

magnetically dilute single crystals of known structure, we have concluded that the probable ground-state vacancy configurations are  $|\epsilon\rangle$ ,  $|\epsilon^2y\rangle$ ,  $|\epsilon^2y\rangle$ , and  $|\epsilon^2(0)\rangle$ , respectively. In  $D_{2h}$  symmetry,  $\epsilon \equiv d_{xy}$ ,  $y \equiv d_{yz}$ , and  $(0) \equiv d_{3z^2 - r^2}$ . The  $z$ -axis is perpendicular to the molecular plane, and the  $y$ -axis bisects each ligand. The configurational excitation energies predicted from spin-Hamiltonians have been compared with the optical spectra of solutions of the complexes, and observed weak transitions were assigned. The agreement between predicted and observed optical transition energies is satisfactory considering the uncertainty in the spin-orbit coupling parameter,  $\zeta$ , for the complex. From the value of  $r^{-3}$  and  $\zeta$  required to fit the hyperfine structure, and the optical transition energies of the cobalt complex, the d-orbitals are considerably less covalent in this complex than in the other three. In the other complexes, the hyperfine structure of the paramagnetic resonance and the optical spectra are best fit with  $r^{-3}$  and  $\zeta$  about 0.5–0.6 of the calculated free ion values.

We find that the strength of the tetragonal field of maleonitriledithiolate dianion as measured by the one-electron energy  $\epsilon \rightarrow \mu$  (where  $\mu \equiv d_{x^2 - y^2}$ ) is large, this energy difference being estimated in the region of  $\pm 40,000$  cm.<sup>-1</sup> for the copper, nickel, and cobalt complexes.

The parameter  $g_{xx}$  is reduced in  $\text{CHCl}_3$ -DMF glass of  $[\text{NiS}_4\text{C}_4(\text{CN})_4]^-$  below its value in the single crystal. According to the theory this implies a reduction in the parameter  $c_1$ , or in  $c_3$ . Since  $c_1$  refers to the excitation  $|\epsilon^2y\rangle \rightarrow |\epsilon^2(0)\rangle$ , whereas  $c_3$  refers to  $|\epsilon^2y\rangle \rightarrow |\epsilon^2\mu\rangle$ , it is more reasonable that the solvent would affect the energy of the former excitation, which ap-

pears to be increased by the order of 10% in the glass over its value in the single crystal.

The common feature of our interpretation of the electronic configurations of the d<sup>3</sup>-hole complexes is the proximity of the energies of the configurations  $|\epsilon^2y\rangle$  and  $|\epsilon^2(0)\rangle$ . The splitting is largest in the nickel(III) complex, with  $|\epsilon^2y\rangle$  lower (by about 20,000 cm.<sup>-1</sup>), smaller in the cobalt(II) complex ( $\sim 3500$  cm.<sup>-1</sup>), and the  $|\epsilon^2(0)\rangle$  has become the ground-state configuration in the rhodium(II) complex (with  $|\epsilon^2y\rangle$  at about 8000 cm.<sup>-1</sup>). No reliable estimate can be obtained of the energy of the  $|\epsilon^2x\rangle$  configuration from the theory, but it may be stated that the energy of this configuration is well above that of  $|\epsilon^2y\rangle$ , probably by  $> 15,000$  cm.<sup>-1</sup>. The large splitting of  $|\epsilon^2y\rangle$  and  $|\epsilon^2x\rangle$  implies an extensive interaction of the metal  $|y\rangle$  and  $|x\rangle$  orbitals with  $\pi$ -orbitals of the ligands.

