Electronic Structure of Synthetic Iron(III) Porphyrins in Pyridine and Pyridine—Water Solutions: a Proton Magnetic Resonance Study

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Abstract

The results of variable temperature proton nuclear magnetic resonance, ESR and magnetic moment measurements on tetraphenylporphyrin iron(III) Cl and octaethylporphyrin iron(III) Cl in pure dry pyridine and in pyridine—water mixtures are reported. In pure dry pyridine both Fe(TPP)Cl and Fe(OEP)Cl exist as undissociated adducts. The temperature dependence of the isotropic shifts and magnetic moments in pyridine—water solution is explained in terms of thermal equilibrium between high spin $S = 5/2$ and low spin $S = 1/2$ states with low spin state lying lower.

Introduction

The electronic structure of iron(III) porphyrins in pyridine and pyridine—water solutions has been the subject of several studies [1–7]. Most of these studies have been carried out on naturally occurring porphyrins, which showed a complicated though interesting behaviour. For example, it has been shown by UV—Vis and proton NMR spectroscopy that protoporphyrin iron(III) chloride (hemin chloride, $S = 5/2$) in pure dry pyridine solution produces an equilibrium mixture of six-coordinated mono-pyridine [Fe(PP)(py)Cl] ($S = 5/2$) and bis-pyridine [Fe(PP)(py)$_2$]Cl ($S = 1/2$) ferric complexes [2, 7]. It has also been observed that a slow autoreduction of the ferric porphyrin occurs in the pure dry pyridine [2]. When water is slowly added to the heme chloride—pyridine solution a more complex situation arises. At low concentrations of water (less than 50% by volume) three structurally distinct species exist in equilibrium in the solution: the above mono- and bis-pyridinato ferric complexes and an aquo hemin complex, [Fe(PP)(H$_2$O)(py)]Cl, in which both pyridine and water has been shown to be coordinated to the iron atom [3, 8]. The hydrophilicity of the medium surrounding the heme was found to inhibit the autoreduction and formation of the ferrous state, and the ferric state was favoured [5, 8]. The aquo hemin complex has structural similarity with the chromophore of metmyoglobin and shows interesting electronic structural properties [3].

In view of the complicated behaviour of the natural porphyrin complexes in pyridine and pyridine—water solutions, a similar study on synthetic ferric porphyrins appeared desirable. Castro and Anderson [6], have recently reported UV—Vis spectral studies on synthetic octaethylporphyrin iron(III) chloride, Fe-(OEP)Cl ($S = 5/2$) in pure dry pyridine and observed that it exists predominantly as an undissociated high spin adduct. No detailed proton NMR studies on these systems have yet been reported.

We report here detailed high resolution proton NMR (at 500 MHz) on a number of synthetic ferric porphyrins in pyridine and pyridine—water solutions at different temperatures. The ferric complexes chosen for the study are: Fe(TPP)Cl and Fe(OEP)Cl. Here TPP and OEP are tetraphenyl and octaethyl porphyrin dianions. Some complementary ESR and UV—Vis spectral results are also presented.

Experimental

Fe(TPP)Cl and Fe(OEP)Cl were prepared and purified by the method of Adler *et al.* [9] while the perchlorato complexes were prepared and purified by the method of Reed *et al.* [10]. Pyridine was refluxed over KOH and stored over molecular sieves. Double distilled water was used in UV—Vis spectral studies, while deuterated pyridine and water were used in the NMR measurements.

Proton NMR measurements were done on a Bruker AM 500 MHz FT NMR spectrometer. Temperatures were measured with an accuracy of ±0.5 °C. The paramagnetic shifts are referenced to TMS, and downfield shift is taken as positive. Optical measurements were done on a Cary 17D spectrometer, and ESR studies on an X-band spectrometer using an Oxford continuous flow cryostat for measurements at liquid helium temperature. The concentrations of the solution for NMR and optical studies were in the 10^{-3} and 10^{-5} M range respectively. No effect of aggregation was observed in the NMR studies.

