Low-spin organoiron(III) N-confused pyriporphyrin.

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Rok wydania

2007

Czasopismo

Journal of Porphyrins and Phthalocyanines

Numer woluminu

11

Strony

172-180

DOI

10.1142/S1088424607000229

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Oxidation of (PyPH)$Fe^{II}Br$, an iron(II) complex of 6,11,16,21-tetraaryl-3-aza-m-benziporphyrin (N-confused pyriporphyrin, (PyPH)H) has been followed, in the presence of pyridine, by ^{1}H and ^{2}H NMR spectroscopy. One-electron oxidation with dioxygen, accompanied by deprotonation of a C(22)H fragment and formation of a Fe-C(22) bond, produced a low-spin, six-coordinate iron(III) complex $[(PyP)Fe^{III}(py)_2]^+$ as confirmed by combination of ^{1}H NMR, EPR and structural data. The characteristic patterns of ^{1}H NMR pyrrole and *meso*-aryl resonances resemble features assigned to the less common, low-spin ground electronic state $((d_{xz}d_{yz})^4(d_{xy})^1)$ of iron(III) regular porphyrins. A conformational rearrangement process has been detected which involves two structures differentiated by macrocyclic ruffling. The structure of $\{H[(PyP)Fe^{III}(py)_2]_2\}(Fe^{III}Br_4)_3\cdot CH_2Cl_2$ has been determined by X-ray crystallography. The cationic complex involves a six-coordinate iron atom bound to the N-confused pyriporphyrin through its three nitrogens (Fe-N(23) = 1.924(7), Fe-N(24) = 1.979(7), Fe-N(25) = 1.9343(7) Å) and the pirydyl trigonal C(22) atom (Fe(1)-C(22) = 1.972(10) Å). The porphyrin is strongly ruffled, defining two deep grooves along C_{meso}-C_{meso} axes at right angles to each other. Two axial pyridine ligands are located in the prearranged equatorial ligand grooves. The iron lies in the N_3C plane of the macrocycle defined by coordinating nitrogen and carbon atoms. In the solid, pairs of molecules are positioned along the line defined by Fe(1)-C(22) and Fe(2)-C(91) bonds. The structure demonstrates the head-to-head arrangement of two $[(PyP)Fe^{III}(py)_2]^+$ subunits revealing the adjacency of the two perimeter nitrogen atoms (the N(3)⋯N(72) distance = 2.587(10) Å) linked by the N⋯H⋯N hydrogen bond.

Słowa kluczowe

Carbaporphyrinoids, Core-modified porphyrin, Iron porphyrin, Pyriporphyrin