with pentane, and air dried; mp 63–65°. *Anal.* Calcd for $C_{10}H_{21}NPtCl_2$: C, 28.51; H, 5.02. Found: C, 27.70; H, 4.98.

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Stability Constants and Proton Magnetic Resonance Studies of Zinc $\alpha,\beta,\gamma,\delta$-Tetraphenylporphin and Substituted Pyridines

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The equilibrium constants of ten substituted pyridine derivatives with zinc $\alpha,\beta,\gamma,\delta$-tetraphenylporphin have been measured in benzene at 25°. Only 1:1 complexes are observed. In contrast to iron(II) and magnesium(II) porphyrins, the stability constants parallel the ligand basicity. A linear log K–pK correlation and a Hammett plot with $\rho = +1.50$ was obtained. Proton magnetic resonance studies indicated that the exchange between the coordinated and uncoordinated pyridine was rapid at $-60°$ and that the structures of the zinc(II) and magnesium(II) monopyridinates are similar.

Introduction

The stability constants of reactions between metalloporphyrins (MP) and nitrogenous bases (L) have

$$MP + nL \longrightarrow L_nMP \qquad (1)$$

received considerable attention. With respect to metal ions in reaction 1, Cu(II),[2] VO(II),[3,4] Hg(II),[5] Zn(II),[4] and Cd(II)[5] have $n = 1$, whereas Ni(II)[2,6,7] and Fe(II)[8] show $n = 2$ with no evidence for LMP species. In contrast, magnesium(II) porphyrins normally form LMP and L_2MP complexes.[9] Several studies have focused attention on stability constants of the same metal ion with different types of porphyrins. Using a series of substituted deuteroporphyrins, nickel(II)–pyridine systems[6,7] give linear Hammett plots, whereas magnesium(II)–pyridine systems do not.[9] Work has also been reported on the variation of the stability constants with ligand basicity. Magnesium(II) porphyrins and some Fe(II) derivatives show stability constants that decrease as the ligand basicity increases.[10] Proton magnetic resonance (pmr) studies have been done on magnesium porphyrin–pyridine reactions.[9,11]

We report the stability constants of the reactions between zinc $\alpha,\beta,\gamma,\delta$-tetraphenylporphin[12] and ten substituted pyridine derivatives in benzene at 25°. A pmr study of the zinc porphyrin–pyridine system is also included.

Experimental Section

Tetraphenylporphrin[13] and its zinc complex[14] were synthesized by literature methods. The molar extinction coefficient of the zinc complex in benzene at 550 mμ was 2.27×10^4, the same as that obtained by other workers.[15] Substituted pyridines from various sources were in all cases purified before use.[9]

The stability constants were measured in benzene at 25.0 ± 0.1° by a spectrophotometric titration method using the equations derived by Miller and Dorough.[5] Figure 1 shows a typical titration, in this case of the zinc porphyrin with 4-aminopyridine, and the four isosbestic points were observed. The concentration of the zinc porphyrin was usually in the range of 2×10^{-6} M.

It has been shown[5] that the equilibrium constant, K, for an $n = 1$ process in eq 1 is given by the expression

$$K = \left[\frac{(LMP)}{(MP)}\right]\left[\frac{1}{(L)}\right] = \left[\frac{F_c}{1 - F_c}\right]\left[\frac{1}{B}\right] \qquad (2)$$

F_c is the fraction of the total porphyrin complexed with pyridine and is equal to X/A; $X = D_m - D_u$, and $A = D_u - D_c$, where, at a given wavelength, D_u and D_m are the optical densities of the uncomplexed and fully complexed porphyrin, respectively. D_m is the optical density at a given pyridine concentration. The equilibrium pyridine concentration, B, is equal to the total pyridine concentration, $B_0 - F_cC_t$, with C_t equal to the total porphyrin concentration. Table I shows a typical calculation of K for 4-aminopyridine and the zinc porphyrin using the 550-mμ wavelength in Figure 1.