Finally, molecular orbital calculations of the ground-state configurations of  $[\text{NiS}_4\text{C}_4(\text{CN})_4]^-$  and  $[\text{CoS}_4\text{C}_4(\text{CN})_4]^{2-}$  using the extended Hückel theory correctly predict the  $|\epsilon^2y\rangle$  configuration.<sup>32</sup>

**Acknowledgments.**—Support of this work by the National Science Foundation through grants GP-957 and GP-596, the Advanced Research Projects Agency (Department of Defence) through Contract SD-88, and the Milton Fund of Harvard University is gratefully acknowledged. We wish to thank Professor D. H. Templeton and his associates for informing us of the results of their crystal structure determinations prior to publication. We also thank Mr. A. Kwok for engaging in many helpful discussions.

(32) R. Hoffmann and R. H. Holm, unpublished work.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY, BALTIMORE, MARYLAND 21218]

## Piperidinate Complexes of Nickel and Copper Mesoporphyrin IX<sup>1</sup>

By EARL W. BAKER, MAURICE S. BROOKHART, AND ALSOPH H. CORWIN

RECEIVED FEBRUARY 15, 1964

By spectrophotometric techniques, it is shown that copper and nickel mesoporphyrin IX form, respectively, a mono- and a dicomplex with piperidine. The thermodynamic constants for these reactions are reported. The crystal field stabilization energy of the structure of the transition metal ion is correlated with the structure of metalloporphyrin ligand complexes and a relationship of spectral shifts to ligand number is shown.

The formation of complexes of copper and nickel mesoporphyrin with a variety of ligands was reported by Corwin, Whitten, Baker, and Kleinspehn.<sup>2</sup> Previously, Caughey, Deal, McLees, and Alben<sup>3</sup> had shown that nickel porphyrins form complexes with pyridine. Miller and Dorough studied the formation of pyridine complexes of several metallo derivatives of tetraphenylporphine and reported equilibrium constants of their formation.<sup>4</sup>

This article reports a spectrophotometric study of the reaction of piperidine with copper and nickel meso-

(1) Porphyrin Studies, XXXII. Paper XXXI: E. W. Baker, M. Ruccia, and A. H. Corwin, *Anal. Biochem.*, **8**, 512 (1964). This work was supported in part by Research Grant A-2877 from the National Institutes of Health and in part by the Petroleum Research Fund administered by the American Chemical Society. Presented in part at the 146th National Meeting of the American Chemical Society, Denver, Colo., 1964.

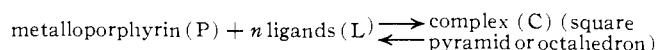
(2) A. H. Corwin, D. G. Whitten, E. W. Baker, and G. G. Kleinspehn, *J. Am. Chem. Soc.*, **85**, 3621 (1963).

(3) W. S. Caughey, R. M. Deal, B. D. McLees, and J. O. Alben, *ibid.*, **84**, 1735 (1962).

(4) J. R. Miller and G. D. Dorough, *ibid.*, **74**, 3977 (1952).

porphyrin IX dimethyl ester. The changes in absorption spectra accompanying complex formation may be used to study the reaction quantitatively. Two distinct electronic transitions in the region of 25,000 cm.<sup>-1</sup> are observed. The shorter wave length transition is associated with the uncomplexed metalloporphyrin and the longer wave length transition with a state of higher liganacy.

The equilibrium under consideration is



for which the equilibrium constant,  $K$ , is given by

$$K = \frac{[\text{C}]}{[\text{P}][\text{L}]^n} \quad (1)$$

where the quantities in brackets are expressed in units of moles/l. Equation 1 may be rewritten as

$$\log O.D._c/O.D._p + \log \epsilon_P/\epsilon_C = n \log [L] + \log K \quad (2)$$

where  $\epsilon_P$  and  $\epsilon_C$  are the extinction coefficients of the porphyrin and the complex at appropriately chosen wave lengths, and  $O.D._p$  and  $O.D._c$  are the optical densities of the porphyrin and the complex at these wave lengths.

