

"This is the peer reviewed version of the following article: [J. Am. Chem. Soc. 2019, 141, 9827–9831] which has been published in final form at [Link to final article using the DOI: DOI: 10.1021/jacs.9b05337]. This article may be used for non-commercial purposes in accordance with the American Chemical Society Terms and Conditions for Self-Archiving."

## A Molecular Complex of Tb in the +4 Oxidation State

Chad T. Palumbo,<sup>a</sup> Ivica Zivkovic,<sup>b</sup> Rosario Scopelliti,<sup>a</sup> and Marinella Mazzanti\*

<sup>a</sup>. Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

<sup>b</sup>. Laboratory for Quantum Magnetism, Institute of Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

### Supporting Information Placeholder

**ABSTRACT:** Lanthanides (Ln) usually occur in the +3, or more recently the +2, oxidation states. The only example of an isolated molecular Ln<sup>+4</sup> so far remains Ce<sup>4+</sup>. Here we show that the +4 oxidation state is also accessible in a molecular compound of terbium as demonstrated by oxidation of the tetrakis(siloxide)terbium(III) ate complex, [KTb(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>4</sub>], **1-Tb**, with the tris(4-bromophenyl)ammonium oxidant, [N(C<sub>6</sub>H<sub>4</sub>Br)<sub>3</sub>][SbCl<sub>6</sub>], to afford the Tb<sup>4+</sup> complex [Tb(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>4</sub>], **2-Tb**. The solid state structures of **1-Tb** and **2-Tb** were determined by X-ray crystallography and the presence of Tb<sup>4+</sup> was unambiguously confirmed by EPR and magnetometry. **2-Tb** displays a similar voltammogram to the Ce<sup>4+</sup> analogue but with redox events that are about 1 V more positive.

The chemistry of lanthanides (Ln) has been limited mostly to the + 3 oxidation state. Only recently it has been shown that the oxidation state + 2 is accessible for all lanthanides by using bulky supporting ligands and appropriate reaction conditions.<sup>1</sup> In contrast, molecular complexes of lanthanides in the oxidation state + 4 remain limited to the special case of the 4f<sup>0</sup> cerium ion.<sup>2</sup> The high oxidizing power of Ce<sup>4+</sup> (the Ce<sup>4+</sup>/Ce<sup>3+</sup> redox potential ranges from 1.87 to -0.86 vs NHE depending on the solvent and supporting ligand)<sup>3</sup> has led to the rapid application of its compounds in various fields ranging from organic syntheses to materials science.<sup>4</sup> Ce<sup>4+</sup> chemistry is well developed, but in order to avoid redistribution products, the rational synthesis of Ce<sup>4+</sup> complexes requires a careful choice of oxidizing agent and solvent and careful consideration of cation effects and ligand exchange dynamics.<sup>3,5</sup>

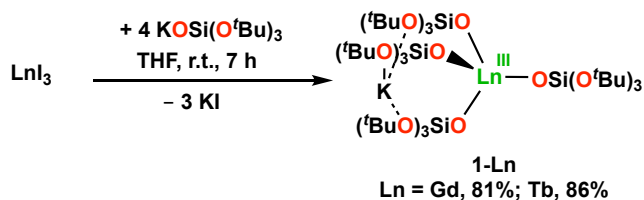
The terbium ion should have the next most accessible +4 oxidation state according to the calculated redox potential of 3.3 V

vs NHE,<sup>6</sup> but Tb<sup>4+</sup> so far has only been observed in concentrated aqueous carbonate solutions<sup>7</sup> and in a few inorganic solids such as metal oxides or fluorides.<sup>6a,8</sup> Further, Tb<sup>4+</sup> in TbO<sub>2</sub> has been recently identified as a potential candidate for solar thermochemical reactions.<sup>9</sup> While a molecular complex of the 5f analogue Bk<sup>4+</sup> has been recently reported,<sup>10</sup> attempts to produce Tb<sup>4+</sup> in molecular compounds were so far not successful,<sup>11</sup> resulting in ligand rather than metal oxidation, leaving the question of the possibility of isolating complexes of Ln<sup>+4</sup> other than Ce<sup>4+</sup> open.<sup>2a</sup>

