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Substitution and Oxidation-Reduction Reactions of a Water-Soluble Porphyrin. Tetrakis(4-*N*-methylpyridyl)porphinecobalt(III)-Pyridine System

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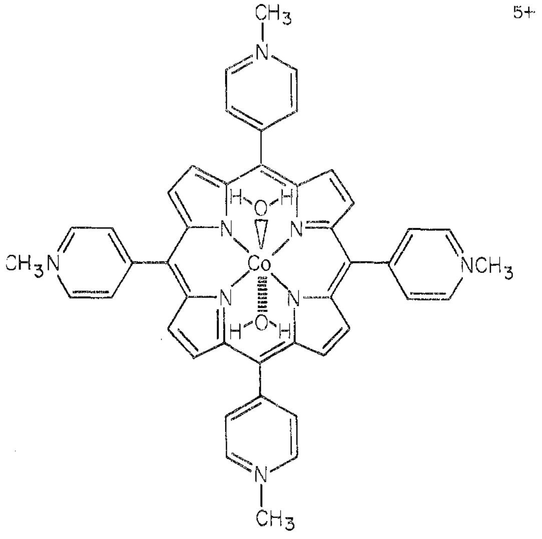
The substitution reactions of tetrakis(4-*N*-methylpyridyl)porphinecobalt(III) (CoTMpyP) with pyridine have been studied as a function of pH at 25° and an ionic strength of 0.5 *M*. The mechanistic pathway proposed for the thiocyanate substitution reactions[8a] is applicable to pyridine as well. A pyridine axial substituent has a smaller influence than does coordinated thiocyanate on the rate of further ligand substitution and on the basicity of the metalloporphyrin. The reductions by dithionite of the diaquo, aquohydroxo, and the bis(pyridine) complexes of CoTMpyP have been investigated. The more active form of the reducing agent is SO_2^- in all cases and the mechanism for the reduction reactions is outer sphere. The rates of reduction correlate with the $\Delta G°$ for the reactions.

Introduction

Proteins containing metal complexes of highly unsaturated ligand ring systems are involved in a variety of essential biological functions. Interest in these substances has led to considerable research activity with model compounds in an effort to understand the role of these metal chelate systems. Compared to most other cobalt(III) complexes, highly unsaturated macrocyclic (N_4) ligands have been shown to enhance the rate of ligand substitution at the metal center by many orders of magnitude.[2-8] Available evidence suggests that these cobalt(III) substitution reactions proceed predominantly *via* either a dissociative or an interchange mechanism. Rate constants for the reaction of a given complex with a series of ligands are relatively insensitive to the nature of the incoming ligand, under similar conditions of pH, temperature, and ionic strength. Thus, it has been found that for a series of seven monoanions, the rate constants for substitution on aquocobalamin vary by about 1 order of magnitude although the stability constants for the formation of the complexes vary by about 12 orders of magnitude.[5,6] The enormous rate enhancement by the unsaturated ligand system can be correlated with the lifetime of the leaving ligand in the inner coordination sphere of the metal complex. However, some dependence of rate on the charge type of the incoming ligand is expected and there is always the possibility of a specific steric effect or "outer-sphere" interaction between the incoming molecule and the metal-containing complex, especially for large unsaturated macrocycles like the corrinoids and porphyrins.

In our previous work on the reactions of thiocyanate with tetrakis(4-*N*-methylpyridyl)porphinecobalt(III) (represented by CoTMpyP), we considered, in the case of the diaquo complex (represented by $CoP(H_2O)_2$, shown as I), a +5,−1 interaction.[8] We found a complicated (but reasonable) reaction pathway in these studies in which the substitution of a water molecule in the inner coordination sphere of CoTMpyP by a thiocyanate leads to a marked trans effect and a large influence on the pK_a of the aquocobalt porphyrin complex. We now report an extension of this study using pyridine as the incoming ligand. Specifically, we consider whether the mechanistic pathway proposed for thiocyanate is also applicable to pyridine, we compare the influences of bound pyridine and bound thiocyanate on the substitution kinetics and basicity of the metalloporphyrin, and we attempt to assess the sensitivity of the substitution rates of the metalloporphyrin to the charge type of the incoming ligand. In addition, we report the kinetics of the reduction of CoTMpyP and its pyridine complex by the potent reducing agent dithionite. These kinetics afford some interesting comparisons with our earlier work[9] on the reduction of CoTMpyP by chromium(II), a study in which we proposed electron transfer through the axial ligands of the cobalt porphyrin.



I

Experimental Section

$(CoTMpyP)I_5$ was prepared, purified, and converted to the chloride form by methods described elsewhere.[8,10] The Evans method[11] had been previously employed to demonstrate that the complex is diamagnetic and, therefore, that the cobalt ion is in its +3 oxidation state.[10] This metalloporphyrin shows no tendency to aggregate in aqueous solution over a wide pH range at the concentration levels used here.[8] Aqueous metalloporphyrin solutions are photosensitive and were protected from visible and fluorescent light.

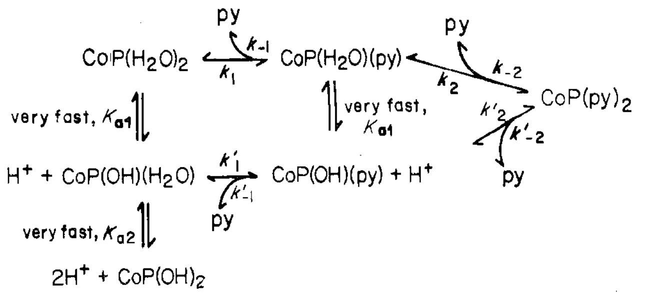
Kinetic and equilibrium measurements were carried out at pH <4 (no buffer), pH 8 (0.002 *M* borate buffer), and pH >11 (no buffer). The free pyridine concentration was calculated using a value of 5.4[12] for the pK_a of the pyridinium ion. Solutions for equilibrium measurements were allowed to stand (tightly sealed and in the dark) for up to 2 days to allow for equilibration.

Solutions of sodium dithionite ($Na_2S_2O_4$) were prepared by adding the solid to 0.5 *M* sodium perchlorate previously deaerated by scrubbing with argon and were used within a few minutes of preparation. The per cent composition of dithionite in the solid stock was determined spectrophotometrically by the reduction of $Fe(CN)_6^{3-}$ (ϵ 1026 M^{-1} cm^{-1} at 420 nm) to $Fe(CN)_6^{4-}$ (ϵ 2 M^{-1} cm^{-1} at 420 nm). Repeated determinations showed that the solid dithionite stock was 93 ± 2% pure and the concentrations quoted in this work have been adjusted accordingly.

Sodium perchlorate stock solutions were prepared by the neutralization of sodium bicarbonate with perchloric acid. All other chemicals were reagent grade and used without further purification.

