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Reversible Sm(III)/Sm(II) Redox Chemistry of an Organosamarium(III) Complex

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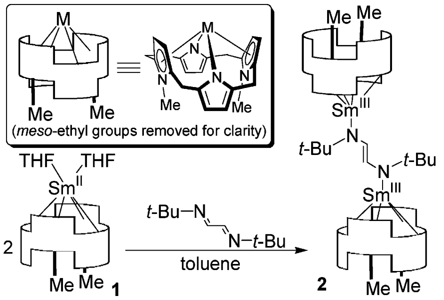
Summary: A binuclear samarium(III) complex featuring the μ-η¹:η¹-bound dianion of 1,4-di-tert-butyl-1,4-diazabuta-1,3-diene has been prepared which exhibits reversible redox behavior, reverting to the samarium(II) precursor when dissolved in tetrahydrofuran. The new samarium(III) complex has been characterized by ^{1}H and ^{13}C NMR spectral data, microanalytical data, magnetic moment measurements in solution, and an X-ray crystal structure determination.

The most commonly exploited reactivity features of organolanthanide complexes (Lewis acidic nature and, for some, reducing abilities) have granted them increasing importance in industrial- and laboratory-scale synthesis. Sm(II) and Sm(III) complexes are most prominent in stoichiometric and catalytic applications,[1] as well as the forerunning breakthroughs in strategic basic organometallic synthesis.[2] This relates to the commercial accessibility of organometallic complexes and precursors in both oxidation states, which in turn is due to the unique Sm(III)/Sm(II) reduction potential (−1.55 V) within the Ln series.[3]

The scope of organosamarium(II) complexes as reducing agents has been greatly limited by their hitherto nonreversible redox behavior in many circumstances. This necessitates the use of stoichiometric amounts of Sm(II) reagents, often making them the reagent of choice only when their advantages of mildness and functional group tolerance/selectivity cannot be attained with a catalytic reducing reagent. Reports of reversible Sm(II)/Sm(III) redox chemistry in organometallic chemistry are limited to the following instances: (i) N_2 and substituted alkene and butadiene complexes of decamethylsamarocene(II)[4] and (ii) N_2 and C_2H_4 complexes of tetrametalated porphyrinogens.[5] A reversible Yb(III)/Yb(II) system[6] based on neutral/radical anion interconversion of 1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene (*t*-BuDAB) and U(IV)/U(III) systems based on N_2 and pyrazine reduction have recently been identified.[7,8] We report here the synthesis of a binuclear Sm(III) complex from a Sm(II) precursor and the reversible redox behavior of these complexes driven by a solvation equilibrium.

Scheme 1. Synthesis of Complex 2



A brown toluene solution of the *trans-N,N*′-dimethyl-modified metallo-*meso*-octaethylporphyrinogen Sm(II) complex[9] **1** reacts quickly with $^1/_2$ equiv of *t*-BuDAB, giving a green solution from which green crystals of **2** were isolated (Scheme 1).

The characterization of **2** included ^{1}H and ^{13}C NMR spectral data, microanalytical data, magnetic moment measurements in solution, and an X-ray crystal structure determination (Figure 1).

The Sm centers in **2** bind to the macrocycles via η^5:η^1:η^5:η^1 interactions (Figure 1a). The reduced diazabutadiene bridges Sm centers, primarily through the nitrogen centers. In addition, close contacts (of the length observed for Sm−C/H agostic interactions) to the

