

equatorial proton undergoing rapid exchange between two sites is given by

$$\Delta\nu_{\text{obsd}} = X_{\delta}\Delta\nu_{\text{eq}} + X_{\lambda}\Delta\nu_{\text{ax}}$$

Here  $\Delta\nu_{\text{eq}}$  and  $\Delta\nu_{\text{ax}}$  are the contact shifts for a given proton in the "frozen" equatorial and axial environments and  $X_{\lambda}$  and  $X_{\delta}$  are the mole fractions of the chelate rings in the  $\lambda$  and  $\delta$  conformations.<sup>28</sup> The methylene protons in the Ni(II) complex of *N*-methylethylenediamine are observed at  $-112$  and  $-127$  ppm.<sup>7</sup> Our results suggest that the "frozen" contact shifts for the primary amine would be the same as for the ethylenediamine complex, namely,  $\Delta\nu_{\text{eq}} = -162$  and  $\Delta\nu_{\text{ax}} = -10$  ppm, and that the primary amine proton would be the one observed at  $\Delta\nu_{\text{obsd}} = -112$  ppm. Making these substitutions and remembering  $X_{\lambda} = 1 - X_{\delta}$ , we can calculate  $X_{\delta} = 0.66$  from eq 4. This means that twice as many methyl groups are in equatorial as axial

(28) When a ring changes from the  $\delta$  to the  $\lambda$  conformation, a proton is moved from an equatorial to an axial position.

positions. Ho and Reilley reported 4 times as many equatorial as axial methyl groups for *N,N'*-dimethylethylenediamine, which has twice as many methyl groups and hence greater preference for the  $\delta$  conformation. Using this value of  $X_{\delta}$  and assuming that the shift of the axial proton for the secondary amine is  $-6$  ppm, as it is in *N,N'*-dimethylethylenediamine, we can write eq 4 for the signal at  $-127$  ppm with only  $\Delta\nu_{\text{eq}}$  as an unknown. We then find  $\Delta\nu_{\text{eq}}$  for the secondary amine is  $-189$  ppm which is in excellent agreement with the  $-188$  ppm reported by Ho and Reilley<sup>7</sup> for *N,N'*-dimethylethylenediamine. Thus the assignment of the peak observed at  $-127$  ppm to proton b is consistent with the reported shifts of ethylenediamine and *N,N'*-dimethylethylenediamine and our calculations.

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## Ligand Binding by Metalloporphyrins. III. Thermodynamic Functions for the Addition of Substituted Pyridines to Nickel(II) and Zinc(II) Porphyrins

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Free energy, enthalpy, and entropy changes for the addition of substituted pyridines to various nickel and zinc porphyrins have been determined in chloroform and benzene solutions. The stoichiometry of the reactions indicates formation of mono pyridinates with some nickel porphyrins and bis pyridinates with others, the latter requiring very high ligand concentrations. In contrast to the situation in iron porphyrin pyridinates, the  $\pi$ -acceptor ability of the ligands has little effect on the enthalpy of reaction of the nickel and zinc complexes. The dependence of the enthalpy of reaction on ligand basicity is strong for nickel porphyrin pyridinates in chloroform and for the corresponding zinc complexes in benzene but is less noticeable when these solvents are reversed. Specific solute-solvent interactions are suggested to explain this behavior. It is suggested that in nickel porphyrins hydrogen bonding between chloroform and the solvent-accessible side of the five-coordinate nickel porphyrins is very sensitive to changes in the metal-ligand bond strength on the opposite side of the porphyrin plane. In agreement with the expectation that zinc compounds will more readily accommodate the forced square-pyramidal structure than nickel, the changes attributed to hydrogen-bond effects in chloroform were found to be smaller in the zinc than the nickel compounds studied. In this respect the zinc porphyrins more closely resemble the iron(II) porphyrins which have been studied previously than do the nickel porphyrins and interactions between the aromatic porphyrin plane and benzene are thought to be more important.

