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**Registry No.** [Co(tbcyclen)Cl]Cl, 60306-18-5; [Co(tbcyclen)-Cl]ClO<sub>4</sub>, 60306-20-9; [Co(tbcyclen)NCS]SCN, 60306-22-1; [Co(tbcyclen)NO<sub>3</sub>]NO<sub>3</sub>, 60326-14-9.

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## Substitution Reactions of Tetracarboxyphenylporphinatocobaltate(III) with Thiocyanate and Pyridine as a Function of pH<sup>1</sup>

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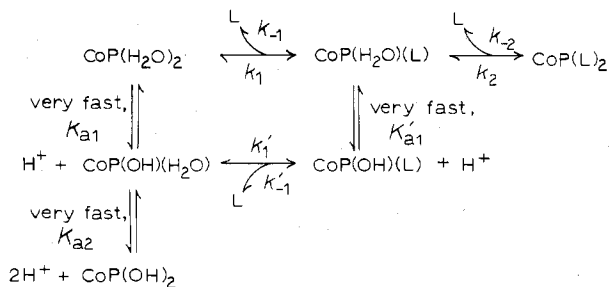
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The substitution reactions of tetracarboxyphenylporphinatocobaltate(III) (CoTCPP) with thiocyanate and with pyridine have been studied as a function of pH at 25 °C and an ionic strength of 0.5 M. While the mechanistic pathway proposed previously for the thiocyanate and pyridine substitution reactions of tetrakis(4-*N*-methylpyridyl)porphinecobalt(III) (CoTMpyP) is generally applicable to CoTCPP as well, some important differences are noted. Where comparisons between the two metalloporphyrins can be made, the change from a positively charged (CoTMpyP) to a negatively charged (CoTCPP) periphery of the macrocycle enhances the respective rate constants by one to three orders of magnitude while the equilibrium constants are altered by factors considerably less than an order of magnitude. These results are discussed with respect to the influence of the electron-withdrawing or -donating properties of the macrocyclic substituents on the electron density at the metal center.

### Introduction

Metalloporphyrin complexes are known to play a crucial role in several biological systems. The presence of such complexes is essential for oxygen transport and storage (hemoglobin and myoglobin), for electron transport (the cytochromes), and as enzymatic cofactors (coenzyme B-12). It seems certain that some of these functions depend on the addition or substitution of a ligand in an axial position of the metal ion. Previous work has shown that metal ions usually considered "inert" to substitution reactions are in fact quite reactive at the axial positions when incorporated in the highly conjugated porphyrin ring system.<sup>3,4</sup> The availability of water-soluble analogues of the naturally occurring porphyrins makes it feasible to carry out detailed kinetic studies of the substitution reactions at these axial positions. Thus it proves possible to gain further insight into the nature of the interactions between the macrocyclic ring system and the metal ion and to determine the effect of these interactions on the substitution properties of the metal center.

### Scheme I<sup>a</sup>

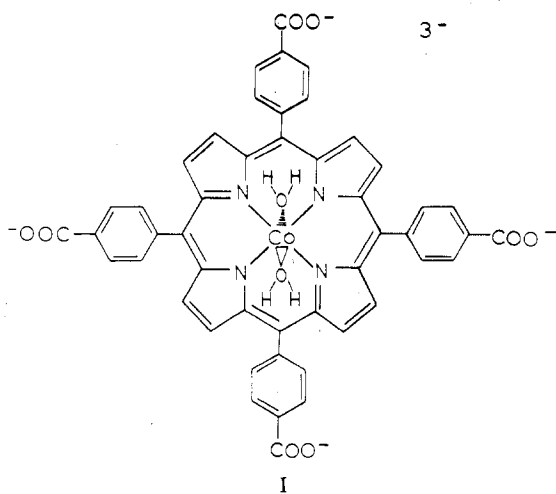


<sup>a</sup> L = ligand (thiocyanate or pyridine); CoP = CoTCPP or CoTMpyP.

We are particularly interested in the manner in which the immediate environment of the metal ion, with respect to the charge on the periphery of the porphyrin, the electron delocalization on the macrocyclic surface, and the nature of the

axial ligands, influences porphyrin ligation, aggregation, and redox properties.<sup>5-11</sup> We have previously reported on the reactions of tetrakis(4-*N*-methylpyridyl)porphyrin cobalt(III) (represented by CoTMpyP) with thiocyanate<sup>7</sup> and with pyridine.<sup>8</sup> A complicated, pH-dependent mechanistic pathway was proposed which could account for the observed results with either ligand (see Scheme I). It was shown that for substitution reactions at the metal center, the charge type of the periphery of the porphyrin molecular ion plays a minor role in Coulombic interactions with the incoming ligand. It was further discovered that the substitution of a thiocyanate ligand for a water molecule in the diaquo complex had an enormous labilizing effect on the second water molecule while the addition of pyridine had only a small labilizing influence and the presence of a hydroxide ion trans to the leaving group had an intermediate effect, the order of labilizing influence being  $\text{SCN}^- > \text{OH}^- > \text{pyridine} > \text{H}_2\text{O}$ .

In the present work we report on the substitution reactions of thiocyanate and pyridine with tetracarboxyphenylporphyrin cobalt(III) (represented by CoTCPP, I). The



mechanistic pathway proposed previously<sup>7,8</sup> for CoTMpyP can satisfactorily account for most but not all of the kinetic results obtained for CoTCPP. For similar processes, the change from a positively charged periphery of the macrocycle in CoTMpyP to a negatively charged periphery in CoTCPP enhances the microscopic rate constants by one to three orders of magnitude. Unlike the situation for CoTMpyP, evidence has been obtained for the existence of dimeric forms of CoTCPP in basic solution (pH > 8).

### Experimental Section

Tetracarboxyphenylporphyrin (TCPP) was prepared and purified as previously described.<sup>5,12</sup> (CoTCPP)Cl was prepared by refluxing TCPP (1 g) and anhydrous  $\text{CoCl}_2$  (0.5 g) in dimethylformamide (200 ml) for up to 6 h. The refluxing solution was then evaporated to about 20 ml and cooled in an ice bath.  $\text{CCl}_4$  (150 ml) was added to the remaining solution and the resulting precipitate filtered, washed with 2 M HCl followed by  $\text{CCl}_4$ , and dried in vacuo. Anal. Calcd for  $\text{C}_{48}\text{H}_{28}\text{N}_4\text{O}_8\text{CoCl}$ : C, 65.27; H, 3.21; N, 6.54. Found: C, 65.16; H, 3.20; N, 6.40.

CoTCPP solutions were prepared by dilution from concentrated stock CoTCPP (which is stored tightly sealed, in the dark) into stock buffer and were used within 48 h of preparation. Phosphate buffer (2 mM) was used for pH  $\leq 8$  and borate buffer (2 mM) was used for pH  $\geq 9$ . All solutions had an ionic strength of 0.5 M utilizing  $\text{NaNO}_3$  as an electrolyte.