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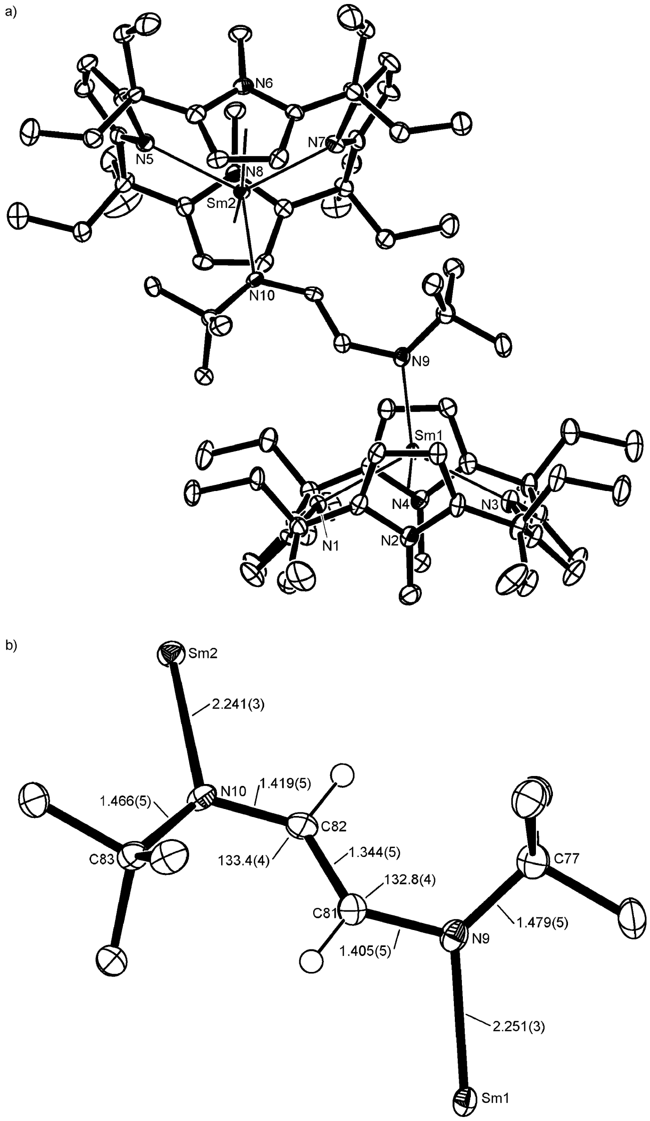
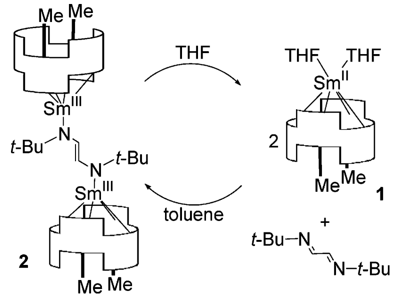


Figure 1. X-ray crystal structure of **2** with 50% probability ellipsoids: (a) general view of the whole molecule (all hydrogens omitted for clarity); (b) reduced diazabutadiene section of the molecule viewed perpendicular to the plane of the diazabutadiene (all hydrogens omitted, except the vinylic hydrogens (calculated)). Selected bond lengths (Å) and angles (deg): Sm1−N1,N3 = 2.504(3), 2.542(3), Sm1−Ct2,Ct4 = 2.6_9, 2.6_5, Sm2−N5,N7 = 2.545(3), 2.520(3), Sm2−Ct6,Ct8 = 2.6_6, 2.6_4, Sm1−C81,H81 = 3.050, 2.8_7, Sm2−C82,H82 = 3.007, 2.8_5; N1−Sm1−N3 = 121.7(1), Ct2−Sm1−Ct4 = $161._5$, N5−Sm2−N7 = 123.1(1), Ct6−Sm2−Ct8 = $161._5$, N9−Sm1−N1,N3 = 112.7(1), 125.6(1), N10−Sm2−N5,N7 = 123.2(1), 113.7(1), Sm1−N9−C77,C81 = 128.0(2), 110.9(2), Sm2−N10−C83,C82 = 129.5(2), 108.4(3).