Previous work<sup>2,3</sup> on the addition of substituted pyridines to iron(II) porphyrins has indicated that measurements of free energy, enthalpy, and entropy changes are necessary to an adequate understanding of the effect of substituent and reaction condition variations on the binding forces involved. Large and variable entropy changes accompany the formation of the complexes with iron(II) porphyrins, rendering conclusions based on stability constants alone invalid and in some cases misleading.

The iron(II) porphyrins are extremely sensitive to solvent change as well as to substitution on both the porphyrin and pyridine and it is important to determine

whether this sensitivity is characteristic of the metalloporphyrin-pyridine system in general or whether it is confined to the Fe(II) complexes.

In addition to an investigation of the stoichiometry of nickel porphyrin addition reactions, this paper reports the thermodynamic parameters of the reactions between substituted pyridines and various nickel and zinc porphyrins in chloroform and benzene.

### Experimental Methods

Methods for the preparation of most of the porphyrin esters used have been described previously.<sup>2</sup>  $\alpha,\beta$ -Dinitrodeuteroporphyrin dimethyl ester was prepared by the method described by Caughey<sup>4a</sup> and mesotetraphenylporphine by the Rothmund procedure.<sup>4b</sup> The method of Caughey was used for the insertion

(1) (a) University of Newcastle. (b) Avondale College. (c) CSIRO.  
 (2) S. J. Cole, G. C. Curthoys, and E. A. Magnusson, *J. Amer. Chem. Soc.*, **93**, 2153 (1971).  
 (3) S. J. Cole, G. C. Curthoys, and E. A. Magnusson, *ibid.*, **92**, 2991 (1970).

(4) (a) W. S. Caughey, W. Y. Fujimoto, and B. P. Johnson, *Biochemistry*, **5**, 3830 (1966); (b) P. Rothmund and A. R. Menotti, *J. Amer. Chem. Soc.*, **63**, 267 (1941); P. Rothmund and A. R. Menotti, *ibid.*, **70**, 1808 (1948).

TABLE I  
THERMODYNAMIC FUNCTIONS FOR THE ADDITION OF PYRIDINE LIGANDS TO ZINC MESOTETRAPHENYLPORPHINE  
IN BENZENE AND CHLOROFORM

Ligand	Solvent	$\Delta G(298^\circ)$ , kcal mol <sup>-1</sup>	$\Delta H(298^\circ)$ , kcal mol <sup>-1</sup>	$\Delta S(298^\circ)$ , cal deg <sup>-1</sup> mol <sup>-1</sup>
4-NH <sub>2</sub> py	Chloroform	-4.8 ± 0.8 <sup>a</sup>	-5.1 ± 0.3 <sup>a</sup>	-1 ± 3 <sup>a</sup>
py	Chloroform	-3.8 ± 0.8	-4.0 ± 0.4	0 ± 3
4-CH <sub>2</sub> COOMe(py)	Chloroform	-4.4 ± 0.8	-4.7 ± 0.5	-1 ± 3
4-CNpy	Chloroform	-2.8 ± 0.8	-4.8 ± 0.4	-1 ± 3
4-NH <sub>2</sub> py	Benzene	-6.3 ± 0.6	-13.9 ± 0.7	-26 ± 4
py	Benzene	-4.9 ± 0.6	-8.8 ± 1.2	-13 ± 5
4-CNpy	Benzene	-3.0 ± 0.6	-4.3 ± 0.5	-1 ± 4

<sup>a</sup> Standard error.

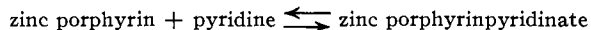
of nickel<sup>5</sup> and a similar procedure using zinc acetate was used for the insertion of zinc. The metalloporphyrin esters were recrystallized from chloroform-methanol.<sup>6</sup>