Concentrated thiocyanate and pyridine solutions were made up in the appropriate buffer solutions, and working solutions of the ligands were prepared by dilution with the same buffer.

The free pyridine concentration,  $[\text{py}]_f$ , was calculated using a value of 5.4 for the  $\text{p}K_a$  of the pyridinium ion.<sup>13</sup> All chemicals were reagent grade and used without further purification.

Spectra in the Soret and visible regions were obtained with a Cary 14 spectrophotometer thermostated at 25 °C.

Kinetic experiments were performed using stopped-flow (Durrum Model D110 apparatus thermostated at 25 °C), temperature-jump (Messanlagen Studiengesellschaft mbH, Goettingen, Germany), and flash photolysis techniques. Stopped-flow and temperature-jump data were displayed on a Tektronix Type 549 storage oscilloscope and photographed for subsequent analysis. The exponential traces were analyzed to about 3 half-lives and linear first-order plots were obtained over this range unless otherwise noted. The flash photolysis experiments were done at the Laboratorio Ricerche di Base, Rome, utilizing the instrumentation described previously.<sup>14</sup>

### Results

**I. Spectral Studies of CoTCPP.** CoTCPP is soluble above pH  $\sim 5$  and Beer's law and temperature-jump studies at pH 5.7 revealed no evidence of aggregation. Thus we conclude that any porphyrin species which may exist in solution at this pH (diaquo, hydroxoquo) are monomeric.<sup>5,6</sup> The Soret band maximum of this material is at 427 nm with a molar absorptivity of  $2.55 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ . Increasing pH causes a slight red shift accompanied by a decrease in absorptivity, presumably due to the conversion of the diaquo complex  $\text{CoTCPP}(\text{H}_2\text{O})_2^{3-}$  to the hydroxoquo complex  $\text{CoTCPP}(\text{H}_2\text{O})(\text{OH})^{4-}$ .<sup>7,8</sup> Attempts to obtain values of  $\text{p}K_{a1}$  (see Scheme I) by titration with base were frustrated by the small magnitude of the spectral changes and by the fact that in the apparent transition region ( $6.5 < \text{pH} < 8.5$ ) reproducible results could not be obtained in unbuffered solutions. Nonetheless, the results of such studies suggest that  $\text{p}K_{a1} \approx 7.5$  indicating that at pH  $< 6$  the metalloporphyrin exists almost entirely in the diaquo form.

Titration studies also indicate  $\text{p}K_{a2} > 9$  although the spectral results above pH 9 are somewhat anomalous. That is, the dependence of the change in absorbance on pH is more complicated than a simple proton loss. The results suggest the presence of additional (probably aggregated) species at high pH. Kinetic evidence for the existence of such species will be presented below.

**II. Spectral Studies with Thiocyanate.** The equilibrium constants  $K_1$  and  $K_2$  (Scheme I) for the addition of thiocyanate to  $\text{CoTCPP}(\text{H}_2\text{O})_2^{3-}$  were determined by spectral measurements in the Soret region. Experiments were carried out at pH 5.7, 0.5 M  $\text{NaNO}_3$ , 2 mM phosphate buffer, and 25 °C. For  $K_1$ , a spectrophotometric titration was performed to obtain absolute values of the absorbance as a function of thiocyanate concentration in the range  $5 \times 10^{-5} \leq [\text{SCN}^-] \leq 3 \times 10^{-3}$  M. An isosbestic point was obtained at 434 nm and a solution of CoTCPP containing no thiocyanate also passed through this point. The data were analyzed by the application of a general minimization technique, Simplex, as described previously.<sup>7</sup> The general equation used was

$$A - A_0 = \frac{K_1 L_0 \Delta \epsilon_1}{1 + K_1 L_0} C_0 \quad (1)$$

where  $\Delta \epsilon_1 = \epsilon_1 - \epsilon_0$ ,  $C_0$  is the total porphyrin concentration, and  $L_0$  is the total ligand concentration. In these experiments  $C_0 < 4 \times 10^{-6}$  M and thus  $L_0 \gg C_0$ . Utilizing data at 427 nm for which  $\epsilon_0 = 2.55 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$  (vide supra), we obtain from the Simplex routine

$$K_1 = \frac{[\text{CoTCPP}(\text{H}_2\text{O})(\text{SCN})^{4-}]}{[\text{CoTCPP}(\text{H}_2\text{O})_2^{3-}][\text{SCN}^-]} = 2.91 \times 10^3 \text{ M}^{-1}$$

and  $\epsilon_1^{427} = 1.41 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ;  $\lambda_{\text{max}}$  for  $\text{CoTCPP}(\text{H}_2\text{O})(\text{SCN})^{4-}$  is 430 nm and  $\epsilon_1^{430} = 1.64 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ . The precise nature of the data and the appropriateness of the model leading to eq 1 can be seen from Figure 1.<sup>7</sup>

$K_2$  was determined under identical conditions except that the thiocyanate concentration was in the range  $8.6 \times 10^{-3} \leq [\text{SCN}^-] \leq 0.5$  M. Data at 427 nm were analyzed using eq

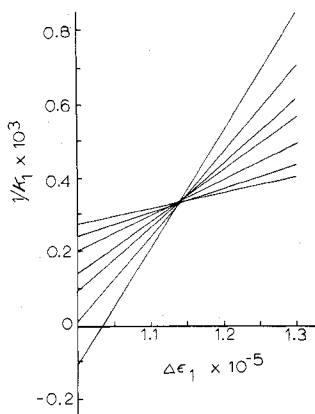


Figure 1. Plot of  $1/K_1$  vs.  $\Delta\epsilon_1$  at 427 nm and pH 5.7 from the Simplex routine for the determination of  $K_1$  (thiocyanate) at 25 °C. The curves are derived from the equation  $1/K_1 = L_0[(C_0\Delta\epsilon_1/(A - A_0)) - 1]$  by systematically varying  $\Delta\epsilon_1$  and calculating values of  $1/K_1$  for each experimentally determined value of  $(A - A_0)$ . The curves should, in theory, intersect at a point and the degree to which this occurs is a measure of the internal agreement of the data.

