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PREPARATION AND CHARACTERIZATION OF IRON(III) COMPLEXES OF N-METHYLOCTAETHYLPORPHYRIN

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Iron(III) complexes of N-methyloctaethylporphyrin, [Fe(III)-(N-CH_3-OEP) (Cl)]$^+$ X^- (X = $FeCl_4$ (1), ClO_4 (2)), were prepared. The central metal of complex (2) is confirmed to be in a high-spin (S = 5/2) state on the basis of magnetic susceptibility and ESR parameters. These complexes form monopyridine adducts in solution.

Much recent interest has been directed to N-alkylporphyrins and their metal complexes. The N-alkyl substituents may cause perturbation on the electronic structure and axial ligation behavior of metal complexes of otherwise symmetric parent porphyrin by their electronic and steric effects.[1] In addition to such basic interest in porphyrin chemistry, there is increasing recent attention to the abnormal catabolism of heme enzymes and proteins which brings about N-alkylation (-arylation) of prosthetic hemes, destruction of hepatic cytochrome P_{450} by various olefinic[2] and acetylenic[3] agents, and phenylhydrazine-induced hemolytic anemia.[4] The oxidation-induced carbon-donor migration from iron to pyrrolic nitrogen in an iron(II)-carbene complex of tetraarylporphine[5,6] would also bear biochemical implication. In the light of these studies, we have initiated studies on the physicochemical characterization of iron complexes of N-alkylporphyrins and the mechanism involved in their biological formation. We report here synthesis and some properties of the iron(III) complex of N-alkylporphyrin.[7]

A tetrahydrofuran (THF) solution (50 ml) of 21-methyloctaethylporphyrin[8] (N-CH_3-OEP) (111 mg) and anhydrous $FeCl_2$[9] (72 mg) was refluxed under nitrogen for 2 h. 2,6-Lutidine (22 mg) was added when the reaction mixture had cooled down to room temperature. The mixture was filtered, the filtrate evaporated, and the

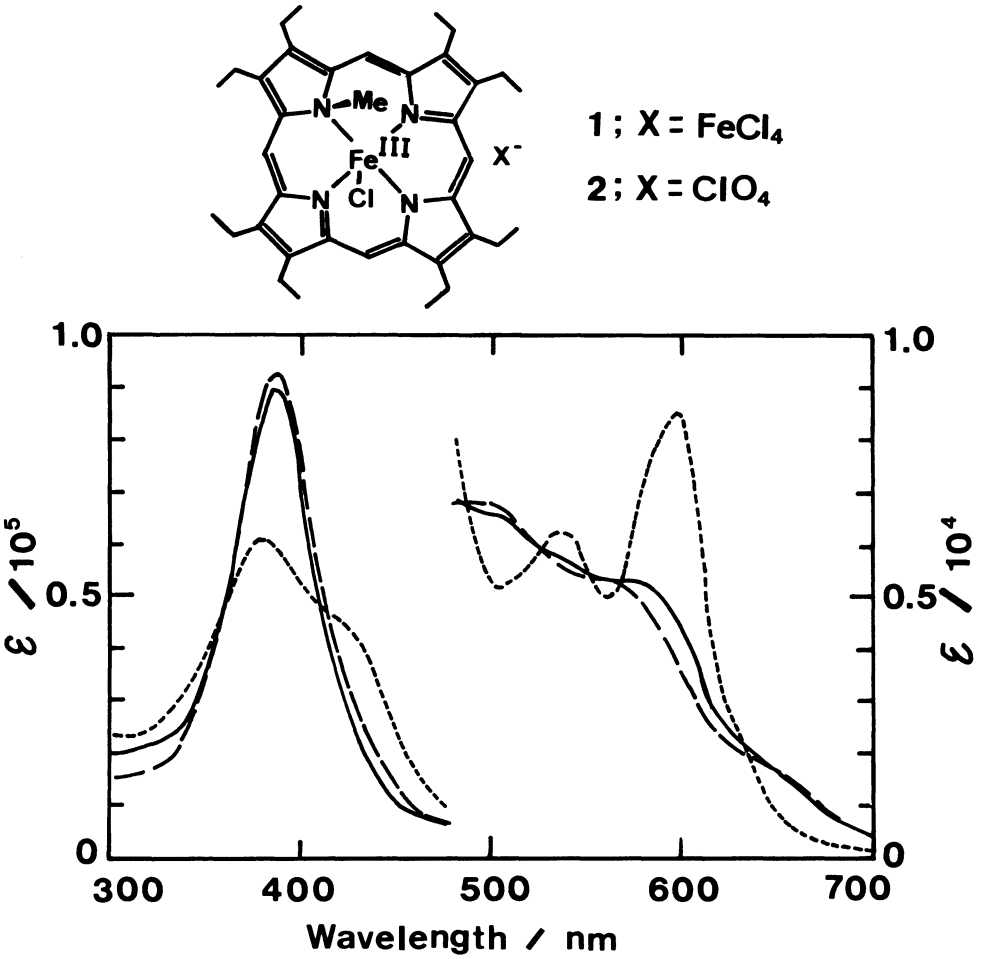

Fig. 1. Electronic absorption spectra of chloroform solutions of (1) (——), (2) (——), and (1) in the presence of pyridine (8.25×10^{-2} mol·dm^{-3}) (-----).

