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Cyclopentadienyl Behavior of Pyrrolyl Anions within the *meso*-Octaethylporphyrinogen-Binding Lanthanides: Carbon−Hydrogen and Metal−Carbon Bond Rearrangements

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The complexation of Ln(III) ions by the *meso*-octaethylporphyrinogen [$Et_8N_4H_4$], **1**, has been achieved by reacting the sodium derivative [$Et_8N_4Na_4\cdot THF_3$], **2**, with [$LnCl_3\cdot THF_2$]. Depending on the reaction or crystallization solvent, a variety of structural categories of Ln−porphyrinogen complexes have been isolated and structurally characterized. When the reaction was carried out in THF and the final complex recrystallized from THF, [$\{(\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-}Et_8N_4)Ln(THF)\}\text{-}\eta^3\text{-}Na(THF)_2$] complexes [Ln = Pr (**3**), Nd (**4**), Sm (**5**), Eu (**6**), Gd (**7**), Yb (**8**)] were obtained in a monomeric form. When their recrystallization was performed in dioxane, a dimerization occurred thanks to dioxane bridging the sodium cations of the monomeric units [$\{(\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-}Et_8N_4)Ln(DME)\}\text{-}\eta^3\text{-}Na](dioxane)_{1.5}$] [Ln = Nd, **14**; Ln = Sm, **15**]. In a third category we isolated complexes where two monomeric monoanions [$(\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-}Et_8N_4)Ln]^-$ are $\eta^2{:}\eta^3$ sandwiching two sodium cations, which are exclusively solvated by the pyrrolyl anions [$\{(\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-}Et_8N_4)Ln\}_2\text{-}\eta^2{:}\eta^3\text{-}Na_2$] [Ln = Pr, **16**; Ln = Sm, **17**]. The three classes of compounds mentioned above, all of them containing the monomeric unit [Ln−porphyrinogen−Na], are characterized by the following structural parameters: Ln−η^5(pyrrole)$_{av}$, 2.490(7) Å for **7**, 2.556(2) Å for **14**, 2.543(2) Å for **16**; Ln−η^1(pyrrole)$_{av}$, 2.43(1) Å for **7**, 2.494(4) Å for **14**, 2.485(4) Å for **16**; centroid−Ln−centroid, 174.6(3)° for **7**, 168.1(1)° for **14**, 169.7(2)° for **16**; Na−η^3(pyrrole), 2.50(1) Å for **7**, 2.515(3) Å for **14**. The recrystallization of complexes **3**−**8** from DME led to dimeric organometallic complexes, where the dimerization has been via the desolvation of the Ln ion and the formation of a Ln−C σ bond with the β-carbon of a pyrrole of an adjacent Ln−porphyrinogen unit. Such dimers occur in the ion-separated form [$(\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-}Et_8N_4)_2Ln_2][NaS_n]_2$ [Ln = Pr (**9**), Nd (**10**), Sm (**11**), Gd (**12**), Eu (**13**)]. Their recrystallization from THF led to the ion-pair derivatives in which two sodium cations are η^2-bonded to the η^1-pyrrolyl anions of the dimer [$\{(\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-}Et_8N_4)_2Ln_2\}\text{-}\eta^2(NaS_n)_2$] [Ln = Pr (**18**), Nd (**19**), Sm (**20**), Gd (**21**); S = DME, THF; n = 2]. When the crystallization of **9**−**13** was carried out from THF/dioxane, polymeric structures were isolated, where cations are bridged by dioxane molecules [$\{(\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-}Et_8N_4)_2Ln\}_2\text{-}\eta^2\{Na(THF)\}_2(\mu\text{-dioxane})$][Ln = Nd, **22**; Ln = Gd, **23**]. In the three classes made up from the dimeric building block, the structural *leit-motiv* is constant and two structural parameters are very close [Ln−η^5(pyrrole)$_{av}$, 2.538(3) Å for **11**, 2.578(1) Å for **18**; centroid−Ln−centroid, 172.3(2)° for **11**, 170.4(1)° for **18**; Ln−C, 2.471(7) Å for **11**, 2.512(2) Å for **18**].

