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where M indicates a metal ion.

The porphyrins were soluble in dimethylformamide (DMF) but practically insoluble in water. The DMF solutions showed the spectra characteristic of the free base porphyrin with the Soret band and the four weak visible bands. Addition of Cu(II) perchlorate to the solution resulted in biphasic spectral changes, an instantaneous change and a subsequent slow change. The latter change was observable at room temperature only under a large excess of Cu(II) over the porphyrin. The spectra after the completion of the first step were ascribed to the formation of $\text{PH}_2(\text{QOCu}^+)_4$. In the spectra after the completion of the second slow step, the four visible bands were replaced by two band characteristic of metalloporphyrin and the change should indicate the formation of $\text{PCu}(\text{QOCu}^+)_4$.

The kinetics of the second step in DMF were measured at 30° by monitoring the absorption at around 523 nm. The formation of the metalloporphyrin followed the first order kinetics under a large excess of Cu(II). The observed first order rate constant, k_0 , increased linearly with the increase of the total concentration of Cu(II). The values of the second order rate constants were 0.92 and 0.41 $\text{M}^{-1}\text{sec}^{-1}$ for the 2- and 5-isomers, respectively.

The addition of HClO_4 to the $\text{PCu}(\text{QOCu}^+)_4$ solution gave rise to the spectra assignable to $\text{PCu}(\text{QOH})_4$, in which the two weak visible bands characteristic of the metalloporphyrin spectrum were blue shifted. The decrease of the absorbance of the Soret band along with the metal chelation of the quinolinol moiety was noted.

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ピリドキサール酵素のモデル

松島美一

〔日本薬学会九州支部第4回研修会(1987年7月, 福岡)における特別講演〕

酵素モデルの代表的研究と言われるピリドキサール酵素のモデルについて, その酵素の理解に果たしてきた役割を概説した。錯体化学の貢献, 反応モデルから分光学的モデルへの変容, 準安定中間体のモデル, 最近のトピックについても論じた。