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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  $\text{LiNO}_3$  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  $\text{LiOSiMe}_3$  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  $\text{NO}_2$ , *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  $1\text{e}^-$  reduction to form **4**. Alternatively, complex **4** could form directly *via*  $\cdot\text{SiMe}_3$  abstraction by **2**.

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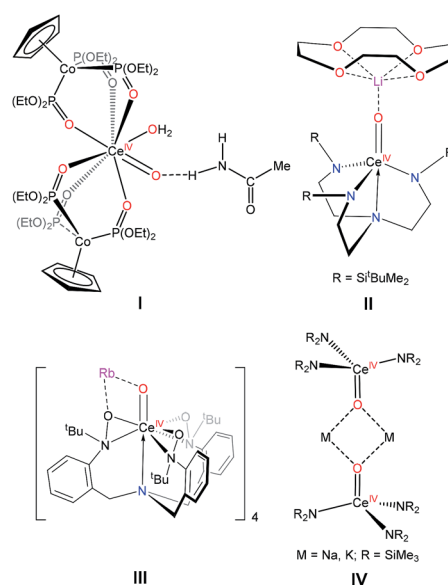
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## Introduction

The past five years has seen significant progress made toward the synthesis of lanthanide complexes containing metal–ligand multiple bonds,<sup>1–6</sup> 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.<sup>2</sup> Similarly, Schelter and co-workers reported the synthesis of a series of Ce(IV) imido complexes,  $[\text{ML}_n][\text{Ce}=\text{N}(3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3)(\text{TriNOx})]$  ( $\text{TriNOx} = \text{N}(o\text{-CH}_2\text{C}_6\text{H}_4\text{N}(\text{tBu})\text{O})_3$ ;  $\text{ML}_n = \text{Li}(\text{THF})(\text{Et}_2\text{O})$ ,  $\text{Li}(\text{TMEDA})$ ,  $\text{K}(\text{DME})_2$ ,  $\text{Rb}(\text{DME})_2$ ,  $\text{Cs}(\text{DME})_2$ ).<sup>5</sup> Significant progress has also been made toward the synthesis of cerium(IV) oxo complexes.<sup>7</sup> 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).<sup>3</sup> 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  $[\text{Li}(12\text{-crown-4})][(\text{NN}'_3)\text{Ce}(\kappa^2\text{-O}_2\text{NO})]$ .<sup>8</sup> 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**).<sup>5</sup> 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.<sup>9</sup> 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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$\text{Ce}(\text{NR}_2)_3$  with  $\text{MNR}_2$ , in the presence of  $\text{O}_2$ ,<sup>9</sup> but they were not completely characterized.

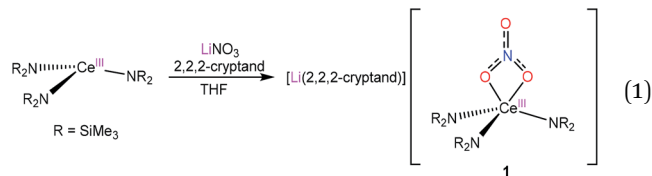
Interestingly, every cerium oxo complex isolated thus far has utilized an external non-covalent interaction to instil stability to this highly reactive functional group. For example, the  $\text{Ce}=\text{O}$  bond in **I** is stabilized by hydrogen bonding to an acetamide solvent molecule.<sup>3</sup> Similarly, the oxo ligands in **II** and **III** are stabilized by their interactions with a capping alkali metal counterion.<sup>5,8</sup> 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  $\pi$  bonds within the  $\text{Ce}=\text{O}$  fragment, concomitant with considerable oxo nucleophilicity.<sup>4,9–11</sup> Indeed, controlling this nucleophilic character has been one of the key challenges to synthesizing a terminal lanthanide oxo complex.<sup>3</sup>