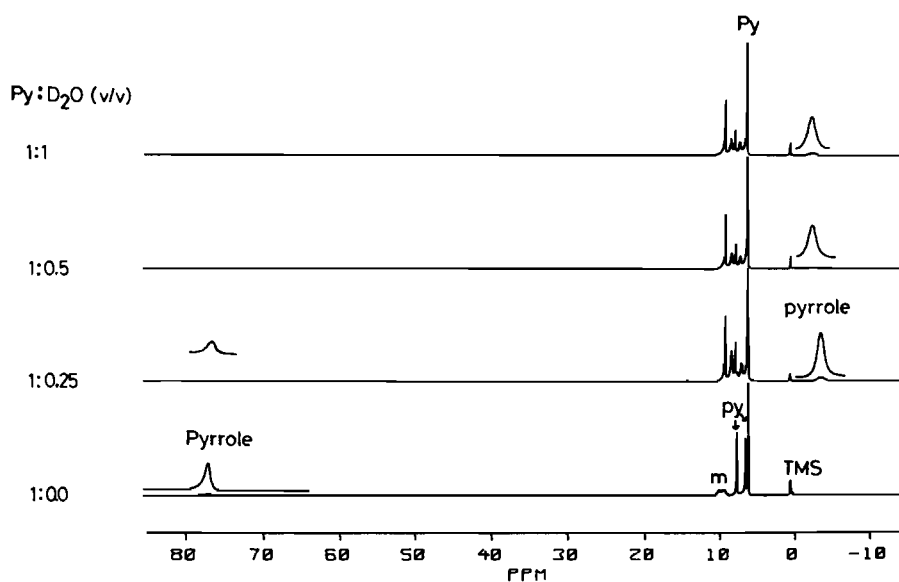*Author to whom correspondence should be addressed.

Fig. 1. ^{1}H NMR spectra of Fe(TPP)Cl in pure pyridine and in pyridine—water solutions.

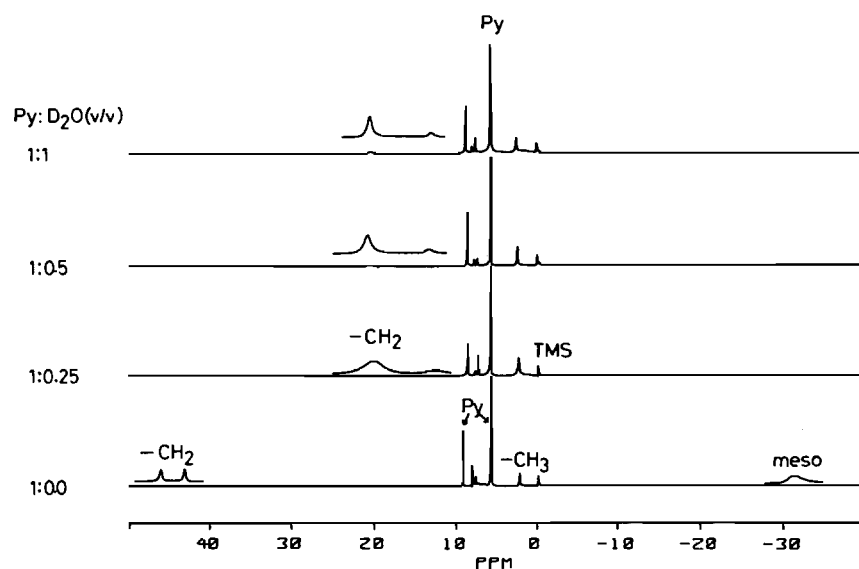Fig. 2. ^{1}H NMR spectra of Fe(OEP)Cl in pure pyridine and in pyridine—water solutions.

Results and Discussion

Figures 1 and 2 show the ^{1}H NMR spectra of Fe-(TPP)Cl and Fe(OEP)Cl in pure dry pyridine and in pyridine—water solutions at room temperature. A summary of the spectral features in pure pyridine and in chloroform solutions is contained in Table I for comparison.