The reported constants are averages of at least two determinations and are those calculated from the 550-mμ peak. It was found that such constants calculated from the longer wavelength peaks had standard deviations within a run usually of 20–30%, even though good isobestic points were obtained. The spectra

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Table I

Calculation of K for Zinc Tetraphenylporphin and 4-Aminopyridine at 25° in Benzene

$[\mathrm{py}]_{\mathrm{initial}} = B_0$	Obsd[a] optical density, D_m	$X = D_m - D_u$	$F_c = X/A$	$[\mathrm{py}]_{\mathrm{eq}} = B = B_0 - F_cC_t$	$K_{\mathrm{eq}} = \frac{F_c}{1-F_c}\left(\frac{1}{B}\right) \times 10^{-4}$, M^{-1}
0.00	0.846 (D_u)				
9.05×10^{-3}	0.297 (D_c)	0.549 (A)	1.000		
2.01×10^{-3}	0.304	0.542	0.987	1.99×10^{-3}	3.81
60.30×10^{-5}	0.323	0.523	0.952	5.85	3.38
10.10	0.407	0.439	0.779	8.56×10^{-5}	4.64
6.03	0.475	0.371	0.675	4.78	4.34
4.02	0.538	0.308	0.561	2.98	4.26
3.02	0.543	0.303	0.551	1.99	6.14
2.71	0.585	0.261	0.475	1.83	4.96
2.41	0.609	0.237	0.431	1.61	4.69
2.01	0.661	0.185	0.336	1.14	4.46
				Av	$(4.52 \pm 0.52) \times 10^4$

[a] Total zinc porphyrin concentration 1.86×10^{-5} M.

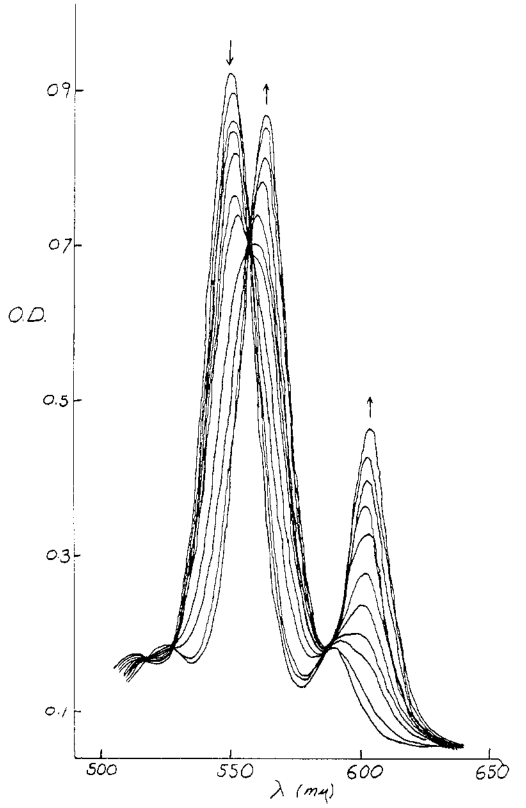

Figure 1.—Optical density *vs.* wavelength curves for the titration of zinc tetraphenylporphin (1.86×10^{-5} M) with 4-aminopyridine in benzene at 25°. The ligand concentrations are given in Table I.

were taken on a Cary Model 14 recording spectrophotometer, with a thermostated cell compartment. The pmr spectra were obtained on a Varian A-60 spectrometer equipped with a variable-temperature probe. The chemical shifts are reported as τ values and were determined from the calibrated paper relative to TMS internal standard, τ 10.

Zinc tetraphenylporphin–monopyridinates can be made by simply evaporating a pyridine solution of the metalloporphyrin at room temperature under vacuum. The composition of the 1:1 complex was determined by proton integration of the porphyrin and pyridine hydrogen atoms.

Results and Discussion

Stability Constants.—The stability constants for the reactions between zinc tetraphenylporphin and ten substituted pyridines are given in Table II. All of the pyridinated derivatives had major peaks at 562 and 602 mμ with molar extinction coefficients in the ranges $(1.9\text{–}2.1) \times 10^4$ and $(1.0\text{–}1.1) \times 10^4$, respectively.

