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 \([\text{Cp}'' = C_5H_5(SiMe_3)_2]\), with potassium graphite in THF in the presence of 2.2.2-cryptand generates \([K(2.2.2\text{-cryptand})][\text{Cp}_3\text{Th}]\), 2, a complex containing thorium in the formal +2 oxidation state. Reaction of 1 with KC₈ in the presence of 18-crown-6 generates the analogous Th^{2+} compound, \([K(18\text{-crown-6})][\text{Th}][\text{Cp}_2\text{Th}]\), 3. Complexes 2 and 3 form dark green solutions in THF with ε = 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 \((\text{Cp}_2\text{Th})^{3+}\) is consistent with a 6d² ground state, the first example of this transition metal electron configuration. Complex 3 reacts as a two-electron reductant with cyclooctatetraene to make \(\text{Cp}_2\text{Th}(\text{C}_8\text{H}_8)\), 4, and \([K(18\text{-crown-6})][\text{Cp}'']\).

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

Previously, it was thought that only the traditional six Ln^{3+} 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, \([K(2.2.2\text{-cryptand})][\text{Cp}_2\text{U}]\) \((\text{Cp}' = C_5H_5SiMe_3)_3\), 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.⁷ 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.⁷⁻² An
analogue of eqn (2) was not possible since Cp₃Th has not yet been synthesized. Despite these issues, thorium reduction chemistry was examined using Cp₃Th [Cp₃ = C₆H₆(SiMe₃)₂-1,3] 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-cryptand)][Cp₃Th], 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)2][Cp₃Th], 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 –H resonance shifted about 0.4 ppm from that of Cp₃M. 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 Cp₃M, respectively. Evans method measurements on both 2 and 3 and SQUID analysis at low temperature suggest the [Cp₃Th]⁻ anion is diamagnetic. No EPR spectra were observed for 2 and 3. Decomposed samples showed the EPR spectrum of Cp₃Th.¹⁵

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 structure of 2, however, is not isomorphous with the lanthanum complex of the same formula, [K(2.2.2-cryptand)][Cp₃La].¹⁶ 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 Cp₃Th. 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 Cp₃Ln Ln³⁺ and the (Cp₃Ln)²⁻ and (Cp₃Ln)³⁻ complexes, respectively, of all the new Ln³⁺ ions that have 4f⁵d¹ ground states instead of the 4f⁴⁵d¹ configurations expected by reduction of a 4f⁴ Ln³⁺ ion. Similarly, the 2.521 Å U–(ring centroid) distance in the U²⁺ complex, [K(2.2.2-cryptand)][Cp₃U], which appears to have a 5f⁶d¹ ground state, is only slightly larger than the 2.508 Å value in the U³⁺ analog, Cp₃U. These small changes in M–(ring centroid) distances match the small changes in radial size commonly seen in transition metal complexes,¹⁷ but contrast with the 0.10–0.20 Å differences generally seen for complexes of 4f⁻¹ Ln³⁺ compared to their 4f⁴ Ln³⁺ counterparts.¹⁸

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 Cp₃Th, 5000 M⁻¹ cm⁻¹. This is similar to the larger intensities observed for the +2 complexes, [K(2.2.2-cryptand)][Cp₃Ln]²⁻ and [K(2.2.2-cryptand)][Cp₃U]²⁺ compared to their +3 analogs, Cp₃Ln and Cp₃U, respectively. However, the absorptions of the Th³⁺ complexes are even more intense and the solutions look like ink.