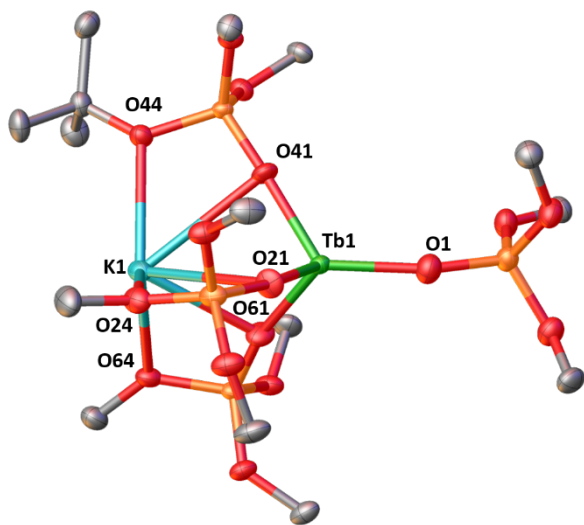
Our group<sup>12</sup> and others<sup>13</sup> have reported the ability of tris(tertbutoxy)siloxide to stabilize lanthanide ions in various oxidation states. In particular, both the Ce<sup>3+</sup> and the Ce<sup>4+</sup> homoleptic tetrakis(tertbutoxy)siloxide complexes [KCe(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>4</sub>], **1-Ce**, and [Ce(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>4</sub>], **2-Ce**, were prepared and crystallographically characterized.<sup>12b</sup> Here we show that the tris(tertbutoxy)siloxide ligand allows the synthesis and characterization of the first example of a molecular complex of Tb<sup>4+</sup>. The 4f<sup>7</sup> terbium complex [Tb(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>4</sub>], **2-Tb**, was prepared by oxidation of the Tb<sup>3+</sup> analogue, [KTb(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>4</sub>], **1-Tb**, using [N(C<sub>6</sub>H<sub>4</sub>Br)<sub>3</sub>][SbCl<sub>6</sub>] as the oxidizing agent. We have also prepared the isoelectronic 4f<sup>7</sup> Gd<sup>3+</sup> complex, [KGd(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>4</sub>], **1-Gd**, for comparison.

The potassium tetrakis(siloxide) Ln<sup>3+</sup> complexes, [KLn(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>4</sub>] (Ln = Gd, Tb), **1-Ln**, were prepared from the reaction of KOSi(O<sup>t</sup>Bu)<sub>3</sub> with the anhydrous lanthanide triiodides GdI<sub>3</sub> and TbI<sub>3</sub> in 81% and 86% yield for Gd and Tb, respectively, Scheme 1.

**Scheme 1. Synthesis of [KLn(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>4</sub>] (Ln = Gd, Tb), 1-Ln.**



The NMR spectrum of **1-Tb** (Figure S1) at 298 K shows only one broad resonance at -26 ppm in toluene-*d*<sub>8</sub>, indicating fluxional behavior of the siloxide ligands that is slowed down at low temperature. Several signals are observed at 193 K, and they coalesce at 223 K into two signals (Figure S2). At 263 K, the four siloxide ligands are equivalent on the NMR time scale (Figure S3). Crystals of **1-Tb** characterizable by X-ray diffraction were grown upon storage of a concentrated toluene solution at -40 °C overnight, Figure 1. Complex **1-Tb** is isostructural with the previously reported [KYb(OSi(O<sup>*t*</sup>Bu)<sub>3</sub>)<sub>4</sub>] complex<sup>12a</sup> and presents a 4-coordinate Tb<sup>3+</sup> ion with one κ<sup>1</sup>-OSi(O<sup>*t*</sup>Bu)<sub>3</sub> ligand and three μ-κ<sup>2</sup>:*O,O*-OSi(O<sup>*t*</sup>Bu)<sub>3</sub> ligands which bridge the Tb<sup>3+</sup> and K<sup>+</sup> cations. In contrast, in the previously reported [KCe(OSi(O<sup>*t*</sup>Bu)<sub>3</sub>)<sub>4</sub>] complex,<sup>12b</sup> the Ce<sup>3+</sup> ion is 5-coordinate with one κ<sup>2</sup>:*O,O*-OSi(O<sup>*t*</sup>Bu)<sub>3</sub> ligand and three μ-κ<sup>2</sup>:*O,O*-OSi(O<sup>*t*</sup>Bu)<sub>3</sub> ligands that bridge the Ce<sup>3+</sup> and K<sup>+</sup>. The difference in structure is attributed to the larger ionic radius of Ce<sup>3+</sup> compared to Tb<sup>3+</sup> and Yb<sup>3+</sup> (6-coordinate Shannon radii: Ce<sup>3+</sup>, 1.01 Å; Tb<sup>3+</sup>, 0.923 Å; Yb<sup>3+</sup>, 0.868 Å).<sup>14</sup>

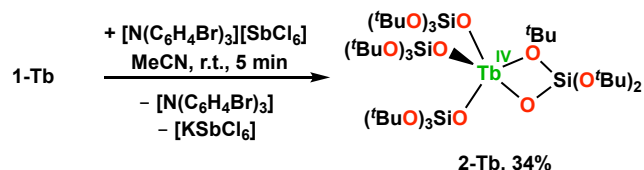


**Figure 1.** Molecular structure of [KTb(OSi(O<sup>*t*</sup>Bu)<sub>3</sub>)<sub>4</sub>], **1-Tb**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, methyl groups on the siloxide ligands, and a second molecule of **1-Tb** present in the unit cell have been omitted for clarity.

