

parison. In all cases the $L_\pi \rightarrow M$ charge-transfer transition is of lower energy for the platinum(IV) complex than for the platinum(II) complex. This trend is expected since the platinum(IV) orbitals are more stable than those of the lower valent platinum(II). The ordering of ligands according to increasing $L_\pi \rightarrow M$ energy is slightly different for platinum(II) and platinum(IV). The ordering for platinum(II) is given as $\text{Br}^- < \text{SeCN}^- \sim \text{N}_3^- \sim \text{SCN}^- < \text{Cl}^- < \text{NO}_2^-$, while that for platinum(IV) is $\text{Br}^- < \text{N}_3^- < \text{SeCN}^- \sim \text{SCN}^- < \text{NO}_2^- < \text{Cl}^-$. The differing position of N_3^- and NO_2^- may be partly due to solvent differences for platinum(II) measurements and assignments of the charge-transfer processes in the nitro complexes. It is clear however the energy variation as a function of ligand is greater for platinum(II) than for platinum(IV), being some $11,000 \text{ cm}^{-1}$ between Br^- and NO_2^- for platinum(II) but only 5400 cm^{-1} between Br^- and Cl^- for platinum(IV). The lower sensitivity of the $L_\pi \rightarrow M$ energies to the nature of the ligand may be an indication of comparatively lower π bonding in the octahedral complexes or a greater involvement of the metal acceptor level, $2e_g(x^2, x^2 - y^2)$, in σ bonding. The metal orbitals of platinum(IV) are expected to be more contracted in the octahedral complexes leading to less favorable overlap than in the case of the square complexes. On the other hand the greater metal charge in the octahedral complexes should facilitate strong σ interaction.

The two-band charge-transfer system with separation $\Delta\sigma-\pi$ of $10,000$ – $16,000 \text{ cm}^{-1}$ has been noted previously¹⁶ as being a characteristic feature of both square-planar and octahedral halide complexes. It is seen in Table V that comparable separations of the $L_\pi \rightarrow M$ and $L_\sigma \rightarrow M$ charge-transfer bands are found for pseudo-halide ligands as well. It is interesting that the polyatomic ligands show slightly larger $\Delta\sigma-\pi$ differences than the halide ligands. Since the changes in $\Delta\sigma-\pi$ are small, they may be due to differences in interelectronic repulsions on the ligands. Electronic repulsion is expected to be somewhat lower on the polyatomic ligands than on the halide ligands.

Another feature which may be noted from the charge-transfer data of Table V is that the $L_\pi \rightarrow M$ band in $\text{Pt}(\text{SeCN})_6^{2-}$ compared to that in $\text{Pt}(\text{SCN})_6^{2-}$ is shifted only 500 cm^{-1} to lower energy. The corresponding shift from PtBr_6^{2-} to PtCl_6^{2-} is 5400 cm^{-1} . It is unlikely that differences in electronic repulsions alone can account for the differences in these energy shifts. In view of the ligand orbital stability, $\text{SeCN}^- < \text{SCN}^-$ and $\text{Br}^- < \text{Cl}^-$, the small shift for the former ligands may be taken as indicating comparatively greater π -donor ability of SeCN^- compared to SCN^- than of Br^- compared to Cl^- in platinum(IV) complexes.

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The Acid-Base Equilibria, Kinetics of Copper Ion Incorporation, and Acid-Catalyzed Zinc Ion Displacement from the Water-Soluble Porphyrin $\alpha,\beta,\gamma,\delta$ -Tetra(4-N-methylpyridyl)porphine

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The preparation and properties of $\alpha,\beta,\gamma,\delta$ -tetra(4-N-methylpyridyl)porphine are described. This porphyrin is water soluble from below pH 0 to above pH 14. Acid-base titrations show only the diacid-free base equilibrium ($\text{p}K_{3,4} = 2.2 \pm 0.2$) in the acid range, and the free base-monocation equilibrium ($\text{p}K_3 = 12.9 \pm 0.2$) in the basic region. The rate law for the dissociation of the Zn(II) chelate is first order in zinc porphyrin and second order in both hydrogen ion and chloride ion concentration. The kinetics of Cu(II) insertion into the free base porphyrin are reported. The properties of this porphyrin are notably different from most other porphyrins in terms of the electrostatic effect of the four positively charged N-methyl groups on the *meso* positions of the porphyrin.