Density functional theory (DFT) using the TPSSh functional¹⁴ was used to examine the (Cp₃Th)¹⁻ anion in 2 and 3. Calculations using scalar-relativistic effective core potentials¹⁹ and triple-zeta valence basis sets, def-TZVP, for thorium¹⁹ predicted trigonal planar structures for Cp₃Th and (Cp₃Th)¹⁻ that match the crystallographic data. The calculated Th–Cp(centroid) lengths of 2.538 Å for Cp₃Th and 2.526 Å for (Cp₃Th)¹⁻ are similar to the experimentally determined distances of 2.52 Å. It
is interesting to note that the calculations for the Th$^{3+}$ complex show a slightly longer metal ligand distance than for the Th$^{4+}$ complex. The calculations indicate a spin-paired ground state of 6d$^2$ for (Cp$_3$Th)$^{3+}$ and a 6d$^4$ ground state for Cp$_3$Th; the latter is consistent with previous analyses of Cp$_3$Th$_2$ ($^{7m}$ ($\text{C}_5\text{Me}_5$)$_2$[$\text{PrN}(\text{Me})\text{NPr}$]Th$^{7m}$ and [K(DME)$_2$]$_2$[Ca$\text{H}_4$(Si$\text{BuMe}_2$)$_2$]Th). Gas-phase studies of Th$^{3+}$ indicate a ground state of 5f$^6$6d$^1$, but the 6d$^2$ configuration is just 63 cm$^{-1}$ higher and the 5f$^7$7s$^1$ is 2527 cm$^{-1}$ higher than the ground state. For (Cp$_3$Th)$^{3+}$ the triplet 5f$^6$6d$^1$ state is computed to be 9–14 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 (Cp$_3$Ln)$^{3+}$ and (Cp$_3$U)$^{4+}$ complexes$^{16,4}$ and noted earlier in the literature for tris(cyclopentadienyl) metal complexes.$^{7,m16}$ Indeed, both the lowest unoccupied molecular orbital (LUMO) of Cp$_3$Th and the highest occupied molecular orbital (HOMO) of (Cp$_3$Th)$^{3+}$ 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$^0$ configurations of the third row transition metals. The 6d$^2$ configuration is that predicted for ions like Rf$^{3+}$ and Db$^{4+}$.

Time-dependent density functional theory was used to simulate the UV-Vis spectra for the (Cp$_3$Th)$^{3+}$ 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 → f and d → 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)$^{1+}$-$^{18}$ and (Cp$_3$U)$^{1+}$-$^{4}$. However, the d → f transitions found for (Cp$_3$Th)$^{3+}$ were not apparent in the analysis of the spectra of (Cp$_3$Ln)$^{1+}$-$^{4}$. The rate of decomposition of [K(18-crown-6)(THF)$_2$][Cp$_3$Th], 3, at room temperature was studied by $^1$H NMR spectroscopy since monitoring by UV-Vis spectroscopy is complicated by the formation of highly colored Cp$_3$Th, as identified by X-ray crystallography.$^{2k}$ The rate of decomposition of 3 is much slower than that of the U$^{2+}$ complex, [K(2.2.2-cryptand)][Cp$_3$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.$^{16,4}$

Complexes 2 and 3 were treated with H$_2$ to determine if a Th$^{3+}$ hydride complex such as “[K(2.2.2-cryptand)][Cp$_3$ThH]” would form in analogy to the complex formed by reaction of [K(2.2.2-cryptand)][Cp$_3$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 state$^{29}$ 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)$^{3+}$ anion displays net two-electron reduction chemistry in its reaction with 1,3,5,7-cyclooctatetraene (C$_8$H$_8$). The Th$^{4+}$ complex Cp$_3$Th(C$_8$H$_8$), 4, is formed as shown in eqn (4) and was characterized by X-ray crystallography, Fig. 4. The (C$_8$H$_8$)$^{2-}$ ring in 4, like that of (C$_5$Me$_5$H)$_2$U(C$_8$H$_8$)$_2$ 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$_8$H$_8$) distances: 2.736(4) to 2.841(4) Å. This 0.105 Å range is similar to the 0.123 Å range in (C$_5$Me$_5$H)$_2$U(C$_8$H$_8$)$_2$. The isolation of the formally Th$^{2+}$ ion in (Cp$_3$Th)$^{3+}$ 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)$^{3+}$ anion$^4$ and in the (Cp$_3$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$_3$Th and (b) the HOMO of the (Cp$_3$Th)$^{3+}$ anion in 3. Contour value is 0.05.

Fig. 4 Molecular structure of Cp$_3$Th(C$_8$H$_8$). 4. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity. Th–C(C$_8$H$_8$) distances (Å): Th–C12, 2.815(4); Th–C13, 2.841(4); Th–C14, 2.769(3); Th–C15, 2.736(4).
potassium-stabilizing chelates, isolation of Th²⁺ appears to be more difficult as described in a 2001 paper by Lappert and co-workers on the formation of Cp₄Th by Na–K reduction of Cp₃ThCl.⁷⁷ 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)]₃[THCp₃] and/or ThCp₂(THF).” They but could not characterize it or obtain reproducible analytical results. Hence, the (Cp₃,Th)₁⁻ anion was probably generated over 10 years ago, but could not be isolated in pure form as a simple [K(THF)]₃ 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 Th³⁺ complexes provide the first examples of an isolable ion with a 6d² electron configuration, the configuration possible for fourth row transition metal congeners of Hf³⁺ or Ta⁵⁺. The synthesis of these complexes demonstrates the power of specific ligand fields to generate new ground states with actinides. The identification of Th³⁺ 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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Notes and references


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