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Synthesis, Structural Characterization, and Properties of Aluminum (III) *meso*-Tetraphenylporphyrin Complexes Axially Bonded to Phosphinate Anions

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Aluminum (III) *meso*-tetraphenylporphyrins axially bonded to phosphinate anions have been synthesized and characterized by NMR and UV–visible spectroscopy, single-crystal X-ray diffraction, and FAB$^+$ mass spectrometry. According to the solvent and the size of the anion, these compounds are able to self-assemble in two different manners.

A self-assembly process can be described as *a spontaneous association of molecules under equilibrium into stable aggregates held together by noncovalent bonds*.[1] Such phenomena are frequent in biological systems, and an outstanding example is provided by bacteriochlorophyll molecules.[2] Metalloporphyrins are attractive compounds for the design of self-assembling chromophores.[3] The axial coordination on the metal center is a powerful synthetic way to synthesize large multiporphyrinic systems.[4] Actually, much attention have been paid to porphyrin containing zinc(II), magnesium(II), tin(IV), or rhodium(III) as metal centers.[5] Although aluminum(III) porphyrins are well known for their catalytic properties and their rich photo- and electrochemistry,[6] their use as molecular building blocks for the design of porphyrin arrays remains limited. The synthesis of porphyrin arrays including aluminum(III) porphyrins is mostly limited to the use of phenolates[7] and carboxylates[8] as the axial ligand. Surprisingly, there is no example of aluminum(III) porphyrins axially bonded to phosphinate anions.

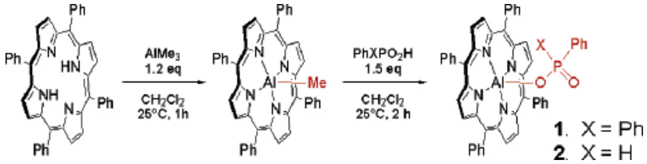

Figure 1. Synthesis of complexes **1** and **2**.

Here we report the synthesis of aluminum(III) *meso*-tetraphenylporphyrin (Al^{III}TPP) complexes axially bonded to phosphinate anions and present their properties as supramolecular building blocks. Complexes **1** and **2** were obtained by a "*one-pot*" strategy using the *meso*-tetraphenylporphyrin free base (H$_2$TPP) as starting material (Figure 1). H$_2$TPP was treated with AlMe$_3$, and the phosphinic acid derivative was added to the reactive intermediate

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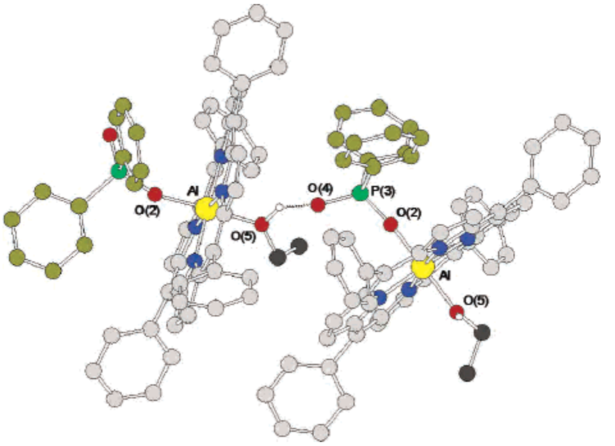

Figure 2. X-ray structure of **[1·EtOH]**$_\infty$ supramolecular chains. Light gray, C porphyrin; dark gray, C ethanol; dark green, C Ph on P(3). Hydrogen atoms, except (O5)H, are omitted for clarity.

Me−Al^{III}TPP. The desired complexes **1** and **2** were isolated by addition of pentane to the reaction mixture and obtained in high yield (85−87%).