Introduction

One of the major limitations in investigating the reactions of metalloporphyrin complexes is their lack of solubility over all pH ranges in aqueous solution. Most naturally occurring porphyrins have carboxylic acid functions which limit their solubility to basic regions, and interesting ligand substitution reactions

have been studied with such Fe(III) and Co(III) derivatives.² Recently a number of acid solution soluble porphyrin complexes have been prepared and their properties examined. With *meso*-tetrapyrrolylporphine,³ the acid-base equilibria,⁴ metal ion electron-

(2) E. B. Fleischer, S. Jacobs, and L. Mestichelli, *J. Amer. Chem. Soc.*, **90**, 2527 (1968).

(3) E. B. Fleischer, *Inorg. Chem.*, **1**, 493 (1962).

(4) E. B. Fleischer and L. E. Webb, *J. Chem. Phys.*, **67**, 1131 (1963).

(1) (a) Author to whom further communications should be addressed at Howard University. (b) Alfred P. Sloan Fellow.

transfer reactions,⁵ and metal ion incorporation mechanisms^{6,7} have been studied. With the disulfonic acid derivative of deuteroporphyrin IX dimethyl ester, the kinetics of Cu(II) incorporation has been investigated.⁸ Also with an ethylenediamine-substituted deuteroporphyrin, the rate of Zn(II) incorporation was found to be catalyzed by pyridine.⁹

We report the preparation and characterization of $\alpha,\beta,\gamma,\delta$ -tetra(4-N-methylpyridyl)porphine, which is water soluble from below pH 0 to above pH 14. This ligand appears to be the most acidic porphyrin known, producing a monoanion species in aqueous solution. The kinetics of the acid-catalyzed dissociation of the Zn(II) chelate and the kinetics of Cu(II) incorporation are also discussed.

Experimental Section

Zinc(II) $\alpha,\beta,\gamma,\delta$ -tetra(4-pyridyl)porphine (ZnTPyP) was synthesized by standard methods.³ The tetra-N-methyl iodide derivative (ZnP) was prepared by refluxing a filtered saturated solution of ZnTPyP ($\sim 10^{-3}$ M) in 10% ethanol-90% chloroform with a 300-fold excess of methyl iodide under nitrogen for 2 hr. The precipitated iodide complex was recovered by filtration, washed with chloroform, and air dried. The iodide salt was dissolved in a minimum amount of water made *ca.* 4 M with NaClO₄ and cooled at 10° overnight. Microcrystals were then filtered off and air dried. *Anal.* Calcd for the tetra-N-methylated zinc complex, Zn(C₄₀N₈H₂₄)(CH₃)₄(ClO₄)₄: Zn, 5.73; C, 46.35; H, 3.18; N, 9.83. Found: Zn, 5.81; C, 46.71; H, 3.34; N, 9.71.

The N-methylated diacid (H₄P²⁺) salt was prepared by dissolving ZnP in 1 M HClO₄ for several hours until the red ZnP turned bright green. The addition of concentrated NaClO₄ precipitated the green hexaperchlorate salt. *Anal.* Calcd for (C₄₀H₂₈N₈)(CH₃)₄(ClO₄)₆: C, 41.35; N, 8.83; H, 3.15. Found: C, 41.32; N, 8.92; H, 3.69. The diacid salt was again prepared 3 years later, and no significantly different analytical results were obtained. Found: C, 41.48; N, 8.90; H, 3.38.