Introduction

Lanthanide coordination chemistry has been well documented by the complexes' high coordination numbers and hard donor atoms,[1] while the most interesting part of their organometallic chemistry[2] is essentially based on the use of cyclopentadienyl ligands.[2,3] A ligand which is particularly appropriate for mimicking the major characteristics of both classes of ligands is the tetraanion derived from the *meso*-octaalkylporphyrinogen[4,5] (Chart 1). In addition to the high negative charge and the sterically protecting cavity, each pyrrolyl anion can function as a cyclopentadienyl-like anion in an η^5 or η^3 bonding mode[4,5] (Chart 1). The conformational flexibility due to the *meso*-sp^3 carbons makes the ligand particularly appropriate to adapt to the metal size. The variety of the cyclopentadienyl rearrangements around a lanthanide ion can be closely simulated in an intramolecular manner using the porphyrinogen tetraanion as a cyclic tetrakiscyclopentadienyl derivative. A few reports have appeared in this field, concerning exclusively Ln(II)[6] and particularly Sm(II).[7] The present paper is focused on the complexation of Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), and

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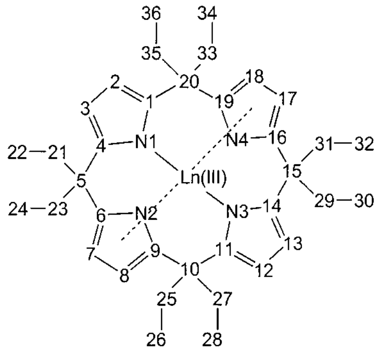
Table 1. Synthetic and Analytical Data for Complexes **3**−**8**

Ln, compd	$LnCl_3(THF)_x$	**2**	THF	pentane	color	yield	X-ray	anal.	μ_{eff}(298 K)
Pr, **3**	11.11 g, 28.4 mmol, $x = 2$	24.2 g, 28.7 mmol	500 mL	80 mL	pale yellow	17.9 g, 74%	THF/pentane	calcd for $C_{44}H_{64}N_4NaPrO_2$: C, 62.55; H, 7.63; N, 6.63. found: C, 62.96; H, 7.45; N, 6.55	3.53 μ_B
Nd, **4**	8.61 g, 21.8 mmol, $x = 2$	18.57 g, 22 mmol	500 mL	80 mL	pale blue	13.3 g, 72%	THF/pentane	calcd for $C_{44}H_{64}N_4NaNdO_2$: C, 62.30; H, 7.60; N, 6.61. found: C, 62.22; H, 7.36; N, 6.66	3.29 μ_B
Sm, **5**	4.97 g, 12.4 mmol, $x = 2$	10.72 g, 12.7 mmol	250 mL	40 mL	yellow	7.5 g, 71%	THF/pentane	calcd for $C_{44}H_{64}N_4NaSmO_2$: C, 61.86; H, 7.55; N, 6.56. found: C, 61.93; H, 7.42; N, 6.34	1.58 μ_B
Eu, **6**	5.52 g, 12.6 mmol, $x = 2.5$	10.72 g, 12.7 mmol	300 mL	60 mL	beige	7.38 g, 68%	THF/pentane	calcd for $C_{44}H_{64}N_4NaEuO_2$: C, 61.74; H, 7.54; N, 6.55. found: C, 61.97; H, 7.92; N, 6.57	5.14 μ_B
Gd, **7**	10.07 g, 19.5 mmol, $x = 3.5$	16.63 g, 19.7 mmol	600 mL	80 mL	white	11.6 g, 69%	THF/pentane	calcd for $C_{44}H_{64}N_4NaGdO_2$: C, 61.36; H, 7.49; N, 6.50. found: C, 60.72; H, 7.54; N, 6.40	7.77 μ_B
Yb, **8**	9.88 g, 23.3 mmol, $x = 2$	19.9 g, 23.6 mmol	500 mL	80 mL	pink	14.4 g, 70%	THF/pentane	calcd for $C_{44}H_{64}N_4NaYbO_2$: C, 60.26; H, 7.36; N, 6.39. found: C, 60.25; H, 7.25; N, 6.54	3.90 μ_B