Visible spectra were determined on a Cary 14 spectrophotometer (25 ± 0.1°) and under anaerobic conditions for the redox systems. Kinetic measurements were made by observing absorbance changes using the Cary 14, the stopped-flow portion of a combined SF-TJ apparatus,[13,14] or, for the redox reactions, a Durrum Model D110 stopped-flow apparatus. All measurements were conducted at 25°

Scheme I



at an ionic strength of 0.5 *M* (in either $NaNO_3$ or $NaClO_4$) and under pseudo-first-order conditions (pyridine or dithionite concentration $\gg$ total porphyrin concentration). Blank experiments were conducted for all systems including a determination of whether dithionite reduces pyridine within the time range of these experiments. For the latter determination a solution of pyridine (1.2×10^{-3} *M*) containing borate buffer (2.5×10^{-3} *M*) was mixed with a freshly prepared solution of dithionite on the Durrum stopped-flow apparatus. The reaction mixture was monitored at 350 nm but no change in absorbance was observed. However, if water which had not been previously degassed was added to the pyridine solution, a change of absorbance occurred consistent with the consumption of dithionite.

Results

I. Substitution Reactions with Pyridine. As for the reactions of CoTMpyP with thiocyanate,[8] the stability and rate constants for the reactions with pyridine are pH dependent. Scheme I best fits the spectral and kinetic data, where $K_1 = k_1/k_{-1}$, $K'_1 = k'_1/k'_{-1}$, and $K_2 = k_2/k_{-2}$. The acid dissociation constants K_{a1} and K_{a2} have been determined previously,[8] $pK_{a1} = 6.0$ and $pK_{a2} = 10.0$. Scheme I is the minimum one consistent with the knowledge that the cobalt(III) porphyrin coordinates two ligands at its axial sites. It has been implicitly assumed that only free pyridine and not the pyridinium ion is the attacking form of the ligand. Experimental evidence for this assumption will be offered later.

The absorption spectra in the Soret region for solutions of pyridine and CoTMpyP at pH <4 show a red shift from 434 nm ($CoP(H_2O)_2$, *ca.* 4×10^{-6} *M*) to 442 nm as pyridine is added ($1.2 \times 10^{-5} \leq [py] \leq 2.5 \times 10^{-3}$ *M*) and an isosbestic point at 440 nm. The porphyrin solution containing no pyridine does not pass through the isosbestic point suggesting that at the pyridine concentrations employed the observed equilibrium is

$$CoP(H_2O)(py) + py \overset{K_2}{\rightleftharpoons} CoP(py)_2$$

and that $K_1 = [CoP(H_2O)(py)]/[CoP(H_2O)_2][py] > 10^5\ M^{-1}$.

A value for the molar absorptivity (ϵ_1) of $CoP(H_2O)(py)$ is needed in order to obtain K_2 from these data. A direct determination of ϵ_1 would require a series of spectral experiments at $[py] < 10^{-6}$ *M* and, as kinetic work to be described later shows, several weeks would be required for the solutions to equilibrate. Decomposition of the porphyrin during this period would render the measurements meaningless. Therefore, to obtain a value of $K_2 = [CoP(py)_2]/([CoP(H_2O)(py)][py])$, we used the equation

$$\log\left(\frac{\epsilon_1 - \epsilon}{\epsilon - \epsilon_2}\right) = n \log\,[py] + \log K_2 \tag{1}$$

where ϵ is the apparent molar absorptivity and ϵ_2 is the molar absorptivity of $CoP(py)_2$. Successive approximations of ϵ_1 were used until the data resulted in a straight line of slope *n* (number of ligands adding to the chromophore) equal to unity. This procedure gave $K_2 = (4.8 \pm 0.4) \times 10^4\ M^{-1}$, $\epsilon_1 = 2.2 \times 10^5\ M^{-1}\ cm^{-1}$, and $\epsilon_2 = 1.5 \times 10^5\ M^{-1}\ cm^{-1}$ at 435 nm.

The determination of k_2 was accomplished by preparing a solution containing CoTMpyP and pyridine ([free pyridine] $\approx 2 \times 10^{-5}$ *M*) and allowing it to equilibrate to a constant absorbance (*ca.* 2 days). Since $K_1 > 10^5\ M^{-1}$, the only porphyrin species present are $CoP(H_2O)(py)$ and $CoP(py)_2$, and addition of further pyridine leads unambiguously to the rate constant for bis-complex formation (k_2) since the reaction with $CoP(OH)(py)$ is certain to be much slower (*vide infra*). The reaction of $CoP(H_2O)(py)$ with pyridine was found to be first order in free pyridine and in porphyrin. A plot of k_2^{obsd} *vs.* [py] where [py] is the concentration of free, unprotonated pyridine is shown in Figure 1 and yields a value of $k_2 = 2.8 \pm 0.2\ M^{-1}\ sec^{-1}$; k_{-2} is too small to measure directly from the intercept but can be calculated from $K_2 = (4.8 \pm 0.4) \times 10^4\ M^{-1}$ to obtain $k_{-2} = (5.8 \pm 0.8) \times 10^{-5}\ sec^{-1}$.

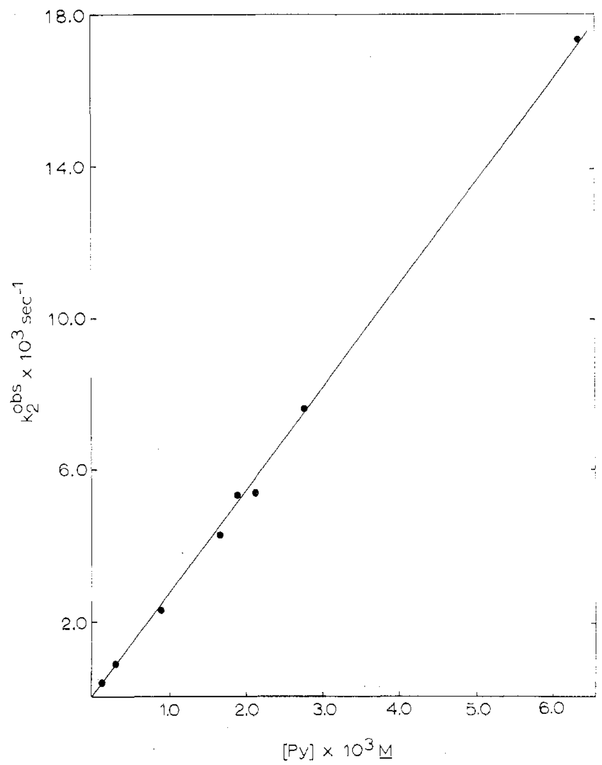


Figure 1. Plot of k_2^{obsd} *vs.* [py] at pH 4 for the reaction $CoP(H_2O)(py) + py \rightarrow CoP(py)_2$ from which k_2 was obtained.

