

## Binding of Nitrogenous Bases to Iron(II) Phthalocyanine in Dimethylsulfoxide

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*An iterative technique employing computer processing of spectrophotometric data has been used to obtain the two formation constants for complexing of nitrogenous bases with Iron(II) phthalocyanine in dimethylsulfoxide. Good correlations of  $K_f$  with  $pK_{BH^+}$  are obtained for the first formation step with a closely related set of ligands.  $\pi$ -bonding does not appear as important as in similar reactions with ferrous porphyrins.*

### Introduction

An attempt has been made<sup>1</sup> to obtain complex formation constants for the binding of bases at the axial positions of Iron(II) phthalocyanine, but the graphical method used to process the data applied precisely for the binding of cyanide alone, as only in this case was there a well defined maximum in the graph of optical density against base concentration per unit of Iron(II) phthalocyanine. Using numerical methods it has proved possible to extend this work, and the formation constants obtained are useful for comparison with those obtained in porphyrin systems.<sup>2</sup>

### Experimental

Solid bases obtained commercially were re-crystallised from ethanol and dried; liquid ones were distilled

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from potassium hydroxide pellets. Physical properties agreed with literature values. The preparation of Iron(II) phthalocyanine and purification of dimethylsulfoxide have already been described in detail.<sup>4</sup> The purity of the Iron(II) phthalocyanine was established by elemental analysis, infra-red spectroscopy, and by the fact that its extinction coefficient, when dissolved quantitatively in pyridine, agreed with that of previous workers<sup>1,3</sup> and gave the wavelength maxima quoted (Table I).

A solution approximately  $10^{-5}M$  in Iron(II) phthalocyanine was prepared under nitrogen in dmsO, and its strength was determined by diluting it accurately with a measured excess of pyridine, such that the solution was at least  $0.5M$  in pyridine. For practical purposes this converts all the Iron(II) phthalocyanine to its bis-base adduct<sup>1</sup> and one can use the extinction coefficients of Table I to calculate the strength of the original Iron(II) phthalocyanine solution. Our results (Table V), giving an overall formation constant of 250 for  $FePc(py)_2$ , show that in a solution  $10^{-5}M$  in  $FePc$ , and  $0.6M$  in pyridine, 99% of  $FePc$  is converted to  $FePc(py)_2$ , and the spectrum in  $0.6M$  pyridine is indistinguishable from that in pyridine (Table I). Even in  $0.1M$  pyridine, where there will be only 73% conversion to  $FePc(py)_2$ , change in absorbance is only significant at 413 nm. A series of solutions (between 12 and 20) each containing the same amount of freshly prepared Iron(II) phthalocyanine/dmsO solution of known concentration, together with known amounts of purified base were made up in volumetric flasks (10 ml). The highest concentration of base used depended on the particular ligand, its value being such that the observed optical density approached the optical density

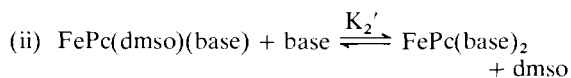
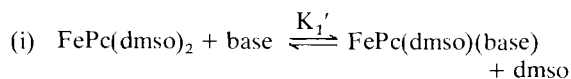
TABLE I. Visible Spectrum of Ferrous Phthalocyanine in Pyridine and in Pyridine/DmsO Solutions.

This work		Whalley <sup>3</sup>		Dale <sup>1</sup>		0.63 M py/dmsO		0.1 M py/dmsO (Dale <sup>1</sup> )	
$\lambda_{max}$ , nm	$\log_{10}\epsilon_{max}$	$\lambda_{max}$	$\log_{10}\epsilon_{max}$	$\lambda_{max}$	$\log_{10}\epsilon_{max}$	$\lambda$	$\log_{10}\epsilon_{max}$	$\lambda$	$\log_{10}\epsilon_{max}$
655	5.07	654	5.03	654	5.11	655	5.07	656	5.08
593	4.47	593	4.47	592	4.48	593	4.49	595	4.49
413	4.32	414	4.29	415	4.31	413	4.32	415	4.29
332	4.82	329.5	4.88	330	4.88	—	—	—	—

in the presence of sufficient base to cause complete conversion to  $\text{FePc}(\text{base})_2$ . After allowing the solutions to equilibrate for at least an hour\* at  $25.0^\circ\text{C}$  the optical density of each solution was measured using a Unicam SP600 single beam instrument at a wavelength having a maximum characteristic of  $\text{FePc}(\text{base})_2$  (Table IV).