$2^7$  since in this ligand concentration range, both thio-

$$A - A_0 = \frac{K_1 L_0 \Delta\epsilon_1 + K_1 K_2 L_0^2 \Delta\epsilon_2}{1 + K_1 L_0 + K_1 K_2 L_0^2} C_0 \quad (2)$$

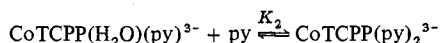
cyanate-containing complexes must be considered. Using the values of  $K_1$  and  $\Delta\epsilon_1$  determined above we obtain (using the Simplex routine)

$$K_2 = \frac{[\text{CoTCPP}(\text{SCN})_2^{5-}]}{[\text{CoTCPP}(\text{H}_2\text{O})(\text{SCN})_4^{4-}][\text{SCN}^-]} = 6.2 \text{ M}^{-1}$$

$\lambda_{\text{max}}$  for  $\text{CoTCPP}(\text{SCN})_2^{5-}$  is at 443 nm with  $\epsilon_2^{443} 1.45 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon_2^{427} 0.53 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ .

The values of the equilibrium constants  $K_1$  and  $K_2$  obtained here are respectively lower by about a factor of 2 than those obtained previously for the reaction of thiocyanate with  $\text{CoTMpyP}$ .<sup>7</sup>

**III. Spectral Studies with Pyridine.** The addition of pyridine to  $\text{CoTCPP}(\text{H}_2\text{O})_2^{3-}$  under equilibrium conditions was also studied by monitoring the absorption in the Soret region. It was assumed that only free pyridine and not the pyridinium ion is the associating form of the ligand.<sup>8</sup> Experiments were carried out at pH 5.6, 0.5 M  $\text{NaNO}_3$ , 2 mM phosphate buffer, and 25 °C. Absorbance spectra were obtained as a function of free pyridine concentration in the range  $4 \times 10^{-6} \leq [\text{py}]_f \leq 1 \times 10^{-3} \text{ M}$ . The data in Figure 2 show a red shift with the final product having an absorbance maximum at 435.5 nm. No change in  $\lambda_{\text{max}}$  or absorptivity is observed on changing  $[\text{py}]_f$  in the range  $3 \times 10^{-4} \leq [\text{py}]_f \leq 1 \times 10^{-3} \text{ M}$ . An isosbestic point is obtained at 433.5 nm but neither  $\text{CoTCPP}$  solutions containing no pyridine nor those solutions at the lowest pyridine concentrations studied pass through the isosbestic point (Figure 2). It is therefore concluded that the observed equilibrium is



Utilizing lower  $[\text{py}]_f$  to obtain  $K_1$  and  $\epsilon_1$  is not experimentally practical.<sup>7,8</sup> However, the data can be analyzed to obtain  $K_2$  by use of eq 3 where  $\epsilon$  is the measured absorptivity (i.e.,

$$\log \left( \frac{\epsilon_1 - \epsilon}{\epsilon - \epsilon_2} \right) = n \log [\text{py}]_f + \log K_2 \quad (3)$$

absorbance/ $C_0$ ),  $\epsilon_1$ , is the absorptivity of  $\text{CoTCPP}(\text{H}_2\text{O})(\text{py})^{3-}$ , and  $\epsilon_2$  is the absorptivity of  $\text{CoTCPP}(\text{py})_2^{3-}$ . Since  $\epsilon_1$  cannot be determined directly, successive approximations

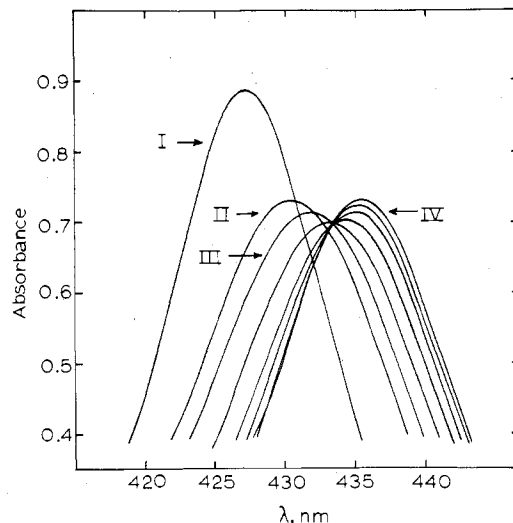


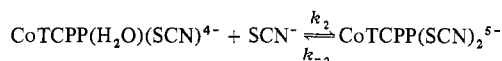
Figure 2. Absorption spectra in the Soret region for  $\text{CoTCPP}(\text{H}_2\text{O})_2^{3-}$  ( $3.5 \times 10^{-6} \text{ M}$ ) and  $\text{CoTCPP}(\text{H}_2\text{O})_2^{3-}$  plus pyridine at pH 5.6, 25 °C.  $[\text{py}]_f$ : I, 0; II,  $4 \times 10^{-6} \text{ M}$ ; III,  $8 \times 10^{-6} \text{ M}$ ; IV,  $8 \times 10^{-4} \text{ M}$ . The final product (IV) is  $\text{CoTCPP}(\text{py})_2^{3-}$  and has  $\lambda_{\text{max}}$  at 435.5 nm and  $\epsilon^{435.5} = 2.08 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ . The isosbestic point is at 433.5 nm.

were used until the data resulted in a straight line of slope  $n$  (number of ligands added to the chromophore) equal to unity. Three separate determinations resulted in the following average values:  $K_2 = (9.5 \pm 1.5) \times 10^4 \text{ M}^{-1}$ ,  $\epsilon_2^{435.5} = (2.08 \pm 0.03) \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $\epsilon_1^{435.5} = (1.70 \pm 0.03) \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ . If we assume that at the lowest  $[\text{py}]_f$  which passes through the isosbestic point,  $[\text{CoTCPP}(\text{H}_2\text{O})(\text{py})^{3-}]/[\text{CoTCPP}(\text{H}_2\text{O})_2^{3-}] \gtrsim 10$ , we can estimate that  $K_1 \gtrsim 10^6 \text{ M}^{-1}$ .

**IV. Kinetic Studies with Thiocyanate.** Earlier work has shown that Scheme I can satisfactorily account for the pH-dependent substitution reactions of  $\text{CoTMpyP}$  with thiocyanate<sup>7</sup> and with pyridine.<sup>8</sup> While the individual rate constants might be expected to show substantial differences for substitution in  $\text{CoTCPP}$  due to the change from a positively to a negatively charged periphery of the porphyrin macrocycle, there is no a priori reason to expect major variations in the mechanistic pathway for substitution. Thus the kinetic experiments reported here were designed and will be discussed using Scheme I as a basic starting point. The results indicate that this approach is well founded although some modifications become necessary for experiments conducted at a pH  $> 8$  (vide infra).