Thus when  $\log O.D._c/O.D._p$  is plotted against  $\log [L]$ , the slope is  $n$ , the number of ligands complexed. Table I gives the optical density ratios as a function of

TABLE I

COMPLEX FORMATION AS A FUNCTION OF  
LIGAND CONCENTRATION

Piperidine, <sup>a</sup> moles/l.	O.D. <sub>c</sub>	O.D. <sub>p</sub>	O.D. <sub>c</sub> /O.D. <sub>p</sub>	$K \times 10^{-3}$
Nickel mesoporphyrin IX dimethyl ester <sup>b</sup>				
10.12	0.625	0.720	0.868	0.82
10.12	0.627	0.715	0.876	0.83
9.12	0.558	0.780	0.716	0.83
9.12	0.562	0.778	0.721	0.84
8.10	0.482	0.843	0.571	0.84 <sup>d</sup>
8.10	0.480	0.841	0.572	0.84 <sup>d</sup>
7.09	0.410	0.918	0.447	0.86 <sup>d</sup>
Copper mesoporphyrin IX dimethyl ester <sup>c</sup>				
10.12	0.518	0.487	1.062	0.21 <sup>e</sup>
9.12	0.505	0.533	0.947	0.21
9.12	0.510	0.537	0.948	0.21
8.10	0.480	0.575	0.835	0.21
8.10	0.480	0.573	0.837	0.21
7.09	0.456	0.625	0.740	0.21
6.07	0.443	0.697	0.637	0.21
6.07	0.457	0.713	0.640	0.21

<sup>a</sup> Piperidine, dielectric constant 5.8, and tetrahydrofuran, dielectric constant 7.8, mixtures were used. <sup>b</sup> Concentration  $3.32 \times 10^{-6}$  mole/l., temp. 308°K.,  $O.D._c$  and  $O.D._p$  taken at 417 and 393  $m\mu$ . <sup>c</sup> Concentration  $3.71 \times 10^{-6}$  mole/l., temp. 280°K.,  $O.D._c$  and  $O.D._p$  taken at 409 and 397  $m\mu$ . <sup>d</sup> Equilibrium constant calculated from eq. 2, letting  $n = 2$ ,  $\epsilon_P$  and  $\epsilon_C$  values taken from Table II. <sup>e</sup> The following values calculated from eq. 2 letting  $n = 1$ ,  $\epsilon_P$  and  $\epsilon_C$  from Table II.

the ligand concentration and Fig. 1 shows a plot of the  $\log (O.D._c/O.D._p)$  against  $\log [L]$  for copper and nickel mesoporphyrin. The slope of 0.97 for copper and 1.93 for nickel shows that  $n = 1$  and 2, respectively.

The sharpness of the Soret transitions in the porphyrins permits direct observation of the  $O.D.$  ratio of the complexed and uncomplexed material. By keeping the peak ratios between 0.5 and 2.0, the small mutual interference between the peaks tends to cancel and the  $O.D.$  ratio can be calculated directly from the observed  $O.D.$ 's.

Since the position of the equilibrium is a function of the dielectric constant as well as the ligand concentration, the second member of the solvent-ligand pair must have a dielectric constant close to that of the ligand. It, of course, must not be a competing ligand. That tetrahydrofuran is a suitable diluent for piperidine is shown by lack of variation in equilibrium constants with solvent concentration.

As shown in eq. 2, the value of  $\epsilon_C$  is required to evaluate  $K$ . Since the association constants are quite low

for these complexes, it is not possible to make direct measurements of  $\epsilon_C$  even in concentrated piperidine solutions. The method of Benesi and Hildebrand<sup>5</sup> was therefore used; the relation may be expressed

$$\frac{C_P}{O.D._c} = \frac{1}{[L]\epsilon_C K} + \frac{1}{\epsilon_C}$$

where  $C_P$  = the initial concentration of metalloporphyrin. Thus for the case of copper, a plot of  $C_P/O.D._c$  against  $[L]^{-1}$  yields a straight line with an intercept of  $\epsilon_C^{-1}$ . For the nickel case where two ligands are added,  $[L]^{-2}$  is plotted against  $C_P/O.D._c$ . The linearity of such a plot is taken as further proof that the correct stoichiometry of the complex has been chosen. The extinction coefficients for copper and nickel mesoporphyrin IX dimethyl ester and their piperidine complexes are given in Table II.