Table 2. Synthetic and Analytical Data for Complexes **9**−**13**

Ln, compd	$LnCl_3(THF)_2$	**2**	THF	pentane	color	yield	X-ray	anal.	μ_{eff}(298 K)
Pr**, 9**	2.10 g, 1.70 mmol	4.59 g, 5.44 mmol	200 mL	40 mL	pale yellow	2.94 g, 62%	DME	calcd for $C_{44}H_{68}N_4NaPrO_4$: C, 59.72; H, 7.65; N, 6.39. found: C, 59.31; H, 7.79; N, 6.61	3.00 μ_B
Nd**, 10**	1.70 g, 4.31 mmol	3.76 g, 4.45 mmol	200 mL	40 mL	pale blue	2.28 g, 60%	DME	calcd for $C_{44}H_{68}N_4NaNdO_4$: C, 59.76; H, 7.75; N, 6.33. found: C, 59.24; H, 7.62; N, 6.61	4.18 μ_B
Sm, **11**	2.04 g, 5.08 mmol	4.33 g, 5.13 mmol	200 mL	40 mL	yellow	2.83 g, 63%	DME	calcd for $C_{44}H_{68}N_4NaSmO_4$: C, 59.35; H, 7.70; N, 6.29. found: C, 59.64; H, 7.69; N, 6.32	1.26 μ_B
Gd**, 12**	2.43 g, 5.48 mmol	4.67 g, 5.53 mmol	200 mL	40 mL	white	3.52 g, 72%	DME	calcd for $C_{44}H_{68}GdN_4NaO_4$: C, 58.90; H, 7.64; N, 6.24. found: C, 58.92; H, 7.67; N, 6.09	8.05 μ_B

Chart 1



Yb(III) by the *meso*-octaethylporphyrinogen, using a synthetic methodology which avoids the lithium derivative of the porphyrinogen. As a matter of fact, the generation of the lithium−porphyrinogen in THF causes its decomposition and led to the presence of oxygenated ligands (enolates) in the final complexes.[7] The Ln(III)−porphyrinogen complexes reported here are obtained in an anionic form occurring as an ion pair associated to an alkali metal cation. Their structure is very much affected by the reaction or crystallization solvent,[8] which is a determining factor not only of the nature of the ion pair formed but also of the molecular complexity and the binding mode rearrangements of the pyrrolyl anions. In the latter case, a particularly relevant intermolecular Ln−C σ bond formation, followed by a C−H bond cleavage has been observed.

This is the first detailed report on the synthesis of lanthanide−*meso*-octaalkylporphyrinogen complexes by the use of an appropriate synthetic method, thus getting rid of other ligands, and on the role played by the reaction or crystallization solvent on the structural diversity.

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Table 3. Crystal Data and Structure Refinement for **7**, **11**, **14**, **16**, and **18**

	7	**11**	**14**	**16**	**18**
formula	$C_{48}H_{72}GdN_4NaO_3$	$C_{72}H_{96}N_8Sm_2 \cdot 2Na(C_4H_{10}O_2)_3$	$C_{92}H_{140}N_8Na_2Nd_2O_{10}$	$C_{80}H_{112}N_8Na_2O_2Pr_2$	$C_{88}H_{136}N_8Na_2O_8Pr_2$
fw	933.34	1960.97	1852.58	1545.58	1761.85
T, K	143	173	143	183	296
λ, Å	0.710 70	0.710 70	0.710 70	0.710 70	0.710 70
cryst system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$C2/c$
a, Å	12.426(3)	12.556(3)	16.236(2)	11.726(3)	20.742(3)
b, Å	16.322(3)	24.187(4)	13.460(2)	13.460(2)	21.152(6)
c, Å	22.572(5)	18.759(3)	21.626(6)	14.693(5)	20.474(3)
α, deg	90	90	90	77.86(3)	90
β, deg	94.05(3)	99.61(3)	108.11(2)	72.47(3)	94.801(10)
γ, deg	90	90	90	67.738(10)	90
V, Å^3	4566.6(16)	5616.9(19)	4491.9(15)	2034.4(9)	8951(3)
Z	4	2	2	1	4
D_{calc}, g/cm^3	1.358	1.159	1.370	1.262	1.307
μ, mm-$^{-1}$	1.506	1.096	1.214	1.241	1.142
reflcns collcd	15 927	38 316	9832	11 966	27 859
data/params	5531/528	8971/542	5168/515	6154/425	7817/488
R1 [$I > 2\sigma(I)$]	0.0747	0.0640	0.0407	0.0434	0.0340
wR2 (all data)	0.2187	0.2127	0.1304	0.1402	0.0997

Experimental Section

General Procedure. All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. Infrared spectra were recorded with a Perkin-Elmer FT 1600 spectrophotometer, and NMR spectra on AC-200E and DPX-400 Bruker instruments. Magnetic susceptibility measurements were made on an MPMS5 SQUID susceptometer (Quantum Design Inc.), operating at a magnetic field strength of 1 kOe. The syntheses of $LnCl_3(THF)_2$,[9] **1**,[4a] and **2**[10] were carried out as reported elsewhere.

The syntheses of **3** and **12** are reported in detail, while, for the analogous series of complexes **4**−**8** and **9**−**12**, the most important synthetic route and analytical data are listed in Tables 1 and 2, respectively. Complexes **13**−**23** were obtained upon crystallization of **3**−**12** according to the solvent mixtures reported below.

