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Stabilization of Imidosamarium(III) Cubane by Amidinates

Cheng-Ling Pan,[†] Wan Chen,[†] Shuyan Song,[†] Hongjie Zhang,*[,†] and Xingwei Li*[,‡]

[†]*State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Science, Changchun 130022, Jilin, People's Republic of China, and* [‡]*The Scripps Research Institute, Scripps, Florida, Jupiter, Florida 33458*

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An imidosamarium(III) cubane has been prepared from the reductive cleavage of azobenzene by a divalent samarium bis (amidinate) complex, indicating that the "spectrator" bis(amidinate) and the resulting imido ligands help to stabilize the cubane framework. The cubane-type imido cluster is a novel unit in lanthanide chemistry.

Ever since the report of a series of studies on the unique yet rich chemical reactivity of Sm^{II} in the 1980s, the chemistry of lanthanide complexes has been increasingly attractive and has become an important field in inorganic chemistry.[1] Isolable divalent samarium complexes can be stabilized by various ligands, but most of the previous work deals with samarocene and its derivatives.[1,2] In particular, the formation of $[\{Sm(\eta^5\text{-}C_5Me_5)_2\}_2N_2]$ during the recrystallization of $[Sm(\eta^5\text{-}C_5Me_5)_2]$ under a dinitrogen atmosphere represents important progress and has broadened the scope of the solution chemistry of divalent lanthanide.[3] This is due to the significance of the side-on coordination of dinitrogen to lanthanide centers and the subsequent activation of the strong N≡N bond under mild conditions, as were independently reported by Evans and Gambarotta.[4]

Metal imido complexes have been identified as key intermediates in both industrial and biological processes such as model studies of dinitrogen fixation.[5] Lanthanide-containing cubane-like clusters are ubiquitous and are closely correlated to their chemical reactivity.[5] These clusters have drawn much attention primarily because of their relevance to metalloenzymes[6] and industrial metal sulfide catalysts.[7] To the best of our knowledge, only two examples of nitrogen-bridged lanthanide cubic clusters have been reported to date. In one example, complex $[\{Cp'Ln(\mu_3\text{-}NCH_2Ph)\}_4]$ (Ln = Y or Lu; Cp′ = $C_5Me_4SiMe_3$), which adopts a cubane-type Ln_4N_4 structure, was isolated from the reaction of lanthanide polyhydrides and PhCN.[8] The other example was obtained by the imido transfer reaction from $[\{PhNMg(THF)\}_6]$ (THF = tetrahydrofuran) to NdI_3.[9]

We have recently successfully synthesized a series of samarium complexes stabilized by a silyl-linked dianionic bis(amidinate) ligand $[Me_2Si\{NC(Ph)N(2,6\text{-}Pr^i{}_2Ph)\}_2]^{2-}$ (**1**). We now report the ligation of **1** and the synthesis of a stable divalent samarium complex, $[(\mathbf{1})SmI_2Li_2(THF)(Et_2O)_2]$ (**2**), and its subsequent reaction with azobenzene, leading to a rare example of cubane-type samarium clusters. This system represents the first example of imido-bridged lanthanide cubane-type clusters as a result of N=N bond cleavage and is possibly relative to dinitrogen fixation and reduction process.

The reaction of the lithium salt of dianion **1**[10] with $SmI_2(THF)_2$ in THF yielded a black solution, from which complex **2** was isolated in 66% yield. Addition of azobenzene (1:4 equiv) to a THF solution of **2** at room temperature gave a

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*To whom correspondence should be addressed. E-mail: xli@scripps.edu (X.L.), hongjie@ciac.jl.cn (H.Z.).

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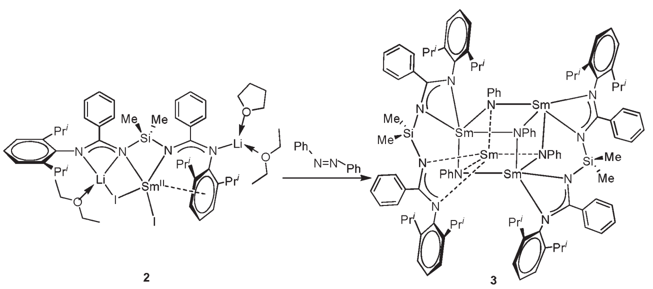
Scheme 1



brown solution, and thus **3** was isolated in 22% yield (Scheme 1). These two complexes have been fully characterized by elemental analysis, IR spectroscopy, NMR spectroscopy, and X-ray crystallography.[11]

Single crystals of complexes **2** and **3** were obtained from their Et_2O solutions. Both lithium and iodide are incorporated in complex **2**, and the coordination sphere of the Sm atom includes the two central N atoms of this $SiMe_2$-tethered amidinate unit [Sm−N2 2.636(7) Å; Sm−N3 2.562(6) Å], a terminal iodide [Sm−I2 3.1801(7) Å], a bridging iodide [Sm−I1 3.2001(7) Å], and an adjacent η^6 arene (Figure 1). Contrary to the typical chelating binding mode of typical amidinates, the two amidinate units coordinate to the Sm center with the two central N atoms. The observation of this rare binding mode indicates that ligand **1** is perhaps a valid alternative to the more common cyclopentadienyls, and it helps to stabilize the divalent metal center in complex **2**.

