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Single Crystal to Single Crystal Transformation and Hydrogen-Atom Transfer upon Oxidation of a Cerium Coordination Compound

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Supporting Information

ABSTRACT: Trivalent and tetravalent cerium compounds of the octamethyltetraazaannulene (H_2omtaa) ligand have been synthesized. Electrochemical analysis shows a strong thermodynamic preference for the formal cerium(IV) oxidation state. Oxidation of the cerium(III) congener Ce(Homtaa)(omtaa) occurs by hydrogen-atom transfer that includes a single crystal to single crystal transformation upon exposure to an ambient atmosphere.

Binary cerium oxides show reversible redox behavior in the solid state that is important in heterogeneous catalytic processes, including applications in fuel cells and three-way catalytic converters.[1] This reactivity is predicated on the oxidation of cerium(III) sesquioxide, Ce_2O_3, to cerium(IV) oxide, CeO_2, in the presence of molecular oxygen.[2] In its molecular chemistry, cerium is typically most stable in its trivalent state; cerium(IV) ions show a formal oxidation potential of +1.3 V versus Fc/Fc^+ in $HClO_4$.[3] However, recent work has shown that the cerium(III/IV) couple has a highly tunable redox potential in response to the electronic nature of its environment.[4] In nonaqueous systems, cerium ions can demonstrate dramatically different redox behavior, with reported metal-based waves shifted to reducing potentials.[4a−c,f,g] As part of an ongoing study of cerium redox chemistry, we sought to characterize a series of related cerium compounds in an electron-donating double-decker framework in order to harness the reducing capability of cerium(III) ions on a molecular scale.

Rare-earth ions typically form 1:2 sandwich complexes with anions of the 6,8,15,17-tetramethyldibenzotetraaza[14]annulene (tetramethyltetraazaannulene, H_2tmtaa) ligand, although 2:3 "triple-decker" compounds have also been reported.[5] Double-decker sandwich structures of this type include a central trivalent rare-earth cation stabilized by 2 equiv of the tetradentate dianionic ligand as well as 1 equiv of an alkali-metal cation.[6] Rare-earth double-decker compounds have also been reported with their charges stabilized by one fully deprotonated dianionic tmtaa^{2-} ligand and one singly protonated monoanionic Htmtaa$^-$ ligand.[5b,7] Recently, the cerium(III) compound Ce(Htmtaa)(tmtaa) was reported and was shown to undergo facile conversion to the cerium(IV) compound Ce(tmtaa)$_2$ in the presence of mild oxidants including O_2, benzoquinone, and $[Cp_2Fe][PF_6]$.[5b] The oxidation state of Ce(tmtaa)$_2$ was confirmed as cerium(IV) using X-ray absorption spectroscopy.[8] Of the reported compounds, only the cerium(IV) compound Ce(tmtaa)$_2$ was structurally characterized.

In order to better understand the electrochemical and chemical implications of oxidation from cerium(III) to cerium(IV) observed for Ce(Htmtaa)(tmtaa), we have synthesized and characterized new cerium complexes of the 2,3,6,8,11,12,15,17-octamethyldibenzotetraaza[14]annulene (octamethyltetraazaannulene, H_2omtaa) ligand (Scheme 1). Upon exposure to an ambient atmosphere, Ce(Homtaa)(omtaa) (**1**) undergoes a single crystal to single crystal (SCSC) transformation with only minor perturbations to the primary coordination environment of the metal ion. Furthermore, the solution-phase redox behavior of **1** shows that it is a potent reductant that undergoes concomitant loss of a proton and an electron.

