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Kinetic and Equilibrium Study of the Reaction of (*meso*-Tetrakis(*p*-sulfonatophenyl)porphinato)diaquochromate(III) with Imidazole in Aqueous Solution

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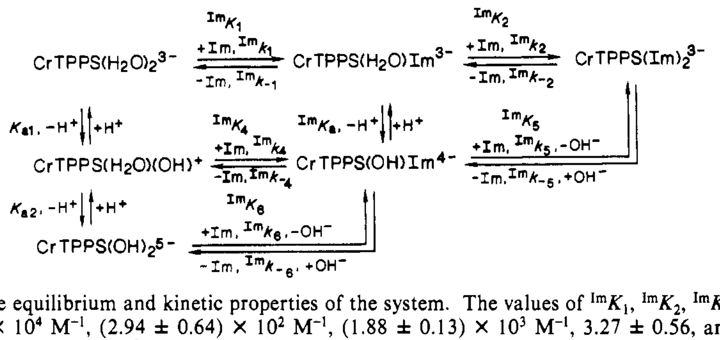
The reaction of imidazole (Im) with (*meso*-tetrakis(*p*-sulfonatophenyl)porphinato)diaquochromate(III) has been studied at 15, 25, and 35 °C at μ = 1.00 M (NaClO$_4$) from pH 6.00 to 0.100 M NaOH. The scheme



adequately describes the equilibrium and kinetic properties of the system. The values of $^{Im}K_1$, $^{Im}K_2$, $^{Im}K_4$, $^{Im}K_5$, and $^{Im}K_6$ at 25 °C are $(1.03 \pm 0.23) \times 10^4$ M^{-1}, $(2.94 \pm 0.64) \times 10^2$ M^{-1}, $(1.88 \pm 0.13) \times 10^3$ M^{-1}, 3.27 ± 0.56, and $(1.23 \pm 0.41) \times 10$, respectively. The values of $^{Im}k_1$, $^{Im}k_2$, $^{Im}k_4$, $^{Im}k_5$, and $^{Im}k_6$ at 25 °C are 2.40 ± 0.09, $(3.05 \pm 0.12) \times 10^{-1}$, $(9.82 \pm 0.32) \times 10$, $(7.96 \pm 0.20) \times 10^{-3}$, and 3.78 ± 0.14 (M s)$^{-1}$, respectively. The values at 25 °C of $^{Im}k_{-2}$, $^{Im}k_{-5}$, and $^{Im}k_{-6}$ are $(2.44 \pm 0.49) \times 10^{-4}$ s^{-1}, $(3.01 \pm 0.06) \times 10^{-2}$ (M s)$^{-1}$, and $(9.29 \pm 0.86) \times 10^{-1}$ (M s)$^{-1}$, respectively. The values of the activation parameters for the paths are ($^{Im}k_i$, ΔH^* (kcal/mol), ΔS^* (cal (deg mol)$^{-1}$)) as follows: $^{Im}k_1$, 16.4 ± 0.5, 1.88 ± 1.64; $^{Im}k_2$, 10.1 ± 0.3, -27.0 ± 1.3; $^{Im}k_4$, 15.6 ± 0.4, 2.87 ± 1.22; $^{Im}k_5$, 18.1 ± 0.1, -7.55 ± 0.47; $^{Im}k_6$, 16.5 ± 1.9, -1.02 ± 6.30; $^{Im}k_{-2}$, 26.3 ± 2.9, $+13.4 \pm 9.7$; $^{Im}k_{-5}$, 16.5 ± 1.9, -1.02 ± 6.30; $^{Im}k_{-6}$, 14.8 ± 2.7, -9.40 ± 9.10. The porphyrin and OH$^-$ ligands labilize the Cr(III) to axial substitution, but there are no apparent trends reflected in the values of the activation parameters of the various paths.

Introduction

The equilibrium and kinetic properties of axial ligation reactions of metalloporphyrins in aqueous solution have been of continued interest for the past 20 years. Most of the reported studies have involved the meso-substituted water-soluble porphyrins of cobalt(III),[1-14] chromium(III),[14-19] and rhodium(III).[14,20,21] The general conclusion has been that the reactions are dissociatively activated. This conclusion has been based on the values of the activation parameters. Generally, positive or small negative values of ΔS^* and positive values for ΔV^* are observed.

In the case of the ligation reactions of meso-substituted porphyrin complexes of chromium(III), the mode of activation is not so certain. In the reactions of CrTPPS(H$_2$O)$_2$$^{3-}$ with NCS$^-$, the values of ΔS^* and ΔV^* are -12.8 cal (deg mol)$^{-1}$ and $+7.4$ cm^3 mol^{-1}, respectively.[14,17,22] In the reaction of CrTAPP(H$_2$O)$_2$$^{5+}$ with NCS$^-$, the values of ΔS^* and ΔV^* are -15.3 cal (deg mol)$^{-1}$ and $+9.2$ cm^3 mol^{-1}, respectively.[19,22] In the reaction of CrTMPP(H$_2$O)$_2$$^{5+}$ with NCS$^-$, the value of ΔS^* is -5.5 cal (deg mol)$^{-1}$.[18,22] When these values are compared to those of the reactions of the Co(III) porphyrins, the values of ΔS^* imply associative activation and those of ΔV^* imply dissociative activation.[14]

The ligation reaction of CrTPPS(H$_2$O)$_2$$^{3-}$ with imidazole (Im) has been studied at pH 6.6 and 10.0.[16] Under these conditions CrTPPS(H$_2$O)$_2$$^{3-}$, CrTPPS(OH)H$_2$O^{4-}, and CrTPPS(OH)$_2$$^{5-}$ are all present and are potential reactants. Hence, a complete elucidation of the kinetics of this system must consider the rate constant–pH profile of the reactions. This detailed rate constant–pH profile investigation was in progress when the above study was published. This is a report of the detailed study of the kinetics and equilibrium properties of the axial ligation reaction of Im with CrTPPS(H$_2$O)$_2$$^{3-}$ from pH 6.00 to 0.100 M OH$^-$ at 15, 25, and 35 °C.

