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Stabilization of the + IV oxidation state in siloxide supported terbium compounds

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Abstract: The synthesis of lanthanides, other than cerium, in the oxidation state +IV has remained a desirable but unmet target until recently when two examples of Tb(IV) with saturated coordination spheres were isolated. Here we report the third example of an isolated molecular complex of terbium(IV) where the siloxide supporting ligands do not saturate the coordination sphere. The fully characterized six-coordinate complex $[\text{Tb}^{\text{IV}}(\text{OSiPh}_3)_4(\text{MeCN})_2]$, **2-Tb^{Ph}**, shows high stability and the labile MeCN ligands can be replaced by phosphinoyl ligands to yield stable Tb(IV) complexes. Computational studies suggest that such stability is due to a strong $\pi(\text{O}-\text{Tb})$ interaction which is greater than in the previously reported Tb(IV) complexes. Importantly, cyclic voltammogram experiments demonstrate that non-binding counterions contribute to the Tb(IV) solution stability by destabilizing the +III oxidation state, while alkali ions promote Tb(IV)/Tb(III) electron-transfer.

Up to 2019, the chemistry of molecular compounds of lanthanides in the oxidation state + IV has been limited to cerium.^[1] Molecular cerium(IV) compounds have led to an increased understanding of lanthanide-ligand bonding^[2] and demonstrated a broad range of reactivity and physical properties that have found application in material science, organic chemistry and catalysis.^[2b, 3a-g] Because of its high redox potential (3.3 V vs NHE (2.5 V vs Fc)),^[4] until recently Tb(IV) had only been identified in bulk terbium oxides and fluorides^[2a, 4a, 5] and in concentrated carbonate solutions.^[6] Beside the intrinsic fundamental interest for the electronic properties of this isotropic $4f^7$ ion, the redox properties of Tb(IV) are well poised for expanding the application of lanthanide ions in catalysis and in material science.^[1a, 7] Seminal attempts to isolate a molecular complex of Tb(IV) using electron-rich nitroxide alkyl or carbene ligands that can stabilize highly oxidizing Ce(IV) compounds led to ligand oxidation or cation exchange.^[8] However, in 2019 the first two molecular compounds of Tb(IV), **2-Tb^{OTBu}**^[9] (**OTBu** = tris(tert-butoxy)siloxide) and **2-Tb^{N=P}**^[10] (**N=P** = tris(amidyl)imidophosphorane) were isolated from the

reduction of **1-Tb^{OTBu}**^[9] and **1-Tb^{N=P}**^[10], using bulky, σ and π donor supporting ligands that completely saturate the coordination sphere of the terbium ion (see Chart 1).

Here we show that the monodentate siloxide ligand $^t\text{OSiPh}_3$ leads to the isolation of the third example of a molecular compound of terbium(IV) in spite of its inability to saturate the coordination sphere of Tb(IV). The six-coordinate $[\text{Tb}^{\text{IV}}(\text{OSiPh}_3)_4(\text{MeCN})_2]$, **2-Tb^{Ph}**, presents solvent molecules in the coordination sphere and shows a reversible redox wave in the presence of alkali ions as a result of a metal-ion coupled redox transfer that stabilizes Tb(III).

