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(TETRABENZPORPHINATO)IRON

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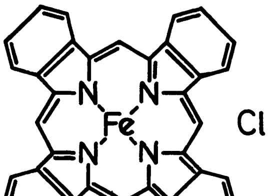
The iron complex of tetrabenzporphine was prepared and characterized. Cyclic voltammetry, and UV absorption, EPR, and MCD spectroscopy have revealed that its monochloride and bisimidazole complexes are trivalent iron high- and low-spin complexes, respectively.

Ample metal porphyrins (Pors), especially iron derivatives, have been prepared and characterized to date because of their relevance to the biologically important hemoproteins. Phthalocyanines (Pcs) which are classified into tetraazaporphyrins have also appeared frequently for reasons including their classical use as dyestuffs and their developing use as components of various solar energy conversion devices. However, reports on tetrabenzporphyrin (H_2TBP) which is a structural intermediary connecting Pors and Pcs are still very scarce. One possible reason for this had been the difficulty in its synthesis.[1)] Although this difficulty was overcome to some extent by the introduction of matrix method,[2)] little is known on its iron complex, FeTBP,[3)] irrespective of special importance of iron porphyrins in connection with hemoproteins. Hence, some fundamentals on FeTBP are presented in this report.



FeTBP·Cl

FeTBP was prepared according to the procedure described in the Note[4)] as a monochloride derivative, FeTBP·Cl. Different from H_2TBP, ZnTBP, and FePc, FeTBP·Cl was not purified by sublimation.

Figure 1 shows the cyclic voltammograms (i-E curves) for H_2TBP (curve A) and FeTBP·Cl (curve B) in DMF. As seen, the redox couple at *ca.* -0.24 V vs. SCE is due to iron (as substantiated below, this corresponds to $Fe^{III/II}$TBP·Cl redox couple), and further reductions and oxidations to Fe^{I}TBP·Cl, $Fe^{I}TBP^{\overline{\cdot}}$Cl, $Fe^{III}TBP^{\dot{+}}$Cl, and probably $Fe^{III}TBP^{2\dot{+}}$Cl or $Fe^{IV}TBP^{\dot{+}}$Cl[5)] occur at *ca.* -1.38, -1.78, 0.52, and 0.99 V vs. SCE, respectively. Thus the difference between the potentials for the second- and third- reduction is 0.40 V, and for the first- and second-oxidations, 0.47 V, the latter value being much smaller than that of other porphyrins (1.2-1.3 V).[6)]

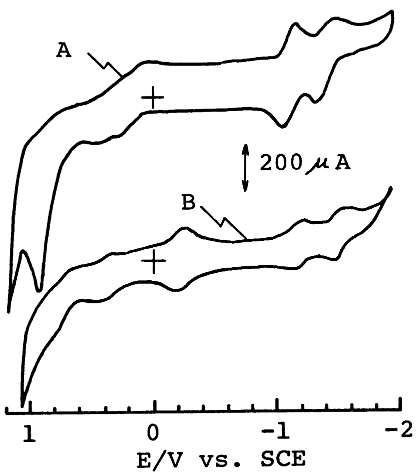


Fig.1 Cyclic voltammograms of H_2TBP (curve A) and FeTBP•Cl (curve B) in N_2-saturated DMF containing 0.1 M (1M = 1 mol/l) TEAP. Scan rate/V•s^{-1} = 0.126. Area of electrode (glassy carbon)/cm^2 = 0.77. [H_2TBP]/M = 1.5×10^{-3}, [FeTBP•Cl]/M = 8.0×10^{-4}.