$Ce[N(Si(CH_3)_3)_2]_3$ was synthesized according to a published procedure[9] and reacted with 2 equiv of H_2omtaa to produce red-brown **1** in good yields (Scheme 1).[5b] The solubility of complex **1** enabled the growth of well-defined single crystals for its structural determination. Whereas the crystallographic structure of the reported Ce(Htmtaa)(tmtaa) could not be refined due to disorder,[5b] compound **1** provided a good X-ray solution and refinement. The structure of **1** shows the expected 1:2 sandwich structure with eclipsed saddle-shaped omtaa^{2-} ligands in an approximate D_{2d} geometry about the cerium ion (Figure 1).[5b,6,7b,10] The hydrogen cations required for charge balance of the cerium(III) complex **1** could not be specifically located in the structure in **1**. However, the Ce−N bond distances in **1**, ranging from 2.5260(16) to 2.5690(16) Å, are consistent with the assigned cerium(III) oxidation state.[6a] Unlike other structurally characterized complexes that include a trivalent rare-earth ion in a double-decker tetraazaannulene framework, the bonds between the cerium ion and the nitrogen atoms in each of the omtaa^{2-} ligands are equivalent by crystallographically imposed symmetry. While the crystal data show a very symmetric environment about the cerium(III) center, 11 resonances were observed in the ^{1}H NMR analysis of **1** in C_6D_6, corresponding to a desymmetrized compound. We attribute this solution behavior to the coordination of two distinctly different ligands to the cerium(III) ion: one that is best described as Homtaa$^-$ and the other as omtaa^{2-}. These data suggest that the equivalent bond lengths between the cerium(III) ion and the nitrogen atoms in each of the omtaa^{2-} ligands in the solid-state structure result from disorder of the hydrogen atoms in the lattice of **1**.

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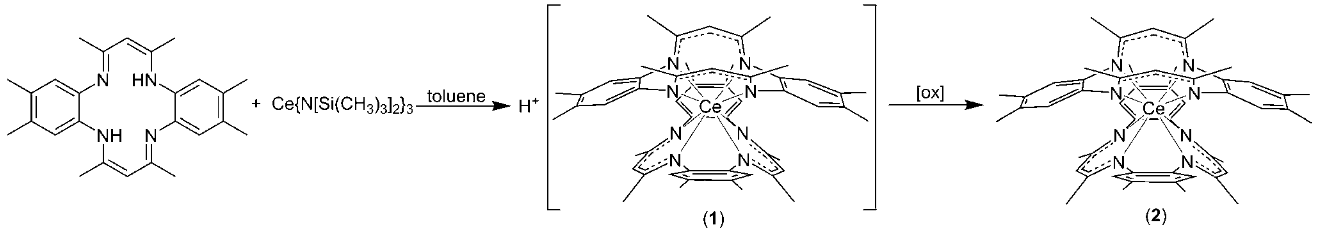
Scheme 1. Syntheses of 1 and 2, Where [ox] = TEMPO or O_2



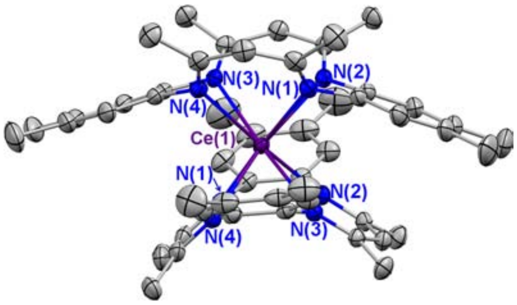


Figure 1. Thirty percent probability thermal ellipsoid plot of compound **1**. Hydrogen atoms have been removed for clarity. Selected bond distances (Å): Ce(1)−N(1) 2.5517(17), Ce(1)−N(2) 2.5690(16); Ce(1)−N(3) 2.5570(17); Ce(1)−N(4) 2.5260(16).