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  $\text{N}_2\text{O}$ , pyridine-N-oxide, and peroxyacids, are  $2e^-$  oxidants.<sup>12</sup> 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,<sup>13–16</sup> 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  $\text{Ru}_2(\text{chp})_4(\text{NO}_3)$  ( $\text{chp}$  = 6-chloro-2-hydroxypyridinate) generated a metal oxo with concomitant release of  $\text{NO}_2$ .<sup>13</sup> 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  $\text{NO}_2$ .<sup>15</sup> 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  $\text{LiNO}_3$  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  $^1\text{H}$  NMR spectrum of **1** in  $\text{py-d}_5$  displays a broad singlet at  $-1.32$  ppm, assignable to the  $\text{SiMe}_3$  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  $\kappa^2$  coordination mode of the nitrate ligand, similar to that observed for the cerium(III) nitrate TREN complex,  $[\text{Li}(12\text{-crown-4})][(\text{NN}')_3\text{Ce}(\text{NO}_3)]$ .<sup>8</sup> 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 Li–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.<sup>17–20</sup> For comparison, the  $\text{Ce}-\text{N}$  distances in  $\text{Ce}(\text{TMP})_3(\text{THF})$  ( $\text{TMP}$  = 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.<sup>18,19</sup> 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.<sup>21–24</sup>

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  $\text{py-d}_5$  solution of **1**, which was stored

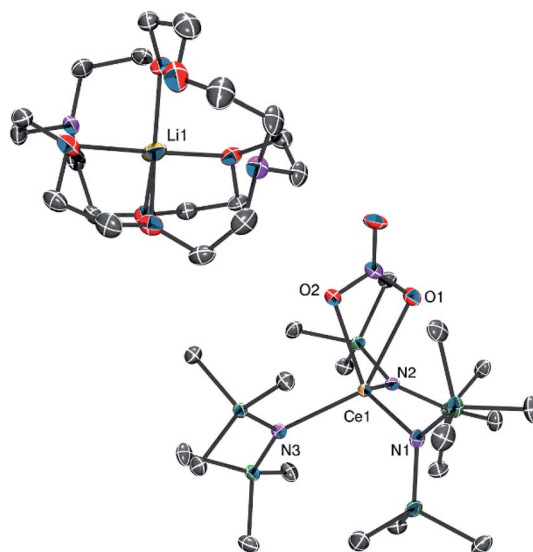


Fig. 1 ORTEP diagram of **1** shown with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°):  $\text{Ce1}-\text{O1} = 2.653(2)$ ,  $\text{Ce1}-\text{O2} = 2.562(2)$ ,  $\text{Ce1}-\text{N1} = 2.385(3)$ ,  $\text{Ce1}-\text{N2} = 2.367(2)$ ,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



for 24 h at room temperature in the absence of light, still consisted primarily of complex **1**, as determined by  $^1\text{H}$  NMR spectroscopy. However, we do observe the formation of several new species in this sample, in small amounts, as revealed by resonances at 0.69, 0.20, and  $-0.58$  ppm (see Fig. S10 in the ESI†). These were later identified as belonging to  $[\text{Li}(2,2,2\text{-cryptand})][\text{Ce}(\text{O})(\text{NR}_2)_3]$  (**2**),  $[\text{Li}(2,2,2\text{-cryptand})]_2[(\mu_3\text{-O})\{\text{Ce}(\mu\text{-O})(\text{NR}_2)_2\}_3]$  (**3**), and  $[\text{Li}(2,2,2\text{-cryptand})][\text{Ce}(\text{OSiMe}_3)(\text{NR}_2)_3]$  (**4**), respectively (*vide infra*). These three complexes were present in a relative ratio of 2 : 27 : 1. The relatively high thermal stability of **1** led us to conclude that formation of a terminal Ce(IV) oxo complex through thermal activation of the nitrate co-ligand in **1** was not synthetically viable.

Given the relatively high thermal stability of **1**, we sought an alternative route to reduce its nitrate co-ligand. Schelter and co-workers previously reported that photolysis of  $[\text{Ce}(\text{NR}_2)_3]$  resulted in formation of a relatively long-lived excited state.<sup>25,26</sup> This excited state species is strongly reducing, and can elicit homolytic cleavage of the C–Cl bond in  $\text{PhCH}_2\text{Cl}$ , resulting in formation of  $[\text{Ce}(\text{Cl})(\text{NR}_2)_3]$  and bibenzyl.<sup>25</sup> The UV-vis spectrum of **1** features two absorptions at 380 nm ( $\epsilon = 200 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 336 nm ( $\epsilon = 140 \text{ M}^{-1} \text{ cm}^{-1}$ ) (Fig. S14†), and is similar to that reported for  $[\text{Ce}(\text{NR}_2)_3]$ .<sup>25</sup> We have assigned the former absorption to a metal-based  $4f \rightarrow 5d_{z^2}$  transition and the latter to a  $4f \rightarrow 5d_{xz/yz}$  transition, by analogy with the assignments reported for  $[\text{Ce}(\text{NR}_2)_3]$ . For comparison, these transitions occur at 413 nm and 341 nm, respectively, in  $[\text{Ce}(\text{NR}_2)_3]$ . We attribute the *ca.* 30 nm blue shift observed for the  $4f \rightarrow 5d_{z^2}$  transition in **1** to the presence of the additional nitrate co-ligand, as well as its overall negative charge.