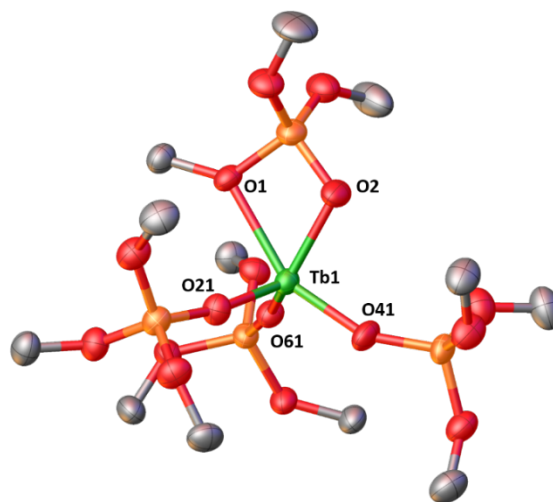
Treatment of **1-Tb** with AgI in either THF or CH<sub>2</sub>Cl<sub>2</sub> gave no reaction. However, treatment of **1-Tb** with a stronger oxidizing agent, namely, the tris(4-bromophenyl)amminium hexachloroantimonate salt, [(N(C<sub>6</sub>H<sub>4</sub>Br)<sub>3</sub>][SbCl<sub>6</sub>)]<sup>15</sup> resulted in an immediate color change and gave an intense orange colored solution. Removal of THF and recrystallization from hexane yielded bright orange single crystals of **2-Tb**, which were characterized by X-ray crystallography, Figure 2. The UV-visible spectrum generated from crystals of **2-Tb** dissolved in toluene shows a broad absorption at λ<sub>max</sub> = 371 nm with a molar extinction

coefficient ε of 4200 M<sup>-1</sup>·cm<sup>-1</sup> (Figure S4). A similar feature (λ<sub>max</sub> = 365 nm) was reported for electrochemically generated solutions of Tb<sup>4+</sup> in 5.5M of K<sub>2</sub>CO<sub>3</sub>. Complex **2-Tb** is stable in toluene for several days, but in THF, the orange solution immediately begins to decolorize and within hours is completely colorless. We found that the synthesis of **2-Tb** is improved in MeCN, likely due to the higher stability of MeCN towards oxidation and to the lower solubility of **2-Tb** which allows it to precipitate from the reaction mixture and avoid side reactions. The optimized synthesis of **2-Tb** is shown in Scheme 2.

### Scheme 2. Synthesis of [Tb(OSi(O<sup>*t*</sup>Bu)<sub>3</sub>)<sub>4</sub>], **2-Tb**.



The complex **2-Tb** is isomorphous with the previously reported **2-Ce**.<sup>12b</sup> Both Ln<sup>4+</sup> ions are 5-coordinate and bound by three κ<sup>1</sup>-OSi(O<sup>*t*</sup>Bu)<sub>3</sub> and one κ<sup>2</sup>:*O,O*-OSi(O<sup>*t*</sup>Bu)<sub>3</sub> ligands despite a 0.11 Å difference in their Ln<sup>4+</sup> ionic radii (6-coordinate Shannon radii: Ce<sup>4+</sup>, 0.87 Å; Tb<sup>4+</sup>, 0.76 Å) and the ability of **2-Ce** to bind an additional ligand.<sup>11c</sup> The 0.09 Å difference in (Ln-O)<sub>avg</sub> bond distances between **1-Tb** and **2-Tb** is less than the 0.15 Å difference in the 6-coordinate ionic radii, but if one considers the decrease in ionic radius from Tb<sup>3+</sup> to Tb<sup>4+</sup> (0.163 Å), and the increase in Shannon<sup>14</sup> radii between coordination numbers *n* and *n*+1 (0.06 Å), the 0.09 Å difference is close to the 0.103 Å difference expected as a result of these influences. The metrical parameters of the **2-Ln** complexes are given in Table 1 together with those of their Ln<sup>3+</sup> analogues **1-Ln**.



