Synthesis and characterization of high-spin iron(III) 2-hydroxy-5,10,15,20-tetraphenylporphyrin. The unprecedented example of the cyclic iron porphyrin trimer.

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Streszczenie

The oligomerization process of a monomeric iron(III) 2-hydroxy-5,10,15,20-tetraphenylporphyrin complex, (2-OH-TPP)(FeCl)-Cl-III, affords the unprecedented cyclic trimeric complex [(2-O-TPP)Fe-III](3). The spectroscopic evidences indicate that this compound has a head-to-tail cyclic trimeric structure with the pyrrolic-alkoxide groups forming bridges from one macrocycle to the iron(III) ion in the adjacent macrocycle PFe-O-PFe-O-PFe-O. The inherent optical asymmetry of the basic oligomerization (2-OH-TPP)Fe-III- unit leads to formation of the enantiomeric iron(III) porphyrin trimers. The H-1 NMR spectrum of trimeric [(2-O-TPP)Fe-III](3) is presented and analyzed. The presence of the three paramagnetic, weakly coupled high-spin iron(III) centers produces marked variation of positions and line widths for the pyrrole resonances. The characteristic upfield positions of the 3-H pyrrole resonances were determined and considered as the diagnostic feature for the iron(III)-pyrrole alkoxide coordination. The large upfield contribution to the 3-H pyrrole contact shift was accounted for by the donation of the electron density from the 2-oxygen on the half-occupied d(z)(2) orbital of the external iron(III) ion. [(2-O-TPP)Fe-III]3 was cleaved by protic acids (HX) to form high-spin, five-coordinate species (2-OH-TPP)Fe(III)X whose H-1 NMR spectra were analyzed, The stepwise cleavage mechanism was determined in the course of the titration with TFA. The process involved the formation of a linear dimeric intermediate [(2-OH-TPP)Fe-III-(2-O-TPP). Fe-III(TFA)]. Addition of an excess of oxygen base (methoxide ion, hydroxide ion in methanolic solutions) to a solution of [(2-O-TPP)Fe-III](3) in chloroform-d resulted in the conversion to the five-coordinate, high-spin complexes [(2-O-TPP)Fe(III)X](-) (X = CH3O-, OH-), The base-catalyzed exchange of the proton at the position next to the hydroxy group (3-H) was observed for [(2-O-TPP)Fe(III)X](-) species due to the keto-enol tautomerism. The characteristic shifts of the 3-H resonances in [(2-O-TPP)Fe-III(OH)](-) (33.4 ppm), (2-OH-TPP)(FeBr)-Br-III (79.1 ppm), and (2-benzoyloxy-TPP)(FeCl)-Cl-III (91.4 ppm) provided direct insight into the electronic structure of tautomeric forms.