Synthesis of 3. $PrCl_3(THF)_2$ (11.11 g; 28.4 mmol) was added to a THF (500 mL) solution of **2** (24.2 g; 28.7 mmol) to give a pale yellow suspension. The mixture was stirred at room temperature for 12 h; the NaCl was filtered off and the yellow-green solution evaporated to dryness. The residue was dissolved in pentane (80 mL), and the pale yellow solid was collected and dried (17.9 g; 74%). Crystals suitable for X-ray analysis were obtained by recrystallizing from THF/pentane. Anal. Calcd for $C_{44}H_{64}N_4NaPrO_2$: C, 62.55; H, 7.63; N, 6.63. Found: C, 62.96; H, 7.45; N, 6.55. $\mu_{eff} = 3.53\ \mu_B$ at 298 K.

Synthesis of 12. Addition of $GdCl_3(THF)_2$ (2.43 g; 5.48 mmol) to a solution of **2** (4.67 g; 5.53 mmol) in DME (200 mL) caused the formation of a white suspension, which was stirred at room temperature for 12 h. Removal of NaCl by filtration and standing of the filtrate overnight at room temperature gave colorless crystals suitable for X-ray crystallography. The solvent was evaporated to dryness, the residue was dissolved in pentane (40 mL), and a white solid was collected (3.52 g; 72%). Anal. Calcd for $C_{44}H_{68}GdN_4NaO_4$: C, 58.90; H, 7.64; N, 6.24. Found: C, 58.92; H, 7.67; N, 6.09. $\mu_{eff} = 8.05\ \mu_B$ at 298 K.

Complexes **16**, **14**, **15**, and **17** were obtained recrystallizing **3** (**16**), **4** (**14**), and **5** (**15** and **17**) from a DME/dioxane mixture. Complexes **13**, **18**, and **20** were obtained recrystallizing **6**, **9**, and **11**, respectively, from DME. Complexes **19** and **21** were obtained recrystallizing **10** and **12** from THF. Complexes **22** and **23** were obtained recrystallizing **10** and **12** from a THF/dioxane mixture.

X-ray crystallography for Complexes 7, 11, 14, 16, and 18. Crystals of **7, 11, 14, 16**, and **18** were mounted in glass capillaries and sealed under nitrogen. Crystal data and structure refinement details are listed in Table 3. Diffraction data have been collected at different temperatures (Table 3) on a mar345 imaging plate and reduced with marHKL release 1.9.1.[11] No absorption correction was performed. The structure solution was performed with ab initio direct methods.[12] All structures were refined using the full-matrix least-squares on F^2 with all non-H atoms anisotropically defined. Hydrogen atoms were placed in calculated positions using the "riding model" with $U_{iso} = aU_{eq}(X)$ (where a is 1.5 for methyl hydrogens and 1.2 for others, while X is the parent atom); in some cases for methyl hydrogens and for hydrogens belonging to solvent molecules a common isotropic displacement parameter ($U_{iso} = 0.08$ Å^2) was used. Structure solution, refinement, molecular graphics, and geometrical calculations have been carried out on all structures with the SHELXTL software package, release 5.1.[13] Final atomic coordinates, thermal and geometrical parameters, and hydrogen coordinates are listed in the Supporting Information.[14]

Results and Discussion

The synthesis of the lanthanide−*meso*-octaethylporphyrinogen has been performed using the anhydrous $[LnCl_3(THF)_2]$[6,7] and the sodium derivative of the porphyrinogen ligand.[10] The use of the sodium instead of the commonly employed lithium derivative[4,5] was suggested by the much easier, available method for removing the alkali metal halide and the decomposition products from THF when lithium derivatives were used.[7] Depending on the reactions solvent, namely THF and DME, two different classes of compounds have been obtained, i.e. the monomeric forms **3**−**8** from THF and the dimeric ones **9**−**13** from DME (see Scheme 1). The solvation degree shown in Scheme 1 refers to the forms recrystallized from THF and DME, respectively, though the products obtained from the reaction and dried in vacuo usually have a lower degree of solvation. The understanding of how complexes **3**−**8** and **9**−**13** display a structural diversity is particularly complicated by the contemporaneous presence of variable degrees of solvation of the lanthanide and alkali metal ions and of the pyrrolyl anions. In fact, the pyrrolyl anion functions intra- and intermolecularly as a binding site in competition with the oxygenated solvents.[5] The basis of all structural forms observed in this study are the monomeric form exemplified for **3**−**8** and the dimeric one