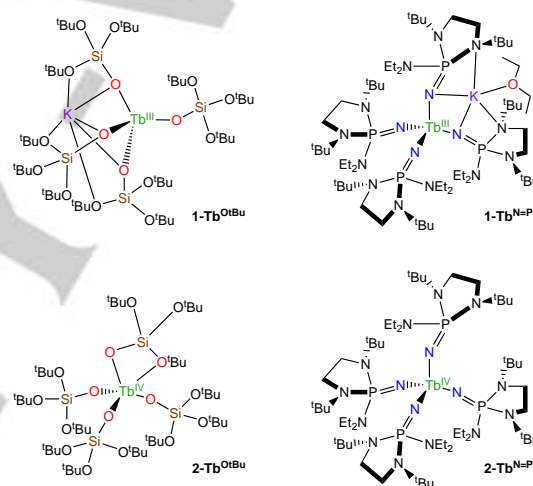
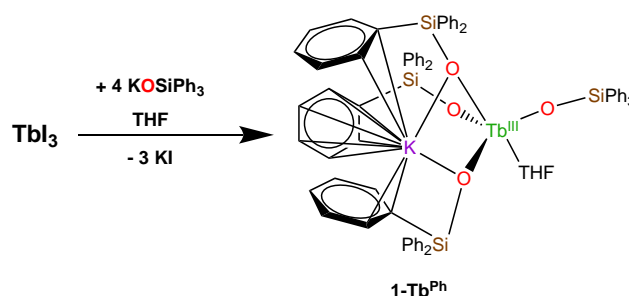


Chart 1. Drawing of the previously published Tb(III) complexes **1-Tb^{OTBu}** (top left)^[9], **1-Tb^{N=P}** (top right)^[10] and Tb(IV) complexes **2-Tb^{OTBu}** (bottom left)^[9], **2-Tb^{N=P}** (bottom right)^[10].

The salt metathesis reaction of the triiodide terbium salt TbI_3 with 4 equivalents of KOSiPh_3 afforded the potassium tetrakis(triphenylsiloxide) terbium(III) complex $[\text{KTb}(\text{OSiPh}_3)_4(\text{THF})]$, **1-Tb^{Ph}**, in 76 % yield (Scheme 1).



Scheme 1. Synthesis of complex **1-Tb^{Ph}**.

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The solid-state molecular structure of complex **1-Tb^{Ph}** is presented in Figure 1. The structure shows a five-coordinate Tb(III) ion bound in a distorted trigonal bipyramidal geometry by four triphenylsiloxide ligands and one molecule of THF. One triphenylsiloxide is coordinated in a κ^1 fashion to the Tb(III) while the three other triphenylsiloxides bridge the Tb(III) and the K⁺ ions via the anionic oxygen and η^6 and η^2 binding by the phenyl rings (K–C distances ranging from 3.159(4) to 3.492(4) Å).

The occurrence of potassium binding in THF solution was confirmed by addition of 1 equivalent of 2.2.2-cryptand to **1-Tb^{Ph}** in THF-*d*₈ which resulted in significant changes in the ¹H NMR spectrum attributed to potassium removal (Figure S3).

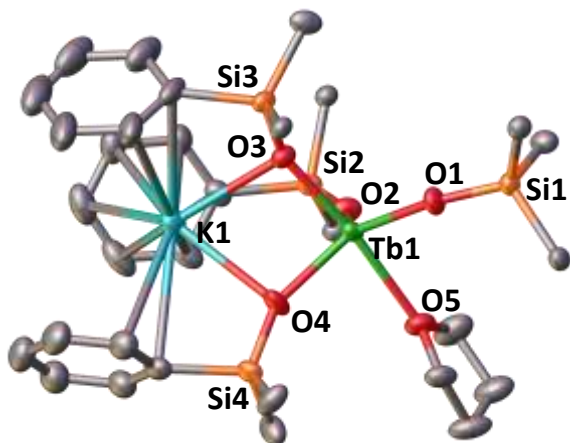
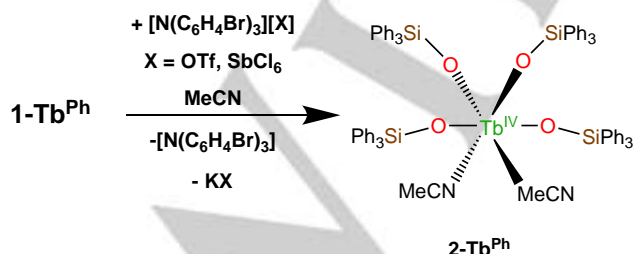


Figure 1. Solid-state molecular structure of **1-Tb^{Ph}** (50% probability ellipsoids). Hydrogen atoms, phenyl groups not bound to the potassium ion and residual solvent molecules are omitted for clarity. Selected distances (Å): Tb1–O_{siloxide} = 2.138(2) – 2.194(2); Tb1–O_{THF} = 2.443(2); K–C_{Ph}(η^6) = 3.265(4) – 3.317(3); K–C_{Ph}(η^2) = 3.159(4) – 3.492(4).

