $(\text{Cp}_3\text{Ln})^{1b-d}$ and $(\text{Cp}_3\text{U})^{1-}$.⁴

The rate of decomposition of $[\text{K}(\text{18-crown-6})(\text{THF})_2][\text{Cp}_3\text{Th}]$, 3, at room temperature was studied by ^1H NMR spectroscopy since monitoring by UV-Vis spectroscopy is complicated by the formation of highly colored Cp_3Th , as identified by X-ray crystallography.^{7k} The rate of decomposition of 3 is much slower

than that of the U^{2+} complex, $[\text{K}(\text{2.2.2-cryptand})][\text{Cp}_3\text{U}]$, which has a half-life of 1.5 h in THF at room temperature.⁴ 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 $[\text{K}(\text{2.2.2-cryptand})][\text{Cp}_3\text{ThH}]$ would form in analogy to the complex formed by reaction of $[\text{K}(\text{2.2.2-cryptand})][\text{Cp}_3\text{U}]$ 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_3Th , which does not react under analogous conditions.

The $(\text{Cp}_3\text{Th})^{1-}$ anion displays net two-electron reduction chemistry in its reaction with 1,3,5,7-cyclooctatetraene (C_8H_8). The Th^{4+} complex $\text{Cp}_2\text{Th}(\text{C}_8\text{H}_8)$, 4, is formed as shown in eqn (4) and was characterized by X-ray crystallography, Fig. 4. The $(\text{C}_8\text{H}_8)^{2-}$ ring in 4, like that of $(\text{C}_5\text{Me}_4\text{H})_2\text{U}(\text{C}_8\text{H}_8)$,²⁰ displays considerable distortion from the normal planar geometry with several atoms 0.095 \AA out of the best plane of the eight carbon atoms. This is reflected by a large range of $\text{Th}\text{--C}(\text{C}_8\text{H}_8)$ distances: $2.736(4)$ to $2.841(4)\text{ \AA}$. This 0.105 \AA range is similar to the 0.123 \AA range in $(\text{C}_5\text{Me}_4\text{H})_2\text{U}(\text{C}_8\text{H}_8)$.²⁰



The isolation of the formally Th^{2+} ion in $(\text{Cp}_3\text{Th})^{1-}$ 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 $(\text{Cp}_3\text{U})^{1-}$ anion⁴ and in the $(\text{Cp}_3\text{Ln})^{1-}$ complexes of the new Ln^{2+} ions.¹ In the absence of these



Fig. 3 Contour plots of (a) the LUMO of Cp_3Th and (b) the HOMO of the $(\text{Cp}_3\text{Th})^{1-}$ anion in 3. Contour value is 0.05.

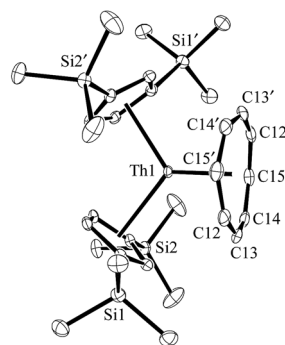


Fig. 4 Molecular structure of $\text{Cp}_2\text{Th}(\text{C}_8\text{H}_8)$, 4. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity. $\text{Th}\text{--C}(\text{C}_8\text{H}_8)$ distances (\AA): $\text{Th}\text{--C12}$, $2.815(4)$; $\text{Th}\text{--C13}$, $2.841(4)$; $\text{Th}\text{--C14}$, $2.769(3)$; $\text{Th}\text{--C15}$, $2.736(4)$.



potassium-stabilizing chelates, isolation of Th^{2+} appears to be more difficult as described in a 2001 paper by Lappert and co-workers on the formation of Cp_3Th by Na–K reduction of Cp_3ThCl .^{7m} In that paper, Lappert reports that treatment of Cp_3ThCl with excess Na–K alloy caused the initially blue solution (presumably Cp_3Th) to change to dark green. They isolated a diamagnetic green compound they postulated to be “[$\text{K}(\text{THF})_x$][ThCp_3]” and/or $\text{ThCp}_2(\text{THF})_x$ but they could not characterize it or obtain reproducible analytical results. Hence, the $(\text{Cp}_3\text{Th})^{1-}$ anion was probably generated over 10 years ago, but could not be isolated in pure form as a simple $[\text{K}(\text{THF})_x]^{1+}$ salt.

In summary, although it is difficult to obtain Th^{3+} complexes, further reduction is still possible with thorium: the +2 formal oxidation state of this metal is accessible in soluble molecular complexes. The Th^{2+} complexes provide the first examples of an isolable ion with a $6d^2$ electron configuration, the configuration possible for fourth row transition metal congeners of Hf^{2+} or Ta^{3+} . The synthesis of these complexes demonstrates the power of specific ligand fields to generate new ground states with actinides. The identification of Th^{2+} 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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