Tetrametallic Divalent Samarium Cluster Hydride and Dinitrogen Complexes

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Reduction of trivalent samarium complexes obtained via reaction of $SmCl_3(THF)_3$ with the disodium salt of the dipyrrolide dianion $[R_2C(H_3C_4N)_2]^{2-}$ (R = Ph, $^1/_2$ $-(CH_2)_5-$) were carried out with sodium in THF and under nitrogen. The two reactions respectively yielded the tetranuclear divalent hydride $\{Na(THF)_6\}\{([Ph_2C(C_4H_3N)_2]Sm)_4(H)(THF)_2\}$ (**1**) and the tetranuclear dinitrogen complex $\{[(CH_2)_5C(C_4H_3N)_2]Sm\}_4(THF)_2(\mu\text{-}N_2)[Na(THF)]_2\cdot 2THF$ (**2**). Transmetalation of $[(Me_3Si)N]_2Sm(THF)_2$ with 1,1-dipyrrolylcyclohexane afforded the dinitrogen complex $\{[(CH_2)_5C(C_4H_3N)_2]Sm\}_4(\mu\text{-}N_2)\cdot 0.5THF$ (**3**). Despite the different oxidation states of **2** and **3** and the presence/absence of alkali-metal cation the two complexes display the same N−N distance.

Introduction

Among the few lanthanides that can be made available as low-valent complexes,[1] samarium certainly occupies a very special place because of the unique richness and variety[2] of the chemical transformations displayed by the cyclopentadienyl divalent samarium derivatives. As usual, the nature of the ancillary ligand plays a prominent role in determining the reactivity of these species. Thus, it is no surprise that during the past decade considerable efforts have been made to develop the chemistry of divalent samarium supported by ligand systems other than cyclopentadienyl derivatives.[3] However, although these species display interesting structural features, the ligand systems employed so far do not seem to support the same extreme level of reactivity as promoted by the Cp systems.

The occurrence of dinitrogen fixation is perhaps a good probe for assessing the level of reactivity of low-valent samarium complexes. The first observation of a reversible dinitrogen fixation on decamethylsamarocene residues was made by Evans.[2d] More recently, we found that calix-tetrapyrrole anions are able to perform dinitrogen four-electron reduction,[4] to stabilize very reactive divalent samarium complexes,[5] to promote ethylene reversible coordination,[6] and to form dinuclear species.[3h,5a] In all these complexes the ligand pyrrolyl rings adopted both the π- and σ-bonding modes, thus enforcing a configuration around the metal center which is strongly reminiscent of a bent-metallocene structure.

This promising behavior and the structural and electronic similarity between the pyrrolide and Cp anions prompted us to embark on a study on the

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behavior of divalent samarium derivatives of other pyrrolide anions. The diphenylmethyldipyrrolide dianion[7] seemed particularly promising due to its close structural resemblance to the *ansa*-metallocene ligand system. In addition, the direct incorporation of the nitrogen donor atom in the ring increases the potential for assembling polynuclear structures. This is, of course, another attractive feature, given that divalent samarium may only act as a one-electron reductant. Thus, the possibility of assembling cluster structures may increase the possibility of achieving multielectron transformations via the cooperative interaction of several metal centers. In this respect, we have recently described the preparation and characterization of a series of divalent and mixed-valence cluster compounds[8] and of a unique trivalent and tetranuclear dinitrogen complex assembled by this promising ligand system.[9]

In this paper, we describe the isolation and characterization of an unprecedented tetranuclear divalent samarium hydride cluster, as well as of two tetranuclear tri- and mixed-valence dinitrogen samarium complexes.

Experimental Section

All operations were performed under an inert atmosphere of a nitrogen-filled drybox or by using standard Schenk-type glassware in combination with a nitrogen-vacuum line. $SmCl_3(THF)_3$,[10] $[(Me_3Si)_2N]_2Sm(THF)_2$,[3l] diphenyldipyrrolylmethane,[7] and dipyrrolylcyclohexane[7] were prepared according to literature procedures. C_6D_6 and THF-d_8 were dried over Na/K alloy, vacuum-transferred into ampules, and stored under nitrogen prior to use. NMR spectra were recorded on a Bruker AMX-500 spectrometer using NMR tubes prepared inside a drybox and vacuum-sealed. Infrared spectra were recorded on a Mattson 3000 FTIR instrument from Nujol mulls or KBr pellets prepared inside the drybox. Samples for magnetic susceptibility measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods,[11] and corrections for underlying diamagnetism were applied to the data.[12] Elemental analyses were carried out using a Perkin-Elmer Series II CHN/O 2400-analyzer.