When the initial pyridine concentration in the porphyrin solution was zero, monophasic kinetic curves were obtained for the reaction of $CoP(H_2O)_2$ with pyridine at pH 3. The observed rate constant was independent of the wavelength chosen and the observed absorbance change corresponded to the full absorbance change predicted from the spectra. The spectrum of the product had λ_{max} 442 nm; *i.e.*, it corresponds to $CoP(py)_2$. These results imply that $k_2 > k_1$ and that the observed rate constant is for the formation of the monopyridine complex. If $k_1 \geq k_2$, a two-stage reaction corresponding to the formation of both $CoP(H_2O)(py)$ and $CoP(py)_2$ would be observed. Therefore, the rate constant obtained from a first-order plot of the observed absorbance change is k_1^{obsd}, the rate constant for formation of $CoP(H_2O)(py)$. In terms of Scheme I the complex may be produced by two parallel pathways[8] and as a consequence k_1^{obsd} is given by eq 2.

$$k_1^{obsd} = \left(\frac{k_1 + K_{a1}k'_1/[H^+]}{1 + K_{a1}/[H^+]}\right)[py] + \left(\frac{k_{-1} + K'_{a1}k'_{-1}/[H^+]}{1 + K'_{a1}/[H^+]}\right) \tag{2}$$

From work at pH 8.1 (*vide infra*) we determined that $k'_1 = 220\ M^{-1}\ sec^{-1}$. Therefore, since $K_{a1}/[H^+] \ll 1$ and if we

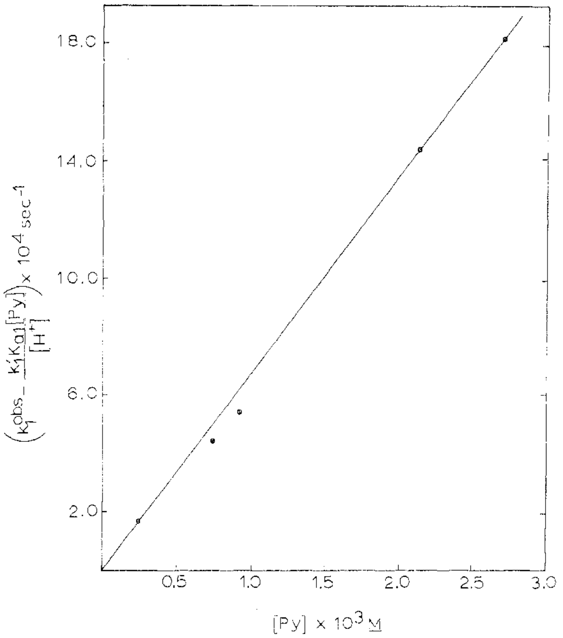


Figure 2. Plot of $k_1^{obsd} - k'_1K_{a1}[py]/[H^+]$ *vs.* [py] using $K_{a1} = 1 \times 10^{-6}$ M and $k'_1 = 220$ M^{-1} sec^{-1}.

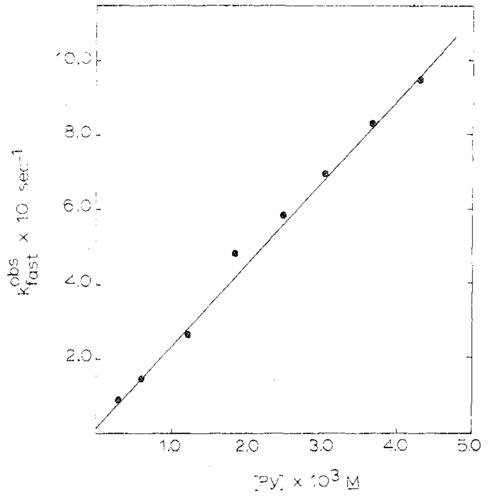


Figure 3. Plot of k_{fast}^{obsd} *vs.* [py] at pH 8 from which k'_1 was obtained.

neglect the terms for the reverse reaction, we obtain $k_1^{obsd} = (k_1 + k'_1K_{a1}/[H^+])[py]$, and a plot of $k_1^{obsd} - k'_1K_{a1}[py]/[H^+]$ *vs.* [py] should be linear, pass through the origin (if the approximation of neglecting reverse terms is valid), and have a slope equal to k_1. This plot is shown in Figure 2 and $k_1 = 0.7 \pm 0.4$ M^{-1} sec^{-1}. The large error limits on k_1 reflect that the determination of this rate constant involves two variables, ([py] and [H$^+$]), and is obtained by substraction of two large numbers. Since the observed kinetics are indeed monophasic, the value of k_1 probably represents an upper limit.

Intermediate pH. There are so many species present in substantial concentration at pH ~8 (*i.e.*, CoP(OH)(H$_2$O), CoP(OH)(py), CoP(H$_2$O)(py), and CoP(py)$_2$) and the spectral changes are so small that the spectral method for determining equilibrium constants proved unproductive. However, the study of the kinetics of the reactions involving these species allows for a rather complete analysis of the system. The mixing of the porphyrin with pyridine at pH 8.1 leads to biphasic kinetics but the observed kinetic processes are sufficiently different in rate to permit independent determinations of the observed rate constants for each phase, k_{fast}^{obsd} and k_{slow}^{obsd}.

The faster process could be studied conveniently using the stopped-flow technique and the results are shown in Figure 3. The reaction proved to be first order in pyridine and in porphyrin. A plot of k_{fast}^{obsd} *vs.* pyridine concentration is linear giving a slope of 220 ± 20 M^{-1} sec^{-1} and an intercept of about 1×10^{-2} sec^{-1}. To obtain a more precise value for the intercept, the pyridine concentration was extended to lower [py] (but in all cases $[py]_0 \gg [CoP]_0$) and the reaction was studied on the Cary 14. The results of these experiments are shown in Figure 4 and the value of the intercept is 1.2×10^{-2} sec^{-1}; thus $k_{fast}^{obsd} = 220[py] + 1.2 \times 10^{-2}$ sec^{-1}. This faster process was interpreted as the formation of the monopyridine complex since when the cobalt porphyrin was allowed to equilibrate with low concentrations of pyridine and additional pyridine was added to this mixture, only the slower process was observed. At this pH (8.1) the initial major porphyrin species is CoP(H$_2$O)(OH) and the monopyridine complex may be formed *via* two pathways. An analysis of Scheme I leads to the identical expression for k_{fast}^{obsd} as is given by eq 2 for k_1^{obsd}. To be consistent with results obtained at low pH, $k'_1 \gg k_1$ and $k_{-1} \ll k'_{-1}$ and, therefore, $k'_1 = 220$ M^{-1} sec^{-1} and $k'_{-1}/(1 + [H^+]/K'_{a1}) = 1.2 \times 10^{-2}$ sec^{-1} at pH 8.1.