Considering Scheme I and the spectral results described above, determination of  $k_2$  at low pH presents the fewest experimental complications. In addition, if it can be shown that for thiocyanate as the attacking ligand  $k_2 \gg k_1$  (as was the case with  $\text{CoTMpyP}$ ), the study of  $k_1$  and  $k_1'$  is greatly simplified. Preliminary results showed that at the thiocyanate concentrations necessary to ensure a substantial amount of the dithiocyanate complex in the final product, the reaction was too fast to measure by either stopped-flow or conventional temperature-jump techniques. However, an estimate of  $k_2$  has been obtained through the use of flash photolysis methods. Similar techniques have been used previously to study the ligation of carbon monoxide in hemoglobin.<sup>15</sup> The apparatus used in this work was a combined laser-temperature-jump-flash photolysis instrument which has been described previously.<sup>14</sup> The excitation wavelength may be varied over a considerable range by use of a tunable laser. In the flash photolysis mode, the excitation wavelength is in the visible or near-infrared region and very little heating of the solution occurs. However, the energy of the excitation beam is sufficient to cause photodissociation of ligands and thus their

subsequent recombination may be followed with appropriate fast detectors. In these experiments the excitation wavelength was 562 nm and recombination was monitored at 405 nm. The laser pulse duration was  $\sim 100$  ns with a repetition rate of 75 Hz. Experiments were performed at pH 5.6 at thiocyanate concentrations of 0.2 and 0.5 M. The total porphyrin concentration was about  $3 \times 10^{-5}$  M in both cases. The photochemical effects observed were extremely small (but reproducible) and thus the relative errors in the relaxation times were correspondingly large. It should be noted that a solution containing no  $\text{SCN}^-$  showed no relaxation effect. The relaxation times,  $\tau$ , observed were  $1.6 \pm 0.5 \mu\text{s}$  for  $[\text{SCN}^-] = 0.2$  M and  $0.8 \pm 0.4 \mu\text{s}$  for  $[\text{SCN}^-] = 0.5$  M. For the relaxation reaction



under pseudo-first-order conditions ( $[\text{SCN}^-] \gg [\text{CoTCPP}]$ ),  $1/\tau = k_2([\text{SCN}^-] + 1/K_2)$  and we obtain  $k_2 = (1.8 \pm 0.8) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ .

Kinetic analysis of Scheme I for the substitution of the first ligand leads to the result<sup>7</sup>

$$k_{\text{obsd}} = \left( \frac{k_1}{1 + K_{a1}/[\text{H}^+]} + \frac{k_1'}{1 + [\text{H}^+]/K_{a1}} \right) [\text{L}] + \left( \frac{k_{-1}}{1 + K_{a1}'/[\text{H}^+]} + \frac{k_{-1}'}{1 + [\text{H}^+]/K_{a1}'} \right) \quad (4)$$

Thus plots of  $k_{\text{obsd}}$  vs.  $[\text{L}]$  should be linear with slope

$$k_f = \frac{k_1}{1 + K_{a1}/[\text{H}^+]} + \frac{k_1'}{1 + [\text{H}^+]/K_{a1}}$$

and intercept

$$k_r = \frac{k_{-1}}{1 + K_{a1}'/[\text{H}^+]} + \frac{k_{-1}'}{1 + [\text{H}^+]/K_{a1}'}$$

Stopped-flow studies of the substitution of the first ligand were carried out by mixing CoTCPP solutions containing no thiocyanate with thiocyanate solutions of various concentrations; the final ligand concentration was in the range  $4 \times 10^{-4} \leq [\text{SCN}^-] \leq 2 \times 10^{-2}$  M while the total porphyrin concentration was  $\sim 2 \times 10^{-6}$  M in all cases. Experiments were conducted at 25 °C at pH 5.6 and 6.4, all solutions containing 0.5 M  $\text{NaNO}_3$  and 2 mM phosphate buffer. The reactions were monitored at 427 nm and monophasic kinetic curves were obtained. Pseudo-first-order kinetics and linear plots of  $k_{\text{obsd}}$  vs.  $[\text{SCN}^-]$  were obtained over the entire range of thiocyanate concentrations at both pH's. Analysis of the data leads to  $k_f = 495 \pm 25$  and  $733 \pm 35 \text{ M}^{-1} \text{ s}^{-1}$  at pH 5.6 and 6.4, respectively. Thus  $k_f$  is seen to be pH dependent as expected from Scheme I. However, since we do not as yet have a precise value for  $K_{a1}$ , we cannot without additional information use eq 4 to determine  $k_1$  or  $k_1'$ .

At pH  $\geq 9$ , spectral results indicate that  $[\text{CoTCPP}(\text{OH})(\text{H}_2\text{O})^{4-}] \gg [\text{CoTCPP}(\text{H}_2\text{O})_2^{3-}]$ . If, in addition, it is assumed that  $k_1' > k_1$  (by analogy with results for CoTMpyP<sup>7,8</sup>), the expression for  $k_f$  reduces to  $k_f \approx k_1'$ . The temperature-jump technique proved useful for studying the substitution kinetics at this pH. If the above assumptions are correct, kinetic analysis of the relaxation process requires that we consider only the following portion of Scheme I

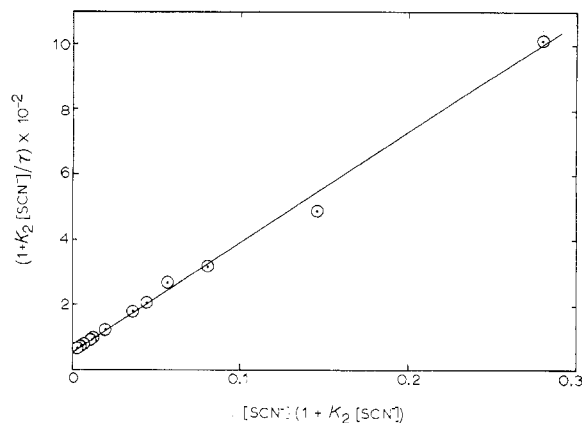
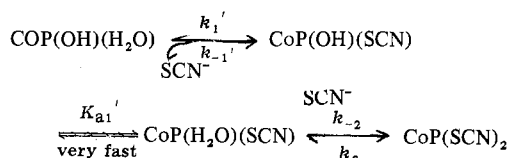


Figure 3. Plot of  $(1 + K_2[\text{SCN}^-])/\tau$  vs.  $[\text{SCN}^-](1 + K_2[\text{SCN}^-])$  for temperature-jump data obtained at pH 9.2 ( $[\text{CoTCPP}] = 8.75 \times 10^{-6}$  M). Slope is  $k_1' = 3.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ . See text and Appendix for mathematical development and additional details.

Use of standard mathematical techniques for deriving relaxation expressions (see Appendix) leads to the result

$$\frac{1 + K_2[\text{SCN}^-]}{\tau} = k_1' \{ [\text{SCN}^-](1 + K_2[\text{SCN}^-]) \} + \frac{k_{-1}'K_{a1}'}{[\text{H}^+]} \quad (5)$$

Thus a plot of  $(1 + K_2[\text{SCN}^-])/\tau$  vs.  $[\text{SCN}^-](1 + K_2[\text{SCN}^-])$  should give a straight line of slope  $k_1'$  and intercept  $k_{-1}'K_{a1}'/[\text{H}^+]$ .