Preparation of $\{Na(THF)_6\}\{([Ph_2C(C_4H_3N)_2]Sm)_4(H)(THF)_2\}$ (1). A solution of diphenylmethyldipyrrole (3.2 g, 10.7 mmol) in THF (200 mL) was treated at room temperature with NaH (0.5 g, 22.5 mmol). The resulting suspension was stirred for 2 h at room temperature until no further effervescence was observed. Subsequent addition of $SmCl_3(THF)_3$ (4.9 g, 10.4 mmol) resulted in an instantaneous color change to light yellow. After the mixture was stirred at 60 °C for 30 min, sodium metal (0.3 g, 13.0 mmol) was introduced in the presence of a catalytic amount of $C_{10}H_8$ (10 mg, 78 μmol). Vigorous stirring at room temperature for 18 h produced a deep purple-brown solution, which was filtered to remove an appreciable amount of insoluble solid. Addition of toluene (75 mL), concentration to small volume and standing overnight at room temperature resulted in the separation of dark purple crystals of **1** (2.5 g, 1.05 mmol, 39%). Anal. Calcd (found) for $C_{116}H_{128}N_8NaO_8Sm_4$: C, 58.37 (58.31); H, 5.41 (5.35); N, 4.69 (4.64). IR (Nujol mull, cm^{-1}): ν 3190 (w), 3051 (w), 2729 (w), 2671 (w), 1595 (w), 1577 (w), 1489 (m), 1456 (vs), 1377 (vs), 1261 (w), 1147 (m), 1092 (br, m), 1043 (s), 984 (w) 891 (w), 848 (m), 798 (m), 740 (s), 700 (s), 656 (w), 634 (w). ^{1}H NMR (THF-d_8, 500 MHz, 23 °C): δ 31.01 (s, pyrrole, 8H), 25.25 (s, pyrrole, 8H), 8.59 (s, phenyl, 4H), 8.45 (q, phenyl, 8H), 7.15 (s, phenyl, 16H), 7.01 (q, phenyl, 8H), 5.92 (dd, phenyl, 4H), 4.17 (br s, pyrrole, 8H), 3.75 (m, THF, 32H), 1.86 (m, THF, 32H), −3.91 (br s, hydride, 1H). ^{13}C NMR (THF-d_8, 125.72 MHz, 23 °C): δ 145.29, 38.23, −23.31 (C−H, pyrrole), 153.32, 133.43, 131.47, 129.97, 126.13, 124.75 (C−H, phenyl), 86.13 (quaternary; the other quaternary carbons could not be located), 68.24, 67.43, 67.08, 26.36, 25.46, 25.14, 24.98 (CH_2, THF). $\mu_{eff} = 7.07\ \mu_B$.

Preparation of $\{[(CH_2)_5C(C_4H_3N)_2]Sm\}_4(THF)_2(\mu\text{-}N_2)[Na(THF)]_2\cdot 2THF$ (2). Method A. Solid NaH (0.7 g, 30.1 mmol) was added to a THF solution (150 mL) of 1,1-cyclohexyldipyrrole (3.4 g, 15.0 mmol). The mixture was stirred for 30 min at room temperature until no further effervescence was observed. Addition of $SmCl_3(THF)_3$ (6.9 g, 14.6 mmol) resulted in a bright yellow suspension, which was heated to 60 °C for 30 min. Excess metallic sodium (0.5 g, 21.7 mmol) and a catalytic amount of naphthalene (10 mg, 78 μmol) were introduced, and the mixture was stirred at room temperature for 16 h. The resulting dark greenish brown solution was filtered, concentrated to 50 mL, and layered with hexanes (50 mL). Standing at room temperature for 2 days yielded crystals of **2** (3.0 g, 1.5 mmol, 42%). Anal. Calcd (found) for $C_{80}H_{112}N_{10}Na_2O_6Sm_4$: C, 49.09 (48.77); H, 5.77 (5.66); N, 7.16 (7.00). IR (Nujol mull, cm^{-1}): ν 3107 (w), 3091 (w), 1597 (w), 1462 (s), 1377 (vs), 1278 (m), 1261 (m), 1149 (m), 1151 (m), 1124 (m), 1078 (m, br), 1038 (m), 1024 (s), 956 (m), 902 (m), 874 (w), 829 (w), 760 (vs), 729 (w), 632 (m), 571 (s). Very poor solubility in the most common inert solvents, including THF and pyridine, has prevented NMR characterization. $\mu_{eff} = 4.05\ \mu_B$.

