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SYNTHESIS OF MONO(PYRIDINE)- AND MONO(4-SUBSTITUTED PYRIDINE)-OCTAETHYLPORPHYRINATOIRON(III) PERCHLORATE

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Mono(pyridine)- and mono(4-substituted pyridine)octaethylporphyrinatoiron(III) perchlorate were prepared by treatment of octaethylporphyrinatoiron(III) chloride with silver perchlorate and successive addition of pyridine and 4-substituted pyridine, respectively. The spin states of monoamine adducts were found to be in equilibrium between high (S = 5/2) and low (S = 1/2) spin states.

Naturally occurring heme is an iron-porphyrin complex, the fifth coordination position of which is generally occupied by a histidyl imidazole ligand.[1)] Although many reports on the isolation and structure of bisamine complexes of synthetic heme have been published,[2-6)] little is known as for the monoamine adduct which is considered to be a simplest model of heme. For the ferrous complex, the preparation of TPPFe(N-methylimidazole), ($TPPH_2$ = α,β,γ,δ-tetraphenylporphin) has been reported recently.[7)] However, the existence of monoamine adduct of the ferric complex has been suggested only by NMR[8-10)] and T-jump study[11)] in solution. We report here the preparation and characterization of some monopyridine adducts of octaethylporphyrinatoiron(III).

Reaction of OEPFeCl[12)] with $AgClO_4$ in benzene under reflux, followed by crystallization after filtration of the hot reaction mixture, afforded dark brown needles $OEPFeClO_4$ (1) in 85% yield. Anal. Found: C, 62.94; H, 6.48. N, 8.04%. Calcd for $C_{36}H_{44}N_4O_4ClFe$: C, 62.84; H, 6.45; N, 8.14%. The reddish purple complex OEPFe(py)ClO_4 (2) was obtained by treatment of 1 with an equimolar amount of pyridine. Recrystallization from benzene-chloroform gave purple crystalline 2 in 80% yield. Anal. Found: C, 64.33; H, 6.34; N, 8.95%. Calcd for $C_{41}H_{49}N_5O_4ClFe$: C, 64.19; H, 6.44; N, 9.13%. Dark brown crystalls, OEPFe(4-CHO·py)ClO_4 (3), and OEPFe(4-CN·py)ClO_4 (4) were also obtained almost quantitatively according to the similar procedure. Anal. Found: C, 63.36; H, 6.28; N, 8.89%. Calcd for $C_{42}H_{49}N_5O_4ClFe$ (3): C, 63.44; H, 6.21; N, 8.81%. Found: C, 63.40; H, 6.26; N, 10.32%. Calcd for $C_{42}H_{48}N_6O_4ClFe$ (4): C, 63.67; H, 6.10; N, 10.61%. Addition of a large excess of amine resulted only in the formation of the corresponding monoamine adduct as crystals in all cases.

These monopyridine adducts are moderately stable in air. In chloroform, however, all are dissociated completely into 1 and pyridine on the basis of the visible spectra. Table 1 summarizes characteristic IR bands and magnetic susceptibility data of the complexes in solid state. The presence of a coordinated amine is confirmed by the characteristic IR bands of skeltal stretching and substituent (at the 4-position) of pyridine. Moreover the red shift of Soret band of reflectance visible spectrum ($\sim$10 nm) comparing with 1 may likely be ascribed to axial ligation of nitrogenous base. These phenomena are commonly observed for metalloporphyrin.13) For 3 and 4, the IR frequencies of carbonyl and cyano stretching vibration are found in the same region as the free ligand. These facts indicate that the pyridine coordinates with iron not by carbonyl or cyano group, but iminonitrogen.

Table 1. Characteristic Spectral Data of OEP Ferric Complexes

No.	Characteristic IR bands[a] (cm^{-1}) ν (ClO_4^-)	 ν (pyridine ring)	 others	μ_{eff} (BM) 77°K	 288°K	Soret[b] (nm)
1	1162, 1150, 1114, 1093, 1067, 1060 (s)		878 (m, br)[c]		4.8	398
2	1145, 1093, 1066, 1658 (s)	1604, 1490 (m)		1.7	3.2	408
3	1149, 1114, 1091, 1060 (s)	1566, 1411 (m)	1710 (s)[d]	4.3	5.4	406
4	1150, 1095, 1060 (s)	1607, 1410 (m)	2215 (w)[e]	3.3	4.7	410

[a] Measured on pressed KBr disks; w = weak, m = medium, s = strong, br = broad.
[b] Reflectance spectra. [c] ν(Fe-O). [d] ν(C=O). [e] ν(C≡N).