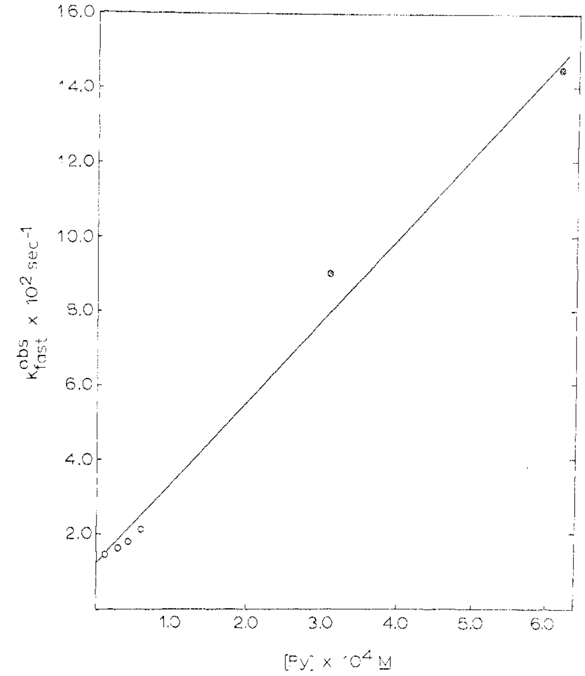
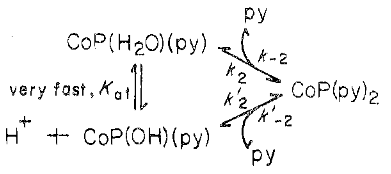


Figure 4. Plot of k_{fast}^{obsd} *vs.* [py] from stopped-flow data (●) and Cary 14 data (○) at pH 8 from which k'_{-1} was obtained. The points represented as closed circles and the line shown are taken directly from Figure 3.

The slower phase is also first order in pyridine and in porphyrin and a plot of k_{slow}^{obsd} *vs.* [py] leads to a slope of 1.4 ± 0.2 M^{-1} sec^{-1} at a pH of 8.1. A value of K'_{a1} and, hence, k'_{-1} can be obtained from a study of the slow-step rate as a function of pH. Consider the section of Scheme I which leads to the formation of CoP(py)$_2$



We thus obtain

$$k_{slow}^{obsd} = \left(\frac{k_2 + K'_{a1}k'_2/[H^+]}{1 + K'_{a1}/[H^+]}\right)[py] + (k_{-2} + k'_{-2}[OH^-]) \quad (3)$$

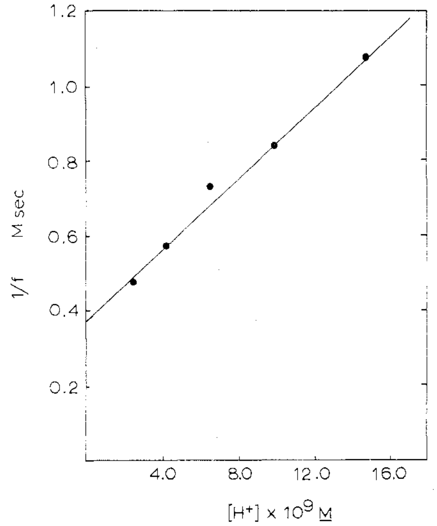


Figure 5. Plot of $1/f$ *vs.* $[H^+]$ from which K'_{a_1} and k'_2 were calculated.

At sufficiently high pyridine concentration ($[\text{py}] \geq 2 \times 10^{-3}$ M) the reverse terms in k_{-2} and k'_{-2} may be neglected and defining $f = k_2 - k_{\text{slow}}^{\text{obsd}}/[\text{py}]$ leads to

$$\frac{1}{f} = \left(\frac{1}{k_2 - k'_2}\right)\left(1 + [H^+]/K'_{a1}\right) \qquad (4)$$

The analysis requires the value for k_2 obtained at low pH, 2.8 M^{-1} sec^{-1}. A plot of $1/f$ *vs.* $[H^+]$, as shown in Figure 5, leads to a value of $K'_{a1} = 8.0 \times 10^{-9}$ (or $pK'_{a1} = 8.1$) and $k'_2 = 0.09$ M^{-1} sec^{-1}, this value being zero within experimental error. Thus we have shown that a pathway involving loss of OH^- directly from the inner coordination sphere is considerably less favorable than that involving loss of water. Using $pK'_{a1} = 8.1$ we also may now calculate that $k'_{-1} = 2.4 \times 10^{-2}$ sec^{-1} and that $K'_1 = k'_1/k'_{-1} = [\text{CoP(OH)(py)}]/[\text{CoP(OH)(H}_2\text{O)}][\text{py}] = (9 \pm 2) \times 10^3$ M^{-1}. Furthermore, a value of K_1 may now be calculated

$$K_1 = \frac{K'_1 K_{a1}}{K'_{a1}} = 1 \times 10^6 \, M^{-1}$$

which is consistent with our estimate from spectral data.

As a confirmation of our postulated scheme, k^{obsd} for the monopyridine complex formation was measured as a function of pH in the range pH 4.2–5.4. In this range k_1^{obsd} becomes greater than k_2^{obsd} and the second complexation is observed as a "tail" on the observed first-order curve. This complication was minimized by observing at 428 nm where the absorbance change due to $\text{CoP(H}_2\text{O)(py)} \rightarrow \text{CoP(py)}_2$ is very small but $\text{CoP(H}_2\text{O)}_2 \rightarrow \text{CoP(H}_2\text{O)(py)}$ is large. A plot of $k^{\text{obsd}}/[\text{py}]$ *vs.* pH gives an independent determination of $pK_{a1} = 6.1$ in good agreement with the previously measured value[8] of 6.0 ± 0.1. It might be noted that the pH dependence of the observed rate constants could be interpreted completely without recourse to considering the pyridinium ion as an attacking form of the ligand. Consistent with kinetic results obtained for binary complex formation,[15] the rate constant for attack by pyridinium ion is within the experimental error.

Scheme II

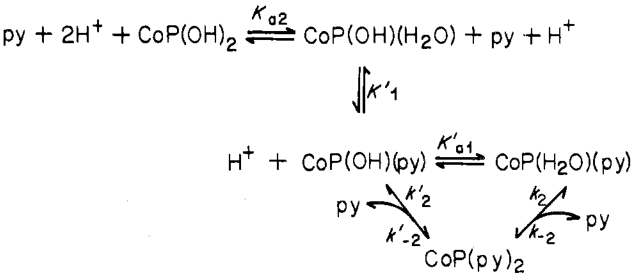


Table I. Kinetic and Thermodynamic Results at 25°, $\mu = 0.5$ M

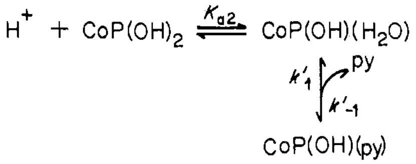
(i) CoTMpyP + SCN^- or py

	k_1, M^{-1} sec^{-1}	k_{-1}, sec^{-1}	K_1, M^{-1}	
py	0.7	6×10^{-7}	1×10^6	
SCN^-	2.1	3.1×10^{-4}	6.4×10^3	
	k_2, M^{-1} sec^{-1}	k_{-2}, sec^{-1}	K_2, M^{-1}	k'_2, M^{-1} sec^{-1}
py	2.8	5.8×10^{-5}	4.8×10^4	~0.09
SCN^-	2.8×10^4	3.0×10^3	13	
	k'_1, M^{-1} sec^{-1}	k'_{-1}, sec^{-1}	K'_1, M^{-1}	
py	220	2.4×10^{-2}	9×10^3	
SCN^-	110			
	pK_{a_1}	pK_{a_2}	pK'_{a_1}	
py	6.0	10.0	8.1	
SCN^-	6.0	10.0	>9	

