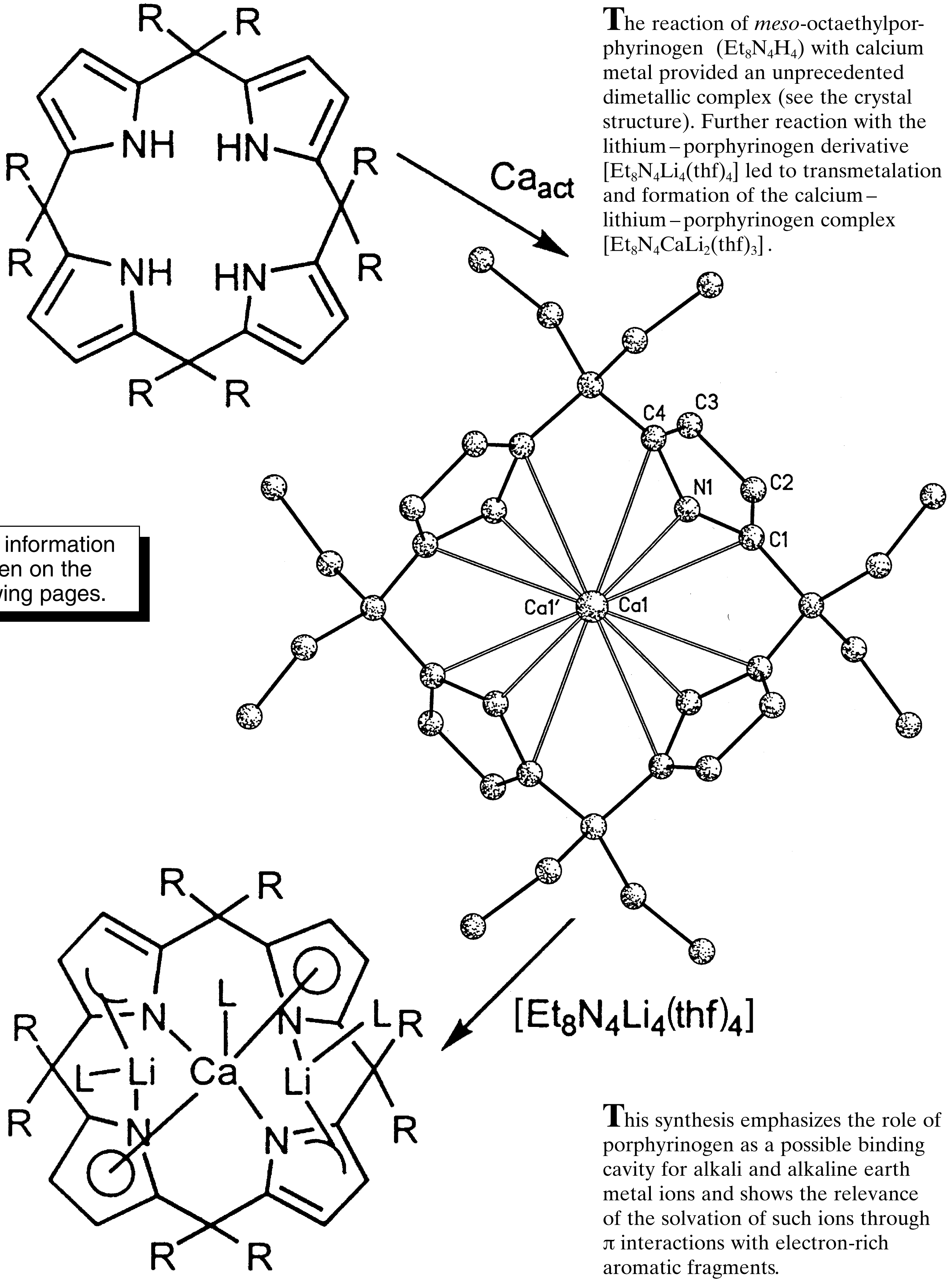
The reaction of *meso*-octaethylporphyrinogen ($Et_8N_4H_4$) with calcium metal provided an unprecedented dimetallic complex (see the crystal structure). Further reaction with the lithium–porphyrinogen derivative $[Et_8N_4Li_4(thf)_4]$ led to transmetalation and formation of the calcium–lithium–porphyrinogen complex $[Et_8N_4CaLi_2(thf)_3]$.



