H^1 NMR investigations of triphenylporphyrin metal complexes and electronic interactions in iron(III) complexes of *meso-meso*-linked 5,5'-bis(10,15,20-triphenylporphyrin).

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Streszczenie

The ^{1}H NMR spectra of iron(III) complexes of dimeric 5,5‘-bis(10,15,20-triphenylporphyrin) [$(TrPPH_2)_2$], 5,5‘-bis(10,15,20-tris(*p*-methoxyphenyl)porphyrin) [$(Tr(p\text{-}MeOP)PH_2)_2$], and hybrid $(TrPPH_2)(Tr(p\text{-}MeOP)PH_2)$ and the respective monomeric 5,10,15-triphenylporphyrin ($TrPPH_2$) and 5,10,15-tris(*p*-methoxyphenyl)porphyrin [$Tr(p\text{-}MeOP)PH_2$] have been investigated in order to elucidate an impact of a direct *meso*−*meso* linkage on the electronic structure of corresponding high- and low-spin iron(III) porphyrins. The following species, covering the representative spin/oxidation states, have been investigated: $(TrPP)_2(Fe^{III}Cl)_2$ (high spin); $[(TrPP)_2(Fe^{III}(CN)_2)_2]^{2-}$ (low spin); $[(TrPP)_2(Fe^{III}Cl)_2]^{+}$ (high-spin iron(III), diporphyrin radical); $[(TrPP^{\bullet})_2(Fe^{III}Cl)_2]^{2+}$ (high-spin iron(III), diradical of diporphyrin). The iron(III) diporphyrins $(TrPP)_2(Fe^{III}Cl)_2$, $[(TrPP)_2(Fe^{III}(CN)_2)_2]^{2-}$, $\{[(TrPP)Fe^{III}(CN)_2][(Tr(p\text{-}MeOP)P)Fe^{III}(CN)_2]\}^{2-}$, and $[(TrPP)_2(Fe^{III}Cl)_2]^{2+}$ revealed the ^{1}H NMR features which have been typically encountered in the spectra of the relevant monomeric complexes. Thus magnetic interactions between two subunits via skeleton appear to be minor. The characteristic broadening and/or paramagnetic shifts of 3-H and 7-H resonances were determined and are diagnostic features of the *meso*−*meso* linkage. One-electron, ligand-based oxidation of $(TrPP)_2(Fe^{III}Cl)_2$ to produce $[(TrPP)_2(Fe^{III}Cl)_2]^{+}$ was observed with the unpaired electron delocalized over both macrocycles. The structure of $(Tr(p\text{-}MeOP)P)Zn^{II}\cdot 0.4CH_2Cl_2$, the fundamental building block in synthesis of diporphyrins, was determined by X-ray crystallography. $(Tr(p\text{-}MeOP)P)Zn^{II}$ crystallizes in the monoclinic space group *C*2/*c* with a = 47.744(9) Å, b = 9.090(2) Å, c = 15.571(2) Å, β = 93.770(13)°, and Z = 8. The refinement of 494 parameters and 4361 reflections yields R_1 = 0.0756, wR_2 = 0.2169. The $(Tr(p\text{-}MeOP)P)Zn^{II}$ presents characteristic features of zinc(II) tetraphenylporphyrin. The molecular periphery of $(Tr(p\text{-}MeOP)P)Zn^{II}$ has a fully exposed *meso* position and two partially exposed pyrrole rings.

Słowa kluczowe

Group theory, Pyrroles, Ions, Nuclear magnetic resonance spectroscopy, Resonance structures