Monomeric and dimeric iron(III) complexes of 5-hydroxy-10,15,20-triphenylporphyrin: formation of cyano and pyridine complexes of (5-oxo-10,15,20-triphenylphlorin)iron.

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Streszczenie

The reaction of [(TrPP)$Fe^{II}(py)_2$] (TrPP = dianion of 5,10,15-triphenylporphyrin) with hydrogen peroxide results in oxygenation of the (porphyrin)iron and the formation of (10,15,20-triphenyl-5-oxophlorin)iron [(5-O-TrPP)$Fe(py)_2$]. Coupled oxidation of [(TrPP)Fe^{III}Cl] in the presence of ascorbic acid and potassium cyanide in methanol leads to oxidative hydroxylation of the porphyrin ring to form a cyclic dimer [(5-O-TrPP)$Fe^{III}]_2$. Three out of four pyrrole ^{1}H NMR resonances of the dimeric complex present the characteristic displacement with respect to the typical position for the high-spin (tetraphenylporphyrin)iron(III) complexes. The linewidths of the β-H pyrrole resonances correlate with specific locations of the respective protons within the dimeric structure. Addition of HCl to [(5-O-TrPP)$Fe^{III}]_2$ results in cleavage of the dimer producing [(5-OH-TrPP)Fe^{III}Cl]. [(5-O-TrPP)$Fe^{III}]_2$ is also split with acetic anhydride to give (5-acetoxy-10,15,20-triphenylporphyrin)iron(III). In the presence of [D_5]pyridine or a large excess of cyanide ion, [(5-O-TrPP)$Fe^{III}]_2$ undergoes cleavage to form air-sensitive [(5-O-TrPP)$Fe(py)_2$] or [(5-O-TrPP)$Fe(CN)_2]^{2-}$. The pyrrole pattern observed for [(5-O-TrPP)$Fe(py)_2$] is similar to that determined on the basis of an analysis carried out for four (oxophlorin)iron regioisomers obtained from hemes. For comparison, the characteristic ^{1}H NMR features of the typical (5-substituted-10,15,20-triphenylporphyrin)iron(III) complexes have been investigated for the series of high-spin and low-spin complexes. The spin-density distribution in the (oxophlorin)iron skeleton is dominated by the radical-like electronic structure. (© Wiley-VCH Verlag GmbH, 69451 Weinheim, Germany, 2002)

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