Kinetics of Substitution Reactions of $\alpha,\beta,\gamma,\delta$-Tetra(4-*N*-methylpyridyl)porphinediaquocobalt(III)

Kenneth R. Ashley,* Margot Berggren, and Meirong Cheng

Contribution from the Department of Chemistry, East Texas State University, Commerce, Texas 75428.

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Abstract: The compound $\alpha,\beta,\gamma,\delta$-tetra(4-*N*-methylpyridyl)porphinediaquocobalt(III) ($CoP(H_2O)_2^{5+}$) has been prepared and characterized in aqueous solution at μ = 1.00 *M* ($NaClO_4$). The complex ion was a monomer at 0.100 *M* H^+ and OH^-. It was a diprotic acid with pK_a's of 5.5 and 10.7. The stability constants of $CoP(SCN)(H_2O)^{4+}$, $CoP(SCN)_2^{3+}$, and $CoP(I)(H_2O)^{4+}$ were determined spectrophotometrically. The values were 6400 ± 1500, 13.7 ± 1.1, and 34.0 ± 5.6 M^{-1}, respectively, at 25°. The stability constants for $CoP(Br)(H_2O)^{4+}$ and $CoP(Cl)(H_2O)^{4+}$ were found to be, respectively, 0.14 ± 0.08 and 0.08 ± 0.2 M^{-1} by kinetic methods at 25°. The pseudo-first-order rate constant for the formation of $CoP(SCN)(H_2O)^{4+}$ had the form $k_{obsd} = a[NCS^-]/([NCS^-] + b)$. This was interpreted to imply a D mechanism. The activation parameters for loss of a water ligand were 19 ± 2 kcal/mol and 7 ± 7 cal/(deg mol) for $\Delta H^\ddagger$ and $\Delta S^\ddagger$, respectively. The pseudo-first-order rate constants for X = I^-, Br^-, and Cl^- had the form $k_{obsd} = a + b[X^-]$. A pseudo-first-order approach to equilibrium was implied. The activation parameters for the reaction with I^- were $\Delta H^\ddagger$ = 20.3 ± 0.5 kcal/mol and $\Delta S^\ddagger$ = 10.4 ± 1.5 cal/(deg mol). The values of the rate constants and stability constants for the reactions with I^-, Br^-, and Cl^-, as well as the activation parameter for the reaction with I^- were all consistent with dissociative activation.

The reactions of the porphinecobalt(III), corrincobalt(III), and bis(dimethylglyoximato)alkylcobalt(III) complexes have attracted considerable interest in the past several years.[1-16] The two major points of interest have been the obvious biological implications of the reactions and the increased lability of cobalt(III) toward substitution reactions. In an attempt to better understand the aqueous reaction patterns of a porphinecobalt(III) complex, the present study was undertaken. The compound $\alpha,\beta,\gamma,\delta$-tetra(4-*N*-methylpyridyl)porphinediaquocobalt(III), ($CoP(H_2O)_2^{5+}$), was chosen as the compound to study because of its favorable solubility properties. After this present study was almost completed, there appeared an independent report of one of the reactions studied in this investigation.[14] However, the conditions were slightly different and this study is more extensive than the previous one.

Experimental Section

Materials. The chemicals used were analytical grade unless otherwise specified. The practical grade pyrrole, 4-pyridinecarboxaldehyde, pyridine, and methyl iodide were obtained from Aldrich Chemical Co. The stock solutions of sodium perchlorate were prepared and standardized as previously reported.[17] The solid cobalt perchlorate was prepared similarly except that the solid was obtained by drying at 200° for 24 hr. Stock standard solutions of perchloric acid, sodium thiocyanate, sodium bromide, sodium chloride, and carbonate free sodium hydroxide were prepaed by usual procedures.

