©*Proc. Indian natn. Sci. Acad.*, **52**, A, No. 4, 1986, pp. 886–890
Printed in India.

MAGNETIC TITRATIONS OF Fe^{III} PORPHYRIN COMPLEXES WITH NITROGENEOUS BASES USING NMR METHOD*

D F EVANS *and* T A JAMES

Inorganic Chemistry Laboratories, Imperial College, London SW7 2AY, UK

(*Received 7 March 1986*)

An nmr method has been used to measure the paramagnetic susceptibilities of Fe^{III} porhyrin halides in chloroform solution in the presence of imidazole. 1-methylimidazole, pyridine and 4-dimethylaminopyridine. By carrying out the magnetic titrations in the nmr tube, only *ca* 3mg of the prophyrin complex is required. Constants β_2 are reported for the equilibria:

$$Fe(P)\ X + 2L \rightleftharpoons Fe(P)\ L_2^+X^-.$$

Key Words : Magnetic Titration by NMR; Iron Porphyrins

INTRODUCTION

A number of years ago, an nmr method was introduced[1] for measuring the paramagnetic susceptibilities of substances in dilute solution. In this method, a coaxial nmr tube is used, with the solvent and reference in one compartment, and the solution and reference in the other. The difference in frequency, Δf, between the two reference signals is given by the expression[2]

$$\frac{\Delta f}{f} = \frac{2\pi}{3}\Delta K, \qquad \ldots (1)$$

where ΔK is the difference in volume susceptibilities caused by the paramagnetic solute. Combining this equation with the Wiedeman adductivity relationship for magnetic susceptibilities gives

$$\chi_g = \frac{3\Delta f}{2\pi f m} + \chi_0 + \frac{\chi_0(d_0 - d_s)}{m}, \qquad \ldots (2)$$

where χ_g is the magnetic susceptibility of the solute, χ_0 that of the solvent, m is g/cm^3 of solute, d_0 is the density of the solvent and d_s that of the solution. This expression is rather inconvenient to use since it involves the accurate measurement of densities. If it is assumed that for a paramagnetic metal complex, the diamagnetic contribution is equal to that of the solvent we obtain[3] the following simple expression for the magnetic moment μ_{eff} of the metal ion :

$$\mu_{eff} = 0.0618\left(\frac{\Delta f M}{f T}\right)^{1/2}, \qquad \ldots (3)$$

*Presented at the INSA Golden Jubilee Symposium on *Recent Trends in Inorganic Chemistry* held in Calcutta in December 1985.

where f is the oscillator frequency (expressed in MHz), T is the absolute temperature and M is the molarity of the solution. A comparison of the full expression and the approximate equation (3) for a number of systems has shown that the latter is a good approximation.[3] For a binuclear or polynuclear complex, equation (3) will give the magnetic moment per metal ion if the molarity M is expressed in terms of the metal. It should be noted that for nmr spectrometers using superconducting solenoids, because of the vertical magnetic field axis, f in equation (3) should be replaced by $2f$. A 500MHz spectrometer will thus have values of Δf which are 16.7 × those for a routine 60 MHz spectrometer, enabling very dilute solutions, such as those obtained with metal enzymes, to be studied.

The nmr method is very suitable for magnetic titrations, including those in which the spin state of a metal ion changes on addition of a ligand. For this purpose, a different experimental arrangement is more convenient.[4] A normal nmr tube is used, which contains a capillary held centrally by PTFE spacers. Sealed in this capillary is a suitable external reference whose resonance lies a few Hz downfield of the internal reference. Magnetic titrations can be carried out by directly adding the titrant to the nmr tube with a microlitre syringe. A calculation of the initial magnetic moment then requires a separate measurement with solvent and reference in the nmr tube. Addition of the titrant will, of course, cause slight changes in Δf due to differences in the diamagnetic susceptibilities of the titrant and of the solvent. For comparatively small additions of titrant (< 10 per cent by volume), these shifts change linearly with the concentration of titrant. Accordingly, a further measurement with solvent, reference and the maximum amount of titrant will allow accurate values of Δf in equation 3 to be obtained throughout the titration.