residue recrystallized from dichloromethane-ether (1:5 v/v) and/or chloroform-benzene (2:3 v/v) to give 118 mg (70%) of the ferric chloride complex of N-CH_3-OEP (1). Found: C, 53.15; H, 5.82; N, 6.69%. Calcd for $C_{37}H_{47}N_4Cl_5Fe_2$: C, 53.11; H, 5.66; N, 6.70%. An anion exchange treatment on (1) was performed with a $CHCl_3$ solution of (1) by adding a saturated aqueous solution of $NaClO_4$ to afford (2) in about 40% overall yield from N-CH_3-OEP. Found: C, 60.51; H, 6.41; N, 7.72%. Calcd for $C_{37}H_{47}N_4O_4Cl_2Fe$: C, 60.17; H, 6.41; N, 7.59%. The IR spectra (650-4000 cm^{-1}) of (1) and (2) by the KBr disk method resemble each other except for a strong absorption at 1093 cm^{-1} (ν(Cl-O) of ClO_4^-)[10] for the latter. The electronic spectra of (1) and (2) in $CHCl_3$ solutions are also almost mutually superimposable (Figure 1). These results suggest that both $FeCl_4$ and ClO_4 anions are essentially not coordinated to the central iron(III).

The magnetic susceptibility parameter for (2) by the Faraday method at 14°C

was determined to be μ_{eff} = 5.95. This value is in a good agreement with the spin-only value (μ_{eff} = 5.92) for high-spin iron(III) (S = 5/2). Furthermore, the ESR spectrum of (2) in frozen $CHCl_3$ gave g-values of 6.13 and 2.00 characteristic of a high-spin iron(III) porphyrin complex.[11]

Addition of pyridine to a $CHCl_3$ solution of (1) (2.093×10^{-5} mol·dm^{-3}) resulted in successive spectral change consistent with an equilibrium involving formation of a single pyridine adduct ((1) + nPy $\rightleftharpoons$ adduct; equilibrium constant, K); a set of clear isosbestic points at intermediate concentrations of pyridine and no further spectral change at higher concentration range of pyridine (>10^{-2} mol·dm^{-3}).[12] The spectrum (Figure 1) observed at such high pyridine concentrations was the same as that of (1) dissolved in neat pyridine. Referring to the relation, $K = [\text{adduct}]/[(1)][\text{Py}]^n$, a plot of log [adduct]/[(1)] readily evaluated from absorbance change at 383 nm *vs.* log [Py] gave a straight line with slope (n) = 1.0 (Figure 2). Thus, the present equilibrium involves formation of a monopyridine adduct with $K = 1.66 \times 10^3$ mol^{-1}·dm^3 as a sole pyridine-binding species persisting even in neat pyridine. The axial coordination behavior of amine bases including pyridines in the iron(III) porphyrin systems has been rather extensively studied.[13] A major problem anticipated here is the possibility of forming more than one adduct,

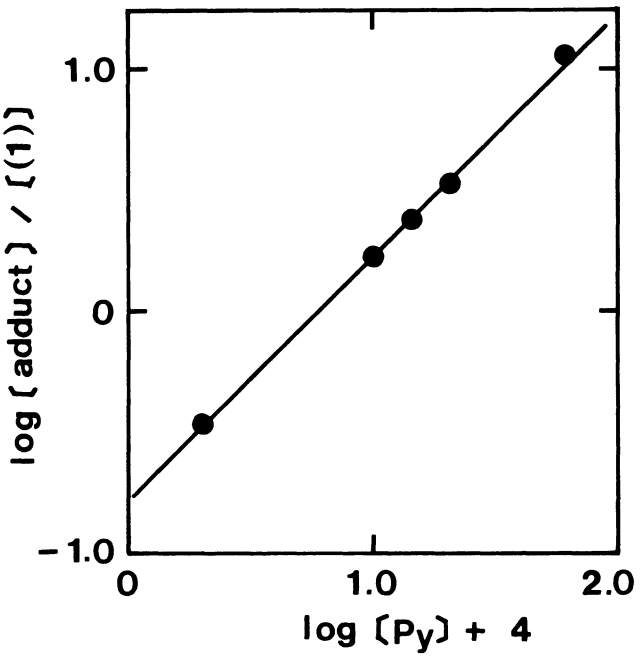

Fig. 2. Analysis of spectral data according to the relation, log [adduct]/[(1)] = log K + nlog [Py]; concentrations are given in mol·dm^{-3}.

monoamine and bisamine adducts. The formation of a monopyridine adduct derived from the simple pyridine-binding equilibrium as stated above seems to be most reasonably due to the steric constraint effect of the N-methyl substituent provided at the sixth coordination site.

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8) Prepared in 55% yield (after chromatography on alumina (Merck, activity grade II-III) with chloroform as eluant, followed by recrystallization from chloroform-methanol (1:5 v/v)) from reaction of OEP and CH_3SO_3F after published procedure (R. Grigg, G. Shelton, A. Sweeney, and A. W. Johnson, J. Chem. Soc., Perkin I, 1789 (1972)) with some modification.
9) Prepared either by recrystallization of commercial $FeCl_2$ from chloroform-ethanol or by *in situ* reduction of $FeCl_3$ with iron powder in THF.
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11) K. M. Smith, Ed., "Porphyrins and Metalloporphyrins," Elsevier, Amsterdam (1975), Chap. 13.
12) The resulting pyridine adduct undergoes gradual demethylation to give Fe(III)-(OEP)(Cl). Similar demethylation has been reported for divalent metal complexes of N-methyltetraphenylporphin.[7b, 7c]
13) Reference 11, Chap. 5.

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