#### Method of Data Treatment

The equilibria involving species based on Iron(II) phthalocyanine were assumed to be:



Let two equilibrium constants,  $K_1$  and  $K_2$  now be defined which do not include the solvent concentration ( $K_1'$ ,  $K_2'$  do)

$$(iii) K_1 = \frac{[\text{FePc}(\text{dmsO})(\text{base})]}{[\text{FePc}(\text{dmsO})_2][\text{base}]} = \frac{K_1'}{[\text{dmsO}]}$$

$$(iv) K_2 = \frac{[\text{FePc}(\text{base})_2]}{[\text{FePc}(\text{dmsO})(\text{base})][\text{base}]} = \frac{K_2'}{[\text{dmsO}]}$$

Let these further terms be defined.

- $a_s$ : Concentration of  $\text{FePc}(\text{dmsO})_2$  before reaction
- $a_e$ : Equilibrium concentration of  $\text{FePc}(\text{dmsO})_2$
- $b_s$ : Concentration of base before reaction
- $b_e$ : Equilibrium concentration of base
- $c_e$ : Equilibrium concentration of  $\text{FePc}(\text{dmsO})(\text{base})$
- $d_e$ : Equilibrium concentration of  $\text{FePc}(\text{base})_2$
- $\epsilon_A$ : Molar extinction coefficient of  $\text{FePc}(\text{dmsO})_2$  at the particular wavelength used for measurements
- $\epsilon_B$ : Molar extinction coefficient of base at the particular wavelength used for measurements (equal to zero)
- $\epsilon_C$ : Molar extinction coefficient of  $\text{FePc}(\text{dmsO})(\text{base})$  at the particular wavelength used for measurements
- $\epsilon_D$ : Molar extinction coefficient of  $\text{FePc}(\text{base})_2$  at the particular wavelength used for measurements
- $A_e$ : The optical density of the solution at the particular wavelength used for measurements

Then:

$$(v) A_e = \epsilon_A a_e + \epsilon_C c_e + \epsilon_D d_e \quad (\text{path length is 1 cm}).$$

In equilibrium measurements the ferrous phthalocyanine concentration,  $a_s$ , was kept constant and the base concentration,  $b_s$ , varied,  $A_e$  being measured for each value of  $b_s$ . For any particular values of  $b_s$ , and

$a_s$  the quantities  $a_e$ ,  $c_e$  and  $d_e$  could be related to  $b_s$ ,  $a_s$ ,  $K_1$  and  $K_2$  by these equations:

$$(vi) \quad a_e = a_s / \{1 + K_1 b_e + K_1 K_2 b_e^2\}$$

$$(vii) \quad c_e = K_1 a_s b_e / \{1 + K_1 b_e + K_1 K_2 b_e^2\}$$

$$(viii) \quad d_e = K_1 K_2 a_s b_e^2 / \{1 + K_1 b_e + K_1 K_2 b_e^2\}$$

If  $K_1$  and  $K_2$  are each less than 100 and  $b_s$  is much greater than  $a_s$ , then  $b_e \sim b_s$ , and provided  $\epsilon_A$ ,  $\epsilon_C$  and  $\epsilon_D$  are known, measurements of  $A_e$  with constant  $a_s$  and various  $b_s$  values should be perfectly capable of giving  $K_1$  and  $K_2$ . To a greater degree of sophistication  $b_e$  was calculated from the cubic equation below:

$$(ix) \quad 0 = K_1 K_2 b_e^3 + (2K_1 K_2 a_s + K_1 - K_1 K_2 b_s) b_e^2 + (K_1 a_s + 1 - K_1 b_s) b_e - b_s$$

TABLE II. Isophthalic Acid, Observed and Calculated Optical Densities Using  $K_1 = 2.39 \times 10^{-4}$ ,  $K_2 = 3.31 \times 10^{-5}$ ,  $\epsilon_C = 2.88 \times 10^3$ , data from ref. 5b.

