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Isolation and Characterization of Linear Polymeric $\{[1,1\text{-}H_{10}C_6(\alpha\text{-}C_4H_3N)_2]_2Sm[Na(THF)]_2\}_n$: A 30-Electron Species with a $(\eta^5\text{-}Cp)_4Ln$ Type Structure

Mani Ganesan, Mathieu P. Lalonde, Sandro Gambarotta,* and Glenn P. A. Yap

Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

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Summary: Reduction of the tetranuclear dinitrogen cluster $\{[1,1\text{-}H_{10}C_6(\alpha\text{-}C_4H_3N)_2]Sm\}_4(THF)_2(\mu\text{-}N_2)$ *with Na sand in THF afforded the linear polymeric divalent Sm complex* $\{[1,1\text{-}H_{10}C_6(\alpha\text{-}C_4H_3N)_2]_2Sm[Na(THF)]_2\}_n$, *where each samarium atom is surrounded by four* η^5*-bonded pyrrolide rings, thus giving the metal center a formal 30-electron configuration.*

Dipyrrolide dianions[1] are structurally and electronically similar to *ansa*-cyclopentadienyl ligand systems. However, the presence of deprotonated N atoms in the pyrrolide rings allows additional σ-bonding interactions, which play an important role in assembling polynuclear structures. In fact, these ligands enabled the preparation of a series of cyclic and planar divalent[2] and mixed-valence[3] Sm clusters of variable nuclearity. A common characteristic in this family of complexes is the particular bonding mode adopted by the ligand, which, by crossing σ- and π-interactions, confers a bent-metallocene geometry to each metal center. This feature is more than likely responsible for the pronounced reactivity of divalent samarium polypyrrolide complexes,[4] which is otherwise observed only with the samarocenes and whose reactivity[5] has to date never been reproduced by any other ligand system.[6] Conversely, divalent samarium pyrrolide complexes react with N_2 to perform a four-electron reduction, resulting in tetranuclear trivalent flat clusters that encapsulate an $[N_2]^{4-}$ moiety.[2−4] Given the low energy requirement for the cleavage of a single N−N bond (157 kJ/mol) and the availability of several Sm(II) centers in the cluster structure, the resistance of the N−N single bond to cleavage is at least surprising. Somehow, the encapsulation of reduced N_2 into a tetranuclear cluster prevents further reduction. Herein we describe the result of an attempt to cleave the N−N bond of coordinated N_2.

Reaction of $\{[1,1\text{-}H_{10}C_6(\alpha\text{-}C_4H_3N)_2]Sm\}_4(THF)_2(\mu\text{-}N_2)$ with an excess of finely dispersed Na in THF and under N_2 afforded the novel divalent samarium complex $\{[1,1\text{-}H_{10}C_6(\alpha\text{-}C_4H_3N)_2]_2Sm[Na(THF)]_2\}_n$ (**1**)[7] (Scheme 1), which no longer contains N_2. The complex has a linear polymeric structure[8] consisting of samarium atoms surrounded by four π-coordinated pyrrolide rings originating from two ligands (Figure 1). The coordination geometry around each Sm atom is therefore pseudo-tetrahedral, with the centroids of the four rings defining the vertexes of the coordination tetrahedron. The N atoms are σ-bonded to two Na(THF) units, which are in turn σ-bonded to two other N atoms of another asymmetric unit, thus building a polymeric structure where the Sm atoms form a nearly linear array. The coordination geometry around each Na atom is tetrahedral and is defined by three N atoms of three σ-bonded pyrrolide rings and one O atom from coordinated THF.