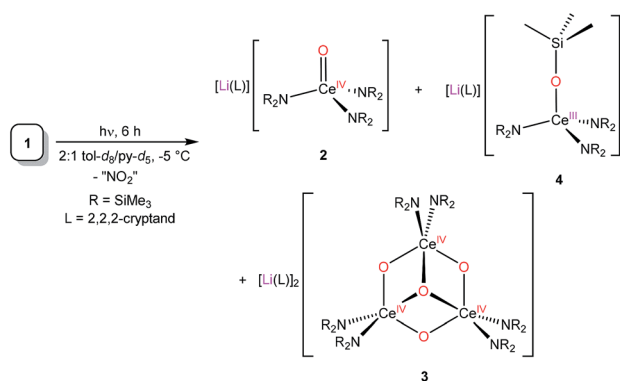
Given the similar optical properties of **1** and  $[\text{Ce}(\text{NR}_2)_3]$ , we hypothesized that photolysis of **1** would induce reduction of the nitrate ligand to afford a Ce(IV) oxo complex. To this end, a 2 : 1 *tol-d*<sub>8</sub>/*py-d*<sub>5</sub> solution of **1**, in an NMR tube equipped with a J-Young valve, was exposed to light from a 380 nm LED lightstrip for 6 h at  $-5^\circ\text{C}$  (Scheme 2). A  $^1\text{H}$  NMR spectrum of this sample revealed an approximately 80% consumption of **1**, as evidenced by the attenuation of its  $\text{SiMe}_3$  resonance at  $-1.18$  ppm. In addition, we observe the appearance of a sharp singlet at 0.80 ppm, as well as the appearance of broad singlets at 0.28,  $-0.21$ , and  $-0.43$  ppm (see Fig. S3 in ESI†). We assigned

the sharp singlet at 0.80 ppm to the terminal Ce(IV) oxo complex  $[\text{Li}(2,2,2\text{-cryptand})][\text{Ce}(\text{O})(\text{NR}_2)_3]$  (**2**), while we have tentatively assigned the resonance at 0.28 ppm to the Ce(IV) oxo cluster  $[\text{Li}(2,2,2\text{-cryptand})]_2[(\mu_3\text{-O})\{\text{Ce}(\mu\text{-O})(\text{NR}_2)_2\}_3]$  (**3**). In addition, the resonances at  $-0.21$  and  $-0.43$  ppm, which integrate to 9 and 54 protons, respectively, are assignable to the Ce(III) silyloxo  $[\text{Li}(2,2,2\text{-cryptand})][\text{Ce}(\text{OSiMe}_3)(\text{NR}_2)_3]$  (**4**). After 6 h of photolysis, these three species were present in an approximately 11 : 2.5 : 1 ratio, according to NMR spectroscopy (Fig. S4†). Attempts to photolyse the reaction mixture for longer times, in an attempt to get complete consumption of **1**, lead to decreased yields of **2**. We also found that the use of the 2 : 1 *tol-d*<sub>8</sub>/*py-d*<sub>5</sub> solvent system was critical to maximize the amount of **2** formed in the reaction mixture. If we perform the photolysis in neat *py-d*<sub>5</sub>, the relative amount of **2** decreased substantially; under these conditions complexes **2** and **3** are formed in nearly equal amounts. Moreover, photolyses performed in neat *tol-d*<sub>8</sub> proved impractical because of the low solubility of complex **1** in that solvent. Finally, we observed that photolyses conducted in NMR tubes result in the most efficient consumption of **1**, likely due to their high surface-to-volume ratio.

Work-up of the reaction mixture resulted in the isolation of complex **2** as yellow plates in 33% yield. Its formulation was confirmed by X-ray crystallography (see below). In one instance, we also observed the deposition of small amounts of pale yellow crystals and colorless plates, which were subsequently identified as **3** and **4**, respectively, by X-ray crystallography.