Cu^{II}, VO^{II}, Ni^{II}, Co^{II}, Mn^{III}, and Fe^{III} complexes of the tetra-N-methylated derivative can be prepared by refluxing an excess of the divalent metal perchlorate with the free base (H₂P) porphyrin in water and precipitating with NaClO₄. *Anal.* Calcd, for example, for the ferric derivative, Fe(C₄₀N₈H₂₄)(CH₃)₄(ClO₄)₃: C, 42.9; N, 9.1; Cl, 14.3; H, 2.9. Found: C, 42.4; N, 9.0; Cl, 14.4; H, 3.3.

The spectrophotometric titrations and kinetics were followed on a Cary Model 14 spectrophotometer, at 27°. Analyses were done by Alfred Bernhardt Laboratories.

Results

$\alpha,\beta,\gamma,\delta$ -Tetra(4-N-methylpyridyl)porphine is water soluble from below pH 0 to above pH 14, due to the four positively charged N-methyl groups. Spectrophotometric titrations were used to determine the acid-base equilibria present.

Equilibria at pH 0-7.—Figure 1 shows the absorption spectra of the metal-free N-methylated derivative at various pH values. In 1 M HCl, the compound had bands at λ 534 m μ (ϵ 1.47 \times 10⁴) and λ 590 m μ (ϵ 1.13 \times 10⁴) and a Soret peak at λ 446 m μ (ϵ 1.93 \times 10⁵). The band positions are similar to those of the non-N-methyl-

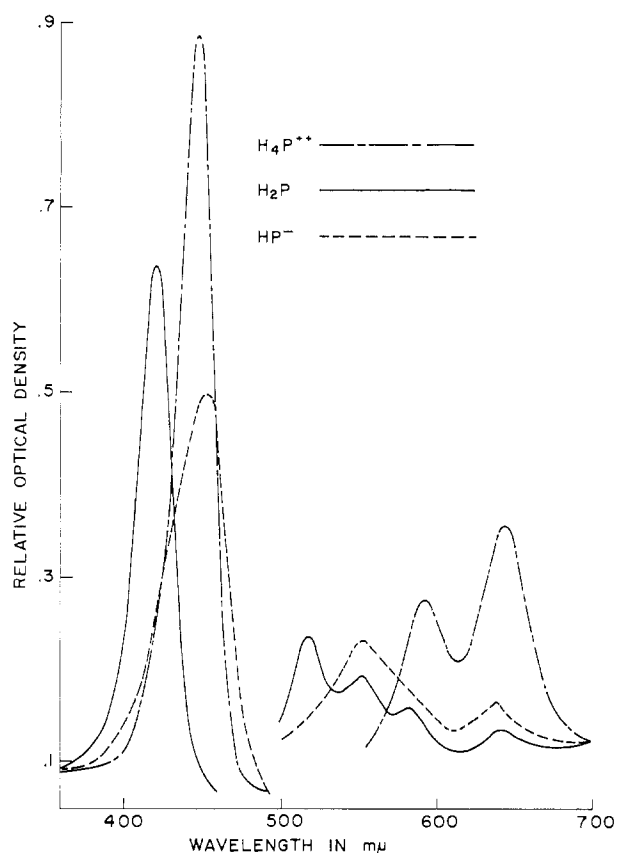


Figure 1.—Absorption spectra of H₄P²⁺ at pH 0.0, H₂P at pH 7.0, and HP⁻ at pH 14.0. The Soret bands are recorded at one-fifth the concentration (2.3×10^{-6} M) used for the visible bands.

ated species,^{3,4} H₄TpyP²⁺, and resemble other diacid porphyrin spectra.¹⁰ The absorption spectrum from pH 4 to 7 was acid independent with four bands in the visible region at 641, 585, 551, and 518 m μ with intensities relative to the 518-m μ band (ϵ 9.18 \times 10³) of 1:0.740:0.405:0.129. The Soret band was at λ 422 m μ (ϵ 1.49 \times 10⁵). This pattern is observed for most *meso*-substituted porphyrins in organic solvents¹⁰ and in particular for the free base H₂TPyP.³ Using the 422- and 446-m μ bands at pH 0 and 7, respectively, it was shown that Beer's law holds over a 100-fold range (*ca.* 10⁻⁴-10⁻⁶ M), indicating that the diacid (H₄P²⁺) and free base (H₂P) forms of the N-methylated porphyrin are presumably monomeric.