This synthesis emphasizes the role of porphyrinogen as a possible binding cavity for alkali and alkaline earth metal ions and shows the relevance of the solvation of such ions through π interactions with electron-rich aromatic fragments.

More information is given on the following pages.

The π Complexation of Calcium inside the *meso*-Octaethylporphyrinogen Tetraanion Cavity**

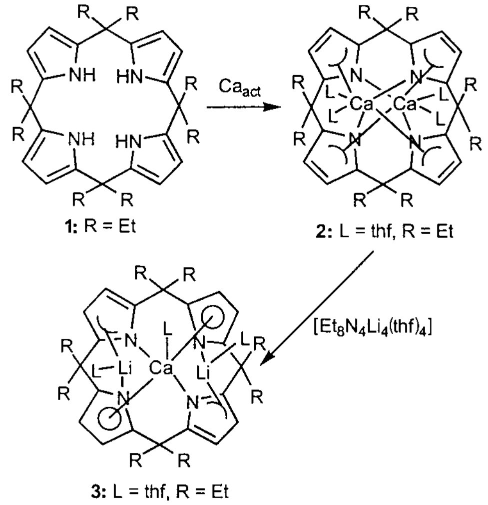
Lucia Bonomo, Olivier Dandin, Euro Solari,
Carlo Floriani,* and Rosario Scopelliti

Solvation of alkali and alkaline earth metal cations by a π cavity is a quite remarkable phenomenon in the context of the role played by cation–π interactions in chemistry and biology.[1–3] Three dimensionally shaped cavities functioning for the π solvation of alkali or alkaline earth metal cations are quite rare. A limited number of examples comes from the transition metal calix[4]arene chemistry,[4, 5] where the transition metal shapes the cavity, thus incapsulating alkali metal cations, even though the alkali metal cation–oxygen interaction remains by far the strongest one. The macrocyclic tetraanion derived from *meso*-octaalkylporphyrinogen, owing to the presence of *meso* sp^3-hybridized carbon atoms, is particularly suited to arrange the pyrrolyl anions to function as η^3 or η^5 binding sites.[6] Such bonding modes allowed the development of novel aspects of organometallic chemistry based on *meso*-octaalkylporphyrinogen as ancillary ligand.[7] In some of those metal–porphyrinogen complexes the pyrrolyl anions function also as η^1, η^3, or η^5 binding sites outside the cavity for lithium or sodium counter cations.[7]

We report here how all four pyrrolyl anions function together as π binding sites for alkali or alkaline earth metal cations inside the porphyrinogen cavity. The synthetic method we devised, in order to avoid any other ligand for the alkali or alkaline earth metal ion,[8] makes use of the metal itself for the metalation of porphyrinogen. We addressed our attention to the calcium atom, among other reasons, because of the possible relevance of π solvation of this cation in biological-type systems,[1] and because of the lack of synthetic and structural information on Ca macrocycles which do not contain oxygen donor atoms.[8, 9]

The reaction of *meso*-octaethylporphyrinogen (**1**, $Et_8N_4H_4$)[10] with calcium metal[11] in the presence of naphthalene led to the synthesis of the unprecedented dimetallic complex **2** ($[Et_8N_4Ca_2(thf)_4]$) containing two Ca^{2+} ions (Scheme 1). The further reaction of **2** with the lithium–porphyrinogen derivative $[Et_8N_4Li_4(thf)_4]$[6a] led to transmetalation with the formation of the calcium–lithium–porphyrinogen complex **3** ($[Et_8N_4CaLi_2(thf)_3]$).