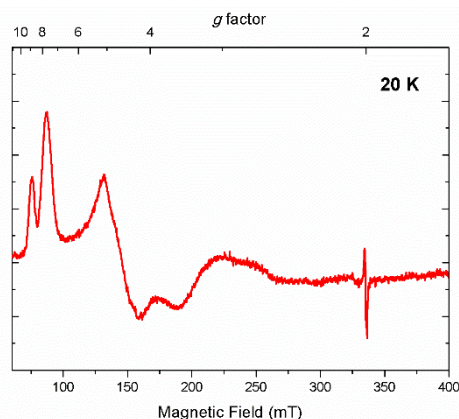
**Figure 2.** Molecular structure of [Tb(OSi(O<sup>*t*</sup>Bu)<sub>3</sub>)<sub>4</sub>], **2-Tb**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and methyl groups on the siloxide ligands have been omitted for clarity.

**Table 1.** Selected bond lengths (Å) and angles (°) of [KLn(OSi(O<sup>*t*</sup>Bu)<sub>3</sub>)<sub>4</sub>], **1-Ln**, and [Tb(OSi(O<sup>*t*</sup>Bu)<sub>3</sub>)<sub>4</sub>], **2-Ln** (Ln = Ce,<sup>12b</sup> Tb).

	<b>1-Tb</b>	<b>2-Tb</b>	<b>1-Ce<sup>12b</sup></b>	<b>2-Ce<sup>12b</sup></b>
Ln-O	2.103(3)-	2.023(3)-	2.221(3)-	2.084(2)-
range	2.152(2)	2.093(3)	2.297(3)	2.160(2)
(Ln-O) <sub>avg</sub>	2.13(2)	2.04(3)	2.26(3)	2.11(3)
Ln-O <sub>tBu</sub>	-	2.474(3)	2.721(3)-	2.581
range			2.764(3)	

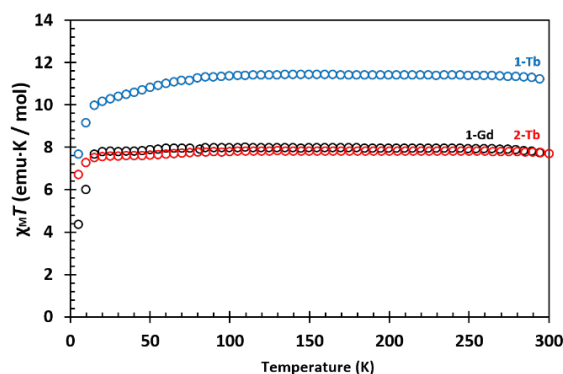
X-band electron paramagnetic resonance (EPR) spectra were measured at 20 K and 298 K on 1 mM solutions prepared by dissolving crystals of **1-Tb**, **1-Gd** and **2-Tb** in toluene (Figures S5-S9 in the Supporting Information). The **1-Tb** spectrum does not show intense features as expected for the non-Kramers Tb<sup>3+</sup> (4f<sup>8</sup>) ion.<sup>16</sup> In contrast, the 20 K spectrum produced from **2-Tb** (Figure 3) shows strong features at g= 8.9, g= 7.7 and g = 5.0 that are consistent with spectra reported for fluoride phosphate glasses and silicates containing Tb<sup>4+</sup>.<sup>17-18</sup> Complex EPR spectra with highly anisotropic g-values have been previously observed in complexes of 4f<sup>7</sup> ions and have been interpreted in term of a large zero field splitting (ZFS).<sup>18-19</sup> Similar strong features were observed in the EPR spectrum of the isoelectronic **1-Gd** complex. The differences in the spectra of the Gd<sup>3+</sup> and Tb<sup>4+</sup> complexes may be ascribed in part to differences in the **1-Ln** and **2-Ln** structures and the increased ZFS resulting from the more charged Tb<sup>4+</sup> ion.<sup>18</sup>

Magnetic susceptibility measurements as a function of temperature were performed on crushed crystalline samples of the 4f<sup>8</sup> **1-Tb** and the 4f<sup>7</sup> complexes, **2-Tb** and **1-Gd**, Figure 4. The  $\chi_M T = 7.78$  and  $7.77$  emu·K/mol measured at 294 K for **1-Gd** and **2-Tb**, respectively, are in agreement with the  $\chi_M T = 7.88$  emu·K/mol predicted for a 4f<sup>7</sup> complex by a first approximation using LS coupling for 4f<sup>7</sup> ion ( $L = 0, S = 7/2$ ),<sup>6a</sup> and both are significantly lower than the 11.2 emu·K/mol observed for 4f<sup>8</sup> Tb<sup>3+</sup> in **1-Tb** (predicted 11.8 emu·K/mol,  $L = 3, S = 5/2$ ). For the isotropic Gd<sup>3+</sup> ion in **1-Gd**, the  $\chi_M T$  data are linear over the temperature range from 300 to 15 K.