The temperature-jump experiments were carried out at pH 9.2 in 2 mM borate buffer, 0.5 M  $\text{NaNO}_3$ , and a final temperature of 25 °C. The thiocyanate concentration was varied over the range  $3.75 \times 10^{-3} \leq [\text{SCN}^-] \leq 0.25$  M while the total CoTCPP concentration was held constant at  $8.75 \times 10^{-6}$  M. A plot of  $(1 + K_2[\text{SCN}^-])/\tau$  vs.  $[\text{SCN}^-](1 + K_2[\text{SCN}^-])$  is shown in Figure 3. From this plot,  $k_1' = (3.3 \pm 0.2) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{-1}'K_{a1}'/[\text{H}^+] = 48 \pm 6 \text{ s}^{-1}$  at pH 9.2.

We can now utilize the expression for  $k_f$  to determine values of  $k_1$  and  $K_{a1}$  which best fit the observed results. The best agreement with experiment was obtained with  $K_{a1} = 4.0 \times 10^{-8}$  M ( $\text{p}K_{a1} = 7.4$ ) and  $k_1 = 450 \text{ M}^{-1} \text{ s}^{-1}$ . These values resulted in a calculated value of  $k_f = 494 \text{ M}^{-1} \text{ s}^{-1}$  at pH 5.6 ( $k_f^{\text{exptl}} = 494 \text{ M}^{-1} \text{ s}^{-1}$ ) and  $k_f = 720 \text{ M}^{-1} \text{ s}^{-1}$  at pH 6.4 ( $k_f^{\text{exptl}} = 733 \text{ M}^{-1} \text{ s}^{-1}$ ). The value for  $\text{p}K_{a1}$  agrees well with the value estimated from spectral studies and the internal agreement of the data supports the assumptions used in determining  $k_1'$ .

Experiments with thiocyanate at pH 9 were also conducted using stopped-flow techniques. At low thiocyanate concentrations ( $10^{-2}$  M) a fast, pseudo-first-order reaction was observed which yielded the same rate constant as was obtained from the temperature-jump studies. This result provides an independent verification of  $k_1'$ . However, a second, slower reaction of much smaller amplitude was also observed with the stopped-flow experiments. The apparent rate constant for this secondary process was approximately three orders of magnitude less than  $k_1'$ . Although the amplitude of this reaction is quite small, the results are fully reproducible and blank experiments conducted without thiocyanate ruled out the possibility of an instrumental artifact. The reaction was studied as a function of thiocyanate concentration in the range  $1 \times 10^{-2} \leq [\text{SCN}^-] \leq 1.0$  M. Pseudo-first-order kinetics were obeyed at each thiocyanate concentration. A plot of  $k_{\text{obsd}}$  vs.  $[\text{SCN}^-]$  shows strong curvature and eventual saturation; a plot of  $k_{\text{obsd}}^{-1}$  vs.  $[\text{SCN}^-]^{-1}$  (Figure 4) gives a straight line. The kinetic data can be accounted for by a rate law of the form

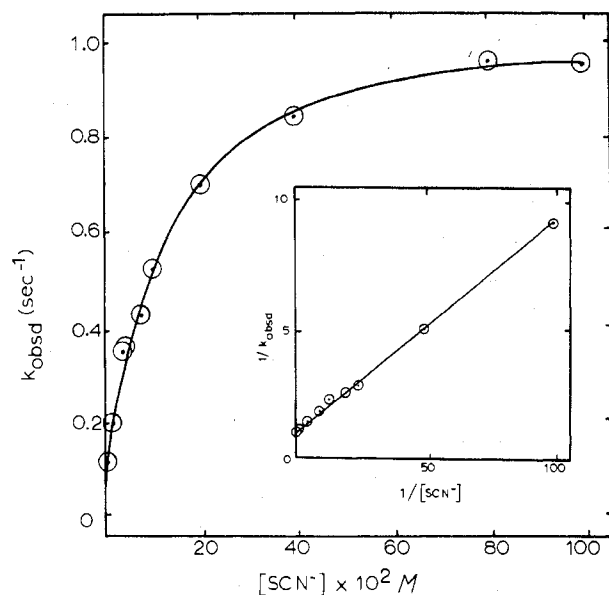


Figure 4. Plot of  $k_{\text{obsd}}$  vs.  $[\text{SCN}^-]$  from stopped-flow data at pH 9.0, 25 °C. This reaction is of much smaller amplitude and almost three orders of magnitude slower than  $k_1'$  observed by temperature-jump methods (see Figure 3). The inset shows the same data plotted as  $k_{\text{obsd}}^{-1}$  vs.  $[\text{SCN}^-]^{-1}$ .

$k_{\text{obsd}} = kK_e[\text{L}]/(1 + K_e[\text{L}])$ , where  $K_e$  is an equilibrium constant and  $[\text{L}]$  represents the ligand concentration. This expression may be rearranged to

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{kK_e[\text{L}]} + \frac{1}{k}$$

and a plot of  $k_{\text{obsd}}^{-1}$  vs.  $[\text{L}]^{-1}$  should yield a straight line with slope  $k^{-1}K_e^{-1}$  and an intercept equal to  $k^{-1}$ . From Figure 4 we obtain  $k = 1.0 \pm 0.1 \text{ s}^{-1}$  and  $K_e = 12 \pm 1 \text{ M}^{-1}$ . The interpretation of this result and the derivation of the rate law will be considered in the Discussion.

**V. Kinetic Studies with Pyridine.** All kinetic measurements for pyridine substitution were done with the Durrum stopped-flow apparatus thermostated at 25 °C. Solutions were at 0.5 M ionic strength with  $\text{NaNO}_3$  and the pH was maintained with 2 mM buffer;  $[\text{CoTCPP}]$  was about  $2 \times 10^{-6} \text{ M}$  in all cases.

To determine  $k_2$ , various concentrations of pyridine were mixed with a CoTCPP solution which had been preincubated with  $10^{-5} \text{ M}$   $[\text{py}]_f$ . Under these conditions the major species present is  $\text{CoTCPP}(\text{H}_2\text{O})(\text{py})^{3-}$  with a small amount of  $\text{CoTCPP}(\text{py})_2^{3-}$ . Thus on mixing with additional pyridine the reaction observed is  $\text{CoTCPP}(\text{H}_2\text{O})(\text{py})^{3-} + \text{py} \rightarrow \text{CoTCPP}(\text{py})_2^{3-}$ . The absorbance change for this process was monitored at 435.5 nm, the absorption maximum of the bis(pyridine) complex. If the reaction is monitored at the isobestic point (433.5 nm), no change in absorbance is seen, thus verifying the assumption that little or no unliganded porphyrin is present in the initial solution. The reaction was studied at pH 5.6 over the range  $4 \times 10^{-4} \leq [\text{py}]_f \leq 5 \times 10^{-3} \text{ M}$ . Under these conditions the final solution contains almost exclusively the bispyridine complex and the reaction rate is expected to be pseudo first order in  $[\text{py}]_f$ ; indeed monophasic first-order kinetic plots were obtained at all pyridine concentrations, and from a plot of  $k_{\text{obsd}}$  vs.  $[\text{py}]_f$  we obtain  $k_2 = (2.1 \pm 0.1) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ . The intercept is too small to be measured reliably, but since  $K_2 = 9.5 \times 10^4 \text{ M}^{-1}$ , we can calculate that  $k_{-2} = (2.2 \pm 0.2) \times 10^{-2} \text{ s}^{-1}$ .

