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Synthesis of a terminal Ce(IV) oxo complex by photolysis of a Ce(III) nitrate complex†

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Reaction of $[\text{Ce}(\text{NR}_2)_3]$ ($\text{R} = \text{SiMe}_3$) with LiNO_3 in THF, in the presence of 2,2,2-cryptand, results in the formation of the Ce(III) "ate" complex, $[\text{Li}(2,2,2\text{-cryptand})][\text{Ce}(\kappa^2\text{-O}_2\text{NO})(\text{NR}_2)_3]$ (**1**) in 38% yield. Photolysis of **1** at 380 nm affords $[\text{Li}(2,2,2\text{-cryptand})][\text{Ce}(\text{O})(\text{NR}_2)_3]$ (**2**), in 33% isolated yield after reaction work-up. Complex **2** is the first reported example of a Ce(IV) oxo complex where the oxo ligand is not supported by hydrogen bonding or alkali metal coordination. Also formed during photolysis are $[\text{Li}(2,2,2\text{-cryptand})]_2[(\mu_3\text{-O})\{\text{Ce}(\mu\text{-O})(\text{NR}_2)_2\}_3]$ (**3**) and $[\text{Li}(2,2,2\text{-cryptand})][\text{Ce}(\text{OSiMe}_3)(\text{NR}_2)_3]$ (**4**). Their identities were confirmed by X-ray crystallography. Complex **4** can also be prepared *via* reaction of $[\text{Ce}(\text{NR}_2)_3]$ with LiOSiMe_3 in THF, in the presence of 2,2,2-cryptand. When synthesized in this fashion, **4** can be isolated in 47% yield. To rationalize the presence of **2**, **3**, and **4** in the reaction mixture, we propose that photolysis of **1** first generates **2** and NO_2 , *via* homolytic cleavage of the N–O bond in its nitrate co-ligand. Complex **2** then undergoes decomposition *via* two separate routes: (1) ligand scrambling and oligomerization to form **3**; and, (2) abstraction of a trimethylsilyl cation to form a transient Ce(IV) silyloxide, $[\text{Ce}^{\text{IV}}(\text{OSiMe}_3)(\text{NR}_2)_3]$, followed by $1e^-$ reduction to form **4**. Alternatively, complex **4** could form directly *via* $\cdot\text{SiMe}_3$ abstraction by **2**.

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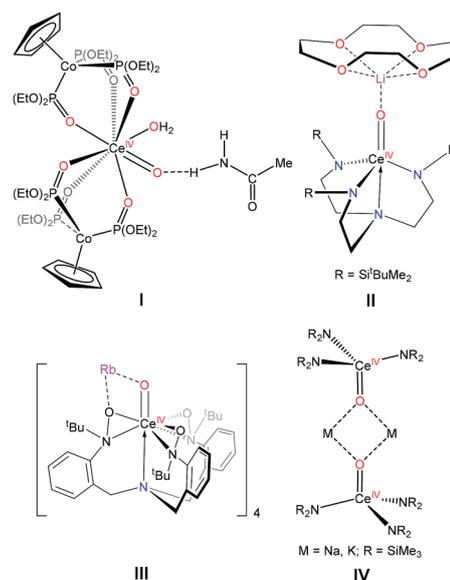
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Introduction