Experimental Section

General Comments. The general reagents used have been described previously.[6,23] The imidazole was purchased from Aldrich Chemical Co. and recrystallized from water. Stock solutions of Im were standardized by titration with standard HCl to the methyl red end point. Na$_3$[CrTPPS(H$_2$O)$_2$]·12H$_2$O was prepared as described previously.[17]

Equilibrium Constants. The acid dissociation constants of the imidazolium ion were determined by potentiometric titration of a 0.100 M solution of Im in 1.00 M NaClO$_4$ with 0.100 M HClO$_4$ in 0.900 M NaClO$_4$ at ±0.10 °C of the desired temperature. The calomel reference electrode contained 4.0 M NaCl instead of saturated KCl solution in order to prevent precipitation of KClO$_4$ at the junction.

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(22) Abbreviations: TPPS = *meso*-tetra(*p*-sulfonatophenyl)porphine; TAPP = *meso*-tetrakis((trimethylammonio)phenyl)porphine; TMPP = *meso*-tetrakis(*N*-methyl-4-pyridiniumyl)porphine; TCPP = meso-tetrakis(*p*-carboxyphenyl)porphine; TPP = tetraphenylporphine; PPh$_3$ = triphenylphosphine; P(OPr)$_3$ = triisopropyl phosphite; P(C$_2$H$_4$CN)$_3$ = tris(2-cyanoethyl)phosphine; py = pyridine; MeIm = *N*-methylimidazole.
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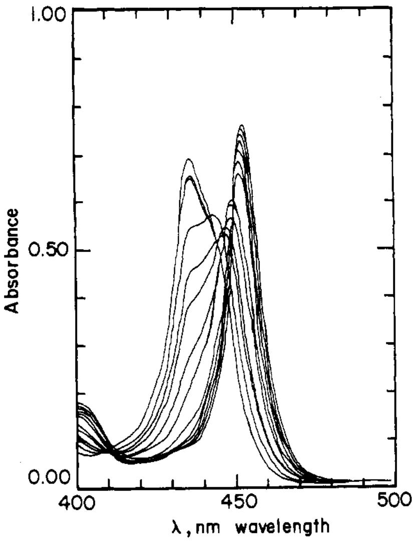
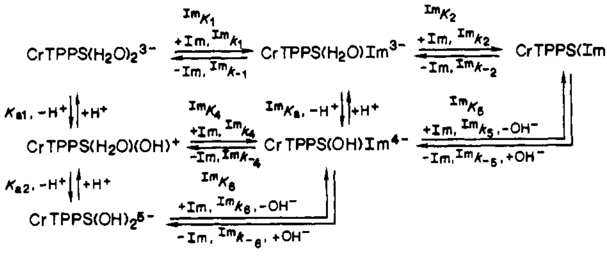


Figure 1. Spectral changes at pH 9.31, 25 °C, μ = 1.00 M ($NaClO_4$), and [Im] = (1.00×10^{-4})–1.00 M.

Scheme I



The $CrTPPS(H_2O)_2{}^{3-}$–NCS^- stability constants were determined spectrophotometrically on a Beckman DU-8a instrument with the temperature maintained at 25.0 ± 0.1 °C.[6] The pH was adjusted to that desired by adding $HClO_4$ or NaOH. The ionic strength, μ, was maintained at 1.00 M ($NaClO_4$).

Kinetics. The kinetic studies of the ligation reactions were spectrophotometrically performed on a Beckman DU-8a or Aminco-Morrow stopped-flow spectrophotometer.[6] The temperature was constant to within ±0.1 °C, and μ = 1.00 M ($NaClO_4$). No added buffer was used. The pH was adjusted to that desired by the addition of $HClO_4$ or NaOH, and the pH was checked both before and after a kinetic run to insure constancy of the pH.

Results and Discussion

Equilibrium. The data from the potentiometric titration of Im were fit by a nonlinear least-squares program to eq 1, where $[H^+] = 10^{-pH}$, V_a is the volume of $HClO_4$ added, V_t is the volume

$$[H^+] = K_a\{V_a/(V_t - V_a)\} \qquad (1)$$

required to reach the end point, and K_a is the acid dissociation constant for ImH^+.[24] Three determinations were made at each temperature. The values of K_a are (5.58 ± 0.32) × 10^{-8}, (7.46 ± 0.47) × 10^{-8}, and (1.00 ± 0.07) × 10^{-7} M at 15, 25, and 35 °C, respectively. These uncertainties, and all others reported, are the estimated 1 standard deviation of the measurement. These values of K_a were used to calculate the [Im] and [ImH^+] present in the solutions. The value of K_a at 25 °C compares favorably to that of (4.90 ± 0.34) × 10^{-8} M at 25 °C and μ = 0.50 M reported in the literature.[25]

Figure 1 shows typical spectra of $CrTPPS(H_2O)_2{}^{3-}$ and Im between 400 and 500 nm as [Im] is varied at pH 9.31. Similar spectra were obtained at pH 6.00 and 0.100 M OH^-. The appearance of isosbestic points in all of these spectral sets at low and then again at high [Im] was taken to imply that at all pH values studied the stepwise formation of the mono- and bis(imidazole) species occurred. Scheme I adequately describes the system under investigation. The rate constant for a reaction will be used to label that path. The values of K_{a_1} and K_{a_2} at 25 °C are (2.33 ± 0.07) × 10^{-8} and (3.53 ± 0.17) × 10^{-12} M.[17]

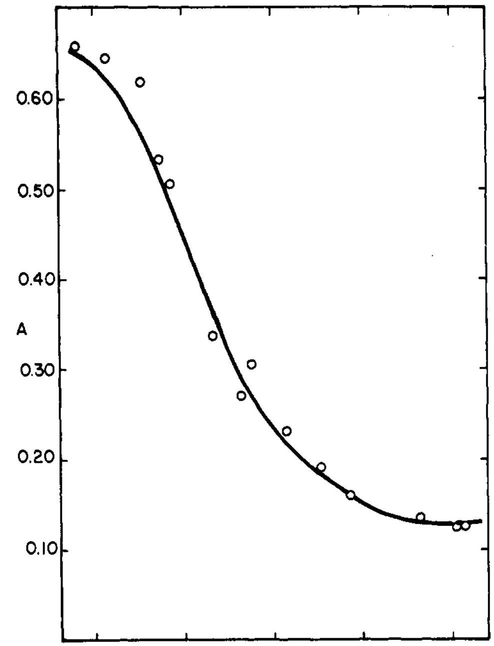


Figure 2. Absorbance as a function of [Im] at pH 6.00, μ = 1.00 M ($NaClO_4$), [Im] = 2.0×10^{-6}–1.4×10^{-1} M, and λ = 444 nm. The solid line is the calculated one from eq 2.