TABLE II

EXTINCTION COEFFICIENTS OF METALLOPORPHYRINS  
AND COMPLEXES

Porphyrin	$\epsilon^a \times 10^{-5}$	$\lambda_{max}, m\mu$
Nickel mesoporphyrin IX DME	3.3	393
Nickel mesoporphyrin IX DME-2 piperidine	3.4	417
Copper mesoporphyrin IX DME	4.7	397
Copper mesoporphyrin IX DME-piperidine	2.3	409

<sup>a</sup> In l. mole<sup>-1</sup> cm.<sup>-1</sup>.

Changes in the visible spectra also occur on complex formation. In nonligands, nickel mesoporphyrin has absorption maxima at 517 and 553  $m\mu$ . The complex absorbs at 543 and 574  $m\mu$ . A lesser shift occurs with copper porphyrin. The uncomplexed bands at 528 and 563  $m\mu$  are shifted to *ca.* 535 and 570  $m\mu$  and broadened, making it difficult to determine the exact positions of the maxima.

Table III gives the variation in complex formation as a function of temperature.  $\Delta H$  was obtained graphically from these data.  $\Delta S^\circ$  was calculated from  $\Delta H$  and the  $\Delta F^\circ$  determined from the equilibrium constant. Table IV gives the thermodynamic constants for the formation of the piperidinate complexes of copper and nickel mesoporphyrin dimethyl ester.

From the data of Corwin, *et al.*,<sup>2</sup> values for  $\Delta H$  and  $\Delta S^\circ$  of the complexes of copper and nickel mesoporphyrin with pyrrolidine and pyridine can be estimated. The values obtained are not very precise since the data are given only at two temperatures, but they do indicate that  $\Delta H$  and  $\Delta S^\circ$  for these bases lie in the same range as piperidine. The data of Caughey, *et al.*,<sup>3</sup> for nickel 2,4-diacetyldeuterioporphyrin dimethyl ester complexed with pyridine also gives a similar value. That is, the  $\Delta H$  for the metal-to-ligand bond is about 2.3 kcal./mole in all of the above cases. The values for  $\Delta S^\circ$  show a change of about -12 e.u. for each mole of ligand complexed. This is in quite good agreement with the values obtained by Davies, Singer, and Staveley<sup>6</sup> who studied the complexation of Cd, V, and

(5) (a) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949); (b) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 578.

(6) T. Davies, S. S. Singer, and L. A. K. Staveley, *J. Chem. Soc.*, 2304 (1954).

TABLE III

## COMPLEX FORMATION AS A FUNCTION OF TEMPERATURE

Temp., °C.	O.D.C	O.D.P	O.D.C/O.D.P
Copper mesoporphyrin IX DME in piperidine <sup>a</sup>			
284.1	0.803	0.812	0.989
287.2	0.786	0.826	0.952
291.0	0.768	0.843	0.912
293.2	0.758	0.858	0.884
299.4	0.728	0.895	0.814
303.2	0.715	0.917	0.780
306.9	0.710	0.959	0.740
310.2	0.690	0.981	0.704
Nickel mesoporphyrin IX DME in piperidine <sup>b</sup>			
277.1	0.997	0.501	1.992
277.8	0.989	0.507	1.952
283.2	0.919	0.545	1.688
290.9	0.799	0.603	1.326
297.3	0.708	0.649	1.091

<sup>a</sup> Concentration  $3.71 \times 10^{-6}$  mole/l., O.D.C and O.D.P taken at 409 and 397  $m\mu$ . <sup>b</sup> Concentration  $3.32 \times 10^{-6}$  mole/l., O.D.C and O.D.P taken at 417 and 393  $m\mu$ .