In the present work, this technique has been applied to the magnetic titration of Fe^{III} porphyrin halides in chloroform solution with a number of ligands. The prophyrins used were protoporphyrin IX dimethyl ester, tetraphenylporphyrin and tetra (*p*-methoxyphenyl) porphyrin.

Experimental

The Fe^{III} porphyrin halides were prepared by standard routes, and gave satisfactory analyses. The chloroform was passed through an alumina column to remove ethanol. Magnetic susceptibilities were measured using a Perkin Elmer R32 90MHz spectrometer. The internal reference was 3 per cent hexamethyldisiloxane, and the capilliary contained 53 per cent hexamethyldisiloxane and 47 per cent bromoform by volume. The ligand was added, either as the pure liquid or as a concentrated solution in chloroform, from a 5μl syringe. An allowance for the change in concentration during the titration was made.

The Fe^{III} porphyrin complex was weighed on a Beckmann LM-500 microbalance and washed into the nmr tube with dihloromethane which was subsequently evaporated. In this way, only *ca* 3mg was needed for each titration. The concentrations of Fe(P) X were normally 0.01M.

Results and Discussion

In the solid state[5] and in solution in organic solvents, the Fe^{III} porphyrin halides are 5 coordinate, with high spin Fe^{III}(μ *ca* 5.9). Studies of visible absorption spectra,[6] and of paramagnetic shifts in the ^1H nmr spectra[7] have shown that with nitrogenous ligands such as imidazole, the predominant equilibrium in solution is :

$$\underset{a-x}{Fe(P)\,Cl} + \underset{b-2x}{2L} \leftrightarrows \underset{x}{Fe(P)\,L_2^+\,Cl^-}, \quad \beta_2 = K_1K_2 \qquad \ldots(4)$$

The 2 : 1 complexes normally contain low-spin Fe^{III}, with μ *ca* 2.0 B.M. K_2 is usually much greater than K_1 and this has been attributed[7] to a change from high spin Fe^{III} to low-spin Fe^{III} which occurs in going from the 1:1 complex to the 2:1 complex. This was confirmed by Sweigart *et al*[8] who characterised transient 6 coordinate high spin intermediates of the type Fe*PLX*, which rapidly convert to the low spin 2 : 1 adducts.

For the above equilibrium, it can be shown that

$$X^3 - (a + b)\,X^2 + [b^2\beta_2 + 4ab\,\beta_2 + 1]\,X/4\beta_2 - ab^2/4 = 0 \qquad \ldots(5)$$

A computer programme solved this expression for x with an assumed value of β_2 for each point on the titration curve. These values of x were then compared with those calculated from the expression

$$\mu^2 = \mu^2_{HS}\,(a - x) + \mu^2_{LS}\,(x),$$

where μ is the actual magnetic moment, μ_{HS} is that for the halide, and μ_{LS} that for the adduct. μ_{HS} and μ_{LS} can be obtained from the initial and final parts on the titration curve. The programme varied β_2 until the best least squares fit was obtained i.e. one which minimizes $\Sigma\,(\mu^2_{calc}-\mu^2)^2$.

Typical results are shown graphically in Fig. 1. The calculated and experimental values of μ are in quite good agreement, indicating that equation (4) does indeed represent the main equilibrium. The values of β_2 obtained are given in the Table, together with some related results obtained by other workers.

