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Use of Calix[4]arenes in the Redox Chemistry of Lanthanides: the Reduction of Dinitrogen by a Calix[4]arene–Samarium Complex

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The synthesis and structural characterization of a samarium–dinitrogen complex supported by a calix[4]arene ligand in which the N–N bond distance has been stretched to 1.611(16) Å are described. The central μ_3-η^2:η^2:η^2-hydrazido tetraanion formed is bonded to three Sm^{III} centers with an overall butterfly-type arrangement.

Since the discovery that a biologically unrelated transition-metal complex was able to bind dinitrogen,[1] formidable efforts have been pursued in the field of its coordinative and reductive binding.[2] For a long time, the use of lanthanides was disregarded within this context, mostly because reaction of the soft and poor ligand dinitrogen was not expected to occur with such hard metal ions. A key date is 1988, when Evans et al. communicated the first planar side-on bound dinitrogen complex $(Cp^*_2Sm)_2-(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$ in which the coordinated dinitrogen unit is unactivated.[3] In the chemistry of early transition metals, the side-on bonding mode of dinitrogen, compared to the end-on bonding mode, is recognized to enhance its reduction, as revealed by the N−N bond distance observed in a wide variety of metal complexes.[4] Nonetheless, despite the fact that in the case of lanthanides[5] this has been the only coordinating mode ever observed since the seminal report by Evans et al., only a few examples of four-electron reduction of dinitrogen by samarium complexes have been reported.[6] Interestingly, they appear to result from a multimetallic cooperative process in which each divalent metal ion contributes one electron to the overall four-electron process.[7] In this context, particular attention should be addressed by the choice of the supporting ligands. First, the coordinating environment should enhance the reductive behavior of the metal, and, second, its geometry should be such that multimetallic reductive pathways remain accessible.

Therefore, the use of calix[4]arene[8] anions as ligands brings two significant peculiarities. First, the electron-rich environment provided by the oxygen donor atoms forms an ideal platform for developing the organometallic and redox chemistry of lanthanides. Second, the preorganization of the quasi-planar O_4 set leads to the formation of "half-sandwich"-type metallic complexes, thereby limiting the steric hindrance on one side. Moreover, a successful precedent in the use of calix[4]arene anions in the reduction and cleavage of dinitrogen has been obtained with low-valent niobium.[9]

The starting materials that we devised for this study are displayed in Scheme 1. The use of the bis-O-alkylated calix[4]arene allows tuning of the macrocycle charge[10] to a value appropriate for entering the chemistry of lanthanides within an oxygen donor environment. The reaction of $LnCl_3(THF)_2$ with the lithium or sodium salt of calix[4]arene [*p*-^{t}Bu-calix[4]-$(OMe)_2(OH)_2$] (**1**)[11] led to the formation of dimeric

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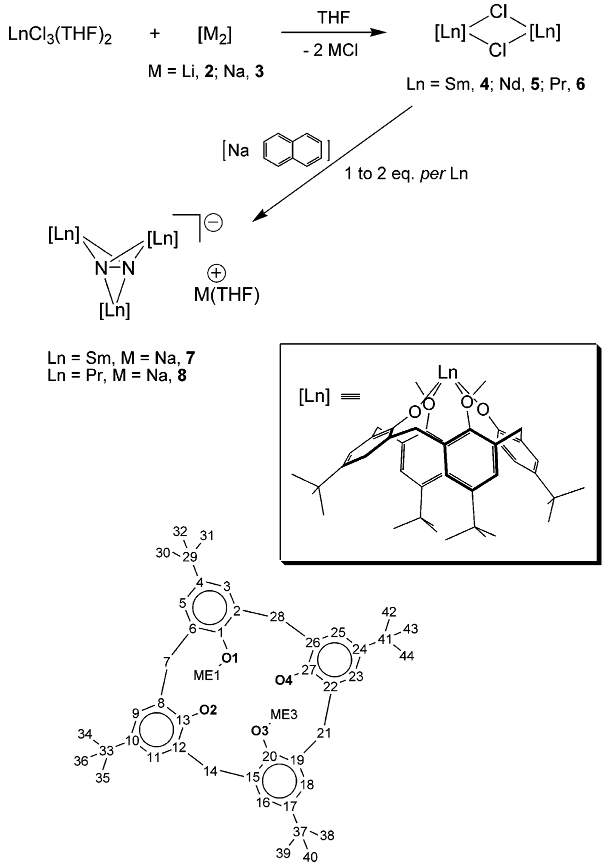
Scheme 1. (Top) Reaction Pathway for the Synthesis of **4**−**6**, **7**, and **8** (Brackets Stand for Calix[4]-(OMe)$_2$(O$^-$)$_2$; (Bottom) Numbering Scheme Adopted for the Calix[4]arene Skeleton (Carbon Atoms Are Labeled with Their Number Only)



