The fixation and reduction of dinitrogen using lanthanides: praseodymium and neodymium *meso*-octaethylporphyrinogen–dinitrogen complexes

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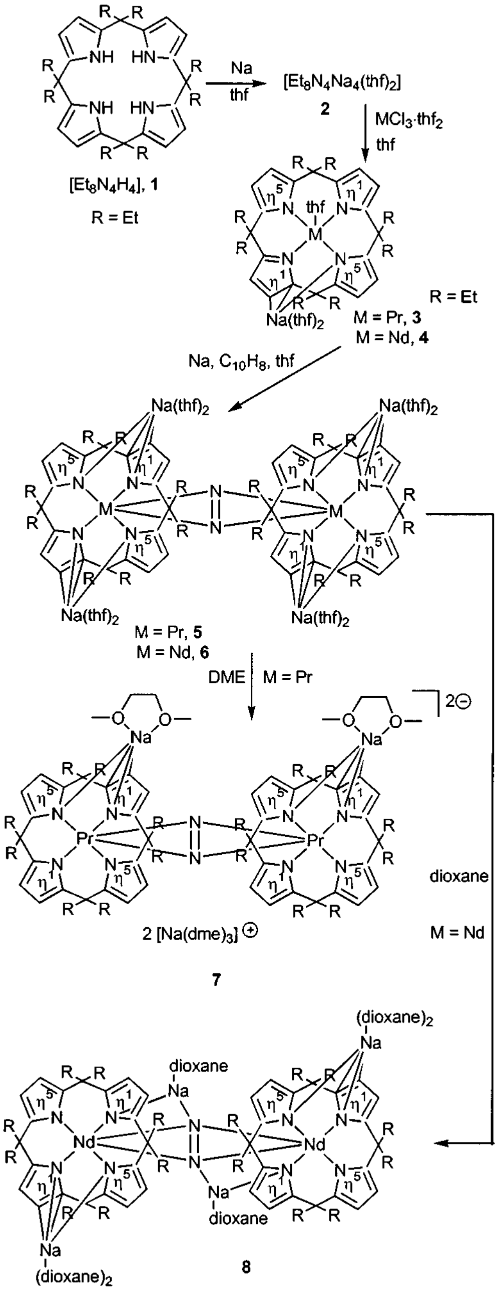
The *meso*-octaethylporphyrinogen–sodium–lanthanide complexes, [{(η^5 : η^1 : η^5: η^1-Et_8N_4)M}Na(thf)$_2$], in the presence of Na metal and under a nitrogen atmosphere, fix and reduce dinitrogen to the $[N_2]^{2-}$ anion, as shown by the isolation of the dinuclear complexes containing the [M(μ-η^2 : η^2-N_2)M] moiety [M = Pr, Nd].

Lanthanide metals can be particularly appropriate in the exploitation of the electron-rich nature of the *meso*-octaalkylporphyrinogen tetraanion. The ligand in turn can provide between 8 and 24 electrons as it adapts the bonding mode of each pyrrolyl anion from η^1 to η^5 based on the requirements of the metal.[1,2] The unique nature of this ligand, which has been recently widely explored in early transition metal organometallic chemistry, centers on its ability to function in a bifunctional manner[1,2] when bonded to acid metals, and through its peculiar redox chemistry.[3] These properties seem to be particularly suitable for exploring the reactivity of lanthanide–porphyrinogen complexes towards dinitrogen. Surprisingly, only one dinitrogen–lanthanide derivative is known for samarium.[4]

Herein we report dinitrogen complexes of Pr and Nd. The synthesis of the unknown starting compounds **3** and **4** has been carried out according to the sequence in Scheme 1. Owing to the potential complication of using lithium, which could eventually reduce N_2,[4b] all preparations and subsequent reactions involved the use of sodium.

