# Magnetic Properties of Hemichrome Salts [Derivatives of Iron(III) Octaethylporphyrin Complexes]: the Presence of a 'Spin-Equilibrium'

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*Summary* The temperature dependence of the effective magnetic moments of hemichrome salts, namely bis(pyridine)octaethylporphinato iron(III) perchlorate and hexafluorophosphate, in both the solid state and in solution are interpreted in terms of a spin-equilibrium between two states, predominantly $S' = \frac{1}{2}$ and $S' = \frac{5}{2}$.

SOME of us have previously reported[1] the investigation of the $^1$H n.m.r. spectra of bis-pyridine complexes of the protoporphyrin iron(III) cation. The temperature dependence of the paramagnetic shifts led the authors to postulate the presence of a spin-equilibrium presumably between states characterised as low-spin, ($S = \frac{1}{2}$) and high-spin ($S = \frac{5}{2}$) though the possible intervention of the intermediate spin-state, $S = \frac{3}{2}$, was alluded to. At the time it was suggested that both states belonged to the same chemical species, *i.e.* $[\mathrm{Fe(Proto\text{-}DME)(Py)_2}]^+$.[†] The possibility that the high-spin form corresponded to the monopyridine complex Fe(Proto-DME)(Py) was considered but the absence of a dependence of the paramagnetic shifts of the porphyrin resonance on the concentration of the pyridine rendered this possibility unlikely. However it could not be completely excluded and recently others[2,3] have reconsidered this problem. In this paper we compare the temperature

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[†] Abbreviations used: $(\mathrm{Proto\text{-}DME})^{2-}$ or $(\mathrm{OEP})^{2-}$ = dianions of protoporphyrin IX dimethyl ester or octaethylporphyrin; Py = pyridine, 3-ClPy = 3-chloropyridine, 4-$\mathrm{NH_2}$Py = 4-aminopyridine, 1-MeIm = 1-methylimidazole.

dependence of the effective magnetic moment of octaethylhemichrome cations, $[Fe(OEP)L_2]^+$ where L = Py, 3-ClPy, 4-$NH_2$Py, or 1-MeIm, in solution *and in the solid state*. The Faraday balance and the techniques used for the latter measurements are described elsewhere.[4]

The perchlorates were prepared by a slight modification of a previously published method.[5] The hexafluorophosphates were readily obtained from a hot solution of octaethylhemin in a mixture of the nitrogeneous base (L), dichloromethane, and methanol (1 : 10 : 8, v/v) by adding a hot, concentrated aqueous solution of ammonium hexafluorophosphate (*ca.* 1 vol) and reducing the volume until crystallization started.[6] All salts had satisfactory analyses.

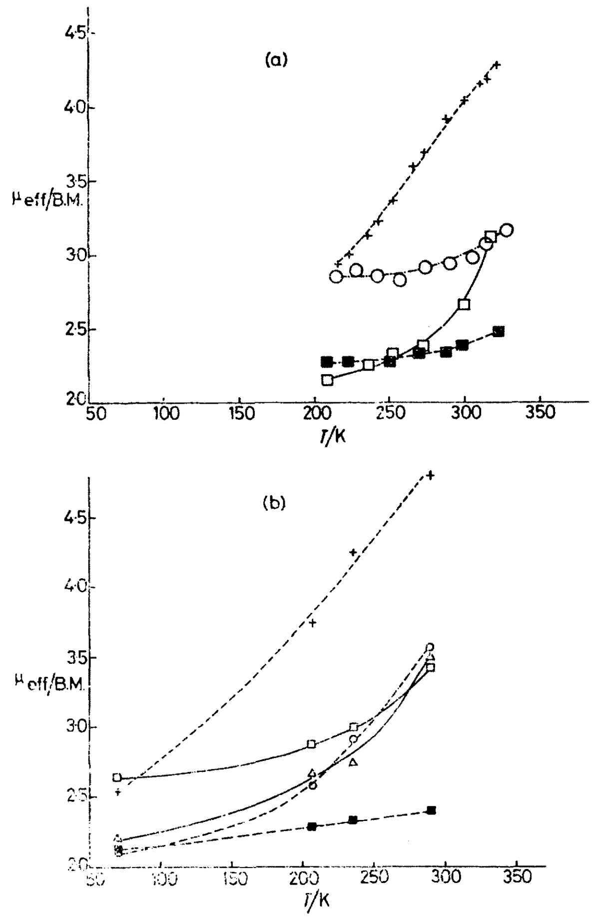

FIGURE (a) Temperature dependence of the effective magnetic moments, $\mu_{eff}$, of hemichrome salts; (a) in chloroform at the concentrations shown: +, [Fe(OEP) (3-ClPy)$_2$]$^+$ $ClO_4^-$ (0·027M); ○, [Fe(OEP) (4-$NH_2$Py)$_2$]$^+$ $ClO_4^-$ (0·021M); □, [Fe(OEP) (Py)$_2$]$^+$ $ClO_4^-$ (0·049M); ■, [Fe(OEP) (1-MeIm)$_2$]$^+$ $ClO_4^-$ (0·034M); (b) determined by susceptibility measurements on solid samples: +, [Fe(OEP) (3-ClPy$_2$)]$^+$ $PF_6^-$; □, [Fe(OEP) (Py)$_2$]$^+$ $ClO_4^-$; △, [Fe(OEP) (Py)$_2$]$^+$ $PF_6^-$; ○, [Fe(OEP) (4-$NH_2$Py)$_2$]$^+$ $PF_6^-$; ■, [Fe(OEP) (1-MeIm)$_2$]$^+$ $PF_6^-$. In all plots the lines through the experimental points are illustrative only.

The temperature dependence of the effective magnetic moments of the complexes in solution (Figure, a) and as solids (Figure, b) indicate that in *both* physical states there is a marked dependence of $\mu_{eff}$ on $T$, typical of that expected for an equilibrium between states characterised by different spin multiplicities. The values of $\mu_{eff}$ of the complexes in solution are not concentration dependent. The effect of adding excess of pyridine ligand is within the experimental error. The behaviour in both solution and solid states is similar though there are differences in detail, just as there are in the solid state between perchlorates and hexafluorophosphates of the same cation (Figure, b). This suggests that the position of the equilibrium at a given temperature is sensitive to the immediate environment of the iron(III) porphyrin cation. This obviously includes the axial pyridine ligand but the results suggest that the magnetic behaviour is responsive to the counter-ion and even the state of solvation. The extreme values of the effective magnetic moment observed, *e.g.* 2·2 and 4·8 B.M., and the behaviour of the curves at temperatures above 300 K suggest that the equilibrium is between two states, one of which is[7] predominantly $S' = \frac{1}{2}$, and the other, $S' = \frac{5}{2}$. Though there are differences in detail, the overall similarity between the magnetic behaviour in solution and in the solid state suggests that the equilibrium present is between two spin-states of the same chemical species $[Fe(OEP)(Py)_2]^+$. As in the previous work[1] the equilibrium is most dependent on the ligands co-ordinated to the iron, the imidazole complexes being essentially low-spin, and the 3-chloro-pyridine complexes showing, in the accessible temperature range, properties characteristic of both spin states. As expected, there is an increasing contribution of the high-spin state as the ligand field strength of L decreases. It is interesting that, as in the iron(II) porphyrin complexes, the variation of the axial ligand can result in a change in spin-state (and concomitant structural changes[8]). Whether those in the iron(III) complexes are of any biological relevance remains to be seen.

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