(ii) $\text{CoP(H}_2\text{O)(py)} + SCN^-$

k_{12}, M^{-1} sec^{-1}	k_{21}, sec^{-1}	K_{12}, M^{-1}
4.5	3.3×10^{-3}	1.4×10^3

High pH. Attempts to determine the equilibrium constants above pH 11.5 where the predominant porphyrin species is CoP(OH)_2 were frustrated by the lack of a sizable spectral shift on addition of py since CoP(OH)_2 has λ_{max} 445 nm, CoP(OH)(py) has λ_{max} ~438 nm, and CoP(py)_2 has λ_{max} 442 nm. Kinetic experiments were limited to pyridine concentrations greater than 0.03 M; below this value the amplitudes of the kinetic curves were too small to allow measurement of k^{obsd}. At these concentrations, the product formed was CoP(py)_2. Consider the following section of Scheme I



For this reaction the pseudo-first-order rate constant is

$$k^{\text{obsd}} \approx \frac{k'_1[\text{py}]}{1 + K_{a2}/[H^+]}$$

assuming that reverse reactions may be neglected and that, as discussed earlier, CoP(OH)_2 does not react directly with pyridine. We calculate that $k^{\text{obsd}}/[\text{py}] \approx 5.5$ sec^{-1} at pH 11.6. This value is several orders of magnitude greater than the measured value. Therefore, we may consider the above as a rapid preequilibrium in the formation of the bis complex (see Scheme II). Since $k_2 \gg k'_2$ we obtain eq 5 which under the

$$k^{\text{obsd}} = \frac{k_2[\text{py}]}{1 + K'_{a1}/[H^+] + \dfrac{K'_{a1}}{K'_1[\text{py}][H^+]}\left(1 + \dfrac{K_{a2}}{[H^+]}\right)} + k_{-2} \qquad (5)$$

prevailing experimental conditions reduces to $k^{\text{obsd}}/[\text{py}] \approx k_2[H^+]/K'_{a1}$. A plot of k^{obsd} *vs.* $[H^+]$ obtained at constant $[\text{py}] = 0.31$ M is a straight line of slope $k_2[\text{py}]/K'_{a1} = 9.6 \times 10^7$ M^{-1} sec^{-1} and since $k_2 = 2.8$ M^{-1} sec^{-1}, we obtain an independent determination of pK'_{a1} as 8.0 in excellent agreement with the value obtained at lower pH.

Further kinetic experiments at high pH with increased concentration of pyridine lead to a saturation phenomenon not readily explicable on the basis of experiments at lower pH. Perhaps at these very high pyridine concentrations we are viewing a solvation effect not directly related to the processes we have thus far described.[10] A summary of the stability and rate constants obtained in this study is shown in Table I. The results we have obtained for thiocyanate are included for comparison.

II. Mixed-Complex Experiments. Pyridine (concentration $\sim 10^{-5}$ *M*) was allowed to equilibrate with the cobalt porphyrin over a period of 2 days at pH 4. The only porphyrin complexes present in solution after equilibration were $CoP(H_2O)(py)$ and $CoP(py)_2$. This solution was then mixed with a solution of thiocyanate (pH 4, $\mu = 0.5$ *M*) and the kinetics were observed on the Cary 14. Blank experiments in which the porphyrin solution was mixed with an aqueous solution containing no thiocyanate gave no effect in the same time range. The reaction being observed is therefore

$$CoP(H_2O)(py) + SCN^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} CoP(py)(SCN)$$

A plot of k^{obsd} *vs.* [SCN⁻] is linear, $k_{12} = 4.5 \pm 0.4\ M^{-1}\ sec^{-1}$, $k_{21} = (3.3 \pm 0.3) \times 10^{-3}\ sec^{-1}$, and thus $K_{12} = [CoP(py)(SCN)]/([CoP(H_2O)(py)][SCN]) = k_{12}/k_{21} = (1.4 \pm 0.3) \times 10^3\ M^{-1}$. The mixed complex has its Soret maximum at 439 nm (ϵ $1.9 \times 10^5\ M^{-1}\ cm^{-1}$) which is different from that of the dithiocyanato complex.

III. Reduction of CoTMpyP with Dithionite. Spectral Results. Because of the instability of dithionite in acid solution,[16] most experiments were conducted at pH 8.0 (2.5×10^{-3} *M* borate buffer) where the predominant porphyrin species is $Co^{III}P(OH)(H_2O)$ having a Soret band maximum at 437 nm (ϵ $1.7 \times 10^5\ M^{-1}\ cm^{-1}$). Addition of excess dithionite ion ($\sim 10^{-3}$ *M*) under anaerobic conditions leads to a blue shift, a band of Soret intensity appearing at 420 nm when the spectrum is determined within 2 min of mixing. Bubbling oxygen through this solution returns the peak to 437 nm although only 70% of the full intensity is restored after 5 min under anaerobic conditions. If the solution containing dithionite is allowed to remain under anaerobic conditions, the Soret band decays completely over a period of 2 hr and this step is irreversible. In contrast, when dithionite ion is added to a deaerated solution of TMpyP at a pH of 8, the Soret band disappears irreversibly within a matter of minutes.

Experiments involving the reduction of $CoP(py)_2$ ([py] = 1.2×10^{-3} *M* such that $CoP(py)_2$ is the only porphyrin species present in significant concentrations) were conducted at pH 8.0. Addition of excess dithionite ion to such a solution shifts the Soret peak reversibly from 442 to 423 nm followed by an irreversible decay of the Soret band in a manner similar to that described for $Co^{III}P(OH)(H_2O)$. That the Soret peak obtained for the reduced product in the presence of pyridine is shifted to the red relative to that obtained in the presence of pyridine suggests that at least some of the reduced porphyrin product contains one or two molecules of the base.

These spectral results imply that the first reduction step occurs at the metal site and that the metalloporphyrin remains intact but that, in a subsequent step, the porphyrin ring system itself is reduced. Kinetic results, to be described below, suggest that the major reducing species is the SO_2^- radical, a one-electron reducing agent. Therefore, although cobalt(I) porphyrins have been reported,[17] it appears that the initial product of the reduction by dithionite ion is a cobalt(II) porphyrin.

The reduction of Co^{III}TMpyP by chromium(II) has been studied at low pH.[9] As in the present study, the Soret band of the product was blue-shifted from that of the reactant. However, the peak of the chromium(II)-reduced product appeared at 428 rather than at 420 nm as found here. The addition of chromium(II) to a CoTMpyP solution already treated with dithionite leads to no change in the Soret maximum from 420 nm. When a solution of Co^{III}TMpyP at low pH is treated with $Ru(NH_3)_6^{2+}$, a rather mild one-electron reducing agent, the Soret maximum appears at 428 nm consistent with the chromium(II) result. Millimolar $Ru(NH_3)_6^{2+}$ is incapable of completely reducing micromolar Co^{III}TMpyP at higher pH and the Soret region is characterized by a broad band which appears to be comprised of two bands at about 437 and 428 nm. The Soret maximum of $Co^{III}P(OH)(H_2O)$ is at 437 nm and the latter band is of the reduced product. Therefore, it appears that the reduction of Co^{III}TMpyP by dithionite leads to a final product which is not Co^{II}TMpyP.