Table I. Values of the Stability Constants at 25 °C for the Reaction of Im with $CrTPPS(H_2O)_2{}^{3-}$ [a]

path	${}^{\mathrm{Im}}K_i$, M^{-1}	${}^{\mathrm{Im}}k_i/{}^{\mathrm{Im}}k_{-i}$, M^{-1}
${}^{\mathrm{Im}}k_1{}^{b}$	(1.03 ± 0.23) × 10^4	(1.52 ± 1.38) × 10^{4} [c]
${}^{\mathrm{Im}}k_2{}^{b}$	(2.94 ± 0.64 × 10^2	(1.25 ± 0.26) × 10^3
${}^{\mathrm{Im}}k_4{}^{d}$	(1.88 ± 0.13) × 10^3	(1.52 [illegible] 0.29) × 10^3
${}^{\mathrm{Im}}k_5{}^{d,e}$	1.24 ± 2.21	(2.64 ± 0.08) × 10^{-1}
${}^{\mathrm{Im}}k_5{}^{e,f}$	3.27 ± 0.56	
${}^{\mathrm{Im}}k_6{}^{e,f}$	(1.23 ± 0.41) × 10	4.07 ± 0.41

[a] The paths and constants are defined in Scheme I. [b] pH 6.00 and λ = 444 nm. [c] 35 °C. [d] λ = 454 nm and pH 9.31. [e] The constant has no dimensions. [f] λ = 451 nm and [OH^-] = 0.10 M.

Figure 2 is a plot of the absorbance A versus Im concentration for the ligation reaction at pH 6.00 and a wavelength of 444 nm. These data, along with the isosbestic point observations, clearly indicate the stepwise nature of the $CrTPPS(H_2O)_2{}^{3-}$–Im interaction. From the definition of the stability constants in Scheme I, the mass balance, and Beer's law, the general equation (2) can

$$A = \frac{A_0 + A_1K_i[\mathrm{Im}] + A_2K_iK_j[\mathrm{Im}]^2}{1 + K_i[\mathrm{Im}] + K_iK_j[\mathrm{Im}]^2} \qquad (2)$$

be derived. A is the absorbance at a particular [Im]; A_0, A_1, and A_2 are the absorbances of solutions of Cr(III) containing zero, one, and two Im ligands, respectively, and K_i and K_j are the stepwise stability constants. The data at pH 6.00 and at λ = 444 nm were fit to eq 2 by using a nonlinear least-squares program.[24] The solid line in Figure 2 is the calculated line from the resulting values of ${}^{\mathrm{Im}}K_1$ and ${}^{\mathrm{Im}}K_2$. The values of ${}^{\mathrm{Im}}K_4$ and ${}^{\mathrm{Im}}K_5$ were obtained in the same manner by using data at pH 9.31 and λ = 454 nm. Likewise, the values of ${}^{\mathrm{Im}}K_6$ and ${}^{\mathrm{Im}}K_5$ were obtained by using data at 0.100 M OH^- and λ = 451 nm. All of these values are reported in Table I.

The previously reported values of ${}^{\mathrm{Im}}K_1$ and ${}^{\mathrm{Im}}K_2$ (pH 6.0) and of ${}^{\mathrm{Im}}K_4$ and ${}^{\mathrm{Im}}K_5$ (pH 10.0) are (7.9 ± 0.2) × 10^3 M, (4.9 ± 0.2)

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× 10² M, (5.89 ± 0.16) × 10² M, and (7.4 ± 0.2) × 10, respectively. The agreement among the values of ${}^{\mathrm{Im}}K_1$, ${}^{\mathrm{Im}}K_2$, and ${}^{\mathrm{Im}}K_4$ is reasonably good. However, the values of ${}^{\mathrm{Im}}K_5$ are appreciably different. It is difficult to resolve this discrepancy. However, it should be remembered that a complex equilibrium exists that is sensitive to pH.

Also, an examination of the method by which the previously reported values were determined reveals an error in the treatment of the data. The data were obtained at isosbestic points. That is, the determination of ${}^{\mathrm{Im}}K_1$ was performed at a wavelength such that $A_2 = A_3$ in eq 2. It was then assumed that eq 2 reduced to eq 3, instead of eq 4, the correct one. If the value of ${}^{\mathrm{Im}}K_2[\mathrm{Im}]$

$$A_0 = \frac{A_0 + A_1{}^{\mathrm{Im}}K_1[\mathrm{Im}]}{1 + {}^{\mathrm{Im}}K_1[\mathrm{Im}]} \tag{3}$$

$$A = \frac{A_0 + A_1{}^{\mathrm{Im}}K_1[\mathrm{Im}]\{1 + {}^{\mathrm{Im}}K_2[\mathrm{Im}]\}}{1 + {}^{\mathrm{Im}}K_1[\mathrm{Im}]\{1 + {}^{\mathrm{Im}}K_2[\mathrm{Im}]\}} \tag{4}$$

is less than about 0.05, then eq 4 reduces to eq 3. The amount of error that is introduced, of course, depends upon the value of ${}^{\mathrm{Im}}K_2[\mathrm{Im}]$. The value of ${}^{\mathrm{Im}}K_4$ was determined in a similar manner. Equivalent considerations show that an error results in using an equation of the form of eq 3 to determine ${}^{\mathrm{Im}}K_4$ and ${}^{\mathrm{Im}}K_5$.

