An integrated approach to the mid-spin state (S=3/2) in six-coordinate iron(III)chiroporphyrins.

Autorzy

J. P. Simonato

J. Pécaut

L. Le Pape

Jean-Louis Oddou

C. Jeandey

M. Shang

W. R. Scheidt

Jacek Wojaczyński

Stanisław Wołowiec

Lechosław Latos-Grażyński

J. C. Marchon

Rok wydania

2000

Czasopismo

Inorganic Chemistry

Numer woluminu

39

Strony

3978-3987

DOI

10.1021/ic000150a

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

An intermediate-spin state very close to the mid-spin state (S = 3/2) can be stabilized in a ferric porphyrin by an integrated approach which combines the favorable effects of a weak axial field strength and of a small macrocycle hole. Axial ligand exchange by reaction of chloroiron(III)tetramethylchiroporphyrin [(TMCP)FeCl] with silver perchlorate in ethanol−chloroform leads to ethanol-ligated ferric chiroporphyrins. Two distinct crystalline products containing a bisethanol complex [[(TMCP)$Fe^{III}(EtOH)_2$]ClO_4] and three variants of a mixed ethanol−water complex [[(TMCP)$Fe^{III}(EtOH)(H_2O)$]ClO_4] have been structurally characterized in the solid state. The small hole of the ruffled chiroporphyrin and the weak axial oxygen ligation result in strongly tetragonally distorted complexes. The six-coordinate species exhibit long axial Fe−O bond distances (2.173(5)−2.272(4) Å) and the shortest equatorial Fe−N(av) distances (1.950(5)−1.978(7) Å) found as yet in a ferric porphyrin, reflecting a singly occupied d_{z^2} orbital and a largely depopulated $d_{x^2-y^2}$ orbital. An intriguing case of bond-stretch isomerism is seen for the axial Fe−O bonds in two crystallographically independent mixed ethanol−water species, and it is accounted for by their distinct intra- and intermolecular hydrogen-bond arrays. The Mössbauer spectrum (δ = 0.35(1) mm s^{-1} and ΔE_Q = 3.79(1) mm s^{-1} at 77 K) indicates a strong tetragonal distortion around the ferric ion, in agreement with the structural data. The value of the magnetic moment (μ_{eff} = 3.8 μ_B in the range 50−300 K) strongly supports a mid-spin state (S = 3/2). The EPR spectrum at 80 K ($g_\perp \approx 4.0, g_\parallel \approx 2.00$) is consistent with a nearly pure mid-spin state ($^4A_2$) with little rhombic distortion. The ^{1}H NMR spectra in $CDCl_3$−EtOH exhibit upfield-shifted resonances for the pyrrole protons ($\delta \approx -30$ ppm) which are consistent with the depopulated iron $d_{x^2-y^2}$ orbital. Solution equilibria with water and various alcohols, and the spin state of the corresponding species, are discussed on the basis of the NMR data. The bisethanol and ethanol−water species are potential models of unknown hemoprotein ligation states such as Tyr(OH)/Tyr(OH) or Tyr(OH)/H_2O that could be obtained by site-directed mutagenesis.

Adres publiczny

https://doi.org/10.1021/ic000150a