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CYCLOPHANE PORPHYRIN - II

ACCESS CONTROL IN AXIAL LIGATION TO IRON COMPLEX OF CYCLOPHANE PORPHYRIN.

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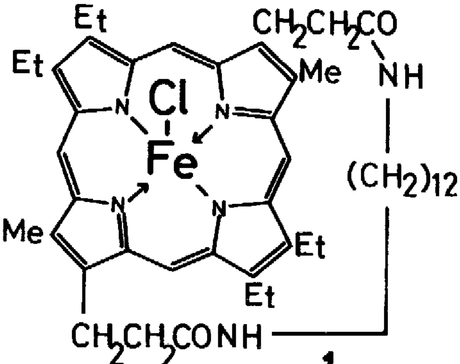
Iron complexes of synthetic porphyrins have provided an attractive tool to elucidate the relationship between function and structure of the hemeproteins such as hemoglobin and myoglobin.[1] The first iron complex of cyclophane porphyrin has been prepared by Baldwin and his coworkers.[2] This ferrous complex is capable of reversible oxygenation at low temperature. We wish to report the first synthesis of the iron complex of the ETIO type cyclophane porphyrin and access control in axial ligation to the hemin due to steric constraint in small cavity of the cyclophane.

The iron complexes 1 and 2 were obtained from treatment of the cyclophane porphyrin 3 and reference porphyrin 4[3] with $FeSO_4$ in glacial acetic acid respectively, followed by addition of aqueous solution of 5% NaCl. The chlorohemins 1 and 2 were purified by recrystallization from benzene-CH_2Cl_2. Both chlorohemins show visible absorption maxima at 385nm($\log\varepsilon$ 4.92), 506(3.88) 536(3.89), 640(3.55) for 1 and 385(4.92), 506(3.87), 536(3.89) and 640(3.54) for 2. Ferric porphyrin exists in the high spin state (S=5/2) or in the low spin state (S=1/2). It is well known that the spin state of the ferric porphyrin is dependent upon axial coordination. Five-coordinate ferric porphyrin such as chlorohemin is of high spin state. Axial coordination of two amine molecules to the ferric complex gives the six-coordinate ferric complex of the low spin state. It is naturally expected that steric constraint due to the dodecamethylene chain of 1 may reduce formation of the six-coordinate ferric complex. In other words, interaction between axial



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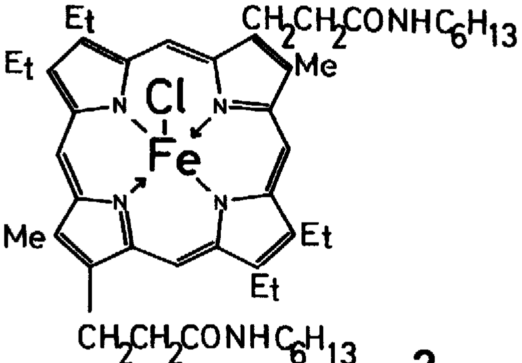

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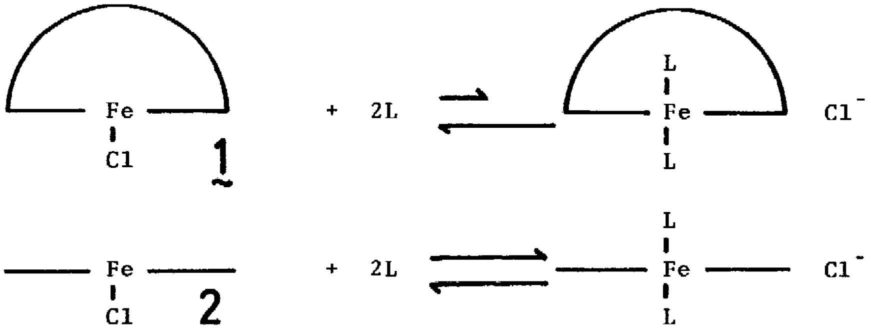
ligand and dodecamethylene group results in an anomalous behavior in equilibrium of spin state as is seen in the usual hemin. Fig. 1 indicates the visible spectra of the chlorohemin **1** and **2** in the presence of 4-benzylpyridine. Addition of amine to the ferric complex **2** causes marked decrease in the strength of the absorption at 630nm assignable to the high spin complex. In



L=4-benzylpyridine

contrast with the reference ferric complex **2** the change in absorption strength of 630nm for the cyclophane porphyrin ferric complex **1** is found to be very small with addition of ten times molar amount of amine in comparison with the case of **2**. These facts lead us to conclude that access of the sixth ligand to the central iron(III) atom from the protected face is remarkably restrained by considerable van der Waals interaction between the long methyl-