pH	OD <sub>obs</sub>	OD <sub>calc</sub>
0.3	0.354	0.3529
1.19	0.354	0.3533
2.09	0.355	0.3560
2.73	0.365	0.3653
2.77	0.367	0.3663
2.93	0.372	0.3712
2.98	0.372	0.3730
3.05	0.375	0.3757
3.095	0.378	0.3776
3.17	0.381	0.3809
3.21	0.382	0.3828
3.31	0.386	0.3876
3.405	0.393	0.3924
3.47	0.397	0.3957
3.49	0.397	0.3967
3.58	0.403	0.4011
3.68	0.404	0.4054
3.69	0.407	0.4058
3.79	0.408	0.4092
3.89	0.410	0.4114
3.99	0.414	0.4122
4.09	0.413	0.4116
4.11	0.410	0.4112
4.18	0.409	0.4112
4.28	0.405	0.4063
4.38	0.401	0.4017
4.49	0.397	0.3956
4.60	0.390	0.3889
4.675	0.383	0.3842
4.77	0.379	0.3783
4.87	0.373	0.3723
4.97	0.367	0.3668
5.22	0.355	0.3556
5.29	0.350	0.3531
5.54	0.348	0.3463
5.86	0.343	0.3412
6.75	0.337	0.3379
7.37	0.337	0.3364

\* Calculations using formation rate constants already determined,<sup>4</sup> and some unpublished, showed that this is many times the period required for complete reaction.

TABLE III. Results of Calculations on Isophthalic Acid.<sup>a</sup>(a)  $\lambda = 248$  nm, data from 5(b).

Values	$K_1$	$K_2$	$\epsilon_{HA^-}$	$\Sigma (\text{relative deviation})^2/n$
Starting	$1 \times 10^{-4}$	$1 \times 10^{-5}$	$3 \times 10^3$	$2.9 \times 10^{-3}$
Final	$2.39 \times 10^{-4}$	$3.31 \times 10^{-5}$	$2.88 \times 10^3$	$9.2 \times 10^{-6}$
Literature	$2.24 \times 10^{-4}$	$3.63 \times 10^{-5}$	$2.92 \times 10^3$	$1.1 \times 10^{-5}$

(b)  $\lambda = 246$  nm, data from 5(a).

Values	$K_1$	$K_2$	$\epsilon_{HA^-}$	$\Sigma (\text{relative deviation})^2/n$
Starting	$1 \times 10^{-5}$	$1 \times 10^{-5}$	$3 \times 10^3$	$5.3 \times 10^{-3}$
Final	$2.73 \times 10^{-4}$	$4.40 \times 10^{-5}$	$3.28 \times 10^3$	$9.3 \times 10^{-6}$
Literature	$2.80 \times 10^{-4}$	$4.00 \times 10^{-5}$	$3.23 \times 10^3$	$1.4 \times 10^{-5}$

(c)  $\lambda = 247.6$  nm, data from 5(a).

Values	$K_1$	$K_2$	$\epsilon_{HA^-}$	$\Sigma (\text{relative deviation})^2/n$
Starting	$1 \times 10^{-5}$	$1 \times 10^{-5}$	$3 \times 10^3$	$3.5 \times 10^{-3}$
Final	$2.36 \times 10^{-4}$	$4.16 \times 10^{-5}$	$4.08 \times 10^3$	$7.9 \times 10^{-6}$
Literature	$2.8 \times 10^{-4}$	$4.0 \times 10^{-4}$	$4.02 \times 10^3$	$1.6 \times 10^{-5}$

<sup>a</sup> Relative deviation =  $[\text{OD}_{\text{obs}} - \text{OD}_{\text{calc}}]/\text{OD}_{\text{obs}}$ . n = number of observations.

Input parameters in our computer aided calculations consisted of  $a_s$ ,  $\epsilon_A$ ,  $\epsilon_D$ , approximate values of  $K_1$ ,  $K_2$  and  $\epsilon_C$  ( $\epsilon_C$  was assumed to be the mean of  $\epsilon_A$  and  $\epsilon_D$ ) together with a ( $b_s$ ,  $A_e$ ) data set. The programme, involving a Simplex\* minimisation method, then refined the values of  $K_1$ ,  $K_2$ , and  $\epsilon_C$  so as to obtain a minimum of the sum of the squares of the relative deviations between observed and calculated optical densities.

