TABLE I

HIGH-PRESSURE PHASES

B-Dy_2O_3		DyOOH		Crystallized in NH_4Cl soln[a]	
d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0
3.115	75	5.68	100	5.47	25
3.076	45	4.067	30	3.985	10
2.998	85	3.978	50	3.907	10
2.935	75	3.904	15	3.203	100
2.842	70	3.076	95	3.078	20
2.788	100	2.894	80	2.987	15
2.720	80	2.862	05	2.884	10
2.172	20	2.837	65	2.850	10
2.104	35	2.792	65	2.792	60
1.899	45	2.724	30	2.726	25
1.760	20	2.698	50	2.694	10
1.738	20	2.244	60	2.272	15
1.679	30	2.202	10	2.245	35
1.631	30	2.152	30	1.975	25
		2.036	20	1.953	30
		1.891	55	1.778	10
		1.867	15	1.762	10
		1.782	55	1.681	30
		1.748	25	1.653	10
		1.741	45	1.597	10
		1.683	10		
		1.577	20		
		1.556	20		

[a] See text.

equilibrium curve. This has been noted generally for the rare earth sesquioxides.[5] Figure 1 shows that the equilibrium curve for the C–B transformation of Dy_2O_3 is a straight line within the experimental error. The equilibrium pressure is lowered by slightly less than 9.3 bars/deg. The calculated molar volume difference of the two phases at room conditions is 3.66 cm^3. If constancy of ΔV is assumed over the p–t range in question ΔH must vary considerably with temperature in accordance with the Clapeyron equation. At atmospheric pressure, the phase change takes place at about 2150° with a calculated ΔH of almost 2 kcal/mol and an entropy change of 0.8 eu.

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Kinetics of the Incorporation of Copper(II) into a Water-Soluble Porphyrin

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Kinetic studies of the incorporation of divalent metal ions (M(II)) into porphyrin molecules (PH_2) to form metalloporphyrins ($M^{II}P$) (reaction 1) have shown that

$$M(II) + PH_2 \longrightarrow M^{II}P + 2H^+ \qquad (1)$$

a multiplicity of factors determines the rates and rate laws observed. In general, increasing the basicity of the porphyrin,[1] substituting anionic for cationic or neutral detergents,[2] and increasing the number of ionized carboxylic acid functions on the porphyrin[3] increase the rate of metal ion incorporation. The effects of complexing[4] M(II) and changing its geometry have been investigated.[5]

Four types of rate laws have been observed: $R_1{}^2 = k_1(M)(PH_2)$, $R_2{}^5 = k_2(M)(PH_2)/(H^+)$, $R_3{}^6 = k_3(M)^2 \cdot (PH_2)/(H^+)$, and $R_4{}^7 = [k_4(PH_2)/(H^+)] + [k_4'(M) \cdot (PH_2)(\text{pyridine})/(H^+)]$. Although R_1 may be a special case of R_2, the aims of a particular investigation have precluded a demonstration that this is true for most porphyrins. R_3 involves a "sitting atop" mechanism and has only appeared with *meso*-tetrapyridylporphine in aqueous solution.[6] (The addition of acetic acid to this porphyrin solution gives rise to R_2 behavior.) R_4 involves a pyridine catalysis of Mg(II) incorporation into deuteroporphyrin in buffered methanol solutions. A central problem is the origin of the 1/(H) terms in R_2, R_3, and R_4. Porphyrins can formally exist in diacid ($PH_4{}^{2+}$), monocation ($PH_3{}^+$), free base (PH_2), and monoanion (PH^-) forms. In R_2 and R_3, there is no evidence for $PH_3{}^+$ or PH^-; thus the $1/(H^+)$ term was tenatively ascribed[5,6] to either a metal ion hydrolysis or an unspecified porphyrin–proton preequilibrium. In R_4, the reactant was stated to be the free base (PH_2), with the rate-determining step involving either PH_2 or PH^-, which were kinetically indistinguishable.[7]

We report the kinetics of the incorporation of Cu(II) into deuteroporphyrin IX 2,4-disulfonic acid dimethyl ester[8] in buffered aqueous solutions. Neuberger and Scott[9] have shown this porphyrin to be monomeric and to exist as $PH_4{}^{2+}$, $PH_3{}^+$, and PH_2. We present evidence that the $1/(H^+)$ term in this reaction arises from a porphyrin rather than from a metal ion preequilibrium, with the rate-determining step involving the free base (PH_2).

