Regulation of Geometric Stability and Spin-State of Iron(III) by Isomeric Porphyrinoids.

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The iron atom in porphyrin is placed in the square N₄-cavity formed by the four pyrrole rings. Shuffling of the pyrrole rings and meso-carbons in porphyrin (P) affords isomeric porphyrinoids of porphycene (Pc), corrphycene (Cn), and hemiporphycene (Hpc). They have characteristic metallo-cores which are rectangular, trapezoidal, and distorted quadrilateral, respectively. We have examined the geometric stability of the iron atom in the modified macrocycles.¹ Binding of 1-methylimidazole (1-MeIm) to the 5-coordinate Fe(III)I derivatives proceeded in two steps through a 6-coordinate Fe(III)I·1-MeIm intermediate. The first and second association constants, $K₁$ and $K₂$, varied with the N₄-core variation. The $K₁$ is in the order of $P < Pc < Hpc < Cn$; the iron atom in Cn is most easily displaced toward the 1-MeIm. The $K₂$ varies as $Hpc < Cn < P < Pc$. The $K₂$ increases with decreasing the axial Fe(III)-I interactions that directly reflects the modified equatorial interactions.

Spin-state of the four Fe(III) macrocycles bearing 1-MeIm and azide (N₃⁻) as axial ligands were analyzed with infrared (IR) spectroscopy.² The azide stretching-band split into two peaks around 2047 and 2017 cm⁻¹, reflecting an equilibrium between the high- ($S = 5/2$) and low- ($S = 1/2$) spin states. The high-spin fraction was found to change over a 0-90% range with the N₄-core arrangement. The result suggests that the iron-bound azide is an excellent probe to monitor the subtle heme deformation in the protein matrix.

References