There is a dearth of equilibrium data with which to compare the values of K_i. The values of ${}^{\mathrm{NCS}}K_1$ for $\mathrm{CrTPPS(H_2O)_2}^{3-}$, $\mathrm{CrTMPP(H_2O)_2}^{5+}$, and $\mathrm{CrTAPP(H_2O)_2}^{5+}$ are 2.45 ± 0.13, 1.2 ± 0.2, and 2 M^{-1}, respectively.[17-19] It appears that neither the charge on the complex (porphyrin) nor the electron-donating ability of the porphyrin affects the value of ${}^{\mathrm{NCS}}K_1$. This has been noted also for $\mathrm{CoTPPS(H_2O)_2}^{3-}$, $\mathrm{CoTMPP(H_2O)_2}^{5+}$, and $\mathrm{CoTCPP(H_2O)_2}^{3-}$.[9,22] It has been reported that the groups substituted at the para position have a substantial effect on the electron available at the pyrrole nitrogens.[26]

The increase in ${}^{\mathrm{Im}}K_1$ to 10^4 M^{-1} and ${}^{\mathrm{Im}}K_4$ (${}^{\mathrm{NCS}}K_4$ = 0.69 ± 0.09 M^{-1}) to 10^3 is substantial. However, it should be noted that the value of $\mathrm{p}K_\mathrm{a}$ for Im is 7.13, whereas the value for NCS^- is 0.9.[24,27] The large difference in the values of K_1 and K_4 might simply be that the affinity of the ligand for bonding to H^+ is also displayed toward Cr(III).

The only other Cr(III) comparison is the CrTPP(Cl)L + X system in toluene, where L = PPh, $\mathrm{P(OPr)_3}$, $\mathrm{P(C_2H_4CN)_3}$, and py and X = MeIm, py, and $\mathrm{PPh_3}$.[22,28] In this system, the values of K range from about 10 to 10^5, with the values for MeIm being about 10^2 times larger than for py and 10^4 larger than for $\mathrm{PPh_3}$. However, the value of 10^4 for MeIm is similar to that of 10^4 for Im. Since the solvents are so different, this value of K might reflect the inherent affinity of the chromium(III) porphyrin for Im.

Kinetics. Previous reports indicated that a complex kinetic scheme similar to Scheme I could describe the ligation reactions of NCS^- and $\mathrm{Cr(TPPS)(H_2O)_2}^{3-}$.[17] Hence, a complex kinetic scheme was anticipated in this case also. Preliminary experiments indicated that the kinetics of the system were pseudo-first-order in [Cr(III)] and first-order in [Im] at all pH values. The values of the stability constants, rate constants, and Im concentrations were such that eq 5 best describes the kinetic system observed at pH 6.00.

$$\mathrm{CrTPPS(H_2O)_2}^{3-} \xrightarrow{+\mathrm{Im},\ {}^{\mathrm{Im}}k_1} \mathrm{CrTPPS(H_2O)Im}^{3-} \underset{-\mathrm{Im},\ {}^{\mathrm{Im}}k_{-2}}{\overset{+\mathrm{Im},\ {}^{\mathrm{Im}}k_2}{\rightleftharpoons}} \mathrm{CrTPPS(Im)_2}^{3-} \tag{5}$$

At pH 9.31 and 0.10 M OH^-, the first kinetic step can be observed separately from the second. At $[\mathrm{OH}^-]$ = 0.100 M, the first step is observed to be reversible. Equation 6 can be derived from the solutions of the associated differential equations of eq 5, the mass balance, and Beer's law. A is the absorbance at time t; A_∞ is the absorbance at the end of the reactions, and C_1 and C_2 are constants comprised of molar absorptivities, rate constants, and the cuvette length. Equation 6 can be solved graphically to give the two observed pseudo-first-order composite rate constants, k' (first step) and k'' (second step).[29]

$$A - A_\infty = C_1e^{-k'} + C_2e^{-k''} \tag{6}$$

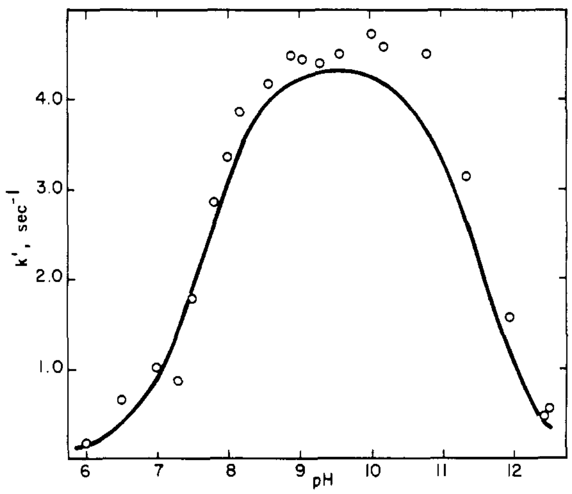

Figure 3. Value of k' as a function of pH at 25.0 °C and μ = 1.00 M ($\mathrm{NaClO_4}$). The solid line is the calculated one from eq 7 (see text).

The value of k', the observed pseudo-first-order rate constant for the addition of the first imidazole ligand, at [Im] = 0.0500 M as a function of pH is plotted in Figure 3. Equation 7 expresses

$$k' = \frac{\{{}^{\mathrm{Im}}k_1[\mathrm{H}^+]^2 + {}^{\mathrm{Im}}k_4K_{\mathrm{a}_1}[\mathrm{H}^+] + {}^{\mathrm{Im}}k_6K_{\mathrm{a}_1}K_{\mathrm{a}_2}\}[\mathrm{Im}]}{[\mathrm{H}^+]^2 + K_{\mathrm{a}_1}[\mathrm{H}^+] + K_{\mathrm{a}_1}K_{\mathrm{a}_2}} + \frac{\{{}^{\mathrm{Im}}k_{-4} + {}^{\mathrm{Im}}k_{-6}[\mathrm{OH}^-]\}{}^{\mathrm{Im}}K_\mathrm{a} + {}^{\mathrm{Im}}k_{-1}[\mathrm{H}^+]}{[\mathrm{H}^+] + {}^{\mathrm{Im}}K_\mathrm{a}} \tag{7}$$

the form of k' if all three paths depicted in Scheme I were operative. An attempt to fit the data to eq 7 was unsuccessful.[24] The algorithm of the program would not give convergent values for the parameters, or parameters in the numerator and denominator would simultaneously become very, very large.

