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Communication

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Chad T. Palumbo, Ivica Zivkovic, Rosario Scopelliti, and Marinella Mazzanti

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A Molecular Complex of Tb in the +4 Oxidation State

Chad T. Palumbo,[a] Ivica Zivkovic,[b] Rosario Scopelliti,[a] and Marinella Mazzanti*

[a] Insititut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

[b] 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^{+4} so far remains Ce^{4+}. 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, $[KTb(OSi(O^tBu)_3)_4]$, **1-Tb**, with the tris(4-bromophenyl)amminium oxidant, $[N(C_6H_4Br)_3][SbCl_6]$, to afford the Tb^{4+} complex $[Tb(OSi(O^tBu)_3)_4]$, **2-Tb**. The solid state structures of **1-Tb** and **2-Tb** were determined by X-ray crystallography and the presence of Tb^{4+} was unambiguously confirmed by EPR and magnetometry. **2-Tb** displays a similar voltammogram to the Ce^{4+} analogue but with redox events that are about 1 V more positive.

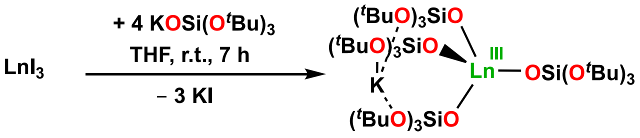
The chemistry of lanthanides (Ln) has been limited mostly to the + 3 oxidation state. Only recently it has been shown that the oxidation state + 2 is accessible for all lanthanides by using bulky supporting ligands and appropriate reaction conditions.[1] In contrast, molecular complexes of lanthanides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

The terbium ion should have the next most accessible +4 oxidation state according to the calculated redox potential of 3.3 V vs NHE,[6] but Tb^{+4} so far has only been observed in concentrated aqueous carbonate solutions[7] and in a few inorganic solids such as metal oxides or fluorides.[6a, 8] Further, Tb^{4+} in TbO_2 has been recently identified as a potential candidate for solar thermochemical reactions.[9] While a molecular complex of the 5f analogue Bk^{4+} has been recently reported,[10] attempts to produce Tb^{4+} in molecular compounds were so far not successful,[11] resulting in ligand rather than metal oxidation, leaving the question of the possibility of isolating complexes of Ln^{+4} other than Ce^{4+} open.[2a]

Our group[12] and others[13] have reported the ability of tris(tertbutoxy)siloxide to stabilize lanthanide ions in various oxidation states. In particular, both the Ce^{3+} and the Ce^{4+} homoleptic tetrakis(tertbutoxy)siloxide complexes $[KCe(OSi(O^tBu)_3)_4]$, **1-Ce**, and $[Ce(OSi(O^tBu)_3)_4]$, **2-Ce**, were prepared and crystallographically characterized.[12b] Here we show that the tris(tertbutoxy)siloxide ligand allows the synthesis and characterization of the first example of a molecular complex of Tb^{4+}. The $4f^7$ terbium complex $[Tb(OSi(O^tBu)_3)_4]$, **2-Tb**, was prepared by oxidation of the Tb^{3+} analogue, $[KTb(OSi(O^tBu)_3)_4]$, **1-Tb**, using $[N(C_6H_4Br)_3][SbCl_6]$ as the oxidizing agent. We have also prepared the isoelectronic $4f^7$ Gd^{3+} complex, $[KGd(OSi(O^tBu)_3)_4]$, **1-Gd**, for comparison.

The potassium tetrakis(siloxide) Ln^{3+} complexes, $[KLn(OSi(O^tBu)_3)_4]$ (Ln = Gd, Tb), **1-Ln**, were prepared from the reaction of $KOSi(O^tBu)_3$ with the anhydrous lanthanide triiodides GdI_3 and TbI_3 in 81% and 86% yield for Gd and Tb, respectively, Scheme 1.

Scheme 1. Synthesis of $[KLn(OSi(O^tBu)_3)_4]$ (Ln = Gd, Tb), 1-Ln.