Figure 2 shows the decrease in the 422-m μ H₂P band and the increase in the 446-m μ H₄P²⁺ peak as the free base is titrated with aqueous HCl. The isosbestic points at 490 and 430 m μ indicate that two linearly related absorbing species are present whose relative concentrations are determined by the hydrogen ion concentration.

It is assumed that the free base-diacid equilibrium



is being observed and neglecting activities

$$\log ([\text{H}_2\text{P}]/[\text{H}_4\text{P}^{2+}]) = \log K_{3,4} - 2(\text{pH}) \quad (2)$$

(5) P. Hambright and E. B. Fleischer, *Inorg. Chem.*, **4**, 912 (1965).

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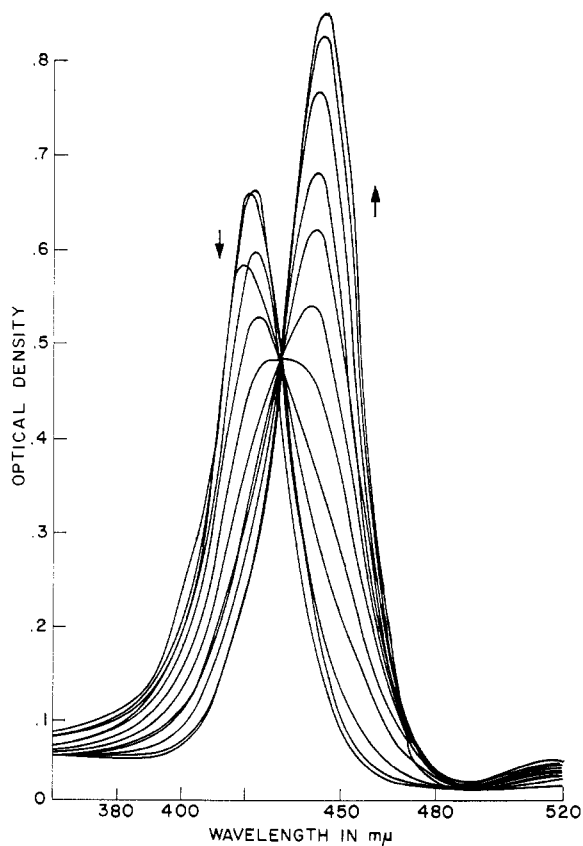
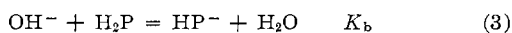


Figure 2.—Spectrophotometric titration of H_2P with HCl forming H_4P^{2+} .

Thus a graph of the left-hand side of (2) vs. pH should be linear with a slope of 2.¹¹ Figure 3 shows the results of such a graph, with the average of two experiments at both the 422- and 446- $m\mu$ peaks giving a slope of 2.1 ± 0.1 and a $pK_{3,4}$ of 2.2 ± 0.2 . Thus the equilibria from pH 0 to 7 are accounted for by the $H_2P-H_4P^{2+}$ reaction with no evidence of a monocation (H_3P^+) species.

Equilibria at pH 7–14.—The acidity of H_2P was investigated from pH 7 to 14 by a spectrophotometric titration with NaOH. The spectra at pH 14.0 (Figure 1) show two visible bands at 578 $m\mu$ ($\epsilon 1.0 \times 10^4$) and at 630 $m\mu$ ($\epsilon 1.0 \times 10^4$) and 630 $m\mu$ ($\epsilon 8.91 \times 10^4$). No differences were noted in titrations run at a constant ionic strength of 1.0 by the addition of NaCl, or without NaCl. Figure 4 shows the resulting titration of H_2P with NaOH and the isosbestic points at 555, 503, and 435 $m\mu$.