Complexes **2** (Figure 1)[12] and **3** (Figure 2) have quite similar structural features. In both compounds the porphyrinogen tetraanion has a 1,3 alternate conformation (two N atoms "up", two N atoms "down"). The two calcium cations are located on opposite sites of the average N_4 plane in **2**



Scheme 1. The synthesis of complexes **2** and **3**. Ca_{act} indicates active calcium.

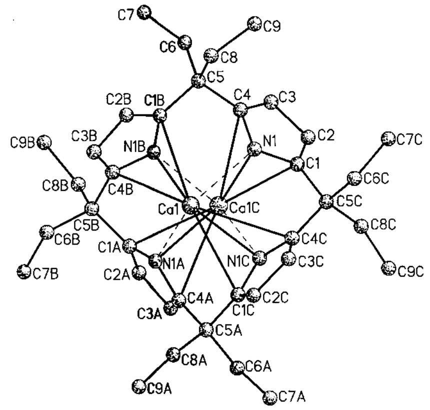


Figure 1. An XP[13] drawing of complex **2**. Selected bond lengths [Å] and angles [°]: Ca–η^3(Pyr) 2.713(2), Ca–η^1(Pyr) 2.634(2), Ca1 ··· Ca1C 3.241(1); η^3(Pyr)-Ca-η^3(Pyr) 125.97(7). η^3(Pyr) indicates the centroid of the pyrrole ligand. The letters A, B, and C denote the following symmetry operations: A = $-x+1$, $-y+½$, z; B = $-y+¾$, $x-¼$, $-z+¾$; C = $y+¼$, $-x+¾$, $-z+¾$. Dashes indicate the η^1 bonding of the two metals. Ca1, N1, N1A are "up"; Ca1C, N1B, N1C are "down". The thf molecules have been omitted for clarity.

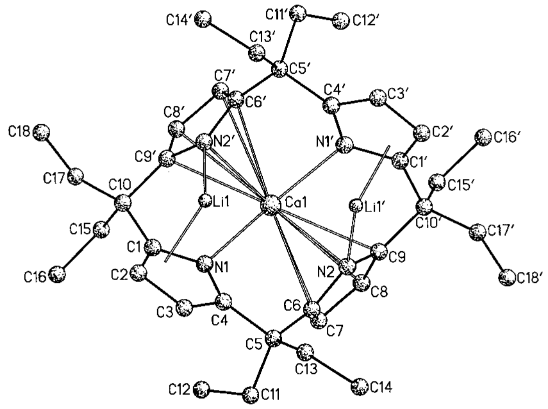


Figure 2. An XP[13] drawing of complex **3**. Selected bond lengths [Å] and angles [°]: Ca–$\eta^5(Pyr)_{av}$ 2.581(2), Ca–$\eta^1(Pyr)_{av}$ 2.467(2), Li–$\eta^3(Pyr)_{av}$ 2.069(5), Li–$\eta^1(Pyr)_{av}$ 2.064(5); $\eta^5(Pyr)_{av}$-Ca-$\eta^5(Pyr)_{av}$ 165.95(7). $\eta^5(Pyr)_{av}$ indicates the centroid of the pyrrole ligand. Letters A and B correspond to the following symmetry operations: A = $-x+3/2$, y, $-z+½$, B = $-x+3/2$, y, $-z+3/2$. The thf molecules have been omitted for clarity.

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(distance ±1.621(1) Å), while the calcium cation is opposite to the two lithium cations in complex **3** with respect to the N_4 average plane (out-of-plane distances: $Ca1 \cdots N_4$ −1.256(2), $Li \cdots N_4$ +1.635(4), $Ca2 \cdots N_4$ +1.242(2), $Li \cdots N_4$ −1.593(4) Å). In complex **2** each pyrrolyl anion displays η^3:η^1 bonding modes and bridging of the two calcium ions; thus, each calcium ion is η^3-bonded (Ca-η^3(C1,N1,C4) 2.713(2) Å) to a pair of *trans*-pyrroles and is η^1-bonded (Ca−N 2.634(2) Å) to the other pair. The two calcium ions force the porphyrinogen to form a dinucleating cavity and to make available the maximum number of binding sites inside the cavity, in the case of complex **2**, in the form of four 2-azaallyl fragments. The binucleating cavity also forces the calcium ions to experience a very close proximity ($Ca \cdots Ca$ 3.241(1) versus $Ca \cdots Ca$ 3.947 Å in calcium metal).[14]