The past five years has seen significant progress made toward the synthesis of lanthanide complexes containing metal–ligand multiple bonds,^{1–6} including those featuring $\text{Ln}=\text{N}$ and $\text{Ln}=\text{C}$ interactions. For example, Anwander and co-workers recently described the synthesis of the first terminal lanthanide imido complex, $[(\text{Tp}^{\text{tBu,Me}})\text{Lu}=\text{N}(3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3)(\text{DMAP})]$, *via* Lewis base-induced methane elimination.² Similarly, Schelter and co-workers reported the synthesis of a series of Ce(IV) imido complexes, $[\text{ML}_n][\text{Ce}=\text{N}(3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3)(\text{TriNOx})]$ ($\text{TriNOx} = \text{N}(o\text{-CH}_2\text{C}_6\text{H}_4\text{N}(\text{tBu})\text{O})_3$; $\text{ML}_n = \text{Li}(\text{THF})(\text{Et}_2\text{O})$, $\text{Li}(\text{TMEDA})$, $\text{K}(\text{DME})_2$, $\text{Rb}(\text{DME})_2$, $\text{Cs}(\text{DME})_2$).⁵ Significant progress has also been made toward the synthesis of cerium(IV) oxo complexes.⁷ For example, Leung and co-workers recently reported the synthesis of a Ce(IV) oxo complex ligated by the tripodal Kläui ligand, $[(\text{L}_{\text{OEt}})_2\text{Ce}(\text{O})(\text{H}_2\text{O})] \cdot \text{MeC}(\text{O})\text{NH}_2$ (**I**, $\text{L}_{\text{OEt}} = \text{CpCo}\{\text{P}(\text{O})(\text{OEt})_2\}_3$, Scheme 1).³ Additionally, our group reported the synthesis of the cerium(IV) oxo complex, $[\text{Li}(12\text{-crown-4})][(\text{NN}'_3)\text{Ce}(\text{O})]$ (**II**, $\text{NN}'_3 = \text{N}(\text{CH}_2\text{CH}_2\text{NR})_3$, $\text{R} = \text{Si}^i\text{BuMe}_2$), which was synthesized by thermal decomposition of a Ce(III) nitrate precursor $[\text{Li}(12\text{-crown-4})][(\text{NN}'_3)\text{Ce}(\kappa^2\text{-O}_2\text{NO})]$.⁸ More recently,

Schelter and co-workers reported the synthesis of a Ce(IV) oxo supported by the tripodal TriNOx ligand, $[(\text{TriNOx})\{\text{Ce}(\text{O})\}\text{Rb}]_4$ (**III**).⁵ Also of note is $[\text{M}]_2[\text{Ce}(\mu\text{-O})(\text{NR}_2)_3]_2$ (**IV**, $\text{M} = \text{Na}, \text{K}$; $\text{R} = \text{SiMe}_3$), reported by Lappert and co-workers in 2010.⁹ These two complexes, which pre-date the other examples mentioned here, were isolated in low yield (*ca.* 20%) upon reaction of



Scheme 1 Selected complexes bearing lanthanide–oxygen multiple bonds.

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† Electronic supplementary information (ESI) available: Further experimental details, figures, spectral, electrochemical, and crystallographic data for 1–4. CCDC 1569781–1569784. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7sc03715e



$\text{Ce}(\text{NR}_2)_3$ with MNR_2 , in the presence of O_2 ,⁹ but they were not completely characterized.

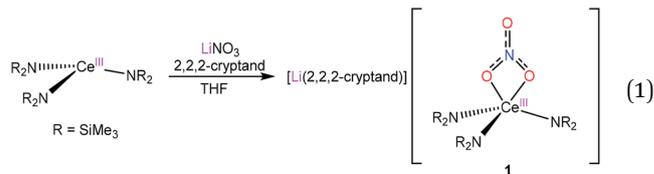
Interestingly, every cerium oxo complex isolated thus far has utilized an external non-covalent interaction to instil stability to this highly reactive functional group. For example, the $\text{Ce}=\text{O}$ bond in **I** is stabilized by hydrogen bonding to an acetamide solvent molecule.³ Similarly, the oxo ligands in **II** and **III** are stabilized by their interactions with a capping alkali metal counterion.^{5,8} The prevalence of these non-covalent interactions can be rationalized by the poor overlap of the metal f and d orbitals with oxygen 2p orbitals, which results in weak π bonds within the $\text{Ce}=\text{O}$ fragment, concomitant with considerable oxo nucleophilicity.^{4,9–11} Indeed, controlling this nucleophilic character has been one of the key challenges to synthesizing a terminal lanthanide oxo complex.³