Crystals of the complex **1·EtOH** were obtained from slow diffusion of pentane into a solution of **1** in a mixture of $CHCl_3$/EtOH in a 98:2 ratio (no crystals were obtained without EtOH). This is the first X-ray structure of a Al^{III}TPP complex axially bonded to a phosphinate anion.[9] Crystallographic analysis showed that complex **1** and ethanol molecules self-assemble to form polymeric *1-D supramolecular chains*, [**1·EtOH**]$_\infty$, where subunits are linked through coordination and hydrogen bonds (Figure 2). The porphyrin is not flat but has a slight saddle shape (the C5−Al−C15 and C10−Al−C20 angles are close to 172°). The coordination geometry around the Al^{III} is slightly distorded octahedral and is coordinated in the equatorial positions by the four nitrogen donors (d_{Al}−N = 2.00 Å). One axial position of the Al^{III} is occupied by the oxygen of the phosphinate ligand which forms a bent interaction with the metal (Al−O(2)−P(3) = 161.5°). The second axial position of the Al^{III} is occupied by the oxygen of one ethanol molecule. The Al−O(2)$_{phosphinate}$ distance is shorter than the Al−O(5)$_{ethanol}$ distance (1.86 compared to 1.98 Å). These distances are close to those found in the literature for Al^{III} Schiff base phosphinate complexes.[10] The O(2)−Al−O(5) linkage is almost linear (~179°). The ethanol molecules link the building blocks **1** together through hydrogen bonds with the P═O functions (O(4)−O(5) = 2.50 Å) and coordination bonds with the Al^{III} (O(5)−Al). The distance between two Al^{III} atoms is 7.75 Å. Two views of one chain are represented in the Figure 3. All the ethyl groups of the ethanol molecules (dark gray) are situated on the same side of the chain.

Complex **1** is air and moisture stable, and no dissociation of the P−O−Al bond is observed in solution even if a large excess of a coordinating solvent is added. The ^{1}H NMR spectrum of the complex **1·CD$_3$OD** in a mixture of C_6D_6/CD_3OD in a 9:1 ratio shows the axially bound phosphinate anion (Figure 4a). The characteristic signals of the TPP ligand are displayed. The three signals at 6.71, 6.54, and 4.88 ppm are due to the protons of the phenyl rings on the phosphorus atom, respectively, H_{para}, H_{meta}, and H_{ortho} strongly shielded by the porphyrinic ring current. These chemical shifts are close to those of a benzoate bound to a six-coordinate Al^{III}TPP.[8] In our case, the second axial ligand is a molecule of CD_3OD.

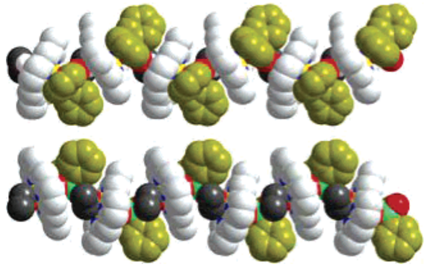

Figure 3. Two different views in CPK of one **[1·EtOH]**$_\infty$ supramolecular chain. Light gray, C porphyrin; dark gray, C ethanol; dark green, C Ph on P(3). (Ph meso and hydrogen atoms, except (O5)H, omitted for clarity).

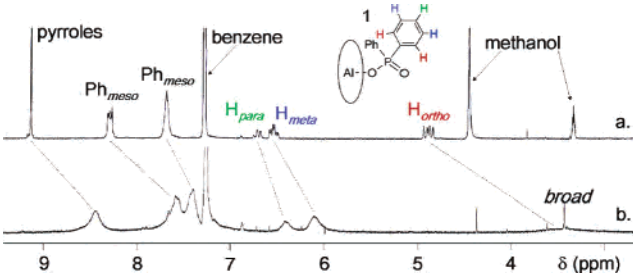

Figure 4. ^{1}H NMR spectra of **1** (200 MHz, 300 K, 20 mM) (a) in C_6D_6 + 10% CD_3OD and (b) in C_6D_6.