The ^{1}H NMR for the two complexes shown in Figs. 1 and 2 are typical of their high spin behaviour [11, 12]. The pyrrole proton in the TPP complex has an isotropic proton shifts (*IPS*) of 72 ppm, which is very close to 72.4 observed in the high spin chloro-

form solution. The linear temperature dependence of the pyrrole *IPS* (Fig. 3) suggests that Fe(TPP)Cl in pyridine solution is high spin. This is further supported by measurement of the magnetic moment in solution (by Evans Method), which gave a value of 5.85 BM. The *IPS* of the CH$_2$ protons in Fe(OEP)Cl at 43 ppm is close to the high spin value in chloroform solution. The observed doublet for the CH$_2$ protons in pyridine solution indicates an out-of-plane displacement of the iron atom as in the chloroform solution. Its linear temperature dependence (Fig. 3) and magnetic moment ($\sim$5.9 BM) again support that, like Fe(TPP)Cl, Fe(OEP)Cl in pure dry pyridine exists

TABLE I. Spectral Features of Fe(TPP)Cl and Fe(OEP)Cl in Pure Pyridine and in Chloroform Solutions

	Solvent	Fe(TPP)Cl	Fe(OEP)Cl
Visible spectra, λ_{max} (nm)	pyridine	695, 655–530, 507, 415	625, 529, 510, 396
	chloroform	690, 656, 572–507, 413	632, 532, 503, 375
NMR (ppm)	pyridine	pyrrole proton 72	43.0, 40.4
	chloroform	72.4	43.1, 40.5
EPR (4.2 K)	pyridine	$g_\perp = 6, g_\parallel = 2$	$g_\perp = 6, g_\parallel = 2$
	chloroform	$g_\perp = 6, g_\parallel = 2$	$g_\perp = 6, g_\parallel = 2$
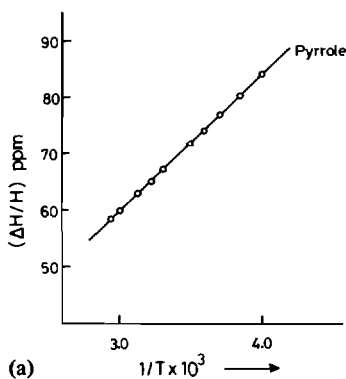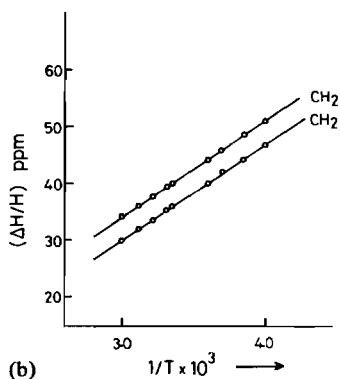
Fig. 3. Curie plots for pyrrole and CH_2 proton resonance of Fe(TPP)Cl (a) and Fe(OEP)Cl (b) in pure pyridine.

Fig. 4. EPR spectra at 4.2 K of Fe(TPP)Cl (a) and Fe(OEP)-Cl (b) in pure pyridine.

in the high spin state. The EPR of these complexes recorded in dry pure pyridine at 4.2 K (Fig. 4) gives a typical high spin resonance ($g_\parallel = 2, g_\perp = 6$) in agreement with above observations.

It has been observed that the ferric ion in hemin chloride/pyridine solution is slowly reduced to the iron(II) complex over a period of days [2, 7]. In contrast, no evidence of the reduction was found in the TPP and the OEP complexes in dry pyridine even over a period of several weeks (Fig. 5).