The scope and applications of SmI_2 and other Sm^{II} π complexes have been widely studied. While most of the previous studies on the chemistry of Sm^{II} have been carried out for samarium(II) cyclopentadienyl (Cp) complexes,[12] there is an increasing interest in the synthesis and applications of divalent σ-bonded organolanthanide complexes RLnX (Ln = Sm, Eu, and Yb; X = Br and I). The first compound of this type was obtained over 30 years ago by Evans and coworkers from organic iodides and lanthanide metals in THF.[13] However, such complexes were poorly characterized in most cases. As a consequence, only limited information is available on the structure of bis(amidinate) complexes.[14]

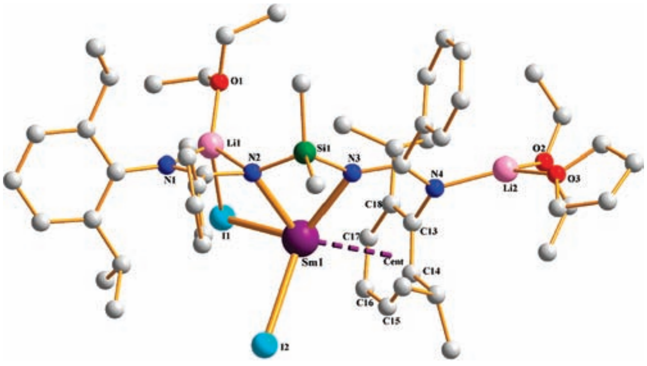


Figure 1. Molecular structure of **2**. Selected bond lengths (Å) and angles (deg): Sm1−N3 2.562(6), Sm1−N2 2.636(7), Sm1−C13 3.001(8), Sm1−C14 3.005(8), Sm1−C16 3.030(8), Sm1−C15 3.045(9), Sm1−C18 3.067 (8), Sm1−Cent 2.696, Sm1−I2 3.1801(7), Sm1−I1 3.2001(7), I1−Li1 2.822(16), Li1−N1 1.962(16), Li1−N2 2.236(16), Li2−N4 1.945(16), Si1−N2 1.737(6), Si−N3 1.731(6), Li1−O1 1.927(16), Li2−O2 1.926(16), Li2−O3 1.929 (17); N3−Sm1−N2 60.97(19), N1−Li1−N2 66.0(5).

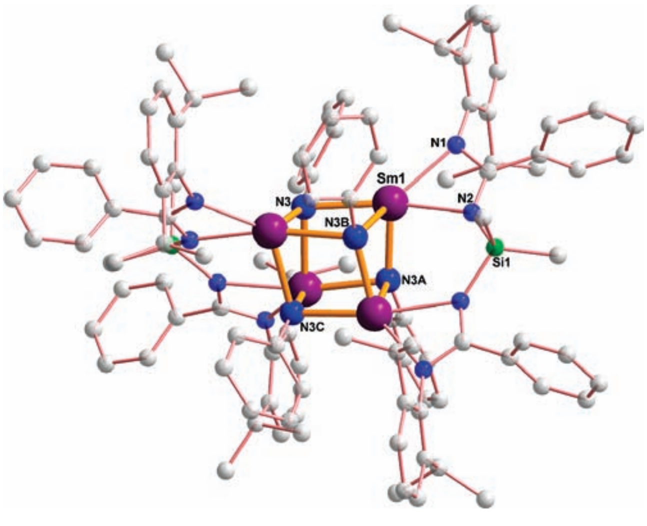


Figure 2. Molecular structure of **3**. Selected bond lengths (Å) and angles (deg): Sm1−N1 2.431(3), Sm1−N2 2.457(3), Sm1−N3 2.238(3), Sm1−N3A 2.450(3), Sm1−N3B 2.459(3), Sm1···Sm1A 3.6999(3), Sm1···Sm1B 3.4398(3), Sm1···Sm1C 3.6699(3); N1−Sm1−N2 55.38(9), N3−Sm1−N3A 82.09(10), N3−Sm1−N3B 83.98 (10).