Method B. A suspension of **3** (see below) (1.0 g, 0.5 mmol) in THF (50 mL) was stirred in the presence of Na sand (0.025 g, 1.0 mmol). The solid rapidly disappeared during the stirring, affording a clear solution without significant color change. The resulting dark brown solution was concentrated to small volume and layered with hexane. Crystalline **2** separated in 35% yield upon standing at room temperature for 2 days.

Preparation of $\{[(CH_2)_5C(C_4H_3N)_2]Sm(THF)_2\}_4(\mu\text{-}N_2)\cdot 0.5THF$ (3). A solution of $[(Me_3Si)_2N]_2Sm(THF)_2$ (1.9 g, 3.0 mmol) in THF (25 mL) was treated with a solution of 1,1-dipyrrolylcyclohexane (0.65 g, 3.0 mmol) in the same solvent (20 mL). The color of the mixture changed instantly to dark brown upon mixing. The resulting solution was concentrated to about 20 mL and allowed to stand at room temperature for a few days, upon which dark brown crystals of **3** separated (1.1 g, 0.7 mmol, 70%). Anal. Calcd (found) for $C_{66}H_{84}N_{10}O_{2.5}Sm_4$: C, 47.78 (47.58); H, 5.10 (4.97); N, 8.44 (8.08). IR (Nujol mull, cm^{-1}): ν 3103 (w), 13450 (w), 1299 (w), 1280 (m), 1262 (m), 1192 (m), 1171 (w), 1151 (m), 1125 (m), 1069 (w), 1061 (w), 1030 (vs), 961 (m), 918 (w), 903 (m), 874 (s), 829 (w), 766 (s), 744 (vs), 691 (w), 670 (w), 630 (m). $\mu_{eff} = 3.24\ \mu_B$.

X-ray Crystallography: Structural Determination of 1−3. Suitable crystals were selected, mounted on thin, glass fibers using paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[13]

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Table 1. Crystal Data and Structure Analysis Results

	1	**2**	**3**
formula	$C_{116}H_{128}N_8NaO_8Sm_4$	$C_{80}H_{112}N_{10}Na_2O_6Sm_4$	$C_{66}H_{84}N_{10}O_{2.5}Sm_4$
fw	2386.65	1957.18	1659.07
space group	monoclinic, *C*2/*c*	monoclinic, *P*2$_1$/*c*	monoclinic, *C*2/*m*
a (Å)	21.464(4)	13.495(4)	12.353(2)
b (Å)	26.796(5)	25.092(7)	17.832(2)
c (Å)	24.835(5)	12.698(4)	14.732(3)
β (deg)	102.345(3)	117.602(5)	104.884(3)
V (Å^3)	13954(5)	3810(2)	3136.2(9)
Z	4	2	2
radiation (Kα; Å)	0.710 73	0.710 73	0.710 73
T (K)	203	203	203
D_{calcd} (g cm^{-3})	1.136	1.706	1.742
μ_{calcd} (cm^{-1})	1.707	3.108	3.741
R, R_w, GOF[a]	1.024, 0.1068, 0.2819	1.010, 0.0581, 0.1460	0.0427, 0.1052, 1.065

[a] $R = \sum|F_o| - |F_c|/\sum|F_o|$; $R_w = [\sum(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Systematic absences in the diffraction data and unit-cell parameters were consistent with *C*2, *Cm*, and *C*2/*m* for **3**, *C*2/*c* and *Cc* for **1**, and, uniquely, *P*2$_1$/*c* for **2**. Refinement in the centrosymmetric space group options yielded computationally stable and chemically reasonable results of refinement. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. The molecular cation of **1** and the compound molecule of **2** were located at inversion centers. The molecular anion in **1** is located at a 2-fold axis. The molecule in **3** is located at the intersection of a mirror plane and 2-fold axis. A cocrystallized thf solvent molecule was located in the asymmetric unit of **2**. The penultimate diffraction map of **3** displayed two significant peaks, located away from the compound molecule, which cannot be modeled as a chemically reasonable solvent molecule and were treated as apparent solvent atoms assigned with carbon atom identities and refined partial occupancies. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHEXTL 5.10 program library (Sheldrick, G. M., Bruker AXS, Madison, WI, 1997). Relevant crystal data and bond distance and angles are given in Tables 1 and 2 respectively.

Results and Discussion

Reduction of a $\{[R_2C(C_4H_3N)_2]Sm\}Cl$ (R = Ph) precursor[9] with sodium under nitrogen and in THF afforded the paramagnetic dark purple crystalline complex **1** (Scheme 1). The molecule is formed by four $\{[Ph_2C(C_4H_3N)_2]Sm\}$units with the four samarium atoms arranged to form a rhomb (Figure 1). Each dipyrromethanyl dianion bridges two metal atoms with the pyrrole rings being in turn π-bonded to one samarium and σ-bonded to another. Each of the two samarium atoms placed on the two acute vertexes of the tetrametallic core bears one molecule of THF. One sodium atom, solvated by six molecules of THF and unconnected to the cluster, completes the structure.