1-Ln
Ln = Gd, 81%; Tb, 86%

The NMR spectrum of **1-Tb** (Figure S1) at 298 K shows only one broad resonance at −26 ppm in toluene-d_8, 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 $[KYb(OSi(O^tBu)_3)_4]$ complex[12a] and presents a 4-coordinate Tb^{3+} ion with one κ^1-$OSi(O^tBu)_3$ ligand and three μ-κ^2:O,O-$OSi(O^tBu)_3$ ligands which bridge the Tb^{3+} and K^+ cations. In contrast, in the previously reported $[KCe(OSi(O^tBu)_3)_4]$

complex,[12b] the Ce^{3+} ion is 5-coordinate with one κ^2:*O*,*O*-OSi(O^{t}Bu)$_3$ ligand and three μ-κ^2:*O*,*O*-OSi(O^{t}Bu)$_3$ ligands that bridge the Ce^{3+} and K^+. The difference in structure is attributed to the larger ionic radius of Ce^{3+} compared to Tb^{3+} and Yb^{3+} (6-coordinate Shannon radii: Ce^{3+}, 1.01 Å; Tb^{3+}, 0.923 Å; Yb^{3+}, 0.868 Å).[14]

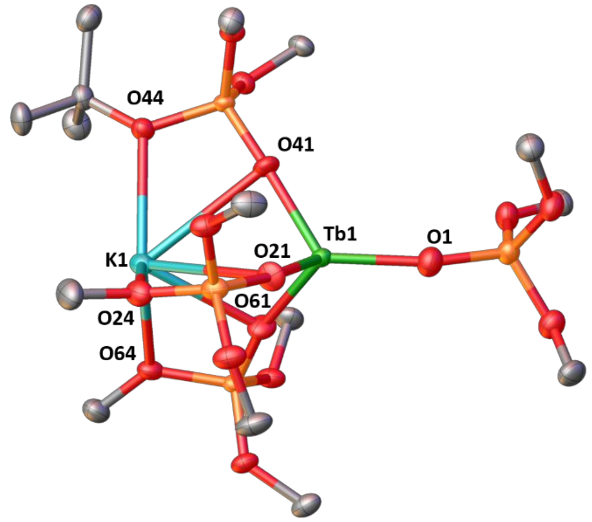
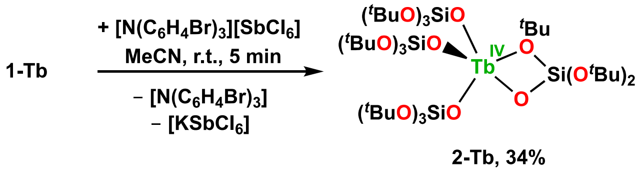


Figure 1. Molecular structure of [KTb(OSi(O^{t}Bu)$_3$)$_4$], **1-Tb**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, methyl groups on the siloxide ligands, and a second molecule of **1-Tb** present in the unit cell have been omitted for clarity.

Treatment of **1-Tb** with AgI in either THF or CH_2Cl_2 gave no reaction. However, treatment of **1-Tb** with a stronger oxidizing agent, namely, the tris(4-bromophenyl)amminium hexachloroantimonate salt, ($[N(C_6H_4Br)_3][SbCl_6]$),[15] 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_{max} = 371 nm with a molar extinction coefficient ε of 4200 $M^{-1}\cdot cm^{-1}$ (Figure S4). A similar feature (λ_{max} = 365 nm) was reported for electrochemically generated solutions of Tb^{4+} in 5.5M of K_2CO_3. 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^{t}Bu)$_3$)$_4$], 2-Tb.



The complex **2-Tb** is isomorphous with the previously reported **2-Ce**.[12b] Both Ln^{4+} ions are 5-coordinate and bound by three κ^1-OSi(O^{t}Bu)$_3$ and one κ^2:*O*,*O*-OSi(O^{t}Bu)$_3$ ligands despite a 0.11 Å difference in their Ln^{4+} ionic radii (6-coordinate Shannon radii: Ce^{4+}, 0.87 Å; Tb^{4+}, 0.76 Å) and the ability of **2-Ce** to bind an additional ligand.[11c] The 0.09 Å difference in $(Ln–O)_{avg}$ 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^{3+} to Tb^{4+} (0.163 Å), and the increase in Shannon[14] 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^{3+} analogues **1-Ln**.