An inspection of Figure 2 and the values of K_{a_1} and K_{a_2} clearly imply that the value of ${}^{\mathrm{Im}}k_4$ is the largest one over the entire pH range and the predominate one at pH 9.31. However, kinetic runs at pH 6.00 and 0.100 M OH^- indicate that paths ${}^{\mathrm{Im}}k_1$ and ${}^{\mathrm{Im}}k_6$ respectively are also important at these conditions. The solid line in Figure 3 is calculated by using eq 7 with the parameters for the ${}^{\mathrm{Im}}k_1$ and ${}^{\mathrm{Im}}k_6$ paths determined at these conditions as well as the values for the ${}^{\mathrm{Im}}k_4$ path determined at pH 9.31. The value of ${}^{\mathrm{Im}}k_\mathrm{a}$ was determined from the k''-pH data (vide infra). One can see that the fit is excellent.

The kinetics of the addition of the first Im at pH 9.31 were studied at [Im] = (1.00–25.0) × 10^{-3} M. The data were fit by a nonlinear least-squares program to eq 8.[24] The resulting values

$$k' = a + b[\mathrm{Im}] \tag{8}$$

of a, assumed to be ${}^{\mathrm{Im}}k_{-4}$, were negative and zero within 1 standard deviation at 15 °C and (6.49 ± 1.21) × 10^{-2} and (1.62 ± 1.60) × 10^{-2} s^{-1} at 25 and 35 °C, respectively. The values of b, ${}^{\mathrm{Im}}k_4$, along with the values of the activation parameters, are reported in Table II.

The values of k' at pH 6.00 were determined at [Im] = (5.00–60.0) × 10^{-3} M. As before, the data were fit to eq 8. The values of a, ${}^{\mathrm{Im}}k_{-1}$, were negative and zero within 1 standard deviation at 15 and 25 °C and (4.18 ± 3.77) × 10^{-4} s^{-1} at 35 °C.

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Table II. Rate Constants and Activation Parameters for the Ligation Reactions of Im and $CrTPPS(H_2O)_2^{3-}$ [a]

rate const	k, 15 °C	k, 25 °C	k, 35 °C	ΔH^*, kcal mol^{-1}	ΔS^*, cal (deg mol)$^{-1}$
k_1, (M s)$^{-1}$	$(9.32 \pm 0.52) \times 10^{-1}$	2.40 ± 0.09	6.37 ± 0.23	16.4 ± 0.5	-1.88 ± 1.64
k_2, (M s)$^{-1}$	$(1.57 \pm 0.14) \times 10^{-1}$	$(3.05 \pm 0.12) \times 10^{-1}$	$(5.28 \pm 0.34) \times 10^{-1}$	10.1 ± 0.3	-27.0 ± 1.3
k_{-2}, s^{-1}	$(6.45 \pm 3.76) \times 10^{-5}$	$(2.44 \pm 0.49) \times 10^{-4}$	$(1.37 \pm 0.18) \times 10^{-3}$	26.3 ± 2.9	$+13.4 \pm 9.7$
k_4, (M s)$^{-1}$	$(3.67 \pm 0.18) \times 10$	$(9.82 \pm 0.32) \times 10$	$(2.30 \pm 0.06) \times 10^2$	15.6 ± 0.4	$+2.87 \pm 1.22$
k_5, (M s)$^{-1}$	$(2.63 \pm 0.80) \times 10^{-3}$	$(7.96 \pm 0.20) \times 10^{-3}$	$(2.18 \pm 0.06) \times 10^{-2}$	18.1 ± 0.1	-7.55 ± 0.47
k_{-5}, (M s)$^{-1}$	$(8.64 \pm 0.23) \times 10^{-3}$	$(3.01 \pm 0.06) \times 10^{-2}$	$(8.29 \pm 0.19) \times 10^{-2}$	19.4 ± 0.8	-0.64 ± 2.63
k_6, (M s)$^{-1}$	1.14 ± 0.04	3.78 ± 0.14	7.84 ± 0.38	16.5 ± 1.9	-1.02 ± 6.30
k_{-6}, (M s)$^{-1}$	$(2.78 \pm 0.37) \times 10^{-1}$	$(9.29 \pm 0.86) \times 10^{-1}$	1.59 ± 0.27	14.8 ± 2.7	-9.40 ± 9.10

[a] The rate constants and their associated paths are defined in Scheme I.

The values of b could not simply be assigned to $^{Im}k_1$. On the basis of the values of K_{a_1} and $^{Im}k_4$, about 98% of the Cr(III) is in the form $CrTPPS(H_2O)_2^{3-}$ at this pH, but about 50% of the ligation reaction occurs via the $^{Im}k_4$ path. Thus, b is defined by eq 9. The

$$b = \frac{^{Im}k_1[H^+] + {}^{Im}k_4K_{a_1}}{[H^+] + K_{a_1}} \tag{9}$$

values of $^{Im}k_1$ were calculated from eq 9 and are reported, along with the activation parameters, in Table II.

The values of $^{Im}k_6$ and $^{Im}k_{-6}$ were determined at 0.100 M OH^- at [Im] = $(3.00\text{–}40.0) \times 10^{-2}$ M. The data were fit to eq 8 with $a = {}^{Im}k_{-6}$ and $b = {}^{Im}k_6$. The values of the rate constants and activation parameters are reported in Table II.

