SYNTHESES AND STRUCTURAL ELUCIDATION OF CYCLOPHANE PORPHYRINS AND THEIR METAL COMPLEXES

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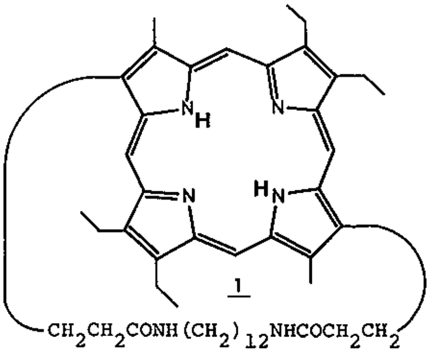
Cyclophane porphyrin **1** has been prepared from condensation of 1,5-di(2-carboxyethyl)porphyrin **2** with 1,12-dodecamethylenediamine by using mixed anhydride method. Similar treatment of **2** with n-hexylamine gave reference porphyrin **3**. Ligation of amine molecule to the ferric chloro complexes of **1** and **3** showed a marked difference in their spin equilibria ($S = 1/2 \rightleftarrows S = 5/2$). When 4-benzylpyridine was used as axial ligand, the former complex remained still at the high spin state, whereas the latter complex was converted to the low spin state. Addition of pyridine showed exclusive existence of the low spin state for both ferric complexes of **1** and **3**. Long dodecamethylene chain of **1** requlates access of relatively large amine molecule to the ferric ion due to steric constraint. Inner space of the ferric complex of **1** permit pyridine to coordinate the iron atom as an axial ligand. Further, it is noted that oxygen binding to the Co(II) complexes of **1** showed clear contrast with that of **3** in the presence of benzimidazole. The former complex gave oxygen binded complex at room temperature within several minutes in air. On the other hand, the reference Co(II) complex was found to be inert at similar condition.

Cyclophane porphyrin **4** bridged by two $-CH_2CH_2CO_2CH_2CH_2CH_2-$ groups was obtained by esterification of **2** with 1,5-di(3-hydroxytrimethyleno)porphyrin. Separation of two porphyrin ring is estimated as 7 ∿ 8 Å and interaction between two ring seems to very small on the basis of visible spectrum of **4**.



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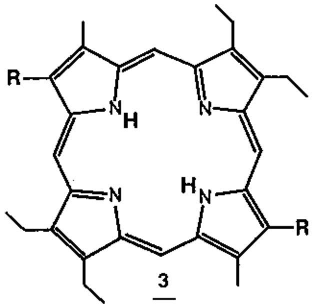

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$R = CH_2CH_2CONHC_6H_{13}$