Table 2. Selected Bond Distances (Å) and Angles (deg)

	Compound **1**		
Sm(1)−N(1)	2.668(17)	Sm(2)−N(2)	2.622(17)
Sm(1)−N(2)	2.842(18)	Sm(2)−N(3)	2.601(17)
Sm(1)−C(5)	2.93(2)	Sm(2)−N(4)	2.795(17)
Sm(1)−C(6)	3.01(2)	Sm(2)−C(1)	2.86(2)
Sm(1)−C(7)	3.01(2)	Sm(2)−C(2)	2.93(2)
Sm(1)−C(8)	2.91(2)	Sm(2)−C(3)	2.95(2)
Sm(1)−O(1)	2.597(14)	Sm(2)−C(4)	2.85(2)
Sm(2)−N(1)	2.801(17)	Sm(1)⋯Sm(2)	3.9132(16)
Sm(1)−Sm(2)−Sm(1a)	102.0(5)	Sm(2)−Sm(1)−Sm(2a)	78.0(5)
	Compound **2**		
Sm(1)−N(1)	2.714(12)	Sm(2)−N(3a)	2.696(11)
Sm(1)−N(2)	2.723(10)	Sm(2)−C(1)	2.766(13)
Sm(1)−N(3)	2.727(11)	Sm(2)−C(2)	2.902(13)
Sm(1)−N(4)	2.731(12)	Sm(2)−C(3)	2.937(14)
Sm(1)−N(5)	2.178(10)	Sm(2)−C(4)	2.815(14)
Sm(1)−O(1)	2.512(9)	Sm(2)−N(5)	2.332(11)
Sm(1)−C(19)	2.875(15)	Sm(2)−N(5a)	2.324(11)
Sm(1)−C(20)	3.116(15)	N(5)−N(5a)	1.371(19)
Sm(1)−C(21)	3.104(15)	N(5)−Na	2.259(12)
Sm(1)−C(22)	2.915(16)	Na−O(2)	2.684(16)
Sm(2)−N(1)	2.719(11)	Sm(1)⋯Sm(2)	3.5848(12)
Sm(1)−N(5)−N(5a)	155.4(11)	Sm(2)−Sm(1)−Sm(2a)	76.6(3)
Sm(1)−Sm(2)−Sm(1a)	103.4(3)	Sm(1)−N(5)−Na	67.2(3)
	Compound **3**		
Sm(1)−N(1)	2.339(3)	Sm(2)−N(3)	2.704(6)
Sm(2)−N(1)	2.160(8)	Sm(1)−C(5)	2.755(7)
N(1)−N(1a)	1.392(16)	Sm(1)−C(6)	2.888(7)
Sm(1)−N(2)	2.596(6)	Sm(1)−C(8)	2.818(7)
Sm(1)−N(3)	2.704(6)	Sm(2)−C(1)	2.814(7)
Sm(2)−N(2)	2.709(7)	Sm(2)−C(4)	2.937(7)
N(3)−Sm(2)−N(3c)	88.8(3)	N(2)−Sm(1)−N(2b)	172.1(3)
O(1)−Sm(2)−N(1)	144.2(3)		

The connectivity of complex **1**, as indicated by the crystal structure, suggests a divalent $\{Na(THF)_6\}\{([Ph_2C(C_4H_3N)_2]Sm)_4(H)(THF)_2\}$ hydride formulation. Chemical degradation carried out by reacting **1** with an excess of gaseous hydrogen chloride was not conclusive, since it produced only 93% of the H_2 expected for a $Sm_4(H)$ hydride formulation. However, the ^1H NMR spectrum of **1** showed a broad peak at −3.91 ppm which did not correlate with any carbon atom. Exposure of a solution of **1** in THF-d_8 to D_2 gas at 1 atm led to the disappearance of this resonance while the rest of the spectrum remained unmodified. A corresponding resonance appeared in the ^2H NMR spectrum. The IR spectrum of the compound, after it was exposed to deuterium gas, showed no modification except for a band at 1261 cm^{-1}, which shifted to 966 cm^{-1}. On the basis of these observations, it seems reasonable to conclude that complex **1** is indeed a divalent tetrasamarium monohydride compound. The magnetic moment of **1** is slightly lower than expected for four Sm(II) centers (μ_{eff} = 7.07 μ_B). On the other hand, the Sm⋯Sm distance (Sm(1)⋯Sm(2) = 3.9132(16) Å) is significantly short, and thus, it may be responsible for some extent of magnetic coupling.