Synthesis of [$\alpha,\beta,\gamma,\delta$-Tetra(4-*N*-methylpyridyl)porphinediaquocobalt(III)] Perchlorate, [$CoP(H_2O)_2$]$(ClO_4)_5$. The synthesis of the porphine was performed in a manner described by Fleischer.[18] However, not enough details were given to allow a ready synthesis. Here the procedure is given in more detail. The pyrrole, pyridine, and isonicotinaldehyde were distilled and kept dry by standard techniques. The zinc acetate was dried at 180° overnight and stored in a desiccator over phosphorus pentoxide. Several 100-ml glass pressure bulbs were two-thirds filled with a solution of 465 ml (7.2 mol) of pyrrole, 650 ml (6.1 mol) of isonicotinaldehyde, 950 ml (12.2 mol) of pyridine, and 280 g (1.5 mol) of zinc acetate. The bulbs were flushed with nitrogen, sealed, and kept at 110° for 48 hr. The bright purple crystals of $\alpha,\beta,\gamma,\delta$-tetra(4-pyridyl)porphinezinc(II) were collected on a filter and washed with ethyl ether. The crystals were dried at 400° under 10 Torr of pressure for 72 hr. This removed some organic materials. The overall yield was 4%. The methylated porphine was prepared by mixing 5 g of the zinc porphine, 5 ml of methyl iodide, and 100 ml of dimethylformamide (DMF) in a standard reflux apparatus. The temperature was raised to 145° and nitrogen was bubbled through the solution. After 20 min, from the time that heating was commenced, the spectrum showed a maximum at 563 nm, a shoulder at 650 nm and the Soret maximum at 436 nm. No additional changes occurred within 17 hr of heating at 140°. The addition of 200 ml of ethyl ether precipitated $\alpha,\beta,\gamma,\delta$-tetra(4-*N*-methylpyridyl)porphinezinc(II) iodide. The product was collected on a funnel and washed with chloroform until the odor of DMF was not detected. The yield for this step was 100%. To remove the zinc from the porphine, 24 ml of 8.0 *M* hydrochloric acid was added to 5 g of zinc N-methylated porphine. The color changed from purple to bright green within a few seconds. The porphine diacid was precipitated by adding 50 ml of 4.0 *M* sodium perchlorate solution. The precipitate was collected on a funnel, washed with ethanol, and dried at 160° for 3 hr. The yield was 75%. Cobalt was incorporated into the porphine ring by refluxing a fourfold excess of $Co(ClO_4)_2 \cdot 9H_2O$ with 5 g of the porphine in 500 ml of DMF at 145° for 30 min. Oxygen was bubbled through the solution during the reaction. Independent experiments confirmed that a fourfold excess was sufficient. Addition of 3 l. of ethanol precipitated the product and the cobalt N-methylated porphine was collected on a funnel. After washing with ethanol until there was no detectable odor of DMF, the product was dried at 110° for 2 hr. The analyses of C, H, and N were performed by Galbraith Laboratories, Inc. The Co analysis was performed using a Perkin-Elmer 303 atomic absorption instrument in this laboratory. Anal. Calcd for $Co(C_{40}H_{28}N_8)(CH_3)_4(ClO_4)_5 \cdot 2(H_2O)$: C, 41.64; N, 8.83; H, 3.15; Co, 4.65. Found: C, 44.02; N, 9.63; H, 3.12; Co, 5.17.

Spectrophotometric Measurements. The determination of the visible spectrum at various $CoP(H_2O)_2^{5+}$ concentrations, at various NCS^- and I^- concentrations, or at various pH was done using a Cary 15 with the commercially available constant temperature block maintained at 25.0 ± 0.1°. Cuvets of the appropriate length were used.

The determination of the acidity constants of $CoP(H_2O)_2^{5+}$ was performed by spectrophotometrically titrating a 8.0×10^{-6} *M* solution of the complex ion, μ = 1.00 *M* $NaClO_4$, with NaOH, μ = 1.00 *M* $NaClO_4$, at 25°. A Beckman Research Model pH meter employing a blue glass electrode and a calomel reference electrode filled with 4.0 *M* NaCl was used.

The spectrophotometric determination of the stability constants of $CoP(SCN)_2^{3+}$ and $CoP(SCN)(H_2O)^{4+}$ was performed in the usual way.[7] The temperature was 25°, $[H^+]$ = 0.100 *M* and μ = 1.00 *M* $NaClO_4$. The absorbance at 453 and 440 nm was measured as quickly as possible after ten half-lives for the anation by NCS^-. The stability constant of $CoP(I)(H_2O)^{4+}$ was determined in the same manner except a wavelength of 433 nm was used and the solutions were prepared by adding the weighted amount of NaI to the nitrogen purged water just before the addition of the $CoP(H_2O)_2^{5+}$.

Kinetics. The kinetics of the anation reactions were studied

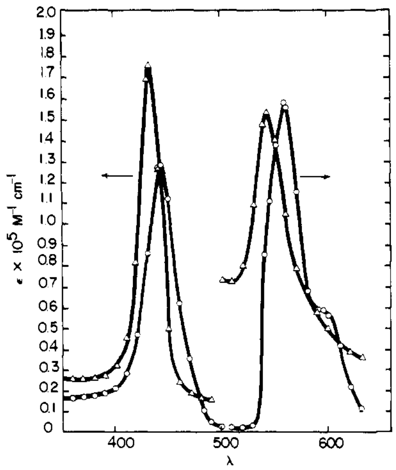

Figure 1. Visible spectra of $[CoP(OH_2)_2{}^{5+}]$ in 0.1 *M* $HClO_4$ and 0.9 *M* $NaClO_4$ (Δ) and of $[CoP(OH)_2{}^{3+}]$ in 0.1 *M* NaOH and 0.9 *M* $NaClO_4$ (O).