The unique redox chemistry of the lanthanides also poses a barrier for the synthesis of lanthanide oxo complexes. In particular, cerium redox chemistry is dominated by the $\text{Ce}(\text{III}/\text{IV})$ redox couple, and thus formation of a $\text{Ce}(\text{IV})$ oxo complex from a $\text{Ce}(\text{III})$ precursor essentially mandates a $1e^-$ O-atom transfer process. However, traditional O-atom transfer reagents, such as N_2O , pyridine-N-oxide, and peroxyacids, are $2e^-$ oxidants.¹² In our recent synthesis of $[\text{Li}(12\text{-crown-4})][(\text{NN}'_3)\text{Ce}(\text{O})]$, the oxo ligand was formed *via* reduction of a nitrate ligand, in a formal $1e^-$ O-atom transfer process. Several other examples demonstrating the use of nitrate as a $1e^-$ O-atom source have emerged in recent years,^{13–16} suggesting that $[\text{NO}_3]^-$ could be a valuable reagent for the generation of f-element oxo complexes. This mode of reactivity can also be promoted with light. For example, Berry and co-workers demonstrated that photolysis of $\text{Ru}_2(\text{chp})_4(\text{NO}_3)$ (chp = 6-chloro-2-hydroxypyridinate) generated a metal oxo with concomitant release of NO_2 .¹³ Similarly, Suslick and co-workers reported that photolysis of $\text{Mn}(\text{TPP})(\text{NO}_3)$ also resulted in metal oxo generation and release of NO_2 .¹⁵ However, it should be noted that in both of these examples the resulting metal oxo was unstable and not isolated.

Drawing on these results, we sought to further develop the use of $[\text{NO}_3]^-$ as an O-atom source for the synthesis of f-element oxo complexes. Herein, we describe the photochemical cleavage of nitrate in a $\text{Ce}(\text{III})$ “ate” precursor to generate the first terminal $\text{Ce}(\text{IV})$ oxo complex.

Results and discussion

Reaction of $[\text{Ce}(\text{NR}_2)_3]$ ($\text{R} = \text{SiMe}_3$) with LiNO_3 in THF, in the presence of 2,2,2-cryptand, results in the formation of the $\text{Ce}(\text{III})$ “ate” complex, $[\text{Li}(2,2,2\text{-cryptand})][\text{Ce}(\kappa^2\text{-O}_2\text{NO})(\text{NR}_2)_3]$ (**1**), which can be isolated as a yellow crystalline solid in 38% yield after work-up (eqn (1)). The ^1H NMR spectrum of **1** in py-d_5 displays a broad singlet at -1.32 ppm, assignable to the SiMe_3 environment, and three resonances at 2.48, 3.45 and 3.51 ppm, assignable to the cryptand moiety. The chemical shift of the methyl resonance, along with its broad appearance, support the presence of a paramagnetic $\text{Ce}(\text{III})$ centre in this complex. The $^7\text{Li}\{\text{H}\}$ NMR spectrum reveals a broad resonance at -1.08 ppm, indicative of a single lithium environment.



The solid-state molecular structure of **1** (Fig. 1) reveals a κ^2 coordination mode of the nitrate ligand, similar to that observed for the cerium(III) nitrate TREN complex, $[\text{Li}(12\text{-crown-4})][(\text{NN}'_3)\text{Ce}(\text{NO}_3)]$.⁸ However, the $\text{Ce}-\text{O}$ distances in **1** (2.653(2) and 2.562(2) Å) are shorter than those observed for $[\text{Li}(12\text{-crown-4})][(\text{NN}'_3)\text{Ce}(\text{NO}_3)]$ (2.724(6) and 2.745(6) Å), likely because of the bulkier TREN ligand in the latter and the absence of $\text{Li}-\text{O}$ interactions in the former. In addition, the $\text{Ce}-\text{N}$ distances in **1** (2.367(2)–2.398(2) Å) are consistent with the $\text{Ce}-\text{N}$ distances reported for other $\text{Ce}(\text{III})$ amido complexes.^{17–20} For comparison, the $\text{Ce}-\text{N}$ distances in $\text{Ce}(\text{TMP})_3(\text{THF})$ (TMP = 2,2,6,6-tetramethylpiperidinato) range from 2.346(2)–2.374(2) Å, while the distances in $[\text{Li}(\text{THF})][\text{Ce}(\text{NCy}_2)_4]$ range from 2.320(2)–2.330(2) Å.^{18,19} The lithium counter-ion in **1** is encapsulated by the 2,2,2-cryptand moiety, rendering **1** a separated cation–anion pair. Interestingly, only five of the eight donor atoms in the cryptand moiety are bound to the lithium ion; two nitrogen atoms and one oxygen atom remain uncoordinated. Similar binding modes have been observed in other $[\text{Li}(2,2,2\text{-cryptand})]^+$ complexes.^{21–24}