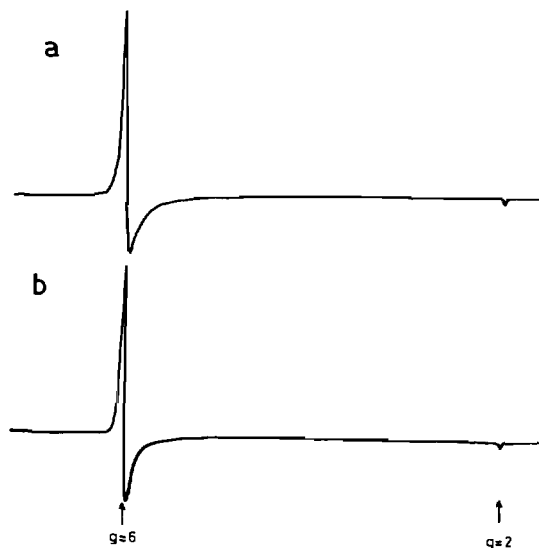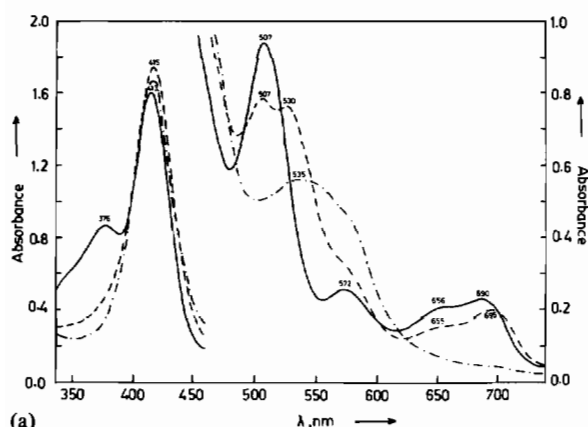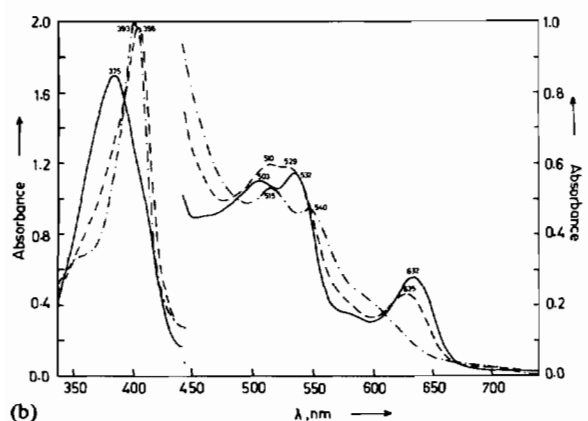The effect of addition of water to the pyridine solution of Fe(TPP)Cl and Fe(OEP)Cl is shown in Figs. 1 and 2. As water is progressively added to the pyridine solution of the TPP complex, the pyrrole proton resonance at 72 ppm decreases in intensity while a new resonance appears at $\sim$−6 ppm. At a pyridine to water ratio of unity (v/v) the high spin resonance completely disappears and only the −6 ppm resonance remains. It is also observed that while the addition of water changes significantly the isotropic shift of the new upfield resonance at $\sim$−6 ppm, the isotropic shift of high spin resonance remains nearly unchanged.

As the water is added to the pyridine solution of Fe(OEP)Cl, the CH_2 signals at $\sim$45 ppm diminish considerably in intensity and a new resonance appears at −23 ppm. Though the position of this peak does not change significantly on further addition of water, it becomes sharp at a pyridine to water ratio of 1:1 (v/v). At this ratio the high spin resonances completely disappear and only low spin resonances remain.