under pseudo-first-order conditions at the desired temperatures, using a stopped-flow apparatus fitted with constant temperature blocks that surrounded both the drive syringes and the mixing chamber. The temperature was maintained to within ±0.1°. The initial absorbance was about 0.9 and the final about 0.5 in the reactions with I^- and NCS^-. The initial absorbance was about 0.900 and the final absorbance was 0.895 to 0.870 in the reaction with Cl^- and Br^-. The mixing chamber path length was about 0.96 cm. The reactions were studied at 435 nm with a spectral band width of 2.5 nm. The final ionic strength of the solutions was 1.00 *M* maintained with $NaClO_4$. The hydrogen ion concentration was 0.100 *M* after mixing.

The pseudo-first-order rate constants were obtained from a nonlinear least-squares fit of the absorbance-time data to the integrated first-order rate equation.

Results

Spectra. The spectra of the $CoP(H_2O)_2{}^{5+}$ in 0.100 *M* $HClO_4$ and 0.900 *M* $NaClO_4$ and in 0.100 *M* NaOH and 0.900 *M* $NaClO_4$ are shown in Figure 1. Later discussion will establish that the species in 0.100 *M* NaOH is probably $CoP(OH)_2{}^{3+}$.

The solutions were checked to see if Beer's law was obeyed. In 0.100 *M* NaOH and 0.900 *M* $NaClO_4$ at 25°, the absorbance of 18 different solutions of $CoP(OH)_2{}^{3+}$ ranging from 1.60×10^{-5} to 1.11×10^{-7} *M* was measured using 10.00, 1.00, and 0.100 cm cuvets. The value of the molar absorptivity at 442 nm was $(1.27 \pm 0.08) \times 10^5\ M^{-1}\ cm^{-1}$. The deviation appeared to be random. In 0.100 *M* $HClO_4$ and 0.900 *M* $NaClO_4$ at 25° the absorbance of 13 different solutions of $CoP(H_2O)_2{}^{5+}$ ranging from 2.99×10^{-5} to 1.34×10^{-7} *M* was measured using 10.00, 1.00, and 0.100 cm cuvets. The value of the molar absorptivity at 432 nm was $(1.78 \pm 0.08) \times 10^5\ M^{-1}\ cm^{-1}$. The deviation appeared to be random.

Table I contains the positions of the Soret band and the values of the molar absorptivities, ε, for the compounds studied. The values of ε for $CoP(SCN)(H_2O)^{4+}$ and $CoP(SCN)_2{}^{3+}$ were calculated since the values of the stepwise stability constants were such that a solution containing only one species could not be prepared.[19]

Acid Dissociation Constants. The A_{433} vs. pH plot from the spectrophotometric titration of $CoP(H_2O)_2{}^{5+}$ is shown in Figure 2. The data were treated as if there were two independent deprotonation steps. The two steps were assumed to be

$$CoP(H_2O)_2{}^{5+} \overset{K_{a1}}{\rightleftarrows} CoP(OH)(H_2O)^{4+} + H^+$$

$$CoP(OH)(H_2O)^{4+} \overset{K_{a2}}{\rightleftarrows} CoP(OH)_2{}^{3+} + H^+$$

Table I. Molar Absorptivities of Some Cobalt Porphines

Compound	λ_{max}, nm[a]	ϵ_{max}, $10^5\ M^{-1}\ cm^{-1}$
$CoP(H_2O)_2{}^{5+}$[b]	432	1.78
$CoP(OH)(H_2O)^{4+}$[c]	433	1.11
$CoP(OH)_2{}^{3+}$[d]	442	1.27
$CoP(I)(H_2O)^{4+}$[e]	428	0.852
$CoP(SCN)(H_2O)^{4+}$[f]	435	0.944
$CoP(SCN)_2{}^{3+}$[g]	453	0.831

[a] Soret band. [b] In 0.10 *M* $HClO_4$, $\mu = 1.00$ *M* $NaClO_4$, and 25°. [c] pH 7.65 and 6.56, $\mu = 1.00$ *M* $NaClO_4$, and 25°. [d] In 0.10 *M* NaOH, $\mu = 1.00$ *M* $NaClO_4$, and 25°. [e] $[I^-] = 0.50$ and 0.90 *M*, 0.10 *M* $HClO_4$, $\mu = 1.00$ *M* $NaClO_4$, and 25°. [f] ε calculated using $K_1{}^{NCS} = 6400\ M^{-1}$; 0.10 *M* $HClO_4$, $\mu = 1.00$ *M* $NaClO_4$, and 25°. [g] ε calculated using $K_2{}^{NCS} = 13.7$; 0.10 *M* $HClO_4$, $\mu = 1.00$ *M* $NaClO_4$, and 25°.