Before employing it on Iron(II) phthalocyanine equilibria the method was checked using data on the variation of the absorbance of dibasic acids<sup>5</sup> with pH, a case where graphical methods work because  $b_e$  is defined by pH measurements, and there is a well defined maximum or minimum in the absorbance–pH plot. Thus, for a dibasic acid  $H_2A$ , the optical density at the wavelength concerned,  $\lambda$ , at pH<sub>i</sub> is:

$$O.D._{\lambda i} = \epsilon_{H_2A}[H_2A]_i + \epsilon_{HA^-}[HA^-]_i + \epsilon_{A^{2-}}[A^{2-}]_i$$

In these systems  $\epsilon_{H_2A}$  and  $\epsilon_{A^{2-}}$  can be obtained from experiments in strongly acid and alkaline solutions. Initially  $K_1$  and  $K_2$  were set at  $1 \times 10^{-4}$  or  $1 \times 10^{-5}$  and an estimate of  $\epsilon_{HA^-}$  was obtained from the maximum in the optical density/pH curve and the total concentration of organic acid used.

Table II shows the observed optical densities for isophthalic acid and those calculated from the final values

\* The procedure is outlined by several authors, e.g. J. A. Nelder and R. Mead, *Comput. J.*, 7, 308 (1965), and the programme was written by M.V.T. in I.C.L. 4100 Algol.

of  $K_1$ ,  $K_2$  and  $\epsilon_{HA^-}$  which produced the minimum sum of the squares of the relative deviations between observed and calculated optical densities. Table III shows that our method gives values of  $K_1$ ,  $K_2$  and  $\epsilon_{HA^-}$  which are similar to the published values but with smaller values for the deviation between observed and calculated optical densities.

TABLE IV. Observed and Calculated Optical Densities (425 nm, 25°C) for 4-aminopyridine Complex Formation Using  $K_1 = 6.18 \times 10^3$ ,  $K_2 = 6.17 \times 10^3$ ,  $\epsilon_A = 4.6 \times 10^3$ ,  $\epsilon_C = 8.5 \times 10^3$ ,  $\epsilon_D = 2.0 \times 10^4$ .  $\Sigma\{\text{relative deviation}\}^2/n = 6.2 \times 10^{-4}$ .

Starting Concentration of Base, $b_s$ $a_s = [\text{FePc}] = 3.63 \times 10^{-5} M$	$A_e$ (obs.)	$A_e$ (calc.)
$2.75 \times 10^{-5}$	0.194	0.199
$5.49 \times 10^{-5}$	0.232	0.230
$8.24 \times 10^{-5}$	0.266	0.264
$1.09 \times 10^{-4}$	0.301	0.298
$1.37 \times 10^{-4}$	0.335	0.332
$1.65 \times 10^{-4}$	0.360	0.364
$1.92 \times 10^{-4}$	0.393	0.392
$2.20 \times 10^{-4}$	0.421	0.418
$2.75 \times 10^{-4}$	0.456	0.462
$3.29 \times 10^{-4}$	0.488	0.497
$5.40 \times 10^{-4}$	0.583	0.577
$1.03 \times 10^{-3}$	0.651	0.648
$1.62 \times 10^{-3}$	0.681	0.671

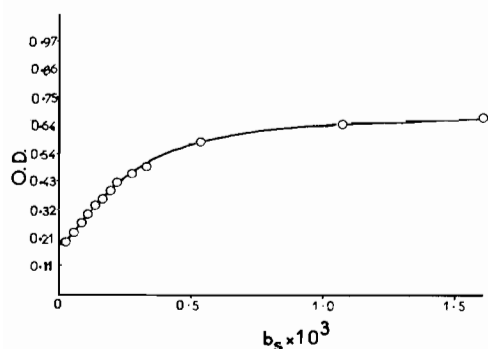


Figure 1. Comparison of calculated and observed absorbance as increasing amounts of 4-aminopyridine are added to a solution of ferrous phthalocyanine in dmsO. (— calculated absorbance; ○ experimental absorbance).