Experimental Section

Deuteroporphyrin IX 2,4-disulfonic acid dimethyl ester[10] was prepared from deuteroporphyrin IX dimethyl ester[11] and N-pyridinium sulfonic acid and purified by column chromatography.[12] The extinction coefficients agreed with literature values.[12] The kinetics were followed at 625.6 mμ at 25° on a Cary Model 14 recording spectrophotometer with a thermostated cell compartment. The ionic strength was maintained at 0.5 with sodium perchlorate using $\mu = 0.1$ acetic acid–sodium acetate to adjust the pH. The reactions were run with an excess amount of metal ion to porphyrin. The pseudo-first-order rate constant k_{obsd} was obtained from ln ($D_t - D_\infty$) *vs.* time plots. D_∞

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is the absorbance at 9 half-lives and D_t is the absorbance at any time. These plots were always linear over 3 half-lives. It can be shown that if $(\text{porphyrin})_{\text{total}} = (\text{PH}_2) + (\text{PH}_3) + (\text{CuP})$, $\ln (D_t - D_\infty) = \ln (\text{PH}_2) + \text{constant}$. The copper porphyrin absorbed at 538 and 572 mμ. Copper perchlorate was analyzed by EDTA titrations.

Results and Discussion

The reaction was found to be first order in porphyrin (eq 2). Table I shows that at pH 3.80 and 4.65, the rate law is also first order in Cu(II). Table II gives the results of the rate dependence on hydrogen ion concentration. A linear relation between $(\text{Cu(II)})/k_{\text{obsd}}$ and (H^+) of the form given in eq 3 was observed.

$$\mathrm{d}(\text{PH}_2)/\mathrm{d}t = k_{\text{obsd}}(\text{PH}_2) \tag{2}$$

$$(\text{Cu(II)})/k_{\text{obsd}} = a + b(\text{H}^+) \tag{3}$$

TABLE I

RATE AS A FUNCTION OF Cu(II) (25°, $\mu = 0.5$)

Expt[a]	$10^3(\text{Cu(II)})_{\text{total}}$, M	10^3k_{obsd}, sec^{-1}	$k_{\text{obsd}}/\text{Cu(II)}_{\text{total}}$, $M^{-1}\ \text{sec}^{-1}$
1	1.76	5.64	3.21
2	2.65	8.72	3.29
3	3.64	10.86	2.99
4	4.42	11.85	2.69
5	5.30	15.20	2.87
6	6.24	16.95	2.72
7	7.06	19.09	3.06
8	8.82	22.78	3.23
9	9.73	26.40	2.99
			Av 3.00 ± 0.17
10	0.44	0.47	1.07
11	1.04	1.22	1.17
12	2.07	2.48	1.19
13	4.44	4.96	1.12
			Av 1.14 ± 0.04

[a] Experiments 1–9: pH 4.65, $(\text{porphyrin})_{\text{total}} = 7.34 \times 10^{-5}$ M. Experiments 10–13: pH 3.80, $(\text{porphyrin})_{\text{total}} = 5.35 \times 10^{-5}$ M.