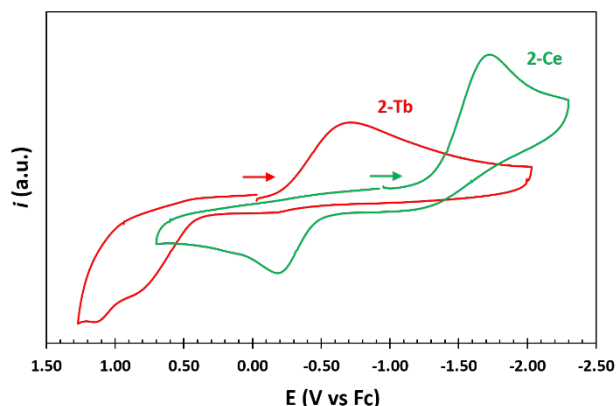
**Figure 3.** X-band EPR spectrum ( $\nu = 9.397323$  GHz,  $P = 0.6335$  mW, modulation amplitude = 0.5 mT,  $T = 20$  K) of **2-Tb**, recorded as a 1 mM solution in toluene.

At temperatures below 15 K, a sharp decrease of the magnetic moment is observed probably due to zero field splitting effects. The  $\chi_M T$  versus T data measured for the **2-Tb** overlap with those measured for **1-Gd** in the temperature range 300 to 15 K as anticipated for an isoelectronic 4f<sup>7</sup> ion.



**Figure 4.** Plot of  $\chi_M T$  versus temperature data for ground crystalline samples of **1-Gd** (black), **1-Tb** (blue), and **2-Tb** (red) collected under an applied magnetic field of 1 T.

Cyclic voltammetry measurements were performed on the homoleptic tetrakis(siloxide) **2-Ce** and **2-Tb** complexes as 2 mM solutions in THF with 0.1 M [NBu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as the supporting electrolyte, Figure 5, Table 2. Cyclic voltammetry experiments previously reported in slightly different conditions (1 mM analyte, [nPr<sub>4</sub>N][B{Ar(3,5-CF<sub>3</sub>)<sub>2</sub>}]<sub>4</sub>) used as electrolyte) for **1-Ce** and **2-Ce** demonstrated irreversibility and wide peak separations for the Ce<sup>4+</sup>/Ce<sup>3+</sup> redox couple which were attributed to ligand reorganization involving the switch between the  $\kappa^1$  and  $\kappa^2$  siloxide coordination modes.<sup>13a</sup> The current–potential curves of **2-Tb** are also characterized by irreversible redox events with wide peak separations between events at the cathodic and anodic electrodes ( $\Delta E = 1.55$  V, **2-Tb**). The  $E_{pc} = -0.70$  V vs Fc reduction potential measured for **2-Tb** is 1.02 V more positive than that observed for **2-Ce** in the same conditions. Similarly, the  $E_{pa} = 0.85$  V vs Fc oxidation event for **2-Tb** is 1.04 V more positive than the  $-0.19$  V vs Fc event measured for **2-Ce**, and is very close to the oxidation threshold for the THF solvent (see Figure S11 for the scan at 50 mV/s, where the  $E_{pc}$  redox event is better resolved). These data are consistent with the more positive potentials expected for Tb<sup>4+</sup> compared to Ce<sup>4+</sup> and suggest that ligand reorganization from the  $\kappa^2$  binding mode in **2-Ln** to  $\kappa^1$  binding in **1-Ln** is also occurring for the terbium system. The oxidation occurs at a potential significantly less positive compared to the calculated value for the Tb<sup>4+</sup>/Tb<sup>3+</sup> redox couple (3.3 V vs NHE),<sup>6</sup> suggesting a stabilizing effect of the Tb<sup>4+</sup> oxidation state by the OSi(O<sup>t</sup>Bu)<sub>3</sub> ligand. The measured value in Table 2, however, is consistent with the applied potential that was reported to generate Tb<sup>4+</sup> ions in concentrated carbonate solutions (1.3 V vs NHE).<sup>7</sup>



**Figure 5.** Cyclic voltammograms of 2 mM solutions of **2-Ce** (green) and **2-Tb** (red) measured in 0.1 M [NBu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in THF versus Fc with a glassy carbon working electrode. The measurements were done at room temperature and scanned at 250 mV/s.

