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Dinitrogen Reduction Operated by a Samarium Macrocyclic Complex. Encapsulation of Dinitrogen into a Sm_2Li_4 Metallic Cage

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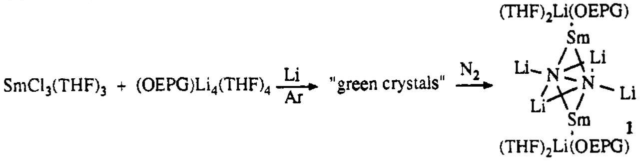
In spite of the considerable number of dinitrogen complexes reported since the discovery of the first example of dinitrogen fixation in $[Ru(NH_3)_5]^{2+}$ 30 years ago,[1] the chemistry of N_2 still remains in its infancy. However, new perspectives for the metal-promoted activation fixation of dinitrogen are opening up, as has been recently seen in both the reversible dinitrogen activation operated by the lithium countercation of an anionic Zr(III) complex[2] and the considerable reduction of N_2 performed by electron deficient low-valent early transition metals.[3] In the latter case, the variety of bonding modes of dinitrogen associated with these systems[4] has been carefully investigated and rationalized.[4a]

Low-valent lanthanides, and in particular Sm(II), are potentially good systems for studying the coordination/reduction of dinitrogen.[5] Samarocene dinitrogen complex $(Cp^*{}_2Sm)_2(N_2)$ provides a puzzling example where the strikingly short N–N distance,[6] which suggests minimal N_2 reduction, is in contrast to the side-on bonding mode. Unfortunately low-valent lanthanides are rare and, besides the bis(cyclopentadienyl) systems,[7] limited to a very few examples.[8] To date, $(Cp^*{}_2Sm)_2(N_2)$ remains the sole case of coordination of dinitrogen in the lanthanide series.

We describe in this paper the preparation of a low-valent Sm macrocyclic complex and its reaction with dinitrogen to form a tetralithium hydrazide salt. The choice of the porphyrinogen tetraanion as a spectator ligand was 2-fold. First, we were interested in studying the behavior of the highly reactive Sm(II) center in a coordination environment sterically and electronically more flexible than that provided by two cyclopentadienyl rings. Second, the alkali cations, easily retained by the porphyrinogen ligand,[10b,c] may play an important role in promoting molecular activation processes at the Sm(II) center.

Scheme 1



The reduction of the mixture obtained from the reaction of $SmCl_3(THF)_3$ with the colorless tetralithium salt of octaethylporphyrinogen (OEPG)[9] $(OEPG)Li_4(THF)_4$[10] under argon may be conveniently carried out in a one-pot preparation forming a gold yellow complex.[11] The subsequent reduction with 1 equiv of metallic lithium proceeds at room temperature in THF under argon to yield a deep-green, extremely air-sensitive crystalline material (Scheme 1). While the extreme air-sensitivity of this species in combination with easy loss of volatile components has prevented formula determination by elemental analysis, recrystallization of this complex from THF under nitrogen yielded moderately air-stable orange-red crystals of $[(THF)_2Li(OEPG)Sm]_2(N_2Li_4)$ (**1**).

The formation of **1** is a perfectly reproducible process, and it can be achieved both by slow recrystallization of the green solid from a dilute THF solution under N_2 (5% yield) and by exposure to an increased pressure of N_2 (7 atm) in an autoclave at 60 °C overnight (45%). In analogy with $(Cp^*{}_2Sm)_2(N_2)$,[6] the formation of **1** at atmospheric pressure was concentration dependent. Crystals of **1** were only obtained from dilute solutions of THF after several days, while concentrated solutions gave either the green crystalline material or a mixture of **1** with green crystalline material.