Although a conclusive explanation for the origin of the hydride in complex **1** cannot be offered at this stage, we observe that its formation is strikingly similar to the case of the reduction of $Cp_2Lu(THF)Cl$ with Na in THF, which afforded a good yield of the corresponding hydride $[Na(THF)_6][(Cp_2LuH)_3H]$.[14] We propose that THF cleavage is the source of the hydride. Degradation of THF is

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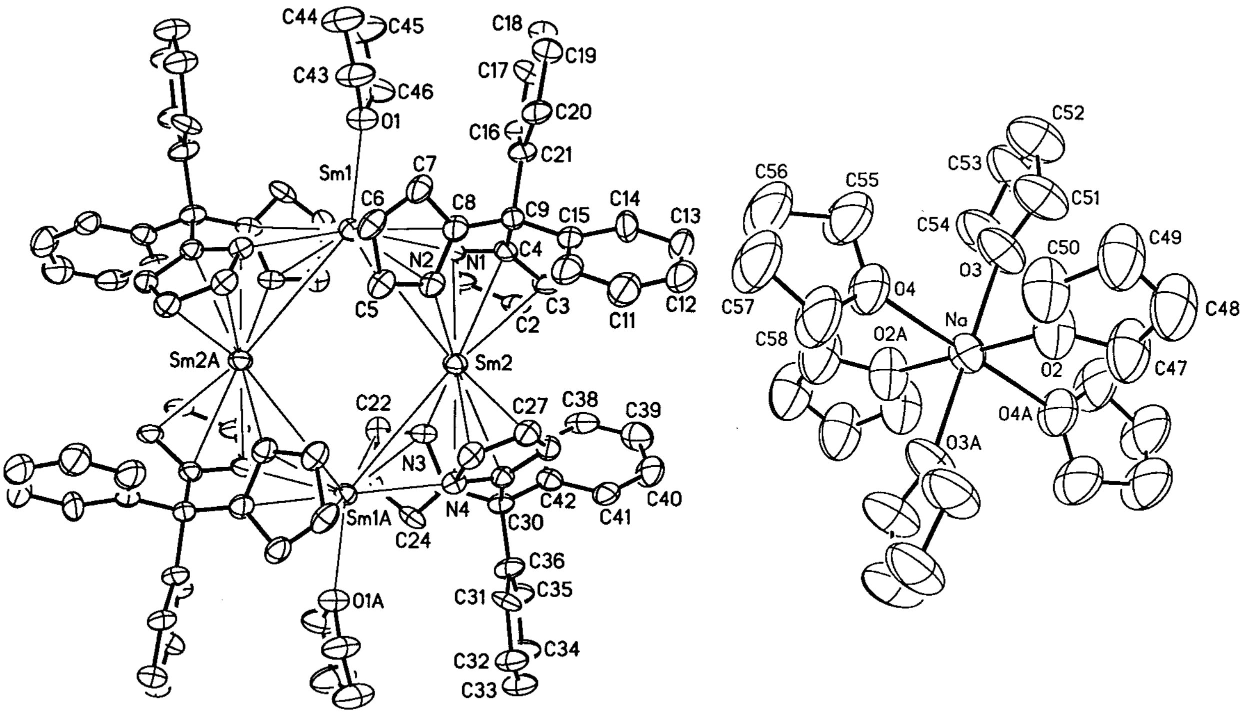
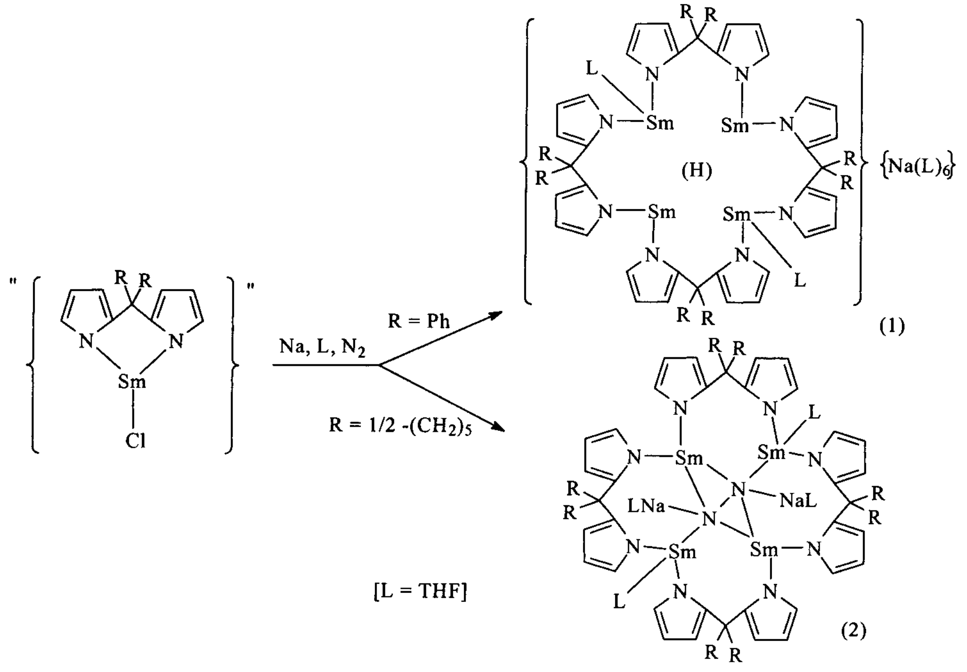