TABLE IV

## THERMODYNAMIC CONSTANTS FOR COMPLEX FORMATION

	$\Delta H \pm 0.05$ , kcal./mole	$\Delta F^\circ_{307} \pm 0.05$ , kcal./mole	$\Delta S^\circ_{307} \pm 0.3$ , e.u.
Ni meso-2 ligands	-4.84	2.92	-25.2
Ni meso per ligand	-2.42	1.46	-12.6
Cu meso-1 ligand	-2.30	1.25	-11.6

Zn with EDTA. They found an entropy decrease of 13-17 units for the third mole of ligand where it is presumed no release of water of hydration occurs.

## Discussion

The use of a porphyrin as a quadridentate ligand places the metal in an essentially square-planar ligand field. The acceptance of one or two additional ligands gives a square pyramid or octahedron. We found that crystal field theory correlated the various observations concerning the structure of the complexes. A correlation of  $\Delta E$ , the difference in crystal field stabilization energy of various transition metal ions in an octahedral and square pyramid complex, and the observed structures of the metalloporphyrin is given in Table V. A gain in stabilization energy favors the formation of the octahedral complex, while energy loss favors a square pyramid. Thus while magnesium(II) mesoporphyrin may be observed as an octahedral complex in high concentrations of ligand, its more stable state is a five-coordinate one.<sup>7</sup> This is to be expected since in the  $d^0$  system no crystal field stabilization energy is gained on conversion to the octahedron. Vanadium actually is present as vanadyl ion and might therefore be considered as a  $d^3$ . From this point of view, the correlation predicts the  $d^3$  to form an octahedron. Vanadium with oxygen on one side and a ligand opposite approaches an octahedral environment. The case of Fe(III) is likewise not so clear-cut. The correlation shows only a small gain in stability upon the formation

(7) A. H. Corwin and R. R. Arellano, unpublished.

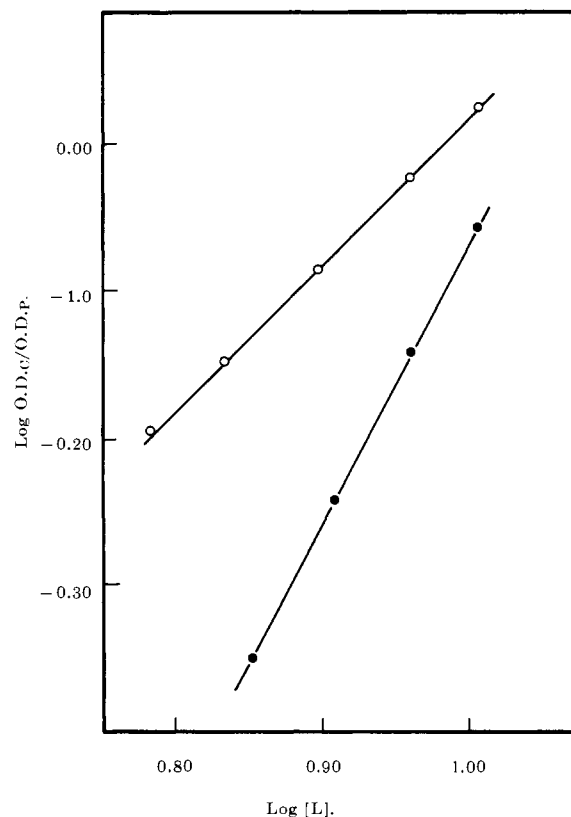


Fig. 1.—Plot of the log O.D.C/O.D.P against log [L] to determine the number of ligands: open circles, copper mesoporphyrin at 280° K. in piperidine, slope = 0.97; closed circles, nickel mesoporphyrin at 308° K. in piperidine, slope = 1.93.

of the octahedral complex. It seems that in moderate fields the more stable state is a five-coordinate one. With strong ligands, an octahedral complex probably

TABLE V

## CORRELATION OF CRYSTAL FIELD STABILIZATION ENERGY WITH STRUCTURE OF METALLOPORPHYRIN COMPLEXES IN STRONG LIGAND FIELDS