The purity of the metalloporphyrins used was checked by thin layer chromatography of the resulting porphyrin or porphyrin esters on alumina and silicic acid. After removal of the central metal atom with acid, uv-visible band positions and relative intensities provided valuable confirmatory evidence of the type of porphyrin obtained but conflicting reported values diminish the values of these data as a criterion of purity of the compounds. Solvent purification methods have been described previously<sup>2</sup> and thermodynamic functions were determined as described previously.<sup>3</sup> As in our previous studies,<sup>2,3</sup> we have deliberately chosen to study a wide range of data rather than obtain fewer values with a higher degree of accuracy. Use was made of only two of the three solvents studied in the earlier work with Fe(II) porphyrins because of very low solubilities of the compounds under investigation. Differential spectroscopy with scale expansion of the absorbance was used to enlarge the small differences in spectra for the nickel porphyrins with and without added ligand. The area of greatest difference corresponded to a very small shoulder found on the red side of the Soret band in normal spectroscopy. The large amount of data obtained prevents publication of all experimental results including concentrations and absorbances obtained. These are available, upon request, from the authors. Interaction between solvent and pyridine ligand is important in subsequent discussion and the heats of interaction at the concentrations used in this study were experimentally determined (Table III) by the method outlined previously.<sup>2</sup>

## Results

### Zinc Tetraphenylporphine-Pyridine Complexes.—

The stoichiometry of the reaction between zinc tetraphenylporphine and pyridine ligands has been established as 1:1 adduct formation.<sup>7,8</sup> The slope of the plot of  $\log R$  vs.  $\log C$  (where  $R$  is the ratio of complexed to uncomplexed species and  $C$  is the concentration of free ligand),  $1.0 \pm 0.2$ , showed that in the present study a 1:1 adduct was also formed, *i.e.*



Free energy, enthalpy, and entropy changes for the reaction in benzene and chloroform for pyridine and various para-substituted pyridines are shown in Table I. The free energy of reaction shows a good linear relationship with the  $pK_a$  of the ligand (Figure 1), in both solvents. The slope of the plot is similar in both solvents.

Equilibrium constants recently determined by Kirksey<sup>8</sup> for the addition of a wide range of pyridine ligands to zinc tetraphenylporphine in benzene (Figure 1) are in good agreement with the values reported here.

The free energies of reaction are lower in chloroform

(5) W. S. Caughey, J. O. Alben, W. F. Fujimoto, and J. L. York, *J. Org. Chem.*, **31**, 2631 (1966).

(6) J. E. Falk in "Porphyrins and Metalloporphyrins," Elsevier, New York, N. Y., 1964, p 130.

(7) J. R. Miller and C. D. Dorough, *J. Amer. Chem. Soc.*, **74**, 3977 (1952).

(8) C. H. Kirksey, P. Hambright, and C. B. Storm, *Inorg. Chem.*, **8**, 2141 (1969).

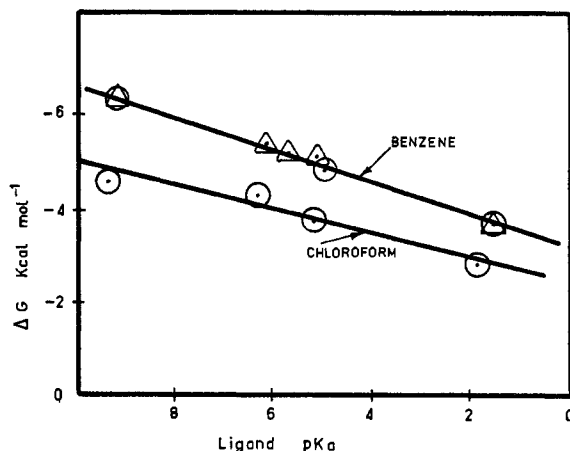


Figure 1.—Free energy of reaction for the addition of pyridine ligands to tetraphenylporphine zinc(II) as a function of ligand base strength:  $\circ$ , data from this study;  $\Delta$ , data from Kirksey, *et al.*<sup>8</sup>

than in benzene by a little more than 1 kcal mol<sup>-1</sup>. The difference is the same, within experimental error, for the three ligands common to both series of measurements.