These results, together with other data in the literature,[6,7] show a number of trends. As regards the halogen, β_2 increases very markedly in the order F < Cl < Br < I (Fe) TPP) F does not form a complex at all with 1-methylomidazole[7]) corresponding to the decrease in Fe*X* bond strength. The ratios of β_2(Br)/β_2(Cl) for the TPP and PPI*X*-DME complexes with 1-methylimidazole are in good agreement (36.5 and 34.4 respectively). As regards the ligand, imidazole forms much more stable complexes than 1-methylimidazole, which has been ascribed to hydrogen bonding between imidazole and the halide ion.[9] For substituted imidazoles and pyridines, the stability constant increase as expected, with increase in basicity of the ligands. However, the values of β_2 are much greater in the imidazole series than in the pyridine series. This has been attributed to π-bonding from the imidazoles to the Fe^{III} ion.[10]

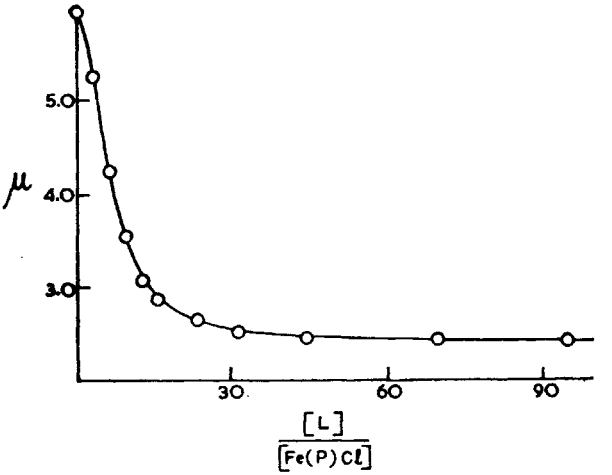

FIG. 1. Magnetic titration of 1-methylimidazole with Fe(TPP)Cl Chlorofrom solutions (0.01M), 35 °C. The solid line represents the magnetic moments calculated from the computer programme and the given values of β_2.

TABLE I

Values of β_2 *for the equilibrium* $Fe(P)\ X + 2L \rightleftharpoons Fe(P)\ L_2^+X^-$

(Solvent chloroform unless otherwise stated)

Complex	*L*	*T* (°C)	This work	β_2 N.M.R.[a]	Abs. Spec [b]
Fe(TPP) Cl	Im	25		10^6	1.58×10^6
,,	1-MeIm	,,	2.05×10^3[c]	1.38×10^3	1.5×10^3
,,	,,	35	5.75×10^2		
,,	,,	25			1×10^4[d]
Fe(TPP) Br	1-MeIm				
,,	,,	35	2.1×10^4		
Fe(TMPP) Cl	1-MeIm	25		4×10^3	3.6×10^3
,,	,,	35	6.5×10^2		
Fe(TPP) I	Py	37.4	2.4×10^2		
	1-MeIm	25			1×10^7
Fe(PPIX–DME) Cl	,,	35	2.85×10^3		
Fe(PPIX–DME) Br	,,	35	9.79×10^4		
Fe(TPP) Cl	Me_2Py	35	2.6×10^2		
Fe(PPIX–DME) Cl	,,	35	8.2×10^2		

(*a*) Ref. 7; (*b*) Ref. 6; (*c*) At 24.6 °C; (*d*) Dichloromethane solution.

REFERENCES

1. D F Evans *J chem Soc* (1959) 2003
2. W C Dickinson *Phys Rev* **81** (1951) 717

3. D F Evans and T A James *J chem Soc Dalton Trans* (1979) 723
4. D F Evans *J chem Soc Dalton Trans* (1973) 1973
5. A H White and B W Skelton *Aust J Chem* **30** (1977) 2655; J L Hoard G H Cohen and M D Glick *J Am chem Soc* **89** (1967) 1992
6. F A Walker M W Lo and M Tutran Ree *J Am chem Soc* **98** (1976) 5552
7. J D Saterlee G N La Mar and J S Frye *J Am chem Soc* **98** (1976) 7275
8. M Qing-jin G A Tonderau J O Edwards and D A Sweigart *J chem Soc Dalton Trans* (1985) 2269 and references therein
9. M Nappa J S Valentine and P A Snyder *J Am chem Soc* **99** 5799
10. L M Epstein D K Straub and C Maricondi *Inorg chem* **6** (1967) 1720