In complex **3**, with less steric constraints, the calcium atom is η^5-bonded ($Ca1 \cdots Pyr(centroid)_{av}$ 2.581(2) Å; Pyr = pyrrole) to the *trans*-pyrroles, giving rise to a bent cyclopentadienyl-type structure (Pyr-Ca1-Pyr 165.95(7)°),[15] and η^1-bonded to the other pair of pyrroles ($Ca1-N_{av}$ 2.467(2) Å), which in turn function as η^3-binding sites for the two lithium cations (Li-η^3(N1,C1,C2) 2.069(5) Å). In both compounds the calcium and lithium atoms complete their coordination sphere with thf molecules. The η^3 and η^5 bonding modes of the pyrrolyl anions have been decided on the basis of the structural parameters and the arbitrary decision that the two $Ca \cdots C$ distances greater than 3.0 Å in complex **2** should be not taken into account as significant interactions. In addition, such parameters are hardly comparable to those of existing structures since they are rather unique. The only comparison could possibly be made with the cyclopentadienyl derivatives,[14] though the pyrrolyl anion in a macrocyclic structure does not have the same function as the Cp ligand. In the latter case, the $Ca \cdots C$ distances are significantly shorter (in these organocalcium compounds, the average metal–carbon bond lengths range from 2.62(2) to 2.73(3) Å).[15b,c]

This synthetic and structural report emphasizes the role of porphyrinogen as a possible binding cavity for alkali and alkaline earth metal ions. Furthermore, it shows how relevant the solvation of such ions can be using π interactions with electron-rich aromatic fragments.

Experimental Section

2: A suspension of active calcium[11] (27.7 mmol) in thf (300 mL) was added to a solution of **1** (7.03 g, 13.0 mmol) in thf (150 mL). The white suspension which suddenly formed was stirred for 2 h, and then the solvent was removed under vacuum. The solid (73 %) was recrystallized from thf/*n*-hexane. Crystals used for the X-ray analysis[12] contain an additional molecule of thf (**2** · thf). ^{1}H NMR ([D$_6$]benzene, 200 MHz, 298 K): $\delta = 6.19$ (s, 8H; C_4H_2N), 3.45 (m, 8H; thf), 2.23 (m, 8H; CH_2), 1.99 (m, 8H; CH_2), 1.23 (m, 8H; thf), 0.92 (t, $J = 7.32$ Hz, 24H; CH_3); elemental analysis calcd for **2** ($C_{52}H_{80}Ca_2N_4O_4$): C 68.98, H 8.91, N 6.19; found: C 68.44, H 8.82, N 6.11.

3: A solution of $[Et_8N_4Li_4(thf)_4]$[6a] (3.22 g, 3.8 mmol) and **2** (3.44 g, 3.8 mmol) in thf (300 mL) was heated under reflux for 24 h. The solution was evaporated to dryness, and the white solid (85 %) recrystallized from thf/*n*-hexane. Crystals for the X-ray analysis contain only three thf molecules. ^{1}H NMR ([D$_6$]benzene, 200 MHz, 298 K): $\delta = 6.26$ (s, 8H; C_4H_2N), 3.44 (brs, 8H; thf), 2.13 (q, $J = 7.32$ Hz, 8H; CH_2), 2.04 (q, $J = 7.32$ Hz, 8H; CH_2), 1.31 (brs, 8H; thf), 1.05 (t, $J = 7.32$ Hz, 12H; CH_3), 0.98 (t, $J = 7.32$ Hz, 12H; CH_3); elemental analysis calcd for **3** · thf ($C_{52}H_{80}CaN_4 \cdot Li_2O_4$): C 71.04, H 9.17, N 6.90; found: C 71.07, H 9.01, N 6.90.

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