The reaction was also studied at pH 9.0. At this pH, the porphyrin solution was preincubated with  $4 \times 10^{-5} \text{ M}$   $[\text{py}]_f$  and the range of  $[\text{py}]_f$  after mixing was  $5 \times 10^{-4} \leq [\text{py}]_f \leq$

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

	$\text{Co}^{\text{III}}\text{TCPP}^a$		$\text{Co}^{\text{III}}\text{TMpyP}^b$	
	py	$\text{SCN}^-$	py	$\text{SCN}^-$
$k_1, \text{M}^{-1} \text{ s}^{-1}$	$1.4 \times 10^3$	450	0.7	2.1
$k_{-1}, \text{s}^{-1}$	$\leq 10^{-3}$	0.15	$6 \times 10^{-7}$	$3.1 \times 10^{-4}$
$K_1, \text{M}^{-1}$	$> 10^6$	$2.9 \times 10^3$	$10^6$	$6.4 \times 10^3$
$k_2, \text{M}^{-1} \text{ s}^{-1}$	$2.1 \times 10^3$	$1.8 \times 10^6$	2.8	$2.8 \times 10^4$
$k_{-2}, \text{s}^{-1}$	$2.2 \times 10^{-2}$	$2.9 \times 10^5$	$5.8 \times 10^{-5}$	$3.0 \times 10^3$
$K_2, \text{M}^{-1}$	$9.5 \times 10^4$	6.2	$4.8 \times 10^4$	13
$k_1', \text{M}^{-1} \text{ s}^{-1}$	$18 \times 10^3$	$3.3 \times 10^3$	220	110
$\text{p}K_{a1}$	7.4	7.4	6.0	6.0
$\text{p}K_{a2}$			10.0	10.0
$\text{p}K_{a1}'$	$> 10$		8.1	$> 9$

<sup>a</sup> This work. <sup>b</sup> R. F. Pasternack and M. A. Cobb, *J. Inorg. Nucl. Chem.*, **35**, 4327 (1973); R. F. Pasternack, M. A. Cobb, and N. Sutin, *Inorg. Chem.*, **14**, 866 (1975).

$4 \times 10^{-3} \text{ M}$ . A plot of  $k_{\text{obsd}}$  vs.  $[\text{py}]_f$  gave a straight line with  $k_2 = (2.4 \pm 0.2) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , in good agreement with the result obtained at pH 5.6. However, at pH 9.0 the amplitude of the reaction is smaller and first-order plots for  $k_{\text{obsd}}$  show some curvature at short times. Thus the value obtained at lower pH is probably more accurate. Nonetheless, the good agreement obtained suggests that the major reaction investigated under these conditions is the conversion of  $\text{CoTCPP}(\text{H}_2\text{O})(\text{py})^{3-}$  to  $\text{CoTCPP}(\text{py})_2^{3-}$ . Then if we assume that  $[\text{CoTCPP}(\text{OH})(\text{py})]/[\text{CoTCPP}(\text{H}_2\text{O})(\text{py})] \leq 0.1$ , we can estimate that  $K_{a1}' \leq 10^{-10} \text{ M}$ .

The kinetics of substitution of the first pyridine ligand were studied as a function of  $[\text{py}]_f$  and pH. In these experiments, CoTCPP solutions containing no pyridine were mixed with pyridine solutions to give a final concentration in the range  $7 \times 10^{-4} \leq [\text{py}]_f \leq 5 \times 10^{-3} \text{ M}$ . Under these conditions the final product is again the bispyridine complex. Unlike the case for thiocyanate substitution, here it is unwarranted to assume that  $k_2 \gg k_1$  and that no complication would arise from the second complexation reaction. However, the reaction of the porphyrin complex with the first pyridine molecule can be conveniently studied by following the change in absorbance at the isobestic point (433.5 nm) for  $\text{CoTCPP}(\text{H}_2\text{O})(\text{py})$  and  $\text{CoTCPP}(\text{py})_2$ . At this wavelength there is no change in absorbance as the second ligand is added. Plots of  $k_{\text{obsd}}$  vs.  $[\text{py}]_f$  at pH 5.6, 6.5, and 7.0 were linear over the entire concentration range studied. From these data,  $k_f$  (in  $\text{M}^{-1} \text{ s}^{-1}$ ) =  $(1.7 \pm 0.1) \times 10^3$ ,  $(3.7 \pm 0.2) \times 10^3$ , and  $(6.1 \pm 0.2) \times 10^3$  at pH 5.6, 6.5, and 7.0, respectively. In all cases a single reaction was observed with pseudo-first-order kinetics.

At pH 9.0 a strongly coupled biphasic reaction is observed at the isobestic point. As with thiocyanate, the second reaction is clearly much slower than either  $k_2$  or the expected  $k_1'$ . First-order plots at all pyridine concentrations used are markedly curved, thus preventing accurate determinations of either  $k_{\text{fast}}$  or  $k_{\text{slow}}$ . By analogy with thiocyanate substitution we conclude that the fast reaction is probably related to  $k_1'$ . Then by taking the initial slope we can establish a lower limit of  $\sim 12 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  for  $k_1'$ . An improved value of the rate constant may be obtained from the kinetic results at lower pH's. Using the expression for  $k_f$  (vide supra), the best fit of the experimental data is obtained with  $k_1 = 1.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_1' = 18 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , and  $\text{p}K_{a1} = 7.4$ . Thus the substitution kinetics of both thiocyanate and pyridine lead to the same value for  $\text{p}K_{a1}$ . The rate and equilibrium constants for pyridine and thiocyanate with both CoTCPP and CoTMpyP (shown for comparison) are summarized in Table I.