System	$\Delta E^a$	Metalloporphyrin	Observed structure
$d^0$	$0Dq$	Mg(II)	Square pyramid or octahedron <sup>b</sup>
$d^1$	$-0.57Dq$	V(IV)	Square pyramid <sup>c</sup>
$d^3$	$2.00Dq$	Mn(IV)	Octahedron <sup>d</sup>
$d^5$	$0.86Dq$	Fe(III)	Square pyramid <sup>e</sup>
$d^6$	$4.00Dq$	Fe(II)	Octahedron <sup>f</sup>
		Co(III)	
$d^7$	$-1.14Dq$	Co(II)	...
$d^8$	$2.00Dq$	Ni(II)	Octahedron
$d^9$	$-3.14Dq$	Cu(II)	Square pyramid
$d^{10}$	$0Dq$	Zn(II)	Distorted octahedron <sup>g</sup>

<sup>a</sup> F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 108.  $\Delta E$  = crystal field stabilization energy of octahedral complex - crystal field stabilization energy of square pyramid. <sup>b</sup> Ref. 4. <sup>c</sup> J. G. Erdman, V. G. Ramsey, N. W. Kalenda, and W. E. Hanson, *J. Am. Chem. Soc.*, **78**, 5844 (1956). <sup>d</sup> G. Engelsma, A. Yamamoto, E. Markham, and M. Calvin, *J. Phys. Chem.*, **66**, 2517 (1962). <sup>e</sup> R. Lemberg and J. W. Legge, "Hematin Compounds and Bile Pigments," Interscience Publishers, Inc., New York, N. Y., 1949, Chapter V. <sup>f</sup> E. S. G. Barron, *J. Biol. Chem.*, **121**, 285 (1937); D. G. Whitten, E. W. Baker, and A. H. Corwin, *J. Org. Chem.*, **28**, 2363 (1963). <sup>g</sup> Ref. 2 and 4.

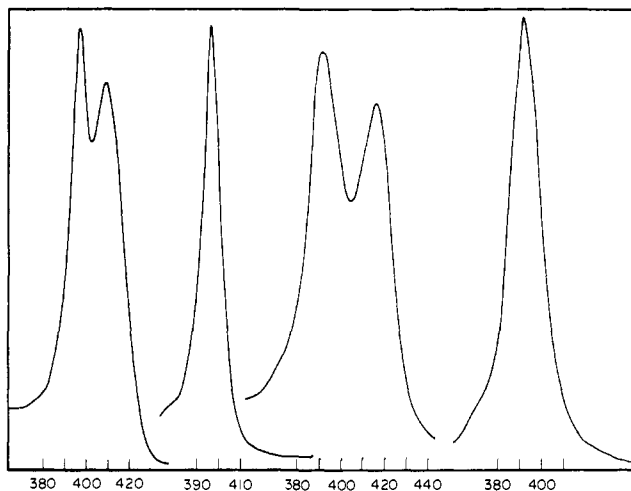


Fig. 2.—Spectral energy shifts (left to right): copper mesoporphyrin IX in piperidine at 20°; copper mesoporphyrin IX in tetrahydrofuran at 20°; nickel mesoporphyrin IX in piperidine at 35°; nickel mesoporphyrin IX in tetrahydrofuran at 35° (wave length in millimicrons).

forms, but this then is in an unstable oxidation state and converts to Fe(II).