We assume the absorbing species to be the free base (H_2P) and monoanion (HP^-) species; thus



and

$$\log \left(\frac{[HP^-]}{[H_2P]} \right) = \log K_b - pOH \quad (4)$$

In accordance with eq 4, Figure 5 shows a linear plot¹²

(11) It is readily shown that $\log \left(\frac{[H_2P]}{[H_4P^{2+}]} \right) = \log \left[\frac{(D_x - D_\infty)}{(D_0 - D_x)} \right]$, where, at constant wavelength, D_∞ is the optical density of H_4P^{2+} at pH 1.0, D_0 that of H_2P at pH 7.0, and D_x the optical density at intermediate pH values.

(12) $\log \left(\frac{[HP^-]}{[H_2P]} \right) \approx \log \left[\frac{(D_0 - D_x)}{(D_x - D_\infty)} \right]$, where D_0 is the optical density of H_2P at pH 7.0, D_∞ is that of HP^- at pH 14.0, and D_x is that of mixtures of HP^- and H_2P , at intermediate pH values.

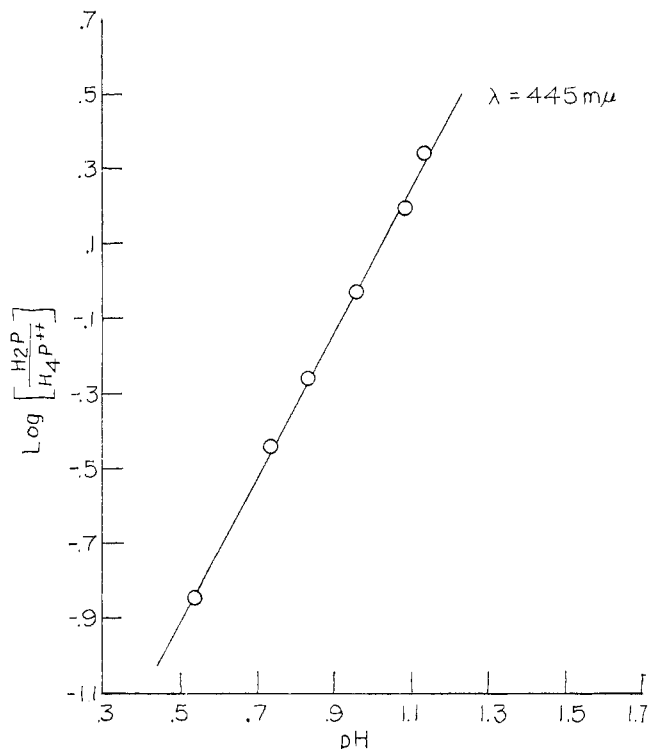


Figure 3.—Determination of $K_{3,4}$ for the $H_4P^{2+}-H_2P$ equilibrium. See eq 2.

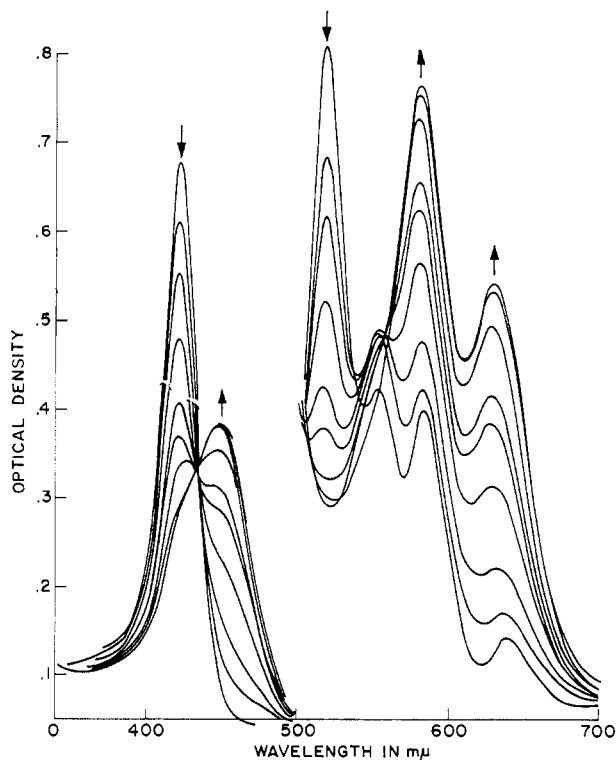


Figure 4.—Spectrophotometric titration of H_2P with NaOH forming HP^- .