Table II

Stability Constant for the Zinc Tetraphenylporphin–Substituted Pyridines Reaction at 25° in Benzene

Reaction	Ligand	Log K	pK of ligand[a]
1	Piperidine	5.05 ± 0.05	11.1
2	4-Aminopyridine	4.65 ± 0.04	9.17
3	4-Methyl	4.02 ± 0.05	6.11
4	3-Methyl	3.81 ± 0.02	5.68
5	4-Hydrogen	3.78 ± 0.02	5.29
6	4-Carboxaldehyde	3.24 ± 0.02	4.77
7	4-Cyano	2.9 ± 0.1	1.91
8	3-Cyano	2.80 ± 0.04	1.45
9	2-Methyl	2.30 ± 0.04	6.11
10	2,4,6-Trimethyl	1.82 ± 0.07	7.42

[a] Data from ref 17.

For all of the ligands studied, the spectral data could be explained by assuming only a 1:1 complex. For example, the magnitude of the equilibrium constant is such that, in 2 M pyridine, the pyridinated complex is completely formed. No further spectral changes were observed up to 11 M pyridine, and thus no higher species are in evidence. This is in agreement with observations in which zinc is coordinated to different porphyrin types.[4,5] It is noted that nickel porphyrins can presumably add one or two ligands, depending on the nature of the porphyrin.[7,16]

Figure 2 shows the linear relationship between log K for the zinc porphyrin–ligand reaction and the pK for the ligand–protonated ligand systems.[17] The relation is of the form

$$\log K = 0.236\mathrm{p}K + 2.47 \qquad (3)$$

and fits over a 10^9-fold range in pK. This equation correlated resonance-conjugated 4-substituents, unconjugated 3-substituents, and piperidine, which lacks a π

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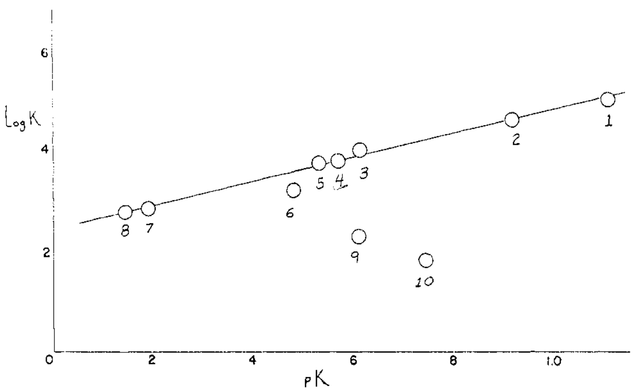

Figure 2.—Graph of log K–pK for the reactions of substituted pyridines with zinc tetraphenylporphin. The numbers correspond to the entries in Table II.

system. While equations of this form have been widely used, there is some debate as to their theoretical interpretation.[18]

The 2-methyl and 2,4,6-trimethyl derivatives deviate markedly from the line and presumably reflect the steric requirement of the reaction close to the zinc center. With respect to hydrogen, the large methyl groups in the 2 and 2,6 positions prevent the ligand from approaching the Zn(II) as closely and therefore should show a lower effective basicity toward Zn(II). The observation that the 2,4,6 derivative has a higher basicity than the 2 derivative whereas its stability constant with the zinc porphyrin is lower than that of the 2-substituted ligand supports this interpretation.

The Hammett equation has been applied to metal ion equilibria with varying degrees of success. Figure 3 shows a plot of the form

$$-\log (K/K_0) = \sigma\rho \qquad (4)$$

where K_0 is the stability constant for the pyridine reaction, and K is the corresponding value for a substituted pyridine. σ is the Hammett substituent constant[19] defined in terms of substituted benzoic acids and ρ is the reaction constant, which is a measure of the effect of the electron density at the reaction site, *i.e.*, the zinc ion. An excellent correlation was obtained with ρ equal to $+1.50$. The positive ρ indicates that the reaction is favored by a low electron density at the reaction site. Insofar as the net positive charge on the coordinated zinc can be increased by adding electron-withdrawing groups to the porphyrin, the stability constants should increase with decreasing porphyrin basicity. This effect was observed previously.[4]

A ρ of -0.58 has been found by May and Jones[20] for the first stability constants of Cu(II) and a series of aromatic carboxylic acids and was interpreted in terms of back-π-bonding from the Cu(II) to the ligand. No Hammett relationship, however, was found with subsituted pyridines and copper acetylacetonate.[21] They noted that where such correlations were observed, the free energy changes were from -4 to -8 kcal/mol. Our data give free energy changes in this range, whereas the magnesium porphyrin results,[9] which do not fit a Hammett plot, show small positive values.