Complex **2** crystallizes in the monoclinic space group  $P2_1/c$  (Fig. 2). In the solid state, **2** displays a terminal Ce=O linkage and a pseudo-tetrahedral geometry about the cerium centre. Its Ce–O bond length (1.840(7) Å) is shorter than those observed for **II** (1.902(2) Å), **III** (1.887(4)–1.902(4) Å), and **IV** (1.908(3) Å),<sup>5,8,9</sup> possibly because of the absence of any alkali metal–oxo interaction in **2**.<sup>5,8</sup> The Ce–O distance in **2** is also shorter than that calculated for  $[\text{K}(18\text{-crown-6})][\text{Ce}(\text{O})(\text{NR}_2)_3]$  (1.904 Å), which also features an alkali metal–oxo interaction.<sup>8</sup> Interestingly, however, the Ce–O distance in **2** is identical to that observed for hydrogen-bond stabilized **I** (1.857(3) Å) by the 3 $\sigma$  criterion,<sup>3</sup> suggesting that the hydrogen bonding interaction in **I** does not substantially disrupt the Ce=O bond. Also of note, the Ce–N distances in **2** (2.353(8)–2.397(8) Å) are slightly longer than those reported for other Ce(IV) amides. For example, the Ce–N distances in  $\text{Ce}(\text{NCy}_2)_4$  range from 2.238(5) to 2.247(6) Å, while those of  $[\text{Ce}(\text{X})(\text{NR}_2)_3]$  (X = Cl, Br) are 2.217(3) and 2.219(7) Å, respectively.<sup>19,27,28</sup> This lengthening may be a consequence of the strongly donating nature of the oxo ligand, along with the complex's overall negative charge, which weakens the Ce–N bonds. For further comparison,  $[\text{Li}(12\text{-crown-4})][(\text{NN}'_3)\text{Ce}(\text{O})]$  also features longer than expected Ce–N distances.<sup>8</sup> Finally, the Li-binding mode of the 2,2,2-cryptand moiety in **2** is similar to that observed in **1**. However, in **2**, six of the eight donor atoms in the cryptand moiety are bound to the lithium ion; only one nitrogen atom and one oxygen atom remain uncoordinated.

Complex **2** is soluble in toluene,  $\text{Et}_2\text{O}$ , benzene, and pyridine, but decomposes when exposed to THF, acetonitrile, and dichloromethane (forming  $\text{HN}(\text{SiMe}_3)_2$  as the only identifiable product). Its  $^1\text{H}$  NMR spectrum in *py-d*<sub>5</sub> features a sharp singlet



Scheme 2 Synthesis of complexes **2**, **3**, and **4** via photolysis of **1**.



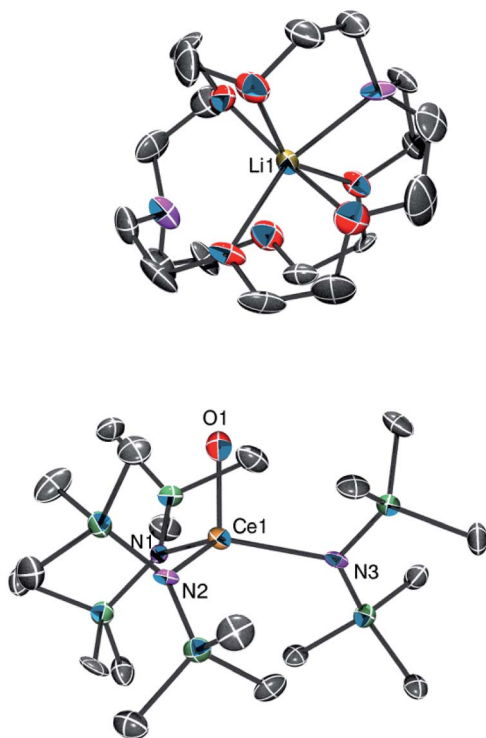


Fig. 2 ORTEP diagram of **2** shown with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ce1–O1 = 1.840(7), Ce1–N1 = 2.397(8), Ce1–N2 = 2.353(8), Ce1–N3 = 2.383(8), N2–Ce1–N1 = 116.4(3), N3–Ce1–N1 = 113.4(3), N2–Ce1–N3 = 116.8(3), O1–Ce1–N1 = 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 SiMe<sub>3</sub> 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 SiMe<sub>3</sub> resonance is nearly identical to that assigned to this complex in the spectrum of the crude reaction mixture (Fig. S4†). The <sup>7</sup>Li{<sup>1</sup>H} 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)]<sup>+</sup> ion.<sup>29,30</sup> 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(SiMe<sub>3</sub>)<sub>2</sub> (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 Ce<sub>3</sub>O<sub>4</sub> core. Each Ce centre is also ligated by two silylamide ligands. Additionally, **3** features two [Li(2,2,2-cryptand)]<sup>+</sup> counterions, confirming the tetravalent oxidation state of each cerium atom. The Ce–O distances observed for the three μ<sub>2</sub>-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)