The enthalpy changes in the zinc-pyridine reactions studied are shown as a function of ligand  $pK_a$  in Figure 2.<sup>9</sup> It can be seen that  $\Delta H$  is much more sensitive to change in ligand in benzene than in chloroform. In

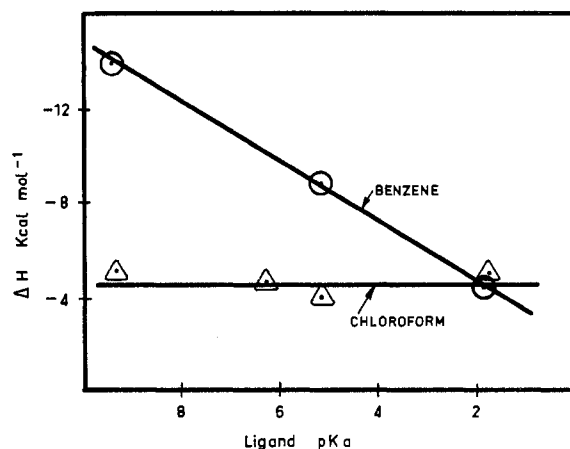


Figure 2.—Relationship between enthalpy change and ligand base strength for the addition of pyridine ligands to tetraphenylporphine zinc(II) in chloroform and benzene.

(9) The use of  $pK$  data of the pyridines which is a free energy term as a basis of comparison rather than the use of  $\Delta H$  values is justified by the constancy of the entropy term for the ionization of the pyridines and the close relationship between  $\Delta G$  and  $\Delta H$  where such data are available for the ionization reaction.

TABLE II  
THERMODYNAMIC FUNCTIONS FOR THE ADDITION OF PYRIDINES TO NICKEL MESOTETRAPHENYLPORPHINE  
IN BENZENE AND CHLOROFORM

Ligand	Solvent	$\Delta G(298^\circ)$ , kcal mol <sup>-1</sup>	$\Delta H(298^\circ)$ , kcal mol <sup>-1</sup>	$\Delta S(298^\circ)$ , cal deg <sup>-1</sup> mol <sup>-1</sup>
4-NH <sub>2</sub> py	Chloroform	-3.5 ± 1.0 <sup>a</sup>	-7.6 ± 0.7 <sup>a</sup>	-14 ± 6 <sup>a</sup>
py	Chloroform	-4.1 ± 1.0	-4.2 ± 0.7	0 ± 6
4-CH <sub>3</sub> COOMe(py)	Chloroform	-4.3 ± 1.2	+1.5 ± 0.7	+6 ± 6
4-CHOpy	Chloroform	-3.1 ± 1.4	+6.0 ± 1.0	+31 ± 8
4-CNpy	Chloroform	-3.5 ± 1.2	+7.0 ± 1.5	+35 ± 8
4-CH <sub>3</sub> py	Benzene	-4.2 ± 1.0	-6.6 ± 1.4	-8 ± 8
py	Benzene	-4.3 ± 1.0	-6.3 ± 0.3	-7 ± 4
4-CNpy	Benzene	-3.9 ± 1.2	-4.3 ± 0.5	-1 ± 6

<sup>a</sup> Standard error.

the latter solvent the differences between the various ligands are of the same order of magnitude as the errors of estimate. In benzene, however, the changes are large, the enthalpy of reaction becoming more favorable as the basicity of the ligand increases.

The pattern of entropy changes produced by change of ligand, like that of enthalpy changes, depends on the solvent. In chloroform there is very little change in entropy with variation of the ligand but in benzene the entropy changes vary by 24 cal deg<sup>-1</sup> mol<sup>-1</sup> between 4-aminopyridine and 4-cyanopyridine. In this solvent the entropy changes are all unfavorable to the reaction, and as the magnitude of  $\Delta H$  for the reaction increases, the  $\Delta S$  term also increases. This largely accounts for the relative insensitivity of the free energy of reaction to the changes in ligand. A plot of  $\Delta H$  against  $\Delta S$  yields a line with slope corresponding to an isoequilibrium temperature of 390°K. This is much further from the temperature at which the reactions were studied than was the case in our previous study with the iron(II) porphyrin-pyridine system,<sup>2</sup> and although changes are not great, we here observe much better correspondence between free energy changes and ligand basicities.