Figure 2. A plot of pH vs. absorbance at 433 nm for $[CoP(H_2O)_2{}^{5+}]$ at 25° and $\mu = 1.00$ *M* ($NaClO_4$).

Either one of these equations can be rearranged into the form $[H^+] = K_a(A - A_b)/(A_a - A)$ where *A* is the absorbance of a $CoP(H_2O)_2{}^{5+}$ solution at a hydrogen ion concentration $[H^+]$ (determined by the equation $pH = -\log [H^+]$), A_b is the absorbance of a solution of one of the deprotonated species, and A_a is the absorbance of a solution of the conjugate acid. The values of K_{a_1} and K_{a_2} were derived from a nonlinear least-squares fit of the data to the rearranged equation.[20] The values of K_{a_1} and K_{a_2} were $(3.45 \pm 0.63) \times 10^{-6}$ and $(1.80 \pm 1.77) \times 10^{-11}\ M^{-1}$. These uncertainties and all others in this report are standard deviations.

Stability Constants. The stability constants for the following reactions were measured at 25° in 0.10 *M* $HClO_4$ and $\mu = 1.00$ *M* $NaClO_4$.

$$CoP(H_2O)_2{}^{5+} + NCS^- \overset{K_1{}^{NCS}}{\rightleftarrows} CoP(SCN)(H_2O)^{4+} + H_2O \quad (1)$$

$$CoP(SCN)(H_2O)^{4+} + NCS^- \overset{K_2{}^{NCS}}{\rightleftarrows} CoP(SCN)_2{}^{3+} + H_2O \quad (2)$$

$$CoP(H_2O)_2{}^{5+} + I^- \overset{K_1{}^{I}}{\rightleftarrows} CoP(I)(H_2O)^{4+} + H_2O \quad (3)$$

The general form of the stability constant is given by the equation

$$K_i{}^X = \frac{[CoP(X)_i(H_2O)_{(2-i)}{}^{(5-i)+}]}{[CoP(X)_{(i-1)}(H_2O)_{(3-i)}{}^{(6-i)+}][X^-]} \quad (4)$$

where X is the ligand NCS^- or I^- and *i* is the integer 1 or 2. It readily can be shown that eq 4 can be rearranged to eq

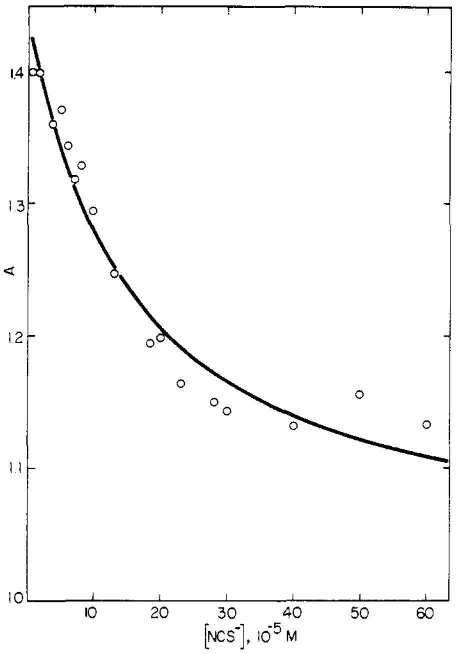

Figure 3. A plot of A vs. [NCS^-] for the determination of K_1^{NCS}. The temperature was 25°, [H^+] = 0.100 M, and μ = 1.00 M ($NaClO_4$). The line is the computer calculated fit of the data.

5, where A_r is the absorbance of a solution of the reactant,

$$A = \frac{(A_r + A_pK_i^X[X^-])}{1 + K_i^X[X^-]} \tag{5}$$

$CoP(H_2O)_2^{5+}$ or $CoPX(H_2O)^{4+}$, A_p is the absorbance of a solution of the product, $CoP(X)(H_2O)^{4+}$ or $CoPX_2^{3+}$, and K_i^X is defined by eq 4.