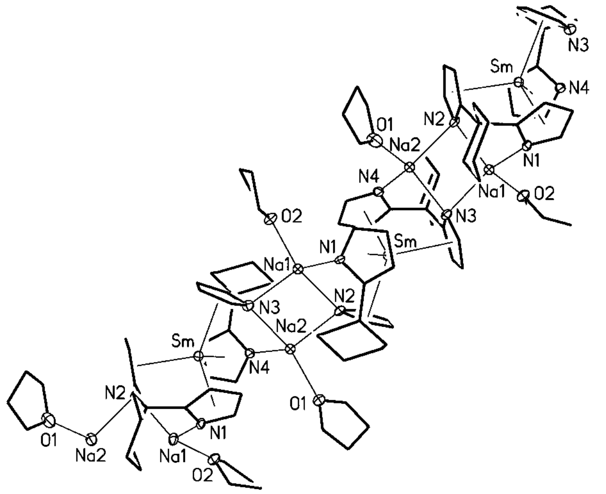

Figure 1. Structure of compound **1**. Bond distances (Å) and angles (deg): Sm−N(1) = 2.811(5), Sm−C(1) = 2.916(6), Sm−C(2) = 3.023(5), Sm−C(3) = 2.978(6), Sm−C(4) = 2.837(5), Sm−N(2) = 2.980(5), Sm−C(5) = 3.037(6), Sm−C(6) = 3.035(5), Sm−C(7) = 2.912(6), Sm−C(8) = 2.883(6), Sm−N(3) = 2.973(5), Sm−C(15) = 2.851(8), Sm−C(16) = 2.884(8), Sm−C(17) = 2.952(6), Sm−C(18) = 2.837(6), Sm−N(4) = 2.822(5), Sm−C(19) = 2.951(6), Sm−C(20) = 2.919(9), Sm−C(21) = 2.961(6), Sm−C(22) = 2.816(5), Na(1)−N(1) = 2.395(5), Na(1)−N(2) = 2.491(6), Na(1)−N(3) = 2.486(5), Na(1)−O(2) = 2.323(5), Na(2)−N(2) = 2.538(6), Na(2)−N(3) = 2.544(6), Na(2)−N(4) = 2.391(5), Na(2)−O(1) = 2.384(5); Centroid(1)−Sm−Centroid(2) = 98.2(3), Centroid(1)−Sm−Centroid(3) = 118.1(3), Centroid(1)−Sm−Centroid(4) = 114.1(3), Centroid(2)−Sm−Centroid(3) = 113.6(4), Centroid (2)−Sm−Centroid(4) = 117.2(3), Centroid(3)−Sm−Centroid(4) = 96.9(3), Sm···Sm···Sm = 153.6(1).

Complex **1** contains samarium in a +2 oxidation state and exhibits the expected magnetic moment.[2−4] The divalent oxidation state and the presence of four symmetrically bonded pyrrolide rings around the same

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[1] See for example: (a) Liu, B. Y.; Bruckner, C.; Dolphin, D. *Chem. Commun.* **1996**, 2141 and references therein. (b) Lee, C. H.; Lindsey, S. *Tetrahedron* **1994**, *50*, 11427.

[2] Dubé, T.; Ganesan, M.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 3716.

[3] (a) Dubé, T.; Conoci, S.; Gambarotta, S.; Yap, G. P. A.; *Organometallics* **2000**, *19*, 1182. (b) Dubé, T.; Gambarotta, S.; Yap, G. P. A.; Conoci, S. *Organometallics* **2000**, *19*, 115.

[4] Dubé, T.; Conoci, S.; Gambarotta, S.; Yap, G. P. A.; Vasapollo, G. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3657.