The potential difference (0.76 V) between the first oxidation and reduction is also much smaller than that for other porphyrins (2.25 V).7)

Though the oxidation state of iron is deduced from the combustion datum4) to be trivalent, EPR spectra on FeTBP•Cl and its bisimidazole complex, $FeTBP(Im)_2$,8) were recorded to manifest it. As shown in Fig.2, g-values were obtained around 6 and 2, suggesting that FeTBP•Cl is a trivalent iron high-spin complex. While $FeTBP(Im)_2$ is a trivalent iron low-spin complex from three g-values around 2 (not shown).9)

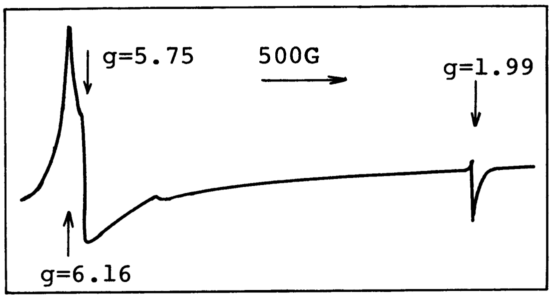


Fig.2 ESR spectrum of FeTBP•Cl in $CHCl_3$-CH_3OH (1:1 v/v) at 6.7 K.

In Fig.3, the UV and MCD spectra for FeTBP•Cl and $FeTBP(Im)_2$ are shown. Compared with those of the corresponding derivatives of (tetraphenylporphinato)iron and (octaethylporphinato)iron,10) these spectra are characteistic in that the Q_{0-0} bands have nearly comparable intensity to that of the Soret bands. FeTBP•Cl showed UV peaks at 762, 668, 616, 578, 543, and 407 nm, and dispersion type MCD curves with approximate inflection points at 756, 614, and 409 nm, and an MCD trough at 693 nm. The band intervals of the peaks at 616, 578, and 543 nm are diagnostic as those of vibrational bands (*ca.* 1100 cm^{-1}), and in particular, MCD features in 820-700 nm region with a change in sign from minus to plus from the longer wavelength side,11) and a trough at 693 nm strongly suggest that FeTBP•Cl is a trivalent iron high-spin complex.12) In the case of $FeTBP(Im)_2$, near infrared bands observed on FeTBP•Cl (charge-transfer bands) disappeared and two dispersion type MCD spectra appeared associated with the absorption maxima at 426 and 626 nm. Since such features were expected in common for both $Fe^{II}TBP(Im)_2$ and $Fe^{III}TBP(Im)_2$, a temperature variation experiment was carried out to confirm the species. As shown in the inset of Fig.3, the intensity of the visible peak and trough