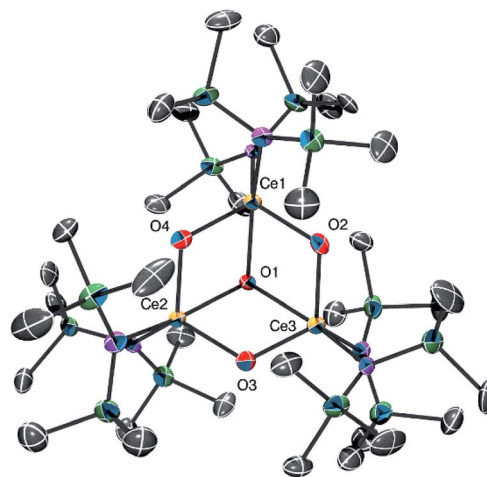


Fig. 3 ORTEP diagram of **3** shown with 50% probability ellipsoids. Hydrogen atoms, diethyl ether solvate and two [Li(2,2,2-cryptand)] counter-ions are omitted for clarity. Selected bond distances (Å) and angles (°): Ce1–O1 = 2.294(7), Ce1–O2 = 2.078(7), Ce1–O4 = 2.133(7), Ce2–O1 = 2.310(7), Ce2–O3 = 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(NR<sub>2</sub>)<sub>2</sub>]<sub>3</sub>],<sup>9</sup> reported by Lappert and co-workers. The Ce–O distances observed for the μ<sub>3</sub>-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 [Ce<sub>3</sub>(μ<sub>3</sub>-oxo)] clusters.<sup>31,32</sup> 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 μ<sub>2</sub>- or μ<sub>3</sub>-hydroxo ligands are anticipated to be substantially longer than the Ce–O distances observed for **2**.<sup>33,34</sup> 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.<sup>19,27,28</sup> 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)]<sup>+</sup> 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<sub>SiPh<sub>3</sub></sub> distance in Ce(OSiPh<sub>3</sub>)<sub>3</sub>(THF)<sub>3</sub> (2.22 Å).<sup>35</sup> 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(OSiPh<sub>3</sub>)<sub>3</sub>(THF)<sub>3</sub> (av. 174°)<sup>35</sup> and [(NN′<sub>3</sub>)Ce(OSiMe<sub>2</sub><sup>t</sup>Bu)] (167.2(2)°).<sup>8</sup>

Conveniently, complex **4** can be synthesized independently via reaction of [Ce(NR<sub>2</sub>)<sub>3</sub>] with LiOSiMe<sub>3</sub> in THF, in the presence of 2,2,2-cryptand (eqn (2)), permitting its complete





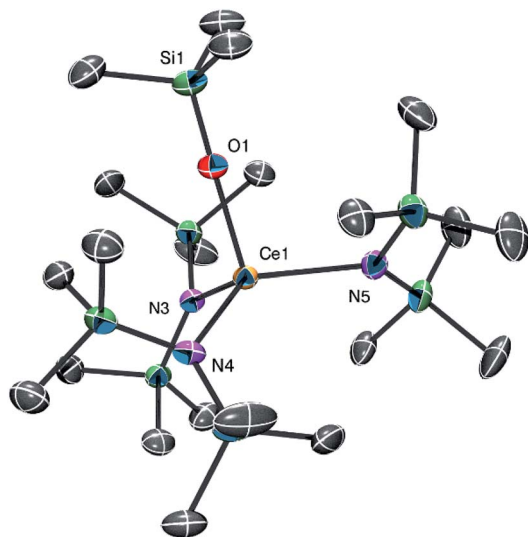
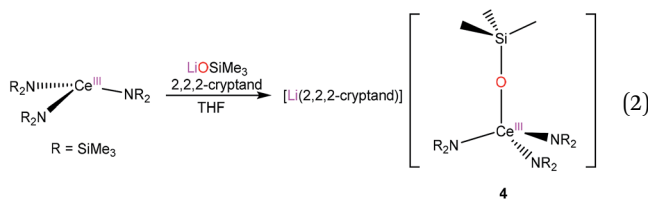