By analogy to the hemin chloride—pyridine—water solution [3, 8], we suggest that addition of water to the pyridine solutions of Fe(TPP)Cl and Fe(OEP)Cl favours the formation of an aquo complex, [Fe(PP)-(py)(H$_2$O)]Cl in which both the pyridine and water
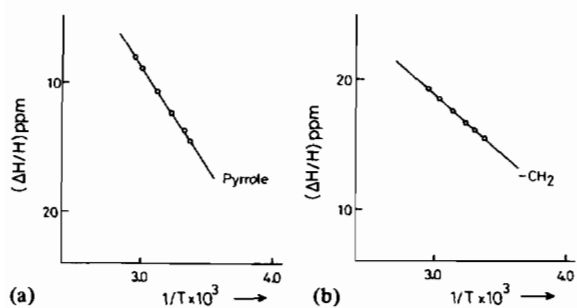
Fig. 5. Electronic absorption spectra of Fe(TPP)Cl (a) and Fe(OEP)Cl (b) in chloroform (———); pure dry pyridine (- - - -) and in pyridine—water solution (— • —).

Fig. 6. Curie plots for Fe(TPP)Cl (a) and Fe(OEP)Cl (b) in pyridine—water solutions.

TABLE II. Variable Temperature Solution Magnetic Moment Data for Fe(TPP)Cl and Fe(OEP)Cl in Pyridine—Water Solutions

T (K)	μ (BM)	
	Fe(TPP)Cl	Fe(OEP)Cl
297	3.78	4.70
310	3.845	4.80
320	3.91	4.86
330	3.97	4.93
840	4.02	5.00

330 K in solution at this pyridine/water ratio are listed in Table II. All these results are consistent with the suggestion that the aquo complex shows a thermal spin-equilibrium $S = 5/2 \rightleftharpoons S = 1/2$ with the $S = 1/2$ state lying lower. In this regard the aquo complex of these synthetic porphyrins is similar to that of the natural porphyrin.

Conclusion

The present proton NMR and magnetic moment measurements establish that high spin ferric complexes of synthetic porphyrins such as Fe(TPP)Cl and Fe-(OEP)Cl exist as high spin species. In pyridine—water solutions six-coordinated mono-aquo mono-pyridine ferric porphyrin complexes exist exclusively at higher concentrations of water and show a thermal spin-equilibrium between the $S = 5/2 \rightleftharpoons S = 1/2$ states.

References

1 W. A. Gallagher and W. B. Elliot, *Biochem. J., 108,* 131 (1968).
2 J. A. Weighman, N. J. Hoyle and R. J. P. Williams, *Biochim. Biophys. Acta, 244,* 567 (1971).
3 H. A. Degani and D. Fiat, *J. Am. Chem. Soc., 93,* 4281 (1971).
4 H. A. O. Hill and K. G. Moralle, *J. Am. Chem. Soc., 94,* 131 (1972).
5 C. Bartocci, F. Scandola, A. Ferri and V. Carassiti, *Inorg. Chim. Acta, 37,* L473 (1979).
6 C. E. Castro and S. E. Anderson, *J. Am. Chem. Soc., 24,* 1113 (1985).
7 L. B. Dugad, O. K. Medhi and S. Mitra, *Inorg. Chem., 26,* 1741 (1987).
8 S. Mazumdar, L. B. Dugad, O. K. Medhi and S. Mitra, *J. Chem. Soc., Dalton Trans.,* in press.
9 (a) A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem., 32,* 476 (1967); (b) A. D. Adler, F. R. Longo, F. Kampus and J. Kim, *J. Inorg. Nucl. Chem., 32,* 2443 (1970).
10 C. A. Reed, T. Mashiko, S. P. Bentler, M. E. Kastner, W. R. Scheidt, K. Spartalion and G. Lang, *J. Am. Chem. Soc., 101,* 2948 (1979).
11 G. N. LaMar and F. M. Walker, in D. Dolphin (ed.), 'The Porphyrins', Vol. IV, Academic Press, New York, 1979, Chap. 2.
12 D. V. Behere, R. Birdy and S. Mitra, *Inorg. Chem., 21,* 386 (1982).

are axially coordinated to the iron. Figures 1 and 2 show that at large concentrations of water ($\geqslant 1:1$ v/v) only the aquo complex is exclusively present in solution. Temperature dependence of the *IPS* of this aquo complex shows a behaviour opposite to the Curie law (Fig. 6). Magnetic moments measured between 297—