Complexes **3**† (light-yellow crystals) and **4**† (light-blue crystals) can occur either in the monomeric or dimeric form, depending on the solvent used during their crystallization. The bonding mode of the lanthanide ion and the sodium cation has been proved by an X-ray analysis on **4**. Complexes **3** and **4** were reduced in THF under a nitrogen atmosphere with sodium, in the presence of small amounts of naphthalene and led to the yellow, **5**,‡ and green, **6**,‡ microcrystalline solids, respectively. Two different solid state forms of the N_2 derivatives have been obtained, depending on the crystallization solvents. Thus, complexes **5** and **6**, when recrystallized from dimethoxyethane (DME) and dioxane, gave **7**‡ and **8**,‡ respectively.

The structures of **7**§ and **8**§ are shown in Figs. 1 and 2 along with selected structural parameters. In both compounds, the porphyrinogen is η^5 : η^1 : η^5 : η^1 bonded[1,2] to the lanthanide ion. Both compounds show two sodium cations η^1 : η^3 bonded to the porphyrinogen and complete their hexacoordination with DME in **7** or two dioxane molecules in **8**. Two additional sodium cations function as countercations in **7**, while in **8** they interact with N_2. The N–N axis is perpendicular to the lanthanide–lanthanide direction, displaying a μ-η^2 : η^2 bonding mode.[4a,5] In both compounds **7** and **8**, unlike in [{(η^5-C_5Me_5)$_2$Sm}$_2$(μ-η^2 : η^2-N_2)][4a] [N–N, 1.088(12) Å] or [{UN($CH_2CH_2NSiBu^tMe_2$)$_3$}$_2$(μ-η^2 : η^2-N_2)] [N–N, 1.109(7) Å] the N–N distance is in good agreement with a bielectronic reduction of N_2.[6] The magnetic moments at 298 K of the complexes **3** and **5**, **4** and **6**, are very close [μ_{eff} = 3.53, **3**; 3.44, **5**; 3.29, **4**; 3.18 μ_B, **6**] and they remain constant over a wide range of temperature (50–320 K). These results allows the assignment of the +III oxidation state to all metal ions in **3–6**, and rules out any significant coupling between the two paramagnetic centres. In compounds **7** and **8** the lanthanide–N distances are relatively short and comparable to those of amido derivatives.[7] The rather short Na–N(N_2) distances support the interaction of the alkali cation with an anionic form of N_2. Unlike in [{(η^5-C_5Me_5)$_2$Sm}$_2$(μ-η^2 : η^2-N_2)] or in [{UN($CH_2CH_2NSiBu^tMe_2$)$_3$}$_2$(μ-η^2 : η^2-N_2)], no loss of N_2 was observed, though complexes **5–8** were kept under vacuum for a rather long time. Dinitrogen was evolved from **5**



Scheme 1

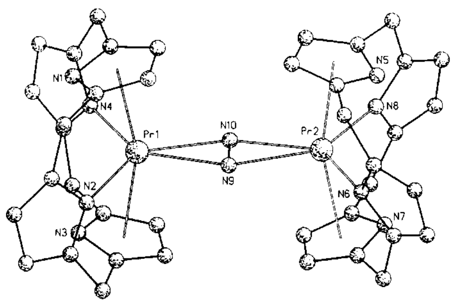


Fig. 1 An XP drawing of complex **7**. Selected bond distances (Å): Pr(1)–η^5(Pyr)$_{av}$ 2.605(6), Pr(1)–η^1(Pyr)$_{av}$ 2.579(5), Pr(1)–N(9) 2.475(5), Pr(1)–N(10) 2.414(5), Pr(2)–η^5(Pyr)$_{av}$ 2.604(6), Pr(2)–η^1(Pyr)$_{av}$ 2.576(5), Pr(2)–N(9) 2.455(5), Pr(2)–N(10) 2.425(4), N(9)–N(10) 1.254(7). η^5(Pyr)$_{av}$ indicates the centroid of the pyrrolyl anion.¶