Although the Soret maximum of TMpyP itself is also at 420 nm, the position of the Soret maximum of the dithionite-reduced product cannot be accounted for in terms of the removal of the metal ion from the ring system by the excess dithionite. As was discussed above, bubbling oxygen into the reaction mixture restores the Soret band to its original position and we observe a large kinetic influence on the reduction of the ring system presumably as a consequence of its coordination to a metal ion. Moreover, although the pH range of the chromium(II) study is different from the dithionite study, the difference in the position of the Soret band is not likely to arise from this cause. M^{II}TMpyP are generally much weaker acids than M^{III}TMpyP, and it is therefore unlikely that the product of the dithionite reduction at pH 8 is $Co^{II}P(OH)(H_2O)$. Consistent with this argument is the inability of $Ru(NH_3)_6^{2+}$ to reduce $Co^{III}P(OH)(H_2O)$ completely and the fact that the (unresolved) peak of the reduction product is at 428 nm as is the peak of the product at low pH. We can, at present, only speculate about the nature of the dithionite–metalloporphyrin interaction. It is possible that subsequent to the reduction of the metalloporphyrin by SO_2^- (*vide infra*) there is a further very rapid reduction of the metalloporphyrin. A second possibility is that dithionite attacks the *N*-methylpyridyl substituents of the porphyrin in a manner which can be reversed by the addition of oxygen. It is known that dithionite rapidly reduces certain pyridine derivatives and that in the process charge-transfer complexes are formed.[18] Interactions of this type might account for the blue-shifted Soret maximum.

Kinetic Results. In all of the kinetic experiments, the exponential nature of absorbance *vs.* time curves for the more rapid (reversible) process is consistent with a first-order dependence on metalloporphyrin. Observations were made at 440 and 420 nm; the curves showed the expected changes in absorbance indicated by the spectra, and the rate constants were independent of the wavelength. Plots of k^{obsd} *vs.* $[S_2O_4^{2-}]$ for experiments at pH 4 (phthalate buffer) and at pH 8 (borate buffer, no pyridine added, and borate buffer, [py] = 1.2×10^{-3} *M*) all showed nonzero intercepts. Plots of k^{obsd} *vs.* $[S_2O_4^{2-}]^{1/2}$ for the results at pH 4 and at pH 8 (the latter in the presence of added pyridine) were linear and passed through the origin

$$k^{obsd} = 7.7 \times 10^3 [S_2O_4^{2-}]^{1/2} \quad \text{pH 4}$$

$$k^{obsd} = 72 [S_2O_4^{2-}]^{1/2} \quad \text{pH 8, py added}$$

Experiments conducted at pH 8 as a function of pyridine concentration showed that, at a fixed dithionite concentration $[S_2O_4^{2-}] = 8.4 \times 10^{-4}$ *M*, k^{obsd} is independent of pyridine for $2.5 \times 10^{-4} \leq [py] \leq 2.5 \times 10^{-2}$ *M*. Throughout this range, the only porphyrin species in significant concentration is $CoP(py)_2$.

The results for the dithionite reduction of Co^{III}TMpyP at pH 8 (no pyridine added) proved more complicated than the two systems discussed above. A plot of k^{obsd} *vs.* $[S_2O_4^{2-}]^{1/2}$ is linear at low dithionite concentration and passes through the origin but, at higher dithionite concentrations, there is a marked deviation from linearity (Figure 6). The data could

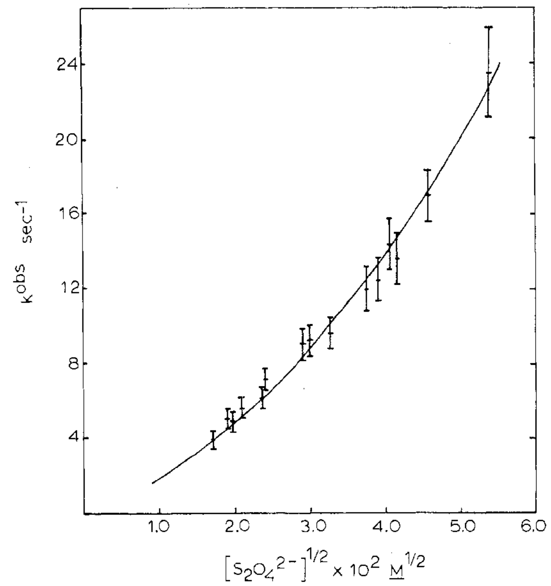


Figure 6. Plot of k^{obsd} *vs.* $[S_2O_4^{2-}]^{1/2}$ for the reduction of CoP-$(OH)(H_2O)$ at pH 8.

be fit quite well (*via* a nonlinear regression method) to a function of the form

$$k^{obsd} = 137[S_2O_4^{2-}]^{1/2} + 5.2 \times 10^3[S_2O_4^{2-}]$$

The curve shown in Figure 6 conforms to these values of the parameters.

Discussion

Substitution Reactions. The present results obtained for pyridine substitution reactions as a function of pH conform to a kinetic picture which very closely parallels the one postulated for the thiocyanate substitution reactions.[8] The substitution reactions of CoTMpyP with thiocyanate and pyridine are very much more rapid than the analogous processes for most cobalt(III) complexes. For example[2a,8]

$$CoP(H_2O)_2{}^{5+} + SCN^- \xrightarrow{2.1\ M^{-1}\ sec^{-1}} CoP(H_2O)(SCN)^{4+}$$

$$Co(NH_3)_5(H_2O)^{3+} + SCN^- \xrightarrow{1.3 \times 10^{-6}\ M^{-1}\ sec^{-1}} Co(NH_3)_5NCS^{2+}$$

Available evidence suggests that both of the preceding reactions proceed *via* an S$_N$1 type mechanism in which the rate-determining step involves the breaking of a cobalt(III)–water bond. The rate constant for this step has been estimated as 2.5 sec^{-1} for the porphyrin complex[8] and 7×10^{-6} sec^{-1} for the ammine complex.[19] Thus, we see that there is a dramatic influence of the porphyrin ligand on the lifetime of a water molecule in the inner-coordination sphere of the complexed cobalt ion. This effect may be interpreted as resulting from the stabilization of the five-coordinate complex, presumed to form enroute to products, relative to the ground-state of the complex. The square-pyramid geometry, often used as a model for the transition state for S$_N$1 mechanisms, is frequently encountered in porphyrin chemistry as, for example, for zinc and high-spin iron complexes.[20]