complexes [*p*-^{t}Bu-calix[4]-(OMe)$_2$(O)$_2$Ln(THF)]$_2$(μ-Cl)$_2$ (Ln = Sm, **4**; Nd, **5**; Pr, **6**), in which the metal ions are bridged by two chloride anions. The structures of **4**−**6** are exemplified by that of **4** (see Figure 1),[12] which possesses a crystallographic C_2 symmetry, with the twofold axis running through the chloride anions. The heptacoordination of the metal ion is completed by a molecule of THF, and the calixarene ligand assumes the elliptical conformation expected in the case of metal complexes of bis-O-alkylated calix[4]arene.[11,13] The ellipticity is shown by the separation between *p*-carbon atoms of opposite aromatic rings [C4···C17, 9.632(13) Å; C10···C24, 6.022(12) Å] and by the dihedral angles between the mean planes through opposite aromatic rings [C1−C6^C15−C20, 82,1(3)°; C8−C13^C22−C27, 13.4(3)°].

The complexes **4**−**6** are therefore well suited for exploring their reduction under dinitrogen. Regardless of the Sm/Na stoichiometry in the starting materials, the reduction of [Sm]$_2$-(μ-Cl)$_2$ (**4**) by sodium naphthalenide under dinitrogen yields the trinuclear complex {[*p*-^{t}Bu-calix[4]-(OMe)$_2$(O)$_2$Sm]$_3$-(THF)(μ_3-η^2:η^2:η^2-N$_2$)}$^-${Na(THF)}$^+$ (**7**), in which three samarium units are arranged around a central side-on dinitrogen moiety. Complex **7** displays a considerable thermal stability, without showing any kind of dinitrogen loss. This observation is in line with an irreversible four-electron reduction of dinitrogen. Such a reduction degree is further supported by the structural parameters of dinitrogen in complex **7** (see below), the structure of which is shown in Figure 2 and a close-up of the core in Figure 3.[14]

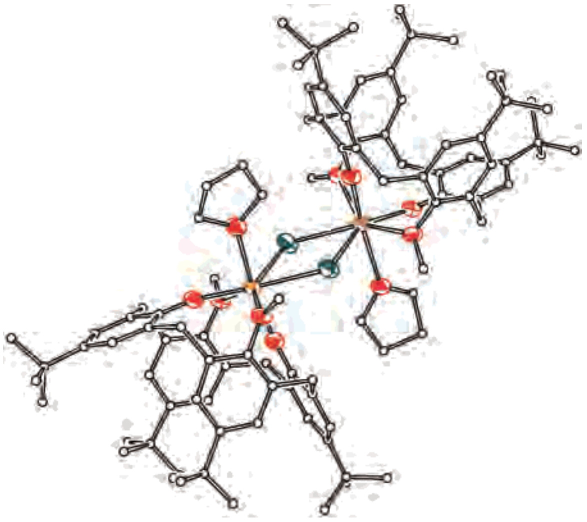


Figure 1. X-ray structure of complex **4**. Protons have been omitted for clarity. Samarium (gold), oxygen (red), and chlorine (green) atoms are represented with 50% probability ellipsoids.

The structure of **7** shows the arrangement of the three [Sm]$^+$ cations, which are linked with each other by two bridging oxygen atoms from calix[4]arenes and a μ_3-η^2:η^2:η^2-N$_2$ molecule. The overall structure is monoanionic according to the 3+ oxidation state for samarium and the presence of the hydrazido tetraanion, while a sodium countercation is hosted in one of the calix cavities.[11] This peculiarity, which is often encountered in metallacalix[4]-arene complexes and emphasizes their ability as alkali-metal ion carriers,[10] is a result of the elliptical conformation displayed by the calix[4]arene skeletons in **7**, which opens the cavity and allows the binding of Na$^+$. Such binding inside the cavity has only a minor effect on the geometrical features of the samarium−calix[4]arene fragment, as shown by the mean value of the Sm−O distances [see the Supporting Information for details]. Dinitrogen displays in **7** a quite unique μ_3-η^2:η^2:η^2 bonding mode,[6a] so that the metal ions and dinitrogen give rise to a butterfly form. We can speculate that for steric reasons the formation of a Sm^{III} tetramer anchoring the dinitrogen moiety is not accessible. The N−N

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[12] Crystal data for **4**: C$_{100}$H$_{132}$Cl$_2$O$_{10}$Sm$_2$·4C$_4$H$_8$O, M = 2154.3, monoclinic, space group $C2/c$, a = 35.136(2) Å, b = 16.798(2) Å, c = 20.627(3) Å, β = 109.00(2)°, V = 11510.9(2) Å^3, Z = 4, ρ_{calcd} = 1.243 g/cm^3, F(000) = 4520, λ(Mo Kα) = 0.710 69 Å, μ(Mo Kα) = 11.14 cm^{-1}, crystal dimensions 0.16 × 0.18 × 0.21 mm. The final R is 0.074 (wR2 = 0.213 calculated on the 8844 unique squared reflections having $I > 0$).