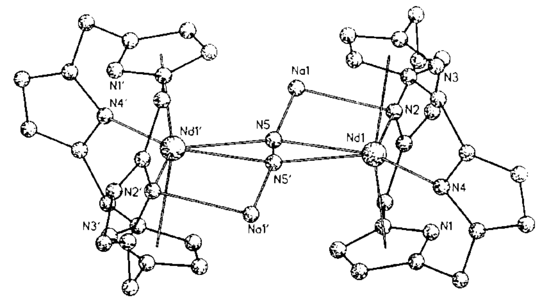


Fig. 2 An XP drawing of complex **8**. Selected bond distances (Å): Nd(1)–η^5(Pyr)$_{av}$ 2.562(5), Nd(1)–η^1(Pyr)$_{av}$ 2.550(4), Nd(1)–N(5) 2.511(4), Nd(1)–N(5′) 2.508(4), Na(1)–N(5) 2.308(4), Na(1)–η^1(Pyr)$_{av}$ 2.433(4), N(5)–N(5′) 1.234(8). Prime denotes a transformation of $-x$, $1 - y$, $-z$. η^5(Pyr)$_{av}$ indicates the centroid of the pyrrolyl anion.¶

and **6** in the expected amount only after oxidation with I_2. The present report deals with some important issues and in particular the use of an electron-rich ligand like porphyrinogen and its role in the fixation of dinitrogen in a reduced form bound to lanthanides like Pr and Nd, which are generally difficult to reduce.

Notes and references

† *Procedures for* **3** *and* **4**: [PrCl$_3$·thf$_2$] (11.2 g, 28.6 mmol) was added to a light-yellow solution of **2** (22.3 g, 28.9 mmol) in THF (600 cm^3). The resulting yellow-green suspension was kept stirring for 12 h at room temperature. The solid, mainly NaCl, was filtered off and the resulting solution evaporated to dryness. The yellow solid was recrystallized from THF–pentane (18.2 g, 75%). (Found: C, 62.63; H, 7.67; N, 6.71. $C_{44}H_{64}N_4NaPrO_2$ requires C, 62.55; H, 7.63; N, 6.63%). Complex **4** was obtained following the same procedure. (Found: C, 62.22; H, 7.36; N, 6.66. $C_{44}H_{64}N_4NaNdO_2$ requires C, 62.30; H, 7.60; N, 6.61%).

‡ *Procedures for* **5**–**8**: Na metal (0.21 g, 9.26 mmol) and naphthalene (0.30 g, 2.31 mmol) were added to a THF (200 cm^3) suspension of **3** (6.51 g, 7.70 mmol) in a 3 dm^3 flask. Stirring gave a red solution after 2 h and was continued for 24 h. Standing for 2 more days resulted in a yellow microcrystalline solid. The amount of solid was increased by partial evaporation of THF until 70 cm^3 and addition of pentane (100 cm^3) (5.8 g, 73%). (Found: C, 60.81; H, 7.60; N, 6.91. $C_{104}H_{160}N_{10}Na_4Nd_2O_8$ requires C, 60.87; H, 7.86; N, 6.86%). The reaction of **5** (1.44 mmol) in THF (100 mL) with I_2 (4.33 mmol) gave N_2 (1.39 mmol). Complex **5** recrystallized from DME gave crystals of **7** suitable for X-ray analysis. The synthesis of **6**, obtained as green crystals, was carried out following the procedure reported for **5**. (Found: C, 60.51; H, 7.95; N, 6.95. $C_{104}H_{160}N_{10}Na_4Nd_2O_8$ requires C, 60.67; H, 7.83; N, 6.80%). Oxidation of **6** (1.43 mmol) with I_2 in THF evolved 1.34 mmol of N_2. The recrystallization of **6** from dioxane gave crystals of **8**, analyzed by X-ray diffraction.