The A vs. [X^-] data were fit to eq 5 using a nonlinear least-squares program with A_r, A_p, and K_i^X allowed to vary. When available, the experimental values of A_r and A_p were the same, within experimental error, of those calculated. The A vs. [NCS^-] plot for reaction 1 is shown in Figure 3. The plots for reactions 2 and 3 were similar. The values of K_1^{NCS}, K_2^{NCS}, and K_1^I were 6403 ± 1549, 13.73 ± 1.13, and 33.99 ± 5.58 M^{-1}, respectively.

The first stability constants of $CoP(Br)(H_2O)^{4+}$ and $CoP(Cl)(H_2O)^{4+}$ could not be measured by equilibrium methods because of the very small changes in absorbance when $CoP(H_2O)_2^{5+}$ reacted with these anions. However, the values of K_1^{Cl} and K_1^{Br} were determined from kinetic data (see below) to be 0.078 ± 0.17 and 0.14 ± 0.08 M^{-1} . The large error is due to the uncertainty in the forward and reverse rate constants.

Kinetics. The anation of $CoP(H_2O)_2^{5+}$ by NCS^-, I^-, Br^-, and Cl^- was studied at various temperatures with [H^+] = 0.10 M and μ = 1.00 M $NaClO_4$. Some runs with NCS^- at 25° were made with [H^+] = 0.020 M and μ = 1.00 M $NaClO_4$. The results were the same as at 0.10 M [H^+]. The anation of $CoP(H_2O)_2^{5+}$ by NCS^-, I^-, Br^-, and Cl^- was pseudo-first-order in $CoP(H_2O)_2^{5+}$. For the reaction with NCS^- the pseudo-first-order rate constant, k_{obsd}, was fit to the equation $k_{obsd} = a[NCS^-]/([NCS^-] + b)$ by a nonlinear least-squares program.[20] The plot of k_{obsd} vs. [NCS^-] is shown in Figure 4. The values of a were 0.904 ± 0.069, 3.54 ± 0.44, and 8.29 ± 0.05 sec^{-1} at 15, 25, and 35°, respectively. At 15, 25, and 35°, the values of b were 0.811 ± 0.069, 1.21 ± 0.18, and 0.920 ± 0.047, respectively. The values of a, which is a first-order rate constant, at 15, 25, and 35° were fit to the Eryling-Polanyi equation to give the activation parameters.[21] The value of $\Delta H^\ddagger$ was 19.0 ± 2.0 kcal/mol and that of $\Delta S^\ddagger$ was 7.35 ± 6.77 cal/(deg mol). The pseudo-first-order rate constants (k_{obsd}) for the anation reactions of $CoP(H_2O)_2^{5+}$ with I^-, Br^-, and Cl^- were fit to the equation $k_{obsd} = c + d[Y^-]$, where Y = I^-, Br^-, or Cl^-. It must be noted that for the reactions with Br^- and Cl^- the signal to noise ratio was six to one or less. Thus, these data are considered to be very approximate. The values of c at 25, 35, and 45° for I^-, Br^-, and Cl^- were 0.024 ± 0.024, 0.027 ± 0.031, and 0.313 ± 0.125; 1.81 ± 0.09, 5.35 ± 0.55, and 12.3 ± 1.2; and 1.18 ± 0.13, 2.78 ± 0.21, and 7.86 ± 0.93 sec^{-1}, respectively. For I^-, Br^-, and Cl^- at 25, 35 and 45°, the values of d were 1.62 ± 0.10, 4.87 ± 0.13, and 14.4 ± 0.5; 0.25 ± 0.15, 0.17 ± 0.95, and 1.93 ± 2.21; and 0.092 ± 0.206, 0.074 ± 0.339, and 1.09 ± 1.57 M^{-1} sec^{-1}, respectively. For I^- the parameter d was fit to the Eryling-Polanyi equation to give the activation parameters.[21] The value of $\Delta H^\ddagger$ was 20.3 ± 0.5 kcal/mol and the value of $\Delta S^\ddagger$ was 10.4 ± 1.5 cal/(deg mol).

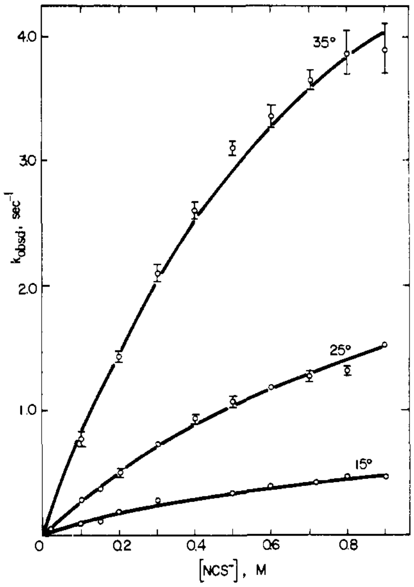

Figure 4. The dependence of the pseudo-first-order rate constant for the anation of [$CoP(H_2O)_2^{5+}$] upon [NCS^-] in 0.100 M [H^+] and μ = 1.00 M ($NaClO_4$). The solid line is the computer calculated least-squares fit of the data.