Addition of AgOTf to a THF solution of **1-Tb^{Ph}** did not result in the oxidation of the Tb(III) complex. In contrast, oxidation of **1-Tb^{Ph}** with the tris(4-bromophenyl)amminium salts, [N(C₆H₄Br)₃][SbCl₆]^[11] or [N(C₆H₄Br)₃][OTf]^[12] in acetonitrile led to the fast color change of the suspension from white to orange (Scheme 2). Careful removal of salts from the orange solid resulted in the isolation of analytically pure [Tb^{IV}(OSiPh₃)₄(MeCN)₂], **2-Tb^{Ph}**, in 21–24 % yield (Scheme 2). The **2-Tb^{Ph}** complex is stable for months in the solid state and in THF solution for several days.



Scheme 2. Synthesis of complex **2-Tb^{Ph}**.

The molecular structure of **2-Tb^{Ph}** is presented in Figure 2 and shows a mononuclear six-coordinate Tb(IV) complex. The metal centre is coordinated to four κ^1 triphenylsiloxide ligands and two molecules of acetonitrile in a distorted octahedral coordination geometry. The Tb1–O_{siloxide}

distances in **2-Tb^{Ph}** (2.028(5)–2.087(5) Å) are shorter than in **1-Tb^{Ph}** (2.138(2)–2.194(2) Å) and are consistent with the Tb(IV)–O_{siloxide} distances found in complex [Tb(OSi(O^tBu)₃)₄], **2-Tb^{OT^tBu}**, (2.023(3)–2.093(3) Å).^[9]

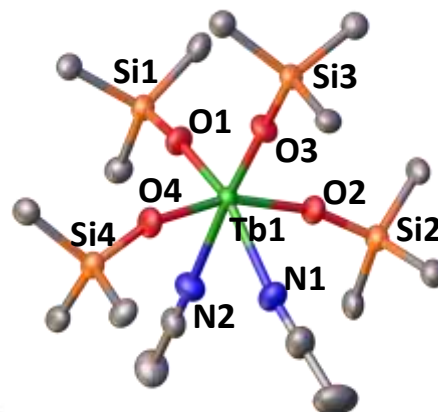


Figure 2. Solid-state molecular structure of **2-Tb^{Ph}** (50% probability ellipsoids). Hydrogen atoms, phenyl groups, residual solvent molecules and a second molecule of **2-Tb^{Ph}** present in the unit cell are omitted for clarity. Selected bond lengths (Å): Tb–O_{siloxide} = 2.028(5) – 2.087(5); Tb–N = 2.451(7) – 2.475(7).

The X-band electron paramagnetic resonance (EPR) spectrum at 20 K of **2-Tb^{Ph}** in a THF/Et₂O mixture (Figure S16) displays a signal with highly anisotropic g-values consistent with the spectra of the only two other reported examples of molecular Tb(IV)^[10] and with the spectra reported for fluoride phosphate glasses and silicates containing Tb(IV).^{[13]–[14]} The spectrum shows two strong features at g = 7.8 and g = 4.7 that can be interpreted in term of a large zero field splitting (ZFS)^[14–15] and corroborate the +IV oxidation state of the terbium metal centre in **2-Tb^{Ph}**.

Magnetic susceptibility was measured as a function of temperature for both **1-Tb^{Ph}** and **2-Tb^{Ph}** as ground solid samples (Figure S23). The measured $\chi_M T$ value for the 4f⁷ **2-Tb^{Ph}** at 294 K is 7.82 emu·K/mol, which is consistent with the value found for the Tb(IV) 4f⁷ ion in the tetrakis(tris(tert-butoxy)siloxide) terbium complex, **2-Tb^{OT^tBu}**, ($\chi_M T$ = 7.77 emu·K/mol at 294 K).^[9] This value is significantly lower than the measured $\chi_M T$ for the 4f⁸ **1-Tb^{Ph}** ($\chi_M T$ = 10.4 emu·K/mol) in agreement with the formation of a Tb(IV) species.