With complex **1** in hand, we explored its suitability as a $\text{Ce}(\text{IV})$ oxo precursor. Unlike $[\text{Li}(12\text{-crown-4})][(\text{NN}'_3)\text{Ce}(\text{NO}_3)]$, however, which is mostly consumed upon standing at room temperature for 24 h, we discovered that complex **1** is not especially temperature sensitive. A py-d_5 solution of **1**, which was stored

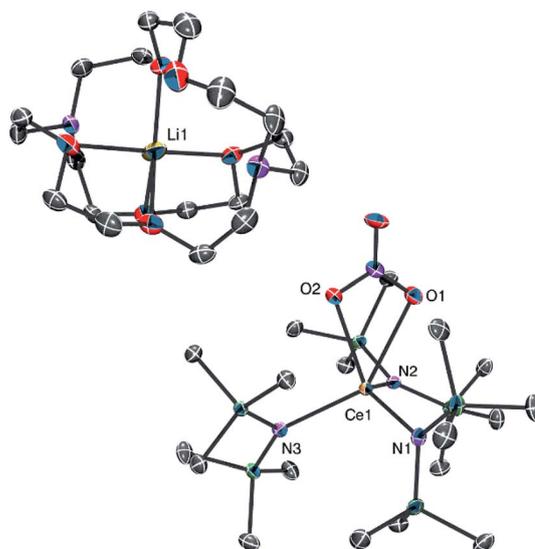


Fig. 1 ORTEP diagram of **1** shown with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): $\text{Ce1}-\text{O1} = 2.653(2)$, $\text{Ce1}-\text{O2} = 2.562(2)$, $\text{Ce1}-\text{N1} = 2.385(3)$, $\text{Ce1}-\text{N2} = 2.367(2)$, $\text{Ce1}-\text{N3} = 2.398(2)$, $\text{N2}-\text{Ce1}-\text{N1} = 121.01(8)$, $\text{N2}-\text{Ce1}-\text{N3} = 112.82(8)$, $\text{N1}-\text{Ce1}-\text{N3} = 101.96(9)$.



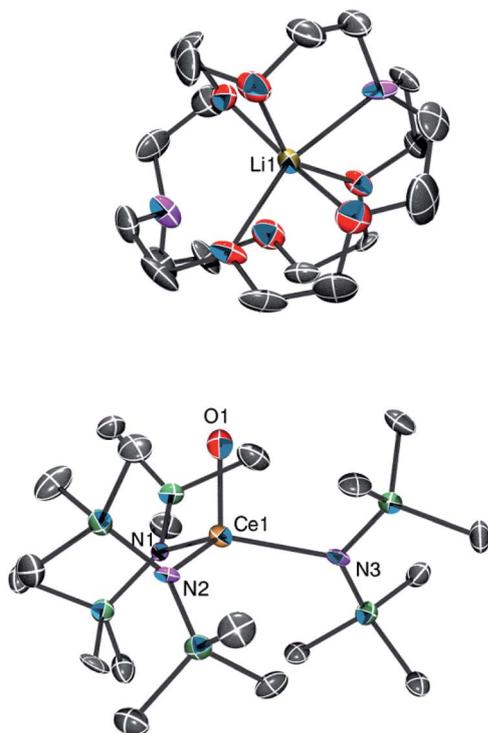


Fig. 2 ORTEP diagram of **2** shown with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ce1–O1 = 1.840(7), Ce1–N1 = 2.397(8), Ce1–N2 = 2.353(8), Ce1–N3 = 2.383(8), N2–Ce1–N1 = 116.4(3), N3–Ce1–N1 = 113.4(3), N2–Ce1–N3 = 116.8(3), O1–Ce1–N1 = 103.9(3), O1–Ce1–N2 = 101.7(3), O1–Ce1–N3 = 101.5(3).