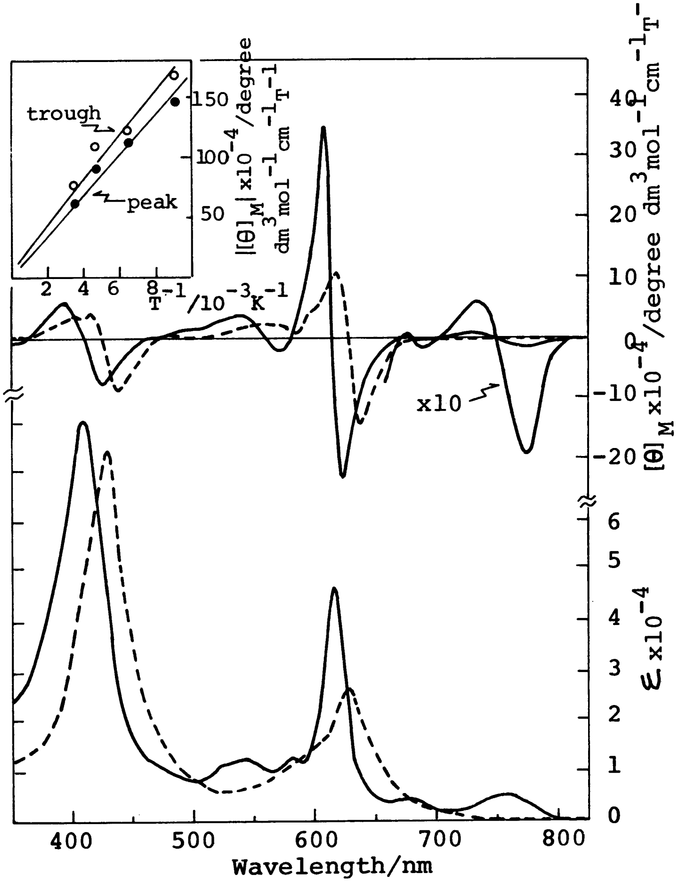


Fig.3 UV (bottom) and MCD (top) spectra of FeTBP•Cl (————) and $FeTBP(Im)_2$ (------) in $CHCl_3$ at room temperature. [FeTBP•Cl]/M = 2.48×10^{-5} and 4.05×10^{-5} for UV and MCD spectra, respectively. $[FeTBP(Im)_2]$/M = 2.48×10^{-5} and 2.56×10^{-5} for UV and MCD spectra, respectively. Path-length/cm = 1. The inset shows the temperature dependence of the MCD intensity of the visible peak and trough of $FeTBP(Im)_2$ in DMF. $[FeTBP(Im)_2]$/M = 2.03×10^{-5}. Path-length/cm = 0.2. Temperature/K = 283, 213, 153, and 110. Magnetic field/T = 1.45.

increased linearly with the reciprocal of the absolute temperature.[10,12) Thus $FeTBP(Im)_2$ was determined to be a trivalent iron low-spin complex, because if it is a divalent iron low-spin complex, such dependence is not expected theoretically[13).

Thus through the above observation, FeTBP•Cl and $FeTBP(Im)_2$ were determined to be trivalent iron high- and low-spin complexes, respectively. In this context, it is concluded that FeTBPs are closer to general iron porphyrins than to iron phthalocyanines whose oxidation state is divalent.

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References

1) R.P.Linstead and E.G.Noble, J.Chem.Soc., 1937, 933.

2) A.Vogler and H.Kunkely, Angew.Chem.Int.Ed.Engl., 17, 760(1978).

3) A.Vogler, B.Rethwisch, H.Kunkely, and J.Hüttermann, Angew.Chem.Int.Ed.Engl., 17, 952(1978).

4) H_2TBP prepared from ZnTBP$^{2)}$ by demetalation was reacted with $FeCl_2$ in refluxing DMF for several hours, and the solution was poured into dilute hydrochloric acid. The resulting precipitate was collected and imposed on a column of basic alumina with DMF or $CHCl_3$-CH_3OH (1:1 v/v). After evaporation of the solvent, the residue was taken up in $CHCl_3$, washed with 10% HCl several times, and dried over anhydrous sodium sulfate. The $CHCl_3$ solution was then evaporated to dryness, and the product was recrystallized from CH_3Cl-benzene. The yield from H_2TBP was 70 %. Anal. Calcd for $C_{36}H_{20}N_4FeCl$: C,72.08; H,3.36; N,9.34; Cl,5.91. Found: C,72.00; H,3.45; N,9.21; Cl,5.56.

5) Detailes will be described in a full paper.

6) R.H.Felton, "The Porphyrins," ed by D.Dolphin, Vol.5, Chap.3, pp53-125.

7) J.H.Fuhrhop in K.M.Smith, "Porphyrins and Metalloporphyrins," Elsevier, Amsterdam (1975), Chap.14.

8) Confirmed from the change of UV spectrum when Im was added to the solution containing FeTBP·Cl; a stepwise change from FeTBP·Cl to FeTBP·Im and further to $FeTBP(Im)_2$ was easily observed in DMF, however, a direct change from FeTBP·Cl to $FeTBP(Im)_2$ was recognized in CH_2Cl_2.

9) Even at 6.7K, a definate spectrum was not obtained.

10) H.Kobayashi, T.Higuchi, and K.Eguchi, Bull.Chem.Soc.Jpn., 49, 457(1976).

11) T.Yamamoto, T.Nozawa, N.Kobayashi, and M.Hatano, Bull.Chem.Soc.Jpn., 55, 3059 (1982).

12) L.Vickery, T.Nozawa, and K.Sauer, J.Am.Chem.Soc., 98, 351(1976).

13) P.J.Stephens, J.Chem.Phys., 52, 3489(1970).

14) A.Vogler, B.Rethwisch, H.Kunkely, and J.Hüttermann, Angew.Chem.Int.Ed.Engl., 17, 951(1978).

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