The UV-Visible spectrum (Figure S4) of **2-Tb^{Ph}** immediately after dissolution in THF shows a broad absorption peak with an absorption maximum at λ_{max} = 386 nm (ϵ = 3000 M^{–1}·cm^{–1}). Similar values of λ_{max} were reported for **2-Tb^{OT^tBu}** (371 nm)^[9] and for electrochemically generated 5.5 M K₂CO₃ Tb(IV) solutions (λ_{max} = 365 nm)^[6b] while a red-shifted maximum absorption was reported for complex **2-Tb^{N=P}** (λ_{max} = 575 nm).^[10]

Monitoring the UV-Visible spectra of **2-Tb^{Ph}** in THF over time showed a surprisingly high solution stability of **2-Tb^{Ph}** compared to the previously reported **2-Tb^{OT^tBu}** complex (See Figure S5–6). Notably after 3 hours in THF at room temperature, more than 90 % of **2-Tb^{Ph}** is still present in solution and 70% of the complex is still present after one day at room temperature. In contrast, after 3 hours in THF at room temperature, only 20 % of the initial absorbance of **2-Tb^{OT^tBu}** was measured.

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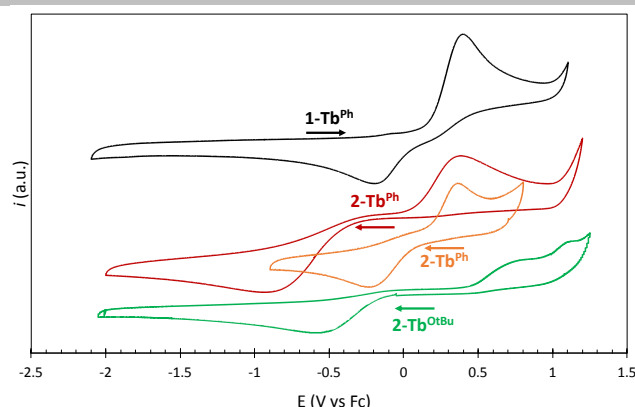


Figure 4. Cyclic voltammograms of 2 mM solutions of **1-Tb^{Ph}** (black), **2-Tb^{Ph}** (red) and **2-Tb^{OTBu}** (green) measured in 0.1 M [NBu₄][B(C₆F₅)₄] and **2-Tb^{Ph}** (orange) measured in 0.1 M [Na][B(C₆H₃(CF₃)₂)₄] in THF versus Fc.

Cyclic voltammograms were measured for the potassium tetrakis(triphenylsiloxy) **1-Tb^{Ph}** and for **2-Tb^{Ph}** complexes in 2 mM THF solutions with [NBu₄][B(C₆F₅)₄] as the supporting electrolyte (Figure 4, Table 1) and compared to those previously reported for the **2-Tb^{OTBu}** complex. The voltammograms of **2-Tb^{Ph}** and **2-Tb^{OTBu}** are both characterized by irreversible redox events and wide peak separations ($E_{pa} - E_{pc} = \Delta E = 1.38$ V for **2-Tb^{OTBu}**^[9] and $\Delta E = 1.36$ V for **2-Tb^{Ph}** at a scan rate of 100 mV/s). The voltammogram of **2-Tb^{Ph}** shows a reduction wave at $E_{pc} = -0.96$ V vs Fc and an $E_{pa} = 0.49$ V vs Fc oxidation potential. These redox potentials are shifted to lower values compared to **2-Tb^{OTBu}** under the same conditions ($E_{pc} = -0.55$ V vs Fc and $E_{pa} = 0.83$ V vs Fc)^[9], but both the **2-Tb^{Ph}** and **2-Tb^{OTBu}** electrochemistry data are consistent with the high potentials expected for a Tb(IV) metal center.