Exposure of crystalline, red-brown samples of **1** to an ambient atmosphere yielded the cerium(IV) complex Ce(omtaa)$_2$ (**2**) quantitatively over a period of 30 min, concomitant with a color change of the crystals to dark green. The ^{1}H NMR spectrum of **2**, recorded in benzene-d_6, revealed changes that support oxidation from a paramagnetic cerium(III) center to a closed-shell formally cerium(IV) complex. The ^{1}H NMR spectrum of **2** shows four sharp resonances from +7.24 to +1.86 ppm. While the transformation of **1** to form **2** necessarily proceeds through the loss of a proton and an electron, attempts to spectroscopically observe the byproducts of the reaction of **1** with O_2 were unsuccessful. Exposure of single crystals of **1** to an ambient atmosphere or O_2 followed by dissolution in C_6D_6 showed only resonances corresponding to **2** by ^{1}H NMR. Similarly, exposure of crystals of the deuterated analogue of **1**, Ce(Domtaa)(omtaa) (**1D**), to an ambient atmosphere or O_2 followed by dissolution in benzene showed no resonances by ^{2}H NMR.

To study the nature of the oxidation reaction in the solid state, single-crystal X-ray diffraction data were collected on a dark-red-brown sample of **1** that had been covered in Paratone oil. Following data collection, the crystal was warmed to room temperature under an ambient atmosphere and was left on the goniometer head for 24 h to induce complete conversion to **2**. A data set was then collected on the same crystal, which had turned dark green. The X-ray data confirmed the SCSC transformation of **1**→ **2** upon exposure to the atmosphere.

The crystal structure of **2** (Figure S2 in the Supporting Information, SI) shows Ce−N bond distances that are contracted in comparison to the structure of **1**; the Ce−N bond distances in **2** range from 2.4367(15) to 2.4600(16) Å and are consistent with the assigned cerium(IV) oxidation state.[5b] A comparison of the unit cell dimensions of **1** and **2** shows conservation of molecular packing (Table 1). The system retains the monoclinic space group *C*2/*c* during oxidation and exhibits only small changes to the unit cell parameters, as shown in Table 1. SCSC transformations have been observed in rare-earth complexes concomitant with changes in solvation, temperature, or exposure to UV light.[11] However, the redox-driven SCSC transformation described here is unprecedented in reported lanthanide coordination chemistry.

Table 1. Crystal Data Showing Similarity of the Structural Data in Compounds 1 and 2, Which Facilitates SCSC Transformation

	1	2
space group	*C*2/*c*	*C*2/*c*
a (Å)	18.524(4)	18.620(3)
b (Å)	18.559(3)	18.510(3)
c (Å)	16.309(3)	16.014(2)
β (deg)	94.435(9)	98.146(7)
V (Å^3)	5590.0(18)	5463.6(14)
Z	4	4
T (K)	143(1)	143(1)
Ce−N (Å)	2.5260(16)−2.5690(16)	2.4367(15)−2.4600(16)

The facile oxidation of compound **1** in the solid state prompted exploration of the solution chemistry of **1** and **2**. Electrochemical analysis of **2** shows a reversible metal-based wave centered at −1.7 V versus Fc/Fc$^+$ in THF with 0.1 M [^{n}Pr$_4$N][BAr$^F{}_4$] (Figure 2). Assignment of this wave as the metal-based feature was made by comparison of the cyclic voltammograms of **2** and the H$_2$omtaa ligand (Figure S4 in the SI). On the basis of this electrochemical analysis, compound **2** represents the most highly reducing, reversible cerium(III/IV) wave that has been described. To the best of our knowledge, two cerium-containing compounds with more reducing potentials than **2** have been reported; both compounds show irreversible electrochemical behavior.[4f,g]