Discussion

Spectra. The spectra of the various compounds studied are similar to other metalloporphyrins.[2] There is the intensive Soret band at about 440 nm with a molar absorptivity of about 10^5 M^{-1} cm^{-1} and a second band around 550 nm with a molar absorptivity of 10^4 M^{-1} cm^{-1}. With the exception of iodide, when a negative ligand replaces the neutral aquo ligand the band maxima shifts to longer wavelengths. Thus, qualitatively, the negative charge on the ligands lowers the energy of the $\pi \rightarrow \pi^*$ transitions in the porphine macrocycle.

It has been established that some porphines aggregate in aqueous solution.[22,23] In general, these are the porphines with negatively charged groups at the periphery. Those with positive charges at the periphery, such as $\alpha,\beta,\gamma,\delta$-tetra(4-$N$-methylpyridyl)porphine, do not dimerize in aqueous solution.

Pasternack reported that $CoP(H_2O)_2^{5+}$ obeyed Beer's law over a wide concentration range and showed no relaxation effects above about 20 μsec.[14] This report shows that Beer's law is obeyed in 0.100 M [H^+] and in 0.100 M [OH^-], μ = 1.00 M $NaClO_4$. These observations support the conclusion that the cobalt porphine is a monomer in solution.

Acid Dissociation Constants. With an understanding of the coordination chemistry of cobalt(III), it was anticipated that at least one of the aquo ligands would be acidic. It was somewhat surprising, but not without precedent, that two acid protons were observed.[24] The values for the two p*K*'s are reasonable and not surprising. However, the low value of 5.46 for pK_{a_1} prevented the study of many potential ligands that would react with $CoP(H_2O)_2^{5+}$, since these ligands are basic.

Stability Constants. The equilibrium constant for reaction 1 was reported by Pasternack to be 6440 M^{-1} and for reaction 2 to be 13 ± 3 M^{-1}.[14] We observed at 25° in 0.100 M $[H^+]$, $\mu = 1.00$ M $NaClO_4$, an equilibrium constant of 6400 ± 1500 M^{-1} for reaction 1 and 13.7 ± 1.1 M^{-1} for reaction 2. This means that in the range of NCS^- concentrations employed in the anation kinetic studies the reaction did not completely form $CoP(SCN)_2^{3+}$ but did completely form $CoP(SCN)(H_2O)^{4+}$.

The values of the stability constants fall in the order $NCS^- > I^- > Br^- > Cl^-$. This indicates that the cobalt in $CoP(H_2O)_2^{5+}$ reacts as a soft acid.[25] This is not surprising since the porphine has so much π electron density associated with it and some of this electron density could be delocalized into the cobalt e_g* orbitals. This extra electron density on the cobalt would make it a soft acid.

Stoichiometry. In the reaction of NCS^- and $CoP(H_2O)_2^{5+}$, both $CoP(SCN)(H_2O)^{4+}$ and $CoP(SCN)_2^{3+}$ were formed. Hence, there was the possibility of observing two consecutive reactions or of observing only one reaction, which might be either the first or second NCS^- reacting. A very detailed examination of the log $(A - A_\infty)$ vs. t kinetic plots indicated only one observable reaction.

The actual reaction studied was reaction 1. This was supported by the observation that the plots of k_{obsd} vs. $[NCS^-]$, Figure 4, have zero intercepts. This implied that the reaction observed substantially went to completion under these reaction conditions. Thus, reaction 1 was observed and reaction 2 was very much faster. This is in agreement with Pasternack.[14] In fact, his value for the rate constant for reaction 2, obtained by means of temperature jump studies, was about 1000 times that for reaction 1. It is tempting to speculate that the apparent additional electron density of NCS^- is enough to labilize the cobalt by this factor of 10^3.

The reaction of $CoP(H_2O)_2^{5+}$ with I^- produced only $CoP(I)(H_2O)^{4+}$ as concluded from the stability constants measurements. Hence, with I^-, reaction 3 was the one studied. Since the absorbance changes were so small in the reactions of $CoP(H_2O)_2^{5+}$ with Br^- and Cl^- and since the decrease in the first stability constant from NCS^- to I^- was so large, it was concluded that the reactions studied were analogous to reaction 3.