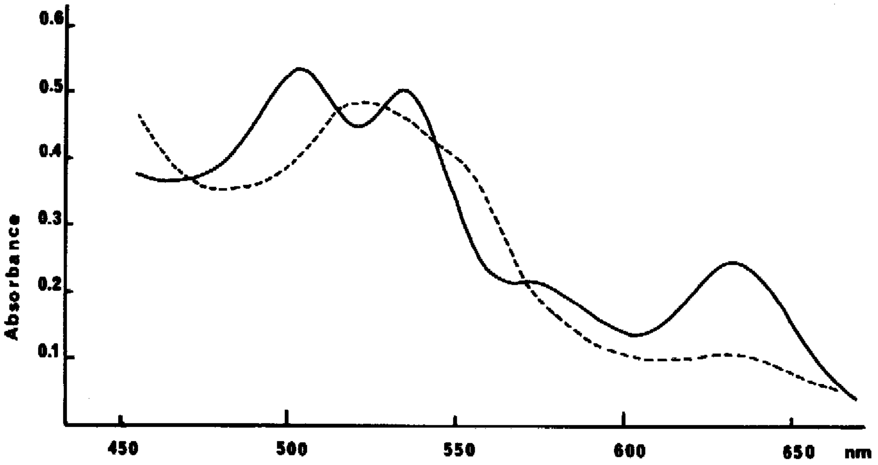


Figure 1. Absorption spectra of the chlorohemin complexes **1** and **2** with 4-benzylpyridine in $CHCl_3$: (——) [the cyclophane porphyrin iron(III)chloride]$=1.0 \times 10^{-4}$M, [4-benzylpyridine]$=1.0 \times 10^{-1}$M, (– – –) [the reference porphyrin iron(III)chloride]$=1.1 \times 10^{-4}$M, [4-benzylpyridine]$=1.1 \times 10^{-2}$M.

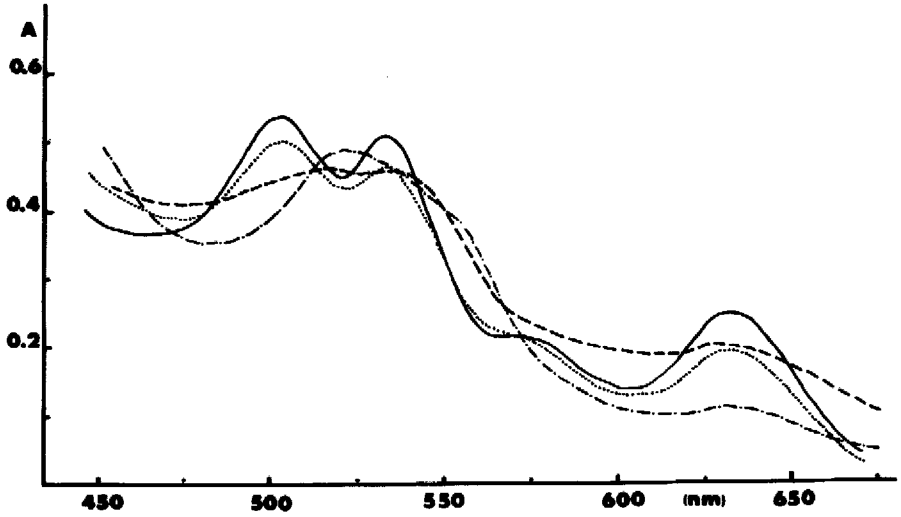


Figure 2. Absorption spectra of the cycliphane porphyrin iron(III) chloride with the 4-substituted pyridines in $CHCl_3$: $[1]=1.0 \times 10^{-4}$M, [4-substituted pyridine]$=1.1 \times 10^{-2}$M, (——) 4-benzylpyridine, (··········) 4-t-butylpyridine, (– – –) 4-ethylpyridine, (—·—·—) 4-methylpyridine.

ene chain and ligand. It is clearly indicated that introduction of the less bulky substituent at the 4-position of pyridine is the more favorable to form the low spin state. Fig. 2 shows the visible spectra of **1** with equi-molar amount of each 4-substituted pyridine. Space-filled molecular model of the cyclophane complex **1** shows that there is enough space to allow access of a pyridine molecule from the bridged face. Larger amine molecules than pyridine seem to meet with steric hindrance to some extent. Further studies are in progress to elucidate anomalous physico-chemical properties of the iron complexes of cyclophane porphyrin.

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