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[14] Crystal data for **7**: C$_{146}$H$_{190}$N$_2$NaO$_{14}$Sm$_3$·7C$_4$H$_8$O, M = 3176.0, triclinic, space group $P1$, a = 19.471(2) Å, b = 20.340(4) Å, c = 25.884(4) Å, α = 103.25(3)°, β = 103.36(3)°, γ = 114.44(3)°, V = 8252(5) Å^3, Z = 2, ρ_{calcd} = 1.278 g/cm^3, F(000) = 3338, λ(Mo Kα) = 0.710 69 Å, μ(Mo Kα) = 11.20 cm^{-1}, crystal dimensions 0.16 × 0.20 × 0.23 mm. The final R is 0.069 (wR2 = 0.225 calculated on the 18 112 unique squared reflections having $I > 0$).

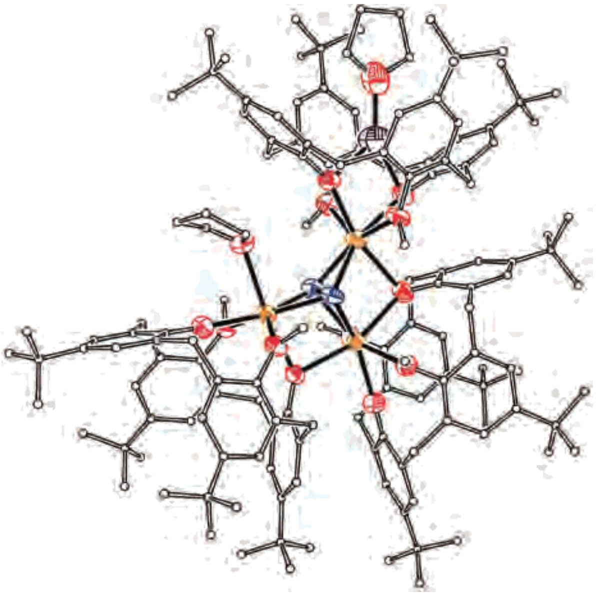

Figure 2. X-ray structure of complex **7**. Protons have been omitted for clarity. Samarium (gold), oxygen (red), nitrogen (blue), and sodium (purple) atoms are represented with 50% probability ellipsoids.

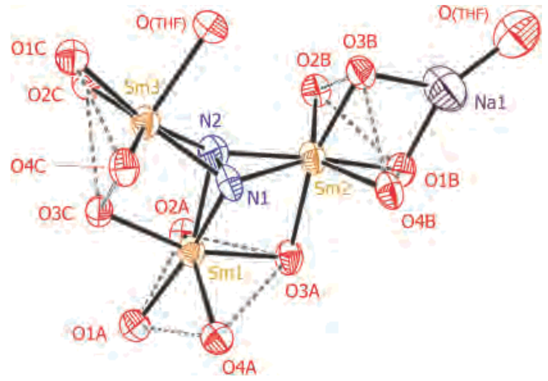

Figure 3. Close-up of the core in complex **7**. Dashed bonds set out the calix[4]arene areas; labels A−C are relative to calix[4]arenes A−C. Bond length: N1−N2, 1.611(16) Å.

bond distance in **7** is stretched to 1.611(16) Å. Notwithstanding the error limit (1.563 and 1.659 Å), this N−N distance is longer than those in the other cases of four-electron-reduced dinitrogen reported for samarium complexes [maximum length observed to date for a samarium *meso*-octaethylporphyrinogen complex: 1.525(4) Å in a N_2Li_4 unit within two samarium ions][15] and also matches with the longest N−N bond distance so far reported for side-on dinitrogen complexes [maximum length observed to date: 1.548(7) Å in a side-on $(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}N_2)\{[PNP]ZrCl\}_2$ complex, where $[PNP] = (^iPr_2PCH_2SiMe_2)_2N$].[16]

The reaction of **6** (a praseodymium analogue of **4**) with $NaC_{10}H_8$ under dinitrogen yields **8**, as evidenced by elemental analysis and gas-volumetric measurements. This result indicates that lanthanides other than samarium can be equally well used for the same purpose. Although the degree of reduction of the dinitrogen unit in **8** could not be ascertained without further structural evidence, this result emphasizes the fact that calix[4]arenes can be used in a quite promising redox chemistry of lanthanides, including those that are not expected to reach a 2+ oxidation state.[5,17]

The chemical and geometrical peculiarities of the electron-rich environment provided by the calix[4]arene dianion, which is expected to disfavor any low oxidation state of a metal,[18] are the major factors that may explain the impressive reduction of the coordinated dinitrogen unit in **7**. Understanding the parameters that favor the coordinative binding of dinitrogen to metal ions but also drive its multielectron reduction is a goal yet to be achieved in the prospect of developing catalytic transformations using dinitrogen as a raw material under mild conditions,[19] as biological systems do.[20] Within this context, the use of a planar matrix of oxygen donor atoms modeled by calixarene ligands may play a key role and opens a novel perspective into the dinitrogen chemistry of the particularly oxophilic lanthanides.

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Supporting Information Available: Experimental details and CIF files for **4** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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