X-ray crystallography also confirmed the cubane-type structure of complex **3** (Figure 2). This cubane-type imido cluster consists of four Sm atoms and four μ_3-imido ligands at the alternating corners of the cube. Each Sm atom is stabilized by a chelating amidinate unit [Sm−N1 2.431(3) Å; Sm−N2 2.457(3) Å] and three bridging imido groups [Sm−N3 2.238(3) Å; Sm−N3A 2.450(3) Å; Sm−N3B 2.459 (3) Å], with the latter resulting from the four-electron reduction of azobenzene. The two silyl-linked bis(amidinate)

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(11) Synthesis for **2** and **3**: All operations were performed under an inert atmosphere (< 5 ppm oxygen or water) in a nitrogen-filled drybox or by using a standard Schlenk-type technique. **2**: THF (20 mL) was added to a mixture of $SmI_2(THF)_2$ (0.84 g, 1.52 mmol) and $[(Me_2Si\{NC(Ph)N(2,6\text{-}Pr^i{}_2Ph)\}_2)_2\text{-}Li_4(THF)_4]$[10] (1.16 g, 0.75 mmol) to give a dark-blue solution. The mixture was stirred for 24 h at 25 °C, after which the solvent was removed under reduced pressure. The black residue was extracted with Et_2O (40 mL) and filtered through a cannula. The black filtrate was concentrated to approximately 5 mL under reduced pressure and stored for 5 days, affording **2** as small dark-purple blocks (1.25 g, 65.8% based on Sm). Anal. Calcd for $C_{52}H_{78}I_2Li_2N_4O_3SiSm$: C, 49.83; H, 6.27; N, 4.47. Found: C, 49.29; H, 5.84; N, 4.21. IR (KBr, cm^{-1}): 1631 (s), 1605 (m), 1574 (m), 1498 (w), 1492 (w), 1447 (w), 1436 (w), 1382 (w), 1361 (w), 1325 (w), 1256 (m), 1203 (w), 1178 (w), 1103 (w), 1057 (w), 1041 (w), 1026 (w), 969 (w), 936 (w), 852 (w), 790 (w), 779 (m), 748 (w), 696 (m). ^1H NMR (C_6D_6, 400 MHz) for **2**: δ 7.66, 7.35−7.14 (Ar*H*), 6.96 (Ar*H*), 3.57 (C*H*Me$_2$), 1.21 (CH*Me*$_2$), 0.41 (Si*Me*$_2$), 3.38, 2.22, 1.11, 0.96 (Et_2O, THF). **3**: A black solution of **2** (1.91 g, 1.51 mmol) in THF (30 mL) was added dropwise to a solution of PhN=NPh (0.07 g, 0.38 mmol) to give a yellow/black suspension. The mixture was vigorously stirred, resulting in a rapid color change to yellow and concomitant formation of a white precipitate (LiI). After 24 h, the THF solvent was removed and extracted with Et_2O. Recrystallization from Et_2O (ca. 2 mL) afforded 0.24 g (21.6%, based on Sm) of **3** as yellow crystals. Anal. Calcd for $C_{104}H_{120}N_{12}Si_2Sm_4$: C, 56.89; H, 5.51; N, 7.65. Found: C, 56.64; H, 5.26; N, 7.36. IR (KBr, cm^{-1}): 1632 (s), 1603 (m), 1575 (w), 1498 (m), 1464 (w), 1447 (w), 1436 (w), 1382 (w), 1361 (w), 1325 (w), 1255 (m), 1204 (w), 1176 (w), 1057 (w), 1041 (w), 1026 (w), 971 (w), 936 (w), 852 (w), 790 (w), 778 (w), 749 (w), 694 (m). ^1H NMR (C_6D_6, 400 MHz) for **3**: δ 8.13, 7.89, 7.36−6.74, 6.46 (Ar*H*), 3.37 (C*H*Me$_2$), 1.22 (CH*Me*$_2$), 0.41 (Si*Me*$_2$).

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ligands surround the nitrogen-bridged cubane unit $[Sm_4(\mu_3\text{-}NPh)_4]^{4+}$.

The assembly of a cluster in complex **3** via reductive scission of the N=N bond is noteworthy. Cleavage of azobenzene substrates has been observed in divalent lanthanide chemistry,[15] but this is the first example of azobenzene cleavage that gives an imidosamarium cubane complex.[15] Interesting analogies could be made between imido ligands and dianionic analogues such as O^{2-} and S^{2-}. In stark contrast, the imido chemistry of lanthanide is much less understood.[8,9] In contrast to d-block transition-metal complexes, the imido- or amidolanthanide complexes have been much less studied. Thus, examples of imido-containing organolanthanide clusters are even rarer.[16] Di-, tetra-, and hexanuclear lanthanide compounds in which the RN^{2-} groups act as bridging or capping ligands have been reported.[9,15,17] The RN^{2-} anion can flexibly adopt a terminal, μ_2-, μ_3-, or μ_4-bridging ligation mode,[9,15,18] thus allowing versatility in structures, reactivity, and physical properties, and these properties can be strongly influenced by the nature of the R substituent.

In summary, the synthesis of imide complexes from the Sm^{II}-mediated reductive cleavage of azobenzene has been achieved to give nitrogen-bridged clusters. The structural versatility and novelty of these samarium compounds encourage us to further carry out investigations on the synthetic scope, reactivity, and mechanisms of these clusters. The chemical reactivity of lanthanide imides, amides, and amidinates will be reported in due course.

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Supporting Information Available: Crystallographic data of complexes **2** (CCDC 715186) and **3** (CCDC 715187) in CIF format, general synthetic consideration, and synthesis, molecular structure, crystal data and structure refinement, and bond lengths and angles of **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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