at 0.69 ppm integrating to 54 protons, which is assignable to the SiMe₃ environment, while the resonances at 2.56, 3.52, and 3.59 ppm, each integrating to 12 protons, are assignable to the cryptand moiety. The chemical shift of its SiMe₃ resonance is nearly identical to that assigned to this complex in the spectrum of the crude reaction mixture (Fig. S4†). The ⁷Li{¹H} NMR spectrum of **2** features a broad singlet centred at –1.00 ppm. This chemical shift is in the range previously reported for the [Li(2,2,2-cryptand)]⁺ ion.^{29,30} We also recorded the Raman spectrum of **2**, but were unable to make a definitive assignment of the Ce=O stretch. Finally, we have found that complex **2** is somewhat thermally sensitive. Upon standing in 2 : 1 toluene/pyridine at room temperature for 4 d, complex **2** decomposes to a mixture of **3**, **4**, and LiN(SiMe₃)₂ (along with other unidentified products) with about 70% conversion (Fig. S12 and S13†). Under these conditions, complexes **3** and **4** are present in an approximately 3 : 1 ratio. Similar results are observed when **2** is left to stand in neat pyridine (Fig. S11†).

Complex **3** crystallizes in triclinic space group $P\bar{1}$ (Fig. 3). In the solid state, complex **3** consists of a partial cubane Ce₃O₄ core. Each Ce centre is also ligated by two silylamide ligands. Additionally, **3** features two [Li(2,2,2-cryptand)]⁺ counterions, confirming the tetravalent oxidation state of each cerium atom. The Ce–O distances observed for the three μ₂-oxo ligands in **3** range from 2.071(7) to 2.133(7) Å, and are comparable to those observed in the structurally related Ce(IV) oxo cluster, [(μ-O)

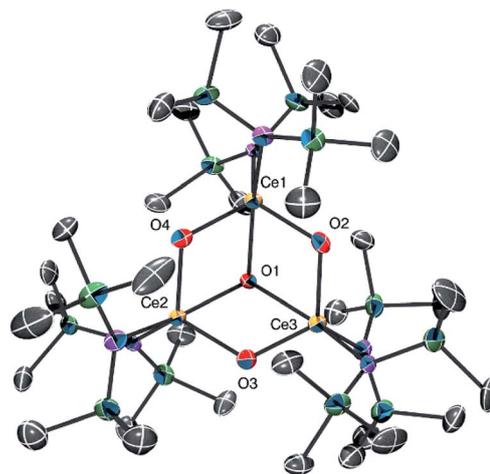


Fig. 3 ORTEP diagram of **3** shown with 50% probability ellipsoids. Hydrogen atoms, diethyl ether solvate and two [Li(2,2,2-cryptand)] counter-ions are omitted for clarity. Selected bond distances (Å) and angles (°): Ce1–O1 = 2.294(7), Ce1–O2 = 2.078(7), Ce1–O4 = 2.133(7), Ce2–O1 = 2.310(7), Ce2–O3 = 2.109(7), Ce2–O4 = 2.071(7), Ce3–O1 = 2.289(7), Ce3–O2 = 2.130(7), Ce3–O3 = 2.100(7), Ce1–N1 = 2.391(8), Ce1–N2 = 2.366(8), Ce2–N5 = 2.389(8), Ce2–N6 = 2.380(9), Ce3–N3 = 2.386(9), Ce3–N4 = 2.415(9), Ce3–O1–Ce1 = 99.8(3), Ce3–O1–Ce2 = 99.6(3), Ce1–O1–Ce2 = 99.5(3).

Ce(NR₂)₂]₃],⁹ reported by Lappert and co-workers. The Ce–O distances observed for the μ₃-oxo ligand in **3** are longer, ranging from 2.289(7) to 2.310(7) Å, but are similar to those reported for other known [Ce₃(μ₃-oxo)] clusters.^{31,32} We can rule out the presence of a hydroxo ligand in **3** on the basis of our structural data. In particular, the Ce–O distances of μ₂- or μ₃-hydroxo ligands are anticipated to be substantially longer than the Ce–O distances observed for **2**.^{33,34} As was observed for **2**, the Ce–N distances in **3** (2.366(8)–2.415(9) Å) are somewhat longer than those typically reported for Ce(IV) amides.^{19,27,28} Unfortunately, we have been unable to isolate pure samples of **3**, and thus have been unable to complete its characterization. As such, the NMR spectroscopic assignments that we report for this complex (see above) should be considered tentative.