TABLE II

RATE AS A FUNCTION OF pH (25°, $\mu = 0.5$)

Expt[a]	pH	10^3k_{obsd}, sec^{-1}	$(\text{Cu(II)})_{\text{total}}/k_{\text{obsd}}$, M sec Obsd	Calcd
1	3.78	1.163	0.891	0.886
2	3.83	1.255	0.825	0.815
3	3.90	1.414	0.733	0.718
4	4.00	1.700	0.609	0.607
5	4.25	2.257	0.459	0.456
6	4.75	3.550	0.292	0.305
7	5.20	3.710	0.279	0.260
8	5.60	4.810	0.215	0.240
9	3.80	...	0.878	0.855
10	4.65	...	0.333	0.323

[a] Experiments 1–8, $(\text{porphyrin})_{\text{total}} = 6.42 \times 10^{-5}$ M. Experiments 9–10, from Table I.

A least-squares analysis of the data in Table II gave $a = 0.235 \pm 0.006$ and $b = (3.93 \pm 0.061) \times 10^3$. This porphyrin has been shown to exist as three proton-related species in acid solutions[9]

$$\text{PH}_4{}^{2+} = \text{PH}_3{}^+ + \text{H}^+ \quad (K_4) \tag{4}$$

$$\text{PH}_3{}^+ = \text{PH}_2 + \text{H}^+ \quad (K_3) \tag{5}$$

$\text{p}K_4 \approx 0.3$ and $\text{p}K_3 \approx 4.7$ at 20°. Under the reaction conditions, PH_2 and $\text{PH}_3{}^+$ are the major species. We postulate the simple mechanism

$$\text{PH}_3{}^+ = \text{PH}_2 + \text{H}^+ \quad (K_3) \tag{6}$$

$$\text{PH}_2 + \text{Cu(II)} \longrightarrow \text{Cu}^{\text{II}}\text{P} + 2\text{H}^+ \quad (k) \tag{7}$$

With eq 7 being rate determining, it is readily shown that

$$k_{\text{obsd}} = kK_3(\text{Cu(II)})/[K_3 + (\text{H}^+)] \tag{8}$$

In relation to eq 3, $a = 1/k$ and $b = 1/kK_3$. Thus, $k = 4.26 \pm 0.11\ M^{-1}\ \text{sec}^{-1}$ and $K_3 = (5.99 \pm 0.29) \times 10^{-5}\ M$. This $\text{p}K_3$ value at 25° (4.2 ± 0.2) is in fair agreement with the independent spectroscopic value[9] of 4.7 at 20°. Using the derived k and K_3 values, Table II shows the good agreement between $(\text{Cu(II)}/k_{\text{obsd}})$ observed and calculated.

The sulfonated deuteroporphyrin has an extremely wide pH solubility range. Most carboxylic acid porphyrins flocculate at pH 4 and *meso*-tetrapyridylporphine (TPyP) is soluble[13] only below pH 3.5. Thus the complications of phase equilibria present when adding detergents to solubilize porphyrins[2] or mixed-solvent systems with varied rate–solvent effects[5] are absent with this compound. No evidence appeared in this reaction for a "sitting atop" intermediate,[14] as found in the incorporation of Cu(II) into TPyP in aqueous solutions.[6]

The reactive species of this porphyrin appears to be the unprotonated free base (PH_2). In contrast to other porphyrin insertion reactions,[5–7] the rate dependence of pH can fairly unambiguously be ascribed to a porphyrin ($\text{PH}_3{}^+$–PH_2) and not a metal ion ($\text{M(H}_2\text{O)}$–M(OH)) preequilibrium. Since the activated complex contains the free base and a copper ion, there is no information on the subsequent steps whereby the two protons are removed and Cu(II) is inserted.

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The Ligand Effects on the N≡N Bond in the Nitrogen Complexes of Cobalt

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We have previously reported that a nitrogen-coordinated complex is prepared by the reduction of cobalt(III) acetylacetonate with triisobutylaluminum in the presence of triphenylphosphine under a nitrogen atmosphere.[1] Yamamoto, *et al.*, also prepared the same complex by an analogous method.[2] Although we

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