

Stabilization of the less common $(d_{xz}d_{yz})^4(d_{xy})^1$ iron(III) porphyrin ground electronic state: ^1H NMR investigations of iron(III) 5,10,15,20-tetracyclohexylporphyrin.

Autorzy

Stanisław Wołowiec

Lechosław Latos-Grażyński

D. Toronto

J. C. Marchon

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Streszczenie

High-spin and low-spin complexes of the iron(III) tetrakis(*meso*-cyclohexyl)porphyrin ((TCHP)Fe^{III}) have been studied by means of 1-D and 2-D ^1H NMR. The complete assignment of porphyrin and R-imidazole ^1H resonances has been done on the basis of 2-D COSY and NOESY techniques as well as by selective deuteration of imidazole. The chemical shifts of pyrrole β -Hs have been used as the probe of the electronic state of an iron(III) metal ion. It has been found that cyanide coordinates to the high-spin (TCHP)Fe^{III}Cl complex, leading to the formation of the low-spin [(TCHP)Fe^{III}(CN)₂]⁻, with the rare $(d_{xz}d_{yz})^4(d_{xy})^1$ ground electronic state (the pyrrole β -H resonance at 12.01 ppm at 293 K in CD₃OD). A contribution of two electronic configurations, $(d_{xy})^2(d_{xz}d_{yz})^3$ and $(d_{xz}d_{yz})^4(d_{xy})^1$, to the ground state of the metal ion has been invoked for the low-spin [(TCHP)Fe^{III}(R-Im)₂]⁺ complexes. Characteristic ^1H NMR shifts for these complexes include the pyrrole resonance at 2.81 ppm accompanied by the markedly upfield shifted imidazole resonances at -19.67 ppm (2-H), -10.58 ppm (4-H), -4.05 ppm (5-H), and 0.97 ppm (1-H). An admixture of a $(d_{xz}d_{yz})^4(d_{xy})^1$ configuration into the ground electronic state increases in the order imidazole (ImH) < 1-methylimidazole (1-MeIm) < 1,2-dimethylimidazole (1,2-diMeIm), following an enlargement of the axial ligand steric hindrance. The rotation of the 1,2-diMeIm around Fe-N bond in the low-spin [(TCHP)Fe^{III}(1,2-diMeIm)₂]⁺ complex is slow on the ^1H NMR time scale even at 293 K. Consequently four β -H resonances and the diastereotopy of the cyclohexyl *meso*-substituents have been observed. The *meso*-cyclohexyl groups rotate freely at temperature above 243 K, whereas the frozen rotation below 233 K leads to the formation of additional rotational isomers as demonstrated by multiplicity of β -H resonances for high-spin and low-spin complexes studied.

Słowa kluczowe

Imidazoles, Ligands, Nuclear magnetic resonance spectroscopy, Pyrroles, Resonance structures

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