The  $d^8$  Ni(II) system clearly forms the octahedral complex, and it is not possible to observe the intermediate five-coordinate complex. In the case of the  $d^8$  Ni(II) system a spectral shift of *ca.* twice that of the copper complex is observed (Fig. 2). No intermediate absorption maximum which would correspond to a five-coordinate complex is found. The plot of the  $\log O.D._c/O.D._p$  against  $\log [L]$  (Fig. 1) with a slope of 2 and the linearity of the Benesi-Hildebrand plot when a second-order ligand dependence is assumed are further evidence that only the octahedral complex is present in an observable concentration. This implies that the second association constant is very much larger than the first. Consideration of the crystal field stabilization energy shows the reason for the stability of the octahedron in nickel complexes. Energy equal to  $2Dq$  is gained when the octahedron is formed from the square pyramid. In strong ligand fields  $2Dq$  is equal to 10–15 kcal./mole. sufficient to prevent the accumulation of an observable amount of the five-coordinate complex. The  $d^9$  Cu(II) system forms the five-coordinate complex with no evidence for the formation of a higher complex even under the highest ligand fields. The correlation predicts the Co(II) to form only the five-coordinate complex. Experimental conditions for the observation of this complex have not yet been devised.

We have interpreted the red shift in the electronic spectra of the metalloporphyrin complexes as an increase in the ground-state energy of the complex over

TABLE VI  
SPECTRAL ENERGY SHIFTS IN METALLOPORPHYRINS  
AND COMPLEXES

Metalloporphyrin <sup>a</sup>	Ligand	Absorption maxima, $m\mu$		$\Delta$ , cm. <sup>-1</sup>	$\Delta$ , kcal./ mole
		Com- plex	por- phyrin		
Nickel meso DME	Piperidine	417	391	1595	4.6
Copper meso DME	Pyrrolidine	412	398	854	2.4
Cobalt meso <sup>b</sup>	Pyridine	416	393	1405	4.1
Manganese etio <sup>c</sup>	Pyridine	427	399	1570	4.5
Vanadyl meso <sup>d</sup>	Piperidine	420	407	760	2.2
Magnesium meso DME <sup>e</sup>	Pyridine	422	411	735	2.1

<sup>a</sup> Meso DME refers to mesoporphyrin IX dimethyl ester, etio refers to etioporphyrin I. <sup>b</sup> Ref. *f*, Table V. <sup>c</sup> Ref. *d*, Table V. <sup>d</sup> E. W. Baker and A. H. Corwin, unpublished. <sup>e</sup> Ref. 7.

that of the uncomplexed metalloporphyrin. It is seen in Table VI that the energy shifts on complex formation fall into two groups. In the complexes of copper, vanadyl, and magnesium porphyrin, the shift is on the order of 800 cm.<sup>-1</sup> or about 2.3 kcal./mole. Structure studies discussed earlier in the paper showed that only one ligand is added in these cases. Thus the copper mesoporphyrin-ligand complex is not an octahedron as was indicated earlier.<sup>2</sup> In the second group, nickel, cobalt, and manganese porphyrins, the shifts are near 1500 cm.<sup>-1</sup> and these are known to be octahedral complexes. Thus the shift caused by two ligands is twice that of a single ligand and is indicative of the greater perturbation of the porphyrin cloud predicted on steric grounds.<sup>2</sup> Interestingly, there is a correspondence between  $\Delta H$  and the spectroscopic energy shift (compare Tables IV and V) for the copper and nickel complexes. However, on intuitive grounds and also in view of the data of Miller and Dorrough,<sup>4</sup> we conclude that this correspondence is coincidental.

### Experimental

Mesoporphyrin IX was prepared from hemin by the method of Baker, Ruccia, and Corwin.<sup>1</sup> The dimethyl ester was prepared by Fischer esterification of the mesoporphyrin.

Copper and nickel mesoporphyrin IX dimethyl esters were prepared from the metal acetates in acetic acid by the method of Fischer and Stangler.<sup>8</sup>

**Spectra.**—All spectra were recorded on a Beckman DK-2 spectrophotometer, using ground-glass stoppered, matched quartz cells. Temperature studies were made by circulating chilled glycol solution through a Beckman cell compartment heating unit. In the low temperature studies, the cell compartment was flushed with dry nitrogen.

(8) H. Fischer and G. Stangler, *Ann.*, **459**, 73 (1927).