Significant broad signals are observed by ^{1}H NMR of the complex **1** in benzene-*d*$_6$ (without CD_3OD) at 25 °C (Figure 4b). The protons resonate at higher fields, showing the close proximity between the porphyrins and suggesting the formation of self-assembled species containing six-coordinate Al^{III}TPP complexes aggregated into chains through bridging phosphinates.[10] When the sample is heated at 75 °C, sharp signals are displayed corresponding to complex **1** with a five-coordinate Al^{III} (the H_{ortho} resonate at 5.20 ppm, see the Supporting Information). The addition of a coordinating solvent such as CD_3OD to the NMR sample leads to sharper signals corresponding to the monomeric complex **1·CD$_3$OD** (Figure 4a). It demonstrates that P═O−Al interactions are involved in the self-assembled structures (π−π stacking interactions are not responsible for the self-assembly process).[11] This process is reversible: when solvents are evaporated and fresh benzene-*d*$_6$ is added, broad signals are displayed again. Sanders and co-workers showed that a six-coordinate Al^{III}−porphyrin complex was never detected with benzoates as the axial ligand (except if a coordinating

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(9) Crystal data for **1.EtOH** ($C_{58}H_{44}N_4O_3PAl$): M_w = 902.97, monoclinic, space group $P12_1/c1$ (No. 14), a = 12.8820(4) Å, b = 26.0619(7) Å, c = 15.0590(4) Å, β = 111.15(2)°, V = 4715.19(70) Å^3, Z = 4, d_{calcd} = 1.268 g·cm^3, T = 173 K, λ(Mo Kα) = 0.71073 Å, μ(Mo Kα) = 0.128 mm^{-1}, 87 791 reflns collected, 15 579 unique reflns, R1$_{obsd}$ for [$I > 2\sigma(I)$]= 0.1037, wR2$_{all}$(F^2) = 0.1017 for all data, GOF on F^2 = 1.301, trans. coeff. = 0.980−0.990.

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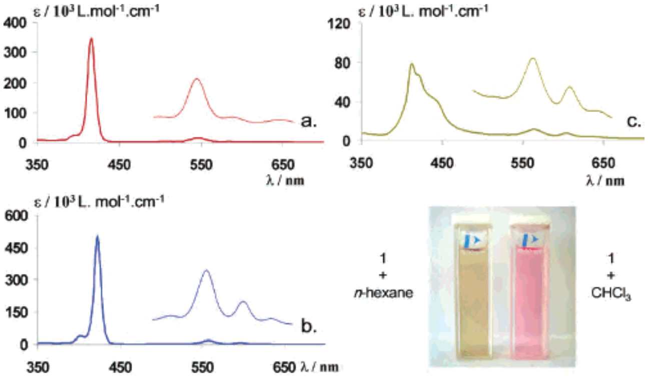

Figure 5. UV−visible absorption spectra of **1** in $CHCl_3$ (a), $CHCl_3$/CH_3OH 9:1 (b), and *n*-hexane/$CHCl_3$ 98:2 (c). Picture inset: quartz cells with self-assembled complex **1** in *n*-hexane/$CHCl_3$ 98:2 (left) and not self-assembled complex **1** in $CHCl_3$ (right) at 24 μM (quartz cells of 1 cm path).

molecule is added).[8] With phosphinates as the axial ligand, six-coordinate Al^{III}TPP are observed in nonpolar solvents. The reciprocal recognition between the donor site P═O and the acceptor site Al^{III} leads to self-assembled structures with P═O−Al interactions.