It has been observed previously<sup>10</sup> that the position of the Soret band of zinc porphyrins is very sensitive to the electron-donating power of the solvent or to the presence of electron-donating ligands in the solvent. A shift toward longer wavelengths as the ligand base strength increases has been observed in these results also (see Figure 3). It is also interesting that the position but not the shape of the Soret peak of zinc tetraphenylporphine differs in benzene and chloroform, being located 200 cm<sup>-1</sup> further to the red in benzene.

**Nickel Porphyrin Complexes. Stoichiometry.**—Varying stoichiometries of the reaction of pyridines with nickel porphyrins have been reported. Miller and Dorough<sup>7</sup> first reported a 1:1 stoichiometry with the complex formed only at very high pyridine concentration. Baker and Corwin reported thermodynamic functions for the addition of pyridine to mesoporphyrin-nickel(II)<sup>11</sup> and mesotetrapyrrolylporphyrin-nickel(II)<sup>12</sup> with two ligands per mole of metalloporphyrin being added at low pyridine concentration. Caughey<sup>13</sup> studied the addition of pyridine ligands to a variety of nickel

porphyrins and concluded that usually two ligands added together to form the bis pyridinate but suggested that a mono pyridinate of ( $\alpha,\beta$ -dinitrodeuteroporphyrin dimethyl ester)nickel(II) may have been formed first. The unit slope of a plot of log (ratio of complexed to uncomplexed species) vs. log free ligand concentration from Caughey's paper<sup>13</sup> also suggests the prior formation of a mono pyridinate.

Other evidence for the 2:1 stoichiometry in some instances comes from Caughey,<sup>14</sup> who found it for the addition of piperidine to deuteroporphyrin-nickel(II) and for the addition of pyridine to 2,4-diacetyldeuteroporphyrin-nickel(II).<sup>13,14</sup>

Storm and coworkers<sup>8,15</sup> have found that the nmr spectra for zinc and magnesium porphyrin complexes show large upfield shifts for the pyridine protons. In this study nmr spectra of solutions with  $7.5 \times 10^{-2} M$  tetraphenylporphyrin-nickel(II) and  $10^{-1} M$  pyridine showed a small shift to high field (about 3 cps) for the resonance of the  $\alpha$  protons. Smaller shifts were noted for the  $\gamma$  proton. Shifts of 6 cps were noted for the protons of 4-aminopyridine. These shifts are much smaller than those observed by Storm and coworkers. There was no evidence of paramagnetic species being present except at high pyridine concentrations.

**Thermodynamic Data.**—Study of the changes in absorption spectrum with changing ligand concentration showed that the stepwise addition of ligands could be observed in  $\alpha,\beta$ -dinitrodeuteroporphyrin-nickel(II) and deuteroporphyrin-nickel(II). Approximate thermodynamic functions for the addition of the second ligand could be obtained for deuteroporphyrin-nickel(II) with pyridine in benzene.  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  values for the addition of the second ligand were (mean  $\pm$  standard error)  $+1.0 \pm 1.5$  kcal mol<sup>-1</sup>,  $-0.8 \pm 1.0$  kcal mol<sup>-1</sup>, and  $-6 \pm 8$  cal mol<sup>-1</sup> deg<sup>-1</sup>, respectively. The small enthalpy change is opposed by the unfavorable entropy change. A small enthalpy change is not unexpected as in the nickel systems the formation of the high-spin octahedral complex must result in the promotion of two electrons to antibonding orbitals. The unfavorable entropy change is explained as due to the binding of the second ligand to the complex.

The thermodynamic functions for the addition of the first ligand for a series of pyridines and tetraphenylporphyrin-nickel(II) in chloroform and benzene were determined. The free energy changes (Table II) observed were small compared with experimental error and show a very poor correlation with ligand basicity.

(10) J. N. Phillips in "Comprehensive Biochemistry," Vol. 9, M. Hoskin and E. H. Stotz, Ed., Elsevier, New York, N. Y., 1963, p 58.

(11) E. W. Baker, M. S. Brookhart, and A. H. Corwin, *J. Amer. Chem. Soc.*, **86**, 4587 (1964); E. W. Baker and A. H. Corwin, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, No. R32.