In the terminology of Langford and Gray,[21] we may consider this bond-breaking mechanism as being either of the dissociative or interchange type. The interpretation of the fact that k_1 for the pyridine reaction is a factor of 3–7 smaller than the analogous rate constant for thiocyanate depends on which mechanism is operating. In terms of the dissociative mechanism, the pyridine molecule competes with water for the vacant site on $CoP(H_2O)$ less well (by the preceding factor) than does thiocyanate. The interchange mechanism interprets this difference in observed rate constant as a difference in the equilibrium constant for outer-sphere complex formation between $CoP(H_2O)_2$ and the ligand L. Either interpretation leads to the conclusion that the rate constants k_1(pyridine) and $k_1(SCN^-)$ are very similar considering the *formal charge type* of the porphyrin. From a calculation of outer-sphere equilibrium constants,[22] which may well not be valid for large molecular ions,[23] this kinetic result implies that the "effective" charge type of the cobalt porphyrin is probably between 1+ and 2+. Thus, for substitution reactions at the metal center, the charge type of the periphery of the porphyrin molecular ion plays little role in coulombic interactions with the incoming ligand. On the other hand, the charge type at the periphery has a quite profound influence on the rate constants for substitution reactions for a given ligand with different porphyrins. The charge type at the periphery of porphyrins influences the distribution of the π-electron density. Positively charged substituents at the meso positions (as, for example, the tetrapyridylporphines (MTpyP) and the tetrakis(4-*N*-methylpyridyl)porphines (MTMpyP)) withdraw electron density from the metal center relative to the negatively charged substituents (*e.g.*, tetraphenylporphinecarboxylates (MTCPP) and tetraphenylporphinesulfonates ($MTPPS_3$ and $MTPPS_4$)). This difference in π-electron delocalization is reflected in the basicity of the metal-free porphyrins,[24,25] the position of the Soret bands,[25] the tendency of the porphyrins to aggregate,[25,26] their tendency to add axial ligands for metals which show variable coordination number,[10,26] and their rates of axial substitution.[8,27] The thiocyanate substitution reactions on tetracarboxyphenylporphinecobalt(III) (CoTCPP) are over 1 order of magnitude faster than the corresponding processes on CoTMpyP although the former porphyrin has a formal negative charge. For Co^{III}TCPP, the rate constant for the reaction of the diaquo form with thiocyanate is 500 M^{-1} sec^{-1}.[27]

The substitution of a hydroxide ion (for a water molecule) trans to the leaving group has a large labilizing effect. For CoTMpyP, the ratio k'_1/k_1 is 50 for thiocyanate and over 300 for pyridine. Furthermore, we have found that k'_1 for $SO_3{}^{2-}$ is $<k'_1$ for SCN^- by a factor of about 2.[28] Thus, there appears to be a small but measurable inverse charge effect on k'_1 which may reflect repulsions between the bound hydroxide ion and the incoming anionic ligands. The trans influence of thiocyanate is even more pronounced than that for hydroxide, being about 10^4. The presence of a pyridine molecule in the inner coordination sphere has a much smaller labilizing influence on the water molecule trans to it as indicated by the ratio $k_2/k_1 \approx 4$–9. Therefore, the following order of labilizing influence has been established with water as the leaving group: $SCN^- > OH^- > py > H_2O$. An identical order is found for SCN^- as the leaving group. The rates of aquation of cobalt(III) cyclam, ammine, and ethylenediamine complexes have been extensively studied and an order of trans labilization has been determined as $OH^- > NO_2{}^- > Cl^- \sim CN^- > H_2O > NH_3 > NCS^-$ with the thiocyanate nitrogen bound.[3] That thiocyanate is so different in its labilizing properties for CoTMpyP suggests that, in this species, it may well be sulfur bound. Certain sulfur-containing ligands and especially sulfite[29] and thiourea[30] have been shown to have a strong labilizing effect on ligands trans to them in cobalt(III) complexes. A recent structural determination[31] of the sulfitopentaamminecobalt(III) complex, in which sulfite shows a large trans-labilizing effect,[29] has established that the sulfite ion is sulfur bound and that there is a significant lengthening of the Co–N bond trans to the Co–S bond. A smaller but similar structural trans effect was determined for the mercaptoacetatobis(ethylenediamine)cobalt(III) complex.[32] A structural determination of the thiocyanate complex of tetraphenylporphineiron(III) has established that in this case the thiocyanate is nitrogen bound.[33] However, the iron is five-coordinate, high spin, and substantially out of plane in this species, and an extrapolation from this complex to the low-spin cobalt(III) derivative of TMpyP is unjustified. Furthermore, sulfur-bound thiocyanate to CoTMpyP would be consistent with the evidence which has been offered that highly unsaturated ligands increase the "soft" character[34] of the cobalt(III) center.[3]

The kinetics of the formation of the mixed complex of CoTMpyP with pyridine and thiocyanate fit quite well with the picture established for binary complex formation of the metalloporphyrin. The rate constant k_{12} is about twice as large as k_1 for SCN^- and about twice as large as k_2 for pyridine. These factors reflect the slight labilizing influence of a bound pyridine and the ligand and metalloporphyrin charge types. It is interesting to note that the stability constant for the addition of SCN^- to $CoP(py)(H_2O)$ is within a factor of 5 of that for the bonding of SCN^- to $CoP(H_2O)_2$. Half of this factor can be interpreted as statistical and, therefore, it seems clear from thermodynamic as well as kinetic grounds that the substitution of pyridine for a water molecule in the inner coordination sphere of the cobalt ion has only a small effect on the electronic distribution and geometry of the cobalt porphyrin complex. This may be contrasted with the influence of thiocyanate in the inner coordination sphere. Equilibrium constants for introduction of SCN^- into the inner coordination sphere follow the pattern $K_1 \approx K_{12} \gg K_2$ and rate constants $k_1^{SCN^-} \approx k_{12} \approx k_2^{py} \ll k_2^{SCN^-}$. Clearly, the presence of SCN^- in the inner coordination sphere has a marked effect on the electronic distribution and/or the geometry of the metalloporphyrin complex. Even a small displacement of the cobalt(III) ion out of the porphyrin plane, for example, would be expected to result in decreased tendency to add an axial ligand on the distal side and a stabilization of the five-coordinate complex presumed to form as an intermediate in substitution reactions.

A comparison of the stability constants for pyridine–cobalt porphyrin complexes with those for pyridine–aquocobalt(III) complexes is difficult because data are sparse for the latter systems. However, for ammonia–aquocobalt(III) complexes the stepwise logarithms of the stability constants have been determined (at $\mu = 2$ *M*) as 7.8, 6.7, 6.1, 5.6, 5.1, and 4.4.[12] In comparing stability constants of a given metal ion with pyridine and ammonia, the latter values are usually larger by from 1 to 3 log units. Therefore, the values of $\log K_1 = 6$ and $\log K_2 = 4.7$ obtained here (especially when the relative number of available sites is considered) lead us to conclude that pyridine has a greater tendency to complex $CoP(H_2O)_2^{5+}$ than $Co(H_2O)_6^{3+}$. This bonding preference of pyridine for the cobalt porphyrin implies the importance of π-back-bonding interactions in this system. The effect of π back-bonding is to lower the electron density on the metal site from that arising from σ donation by the ligand. The "soft" character of the cobalt porphyrin complex may make π back-bonding a more important interaction than might otherwise be the case for a M^{3+}–py bond. This bonding model could well account for the small kinetic and thermodynamic influence of a bound pyridine.

