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

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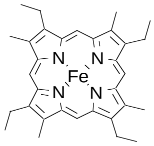
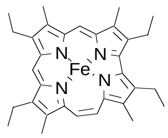
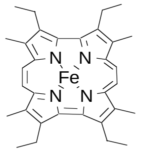


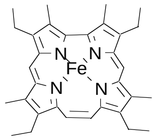
Porphyrin (P)



Hemiporphycene (Hpc)



Porphycene (Pc)



Corrphycene (Cn)

The iron atom in porphyrin is placed in the square N_4-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-methylmidazole (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, K_1 and K_2, varied with the N_4-core variation. The K_1 is in the order of P < Pc < Hpc < Cn; the iron atom in Cn is most easily displaced toward the 1-MeIm. The K_2 varies as Hpc < Cn ~ P < Pc. The K_2 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 (N_3^-) 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 N_4-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

(1) Neya, S.; Hoshino, T.; Hata, M.; Funasaki, N. *Chem. Lett.* **2004**, *33*, 114-115.

(2) Neya, S.; Chang, C. K.; Okuno, D.; Hoshino, T.; Hata, M.; Funasaki, N. *Inorg. Chem.* **2005**, *44*, 1193-1195.