The self-assembly process can also be observed by UV−visible spectroscopy. A solvatochromic behavior induced by self-assembly of the complex **1** is observed. The UV−visible absorption spectrum of **1** in chloroform (Figure 5a) shows the typical absorption bands of Al^{III}TPP derivatives. According to previous studies,[12] the Al^{III} is square pyramidal ($4N_{TPP} + 1O_{phosphinate}$). No self-assembly occurs at 2.4×10^{-5} M in chloroform, and the solution is pink (Figure 5, inset). The sharp Soret band and one intense Q-band appear, respectively, at 415 and 546 nm. When an Al^{III}-ligating entity such as methanol is added, the Soret band and the intense Q-band are bathochromically shifted and appear, respectively, at 422 and 558 nm (Figure 5b). A second intense Q-band appears at 597 nm. This spectral evolution shows that the Al^{III} is octahedral ($4N_{TPP} + 1O_{phosphinate} + 1O_{CH3OH}$). The recognition of the complementary polar functional parts P═O and Al^{III} is effective in nonpolar solvents. When a concentrated solution of **1** in chloroform is diluted by adding *n*-hexane to reach 2.4×10^{-5} M, a change of color from pink to brown is observed (Figure 5, inset). Dramatic changes in the UV−visible absorption spectrum result from the self-assembly process (Figure 5c). The Q bands are red-shifted and show that the Al^{III} is octahedral (two intense Q-bands at 564 and 604 nm). The Soret band is less intense and appears split and broad. This spectral evolution arises from the excitonic coupling between the neighboring chromophores within the self-assembled structures.[13] As expected, the addition of a coordinating solvent such as methanol to a solution of the complex **1** in *n*-hexane leads to complete disassembly.[11]

Spectroscopic analyses tend to show that complex **1** is able to self-assemble alone in solution by P═O−Al interactions, but there is no spectroscopic evidence of the formation of oligomeric species more than the dimer. It was possible to observe by FAB^+ mass spectrometry a weak signal at *m*/*z* = 1715 corresponding to the dimer $[\mathbf{1}]_2$.[14] The exact association constant K_{assoc} for this system could not be extracted, but K_{assoc} for the P═O−Al interaction in *n*-hexane/$CHCl_3$ 98:2 must be greater than 10^5 M^{-1}.[15] Bulky groups on the porphyrin and/or the phosphorus atom prevent the formation of stable P═O−Al interactions. Thus, more stable self-assembled structures are obtained when the size of these groups is decreased. Complex **2** has only one phenyl ring on the phosphorus atom. This structural change dramatically decreases its solubility. This compound is only soluble in the presence of a coordinating molecule. It can be explained by the formation of stable oligomeric structures with P═O−Al interactions which are disassembled by methanol. FAB^+ mass spectrometry provided evidence for oligomeric structures (Figure 6). Signals up to the tetramer fragment (*m*/*z* = 2984.2) are detected, showing the stability of the −[Al−O−P═O]− backbone toward FAB^+ mass spectrometry conditions.

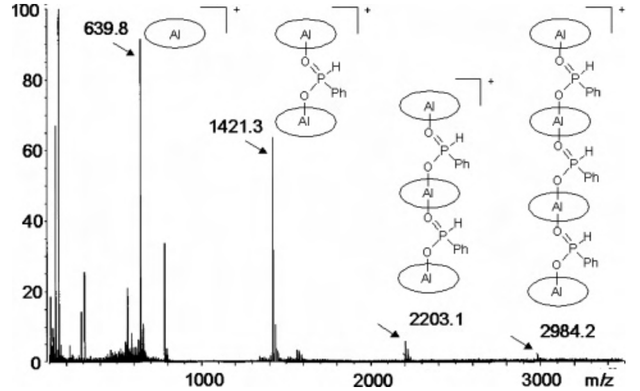

Figure 6. FAB^+ mass spectrum of the complex **2**. The different fragments observed are schematically represented.

In summary, aluminum (III) *meso*-tetraphenylporphyrin complexes axially bonded to phosphinate anions have been prepared and characterized. These compounds are new building blocks to obtain 1-D self-assembled structures. According to the solvent and the size of the anion, two self-assembly pathways are possible to give supramolecular chains like **[1·EtOH]**$_\infty$ or self-assembled structures with P═O−Al interactions.

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Supporting Information Available: General experimental details, full synthetic procedure and characterization of compounds **1** and **2**, estimation of the K_{assoc} for **1**, and crystallographic data for **[1·EtOH]**$_\infty$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) K_{assoc} was estimated on the assumption that the concentration of the free complex **1** is <20% of the total concentration 24 μM. See the Supporting Information.