**Table 2. Electrochemical data in V vs Fc [V vs NHE] of the 2-Ce and 2-Tb complexes (Figure 2).**

	2-Ce	2-Tb
$E_{pc}$	-1.72 [-0.92]	-0.70 [0.10]
$E_{pa}$	-0.19 [0.61]	0.85 [1.65]
$\Delta E_{pc}/E_{pa}$	1.53	1.55

In conclusion, the utilization of the electron-rich tetrakis(tert-butoxy)siloxide ligand environment along with the tris(bromophenyl) ammonium hexachloroantimonate oxidant has allowed the expansion of rare earth oxidation chemistry to a molecular complex of terbium(IV). The isolation of a molecular Tb<sup>4+</sup> suggests that it may be possible to extend the +4 oxidation state to molecular complexes of the other lanthanide ions. In view of the broad range of applications of Ce<sup>4+</sup>, this finding should lead to further development of the redox chemistry of the lanthanides and to unusual oxidative chemistry.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/XXX and includes additional spectroscopic, electrochemical characterization, magnetism, and structural details for **1-Ln** (Ln = Tb, Gd) and [Tb(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>4</sub>], **2-Tb** (PDF). Crystallographic data in CIF format for **1-Tb** and **2-Tb** (CIF).

## AUTHOR INFORMATION

### Corresponding Author

\*Email: [marinella.mazzanti@epfl.ch](mailto:marinella.mazzanti@epfl.ch)

### ORCID

Chad T. Palumbo: 0000-0001-6436-4602  
 Rosario Scopelliti: 0000-0001-8161-8715  
 Marinella Mazzanti: 0000-0002-3427-008X

## Notes

The authors declare no competing financial interests.

## ACKNOWLEDGMENT

We acknowledge support from the Swiss National Science Foundation grant number 200021\_178793 and the Ecole Polytechnique Fédérale de Lausanne (EPFL). We thank Dr. Euro Solari for performing the elemental analysis measurements, Dr. F. Fadaei-Tirani for important contributions to the X-ray single crystal structure analyses, and Dr. A. Sienkiewicz for EPR data collection.