Similar irreversible cathodic and anodic events with analogous large peak separation ($\Delta E \sim 1.2$ V vs Fc) were recently reported by Schelter and Anwander for the cerium tertbutoxysiloxide analogues **1-Ce^{OTBu}**, and **2-Ce^{OTBu}**.^[16] Such behaviour was assigned to kinetic barriers to electron transfer arising from reorganization of the tert-butoxide ligand (from bidentate to monodentate) following/preceding electron transfer. Indeed, the crucial role of ligand re-organization and cation binding is well documented in the redox chemistry of cerium.^[16, 17]

In the case of the **2-Tb^{Ph}** system, the large peak separation is probably due to changes in the coordination sphere concurrent with changes in terbium oxidation state and solvent binding, but also to ion-pair formation effects^[18] occurring in the absence of coordinating cations.

Table 1. Electrochemical data in V vs Fc [V vs NHE] of **1-Tb^{Ph}**, **2-Tb^{Ph}** and **2-Tb^{OTBu}**, measured in a) 0.1 M [NBu₄][B(C₆F₅)₄] THF solution, b) 0.1 M [Na][B(C₆H₃(CF₃)₂)₄] THF solution.

	1-Tb^{Ph} (a)	2-Tb^{Ph} (a)	2-Tb^{Ph} (b)	2-Tb^{OTBu} (a)
E_{pc}	-0.19 [0.61]	-0.96 [-0.16]	-0.22 [0.58]	-0.55 [0.25]
E_{pa}	0.41 [1.21]	0.49 [1.39]	0.37 [1.17]	0.83 [1.63]
$\Delta E_{pc}/E_{pa}$	0.60	1.36	0.59	1.38

Indeed the cyclic voltammograms of the **2-Tb^{Ph}** complex measured as 2 mM solutions in THF using [Na][B(C₆H₃(CF₃)₂)₄] as the supporting electrolyte (Figure 4, Table 1) show a narrower peak separation between the redox events ($\Delta E = 0.59$ V) compared to those measured in [NBu₄][B(C₆F₅)₄] ($\Delta E = 1.36$ V) at the same scan rate. Moreover, the reduction event ($E_{pc} = -0.22$ V vs Fc) occurs at a potential 0.74 V more positive than the potential measured with [NBu₄][B(C₆F₅)₄] as the electrolyte. A similar voltammogram with a narrow peak separation ($\Delta E = 0.60$ V) and a reduction event at $E_{pc} = -0.19$ V vs Fc was also measured for the Tb(III) complex **1-Tb^{Ph}** which presents an inner sphere alkali ion.

Furthermore, the voltammogram of the **2-Tb^{Ph}** complex measured as 2 mM solutions in THF using [Li][B(C₆F₅)₄] did not show any signal due to the immediate decomposition of the complex. These differences suggest that the presence of non-redox active alkali metals in the coordination environment of the terbium metal center facilitates the Tb(IV)/Tb(III) reduction. This could be explained in term of metal-ion coupled electron transfer. Electron transfer processes triggered by concerted ion pairing were shown to play an important role in modulating the redox reactivity of metal-oxo intermediates.^[18a, 19] Thus, the inner-sphere binding of potassium to Tb(III) does not affect the oxidation potential, but results in reduced kinetic stability of the oxidized Tb(IV). Notably, 90% of the initial **2-Tb^{Ph}** complex is still present after 3 hours in a THF solution in presence of 0.1 M [NBu₄][B(C₆F₅)₄], but the complex immediately decomposes in presence of 0.1 M [Li][B(C₆F₅)₄].