The success of the method with the base 4-aminopyridine is indicated in Table IV and Figure 1. The error parameter we used,

$$\left\{ \sum \left( \frac{OD_{\text{calc}} - OD_{\text{obs}}}{OD_{\text{obs}}} \right)^2 / \text{no. of observations} \right\}$$

is larger than that for the very closely defined dibasic acid system used as a test. In those systems a rather better spectrophotometer was used, more data points were taken, and there was no possibility of extraneous equilibria such as the dimerisation of Iron(II) phthalocyanine.<sup>6</sup>

With weak bases there is doubt as to whether  $\text{FePc}(\text{base})_2$  has formed completely enabling  $\epsilon_D$  to be determined correctly. We have indicated the precautions taken earlier in this section, but calculations varying  $\epsilon_D$  by 10% do not move  $K_1$ ,  $K_2$  values outside the observed error limits in Table V.

## Results and Discussion

Table V summarises the results and compares them with results for the binding of the bases to the proton and to the zinc nucleus of zinc  $\alpha, \beta, \gamma, \delta$ -tetraphenylporphyrin in benzene.<sup>7</sup> It also shows  $K_2$  values increased fourfold, to correct for the statistical factor (the second ligand has half the number of binding sites that the first had available, and twice as many as the first had from which it can dissociate) and make  $K_1$  and  $K_2$  directly comparable.

Table VI gives the observed extinction coefficient of Iron(II) phthalocyanine at the wavelength used, the calculated extinction coefficient of the mono-base species and the observed extinction coefficient of the bis-base species.

From Figure 2 it will be seen that there is a good correlation between  $K_1$  and pyridine basicity. Iron(II)

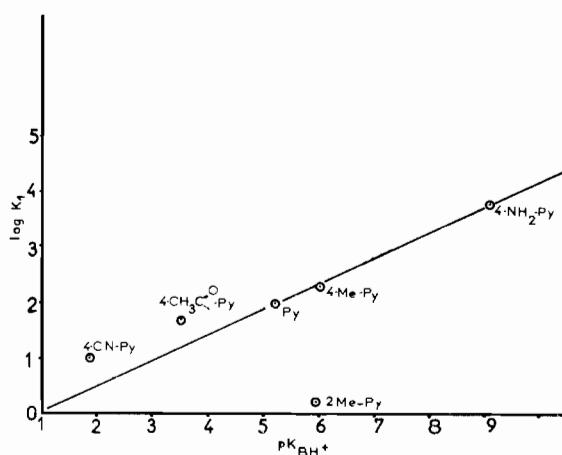


Figure 2. Comparison of first formation constants ( $\log K_1$ ) with ligand basicities ( $pK_{\text{BH}^+}$ ).

TABLE V. Equilibrium Constants at 25°C for the Binding of Heterocyclic Bases to Ferrous Phthalocyanine in DmsO Solution.

Base	$pK_{\text{BH}^+}$	$K_1$	$\log K_1$	$K_2$	$\log K_2$	Corrected $\log K_2$	$\log_{10} K_{\text{Zn}}^{\text{d}}$
Imidazole	6.95 <sup>a</sup>	$(10 \pm 4) \times 10^4$	5.0	$(6.3 \pm 2.0) \times 10^3$	3.8	4.4	—
4-Aminopyridine	9.12 <sup>b</sup>	$(6.2 \pm 2.0) \times 10^3$	3.8	$(6.2 \pm 2.0) \times 10^3$	3.8	4.4	4.65
4-Methylpyridine	6.03 <sup>b</sup>	$200 \pm 40$	2.3	$6.3 \pm 0.6$	0.8	1.4	4.0
Pyridine	5.21 <sup>b</sup>	$100 \pm 18$	2.0	$2.5 \pm 0.16$	0.4	1.0	3.8
4-Acetylpyridine	3.51 <sup>b</sup>	$50 \pm 8$	1.7	$0.40 \pm 0.02$	-0.4	0.2	3.0
4-Cyanopyridine	1.86 <sup>b</sup>	$10 \pm 0.8$	1.0	$4.0 \pm 0.4$	0.6	1.2	2.9
2-Methylpyridine	5.96 <sup>c</sup>	$1.6 \pm 0.5$	0.2	$0.63 \pm 0.05$	-0.2	+0.4	2.3

Errors are standard errors.

<sup>a</sup> from: A. H. M. Kirby and A. Neuberger, *Biochem. J.*, 32, 1146 (1938).