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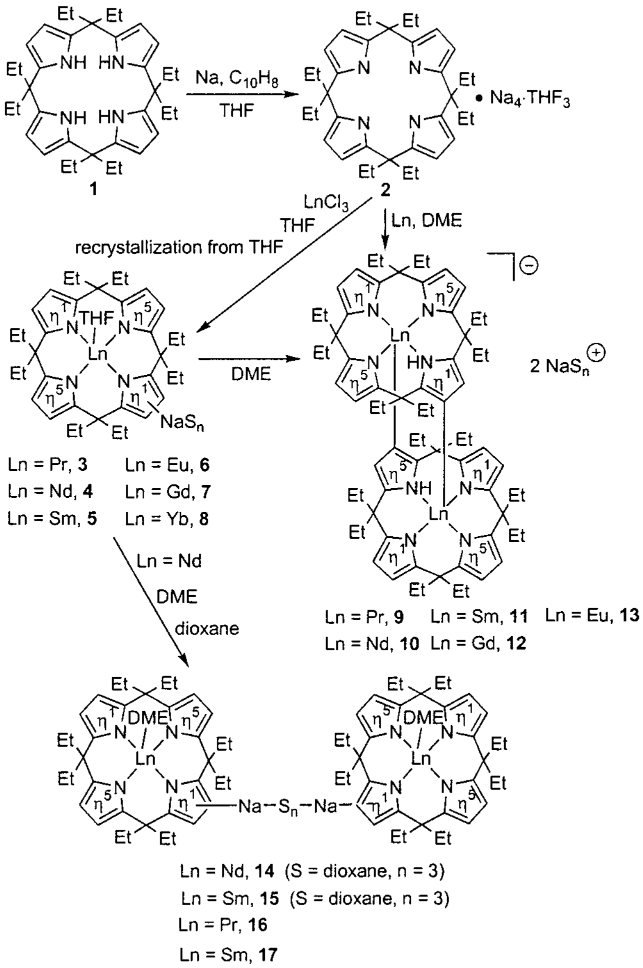
Table 4. Selected Bonds (Å) and Angles (deg) for Complexes **7**, **11**, **14**, **16**, and **18**

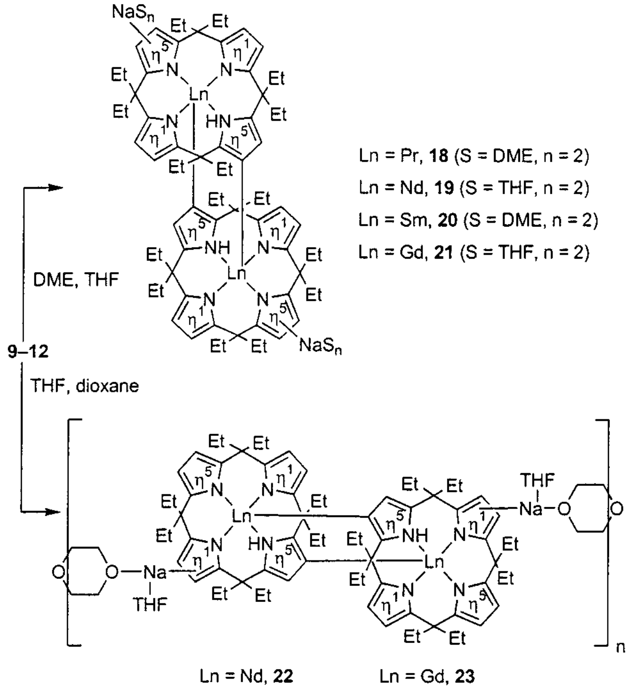
	7	**11**	**14**	**16**	**18**
Ln−η^5(Pyr)[a]	2.522(7)	2.571(3)	2.576(2)	2.568(2)	2.608(1)
Ln−η^5(Pyr)[b]	2.459(8)	2.505(3)	2.536(2)	2.518(2)	2.548(2)
Ln−η^1(Pyr)[c]	2.46(1)	2.461(6)	2.527(4)	2.496(4)	2.506(2)
Ln−η^1(Pyr)[d]	2.41(2)	2.462(6)	2.461(4)	2.473(4)	2.475(2)
η^5(Pyr)−Ln−η^5(Pyr)	174.6(3)	172.3(2)	168.1(1)	169.7(2)	170.4(1)
Na−η^3(Pyr)[e]	2.50(1)		2.515(3)	2.610(3)	
Na−η^2(Pyr)				2.492(4)[f]	2.633(2)[g]
Na−η^1(Pyr)[h]	2.55(1)		2.460(4)		
Ln−C[i]		2.471(7)			2.512(2)