The unusual results were obtained for the magnetic moment of all the complexes at 288°K. The values are intermediate between that expected for high (S = 5/2) and low (S = 1/2) spin iron (III). Temperature dependence study shows that the monopyridine adduct (2) is in low-spin state between 77°K and 240°K, while 3 and 4 have the magnetic moment higher than the low-spin value 2.2 BM even at 77°K. The coordination of the stronger base results in the more favorable population in the low spin state. It has been noted that the spectral behavior of a ferric porphyrin in the visible region an be usually correlated well with the spin state of iron(III).14) The complexes 1, 3 and 4 exhibit similar reflectance spectra with a shoulder at 650 nm (Figure 1). Although 2 shows a spectrum rather similar to that of OEPFe$(imd)_2ClO_4$ (typical low spin complex), there exists a weak shoulder at 640 nm. In any case, all the complexes seem to show intermediate spectra at 25°C between those

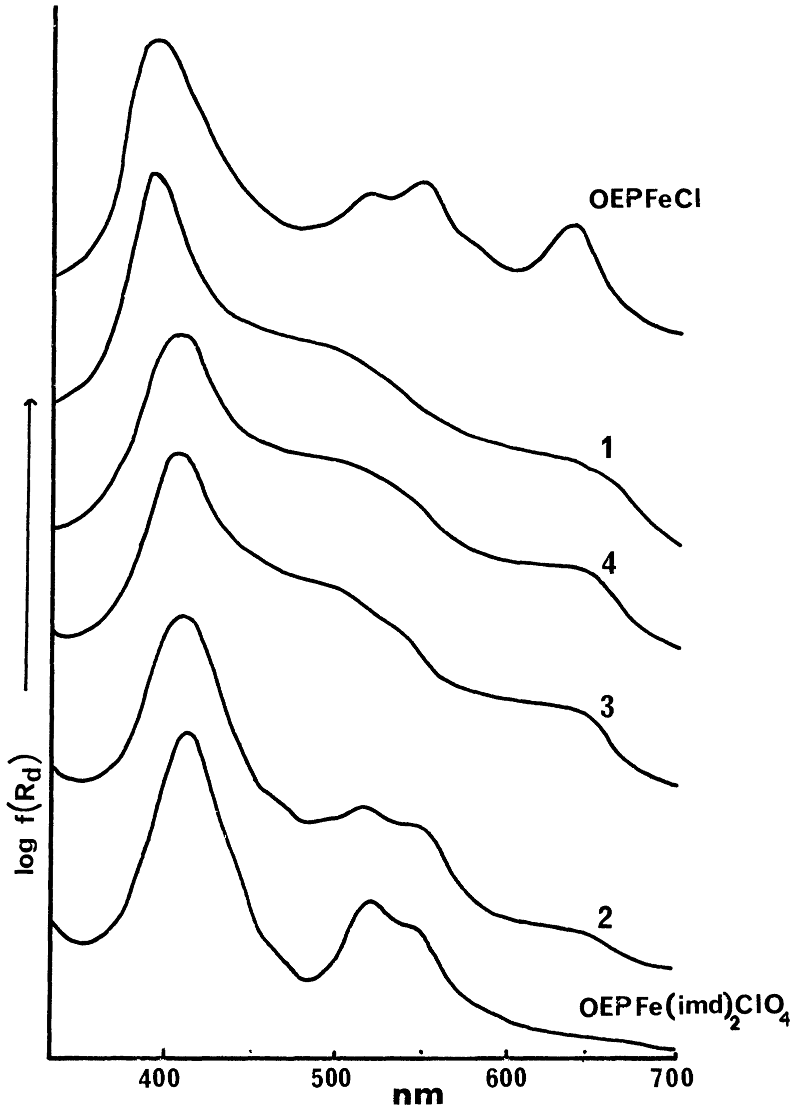

Figure 1. Reflectance spectra of OEPFe(III) complexes at 25°C

of high and low spin hemin as far as characteristic CT band at 650 nm of high spin complex[15] is concerned. Thus, the anomalous temperature dependence of the susceptibility and the behavior of optical spectra have led to the conclusion that the phenomena should be explained by the spin-state equilibrium as follows.[16] Similar

$$^6A_1 \rightleftharpoons {}^2T_2$$

anomalous behavior of the susceptibility have found for ferrimyoglobin hydroxide[14] and pyridine solution of hemin.[8, 17]

The intermediate value of the perchlorate 1 may be accounted for if we assume that the perchlorate ion is not a free ion but acts as a monodentate ligand. The

IR of 1 indicates stretching bands of ClO_4^- with many splittings and a broad band at 890 cm^{-1}. The latter band can be reasonably assigned to ν(Fe-O), which is observed for the oxygen coordinated hemin such as OEPFeOH, OEPFeOMe and OEPFeOEt.[18] The ClO_4^- ion of monoamine adducts seems to be very weak ligand, since their infrared spectra show rather ordinary absorptions of free ClO_4^- group. In the cases of strong base such as imidazole and γ-picoline, we have isolated bisamine adducts as stable complexes.[5] The positive charge of the ferric porphyrin is effectively delocalized among the two amine molecules of the fifth and sixth ligands. For weaker bases such as parent pyridine and pyridines substituted with the electron withdrawing group, a perchlorate ion is probably required to stabilize the positively charged ferric porphyrin in crystalline state. The quantitative magnetic measurement and the crystallographic study of the monoamine adducts are now in progress.

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