(12) P. Hambright, *Chem. Commun.*, 470 (1967).

(13) W. S. Caughey, R. M. Deal, B. D. McLees, and J. O. Alben, *J. Amer. Chem. Soc.*, **84**, 1735 (1962).

(14) J. E. Falk in "Porphyrins and Metalloporphyrins," Elsevier, New York, N. Y., 1964, p 58.

(15) C. B. Storm and A. H. Corwin, *J. Org. Chem.*, **29**, 3700 (1964).

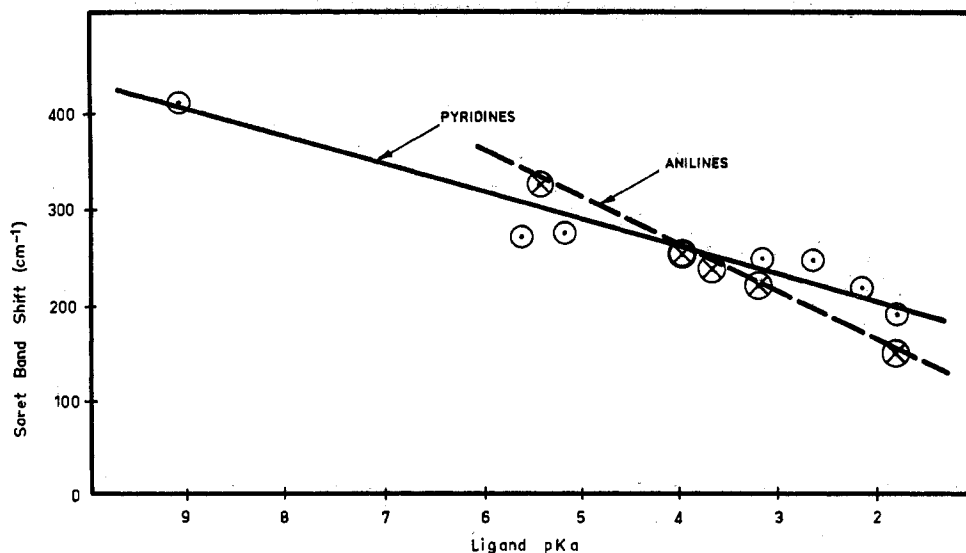


Figure 3.—The relationship between the Soret band shift to longer wavelength and ligand base strength for tetraphenylporphine-zinc(II) complexes in chloroform.

The reason for this will become apparent as the enthalpy and entropy changes are examined.

#### Discussion

The entropy change is most important in the formation of the nickel porphyrin monopyridinates. In fact, the effect on  $\Delta G$  of a large unfavorable enthalpy of reaction for weak bases in chloroform is overcome by the very large favorable entropy of reaction in these cases.

The enthalpy change is not very sensitive to changes in the basicity of the ligand (Figure 4) when benzene is

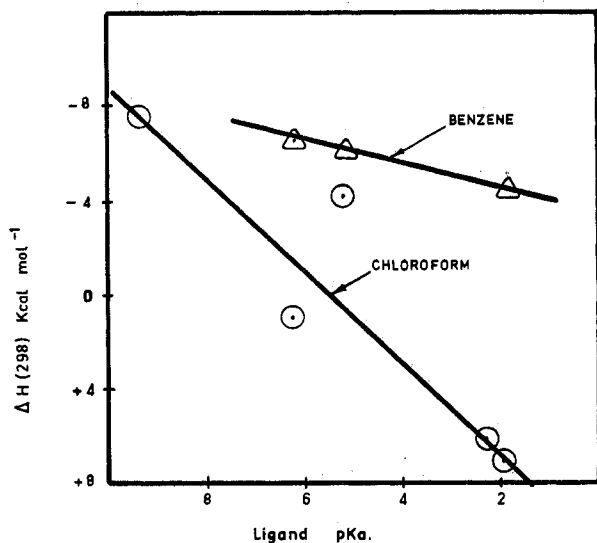


Figure 4.—The relationship between enthalpy change and ligand base strength for the addition of pyridine ligands to tetraphenylporphinenickel(II) in chloroform and benzene.