DFT (B3PW91) calculations were carried out on compounds **1-Tb^{Ph}**, **2-Tb^{Ph}**, and the previously reported complexes **1-Tb^{OTBu}**^[9] and **1-Tb^{N=P}**^[10]. The Tb–O_{siloxy} bond distances are correctly reproduced computationally (2.13–2.20 Å for **1-Tb^{Ph}**, 2.09–2.12 Å for **2-Tb^{Ph}** and 2.07–2.11 Å for **2-Tb^{OTBu}**) indicating the correctness of the method. First of all, the oxidation states of the compounds were studied by computing the unpaired spin densities for all three systems (see Figure S21). As expected for lanthanide complexes, the unpaired spin density is only located at the lanthanide center and its value gives insights on the oxidation state. For complex **1-Tb^{Ph}**, the value is 8.08 whereas it is reduced to 6.36–6.38 for **2-Tb^{Ph}** and **2-Tb^{OTBu}**. These values are consistent with a Tb(III) in **1-Tb^{Ph}** and Tb(IV) for **2-Tb^{Ph}**, **2-Tb^{OTBu}** and **2-Tb^{N=P}** (6.30).

In **2-Tb^{Ph}**, the Tb–O Wiberg Bond Indexes (WBI) are found to be in the 0.60–0.65 range indicating single bonds with an important covalent contribution whereas the Tb–N_{acetonitrile} WBI are only 0.25 in line with a dative interaction. The Tb–O WBI compare well with those found in complex **2-Tb^{OTBu}** (0.54–0.58) and with the Tb–N WBI found in **2-Tb^{N=P}** (0.66). Interestingly, these values of Tb–O WBI are greater than those found in complex **1-Tb^{Ph}** (0.41–0.49). The larger value of Wiberg Bond Index (that only account for covalent interaction) found for Tb(IV) compared to Tb(III) demonstrates the larger covalent character of Tb(IV). The Tb(IV)–O distance decreases compared to Tb(III) as a result of the increased covalency which requires an increased overlap between the more contracted orbitals of Tb(IV) and the O orbitals. The covalency difference between Tb(III) and Tb(IV) is further highlighted using NBO analysis. Indeed, as reported by Maron and Eisentein,^[20] the bonding in trivalent lanthanide complexes is strongly ionic. The same holds true here for complex **1-Tb^{Ph}** as only donations from occupied hybrid sp orbital on each O to empty 5d orbitals on Tb(III) are observed (55 kcal/mol were computed

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for each donation interaction at the second order donor-acceptor NBO level). Moreover, weak π -donation from O to Tb(III) is also found (22 kcal/mol were computed at the second order level for each donation). In **2-Tb^{Ph}**, a slightly polarized Tb–O σ -bond could be located (56% O – 44% Tb). Moreover, the σ - and π -donations from the O to Tb(IV) are greater than for Tb(III) (77 and 42 kcal/mol) indicating some stronger interactions. Interestingly, for **2-Tb^{O^tBu}**, the Tb–O bonds are more strongly polarized toward O (80%) and the σ/π donations are lower than in **2-Tb^{Ph}**. This is line with what found with the WBI (at most a difference of 0.1 between the two complexes), indicating that the bonds are slightly more covalent in **2-Tb^{Ph}** than in **2-Tb^{O^tBu}**. Finally, for **2-Tb^{N=P}**, strongly polarized Tb–N bonds toward N (roughly 90%) and weaker σ/π donations than in **2-Tb^{Ph}** (60 and 22 kcal/mol respectively) are found. The main difference between **2-Tb^{N=P}** and **2-Tb^{Ph}** is the amount of π interaction in the latter. This strong π (O–Tb) interaction evidently contributes to the stability of the complex.