Complex **4** crystallizes in the monoclinic space group $P2_1/n$ and its solid-state molecular structure is shown in Fig. 4. In the solid state, complex **4** consists of a pseudo-tetrahedral Ce(III) anion and a [Li(2,2,2-cryptand)]⁺ cation. Complex **4** features a Ce–O bond length of 2.214(3) Å which is significantly longer than the Ce–O distance found in **2** (1.840(7) Å), further supporting the presence of Ce=O multiple bond character in the latter. However, this distance is similar to the average Ce–O_{SiPh₃} distance in Ce(OSiPh₃)₃(THF)₃ (2.22 Å).³⁵ The average Ce–N distance in **4** (2.41 Å) is comparable to that observed for **1** (2.38 Å), consistent with its anticipated Ce(III) oxidation state. Finally, the Ce–O–Si bond angle (178.9(2)°) is similar to that observed for Ce(OSiPh₃)₃(THF)₃ (av. 174°)³⁵ and [(NN′₃)Ce(OSiMe₂tBu)] (167.2(2)°).⁸

Conveniently, complex **4** can be synthesized independently via reaction of [Ce(NR₂)₃] with LiOSiMe₃ in THF, in the presence of 2,2,2-cryptand (eqn (2)), permitting its complete



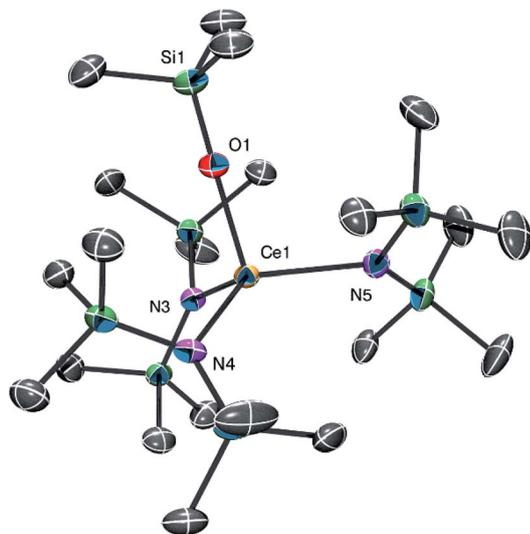
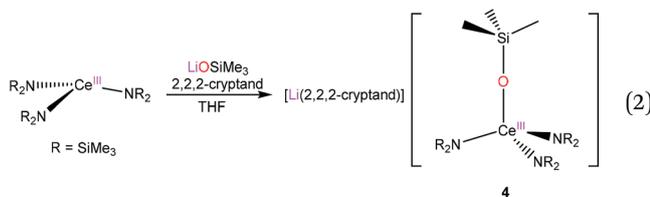


Fig. 4 ORTEP diagram of **4** shown with 50% probability ellipsoids. Hydrogen atoms and [Li(2,2,2-cryptand)] counterion are omitted for clarity. Selected bond distances (Å) and angles (°): Ce1–O1 = 2.214(3), Ce1–N3 = 2.430(4), Ce1–N4 = 2.396(4), Ce1–N5 = 2.413(4), O1–Si1 = 1.607(4), N4–Ce1–N3 = 109.97(13), N4–Ce1–N5 = 117.68(14), N5–Ce1–N3 = 117.42(13), Si1–O1–Ce1 = 178.9(2).

characterization. Synthesized *via* this route, **4** can be isolated as a white solid in 47% yield after work-up.



The ^1H NMR spectrum of **4** in $py-d_5$ features two broad singlets at -0.37 and -0.59 ppm, integrating to 9 and 54 protons, respectively. These resonances are assignable to the OSiMe₃ and N(SiMe₃)₂ methyl environments, respectively. Importantly, these resonances are nearly identical to those assigned to this complex in the spectrum of crude reaction mixture (Fig. S4†). Also observed in the ^1H NMR spectrum of **4** are resonances at 2.56, 3.52 and 3.60 ppm, each integrating to 12 protons, which are assignable to the cryptand moiety. Finally, its $^7\text{Li}\{^1\text{H}\}$ NMR spectrum consists of a single resonance at -0.97 ppm.