the solvent. There is a trend to greater bond strength as the basicity of the ligand strengthens. In chloroform, however, there is a very large change in enthalpy of reaction as the ligand varies. Figure 4 shows that there is no strictly linear relationship between ligand basicity and  $\Delta H$  for the reaction but there is no doubt regarding the overall trend and the sensitivity of the reaction to changes in the ligand. The slope of the

trend line through the points on the  $\Delta H$ -ligand basicity plot is about 5 times greater for the series in chloroform than in benzene.

The variations in the entropy changes oppose the variations in enthalpy. A plot of  $\Delta H$  vs.  $\Delta S$  for the values obtained is reasonably linear ( $r = 0.98$ ) and corresponds to an isoequilibrium temperature of only 310°K. It is because this temperature is so close to that at which the reaction was studied that there is so little change in the free energy values.

In comparing the results obtained for nickel and zinc as the coordinating metal atom it should first be noted that in accordance with the normal coordination chemistry of these metals the octahedral bis pyridinate is more readily formed with nickel than with zinc although it is difficult in both cases. However, both metals fairly readily form the square-pyramidal five-coordinate metal porphyrin complex. The formation of complexes of this geometry is not unusual for zinc but is quite rare for nickel. It is probable that it is the high stability of the planar porphyrin chelate that stabilizes the nickel complex with this geometry.

Square-pyramidal nickel has previously been reported for the pentacyanonickel(II) ion<sup>16</sup> and X-ray structures have revealed square-pyramidal nickel in one or two other cases.<sup>17</sup> However, the nickel atom bonds are strained in this type of coordination compound and slight distortion of the pyramid with the nickel atom movement slightly out of the porphyrin plane occurs to a degree of distortion dependent on the strength of the bond to the fifth ligand. If this is so, the notable difference in the behavior in chloroform and benzene of nickel and zinc tetraphenylporphine-pyridine complexes finds a ready explanation in terms of hydrogen bonding between the metalloporphyrin and the solvent chloroform. Ligand and solvent binding may be cooperative.

The postulate of H bonding between an acceptor chloroform molecule and a donor nitrogen atom as low

(16) F. A. Cotton and G. W. Wilkinson in "Advanced Inorganic Chemistry," 2nd ed, Interscience, London, 1966, p 880.

(17) H. B. Gray, paper presented at the 12th International Conference on Coordination Chemistry, Sydney, Australia, 1969.

in basicity as that in a metalloporphyrin molecule has been queried. Normally, metalloporphyrins would be expected to bind protons only if supplied by much stronger acids than chloroform. However, H bonding by  $\pi$ -electron donation to chloroform from aromatic molecules is well known<sup>18</sup> and between chloroform and benzene in particular, being well attested by studies of heat of mixing,<sup>19</sup> enhancement of the C-D stretching frequency of deuteriochloroform,<sup>20</sup> and the nmr chemical shift of chloroform dissolved in benzene.<sup>21</sup> There is reason for suggesting a similar type of interaction with the highly delocalized pyrrole  $\pi$ -electron system of the metalloporphyrin. Distortion of the metal atom from the plane of the pyrrole nitrogen atoms will alter the nitrogen atom hybridization from trigonal in the direction of tetrahedral and it is therefore likely to enhance the pyrrole nitrogen basicity and increase the extent of H bonding with chloroform in this region. It will also improve the access of solvent molecules to the pyrrole nitrogens—the metal atom is withdrawn from the side of the macrocycle where the lone pairs become available.<sup>22</sup> Finally, interaction is also improved by back-donation from the metal, more so for nickel than for zinc.