[a] Pyr = (N2, C6, C7, C8, C9). [b] Pyr = (N4, C16, C17, C18, C19). [c] Pyr = (N1). [d] Pyr = (N3). [e] Pyr = (N1, C3, C4). [f] Pyr = (C12A,[j] C13A). [g] Pyr = (C2, C3). [h] Pyr = N2. [i] C = C8. [j] The letter A indicates the following symmetry operation: −*x*, −*y*, −*z*. η^5(Pyr), η^3(Pyr), η^2(Pyr), η^1(Pyr) indicate the centroids.

Scheme 1



Scheme 2



displayed for **9**−**13**. All the others are derived from them as a consequence of different solvation of the alkali metal countercation.[4,5] We also found that the monomeric forms can be converted into the dimeric ones via a crystallization in DME, though the reverse transformation cannot be achieved recrystallizing the dimers from THF. The recrystallization of monomers **4** and **5** from a mixture of DME and dioxane led to the dimers **14** and **15**, where the dimerization occurs via sodium cations bridged by dioxane molecules. Under the same conditions, sometimes complexes such as **16** and **17** were obtained with the two sodium cations sandwiched between two monomeric metal−porphyrinogen moieties and without any solvent of crystallization. The dimeric nature of **9**−**13** is maintained during a recrystallization from a mixture DME/THF, pure THF, and THF/dioxane mixture. In all cases the ion-separated forms have been converted into ion-pair dimers, with a sodium cation binding to one of the pyrroles of the porphyrinogen ligand. The solvation of the alkali metal cation is completed by DME in the case of **18** and **20** and by THF in the case of **19** and **21**, while the presence of dioxane in the third case led to a polymerization of the ion-pair dimers via the sodium countercations bridged by dioxane molecules (see complexes **22** and **23**).[15] The latter crystallizations confirmed that THF can affect the structural form by affecting the solvation of the alkali metal countercation[5] in dimers **9**−**13**, but it does not reverse the process back to the monomers.

In both classes of compounds the lanthanide ions display a bonding mode to the porphyrinogen ligand similar to those observed in [Cp_2LnL_3] complexes.[2c] As a matter of fact, two of the pyrrolyl anions within the porphyrinogen ligand display an η^5 bonding mode, while the other two are η^1 bonded to the lanthanide ion. Such a bonding mode of porphyrinogen tetraanion has been observed in the complexation of zirconium(IV) and hafnium(IV)[4] and is particularly relevant to the reactivity of the metal center. The ligand, which is conformationally very flexible, can adapt its bonding mode along the reaction pathway according to requests of the metal. The lanthanide ion in all the monomeric forms completes its coordination sphere with a

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(15) The proposed structures of **22** and **23** are supported by X-ray analyses, which do not show any significant difference from that of **18**.

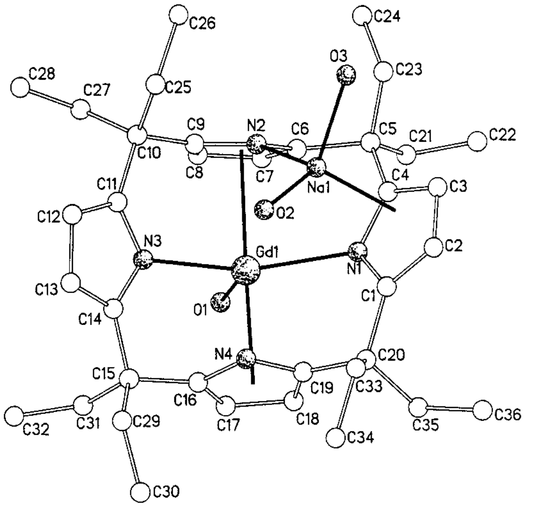

Figure 1. Drawing of complex **7**. Hydrogens have been omitted for clarity, while for THF only oxygens have been included.