Figure 1. ORTEP drawing of **1**. Thermal ellipsoids are drawn at the 30% probability level.

Scheme 1



well-known to proceed through different pathways and to produce a variety of products, including transient “NaH” when the degradation is initiated by the attack of Na on the THF α-hydrogen.[15] Since **1** is produced by a Na reduction in THF, it is possible that its formation is simply the result of the addition of a solvated NaH fragment to a divalent and tetranuclear cluster. Obviously we cannot exclude the possibility that the formation of **1** may actually follow a complex mechanism, perhaps requiring a more direct participation of the samarium atom. In this respect, it is interesting to observe that previous attempts to generate a dinitrogen-free tetrametallic cluster structure, via the same Na reduction reaction of the 1,1-dipyrrolylcyclohexane derivative *and under exclusion of N_2*, led to a different THF-cleavage process (deoxygenation) with formation of a tetrametallic oxo derivative.[8a] Nonetheless, the idea that the hydride may be indeed provided by THF cleavage is corroborated by the fact that a substantial amount of ethylene has been found present in the GC-MS of the reaction mixture.

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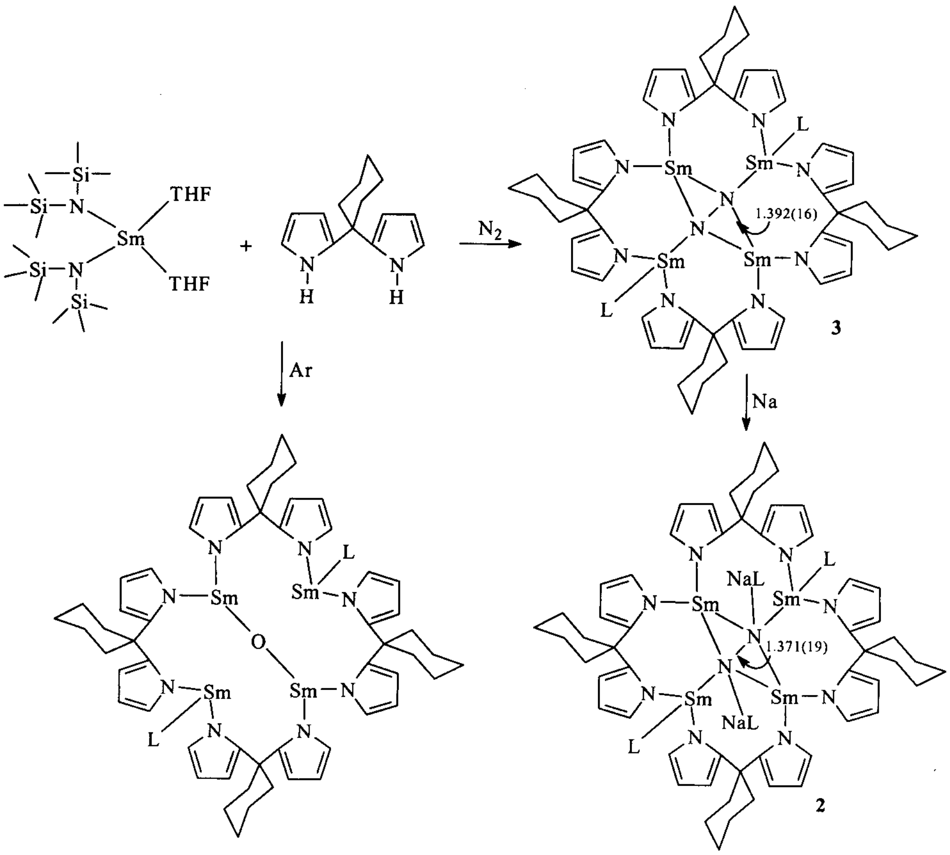
(15) See the following and references therein: (a) Dubé, T.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **1998**, *17*, 3967. (b) Jubb, J.; Gambarotta, S.; Duchateau, R.; Teuben, T. *J. Chem. Soc., Chem. Commun.* **1994**, 2641. (c) Aspinall, H. C.; Tillotson, M. R. *Inorg. Chem.* **1996**, *35*, 2163. (d) Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1291.

