



Iron complexes of C- and N-methylated 2-aza-21-carbaporphyrin: NMR studies.

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Streszczenie

Insertion of iron(II) into methylated derivatives of N-confused porphyrins 2-aza-2-methyl-5,10,15,20-tetraphenyl-21-carbaporphyrin (*MeCTPPH*)H, 2-aza-5,10,15,20-tetraphenyl-21-methyl-21-carbaporphyrin (*CTPPMe*)H₂, and 2-aza-2-methyl-5,10,15,20-tetraphenyl-21-methyl-21-carbaporphyrin (*MeCTPPMe*)H yielded N- or C-methylated high-spin iron(II) complexes (*MeCTPPH*)Fe^{II}Br, (*HCTPPMe*)Fe^{II}Br, and (*MeCTPPMe*)Fe^{II}Br. One electron oxidation of (*Me-CTPPH*)Fe^{II}Br using Br₂, accompanied by deprotonation of a C(21)–H(21) fragment and formation of an Fe–C(21) bond, produces an intermediate-spin, five-coordinate iron(III) complex (*MeCTPP*)Fe^{III}Br. Simultaneously, a high-spin complex [(*MeCTPPH*)Fe^{III}Br]⁺ was formed which preserved the side-on interaction between the metal ion and the inverted pyrrole ring. [(*MeCTPPH*)Fe^{III}Br]⁺ was also obtained by titration of (*MeCTPP*)Fe^{III}Br with TFA due to the C(21) protonation. A titration of (*HCTPPMe*)Fe^{II}Br and (*MeCTPPMe*)Fe^{II}Br with Br₂ yielded solely corresponding high-spin iron(III) species [(*HCTPPMe*)Fe^{III}Br]⁺ and [(*MeCTPPMe*)Fe^{III}Br]⁺. Dioxygen reacts cleanly with (*MeCTPPH*)Fe^{II}Br carbaporphyrin to form solely (*MeCTPP*)Fe^{III}Br. The ¹H NMR spectra of paramagnetic iron(II) and iron(III) complexes were examined. The characteristic patterns of pyrrole, C-methyl, and N-methyl resonances were found diagnostic of the ground electronic state of iron and the coordinating nature of the N-confused pyrrole. The characteristic C–Me resonances occur in a unique window (520–420 ppm) for iron(III) C-methylated N-confused porphyrins which remains in contrast with relatively small values found for iron(II) C-methylated derivatives (50–80 ppm).

Słowa kluczowe

Iron, Nuclear magnetic resonance spectroscopy, Oxidation, Pyrroles, Resonance structures

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