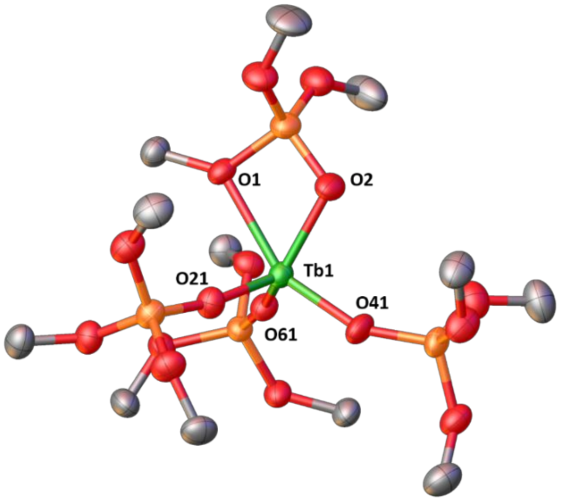


Figure 2. Molecular structure of [Tb(OSi(O^{t}Bu)$_3$)$_4$], **2-Tb**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and methyl groups on the siloxide ligands have been omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) of [KLn(OSi(O^{t}Bu)$_3$)$_4$], 1-Ln, and [Tb(OSi(O^{t}Bu)$_3$)$_4$], 2-Ln (Ln = Ce,[12b] Tb) .

	1-Tb	**2-Tb**	**1-Ce**[12b]	**2-Ce**[12b]
Ln–O range	2.103(3)-2.152(2)	2.023(3)-2.093(3)	2.221(3)-2.297(3)	2.084(2)-2.160(2)
$(Ln–O)_{avg}$	2.13(2)	2.04(3)	2.26(3)	2.11(3)
$Ln–O_{tBu}$ range	-	2.474(3)	2.721(3)-2.764(3)	2.581

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^{3+} ($4f^8$) ion.[16] 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^{4+}.[17-18] Complex EPR spectra with highly anisotropic *g*-values have been previously observed in complexes of $4f^7$ ions and have been interpreted in term of a large zero field splitting (ZFS).[18-19] Similar strong features were observed in the EPR spectrum of the isoelectronic **1-Gd** complex. The differences in the spectra of the Gd^{3+} and Tb^{4+} 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^{4+} ion.[18]

Magnetic susceptibility measurements as a function of temperature were performed on crushed crystalline samples of the $4f^8$ **1-Tb** and the $4f^7$ 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 $4f^7$ complex by a first approximation using *LS* coupling for $4f^7$ ion ($L = 0$, $S = 7/2$),[6a] and both are significantly lower than the 11.2 emu·K/mol observed for $4f^8$ Tb^{3+} in **1-Tb** (predicted 11.8 emu·K/mol, $L = 3$, $S = 5/2$). For the isotropic Gd^{3+} ion in **1-Gd**, the $\chi_M T$ data are linear over the temperature range from 300 to 15 K.

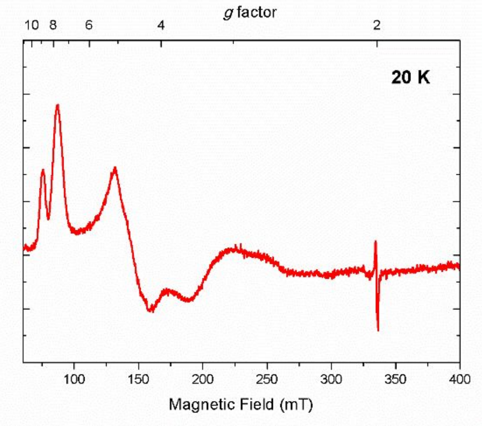


Figure 3. X-band EPR spectrum (υ = 9.397323 GHz, P = 0.6335 mW, modulation amplitude = 0.5 mT, T = 20 K) of **2-Tb**, recorded as a 1 mM solution in toluene.

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 $4f^7$ ion.

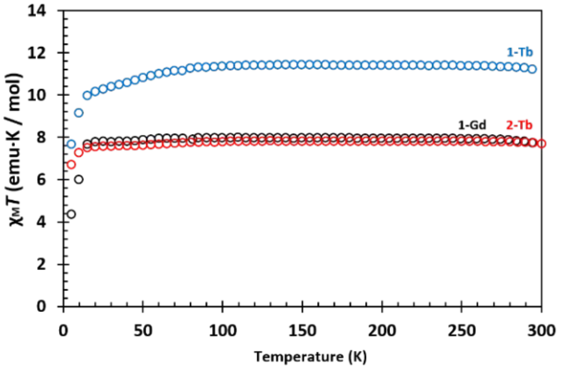


Figure 4. Plot of $\chi_M T$ versus temperature data for ground crystalline samples of **1-Gd** (black), **1-Tb** (blue), and **2-Tb** (red) collected under an applied magnetic field of 1 T.