Kinetics. In the reaction of $CoP(H_2O)_2^{5+}$ and NCS^- the observed rate law was

$$\frac{-d[CoP(H_2O)_2^{5+}]_{total}}{dt} = \frac{a[NCS^-]}{[NCS^-] + b}[CoP(H_2O)_2^{5+}]_{total} \tag{6}$$

Since the rate studies were performed under pseudo-first-order conditions, $k_{obsd} = a[NCS^-]/([NCS^-] + b)$. Two possible mechanisms that fit the experimental rate law were an SN1IP and a D mechanism.[26]

For a SN1IP, the following sequence of reactions could be envisioned to occur

$$CoP(H_2O)_2^{5+} + NCS^- \overset{K_{IP}}{\rightleftharpoons} CoP(H_2O)_2^{5+}\cdots NCS^-$$

$$CoP(H_2O)_2^{5+}\cdots NCS^- \xrightarrow{k_R} CoP(SCN)(H_2O)^{4+} + H_2O$$

with $k_{obsd} = k_R[NCS^-]/\{(1/K_{IP}) + [NCS^-]\}$. The values of k_R would correspond to those of a, and those of $1/K_{IP}$ would correspond to those of b. the values of K_{IP} would be 1.23, 0.83, and 1.09 M^{-1} for 15, 25, and 35°, respectively.

Table II. A Comparison of the First Stability Constants and the Rate Constants for the Reaction between X^- and $CoP(H_2O)_2^{5+}$ at 25°

	X^-			
	NCS^-	I^-	Br^-	Cl^-
K_1^X, M^{-1}	6,400	34	0.14[a]	0.08[a]
K_1^X/K_1^{Cl}	80,000	430	1.7	1
k_f^X, M^{-1} sec^{-1}	2.9[b]	1.6	0.25	0.092
k_f^X/k_f^{Cl}	32	18	2.7	1

[a] Stability constants calculated from d/c. [b] $k_f^{NCS} = a/b$.

These values of K_{IP} are very much too small if one just considers a +5, −1 interaction.[27] However, it would be unrealistic to compare $CoP(H_2O)_2^{5+}$ to the much smaller aquo cations or ammine cations, especially in view of the possible delocalization of charge over a large volume. Thus, the small values of K_{IP} might be reasonable for this system. However, in view of the considerations that will be presented below, this SN1IP mechanism tentatively is considered unlikely.

If a D mechanism were operative, then the following mechanism would be applicable under these experimental conditions.

$$CoP(H_2O)_2^{5+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CoP(H_2O)^{5+} + H_2O$$

$$CoP(H_2O)^{5+} + NCS^- \xrightarrow{k_3^{NCS}} CoP(SCN)(H_2O)^{4+} \tag{7}$$

Here, $k_{obsd} = k_1[NCS^-]/(k_2/k_3^{NCS} + [NCS^-])$, and the values of a corresponded to those of k_1 and the values of b corresponded to those of k_2/k_3^{NCS}.

The conclusive piece of information to support this D mechanism would be the invariance of k_1 as the entering ligand was changed. That is, the value of k_1 should be independent of entering ligand and would be unique to $CoP(H_2O)_2^{5+}$ in a particular solvent system. Unfortunately at this time, no other ligand has been studied that reacts with $CoP(H_2O)_2^{5+}$ to give a rate law similar to eq 6.

Instead, the observed rate law for reaction 8

$$CoP(H_2O)_2^{5+} + X^- \underset{k_r^X}{\overset{k_f^X}{\rightleftharpoons}} CoPX(H_2O)^{4+} + H_2O \tag{8}$$

was of the form

$$\frac{-d[CoP(H_2O)_2^{5+}]}{dt} = d[X][CoP(H_2O)_2^{5+}] - c[CoPX(H_2O)^{4+}]$$

This rate law is indicative, in these systems, of a reaction that did not go to completion.[21] Upon integration of the rate law, $k_{obsd} = c + d[X^-]$. The constant c corresponds to k_r^X and d corresponds to k_f^X.

Since there is no evidence for an intermediate, an I stoichiometric mechanism is assigned to the anation reactions of I^-, Br^-, and Cl^-. A comparison of the stability constants would reveal the mode of activation. These data are tabulated in Table II.

The stability constants vary by a factor of 80,000 whereas the rate constants vary by only a factory of 32. This is clearly indicative of dissociative activation.[10] Since there is evidence for an intermediate in the reaction with NCS^-, a D mechanism is suggested for this reaction.

