

Reactions of the iron(III) tetraphenylporphyrin π cation radical with triphenylphosphine and the nitrite anion. Formation of β -substituted iron(III) porphyrins.

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Artykuł

The formation of iron(III) /S-(triphenylphosphonio)tetraphenylporphyrin ((/3-PPh₃+TPP)Fe^{III}M and iron(III) 0-nitrotetraphenyl-porphyrin (/3-NO₂-TPP)Fe^{III} in the reaction of iron(III) tetraphenylporphyrin cation radical (TPP')Fe^{III}(ClO₄)₂ with tri-phenylphosphine or nitrite anion has been established through a variety of spectroscopic investigations. The reaction mechanism seems to be analogous to that elucidated for a variety of metalloporphyrin cation radicals or arene cation radicals. The structure of (5-PPh₃+TPP)Fe^{III}Cl₂·CHCl₃, C₆₃H₄₃N₄Cl₅PFe, has been determined at 173 K by X-ray diffraction: monoclinic space group

72/a, Z = 8, a = 27.948 (3) Å, b = 11.286 (3) Å, c = 33.633 (5) Å, β = 94.31 (1)°, least-squares refinement of parameters using 3658 reflections (Mo Kα) yielding R = 0.091, wR = 0.06. The structural study of (/3-PPh₃+TPP)Fe^{III}Cl₂ revealed its "zwitterionic" nature. The species belongs to a rather small class of high-spin six-coordinate iron(III) porphyrins and is the first example where two apical positions are occupied by chloride anions. The Fe-Cl distances are Fe-Cl(1) = 2.429(3) Å and Fe-Cl(2) = 2.348 (3) Å. The iron atom is precisely located in the plane of an expanded porphyrin core of a saddlelike conformation with mean Fe-N

= 2.055 (7) Å. This value is in the range of Fe-N distances found in other known high-spin ferric porphyrins. This geometry is also preserved in chloroform and has been established for bromide and iodide axial ligands. The proton NMR spectra of high-spin and low-spin iron(III) /^h-substituted porphyrins have been obtained and analyzed. Functional group assignments have been made with the use of selective deuteration and methyl substitution. The pattern of seven pyrrole resonances reflects the asymmetry that results from /3-substitution. This pattern is diagnostic for mono-/S-substitution. Because of hindrance of the phenyl group, rotation around the pyrrole carbon-phosphorus bond is restricted.

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