## Discussion

Substituted porphine ligands with their highly delocalized  $\pi$ -electron clouds have a marked cis-labilizing influence on "inert" metal ion substitution.<sup>3,4,7,8</sup> The replacement of a

**Table II.** Relative Rate Constants for CoTMpyP and CoTCPP

Step	$k_{\text{CoTCPP}}/k_{\text{CoTMpyP}}$	
	py	SCN <sup>-</sup>
$k_1$	2000	210
$k_1'$	80	30
$k_2$	750	65

water molecule by a thiocyanate ion proceeds some  $10^6$ – $10^9$  times faster for cobalt(III)–porphyrin species than for cobalt(III)–ammine complexes. This kinetic effect which is a manifestation of the extensive mixing of ligand and metal orbitals is unparalleled by model macrocyclic compounds not having a high degree of electron delocalization.<sup>16,17</sup> Thus when we compare the present results obtained with CoTCPP with those obtained previously for CoTMpyP in terms of reactions being slower or faster, our remarks must be taken in this context; the primary influence of the porphyrin ligand is a profound labilization of the axial bonds.

The rate comparisons of Table I show the influence of negatively charged substituents which concentrate electron density at the metal site (as for CoTCPP) relative to the delocalization of electron density by positively charged substituents (as for CoTMpyP). We can, from these results, distinguish between the influence of peripheral charge on the porphyrin molecular orbitals and the Coulombic interactions of the substituents with incoming ligands. Let us consider this latter effect first.

We pointed out earlier that the formal charge type of the porphyrin and the resulting Coulombic interactions with attacking ligands appear to play a measurable but minor role in determining rates of reactions.<sup>8</sup> For CoTMpyP(H<sub>2</sub>O)<sub>2</sub><sup>5+</sup>,  $k_1^{\text{SCN}^-}/k_1^{\text{py}} \approx 3$  which led us to estimate that the "effective" charge type of the metalloporphyrin is about 1+ to 2+. This conclusion concerning the relative importance of Coulombic interactions is borne out by the present study; for CoTCPP(H<sub>2</sub>O)<sub>2</sub><sup>3-</sup>,  $k_1^{\text{SCN}^-}/k_1^{\text{py}} \approx 1/3$ . The relative rates for the neutral ligand and the anion have "crossed over" for the two metalloporphyrins but the entire factor is less than an order of magnitude.

We found in our earlier work that whereas the substitution of a hydroxide ion for a water molecule trans to the leaving group has a large labilizing effect, there appears to be a small but inverse charge effect on  $k_1'$ . For CoTMpyP(H<sub>2</sub>O)(OH)<sup>4+</sup>, pyridine substitutes twice as fast as SCN<sup>-</sup>, the effect amounting to a factor of about 6 since  $k_1^{\text{SCN}^-} = 3k_1^{\text{py}}$ . For CoTCPP(H<sub>2</sub>O)(OH)<sup>4-</sup>, pyridine substitutes 6 times as fast as SCN<sup>-</sup> but is already about 3 times faster for the diaquo complex. Therefore, once again charge interactions of the metalloporphyrins with incoming ligands are of minor importance.

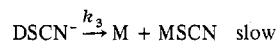
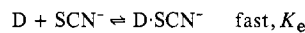
These effects pale in comparison with the influence of the peripheral charge type on the substitution rate for a given ligand. The ratios of rate constants for a pyridine or thiocyanate ligand substituting for a water molecule for the two metalloporphyrins are shown in Table II. The influence is more clearly seen for pyridine where Coulombic effects play no role at all. Changing from positively to negatively charged peripheral substituents increases the metal–water bond-breaking step which appears to be rate determining in these processes by over three orders of magnitude.<sup>3,4,7,8,18</sup> The major influence of these peripheral substituents therefore is to modify the degree of electron delocalization at the porphyrin core which in turn manifests itself in a "cis" effect as well as in determining other kinetic and thermodynamic properties such as ease of metal reduction,<sup>11</sup> coordination number preference,<sup>9</sup> and tendency to aggregate.<sup>5,6,19</sup> Table II also shows that the rate constant ratio is substantially reduced by the presence of a hydroxide ion trans to the leaving water molecule (step  $k_1'$ ).

This suggests to us that the anionic ligand tends to counteract the charge effects of the macrocyclic periphery, probably by providing additional electron density in the case of CoTMpyP and by exerting a repulsive effect on the delocalized  $\pi$  electrons in CoTCPP.

It might be noted that the labilization patterns for bound ligands determined for CoTMpyP are valid for CoTCPP as well. Thus with water as the leaving group, the trans influence order is SCN<sup>-</sup> > OH<sup>-</sup> > py > H<sub>2</sub>O. Arguments made earlier that SCN<sup>-</sup> is likely to be sulfur bonded to cobalt in CoTMpyP seem to be equally applicable here.<sup>7,8,19,20</sup>

Finally, we have observed a cobalt porphyrin species and a reaction pathway for CoTCPP which has no parallel for CoTMpyP. For both thiocyanate and pyridine, we have observed slow reactions at pH 9 which cannot be accommodated within the framework of Scheme I. Our spectral results have indicated that at high ligand concentration, the only chromophore in solution is the diliganded complex (i.e., we obtain the same value of  $\epsilon_2$  at pH 9 as at pH 5.6). Thus, the eventual product of the slow reaction is CoTCPP<sub>2</sub>. The appearance of biphasic kinetics at high pH *even at the isosbestic point for CoTCPP(H<sub>2</sub>O)L and CoTCPP<sub>2</sub>* implies that the unliganded metalloporphyrin exists in two forms at pH 9 which equilibrate slowly relative to the substitution rate. The kinetic results are consistent with these two forms being CoTCPP(H<sub>2</sub>O)(OH)<sup>4-</sup> and an aggregate of this species, presumably a dimer, D. Because this latter species does not appear at low pH, it is likely to be either a  $\mu$ -oxo or dihydroxo dimer but, for this diamagnetic species, one does not have a convenient method for distinguishing between these two forms as can be done for iron(III) species.<sup>21</sup>

The reaction of D with thiocyanate leads to saturation kinetics and can be accounted for by the formation of a dimer–thiocyanate complex in a rapid step followed by a rate-determining breakdown of the dimer



The resultant monomers, M and MSCN, would then be expected to add additional thiocyanates rapidly. Similar pathways have been observed for the well-characterized oxo-bridged iron dimer of tetra(*p*-sulfophenyl)porphine.<sup>22</sup>

For this mechanism

$$\frac{-d[D]}{dt} = \left( \frac{k_3 K_e [\text{SCN}^-]}{1 + K_e [\text{SCN}^-]} \right) [D]$$

$$k_{\text{obsd}} = \frac{k_3 K_e [\text{SCN}^-]}{1 + K_e [\text{SCN}^-]}$$

A plot of  $1/k_{\text{obsd}}$  vs.  $1/[\text{SCN}^-]$  is predicted to be linear; such a plot is shown in Figure 4 from which we obtain  $K_e = 12 \pm 1 \text{ M}^{-1}$  and  $k_3 = 1 \pm 0.1 \text{ s}^{-1}$ . That the reaction of the dimer with pyridine is more severely coupled with the ligand substitution step than is the case for thiocyanate can be accounted for by either a much larger  $K_e$  or  $k_3$  for pyridine. We feel that the main contribution to this effect is a larger  $K_e$  inasmuch as all of the stability constants for pyridine are larger than the respective constants for thiocyanate.