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 $[NBu_4][B(C_6F_5)_4]$ as the supporting electrolyte, Figure 5, Table 2. Cyclic voltammetry experiments previously reported in slightly different conditions (1 mM analyte, $[^nPr_4N][B\{Ar(3,5\text{-}CF_3)\}_4]$ used as electrolyte) for **1-Ce** and **2-Ce** demonstrated irreversibility and wide peak separations for the Ce^{4+}/Ce^{3+} redox couple which were attributed to ligand reorganization involving the switch between the κ^1 and κ^2 siloxide coordination modes.[13a] 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 (ΔE = 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^{4+} compared to Ce^{4+} and suggest that ligand reorganization from the κ^2 binding mode in **2-Ln** to κ^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^{4+}/Tb^{3+} redox couple (3.3 V vs NHE),[6] suggesting a stabilizing effect of the Tb^{4+} oxidation state by the $OSi(O^tBu)_3$ ligand. The measured value in Table 2, however, is consistent with the applied potential that was reported to generate Tb^{4+} ions in concentrated carbonate solutions (1.3 V vs NHE).[7]

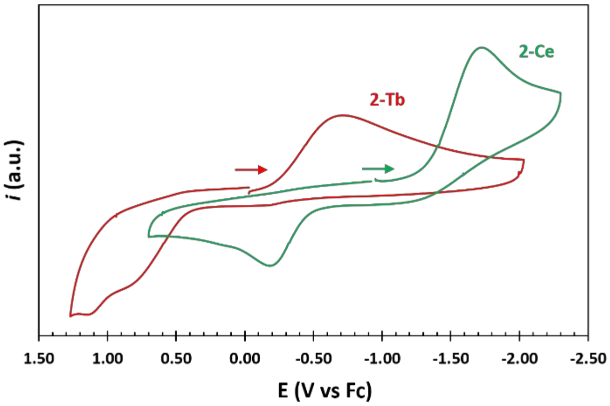


Figure 5. Cyclic voltammograms of 2 mM solutions of **2-Ce** (green) and **2-Tb** (red) measured in 0.1 M $[NBu_4][B(C_6F_5)_4]$ in THF versus Fc with a glassy carbon working electrode. The measurements were done at room temperature and scanned at 250 mV/s.

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(tertbutoxy)siloxide ligand environment along with the tris(bromophenyl) amminium hexachloroantimonate oxidant has allowed the expansion of rare earth oxidation chemistry to a molecular complex of terbium(IV). The isolation of a molecular Tb^{+4} 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^{+4}, 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: 1021/XXX and includes additional spectroscopic, electrochemical characterization, magnetism, and structural details for **1-Ln** (Ln = Tb, Gd) and [Tb (OSi(O^{t}Bu)$_3$)$_4$], **2-Tb** (PDF) . Crystallographic data in CIF format for **1-Tb** and **2-Tb** (CIF).

AUTHOR INFORMATION

Corresponding Author

*Email: 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.

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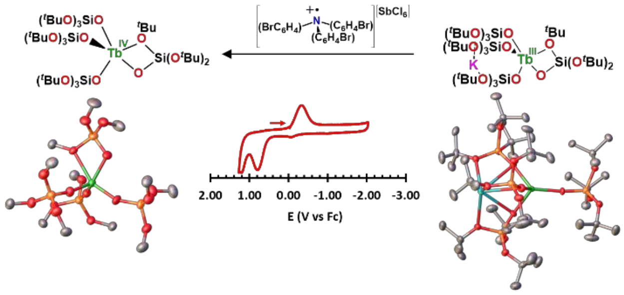
(^{t}BuO)$_3$SiO
(^{t}BuO)$_3$SiO
(^{t}BuO)$_3$SiO
IV
Tb
^{t}Bu
O
O
Si(O^{t}Bu)$_2$
[(BrC$_6$H$_4$)N(C$_6$H$_4$Br)(C$_6$H$_4$Br)]$^{+\bullet}$[SbCl$_6$]
K
III
2.00
1.00
0.00
-1.00
-2.00
-3.00
E (V vs Fc)