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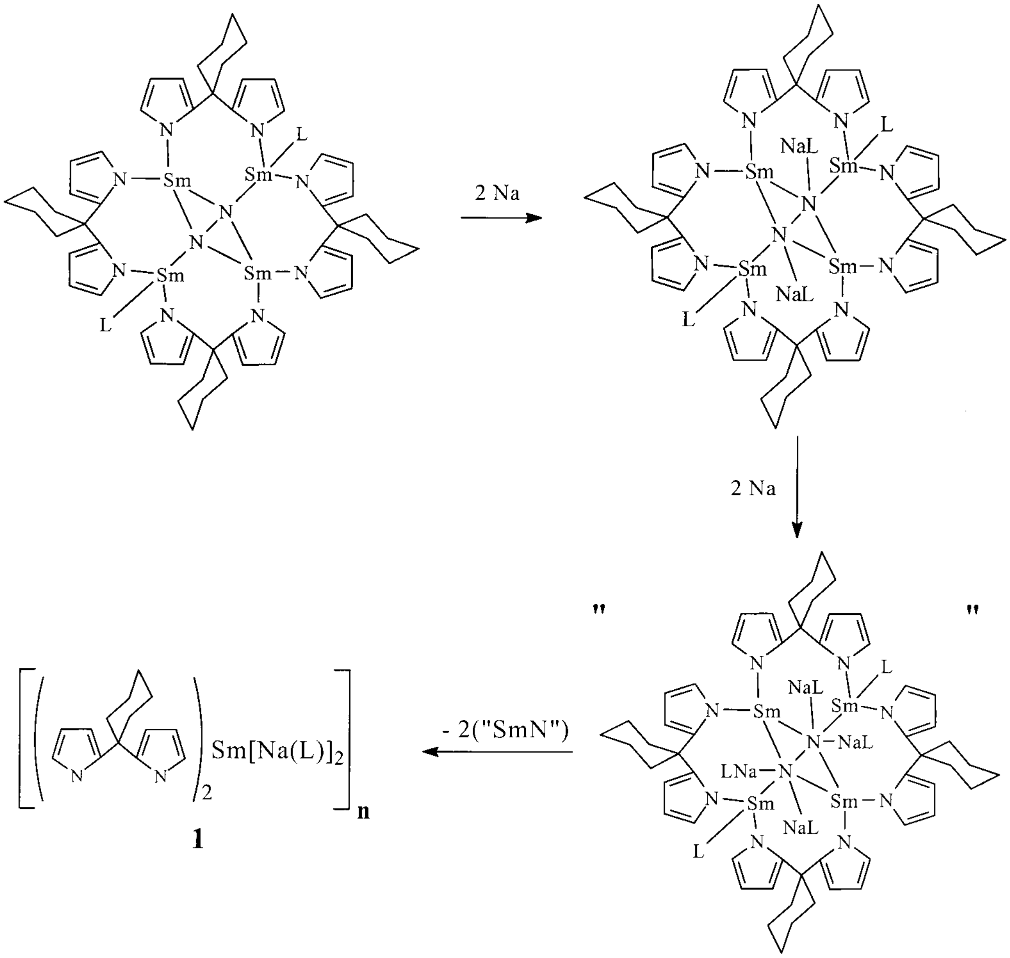
Scheme 1



metal assigns a formal 30-electron count to the Sm center. To the best of our knowledge, complex **1** provides the first example of a lanthanide in a η^5-Cp$_4$M type geometry which has in the tetravalent Cp$_4$U complex the only precedent.[9] The formal 30-electron count is among the highest in lanthanide chemistry, and it is surpassed only by [(COT)$_2$Yb]K$_2$(crown),[10] formally containing a 34-electron configuration. The unique ligand arrangement of **1** stands out even more when compared to other existing Cp$_n$Ln[11] compounds, which have so far indicated that lanthanides can only accommodate up to

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(5) (a) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood,J. L. *J. Am. Chem. Soc.* **1983**, *105*, 140. (b) Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1007. (c) Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. In *Fundamentals of Homogeneous Catalysis*; Tsutsui, M., Ed.; Plenum Press: New York, 1979; Vol. 3. (d) Evans, W. J.; Ansari, M. A.; Ziller, J. W.; Khan, S. I. *Organometallics* **1995**, *14*, 3. (e) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 219. (f) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270. (g) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1285. (h) Evans, W. J.; Drummond, D. K.; Bott, S. G.; Atwood, J. L. *Organometallics* **1986**, *5*, 2389. (i) Evans, W. J.; Keyer, R. A.; Zhang, H.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1987**, 837. (j) Evans, W. J.; Drummond, D. K.; Grate, J. W.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 3928. (k) Evans, W. J.; Drummond, D. K. *J. Am. Chem. Soc.* **1989**, *111*, 3329. (l) Evans, W. J.; Keyer, R. A.; Rabe, G. W.; Drummond, D. K.; Ziller, J. W. *Organometallics* **1993**, *12*, 4664. (m) Evans, W. J.; Grate, J. W.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1671. (n) Evans, W. J.; Ulibarri, T. A. *J. Am. Chem. Soc.* **1987**, *109*, 4292. (o) Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 3728. (p) Evans, W. J.; Drummond, D. K. *J. Am. Chem. Soc.* **1988**, *110*, 2772. (q) Evans, W. J.; Drummond, D. K. *Organometallics* **1988**, *7*, 797. (r) Evans, W. J.; Drummond, D. K.; Chamberlain, L. R.; Doedens, R. J.; Bott, S. G.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 4983. (s) Evans, W. J.; Drummond, D. K. *J. Am. Chem. Soc.* **1986**, *108*, 7440. (t) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2314. (u) Zhang, X.; Loppnow, G. R.; McDonald, R.; Takats, J. *J. Am. Chem. Soc.* **1995**, *117*, 7828. (v) Dubé, T.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 1432. (w) Dubé, T.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **1998**, *17*, 3967. (x) Desurmont, G.; Li, Y.; Yasuda, H.; Maruo, T.; Kanehisa, N.; Kai, Y. *Organometallics* **2000**, *19*, 1811.