In the literature there have been two reports of similar behavior by hematoporphyrindiaquocobalt(III)[13] and

Table III. Activation Parameters for D and I_d Mechanisms

Reaction	Mechanism	ΔH, kcal/mol	ΔS, cal/(deg mol)	Ref
trans-$Co(en)_2SO_3(H_2O)^+$[a] → *trans*-$Co(en)_2SO_3^+ + H_2O$	D	16	0.2	29
trans-$Co(CN)_4SO_3(H_2O)^{3-}$ → *trans*-$Co(CN)_4SO_3^{3-} + H_2O$	D	22	17.4	30
$CoBm(H_2O)$[b] $+ L \rightarrow CoBmL + H_2O$	I_d	15.5	8	5
$CH_3Co(DH)_2H_2O$[c] $+ L \rightarrow CH_3Co(DH_2)L + H_2O$	I_d	19	7	10, 11
trans-$Co(en)_2(SO_3)_2^-$[a] → *trans*-$Co(en)_2SO_3^+ + SO_3^{2-}$	D	20.5	6	29
trans-$Co(en)_2SO_3(OH)$[a] → *trans*-$Co(en)_2SO_3^+ + OH^-$	D	21	4	29
$Co(CN)_5N_3^{3-} \rightarrow Co(CN)_5^{2-} + N_3^-$	D	27.3	−0.6	31
$Co(CN)_5NCS^{3-} \rightarrow Co(CN)_5^{2-} + NCS^-$	D	31.1	11.5	31
$Co(CN)_5I^{3-} \rightarrow Co(CN)_5^{2-} + I^-$	D	29.7	12.5	32
$CoP(H_2O)_2^{5+}$[d] $\rightarrow CoP(H_2O)^{5+} + H_2O$	D	19.0	7.4	This work
$CoP(H_2O)_2^{5+}$[d] $+ I^- \rightarrow CoP(I)(H_2O) + H_2O$	I_d	20	10.4	This work

[a] en is ethylenediamine. [b] $CoBm(H_2O)$ is cobalamine. [c] DH is dimethylglyoximate. [d] P is $\alpha,\beta,\gamma,\delta$-tetra(4-*N*-methylpyridyl)porphine.

tetra(*p*-sulfonate)phenylporphinediaquocobaltate(III).[28] The data for the first complex could be interpreted to mean that either a SN1IP or a D mechanism was operative. The authors preferred the D mechanism because of the somewhat large values of K_{IP} that resulted if an SN1IP mechanism was chosen. However, this work could not be reproduced in this laboratory. The ligation studies of the second complex have been reported only as a private communication and no details were given. The next nearest related system was the anation reactions of cobalamine.[4,5] The entering anions were SCN^-, SO_3^{2-}, $S_2O_3^{2-}$, NCO^-, N_3^-, I^-, and Br^-. The maximum concentration of entering ligand varied from 1.0 *M* for Br^- to 0.012 *M* for NCO^-. The rate constants for anation varied from 0.17×10^3 to 2.3×10^3 M^{-1} sec^{-1} whereas the formation constants varied from 1.9 to 5.6×10^4 M^{-1} (excluding SO_3^{2-}). It is readily obvious that the rate constants were relatively independent of the stability constant; i.e., the rate of anation was independent of entering group. This was indicative of an I_d mechanism.

The ligation reactions of methylbis(dimethylglyoximato)aquocobalt(III) with NCS^-, CN^-, N^-, C_5H_5N, and NH_3 showed this same behavior.[10,11] These reactions were concluded also to occur by an I_d mechanism. Thus, by analogy to these similar systems, dissociative activation was proposed in the anation of $CoP(H_2O)_2^{5+}$.

An additional argument that dissociative activation is occurring can be advanced by observing the data in Table III. For those reactions in which there is dissociative activation for the loss of a water ligand, the value of $\Delta H^\ddagger$ is about 18 kcal/mol and of $\Delta S^\ddagger$ is about 8 cal/(deg mol). Excepting for the somewhat low value of $\Delta H^\ddagger$, the values are what would be expected if the degree of bond breaking exceeded the degree of bond making.

In those cases in cobalt(III) chemistry in which an SN1IP mechanism appears to be in effect there is little or no enhanced lability of the cobalt(III).[33] That is, the reactivity of the ion pair appears to be similar to that of the free ion. Thus, regardless of the stoichiometric mechanism there is a cis labilizing effect operative, and the source of the cis effect arises from the positive $\Delta S^\ddagger$ and the lowered $\Delta H^\ddagger$. This is consistent with a transition state which is five coordinate and which is rearranged enough to strengthen the remaining five bonds.

It has been concluded that the reaction of $CoP(H_2O)_2^{5+}$ with NCS^- occurs by a D mechanism and that the reaction of $CoP(H_2O)_2^{5+}$ with I^-, Br^-, and Cl^- occurs by an I_d mechanism (no reactive intermediate was detected).

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