of $\log \left(\frac{[HP^-]}{[H_2P]} \right)$ vs. pOH. Similar graphs from two separate experiments using the 420-, 580-, and 640- $m\mu$ wavelengths gave an average slope of 1.1 ± 0.2 and a pK_b of 1.1 ± 0.2 . Thus the dissociation constant (eq 5) of the free base at 27° is 12.9 ± 0.2 . The



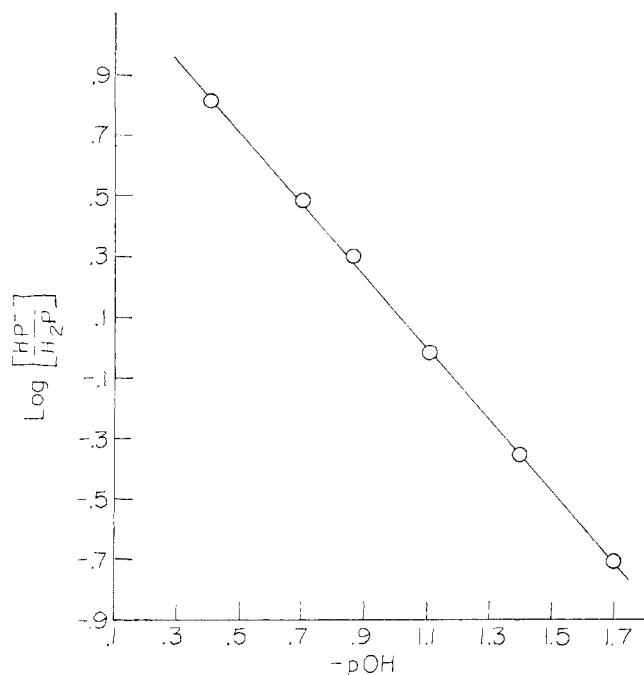
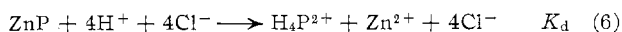


Figure 5.—Determination of K_b for the H_2P - HP^- equilibrium. See eq 4.

equilibrium was shown to be reversible in that the addition of acid to HP^- produced H_2P and H_4P^{2+} , at the appropriate pH's.

Kinetics of the Acid-Catalyzed ZnP Displacement.—

The water-soluble N-methylated zinc complex, ZnP, had bands at $563\text{ m}\mu$ ($\epsilon\ 1.60 \times 10^4$) and $436\text{ m}\mu$ ($\epsilon\ 2.06 \times 10^5$) at pH 7.0. The kinetics of the decomposition of ZnP to H_4P^{2+} (eq 6) were investigated as a



function of $[H^+]$ and $[Cl^-]$ at 27° . The reactions were run under pseudo-first-order conditions with over a 1000-fold excess of $[H^+]$ or $[Cl^-]$ to ZnP (*ca.* 10^{-5} M). At $640\text{ m}\mu$, plots of $-\ln[ZnP]$ vs. time were linear over at least 2 half-lives when the hydrogen and chloride ion concentrations were constant. Thus the reaction was first order in $[ZnP]$. k_{obsd} was obtained from the

$$-d[ZnP]/dt = k_{\text{obsd}}[ZnP] \quad (7)$$

slopes of such plots (eq 7). Table I shows the reaction to be second order in $[H^+]$ over an eightfold range,