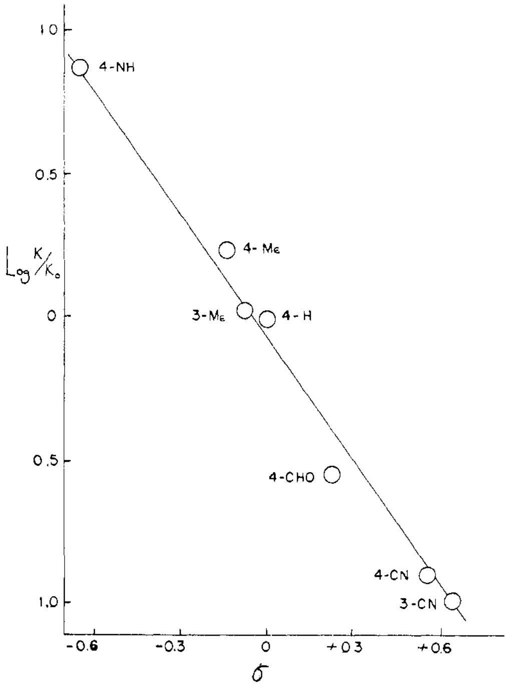

Figure 3.—Hammett plot for the substituted pyridines–zinc tetraphenylporphin equilibria.

The log K–pK correlation, the positive ρ value, and evidence that Zn(II) is not a good π donor[22] tend to indicate that ligand to metal σ bonding predominates in this system. This is in contrast to the iron(II) porphyrin systems, where the stability constants show an inverse dependence of ligand basicity, which was attributed to back-π-bonding involving metal ion d and pyridine π orbitals. Magnesium(II) porphyrins also show this inverse dependence,[9] which cannot be rationalized in terms of d orbitals. The systems are not strictly comparable in that three different equilibria are being followed; with zinc(II) the equilibrium constants refer to a four- to five-, with Fe(II) a four- to six-, and with Mg(II) a five- to six-coördinate change process.

Da Silva and Calados[23] have postulated that π bonding in metal complexes can be detected by the observation of positive ρ' values obtained from plots of the equation

$$\log \frac{\beta_{\mathrm{ML}'}}{\beta_{\mathrm{HL}'}} - \log \frac{\beta_{\mathrm{ML}}}{\beta_{\mathrm{HL}}} = \rho'\sigma \qquad (5)$$

β_{ML} and β_{HL} are the stability constants of a reference metal–ligand and a proton–ligand reaction compared to those of other related (MH′–HL′) reactions. σ is the Hammett sigma and ρ' is a constant which measures the susceptibility of the reaction to substituent effects. They have shown that eq 5 fits data that a straight

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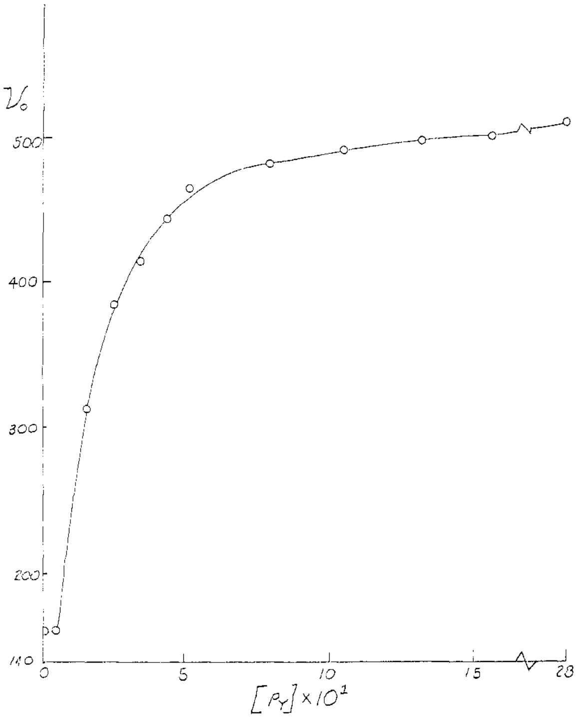

Figure 4.—Graph of the observed frequency of the pyridine protons *vs.* the added pyridine concentration. The concentration of the zinc porphyrin is 0.085 *M*.