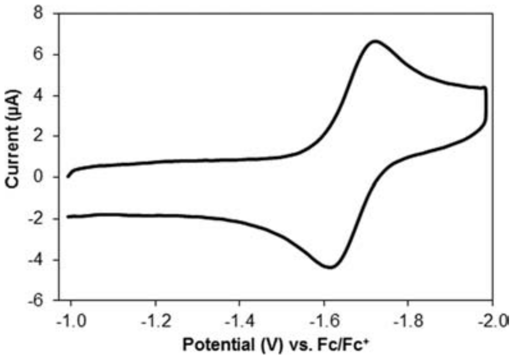
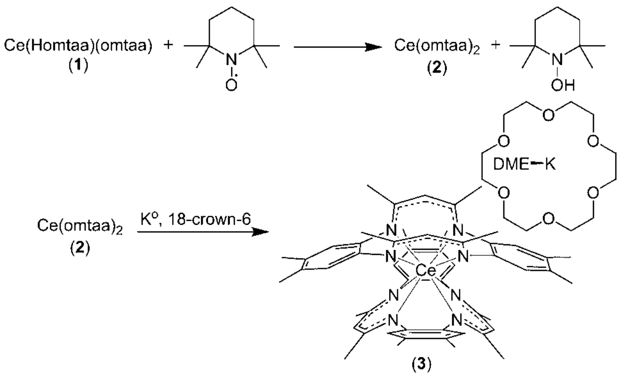


Figure 2. Isolated Ce(III/IV) couple in the cyclic voltammogram of **2** centered at −1.7 V vs Fc/Fc$^+$ in THF with 0.1 M [^{n}Pr$_4$N][BAr$^F{}_4$]; [**2**] = ca. 1 mM; ν = 500 mV/s.

In order to understand the reaction pathway involved in the oxidation of **1** to **2**, chemical oxidation of **1** was explored. In solution, **1** is oxidized in the presence of the stable organic radical TEMPO to yield TEMPO-H and **2**, as detected by ^{1}H NMR spectroscopy (Scheme 2). The production of TEMPO-H results from hydrogen-atom transfer from **1** to TEMPO and is promoted by oxidation of the cerium center. Deuterium-labeling experiments were used to show that compound **1** is the source of the hydrogen atom donated to TEMPO. Reaction of the deuterated compound **1D** with 1 equiv of TEMPO yielded compound **2** and TEMPO-D, as evidenced by a peak in the ^{2}H NMR spectrum at 3.68 ppm, recorded in proteobenzene (Figure S15 in the SI).

Scheme 2. Reaction of 1 with TEMPO (Top) and Reduction of 2 in the Presence of Potassium and 18-Crown-6 (Bottom)



Chemical reduction of the cerium(IV) center in compound **2** was accomplished using potassium metal in the presence of 18-crown-6, yielding [K(DME)(18-crown-6)][Ce(omtaa)$_2$] (**3**; DME = 1,2-dimethoxyethane; Scheme 2). Crystallization of **3** from a mixture of DME and toluene allowed for isolation of pure compound **3**, as confirmed by CHN combustion analysis. Because of the very air-sensitive nature of the compound as well as the high surface area of the platelike crystals, fully refined structural data were not obtained for **3**. However, a preliminary solution collected on **3** did confirm the expected connectivity of the atoms with two disordered omtaa^{2-} ligands sandwiching the cerium(III) center and 1 equiv of 18-crown-6 and DME bound to the potassium ion (Figure S5 and Table S1 in the SI). This structural motif is common to analogous reported compounds, which include a trivalent rare-earth ion sandwiched by two tmtaa^{2-} ligands.[6b]

In summary, the oxidation of compound **1** has been explored in both the solid-state and solution phases. In the solid state, oxidation of the cerium(III) center proceeds through a SCSC transformation upon exposure to an ambient atmosphere. In the solution phase, we have shown reversible redox behavior of **2** at a highly reducing potential and have taken advantage of the facile oxidation of a cerium(III) ion in the omtaa^{2-} ligand framework to promote hydrogen-atom donation to an organic substrate. Although the transformation of **1** to **2** is as yet irreversible, these results illustrate the possibility of manipulating small-molecule equivalents with redox changes, reminiscent of the behavior of CeO$_2$, using a molecular material in a conserved framework. Further work is underway to explore molecular cerium materials in this context.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files (CIFs), full experimental details, cyclic voltammograms, and NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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