## REFERENCES

- (a) Fieser, M. E.; MacDonald, M. R.; Krull, B. T.; Bates, J. E.; Ziller, J. W.; Furche, F.; Evans, W. J., Structural, Spectroscopic, and Theoretical Comparison of Traditional vs Recently Discovered Ln(2+) Ions in the K(2.2.2-cryptand) (C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)(3)Ln Complexes: The Variable Nature of Dy<sup>2+</sup> and Nd<sup>2+</sup>. *J. Am. Chem. Soc.* **2015**, *137*, 369-382; (b) Hitchcock, P. B.; Lappert, M. F.; Maron, L.; Protchenko, A. V., Lanthanum does form stable molecular compounds in the +2 oxidation state. *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 1488-1491; (c) Xemard, M.; Jaoul, A.; Cordier, M.; Molton, F.; Cador, O.; Le Guennic, B.; Duboc, C.; Maury, O.; Clavaguera, C.; Nocton, G., Divalent Thulium Triflate: A Structural and Spectroscopic Study. *Angew. Chem. Int. Ed. Engl.* **2017**, *56*, 4266-4271; (d) MacDonald, M. R.; Bates, J. E.; Ziller, J. W.; Furche, F.; Evans, W. J., Completing the Series of +2 Ions for the Lanthanide Elements: Synthesis Of Molecular Complexes of Pr<sup>2+</sup>, Gd<sup>2+</sup>, Tb<sup>2+</sup>, and Lu<sup>2+</sup>. *J. Am. Chem. Soc.* **2013**, *135*, 9857-9868.
- (a) Anwander, R.; Dolg, M.; Edelman, F. T., The difficult search for organocerium(IV) compounds. *Chem. Soc. Rev.* **2017**, *46*, 6697-6709; (b) Kaltsoyannis, N.; Scott, P., *The f elements*. Oxford University Press: Oxford, 1999; (c) So, Y. M.; Leung, W. H., Recent advances in the coordination chemistry of cerium(IV) complexes. *Coord. Chem. Rev.* **2017**, *340*, 172-197.
- Piro, N. A.; Robinson, J. R.; Walsh, P. J.; Schelter, E. J., The electrochemical behavior of cerium(III/IV) complexes: Thermodynamics, kinetics and applications in synthesis. *Coord. Chem. Rev.* **2014**, *260*, 21-36.
- (a) Schelter, E. J., Cerium under the lens. *Nat. Chem.* **2013**, *5*, 348-348; (b) Montini, T.; Melchionna, M.; Monai, M.; Fornasiero, P., Fundamentals and Catalytic Applications of CeO<sub>2</sub>-Based Materials. *Chem. Rev.* **2016**, *116*, 5987-6041; (c) Sridharan, V.; Menendez, J. C., Cerium(IV) Ammonium Nitrate as a Catalyst in Organic Synthesis. *Chem. Rev.* **2010**, *110*, 3805-3849; (d) Pham, T. A.; Altman, A. B.; Stieber, S. C. E.; Booth, C. H.; Kozimor, S. A.; Lukens, W. W.; Olive, D. T.; Tylliszczak, T.; Wang, J.; Minasian, S. G.; Raymond, K. N., A Macrocyclic Chelator That Selectively Binds Ln(4+) over Ln(3+) by a Factor of 10(29). *Inorg. Chem.* **2016**, *55*, 9989-10002; (e) Broderick, E. M.; Diaconescu, P. L., Cerium(IV) Catalysts for the Ring-Opening Polymerization of Lactide. *Inorg. Chem.* **2009**, *48*, 4701-4706.
- (a) Crozier, A. R.; Bienfait, A. M.; Maichle-Mossmer, C.; Tornroos, K. W.; Anwander, R., A homoleptic tetravalent cerium silylamide. *Chem. Commun.* **2013**, *49*, 87-89; (b) Droese, P.; Crozier, A. R.; Lashkari, S.; Gottfriedsen, J.; Blaurock, S.; Hrib, C. G.; Maichle-Mossmer, C.; Schadle, C.; Anwander, R.; Edelman, F. T., Facile Access to Tetravalent Cerium Compounds: One-Electron Oxidation Using Iodine(III) Reagents. *J. Am. Chem. Soc.* **2010**, *132*, 14046-14047; (c) Levin, J. R.; Dorfner, W. L.; Carroll, P. J.; Schelter, E. J., Control of cerium oxidation state through metal complex secondary structures. *Chem. Sci.* **2015**, *6*, 6925-6934; (d) Robinson, J. R.; Qiao, Y. S.; Gu, J.; Carroll, P. J.; Walsh, P. J.; Schelter, E. J., The role of dynamic ligand exchange in the oxidation chemistry of cerium(III). *Chem. Sci.* **2016**, *7*, 4537-4547; (e) Casely, I. J.; Little, S. T.; Blake, A. J.; Wilson, C.; Arnold, P. L., Tetravalent cerium carbene complexes. *Chem. Commun.* **2007**, 5037-5039; (f) Robinson, J. R.; Gordon, Z.; Booth, C. H.; Carroll, P. J.; Walsh, P. J.; Schelter, E. J., Tuning Reactivity and Electronic Properties through Ligand Reorganization within a Cerium Heterobimetallic Framework. *J. Am. Chem. Soc.* **2013**, *135*, 19016-19024; (g) Damon, P. L.; Wu, G.; Kaltsoyannis, N.; Hayton,