Hammett equation fails to represent. In particular, a positive ρ' of 6.560 was obtained for the iron(II) mesoporphyrin–substituted pyridines reaction, and was used as evidence for the importance of π bonding in iron(II) porphyrins. A similar treatment of our Zn(II) data, however, also gave a linear plot, with a positive ρ' of 4.5. Since the zinc(II) porphyrins do not manifest strong typical π-donor characteristics compared to the Fe(II) complexes, we question, in this case, the use of positive ρ' values to detect back-π-bonding.

Pmr of Zinc Porphyrins.—Zinc tetraphenylporphin–pyridine complexes show a high-field shift for the coordinated pyridine protons similar to that observed for the magnesium porphyrin–monopyridinate.[11] The observed chemical shift of the pyridine protons is a weighted average of the chemical shifts of the free pyridine and of the monopyridine–metalloporphyrin complex. The stability constants for the binding of the pyridine ligand in both the magnesium and zinc monopyridinate complexes are very high. At less than a stoichiometric quantity of pyridine, with the high association constants dealt with here, there is essentially no free pyridine. Thus the chemical shifts of the five-coordinate complexes are readily obtained. This is shown on the low pyridine portion of the plot given in Figure 4. A comparison of the ligand shifts involved is given in Table III. When either the solid monopyridinate or the zinc porphyrin followed by the addition of 1 equiv of pyridine is observed in the pmr, the high-field shifts of the pyridine protons are observed. When more than 1 equiv of pyridine is added, the pyridine peaks shift to lower field, indicating an exchange-averaged spectrum, as shown in Figure 4. The spectrum was examined with *ca.* 2 equiv of pyridine present down to −60°. No line broadening or other evidence of slowing of the exchange rate was observed. This is in agreement with the earlier pmr observations on magnesium porphyrins[11] and the recent fluorometric observations of Whitten, *et al.*,[24] on magnesium and zinc porphyrin–pyridinates. Also the position of the exchange-averaged pyridine absorption line was temperature independent. This is consistent with a five-coordinate complex with a very high association constant and no six-coordinate species accessible.

TABLE III

PMR SHIFTS OF PYRIDINE AND SOME METALLOPORPHYRIN–PYRIDINE COMPLEXES

	α-H	Shift[a]	β-H	Shift	γ-H	Shift
C_5H_5N[b]	1.42[d]		2.79		2.38	
$MgTPP \cdot C_5H_5N$[c]	6.99	5.57	4.29	1.50	3.53	1.15
$ZnTPP \cdot C_5H_5N$	7.34	5.92	4.50	1.71	3.66	1.28

[a] Difference in parts per million from free ligand. [b] "High Resolution NMR Spectra Catalog," Varian Associates, Inc., Palo Alto, Calif. [c] TPP is $\alpha,\beta,\gamma,\delta$-tetraphenylporphin. [d] Chemical shifts reported as τ values relative to tetramethylsilane internal standard, τ 10.

The similarity between the ligand shifts in the zinc and magnesium porphyrin–monopyridinate complexes suggest that their structures are closely related. The chemical shift of the pyridine protons is changing by *ca.* 1.7 ppm/Å relative to the porphyrin.[11] The observed similarities of the chemical shifts mean that the pyridine protons are located within 0.1–0.2 Å of the same position relative to the porphyrin ring. Glick, *et al.*,[25] have recently published a structure of aquozinc tetraphenylporphin. For this structure the zinc(II) ion is in a square-pyramidal configuration and is displaced about 0.20 Å from the basal plane of the porphyrin nitrogens. This comparison then strongly suggests that the five-coordinate magnesium porphyrins will also be puckered with the magnesium lying considerably out of the plane of the porphyrin ring.[26]

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(26) NOTE ADDED IN PROOF. A. Timkovich and A. Tulinsky, *J. Am. Chem. Soc.*, **91**, 4430 (1969), have published the crystal and molecular structure of aquomagnesium tetraphenylporphin. In this structure the magnesium atom is 0.27 Å out of the plane of the porphyrin ring. This confirms our suggestion in this paper, based on nmr evidence, that the five-coordinate magnesium and zinc porphyrins should have similar structures.