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^{1} H NMR investigation of high-spin and low-spin iron(III) *meso*-ethynylporphyrins.

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Streszczenie

The ^{1}H NMR spectra of iron(III) 5-ethynyl-10,15,20-tri(*p*-tolyl)porphyrin [(ETrTP)$Fe^{III}X_n$], iron(III) 5-(phenylethynyl)-10,15,20-tri(*p*-tolyl)porphyrin [(PETrTP)$Fe^{III}X_n$], iron(III) 5-(phenylbutadiynyl)-10,15,20-tri(*p*-tolyl)porphyrin [(PBTrTP)$Fe^{III}X_n$], iron(III) 5,10,15,20-tetra(phenylethynyl)porphyrin [(TPEP)$Fe^{III}X_n$], iron(III) 1,4-bis-[10,15,20-tri(*p*-tolyl)porphyrin-5-yl]-1,3-butadiyne {[(TrTP)$Fe^{III}X_n$]$_2$B}, and 5,10,15-triphenylporphyrin [(TrPP)$Fe^{III}X_n$] have been studied to elucidate the impact of *meso*-ethynyl substitution on the electronic structure and spin density distribution of high-spin ($X = Cl^-$, $n = 1$) and low-spin ($X = CN^-$, $n = 2$) derivatives. The meso substituents, i.e., ethynyl, phenylethynyl, and phenylbutadiynyl, provided insight into the efficiency of spin density delocalization along structural elements that are typically applied to transmit electronic effects along multipart polyporphyrinic systems. The positive spin density localized at the *meso*-carbon of high-spin iron(III) ethynylporphyrins is effectively delocalized along the ethyne or butadiyne fragment as illustrated by the comparison of isotropic shifts of C_{meso}−**H** and −CC−**H** determined for (TrPP)$Fe^{III}Cl$ (−82.6 ppm, 293 K) and (ETrTP)$Fe^{III}Cl$ (−49.5 ppm, 298 K). The replacement of the ethynyl hydrogen by phenyl or phenylethynyl provided evidence for the π spin density distribution around the introduced phenyl ring. An analysis of the isotropic shifts for the low-spin bis-cyanide iron(III) porphyrins series reveals the analogous mechanism of spin density transfer. Treatment of high-spin [(TrTP)$Fe^{III}Cl$]$_2$B with a base resulted in formation of the cyclic [(TrTP)$Fe^{III}OFe^{III}$(TrTP)B]$_2$ complex linked by two μ-oxo bridges. (TPEP)H_2 has been characterized by X-ray crystallography as a porphyrin dication where two molecules of trifluoroacetic acid associate with two coordinated trifluoroacetate anions. The X-ray structure of bis-tetrahydrofuran 1,4-bis[10,15,20-tri(*p*-tolyl)porphyrinatozinc(II)-5-yl]-1,3-butadiyne complex {[(TrTP)Zn^{II}(THF)]$_2$B} reveals two parallel, non-coplanar [(TrTP)Zn(THF)] subunits linked by the linear butadiyne moiety.

Adres publiczny

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