The addition of the second Im was first-order in [Im] at pH 6.00 and 0.100 M OH^- at [Im] = $(5.00\text{–}120) \times 10^{-4}$ and $(5.00\text{–}100) \times 10^{-2}$ M, respectively. The second-order rate constant as a function of pH was studied at 25 °C and [Im] = 0.0500 M. The results are displayed in Figure 4. Assuming only the $^{Im}k_2$ and $^{Im}k_5$ paths, eq 10 can be derived. The solid line in Figure 4 is the calculated curve resulting when $^{Im}k_2$, $^{Im}k_5$, $^{Im}k_{-1}$, and $^{Im}k_{-5}[OH^-]$ are fixed at the independently determined values (vide infra). The value of $^{Im}K_a$ resulting from this fit is $(8.85 \pm 2.42) \times 10^{-10}$ M. At pH 6.00 and $[OH^-]$ = 0.100 M, eq 10 reduces to the form of eq 8, with $a = {}^{Im}k_{-2}$ and $b = {}^{Im}k_2$ and with $a = {}^{Im}k_{-5}[OH^-]$ and $b = {}^{Im}k_5$, respectively. The values of the parameters and the associated activation parameters determined under these conditions are reported in Table II.

$$k'' = \left\{\frac{^{Im}k_2[H^+] + {}^{Im}k_5{}^{Im}K_a}{[H^+] + {}^{Im}K_a}\right\}[Im] + \{^{Im}k_{-2} + {}^{Im}k_{-5}[OH^-]\} \tag{10}$$

The previously reported results by Krishnamurthy are generally consistent with these results.[16] The $^{Im}k_6$ and $^{Im}k_1$ paths were not observed, and the $^{Im}k_2$ path was studied only at 25 °C. The values of $^{Im}k_2$ and $^{Im}k_{-2}$ were $(1.21 \pm 0.05) \times 10^{-1}$ (M s)$^{-1}$ and $(1.7 \pm 0.4) \times 10^{-4}$ s^{-1} compared to the values of $(3.05 \pm 0.1) \times 10^{-1}$ (M s)$^{-1}$ and $(2.44 \pm 0.49) \times 10^{-4}$ s^{-1} respectively reported here.

The $^{Im}k_4$ path was studied at pH 10.00 and 6.50–7.00. The values of $^{Im}k_4$ reported were 60.3 ± 0.8 and 63 (M s)$^{-1}$, respectively.[16] These values compare favorably to the value of 95.1 ± 4.2 (M s)$^{-1}$ calculated from the present data.

The $^{Im}k_5$ path at pH 10.00 was studied up to [Im] = 0.25 M but became less than first order in [Im] above [Im] $\simeq$ 0.15 M.[16] This was not observed in the present study, even though the path was studied at an upper Im concentration of 1.00 M at 0.100 M OH^-. The previously reported value of 0.02 (M s)$^{-1}$ is close to the value of 0.042 (M s)$^{-1}$ calculated by using the data from this study.

The previously reported values of the activation parameters are not too close to the ones reported in Table II.[16] These values of ΔH^* and ΔS^* for the $^{Im}k_4$ and $^{Im}k_5$ paths are 18.2 ± 2 kcal mol^{-1}, 12 ± 6 cal (deg mol)$^{-1}$ and 22.4 ± 0.3 kcal mol^{-1}, 11 ± 1 cal (deg mol)$^{-1}$. However, given the complexity of this kinetic system with all of the variables involves, the agreement between this and the previous incomplete study is very good.

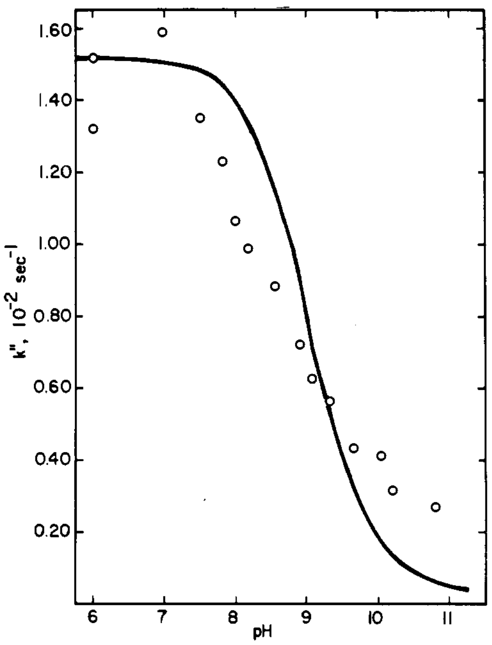

Figure 4. Value of k'' as a function of pH at 25.0 °C and μ = 1.00 M ($NaClO_4$). The solid line is the calculated one from eq 10 (see text).

Table III summarizes the available data for the ligation reactions of chromium(III) porphyrins. The data are arranged in terms of the trans, leaving, and entering ligands. The first observation that can be made is that the reactions are, in general, much faster than usual Cr(III) ligation reactions. The labilization of Cr(III) by a porphyrin ligand appears to be a general phenomenon. However, this labilization is not as great as in the case of cobalt(III) or rhodium(III) porphyrins.[11,21] The labilization is about a factor of 10^2–10^3, 10^3–10^7, and 10^9 for Cr(III), Rh(III), and Co(III), respectively.[21] The amount of labilization is obviously dependent upon the comparison reaction. It is very tempting to ascribe significance to the fact that these last two ions have a d^6 configuration whereas Cr(III) has a d^3 configuration.

One can see from Table III that the labilization is generally accompanied by a decrease of about 8 kcal mol^{-1} in the value of ΔH^* and a less positive to negative value of ΔS^*, of up to −31 cal (deg mol)$^{-1}$ compared to those values for the reaction of $Cr(NH_3)_5H_2O^{3+}$ with NCS^-. Since the ligation reactions are labilized by the porphyrins, it is suggested that the reactions are dissociatively activated. Hence, this decrease in the value of ΔH^* is interpreted as resulting from the stabilization of the activated complex by the porphyrin ligand. However, the decrease in the