Scheme 2



In close analogy with the chemistry of Sm(II) supported by the calix-tetrapyrrole ligand system,[8,9] the reduction of the trivalent $\{[R_2C(C_4H_3N)_2]Sm\}Cl$ precursor displayed a remarkable sensitivity to the nature of the substituents (Scheme 1). The very same reaction which afforded **1** carried out under identical conditions but using the 1,1-dipyrrolidecyclohexane derivative ($R = {}^1/_2\ -(CH_2)_5-$), afforded the dinitrogen complex $\{[(CH_2)_5C(C_4H_3N)_2]Sm\}_4(THF)_2(\mu\text{-}N_2)[Na(THF)]_2\cdot 2THF$ (**2**), which was isolated in crystalline form. The structure, as revealed by X-ray diffraction analysis (Figure 2), consists of four Sm atoms and four 1,1-dipyrrolylcyclohexane dianions defining a rhomb-type structure similar to that of complex **1**. Even in this case four ligands bridge the four metal centers, adopting both σ- and π-bonding modes. A dinitrogen molecule, placed in the center of the tetranuclear core, adopts the side-on bonding mode with two Sm atoms and the end-on bonding mode with the other two. Each nitrogen atom is also coordinated to one sodium atom solvated by one molecule of THF.

Although the geometrical parameters of the Sm_4 core of **2** are comparable to those of **1**, we found no evidence that **1** may react with dinitrogen. The rather long N−N distance (N−N = 1.371(16) Å) is only slightly shorter than expected for a N−N single bond. If we assume that N_2 has undergone only a two-electron reduction, the presence of two Na atoms and of four dianionic ligands gives the four samarium atoms a formal oxidation state of +2. In this event, the complex should be regarded as the adduct of a Na_2N_2 moiety to a *divalent* samarium tetranuclear cluster. This hypothesis contrasts not only with the long N−N distance but also with the magnetic moment ($\mu_{eff} = 4.05\ \mu_B$), which is considerably lower than in the divalent **1** and which suggests instead the presence of trivalent Sm centers. Alternatively, a four-electron reduction of dinitrogen will attribute a formal oxidation state of +2.5 to the four samarium atoms. Although the magnetic moment does not support the presence of divalent Sm centers in complex **2**, on the other hand, it should be observed that the short Sm···Sm distance is nearly in the bonding range (Sm(1)···Sm(2) = 3.5848(12) Å); thus, it is likely to promote magnetic couplings.

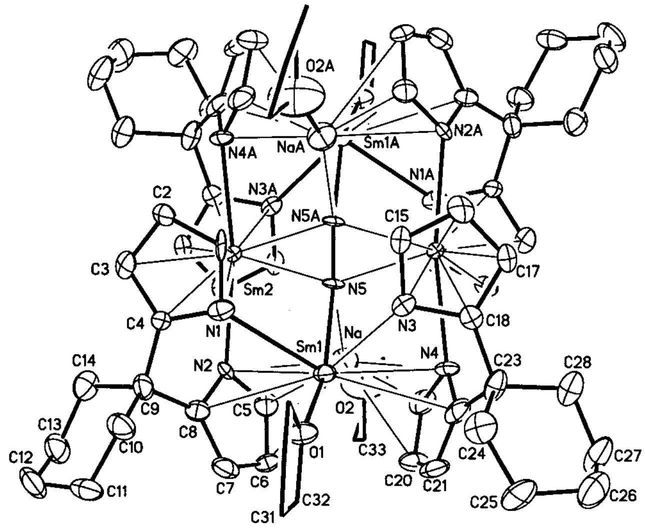


Figure 2. ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 30% probability level.

