Synthesis and characterization of gallium(III) 2-hydroxy-5,10,15,20-tetraphenylporphyrin. A novel example of a cyclic gallium(III) porphyrin trimer.

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Streszczenie

A trimeric [(2-O-TPP)Ga-III](3) complex (2-O-TPP is a trianion of 2-hydroxy-5,10,15,20-tetraphenylporphyrin) was obtained by hydrolysis of the monomeric five-coordinate complex (2-BzO-TPP)(GaCl)-Cl-III (2-BzO-TPP is a dianion of 2-benzoyloxy-5,10,15,20-tetraphenylporphrin) with sodium hydroxide in ethanol. The H-1 NMR spectra of the trimer and its monomeric precursors: (2-BzO-TPP)(GaCl)-Cl-III, (2-OH-TPP)Ga(III)TFA are presented and analyzed. The spectroscopic evidences indicated that the trimeric gallium(III) complex has a head-to-tail cyclic trimeric structure with the pyrrolic-alkoxide groups forming bridges from one macrocycle to the metal in the adjacent macrocycle PGa-O-PGa-O-PGa-O. The three gallium(III) porphyrin subunits are not equivalent. Their spatial proximity produces a marked variation of the chemical shifts due to a contribution of the ring current effect. The unprecedented positions of the 3-H pyrrole resonances (1.82, 2.18, 2.82 ppm), when compared to (2-BzO-TPP)(GaCl)-Cl-III (8.96 ppm), reflect the coordination of 2-0 centers to the adjacent gallium(III) ions. The strong effects were also determined for ortho 20-phenyl resonances ([(2-O-TPP)Ga-III](3), 5.21, 5.36, 5.69, 5.78, 5.93, and 6.33 ppm; (2-BzO-TPP)(GaCl)-Cl-III, 7.9-8.4 ppm). A two-dimensional COSY experiment was effective in connecting the protons within the phenyl and pyrrole rings. The complete peak assignments were derived from the NOESY experiment. In particular, closed loops of the NOE connectivities, which involved interporphyrin contacts between all subunits of the trimer, were analyzed and provided unambiguous spectroscopic evidence for the cyclic trimer formation. The trimer was cleaved in the reversible process to the monomeric complexes: (2-OH-TPP)(GaCl)-Cl-III and [(2-O-TPP)Ga-III(OH)](-) by addition of HCl or OH-, respectively. The formation of the expanded linear intermediate was demonstrated in the course of the acidic cleavage. The differences of pyrrole chemical shifts demonstrated for the gallium(III) monomeric species and the increased lability of the 3-H pyrrole proton resulted from the tautomeric phenol-enol-ketone equilibria typical for the 2-OH-TPPH2 porphyrin.

Słowa kluczowe

MAGNETIC-RESONANCE SPECTROSCOP, ; RAY CRYSTAL-STRUCTURE, RING CURRENT MODEL, 2-SUBSTITUTED 5, solid-phase peptide synthesis, molecular dynamics, 20-TETRAPHENYLPORPHYRINS, BRIDGED METALLOPORPHYRINS

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