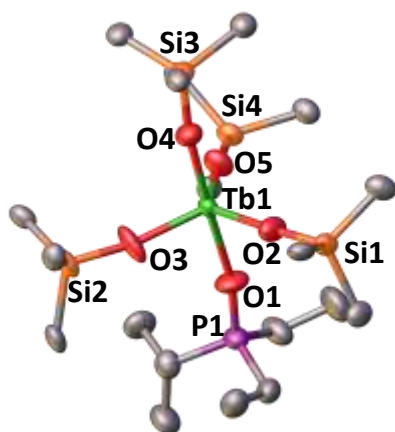


Figure 3. Solid-state molecular structure of $[\text{Tb}^{\text{IV}}(\text{OSiPh}_3)_4(\text{Et}_3\text{PO})]$, **3** (50% probability ellipsoids). Hydrogen atoms and phenyl groups bound to Si atoms are omitted for clarity. Selected bond lengths (Å): Tb–O_{siloxide} = 2.014(3) – 2.047(3); Tb–O_{phosphinoxide} = 2.214(3).

The high solution stability of **2-Tb^{Ph}** and the presence of two open coordination sites in its coordination sphere render reactivity studies accessible. This was confirmed by reactivity studies with phosphinoxide ligands that led, after reaction of **2-Tb^{Ph}** with 1 equiv. of Et_3PO or Ph_3PO , to the replacement of the acetonitrile ligands and the isolation of the complexes $[\text{Tb}^{\text{IV}}(\text{OSiPh}_3)_4(\text{Et}_3\text{PO})]$, **3** (Figure 3) and $[\text{Tb}^{\text{IV}}(\text{OSiPh}_3)_4(\text{Ph}_3\text{PO})]$, **4** which display and (Figure S24). Complexes **3** and **4** display high stability and solubility in toluene. The formation of stable Tb(IV) complexes of trialkyl phosphinoxide ligands is relevant for the development of separation processes contingent on phosphorus-based extractants.^[21]

In conclusion we have isolated and characterized the third example of a molecular complex of terbium(IV), which is highly oxidizing but also shows reasonable solution-phase stability. The stability of the complex could be interpreted in terms of a large covalent contribution to the Tb–O bond not present in the Tb(III) analogue. The isolation of **2-Tb^{Ph}** indicates that ligands capable of saturating the coordination sphere of the terbium ion are not essential for the isolation of stable Tb(IV) compounds. Furthermore, we found that the presence of non-redox active alkali ions at high concentration results in reversible $\text{Tb}^{\text{III}}/\text{Tb}^{\text{IV}}$

redox processes probably enabled by metal-coupled electron transfer. In contrast, in the absence of coordinating alkali ions, a significant destabilization of the terbium(III) compared to the tetravalent oxidation state is observed likely due to ion pairing effects. These results provide key information for the isolation of stable lanthanide(IV) ions with high oxidizing abilities which is key for the expansion of tetravalent lanthanide chemistry and its applications in catalysis and in the development of new separation technologies.

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Keywords: lanthanides • terbium • metal-ion coupled electron transfer • siloxides • rare earths

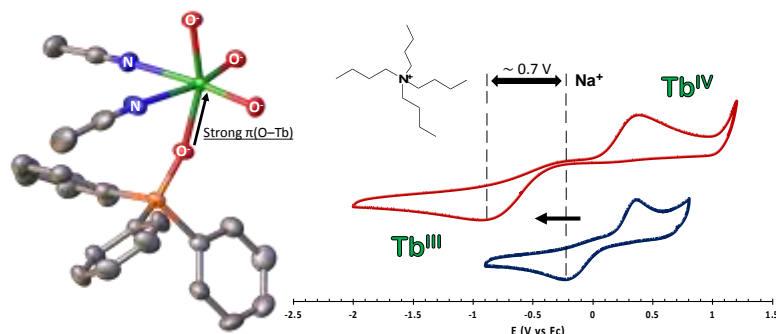
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The complex of terbium(IV) $[\text{Tb}(\text{OSiPh}_3)_4(\text{MeCN})_2]$ contains labile ligands but shows high stability as a result of a strong $\pi(\text{O-Tb})$ interaction. Non-binding counterions contribute to the $\text{Tb}(\text{IV})$ solution stability by destabilizing the +III oxidation state, while alkali ions promote $\text{Tb}(\text{IV})/\text{Tb}(\text{III})$ electron-transfer.

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state in siloxide supported terbium
compounds**