To rationalize the presence of **2**, **3**, and **4** in the reaction mixture, we propose that photolysis of **1** first generates **2** and NO₂, *via* homolytic cleavage of the N–O bond in its nitrate co-ligand. However, **2** is unstable to the reaction conditions and begins to decompose *via* two separate routes: (1) ligand scrambling and oligomerization to form **3**; and, (2) abstraction of a trimethylsilyl cation to form a transient Ce(IV) silyloxyde, [Ce^{IV}(OSiMe₃)(NR₂)₃], followed by 1e[−] reduction to form **4**. Alternatively, complex **4** could form directly *via* ·SiMe₃ abstraction by **2**. To support these hypotheses, we note that complex **2** is thermally unstable, and slowly decomposes to

form a mixture of **3** and **4** in solution (Fig. S12 and S13†). Additionally, we observe a minor resonance at 0.53 ppm in the ^1H NMR spectrum of the photolysis reaction mixture (Fig. S4†), which is assignable to LiN(SiMe₃)₂. Its presence is consistent with the proposed conversion of **2** to **3** *via* ligand scrambling and loss of LiN(SiMe₃)₂. Finally, we previously demonstrated that the Ce(IV) silyloxyde, [(NN′₃)Ce(OSi^tBuMe₂)], was formed as a minor by-product during the conversion of [Li(12-crown-4)][(NN′₃)Ce(κ²-O₂NO)] to the Ce(IV) oxo, [Li(12-crown-4)][(NN′₃)Ce(O)],⁸ presumably *via* a similar adventitious [SiR₃]⁺ abstraction.

To test the thermodynamic favourability of the proposed 1e[−] reduction to form **4**, we investigated its electrochemistry by cyclic voltammetry. The cyclic voltammogram of **4** in THF reveals a redox feature centred at -0.53 V at 200 mV s^{−1} (*vs.* Fc/Fc⁺; see Fig. S23 in ESI†). This feature is marked by a large difference between the potentials of the oxidation and reduction peaks (*i.e.*, 0.72 V at 200 mV s^{−1}), suggestive of an ECE-type process. While the potential of this feature is comparable to those previously reported for cerium complexes with similar ligand frameworks, including [Ce(F)(NR₂)₃] (-0.56 V), [Ce(Cl)(NR₂)₃] (-0.30 V) and [Ce(Br)(NR₂)₃] (-0.31 V),^{36–38} its electrochemical irreversibility suggests that [Ce^{IV}(OSiMe₃)(NR₂)₃] is not particularly stable. Therefore, complex **4** may not be formed *via* a straightforward 1e[−] reduction of a [Ce^{IV}(OSiMe₃)(NR₂)₃] intermediate. Instead, the cyclic voltammetry data may be evidence for a concerted ·SiMe₃ abstraction by **2** to form **4**. A similar ·SiMe₃ abstraction by the uranyl fragment has been reported by Arnold and co-workers.^{39–41}

Conclusions

In summary, we report the synthesis of the first lanthanide oxo complex where the oxo ligand is not supported by hydrogen bonding or alkali metal coordination, namely, [Li(2,2,2-cryptand)][Ce(O)(NR₂)₃] (**2**). This complex was generated by photolysis of the Ce(III) nitrate precursor [Li(2,2,2-cryptand)][Ce(κ²-O₂NO)(NR₂)₃] (**1**), which results in photochemical cleavage of the nitrate co-ligand. Also formed in the photolysis reaction are the Ce(IV) oxo cluster, [Li(2,2,2-cryptand)]₂[(μ₃-O)Ce(μ-O)(NR₂)₂]₃ (**3**), and the Ce(III) silyloxyde complex, [Li(2,2,2-cryptand)][Ce(OSiMe₃)(NR₂)₃] (**4**). We believe these two complexes are formed upon thermal (or photochemical) decomposition of **2** after its initial generation in the reaction mixture. Overall, this work further highlights the utility of [NO₃][−] as a 1e[−] O-atom source for the generation of lanthanide oxo complexes. Indeed, we have now shown that nitrate reduction to form cerium oxos can proceed *via* both thermal and photochemical routes. Going forward, we will attempt to synthesize a Ln(III) oxo complex *via* 1e[−] O-atom transfer from [NO₃][−]. This is anticipated to be a greater synthetic challenge because the lower Ln oxidation state results in reduced Ln–O bond covalency.⁴²

Conflicts of interest

There are no conflicts to declare.



Acknowledgements

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