<sup>b</sup> from: A. Fischer, W. J. Galloway and J. Vaughan, *J. Chem. Soc.*, 3591 (1964).

<sup>c</sup> from: R. J. L. Andon, J. D. Cox and E. F. G. Herrington, *Trans. Far. Soc.*, 50, 915 (1954).

<sup>d</sup> Estimated from data in ref. (6).

TABLE VI. Molar Extinction Coefficients for  $\text{FePc}(\text{dmsO})_2$ ,  $\text{FePc}(\text{dmsO})(\text{base})$ ,  $\text{FePc}(\text{base})_2$  ( $\epsilon_M$  to  $\pm 5\%$ ).

Base	Wavelength of bis-base Maximum (nm)	$\epsilon_M \text{FePc}$ $\epsilon_A$	$\epsilon_M \text{FePc}(\text{base})$ $\epsilon_C$	$\epsilon_M \text{FePc}(\text{base})_2$ $\epsilon_D$
Imidazole	426	$3.2 \times 10^3$	$4.1 \times 10^3$	$2.0 \times 10^4$
4-aminopyridine	425	$4.6 \times 10^3$	$8.5 \times 10^3$	$2.0 \times 10^4$
4-methylpyridine	413	$1.0 \times 10^4$	$3.0 \times 10^4$	$2.1 \times 10^4$
Pyridine	413	$8.9 \times 10^3$	$2.8 \times 10^4$	$2.1 \times 10^4$
4-acetylpyridine	405	$9.5 \times 10^3$	$1.7 \times 10^4$	$1.5 \times 10^4$
4-cyanopyridine	404	$1.7 \times 10^4$	$2.8 \times 10^4$	$1.2 \times 10^4$
2-methylpyridine	406	$7.6 \times 10^3$	$5.4 \times 10^4$	$1.8 \times 10^4$

phthalocyanine in dmsO being half as selective an acid as the proton in water. In low spin  $d^6$  systems such as  $\text{FePc}(\text{axial ligand})_2$  there is always some argument as to whether there is back-bonding involving donation of electrons from full  $t_{2g}$  orbitals of the iron to vacant antibonding orbitals of suitable symmetry and energy on the pyridine.<sup>8</sup> Electron withdrawing substituents on the pyridine (*e.g.* nitro, cyano and acetyl groups) are supposed to change the energy of the pyridine  $\pi^*$  orbitals so that they are at a more suitable energy level to accept electrons from the  $t_{2g}$  orbitals of the iron, thus making complexes involving these pyridines more stable than their proton (*i.e.*  $\sigma$ ) basicity would indicate. First formation constant values provide some evidence of this, the complexes with 4-cyano and 4-acetylpyridine being slightly more stable than their basicity would

predict. But the effect is slight, and involves free energies, where entropies as well as heats of base and complex solvation may play some part: heats of bond formation, corrected for solvation effects, should be used if a serious attempt is to be made to estimate  $\pi$  bonding effects. A good relationship (Figure 3) is obtained between  $\log K_1$  and  $\log K_{Zn}$  for the binding of pyridines to zinc tetraphenylporphyrin. 2-Methylpyridine appears far less basic towards Iron(II) phthalocyanine than its proton basicity would suggest (Figure 2) and obviously steric hindrance is involved; this hindrance should be of equal importance for its binding to zinc tetraphenylporphyrin, and its basicity towards ferrous phthalocyanine indeed parallels its low basicity towards the porphyrin (Figure 3).

Turning now to a correlation of the second formation constant with proton basicity (Figure 4), it can be seen that the binding of the second ligand to  $\text{FePc}(\text{base})(\text{dmsO})$  is twice as sensitive to variation in basicity as is binding of the first ligand. Cyano and acetylpyridine clearly bind much more firmly in the second stage than one would expect from their  $\sigma$ -donor

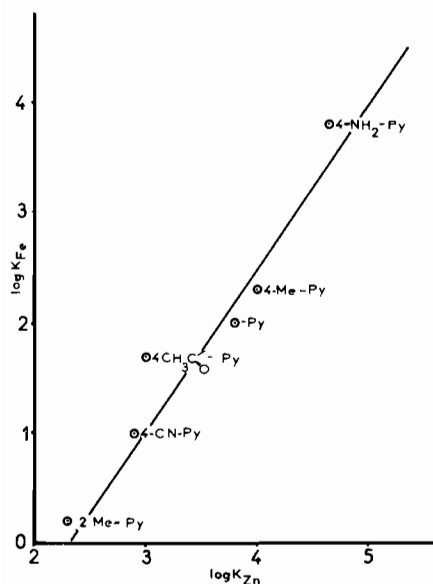


Figure 3. Comparison of first formation constants of pyridines with ferrous phthalocyanine and with zinc  $\alpha,\beta,\gamma,\delta$ tetraphenylporphyrin.