TABLE I
ACID-CATALYZED DISSOCIATION RATES OF Zn(II) FROM ZnP^a (27°)

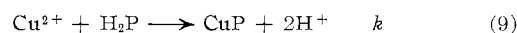
$10^2[H^+], M$	$[Cl^-]_{\text{total}},^b$	$10^2k_{\text{obsd}}, \text{sec}^{-1}$	$10^2k_{\text{obsd}}/[H^+]^2[Cl^-]_{\text{total}}^2, F^{-2} \text{sec}^{-1}$
4.13	2.65	7.78	6.45
8.26	2.70	32.0	6.43
12.4	2.71	79.7	6.92
16.5	2.78	146	6.93
24.8	2.86	350	6.95
33.1	2.94	679	7.20
24.8	1.56	104	6.96
24.8	0.765	25.1	6.99
24.8	0.248	2.24	5.94
			Av 6.75 \pm 0.32

^a Concentration of ZnP *ca.* 10^{-5} M . ^b $[Cl^-]_{\text{total}} = [HCl] + [NaCl]$.

in the presence of a high approximately constant concentration of chloride, where $[Cl^-]_{\text{total}} = [HCl] + [NaCl]$. At constant $[H^+]$, the reaction was second order in $[Cl^-]_{\text{total}}$ over a tenfold range in $[Cl^-]_{\text{total}}$. The ionic strength during the chloride variation could not be controlled, as high concentrations of other electrolytes, such as $NaClO_4$, precipitated the porphyrin. Hence the acid decomposition of ZnP follows the rate law (8) with $k_d = (6.8 \pm 0.3) \times 10^{-2} F^{-3} \text{sec}^{-1}$.

$$\text{rate} = k_d[ZnP][H^+]^2[Cl^-]^2 \quad (8)$$

Kinetics of Cu(II) Incorporation.—The kinetics of Cu(II) incorporation into H_2P (eq 9) were briefly



investigated in unbuffered nitric acid solutions at pH 3.0, under pseudo-first-order conditions. The method has been described previously.⁷ The reaction was shown to be first order in H_2P and first order in $[Cu(II)]$ over a 12-fold range. From the results in Table II, the rate law is

$$\text{rate} = k[H_2P][Cu(II)] \quad (10)$$

where $k = (8.7 \pm 0.2) \times 10^{-2} F^{-1} \text{sec}^{-1}$.

TABLE II
KINETICS OF Cu(II) INCORPORATION INTO
 H_2P AT 27° AND pH 3.0

$10^2[Cu(II)], M$	$10^4k_{\text{obsd}}, \text{sec}^{-1}$	$10^2k_{\text{obsd}}/[Cu(II)], F^{-1} \text{sec}^{-1}$
2.40	1.99	8.3
7.13	6.34	8.9
12.0	10.5	8.7
21.6	18.8	8.7
28.8	25.8	8.9
		Av 8.7

Discussion

Acid-Base Equilibria.—The spectrophotometric titrations of the tetra-N-methylated free base H_2P show it to be an amphoteric electrolyte. It can add two protons to form the diacid H_4P^{2+} or lose one proton to form the monoanion HP^- . $K_{3,4}$ for the $H_4P^{2+} \rightleftharpoons H_2P$ equilibrium is the same as that found for the non-N-methylated TPyP,⁴ which was insoluble due to deprotonation of its pyridyl groups above pH 4. In contrast to several water-soluble deuteroporphyrins¹³ or porphyrins made water soluble by the addition of cationic detergents,¹⁴ the N-methylated derivative shows no evidence of a monocation H_3P^+ . Monocation species can however be stabilized by the addition of anion detergents.¹⁴ The absence of H_3P^+ has been previously explained on the basis of X-ray determinations showing the crystalline H_4P^{2+} compounds to be extremely nonplanar in contrast to H_2P derivatives.¹⁵ Thus once a proton is removed from H_4P^{2+} , the driving

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(15) A. Stone and E. B. Fleischer, *J. Amer. Chem. Soc.*, **90**, 2735 (1968).

force toward planarity of H_2P limits the existence of H_3P^+ .

