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Oxidation and oxygenation of iron complexes of 2-aza-21-carbaporphyrin.

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Streszczenie

Oxidation and oxygenation of (*H*CTPP*H*)$Fe^{II}Br$ an iron(II) complex of 2-aza-5,10,15,20-tetraphenyl-21-carbaporphyrin (CTPP*H*)H_2 have been followed by ^1H and ^2H NMR spectroscopy. Addition of I_2 or Br_2 to the solution of (*H*CTPP*H*)$Fe^{II}Br$ in the absence of dioxygen results in one-electron oxidation yielding [(*H*CTPP*H*)$Fe^{III}Br]^+$. One electron oxidation with dioxygen, accompanied by deprotonation of a C(21)H fragment and formation of an Fe−C(21) bond, produces an intermediate-spin, five-coordinate iron(III) complex (*H*CTPP)$Fe^{III}Br$. In the subsequent step an insertion of the oxygen atom into the preformed Fe^{III}−C(21) bond has been detected to produce [(CTPP*O*)$Fe^{III}Br]^-$. Protonation at the N(2) atom affords (*H*CTPP*O*)$Fe^{III}Br$. The considered mechanism of (*H*CTPP*H*)$Fe^{II}Br$ oxygenation involves the insertion of dioxygen into the Fe−C bond. The ^1H NMR and ^2H NMR spectra of paramagnetic iron(III) complexes were examined. Functional group assignments have been made with use of selective deuteration. The characteristic patterns of pyrrole and 2-NH resonances have been found diagnostic of the ground electronic state of iron and the donor nature localized at C(21) center as exemplified by the ^1H NMR spectrum of intermediate-spin (*H*CTPP)$Fe^{III}Br$: β-H 7.2, −10.6, −19.2, −20.6, −23.2, −24.9, −43.2; 2-NH −76.6 (ppm, 298 K). The structures of two compounds (*H*CTPP)$Fe^{III}Br$ and (*H*CTPP*O*)$Fe^{III}Br$, were determined by X-ray diffraction studies. In the first case, the iron(III) is five-coordinate with bonds to three pyrrole nitrogen atoms (Fe−N distances: 1.985(8), 2.045(7), 2.023(8) Å), and the pyrrolic trigonal carbon (Fe−C: 1.981(8) Å). The iron(III) of (*H*CTPP*O*)$Fe^{III}Br$ forms bonds to three pyrrole nitrogen atoms (Fe−N distances 2.104(5), 2.046(5), 2.102(5) Å). The Fe−O 2.041(5) Å and Fe−C(21) 2.192(5) Å distances suggests a direct interaction between the iron center and the π electron density on the carbonyl group in a η^2 fashion.

Słowa kluczowe

Iron, Nuclear magnetic resonance spectroscopy, Oxidation, Pyrroles, Saturation

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