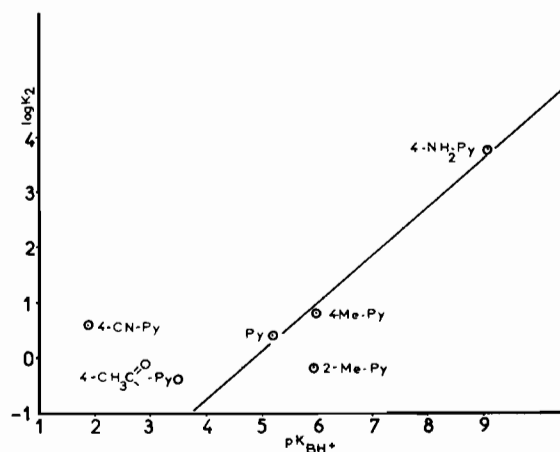


Figure 4. Comparison of second formation constants ( $\log K_2$ ) with ligand basicities.

properties, and it is tempting to say that the binding of the first  $\pi$ -accepting axial ligand has altered the iron  $t_{2g}$  orbitals such that  $\pi$  acceptance by a second axial ligand of the same species is greatly facilitated.\* Applying such arguments to free energy terms is always risky, as entropy effects may be responsible for the increase in stability ascribed to  $\pi$ -bonding. However in this case we will anticipate our results obtained for the first step by the kinetic method<sup>9</sup> and state that enthalpy and entropy self-compensate and no special entropy effects appear to be involved in the cases of those pyridines with electron withdrawing substituents.

Finally, it is of interest to compare the present results with those recently reported by Cole, Curthoys and Magnusson<sup>2c</sup> for pyridines and various Iron(II) haems in benzene. Their results concern an addition reaction at the metal centre whereas ours obtain to a replacement, and they were not able to separate this into two steps as we have our replacements. Correlation between our  $\log K_1 K_2$  values in dmsO and theirs in benzene is poor (Figure 5). In general our formation constants follow ligand basicity, with slight modification when very electronegative substituents are *para* to the pyridine nitrogen, whereas their constants and to a greater extent enthalpy changes are dominated by  $\pi$  back-acceptance from the iron  $t_{2g}$  orbitals of the haems by the ligands chosen by Cole, Curthoys and Magnusson.

### Acknowledgements

M.V. Twigg thanks the Science Research Council for a post-graduate studentship. J.G. Jones thanks the S.R.C. for the award of technical help and the University of Coimbra, Portugal, for hospitality and the use of their excellent library.

\* It could be remarked that  $K_2$  values, apart from that of 4-aminopyridine, span only one order of magnitude, so that it could be argued that  $K_2$  was invariant with pK. But  $K_2$  for 4-aminopyridine is large and subject to less error than smaller  $K_2$  values, so that our feeling is that it cannot be neglected.

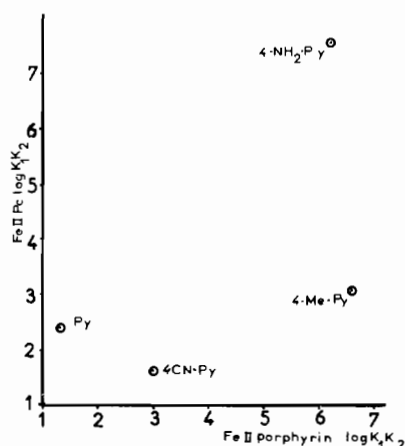


Figure 5. Comparison of overall formation constants ( $\log_{10} K_1 K_2$ ) for the binding of pyridines to ferrous phthalocyanine in dmsO and to Protoporphyrin Iron(II) dimethyl ester in benzene.

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