Of particular interest is the K_2 of 12.9 for the H_2P-HP^- equilibrium. No other porphyrins are sufficiently acidic to show HP^- species in aqueous solution.¹⁰ Spectrophotometric titrations of etioporphyrin I in methanol with sodium triphenylmethyl showed no difference in acidity in removing the two protons from the free base¹⁶ and indicated that the free base acidity was similar to that of methanol ($pK \approx 16$). The relatively lower basicity and higher acidity of the N-methylated porphyrin compared to other porphyrins is presumably a reflection of the four positive charged N-methylpyridinium groups on the porphyrin's periphery. The positive charges will exert an electrostatic effect repelling H^+ and attracting OH^- , producing a lower effective basicity and higher effective acidity, respectively. This is in contrast to most other porphyrins which have a negative field due to ionized carboxylic acid or sulfonic acid side chains.

Kinetics of Cu(II) Incorporation.—The observed kinetics, first order in metal ion and porphyrin, are typical of those found in most porphyrin systems.^{6,9,17,18} We are unable to explain why, under the same conditions, the N-methylated porphyrin forms no sitting-atop complexes whereas the non-N-methylated derivative shows definite sitting-atop equilibria and kinetic behavior. The positive field of the N-methyl groups would repel Cu(II) whereas the negative field of the ionized sulfonic acid groups on certain substituted deuteroporphyrins would attract Cu(II). This is clearly shown by their rate behavior, the sulfonated species reacting by the same rate law about 50 times faster⁸ than the N-methylated free base. This type of electrostatic effect has also been noted in the reactions of Fe(II) with porphyrins containing various numbers of ionized carboxylic acid functions.¹⁸

Kinetics of Zn(II) Dissociation.—The rate law for the dissociation of Zn(II) from ZnP shows an activated complex of the composition $(Cl^-)_2ZnP(H^+)_2$ which can arise from various preequilibria. One interpretation involves additions of hydrogen ions and chloride ions in separate preequilibrium steps with a final rate-determining addition of either H^+ or Cl^- to form H_2P and

chloride-coordinated Zn(II). The protonation of H_2P to H_4P^{2+} , the observed product, would occur in fast steps following the rate-determining step. Since it is energetically improbable to break the four Zn-N bonds simultaneously, the preequilibria involve a succession of reactions in which the two chlorides facilitate the removal of dipositive Zn(II) from the porphyrin with the concerted protonation of the resulting dianion P^{2-} . No large charge separation (Zn^{2+} from P^{2-}) need occur, and a gradual bond making-bond breaking type of mechanism is implied.

The second-order hydrogen ion dependence found here seems to be a general feature of acid-dependent porphyrin or phthalocyanine ligand-metal ion dissociation reactions. Thus in pyridine-buffered methanol solutions containing perchloric acid, the dissociation of Mg(II) from its deuteroporphyrin chelate showed a complicated three-term rate law.¹⁹ The limiting forms of all terms at high $[H^+]$ gave second-order dependencies on $[H^+]$. A succession of protonations and solvations, consistent with our interpretation, was the suggested mechanism. The demetalation of tin(IV) phthalocyanine was also found to be second order in hydrogen ion.²⁰ While the experimental methods have been questioned,^{19,20} the dissociation of Cu(II) from its etioporphyrin complex was interpreted²¹ in terms of a mechanism involving $[H^+]^2$. The squared term presumably reflects the stability of the free base porphyrins or phthalocyanines, compared to the di- or mono-anion.

The kinetics of formation and dissociation of metal-porphyrins show activated complexes in aqueous solution containing a metal ion and formally a free base porphyrin.⁸ It is interesting that the electrophilic substitution of Zn(II) for Hg(II) coordinated in a tetraphenylporphine complex in nonaqueous media gave no indication of free base participation under conditions in which it might be expected to occur, showing that the free base is not a universal intermediate in these systems.²²

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