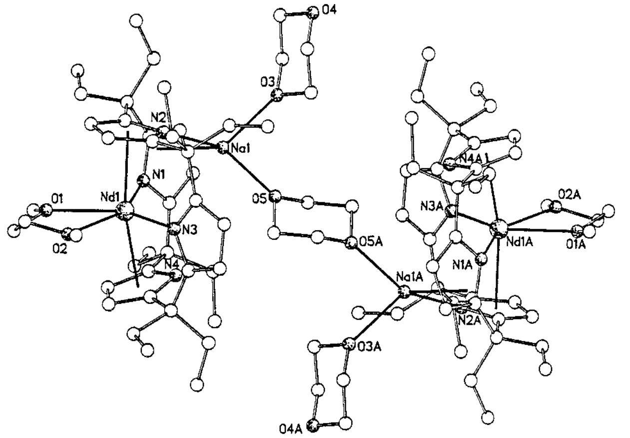

Figure 2. Drawing of complex **14**. Hydrogens have been omitted for clarity. The labeling scheme of the ligand is reported in Chart 1. The letter A corresponds to equivalent atoms obtained by the following symmetry operation: $-x$, $-y$, $-z$.

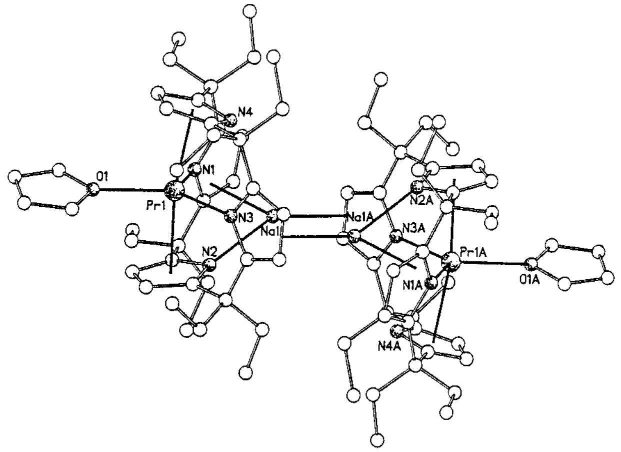

Figure 3. Drawing of complex **16**. Hydrogens have been omitted for clarity. The labeling scheme of the ligand is reported in Chart 1. The letter A indicates the following symmetry operation: $-x$, $-y$, $-z$.

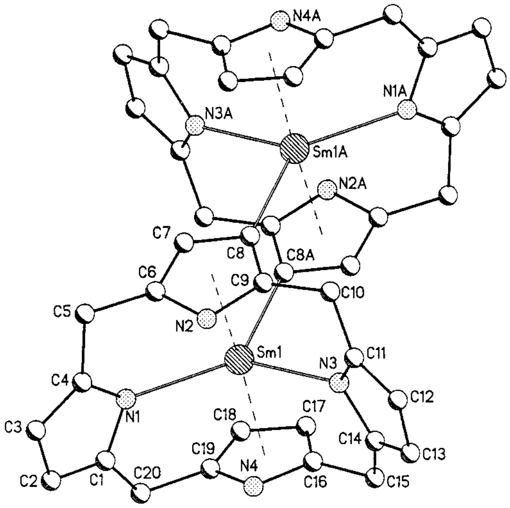

Figure 4. Drawing of the dianion of dimeric complex **11**. Hydrogens and ethyl groups have been omitted for clarity. The letter A indicates the following symmetry transformation: $-x$, $-y$, $-z$.

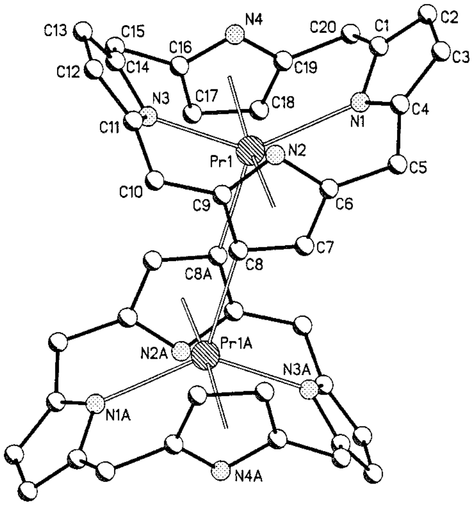

Figure 5. Drawing of the dianion of dimeric complex **18**. Hydrogens and ethyl groups have been omitted for clarity. The letter A indicates the following symmetry transformation: $-x + {}^1/_2$, $-y + {}^1/_2$, $-z$.