The X-ray crystal structure determination of **1**[12] has shown a dimeric complex where two $(THF)_2Li(OEPG)Sm$ units are bridged by a planar N_2Li_4 moiety placed on a symmetry center (Figure 1). The molecule may be conveniently described in terms of a rather regular coordination octahedron bound by two samarium atoms on the vertical axis, and four lithium cations

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[11] A solution of $SmCl_3(THF)_3$ (5.04 g, 10.6 mmol) in freshly distilled anhydrous THF (200 mL) was treated under Ar with colorless $Li_4OEPG(THF)_4$ (9.51 g, 11.1 mmol). The solution immediately became golden yellow, and stirring was continued overnight. Metallic lithium (0.074 g, 10.6 mmol) was then added to the reaction mixture under argon. The color changed from yellow to deep green over several hours, and after stirring overnight, the tiny amount of unreacted lithium was removed by filtration. The solution was concentrated to dryness, and the residue was stirred in hexane. The deep green microcrystalline product was filtered off and dried under vacuum (9.47 g). Recrystallization of 1.00 g of the green solid from THF (200 mL), under nitrogen, afforded orange-red crystals (0.05 g, 5% based on mass of green compound) suitable for X-ray diffraction studies. Exposure of the green powder (1.00 g) to a 7-atm pressure of N_2 in an autoclave at 60 °C overnight gave **1** as an orange-red powder (0.45 g, 45% based on mass of green compound). IR (Nujol, KBr cm^{-1}) ν: 1325 m, 1256 m, 1195 w, 1140 w, 1124 w, 1083 m, 1039 s, 1020 m, 972 m, 926 m, 888 m, 840 m, 783 s, 749 m, 720 m, 670 w, 659 w. Elemental anal. Calcd (found): C, 61.01 (60.88); H, 7.45 (7.39); N, 8.09 (7.88). [$\mu_{eff} = 2.72\ \mu_B$ per dimer (295 K).]

[12] Crystal data for **1** are as follows: $C_{44}H_{63}N_5O_2Li_3Sm$, $M = 866.24$, triclinic, $P\bar{1}$, $a = 13.272(5)$ Å, $b = 14.967(4)$ Å, $c = 12.601(24)$ Å, $\alpha = 111.28(2)°$, $\beta = 117.53(12)°$, $\gamma = 78.87(3)°$, $V = 2067(3)$ Å^3, $Z = 2$, $T = -159$ °C, Mo Kα, $R = 0.023$, $R_w = 0.028$ for 6062 reflections and 496 parameters out of 6799 unique. The structure was solved by direct methods; non-hydrogen atom positions were located and refined anisotropically. Hydrogen atom positions were located and refined with one common isotropic thermal factor.

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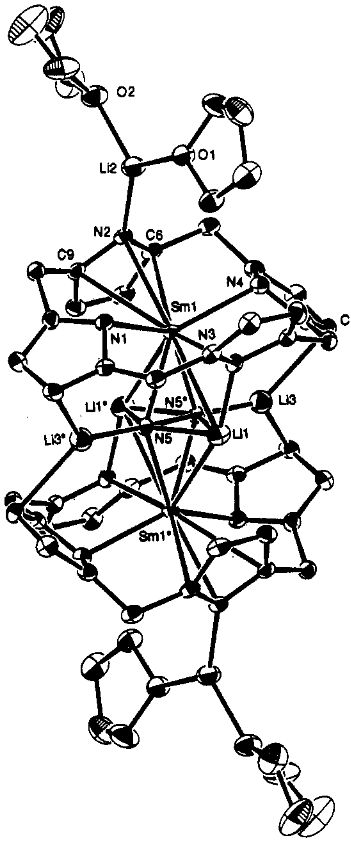

Figure 1. ORTEP plot of **1** with thermal ellipsoids drawn at the level of 50% probability. Ethyl groups have been omitted for clarity. Bond distances (Å) and angles (deg): N5–N5* = 1.525(4); N5–Li1 = 2.030(6); N5–Li3 = 1.873(5); Sm1–N5 = 2.357(2); Sm1–N5* = 2.342(2); Sm1–N2 = 2.462(2); Sm1–C6 = 2.783(3); Sm1–C9 = 2.778(3); Sm1–N1 = 2.462(2); Sm1–N3 = 2.502(3); Sm1–N4 = 2.455(2); Li3–C13 = 2.345(6); Li1–N3 = 2.033(6); Sm1–Li1 = 2.824(5); Sm1–Li1* = 2.999(5); Li2–N2 = 1.982(6); N1–Sm1–N3 = 80.84(8); N1–Sm1–N2 = 83.85(8); N2–Sm1–N4 = 83.07(8); N3–Sm1–N4 = 81.27(8); N5–Sm1–N5* = 37.9(1); N5–Li3–C13 = 128.4(3); Sm1–N3–Li1 = 76.2(2); O1–Li1–N2 = 126.6(3); O2–Li1–N2 = 126.0(3); O1–Li2–O2 = 107.3(3).