The data of Table III show that the results obtained

TABLE III  
HEATS OF SOLUTION (KCAL MOL<sup>-1</sup>) OF SUBSTITUTED  
PYRIDINES<sup>a</sup> IN CHLOROFORM AND BENZENE

	Chloroform	Benzene
4-CNpy	+2.5 ± 0.3 <sup>b</sup>	+4.6 ± 0.3
4-COOBu(py)	-3.1 ± 0.3	+1.0 ± 0.3
py	-1.5 ± 0.3	+0.1 ± 0.3
4-CH=CH <sub>2</sub> py	-1.4 ± 0.3	+0.3 ± 0.3
4-CH <sub>3</sub> py	-2.0 ± 0.3	+0.0 ± 0.3

<sup>a</sup> Pyridine concentration between 10<sup>-2</sup> and 10<sup>-3</sup> M. <sup>b</sup> Average standard error of estimate.

could not be explained in terms of interaction between ligand and solvent. There is a fairly consistent difference of approximately 2–3 kcal mol<sup>-1</sup> between heats of mixing of the pyridines in chloroform and benzene suggesting that hydrogen bonding is quite a significant

(18) G. C. Pimentel and A. L. McClellan in "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960, pp 197, 202; M. L. Joslem and G. Somisacan in "Hydrogen Bonding," D. Hadzi, Ed., Pergamon Press, New York, N. Y., 1959, pp 129–137.

(19) M. Tamres, *J. Amer. Chem. Soc.*, **74**, 3375 (1952).

(20) C. M. Huggins and G. C. Pimentel, *J. Chem. Phys.*, **23**, 896 (1955).

(21) L. W. Reeves and W. G. Schneider, *Can. J. Chem.*, **35**, 251 (1957); A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1651 (1957); C. J. Cresswell and A. L. Allred, *J. Phys. Chem.*, **66**, 1469 (1962).

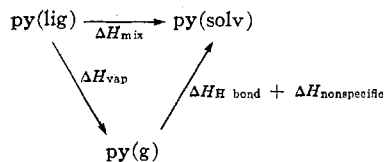
(22) D. M. Collins and J. L. Hoard, *J. Amer. Chem. Soc.*, **92**, 3761 (1970).

factor in the heat of mixing. However, the differences obtained for heats of mixing of the various liquid pyridines and chloroform are very small, the greatest difference being only 1.6 ± 0.5 kcal mol<sup>-1</sup>. This is far too small to explain the results obtained.<sup>23</sup>

In summary, we suggest that the behavior of chloroform and benzene as solvents and of nickel and zinc as metals follows from (a) the ability of chloroform alone to act as an electron acceptor and form H bonds, (b) the distortion of the porphyrin skeleton when bound in a five-coordinate geometry to these metals, and (c) the very different degree of d $\pi$ -p $\pi$  bonding between Ni-N and Zn-N bonds in these complexes.

Nickel and zinc porphyrins are not as sensitive to change of ligand as are their Fe(II) counterparts. However, the solvent in which the reaction is carried out has a large modifying influence on the changes in metal-ligand bond strength which are observed as the ligand changes. Thus, in benzene the metal-ligand bond strength of the zinc porphyrins changes by quite a large amount as the base strength of the ligand is varied. In this respect the zinc porphyrins resemble the iron(II) porphyrins. In chloroform, however, the bond strengths of zinc porphyrinpyridinates are not sensitive to ligand change and therefore behave quite differently from the Fe(II) compounds. For the nickel porphyrins the situation is the reverse. For these complexes it is in chloroform that the bond strength changes resemble the sensitivity to change of those found for the Fe(II) compounds whereas in benzene there is little change in bond strength observed. The results obtained for nickel and zinc show one other area of major difference to the Fe(II) complexes. For the nickel and zinc complexes the contributions of  $\sigma$ - and  $\pi$ -bonding effects are not so nearly balanced as they are in the Fe(II) compounds.  $\sigma$ -Bond effects predominate and the V-shape plots of  $\Delta H$  vs. ligand pK<sub>a</sub> which characterized the Fe(II) results are absent in the nickel and zinc series.

(23) The complexity of heats of mixing has been pointed out to us by a referee who has proposed the cycle



to illustrate this complexity. We would agree with this referee's comment but would point out that the supposition that hydrogen bonding changes are reflected by the differences in heats of mixing seems to us a reasonable interpretation for the purposes of this discussion.