Table III. Summary of the Reaction Data at 25 °C for Ligation Reactions MXL + Y → MXY + L

path	X	L	Y	k, (M s)$^{-1}$	ΔH^*, kcal mol^{-1}	ΔS^*, cal (deg mol)$^{-1}$	K, M^{-1}
				M = CrTPPS[a]			
k_1	H_2O	H_2O	Im	2.4	16	−2	1.0×10^4
k_1	H_2O	H_2O	NCS^-	4.7×10^{-3}	17	−13	2.45
k_{-1}	H_2O	NCS^-	H_2O	1.9×10^{-3}[g]	16	−19	4.1×10^{-1}
k_{-1}	H_2O	Im	H_2O	$<4 \times 10^{-4}$[g]			9.7×10^{-5}
k_4	OH^-	H_2O	Im	9.8×10	16	+3	1.9×10^3
k_4	OH^-	H_2O	NCS^-	2.8×10	17	+4	6.9×10^{-1}
k_6	OH^-	OH^-	Im	3.8	17	−1	1.2×10
k_{-6}	OH^-	Im	OH^-	9.3×10^{-1}	15	−9	8.1×10^{-2}
k_{-4}	OH^-	Im	H_2O	6.0×10^{-2}[g]			5.3×10^{-4}
k_2	Im	H_2O	Im	3.1×10^{-1}	10	−27	2.9×10^2
k_{-5}	Im	Im	OH^-	3.0×10^{-2}	19	−1	3.1×10^{-1}
k_5	Im	OH^-	Im	8.0×10^{-3}	18	−8	3.3
k_{-2}	Im	Im	H_2O	2.4×10^{-4}[g]	26	+13	3.4×10^{-3}
				M = CrTMPP[b]			
k_1	H_2O	H_2O	NCS^-	6.6×10^{-4}[c]	20	−6	1.0[d]
k_{-1}	H_2O	NCS^-	H_2O	2.7×10^{-4}[c,g]	15	−24	1.0
k_4	OH^-	H_2O	NCS^-	4.0	15	−7	1.6×10^{-1}
k_4	OH	H_2O	CN^-	7.9×10^{-1}	10	−27	1.5×10^3
k_{-4}	OH^-	CN^-	H_2O	2.8×10^{-3}[g]	17	−14	6.7×10^{-4}
				M = CrTAPP[e]			
k_1	H_2O	H_2O	NCS^-	4.2×10^{-3}	16	−15	2
				M = $Cr(NH_3)_4$[f]			
k_1	NH_3	H_2O	NCS^-	3.0×10^{-5}	24	3	

[a] This work at 25 °C and μ = 1.00 M ($NaClO_4$) unless otherwise specified. [b] Reference 19. [c] Calculated for 25 °C from data in reference 19. [d] 30 °C. [e] Reference 20. [f] Duffy, N. V.; Early, J. E. *J. Am. Chem. Soc.* **1967**, *89*, 272. [g] In s^{-1}.

value of ΔS^* is harder to rationalize in terms of an I_d mechanism being operative.

The decrease in ΔH^* is observed in other ligation reactions of $MTPPS(H_2O)^{3-}$ where M is Cr(III), Co(III), and Rh(III).[11,17,21] However, the change in ΔS^* in the case of Co(III) is positive but is also negative in the case of Rh(III). The values of ΔV^* for these ligation reactions with NCS^- are all positive.[14] It is a very confusing task to try to draw any generalizations from these data. It might be that while the values of the intrinsic activation parameters for the ligation reactions of any one metal are somewhat similar, the solvation effects are such that they significantly alter the values for each individual reaction, especially the values of ΔS^*. This would be reasonable in view of the charge difference of the entering ligands.

The previously offered explanations for this porphyrin-induced lability all suggest that the porphyrin ligand is able to donate electron density to the metal center to the extent that effectively a lower oxidation state of the metal, which is labile, is produced.[1,15,17,19] Presumably, the lability of the lower oxidation state metal is due to its ability to stabilize the activated complex in a dissociatively activated intimate mechanism. A d^3 metal apparently would not have as much electron density on the metal ion as a d^6 metal, hence the greater lability of the d^6 metals. It is interesting to compare the equilibrium property of $E_{1/2}$, the half-wave potential in aqueous solution. The values for a wide number of Cr(III) complexes are about −1.0 V vs SCE, and for a large number of Co(III) complexes they are about −0.2 V vs SCE.[30] This relative ease of reduction is consistent with the relative labilities of the two metal ions. This line of reasoning would imply that the trans ligand also should have the ability to affect the lability of the metal ion.

A second observation is the additional labilization of the complexes by the trans OH^- ligand. The values of k_4/k_1 for $CrTPPS(H_2O)_2{}^{3-}$ and Y = Im and NCS^- are 41 and 6000, whereas the values of K_4/K_1 are 0.20 and 0.28, respectively. An examination of Table III reveals that the large ratio for NCS^- results from the small value of ${}^{NCS}k_1$. The values of k_4, ΔH_1^*, ΔH_4^*, and ΔS_4^* are all similar. The difference in the comparison arises from the relatively more negative value of ΔS_1^* for NCS^-. This could simply reflect a solvation effect. The positive values of ΔS_4^* could imply an expanded activated complex when OH^- is the trans ligand. The lack of correspondence between k_i and K_i is taken as an indication of dissociative activation.[31]

The value of ${}^{NCS}k_4/{}^{NCS}k_1$ for $CrTMPP(H_2O)_2{}^{5+}$ is 6000 and of ${}^{NCS}K_1/{}^{NCS}K_4$ is 0.16. This large ratio is again the result of the small value of ${}^{NCS}k_1$. The values of ΔS^* are similar, but negative, for the two paths, and the values of ΔH^* differ by 5 kcal mol^{-1}, a totally different situation than with $CrTPPS(H_2O)_2{}^{3-}$. These values might be reflecting the solvation difference resulting from the different charges on the complexes.

The value of ${}^{Im}k_{-6}/{}^{Im}k_{-5}$ for $CrTPPSXIm^{n-}$ where X = OH^- and Im and Y = OH^- is 31, and the value of ${}^{Im}k_{-6}/{}^{Im}k_{-5}$ is 0.26. Here again, OH^- is labilizing the trans position compared to Im. The labilization is reflected by a decrease in the value of ΔH^* but a more negative ΔS^* value. The value of ${}^{Im}k_2/{}^{Im}k_1$ for $CrTPPS(X)H_2O^{3-}$, where X = Im and H_2O and Y = Im, is 0.13 and of ${}^{Im}k_2/{}^{Im}k_1$ is 0.029. The Im ligand is *not* trans-labilizing. Also, the values of the activation parameters are very surprising. The values of 10 kcal mol^{-1} and −27 cal (deg mol)$^{-1}$, respectively, for ΔH^* and ΔS^* are both the extreme of the observed values. These observations of the activation parameters are confusing when one attempts to determine trends and reasons in their values.