defining the equatorial plane. A molecule of N_2 with an elongated N–N distance [N5–N5* = 1.525(4) Å] has been found inside the Sm_2Li_4 octahedron, lying on one Li–Li diagonal [Li3–N5–N5*–Li3* = 0.0°]. The N_2Li_4 core is formed by one N_2 unit with two side-on lithium atoms [N5–Li1 = 2.030(6) Å] and the two other coplanar and coaxial with the N–N vector [N5–Li3 = 1.873(5) Å]. The two samarium atoms are symmetrically placed side-on with respect to the N_2 moiety [Sm1–N5 = 2.357(2) Å; Sm1–N5* = 2.342(2) Å] above and below the N_2Li_4 plane. The OEPG ligand is considerably distorted. One of the four pyrrolyl rings adopts a η^3-bonding mode [Sm1–N2 = 2.462(2) Å, Sm1–C6 = 2.783(3) Å, Sm1–C9 = 2.778(3) Å] with respect to Sm, while the other three rings, although not coplanar with Sm, have in the Sm–N bond [Sm1–N1 = 2.462(2) Å, Sm1–N3 = 2.502(3) Å, Sm1–N4 = 2.455(2) Å] the shortest bonding contact. The coordination geometry of the lithium cations is rather unusual. The two lithium atoms on the N–N axis are trigonal planar with a coordination geometry defined by one nitrogen atom of the N_2 unit and two β carbon atoms from two pyrrolyl rings of the two (OEPG)Sm units. Since the lithium atom is placed perpendicularly with respect to the pyrrolyl plane, the short Li–C distance [Li3–C13 = 2.345(6) Å] possibly indicates interaction with the π ring system. Conversely, the other two lithium cations, coordinated side-on with respect to the N_2 unit, are bonded to one nitrogen of one pyrrolyl ring [Li1–N3 = 2.033(6) Å], which is bridging Sm and Li. Given the presence of short Sm–Li contacts [Sm1–Li1 = 2.824(5) Å, Sm1–Li1* = 2.999(5) Å], the coordination geometry of the alkali cation may be regarded as pyramidal. Finally, two $(THF)_2Li$ moieties are located in the external part of the molecule pointing away from the molecular core. The coordination geometry of these two lithium cations is also trigonal planar, and the bonding with the rest of the molecule is achieved through a Li–N short contact [Li2–N2 = 1.982(6) Å] with the nitrogen of the pyrrolyl ring which is η^3-bonded to the samarium atom.

The crystal structure of **1** indicates that the molecule arises from the aggregation of two $(THF)_2Li(OEPG)Sm$ units, formally containing Sm(III), with a N_2Li_4 unit. The magnetic moment of 2.72 μ_B per dimeric complex is also as expected for a Sm(III) species.[13] The very long N–N distance is consistent with N–N single bond character and, therefore, a four-electron reduction of dinitrogen. On the basis of its extreme air-sensitivity and reactivity with N_2, we speculate that the initially formed green compound is a Sm(II) complex, capable of reducing the dinitrogen to the N_2^{4-} fragment, itself being oxidized in the process to Sm(III). However, since the formal reduction of N_2 to N_2^{4-} implies the transfer of four electrons, it is obvious that the reaction must involve at least four different metal centers and that other products, presently unknown, must be present in the reaction mixture.

A crystallographic determination of the green complex is currently underway together with an extensive study of its chemical reactivity.

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Supplementary Material Available: Details on structure determination and tables listing atomic positional parameters, anisotropic thermal parameters, and bond distances and angles (38 pages); observed and calculated structure factors (41 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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