Fig. 4 ORTEP diagram of **4** shown with 50% probability ellipsoids. Hydrogen atoms and [Li(2,2,2-cryptand)] counterion are omitted for clarity. Selected bond distances (Å) and angles (°): Ce1–O1 = 2.214(3), Ce1–N3 = 2.430(4), Ce1–N4 = 2.396(4), Ce1–N5 = 2.413(4), O1–Si1 = 1.607(4), N4–Ce1–N3 = 109.97(13), 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  $^1\text{H}$  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 OSiMe<sub>3</sub> and N(SiMe<sub>3</sub>)<sub>2</sub> 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  $^1\text{H}$  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 NO<sub>2</sub>, *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) silyloxide, [Ce<sup>IV</sup>(OSiMe<sub>3</sub>)(NR<sub>2</sub>)<sub>3</sub>], followed by 1e<sup>−</sup> reduction to form **4**. Alternatively, complex **4** could form directly *via* ·SiMe<sub>3</sub> 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  $^1\text{H}$  NMR spectrum of the photolysis reaction mixture (Fig. S4†), which is assignable to LiN(SiMe<sub>3</sub>)<sub>2</sub>. Its presence is consistent with the proposed conversion of **2** to **3** *via* ligand scrambling and loss of LiN(SiMe<sub>3</sub>)<sub>2</sub>. Finally, we previously demonstrated that the Ce(IV) silyloxide, [(NN′<sub>3</sub>)Ce(OSi<sup>t</sup>BuMe<sub>2</sub>)], was formed as a minor by-product during the conversion of [Li(12-crown-4)][(NN′<sub>3</sub>)Ce(κ<sup>2</sup>-O<sub>2</sub>NO)] to the Ce(IV) oxo, [Li(12-crown-4)][(NN′<sub>3</sub>)Ce(O)],<sup>8</sup> presumably *via* a similar adventitious [SiR<sub>3</sub>]<sup>+</sup> abstraction.

To test the thermodynamic favourability of the proposed 1e<sup>−</sup> 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<sup>−1</sup> (*vs.* Fc/Fc<sup>+</sup>; 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<sup>−1</sup>), 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)(NR<sub>2</sub>)<sub>3</sub>] ( $-0.56$  V), [Ce(Cl)(NR<sub>2</sub>)<sub>3</sub>] ( $-0.30$  V) and [Ce(Br)(NR<sub>2</sub>)<sub>3</sub>] ( $-0.31$  V),<sup>36–38</sup> its electrochemical irreversibility suggests that [Ce<sup>IV</sup>(OSiMe<sub>3</sub>)(NR<sub>2</sub>)<sub>3</sub>] is not particularly stable. Therefore, complex **4** may not be formed *via* a straightforward 1e<sup>−</sup> reduction of a [Ce<sup>IV</sup>(OSiMe<sub>3</sub>)(NR<sub>2</sub>)<sub>3</sub>] intermediate. Instead, the cyclic voltammetry data may be evidence for a concerted ·SiMe<sub>3</sub> abstraction by **2** to form **4**. A similar ·SiMe<sub>3</sub> abstraction by the uranyl fragment has been reported by Arnold and co-workers.<sup>39–41</sup>

## 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)(NR<sub>2</sub>)<sub>3</sub>] (**2**). This complex was generated by photolysis of the Ce(III) nitrate precursor [Li(2,2,2-cryptand)][Ce(κ<sup>2</sup>-O<sub>2</sub>NO)(NR<sub>2</sub>)<sub>3</sub>] (**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)]<sub>2</sub>[(μ<sub>3</sub>-O)Ce(μ-O)(NR<sub>2</sub>)<sub>2</sub>]<sub>3</sub> (**3**), and the Ce(III) silyloxide complex, [Li(2,2,2-cryptand)][Ce(OSiMe<sub>3</sub>)(NR<sub>2</sub>)<sub>3</sub>] (**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 [NO<sub>3</sub>]<sup>−</sup> as a 1e<sup>−</sup> 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<sup>−</sup> O-atom transfer from [NO<sub>3</sub>]<sup>−</sup>. This is anticipated to be a greater synthetic challenge because the lower Ln oxidation state results in reduced Ln–O bond covalency.<sup>42</sup>

## Conflicts of interest

There are no conflicts to declare.



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