As mentioned above, we have recently reported that a tetranuclear samarium cluster, nearly identical with

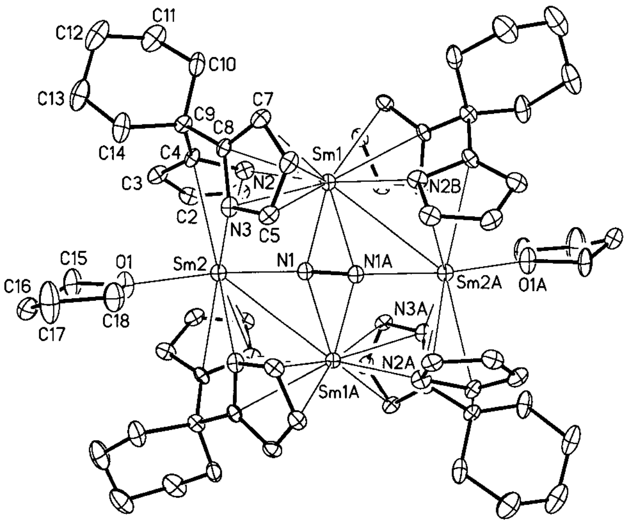


Figure 3. ORTEP drawing of **3**. Thermal ellipsoids are drawn at the 30% probability level.

the anionic moiety of **1,** afforded four-electron reduction of dinitrogen.[9] The magnetic moment of that dinitrogen complex was considerably higher than in **2** ($\mu_{\text{eff}} = 6.55$ μ_B) and sharply contrasts with the presence of comparable Sm···Sm contacts (Sm(1)···Sm(2) = 3.602(9) Å) and an only slightly longer N−N distance (N−N = 1.412(17) Å). On the other hand, a comparison between the two dinitrogen complexes is not completely appropriate, given the diversity of the ligand substituents. Thus, in an effort to define the role of the sodium atoms and of the nature of the ligand substituents in determining in **2** the extent of dinitrogen reduction, the N−N distance, and the magnetic moment, we have attempted the preparation of another tetranuclear compound of the 1,1-dipyrrolylcyclohexane ligand. To avoid retention of alkali-metal cations, we have carried out a transmetalation reaction between $[(Me_3Si)_2N]_2Sm(THF)_2$ and 1,1-dipyrrolylcyclohexane (Scheme 2). Even in this case, the reaction proceeded rapidly upon mixing to form the new dinitrogen complex $\{[(CH_2)_5C(C_4H_3N)_2]Sm(THF)_2\}_4(\mu\text{-}N_2)\cdot 0.5THF$ (**3**), which was isolated in crystalline form upon allowing the reaction mixture to stand for a few days at room temperature. As a common feature among these clusters, the complex could not be redissolved in any common inert solvent once it precipitated from the reaction mixture. The X-ray crystal structure of **3** showed the same arrangement as observed in complex **2** with very similar bond distances and angles, except for the absence of the two solvated Na atoms (Figure 3). Even in this case the Sm···Sm distance is very short and is almost in the bonding range (Sm(1)···Sm(2) = 3.5929(7) Å), while the value of the N−N distance (N(1)−N(1a) = 1.392(16) Å) is, within the experimental error, *equal to that observed in complex **2***. This is particularly surprising, given the absence of the two sodium cations, which implies that the four samarium atoms are likely to be present in their trivalent state. Accordingly, the magnetic moment ($\mu_{\text{eff}} = 3.24$ μ_B) is substantially lower than that in **2**, suggesting a larger extent of oxidation of the samarium centers. The large discrepancy between the magnetic moment of **3** and that of the diphenyl analogue[9] can be attributed only to the different nature of ligand substituents, given that the geometrical parameters of the Sm_4N_2 core are very comparable.

There are a few considerations arising from the structure of this compound which are relevant to the present discussion. The fact that **3** is again a tetranuclear dinitrogen complex reiterates that tetranuclear structures are particularly favored with this ligand system and that these clusters may be used to host a dinitrogen unit or other fragments in the center. The coordinated dinitrogen unit of **2** and **3** as well as that of the other diphenyl complex previously reported[9] is likely to have undergone four-electron reduction. However, complex **2** is clearly the result of the attack of sodium (present in excess in the reaction mixture) on the initially formed **3**, affording partial reduction of samarium rather than N−N cleavage, as one in principle could expect. Accordingly, treatment of **3** with finely dispersed Na in THF indeed afforded **2**. This is rather surprising in the view of the results reported in the recent literature describing N−N cleavage of coordinated dinitrogen via reduction with alkali metals.[16] The implication of this surprising behavior is that divalent samarium, which obviously possesses a reducing potential sufficiently strong to attack dinitrogen and to reduce the N−N triple and double bond, does not have the sufficient reducing power to cleave a N−N single bond. This strikingly contrasts with the fact that considerably less energy is required. On the other hand, the rigid encapsulation of the N_2 moiety in the tetrametallic cage may well be the factor preventing N−N single bond cleavage and favoring instead reduction of the metal centers and formation of the mixed-valence **2**.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Council of Canada (NSERC) and by NATO (travel grant).

Supporting Information Available: Crystallographic data (excluding structure factors) for the structures reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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