Reduction by Dithionite. The kinetic results are consistent with a mechanism involving the dissociation of dithionite into SO_2^- radicals

$$S_2O_4^{2-} \rightleftharpoons 2SO_2^-$$

$$K_{diss} = [S_2O_4^{2-}]/[SO_2^-]^2$$

$$Co^{III}TMpyP + SO_2^- \xrightarrow{k_1} \text{products}$$

$$Co^{III}TMpyP + S_2O_4^{2-} \xrightarrow{k_2} \text{products}$$

The dissociation reaction is known to be sufficiently rapid[35] for equilibrium between $S_2O_4^{2-}$ and SO_2^- to be maintained under the conditions used. As a consequence

$$k^{obsd} = K_{diss}^{1/2}k_1[S_2O_4^{2-}]^{1/2} + k_2[S_2O_4^{2-}]$$

Table II. Rate Constants for the Reduction of $Co^{III}TMpyP$ by SO_2^-, $S_2O_4^{2-}$, and Cr^{2+} at 25° and $\mu = 0.5$ *M*[a]

Conditions (porphyrin species)	SO_2^-	$S_2O_4^{2-}$	Cr^{2+} [b]
pH 4 ($CoP(H_2O)_2$)	3.1×10^8		16
pH 8, no py added ($CoP(OH)(H_2O)$)	5.5×10^6	5.2×10^3	1.3×10^6
pH 8, excess py ($CoP(py)_2$)	2.9×10^6		

[a] All rate constants have units of M^{-1} sec^{-1}. [b] Reference 9.

Using a value of $K_{diss} = 6.25 \times 10^{-10}$ *M* at 25°[36] gives the results summarized in Table II. Evidently the pathway involving direct $S_2O_4^{2-}$ attack on the porphyrin forms $CoP(H_2O)_2$ and $CoP(py)_2$ is of negligible importance under the conditions of this study. Moreover, the observed rates of reduction of the CoTMpyP complexes by dithionite (whether by SO_2^- or $S_2O_4^{2-}$) exceed the rate of substitution into the inner coordination sphere of the metal ion. Therefore, regardless of the exact position of attack, whether it be in the equatorial plane along an edge of the porphyrin or at an axial site through the bound ligand atoms, we may conclude that no bond is formed directly between the cobalt atom and the reducing agent.

The pH dependence of the reductions by SO_2^- may be compared with those obtained with Cr^{2+}. The reduction of $CoP(H_2O)_2$ by SO_2^- proceeds more than 50 times faster than the reduction of $CoP(OH)(H_2O)$ (see Table II). On the other hand, $CoP(H_2O)_2$ is reduced by Cr^{2+} about 10^5 times *more slowly* than is $CoP(OH)(H_2O)$.[9] Very large ratios of k_{OH}/k_{H_2O} are not uncommon in redox chemistry and usually imply that hydyroxide ion is serving as a bridging ligand between the two metal sites (as, for example, $(H_2O)_5Cr–(OH)–CoP–OH_2$).[37] Even though the reduction is more rapid than the substitution reaction, an inner-sphere mechanism is operating in this case.[37] However, as discussed above, the reduction of CoTMpyP by the SO_2^- radical is almost certainly outer sphere. Since $M^{II}TMpyP$ are weaker acids than $M^{III}TMpyP$, substituting a hydroxide ion for a water molecule in the inner coordination sphere of $Co^{III}TMpyP$ stabilizes the +3 oxidation state relative to the +2 oxidation state. Rates of similar outer-sphere reduction reactions generally correlate with their standard free energy changes[37,38] and, therefore, that k_{H_2O}/k_{OH} is greater than unity for the reduction by SO_2^- is expected on the basis of considerations of the overall driving forces for the reactions.

The results show that $CoP(H_2O)_2$ is reduced about 100 times faster than $CoP(py)_2$ by SO_2^-. A corresponding rate difference is not seen, for example, in the (outer-sphere) reduction of $Co(NH_3)_5H_2O^{3+}$ and $Co(NH_3)_5py^{3+}$ by vanadium(II); the latter reactions proceed at approximately equal rates.[39] The difference in the rates of reduction of $CoP(H_2O)_2$ and $CoP(py)_2$ by SO_2^- is undoubtedly due in part to differences in the free energy changes for the reactions. Available evidence indicates that in aqueous solution, pyridine is complexed more strongly by cobalt(III) hematoporphyrin than by the corresponding cobalt(II) porphyrin.[40] If the same stability order also applies to CoTMpyP, then the free energy change for the reduction of $CoP(H_2O)_2$ will be more favorable than that for the reduction of $CoP(py)_2$, tending to enhance the rate of reduction of the former complex. Another factor which needs to be considered in rationalizing the observed rates is the relative heights of the intrinsic barriers (exchange rates) of the cobalt(II)–cobalt(III) reactions. These are not known at this time and a more detailed consideration of the relative rates must await their determination.

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Registry No. CoP(H_2O)$_2$, 51405-04-0; py, 110-86-1; CoP(H_2O)(py), 53993-53-6; SCN^-, 302-04-5; $S_2O_4{}^{2-}$, 14844-07-6; CoP(py)$_2$, 53993-54-7.

Supplementary Material Available. Kinetic data for the substitution reactions CoTMpyP with pyridine and for the reduction of CoTMpyP with dithionite will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number AIC40150X.

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Electron Transfer through Organic Structural Units. XVIII. Titanium(III) Reductions of Coordinated Cobalt(III)[1]

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Specific rates of reduction, with Ti(III), of 17 pentaamminecobalt(III) complexes (containing a variety of carboxylato groups) have been measured at 25°, in aqueous *p*-toluenesulfonate media. All carboxylato complexes are reduced more rapidly than the derivative of *N,N*-dimethylnicotinamide, I, which reacts *via* an outer-sphere path. In most instances, rate laws feature a prominent inverse-(H^+) term, even when the oxidant has no acidic center, thus implicating $TiOH^{2+}$ as the predominant reducing species. In two cases, an important $(H^+)^{-2}$ term, the first to be reported for reduction of a Co(III) species, is observed as well. Large rate increases associated with the attachment of α-OH to the carboxyl ligand strongly indicate an inner-sphere path, with carboxyl bridging, for reactions in this series; such neighboring hydroxyl accelerations are proportionally more pronounced for Ti(III) than for Cr(II) or Eu(II). Very high rates are observed for several substituted salicylato complexes, but in these reductions the acid-independent term, which is generally negligible for complexes in this series, is preferentially enhanced, and the $(H^+)^{-1}$ term is not observed. In contrast to reductions by Cr(II), no acceleration or alteration of the form of the rate law results from incorporation of a carbonyl group in conjugation with $-COOCo^{III}$. This difference in response with the two reductants is in accord with earlier evidence that such enhanced reductions, irrespective of the position of attack, involve preliminary one-electron transfer to the ligand, a reduction for which the potential of Ti(III) is insufficient.

Relatively few kinetic investigations of the reactions of Ti(III), the most powerfully reducing of the readily accessible d^1 metal centers, have been described.[2] Although this reductant can be prepared and stored with ease, choice of a reaction medium in which to carry out quantitative studies presents problems. Ti(III) is most often generated in aqueous HCl or H_2SO_4, but rate laws for redox reactions in such solutions frequently include chloride- or sulfate-dependent