(6) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6877;

(7) A suspension of [{Sm[(CH$_2$)$_5$C(C$_4$H$_3$N)$_2$]}$_4$(THF)$_2$(μ-N$_2$)] (2.4 g, 1.4 mmol) in THF (50 mL) was stirred in the presence of an excess of finely dispersed metallic sodium (0.6 g, 29 mmol) for 24 h. Excess sodium was removed by filtration and the solution concentrated to ca. 30 mL. Dark red crystals of **1** (0.7 g, 0.9 mmol, 16%) were formed upon layering hexane over the THF solution and allowing the mixture to stand at room temperature for a few days. Anal. Calcd (found) for C$_{36}$H$_{48}$N$_4$Na$_2$O$_2$Sm: C, 56.51 (56.56); H, 6.32 (6.22); N, 7.32 (7.25). IR (Nujol, cm^{-1}): ν 3103 (w), 3084 (w), 2665 (w), 1422 (vs), 1345 (m), 1294 (s), 1276 (s), 1263 (s), 1227 (w), 1215 (w), 1193 (m), 1167 (m), 1153 (s), 1129 (m), 1097 (m), 1029 (vs), 948 (s), 897 (vs), 874 (s), 847 (w), 831 (s), 750 (vs), 685 (m), 633 (s). $\mu_{\mathrm{eff}} = 2.76\ \mu_{\mathrm{B}}$.

(8) Crystal data for **1**: C$_{36}$H$_{48}$N$_4$Na$_2$O$_2$Sm, $M_r = 765.11$, monoclinic, $P2_1/c$, $a = 17.946(2)$ Å, $b = 12.191(1)$ Å, $c = 16.840(2)$ Å, $\beta = 110.378(2)°$, $V = 3453.5(7)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.472$ g cm^{-3}, absorption coefficient 1.763 mm^{-1}, $F(000) = 1568$, 27067 (4947) collected (unique) reflections; R1 = 0.0393, wR2 = 0.0657, GOF = 1.035.

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three η^5-bonded Cp rings in their coordination spheres. In addition, the tendency of a pyrrolide anion toward η^5-coordination is expected to be far lower than that of a regular Cp ring due to the possible formation of robust Ln−N σ-bonds. The low oxidation state and consequent expansion of the atomic dimensions may play a significant role in accommodating the four rings in the coordination sphere.

Finally, the formation of **1** implies not only reduction of samarium centers to the divalent state but also removal of one samarium atom from one ligand. Our previous work has shown that the attack of the first two Na atoms on $\{[1,1\text{-}H_{10}C_6(\alpha\text{-}C_4H_3N)_2]Sm\}_4(THF)_2(\mu\text{-}N_2)$ occurs on the dinitrogen moiety with each N atom coordinating one of the two alkali-metal cations.[4] However, rather than cleaving N_2, the reaction results in the reduction of two of the four Sm centers while the N−N single bond remains nearly unperturbed. Assuming that a similar process also occurs during the attack of an additional 2 equiv of Na, the reduction should result in the formation of a divalent "(ligand)$_4$Sm$_4$N$_2$-[Na(THF)]$_4$" intermediate (Scheme 1). The formation of **1** would simply require *formal* elimination of 2 equiv of SmN. Accordingly, no N_2 gas was released during the reduction and no NH_3 or hydrazine could be detected upon hydrolysis of the reaction mixture followed by careful acidification (*warning!* fire hazard). The possible formation of a potentially important binary compound such as SmN via a mild condition reaction pathway and its presumable resistance to hydrolysis is of course just speculation, since no conclusive evidence has been obtained so far. At this stage, it is interesting to observe that in the chemistry of dinitrogen fixation promoted by low-valent Sm and supported by the closely related calix[4]tetrapyrrole ligand system,[12] a Sm metal also deprived of its ligand system was found attached to a N_2 unit, possibly indicating that the elimination of SmN is not an unrealistic possibility.

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Supporting Information Available: Listings of atomic coordinates, thermal parameters, and bond distances and angles for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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