Speculative though these arguments for the difference in behavior between pyridine and thiocyanate may be, the kinetic results do implicate very strongly the existence of a dimer species for CoTCPP whereas none was observed for CoTMpyP. We had, during our investigations of other metal derivatives of these two porphyrins, pointed out that MTCPP derivatives have a greater tendency to aggregate than do MTMpyP derivatives.<sup>19</sup> However, in these earlier cases the aggregation did not involve a covalent link between the metal

atoms. The results of the present study suggest that even when a  $\mu$ -oxo or dihydroxo bridge exists between the two metal sites, the  $\pi$ -electron density of the porphyrin ring system plays a role in stabilizing the aggregate. Thus, no dimer is observed when the  $\pi$  molecular orbitals expand over the surface of the molecule because of the electron-withdrawing influence of the positively charged periphery whereas a dimer is observed when the periphery is negatively charged.

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#### Appendix. Derivation of the Relaxation Expression for the Temperature-Jump Study of Thiocyanate Substitution at pH 9

The reaction of the dimeric species is neglected since  $k_3 \ll k_1'$  (see Discussion). First, consider

$$\frac{-d[\text{CoP(OH)(H}_2\text{O)}]}{dt} = k_1'[\text{CoP(OH)(H}_2\text{O)}][\text{SCN}] - k_{-1}'[\text{CoP(OH)(SCN)}] \quad (1a)$$

Linearizing (1a) yields

$$\frac{-d\delta[\text{CoP(OH)(H}_2\text{O)}]}{dt} = k_1'[\text{CoP(OH)(H}_2\text{O)}]\delta[\text{SCN}] + k_1'[\text{SCN}]\delta[\text{CoP(OH)(H}_2\text{O)}] - k_{-1}'\delta[\text{CoP(OH)(SCN)}] \quad (2a)$$

From material balance and  $\sigma[\text{dimer}] = 0$ , we obtain

$$\delta[\text{CoP(OH)(H}_2\text{O)}] + \delta[\text{CoP(OH)(SCN)}] + \delta[\text{CoP(H}_2\text{O)(SCN)}] + \delta[\text{CoP(SCN)}_2] = 0 \quad (3a)$$

The equilibrium constants  $K_{a1}'$  and  $K_2$  are defined as

$$K_{a1}' = \frac{[\text{CoP(OH)(SCN)}][\text{H}^+]}{[\text{CoP(H}_2\text{O)(SCN)}]} \\ K_2 = \frac{[\text{CoP(SCN)}_2]}{[\text{CoP(H}_2\text{O)(SCN)}][\text{SCN}]}$$

Rearranging and substituting these expressions in (3a) give

$$\delta[\text{CoP(OH)(H}_2\text{O)}] + \delta[\text{CoP(OH)(SCN)}] \left\{ 1 + \frac{[\text{H}^+]}{K_{a1}'}(1 + K_2[\text{SCN}]) \right\} + K_2[\text{CoP(H}_2\text{O)(SCN)}]\delta[\text{SCN}] = 0 \quad (4a)$$

Material balance may also be written as

$$\delta[\text{SCN}] + \delta[\text{CoP(OH)(SCN)}] + \delta[\text{CoP(H}_2\text{O)(SCN)}] + 2\delta[\text{CoP(SCN)}_2] = 0 \quad (5a)$$

Subtracting (3a) from (5a) and again utilizing the equilibrium expressions as well as the fact that  $K_2[\text{CoP(H}_2\text{O)(SCN)}] \ll 1$ , we have

$$\delta[\text{SCN}] = \delta[\text{CoP(OH)(H}_2\text{O)}] - \frac{K_2}{K_{a1}'}[\text{SCN}][\text{H}^+]\delta[\text{CoP(OH)(SCN)}] \quad (6a)$$

Substituting (6a) in (4a) and simplifying yield

$$\delta[\text{CoP(OH)(SCN)}] = \frac{-\delta[\text{CoP(OH)(H}_2\text{O)}]}{1 + ([\text{H}^+]/K_{a1}') (1 + K_2[\text{SCN}])} \quad (7a)$$

Substituting (7a) in (6a) and simplifying give

$$\delta[\text{SCN}] \approx \delta[\text{CoP(OH)(H}_2\text{O)}] \quad (8a)$$

Substituting (8a) and (7a) in (2a) yields

$$\frac{-d\delta[\text{CoP(OH)(H}_2\text{O)}]}{dt} = k_1'[\text{CoP(OH)(H}_2\text{O)}]\delta[\text{CoP(OH)(H}_2\text{O)}] + k_1'\delta[\text{CoP(OH)(H}_2\text{O)}][\text{SCN}] + k_{-1}' \frac{\delta[\text{CoP(OH)(H}_2\text{O)}]}{1 + ([\text{H}^+]/K_{a1}') (1 + K_2[\text{SCN}])} \quad (9a)$$

Therefore

$$\frac{1}{\tau} = k_1'[\text{CoP(OH)(H}_2\text{O)}] + k_{-1}'[\text{SCN}] + k_{-1}' \frac{1}{1 + ([\text{H}^+]/K_{a1}') (1 + K_2[\text{SCN}])} \quad (10a)$$

At the concentrations employed,  $k_1'[\text{CoP(OH)(H}_2\text{O)}] \ll k_{-1}'[\text{SCN}]$ ; therefore

$$\frac{1}{\tau} = k_{-1}'[\text{SCN}] + k_{-1}' \frac{1}{1 + ([\text{H}^+]/K_{a1}') (1 + K_2[\text{SCN}])} \quad (11a)$$

With the additional assumption that  $[\text{H}^+] \gg K_{a1}'$ , (11a) can be rearranged to

$$\frac{1 + K_2[\text{SCN}]}{\tau} = k_{-1}' \{ [\text{SCN}](1 + K_2[\text{SCN}]) \} + \frac{k_{-1}'K_{a1}'}{[\text{H}^+]} \quad (12a)$$

**Registry No.** CoTCPP(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup>, 60489-06-7; py, 110-86-1; SCN<sup>-</sup>, 302-04-5; CoTCPP(H<sub>2</sub>O)(SCN)<sup>4+</sup>, 60489-07-8; CoTCPP(SCN)<sub>2</sub><sup>5+</sup>, 60489-08-9; CoTCPP(H<sub>2</sub>O)(py)<sup>3+</sup>, 60489-09-0; CoTCPP(py)<sub>2</sub><sup>3+</sup>, 60489-10-3.

#### References and Notes

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