C_2H_2 portion are noted (Sm1−C81,H81 = 3.050(4), 2.8_7 Å, Sm2−C82,H82 = 3.007(4), 2.8_5 Å). The only other known bridging $(t\text{-BuDAB})^{2-}$ example exhibits solely μ-η^1:η^1 binding (in a Nb complex[10]); however, it features a syn arrangement of the M−N−C−C fragment which affects interactions involving the C_2H_2 section.[11] In comparison, $[(C_5Me_5)_2Ln(THF)_2]$ (Ln = Sm, Yb) react with *t*-BuDAB, giving $[(C_5Me_5)_2Ln(t\text{-BuDAB})]$, in which the diazabutadiene chelates as a singly reduced radical anion.[6,12] Complex **2** does not react with an additional 1 equiv of *t*-BuDAB.

Scheme 2. Reversible Redox Properties of Complex 2



Quantitatively, the structure of **2** is consistent with the presence of Sm(III) centers and a two-electron-reduced diazabutadiene unit. For example, the Sm−centroid (*N*-methylpyrrolyl) distances of 2.6_4−2.6_9 Å are comparable to those in the analogous Sm(III) bis(trimethylsilyl)amide[9] (2.64_5−2.66_7 Å) and are considerably shorter than in the Sm(II) precursor **1** (2.75_6 Å).[9] Further, the geometry of the reduced diazabutadiene (Figure 1b) confirms this formalism: viz., long−short−long distances within the NCCN unit and typical Sm−N distances for Sm(III) amides (cf. 2.306(2)−2.314(2) Å for the aforementioned bis(trimethylsilyl)amide[9]). In comparison, neutral and singly reduced chelating diazabutadienes (a bridging example of the latter is unavailable for comparison) feature short−long−short or intermediate distances within the NCCN units, respectively, as in $[Li(t\text{-BuDAB})_2]$ (1.236(5)−1.488(5)−1.248(5) and 1.317(6)−1.399(7)−1.317(5) Å).[13]

Magnetic moment measurements on **2** are also consistent with a Sm(III) oxidation state in solution (C_6D_6, 25 °C, Evans method[14]): 2.74 μ_B (1.94 μ_B per Sm for noncommunicating metal centers). Further, the paramagnetic shift effects on the ^1H NMR spectrum of **2** are minimal and are similar to those previously noted for Sm(III) complexes of the same macrocycle (cf. chemical shift range of 42.19 to −21.07 ppm for the Sm(II) complex **1** at 25 °C).[9]

Compound **2** is stable when dissolved in benzene, toluene, and hexane but displays the remarkable property of rapidly reverting to the Sm(II) species **1** when dissolved in THF (quantitatively on the basis of ^1H NMR spectral data). Removal of THF in vacuo forces the equilibrium again toward the green Sm(III) derivative **2**, which can be crystallized from toluene as before (Scheme 2).

The solvation-driven Yb(III)/Yb(II) redox chemistry of $[(C_5R_5)_2Yb(t\text{-BuDAB})]$ (R = Me) is influenced by steric effects, such that the nonmethylated analogue (R = H) does not display this reactivity.[6] Extreme steric interactions between ligands is also known to result in unusual

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organolanthanide redox chemistry: e.g., the "sterically induced reduction chemistry" of $[(C_5Me_5)_3Sm]$.[2c] In a more general sense, solvent dielectric constant effects are known to influence electron exchange reactions,[15] and substantial ligation effects on the reductive ability of Sm(II) have been documented.[16] We are not yet in a position to comment on the principle giving rise to the redox reactivity of **2**, be it linked to steric effects of the macrocycle[17] or the electronic characteristics conveyed onto the Sm center from the metalated modified porphyrinogen.

In conclusion, we have reported a rare example of a reversible Sm(II)/Sm(III) system. We are studying the underlying grounds for this remarkable and highly promising chemistry through theoretical investigations and extending the chemistry to other lanthanides and reducible substrates.

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Note Added after ASAP Publication. There was an inadvertent omission of an author name in the version of the paper that was posted on the Web on April 6, 2005. The author list that now appears is correct.

Supporting Information Available: Text giving experimental preparation details and a CIF file giving crystallographic data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) See, for example: Arnett, E. M.; Troughton, E. B.; McPhail, A. T.; Molter, K. E. *J. Am. Chem. Soc.* **1983**, *105*, 6173–6174.

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