molecule of solvent. When the monomeric form is thermally desolvated, a coordination site on the lanthanide ion is made free, and in the dimers the solvent molecule is replaced by a strong σ-interaction with a pyrrole from an adjacent Ln−porphyrinogen moiety. The lanthanide ion involved in such in an intermolecular process behaves as a strong electrophile toward a metallaporphyrinogen, attacking the β-position of one of the pyrroles. It has been shown that such an attack by an electrophile is followed by a hydrogen shift, which occurs either to β-carbon of on adjacent pyrrole[16] or, as in the present case, to nitrogen of the same pyrrole. Such a metalation of a pyrrole establishes a quite strong Ln−C σ bond (see structural parameters below). The shift of the β-hydrogen to the nitrogen of the same pyrrole has been proved by the appearance of 3500 cm^{-1} band in the IR spectrum of the dimers and is supported by the structural parameters (see below). The monomer → dimer transformation resembles the electrophilic activation of a C−H bond using lanthanide complexes.[17] In the dimeric complexes the lanthanide ion displays a structural form which resembles that occurring in the Cp series with η^5- and η^1-bonded cyclopentadienyl anions.[2d,e] The magnetic moment of the lanthanide ion does not change very much when going from the monomeric to the dimeric form (see Tables 1 and 2).

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(16) Bonomo, L.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1998**, *120*, 12972.

(17) *Selective Hydrocarbon Activation: Principles and Progress*; Davies, J. A., Watson, P. L., Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1990; Chapter 4.

A single example of the X-ray structure is reported for each category of complexes displayed in Schemes 1 and 2 . Selected bond distances and angles are listed in Table 4. The structures of those complexes containing the monomeric fragment [{(η^5:η^1:η^5:η^1-Et$_8$N$_4$)Ln}-η^3-Na], namely **3**−**8**, **14**, **15**, **16**, and **17**, shown in Figures 1−3 differ only for the solvation of the sodium cation. The lanthanide ion achieves a formal octacoodination, like in Cp$_2$ML$_3$ complexes of early transition metals, by the help of the porphyrinogen tetraanion and a molecule of solvent (THF or DME).[2] The two η^5-bonded pyrroles are arranged in a parallel fashion, as proved by the dihedral angles between the two η^5-pyrrole rings and the centroid−Ln−centroid angles [17.7(4), 174.6(3)° for **7**; 25.2(1), 168.1(1)° for **14**; 25.0(3), 169.7(2)° for **16**]. The sodium cation is permanently η^3-bonded [Na−η^3(pyrrole), 2.50(1) Å for **7**, 2.515(3) Å for **14**] to one of the pyrrolyl anion η^1 bonded to the lanthanide ion.[5] In the case of complexes **3**−**8** (see Figure 1), its coordination sphere is completed by THF, while in complexes **14** and **15** dioxane bridges the sodium cations of the two monomeric units making dimers (see Figure 2). In the case of complexes **16** and **17**, two sodium cations are η^2:η^3 sandwiched by two [(η^5:η^1:η^5:η^1-Et$_8$N$_4$)Ln] anions [Na−η^2(pyrrole), 2.492(4) Å; Na−η^3(pyrrole), 2.610(3) Å]. The structure of the dimers **9**−**13** and **18**−**21** is exemplified in Figures 4 and 5 for complexes **11** and **18**, respectively. The major difference between these two categories stays in the ion separated and ion-pair forms, respectively. The overall structure of the dimeric dianion [(η^5:η^1:η^5:η^1-Et$_8$N$_4$)$_2$-Ln$_2$]$^{2-}$ is quite similar. Within each monomeric unit the porphyrinogen is η^1:η^5:η^1:η^5 bonded to the metal, the more significant structural parameters being as follows: Ln−η^5-(pyrrole)$_{av}$ is 2.538(3) Å for **11** and 2.578(1) Å for **18**. Centroid−Ln−centroid is 172.3(2)° for **11** and 170.4(1)° for **18**. The dihedral angle between the two η^5-bonded pyrrole planes is 15.8(4)° for **11** and 15.7(1)° for **18**. One of the pyrrolic nitrogens bears an hydrogen, though maintaining a nearly planar sp^2 geometry. The lanthanide ion is completing its coordination sphere interacting with the β-carbon of a η^5-bonded pyrrole from an adjacent Ln−porphyrinogen moiety, forming a Ln−C(sp^2) σ bond [2.471(7) Å for **11**, 2.512(2) Å for **18**].[1b] This interaction shifted the related hydrogen from the β-carbon to the nitrogen atom of the same pyrrolyl anion.[16] The resulting organometallic dianion is in the ion-separated form in complex **11** (Figure 4), while in complex **18** the two sodium cations are η^2 bonded to one of the η^1-pyrrolyl anions of the dimer [Na−η^2(pyrrole), 2.633(2) Å].

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Supporting Information Available: ORTEP drawings and tables of crystallographic data for **7**, **11**, **14**, **16**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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