§ *Crystal data* for **7**: $C_{104}H_{176}N_{10}Na_4O_{16}Pr_2$, M = 2196.33, monoclinic, space group $P2_1/c$, a = 20.1877(14), b = 19.2513(14), c = 29.745(2) Å, β = 94.134(6)°, V = 11529.8(14) Å^3, Z = 4, D_c = 1.265 g cm^{-3}, F(000) = 4640, λ(Mo-Kα) = 0.71073 Å, μ = 0.912 mm^{-1}; crystal dimensions 0.51 × 0.44 × 0.53. Diffraction data were collected on a KUMA CCD at 173 K. For 16219 observed reflections [$I > 2\sigma(I)$] the conventional R is 0.0687 ($wR2$ = 0.1668 for 22661 independent reflections). *Crystal data* for **8**: $C_{124}H_{200}N_{10}Na_4Nd_2O_{26}$, M = 2627.38, monoclinic, space group $P2_1/c$, a = 12.908(3), b = 15.537(2), c = 32.885(9) Å, β = 94.02(2)°, V = 6579(3) Å^3, Z = 2, D_c = 1.326 g cm^{-3}, F(000) = 2772, λ(Mo-Kα) = 0.71070 Å, μ = 0.865 mm^{-1}; crystal dimensions 0.40 × 0.38 × 0.27. Diffraction data were collected on a mar345 area detector at 173 K. For 8471 observed reflections [$I > 2\sigma(I)$] the conventional R is 0.0546 ($wR2$ = 0.1623 for 10692 independent reflections). CCDC 182/1065. See http://www.rsc.org/suppdata/cc/1998/2603, for crystallographic files in .cif format.

¶ *meso*-Ethyl groups and sodium cations bonded to the periphery of porphyrinogen have been omitted for clarity.

1 D. Jacoby, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Chem. Soc., Chem. Commun.*, 1991, 790; *J. Am. Chem. Soc.*, 1993, **115**, 3595; D. Jacoby, S. Isoz, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1995, **117**, 2793; C. Floriani, in *Stereoselective Reactions of Metal-Activated Molecules*, ed. H. Werner and J. Sundermeyer, Vieweg, Wiesbaden, 1995, pp. 97–106; S. De Angelis, E. Solari, A. Chiesi-Villa and C. Rizzoli, *Organometallics*, 1995, **14**, 4505; D. Jacoby, S. Isoz, C. Floriani, K. Schenk, A. Chiesi-Villa and C. Rizzoli, *Organometallics*, 1995, **14**, 4816; S. Isoz, C. Floriani, K. Schenk, A. Chiesi-Villa and C. Rizzoli, *Organometallics*, 1996, **15**, 337; G. Solari, E. Solari, A. Chiesi-Villa and C. Rizzoli, *Organometallics*, 1997, **16**, 508.

2 C. Floriani, *Pure Appl. Chem.*, 1996, **68**, 1.

3 S. De Angelis, E. Solari, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1994, **116**, 5691; *J. Am. Chem. Soc.*, 1994, **116**, 5702; C. Floriani, *Chem. Commun.*, 1996, 1257.

4 Two reports appeared on Sm–N_2 chemistry, the first one (a) containing a true N_2 bridging two samarium ions, the second one (b) containing the Li_4N_2 unit within two samarium ions: (a) W. J. Evans, T. A. Ulibarri and J. W. Ziller, *J. Am. Chem. Soc.*, 1988, **110**, 6877; (b) J. Jubb and S. Gambarotta, *J. Am. Chem. Soc.*, 1994, **116**, 4477.

5 The unusual μ-η^2 : η^2 bonding mode has been found also in a U(III) derivative: P. Roussel and P. Scott, *J. Am. Chem. Soc.*, 1998, **120**, 1070.

6 R. Ferguson, E. Solari, C. Floriani, D. Osella, M. Ravera, N. Re, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1997, **119**, 10104 and references therein; C. E. Laplaza, M. J. A. Johnson, J. C. Peters, A. L. Odom, E. Kim, C. C. Cummins, G. N. George and I. J. Pickering, *J. Am. Chem. Soc.*, 1996, **118**, 8623 and references therein; A. Zanotti-Gerosa, E. Solari, L. Giannini, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1998, **120**, 437.

7 M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, *Metal and Metalloid Amides. Synthesis, Structures and Physical Properties*, Ellis Horwood, Chichester, UK, 1980, ch. 8.

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