- T. W., Formation of a Ce(IV) Oxo Complex via Inner Sphere Nitrate Reduction. *J. Am. Chem. Soc.* **2016**, *138*, 12743-12746.
6. (a) Cotton, S., *Lanthanides and Actinides Chemistry*. John Wiley & Sons: Chichester, 2006; (b) Soor, F. M.; Edelman, F. T., *The Rare Earth Elements: Fundamentals and Applications*. John Wiley & Sons Ltd: Chichester, 2012.
  7. Hobart, D. E.; Samhoun, K.; Young, J. P.; Norvell, V. E.; Mamanov, G.; Peterson, J. R., Stabilization of praseodymium(IV) and terbium(IV) in aqueous carbonate solution. *Inorg. Nucl. Chem. Letters* **1980**, *16*, 321-328.
  8. (a) Minasian, S. G.; Batista, E. R.; Booth, C. H.; Clark, D. L.; Keith, J. M.; Kozimor, S. A.; Lukens, W. W.; Martin, R. L.; Shuh, D. K.; Stieber, S. C. E.; Tylicszak, T.; Wen, X. D., Quantitative Evidence for Lanthanide-Oxygen Orbital Mixing in CeO<sub>2</sub>, PrO<sub>2</sub>, and TbO<sub>2</sub>. *J. Am. Chem. Soc.* **2017**, *139*, 18052-18064; (b) Doi, Y.; Ninomiya, K.; Hinatsu, Y.; Ohoyama, K., Structure and magnetic properties of the two-dimensional antiferromagnet Na<sub>2</sub>TbO<sub>3</sub>. *J. Phys. Condens. Matter* **2005**, *17*, 4393-4401.
  9. Naghavi, S. S.; Emery, A. A.; Hansen, H. A.; Zhou, F.; Ozolins, V.; Wolverton, C., Giant onsite electronic entropy enhances the performance of ceria for water splitting. *Nat. Commun.* **2017**, *8* (285).
  10. Deblonde, G. J. P.; Sturzbecher-Hoehne, M.; Rupert, P. B.; An, D. D.; Illy, M. C.; Ralston, C. Y.; Brabec, J.; de Jong, W. A.; Strong, R. K.; Abergel, R. J., Chelation and stabilization of berkelium in oxidation state plus IV. *Nat. Chem.* **2017**, *9*, 843-849.
  11. (a) Gregson, M.; Lu, E.; Mills, D. P.; Tuna, F.; McInnes, E. J. L.; Hennig, C.; Scheinost, A. C.; McMaster, J.; Lewis, W.; Blake, A. J.; Kerridge, A.; Liddle, S. T., The inverse-trans-influence in tetravalent lanthanide and actinide bis(carbene) complexes. *Nat. Commun.* **2017**, *8* (14137); (b) Kim, J. E.; Bogart, J. A.; Carroll, P. J.; Schelter, E. J., Rare Earth Metal Complexes of Bidentate Nitroxide Ligands: Synthesis and Electrochemistry. *Inorg. Chem.* **2016**, *55*, 775-784.
  12. (a) Andrez, J.; Pecaut, J.; Bayle, P.-A.; Mazzanti, M., Tuning Lanthanide Reactivity Towards Small Molecules with Electron-Rich Siloxide Ligands. *Angew. Chem. Int. Ed. Engl.* **2014**, *53*, 10448-10452; (b) Kelly, R. P.; Maron, L.; Scopelliti, R.; Mazzanti, M., Reduction of a Cerium(III) Siloxide Complex To Afford a Quadruple-Decker Arene-Bridged Cerium(II) Sandwich. *Angew. Chem. Int. Ed. Engl.* **2017**, *56*, 15663-15666.
  13. (a) Friedrich, J.; Qiao, Y. S.; Maichle-Mossmer, C.; Schelter, E. J.; Anwender, R., Redox-enhanced hemilability of a tris(tert-butoxy) siloxy ligand at cerium. *J. Chem. Soc.-Dalton Trans.* **2018**, *47*, 10113-10123; (b) Lapadula, G.; Conley, M. P.; Coperet, C.; Andersen, R. A., Synthesis and Characterization of Rare Earth Siloxide Complexes, M OSi(OtBu)<sub>3</sub>(3)(L)(x) where L is HOSi(OtBu)<sub>3</sub> and x=0 or 1. *Organometallics* **2015**, *34*, 2271-2277; (c) Friedrich, J.; Maichle-Mossmer, C.; Anwender, R., Synthesis and derivatisation of ceric tris(tert-butoxy)siloxides. *Chem. Commun.* **2017**, *53*, 12044-12047.
  14. Shannon, R. D., Revised Effective Ionic-Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Crystallogr A* **1976**, *32*, 751-767.
  15. Connelly, N. G.; Geiger, W. E., Chemical redox agents for organometallic chemistry. *Chem. Rev.* **1996**, *96*, 877-910.
  16. (a) Abragam, A.; Bleaney, B., *Electron Paramagnetic Resonance of Transition Ions*. Clarendon Press: Oxford, 1970; (b) Hinatsu, Y., Magnetic-susceptibility and electron-paramagnetic resonance studies of tetravalent terbium ions in BaTbO<sub>3</sub> AND SrTbO<sub>3</sub>. *J. Solid State Chem.* **1992**, *100*, 136-140.
  17. Ebsendorff-Heidepriem, H.; Ehrst, D., Electron spin resonance spectra of Eu<sup>2+</sup> and Tb<sup>4+</sup> ions in glasses. *J. Phys. Condens. Matter* **1999**, *11*, 7627-7634.
  18. Hansen, S.; Mosel, B. D.; MullerWarmuth, W.; Fielding, P. E., EPR studies of Tb<sup>4+</sup> in single crystals of zircon and scheelite structure silicates and germanates. *Z. Naturforsch A* **1996**, *51*, 885-894.
  19. Benmelouka, M.; Van Tol, J.; Borel, A.; Nellutla, S.; Port, M.; Helm, L.; Brunel, L. C.; Merbach, A. E., Multiple-Frequency and Variable-Temperature EPR Study of Gadolinium(III) Complexes with Polyamino-carboxylates: Analysis and Comparison of the Magnetically Dilute Powder and the Frozen-Solution Spectra. *Helv. Chim. Acta* **2009**, *92*, 2173-2185.