This labilization by cis or trans OH^- is a generaly observed phenomenon for Cr(III) complexes.[32,33] It has been suggested that the labilization by OH^- is due to its ability to stabilize a dissociatively generated activated complex by donating available electron density from it to the Cr(III).[17,34]

The values of ${}^{Im}k_1$ at 25 °C are surprisingly similar to those for the reaction of MeIm with CrTPP(Cl)L in toluene a system that reacts via a D mechanism. This similarity is probably just a coincidence, especially in view of the difference in solvents. However, it might be significant. An examination of reactions of other neutral nitrogen atom donor ligands might be revealing. The study of the reaction with pyridine is currently under way,

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and the results will be reported in the future.

The reaction of $CrTPPS(H_2O)_2^{3-}$ with Im has been studied at 15, 25, and 35 °C in aqueous solution over the accessible pH range. The values of the equilibrium and rate constants and activation parameters are reported. The porphyrin ligand labilizes the Cr(III) to ligation, with the trans OH^- ligand labilizing even more. There are no clear trends in the values of the activation parameters and the labilization other than, in general, the values of ΔH^* are about 16 kcal mol^{-1}.

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Tetrathiometalate Complexes of Rhodium, Iridium, Palladium, and Platinum. Structures of $[(C_5Me_5)RhCl]_2WS_4$ and $[(C_3H_5)Pd]_2WS_4$

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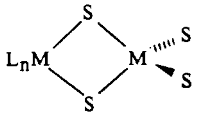
Synthetic routes to tetrathiometalate complexes of rhodium, iridium, palladium, and platinum are described. Acetonitrile solutions of WS_4^{2-} reacted with $[Rh(diene)Cl]_2$ (where diene = 1,5-cyclooctadiene (COD) or norbornadiene (NBD)), $[Ir(COD)Cl]_2$, $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$, and $[Pd(allyl)Cl]_2$ to give good yields of μ-WS_4 complexes $[Rh(diene)]_2WS_4$, $[Ir(COD)]_2WS_4$, $[(\eta^5\text{-}C_5Me_5)RhCl]_2WS_4$, and $[(allyl)Pd]_2WS_4$, respectively. $(COD)PtCl_2$ reacted with MS_4^{2-} to give $(COD)PtMS_4$, M = Mo, W. The latter complexes react further with PPh_3 or WS_4^{2-} to give $(PPh_3)_2PtMS_4$ and $Pt(WS_4)_2^{2-}$, respectively. $[Rh(COD)]_2WS_4$ reacted with *t*-BuNC to give $[Rh(t\text{-}BuNC)_2]_2WS_4$. $RhCl_3\cdot 3H_2O$ and $IrCl_3\cdot H_2O$ react with WS_4^{2-} to give the octahedral complexes $M(WS_4)_3^{3-}$ isolated as their Et_4N^+ salts. The ^{183}W NMR spectrum of $(Et_4N)_3[Rh(WS_4)_3]$ showed a doublet with $J(^{183}W,^{103}Rh) = 4.8$ Hz. Thermal gravimetric analyses of $[Rh(COD)]_2WS_4$ and $(COD)PtWS_4$ indicate that loss of organic coligands and stoichiometric amounts of sulfur occur at moderate temperatures. The compound $[(\eta^5\text{-}C_5Me_5)RhCl]_2WS_4\cdot CHCl_3$ crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 13.179$ (2) Å, $b = 28.725$ (7) Å, $c = 8.258$ (2) Å, $V = 3126$ (2) $Å^3$, and $Z = 4$ and was refined to $R = 0.052$ and $R_w = 0.059$. The compound $[(\eta^3\text{-}C_3H_5)Pd]_2WS_4$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 9.230$ (4) Å, $b = 9.994$ (5) Å, $c = 14.780$ (7) Å, $\beta = 103.54$ (4)°, $V = 1325$ (1) $Å^3$, and $Z = 4$ and was refined to $R = 0.066$ and $R_w = 0.079$.

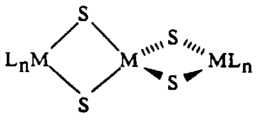
Introduction

In this report we describe the synthesis of tetrathiometalate complexes of rhodium, iridium, palladium, and platinum. At the inception of this investigation[1] little was known about the thiometalate complexes of the platinum metals[2] and no thiometalate complexes of rhodium or iridium had been reported.[3] Given the well-established affinity of platinum for sulfur ligands,[4] this aspect of coordination chemistry seemed likely to be very rich. Two classes of compounds were prepared, square-planar d^8 complexes and octahedral d^6 complexes. Thiometalate complexes of d^8 ions have been known for some time, viz. $M(M'S_4)_2^{3-}$ (where M = Co; M′ = Mo, W)[5,6] and $M(M'S_4)_2^{2-}$ (where M = Ni, Pd, Pt; M′ = Mo, W).[2] Octahedral d^6 thiometalate complexes are much less common.[7,8] We describe the first examples of tris(tetrathiometalate) complexes in the form of $M(WS_4)_3^{3-}$, where M = Rh, Ir.

Thiometalates commonly function as either terminal (A) or bridging (B) bidentate ligands. In type A complexes, the MS_4



A



B

metallo ligand can be viewed as a pseudohalide, 2e chelating agent. It is clear, however, that tetrathiometalates are not simple dithio chelates: whereas 1,1-dithiolenes stabilize metals in high formal oxidation states,[9] MoS_4^{2-} and WS_4^{2-} stabilize metals in their lower oxidation states.[10] In the bridging mode (B), each half of the MS_4 group resembles a dithio acid or 3e ligand. Recent work from this laboratory has shown that such bridging tetrathiometalates can promote strong electronic communication between the terminal metal sites.[11] For example carbonylation of $[CpRu(PPh_3)]_2WS_4$ proceeds only to the monocarbonyl stage despite the fact that the $CpRu(PPh_3)$ centers are equivalent and 5.65 Å apart (eq 1). Intermetallic electronic coupling is also indicated for the one-dimensional semiconductor NH_4CuMoS_4.[12] Recently complexes have been described in which metal atoms bridge adjacent edges of the thiometalate tetrahedron, such as

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