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

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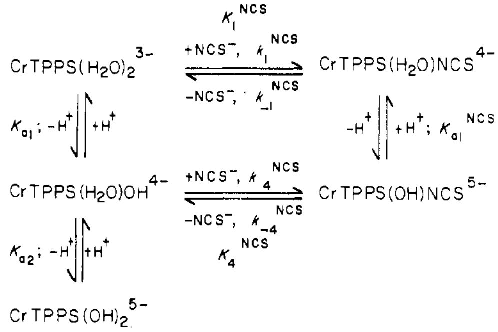
The reaction of NCS^- with (*meso*-tetrakis(*p*-sulfonatophenyl)porphinato)diaquochromate(III) ($CrTPPS(H_2O)_2^{3-}$) has been studied at 15, 25, and 35 °C in $\mu = 1.00$ M ($NaClO_4$) from pH 1 to 13. The following scheme adequately describes the equilibrium and kinetic properties of the system:



The values of pK_{a1}, pK_{a2}, and K_1^{NCS} at 25 °C are 7.63 ± 0.02, 11.45 ± 0.02, and 2.52 ± 0.16 M^{-1}, respectively. The values of pK_{a1}^{NCS} and K_4^{NCS} at 25 °C were determined kineticly to be 8.13 ± 0.06 and 0.69 ± 0.03 M^{-1}, respectively. The value of k_1^{NCS} at 25 °C is (4.67 ± 0.04) × 10^{-3} M^{-1} s^{-1} with ΔH^* and ΔS^* having values of 16.8 ± 0.4 kcal/mol and -12.8 ± 1.4 cal/(deg mol), respectively. The labilization effect of the porphine is only a factor of 10^2 compared to 10^9 for Co(III). The value of k_{-1}^{NCS} at 25 °C is (1.91 ± 0.10) × 10^{-3} s^{-1} with ΔH^* and ΔS^* values of 15.7 ± 1.1 kcal/mol and -18.5 ± 4.2 cal/(deg mol), respectively. The value of k_4^{NCS} at 25 °C is 28.5 ± 1.3 M^{-1} s^{-1} with $\Delta H^* = 16.7 \pm 0.1$ kcal/mol and $\Delta S^* = 4.1 \pm 0.2$ cal/(deg mol). The value of k_{-4}^{NCS} at 25 °C is 41.3 ± 4.9 s^{-1}. The presence of the $TPPS^{6-}$ and OH^- ligands greatly labilizes Cr(III) toward substitution and the reaction probably is dissociatively activated.

Introduction

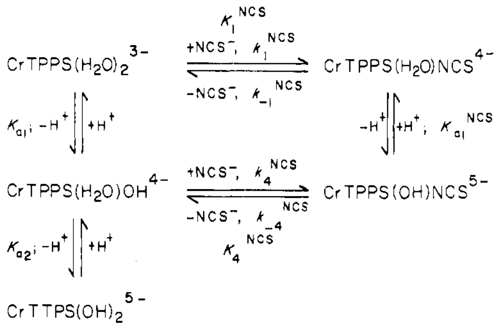
The labilization of the axial water ligands in cobalt(III) porphines has been documented.[2-8] The labilization of the axial water ligands in $RhTPPS(H_2O)_2^{3-}$ (TPPS = *meso*-tetrakis(*p*-sulfonatophenyl)porphine) also occurs but the effect is not as great as in the cobalt(III) porphines.[9,10] It has been reported that $CrTPPS(H_2O)_2^{3-}$ is labile to substitution by F^-, CN^- and C_6H_5N.[11] However, recently it has been reported that the reaction with $C_3H_4N_2$ is slow and shows no labilization effects of the porphine.[9] To further complicate this matter, the previous studies were performed at pH 7-12, and the reactive species was assumed to be $CrTPPS(OH)H_2O^{4-}$. It is known that when OH^- is a ligand on Cr(III) complexes the substitution reactions are substantially faster than when H_2O is the ligand.[12,13]

Table I. The Position and the Molar Absorptivities of the Soret Band of the Compounds Studied

compd	λ, nm	ε, 10^5 M^{-1} cm^{-1}
$Cr(TPPS)(H_2O)_2^{3-}$	444	2.09
$Cr(TPPS)(OH)(H_2O)^{4-}$	436	2.28
$Cr(TPPS)(OH)_2^{5-}$	436	2.55
$Cr(TPPS)(H_2O)NCS^{4-}$	450	1.62[a]

[a] The computer-calculated value from eq 2.

Scheme I



In an attempt to understand the effect of the porphine on the Cr(III) anation reactions, a detailed study of the reaction of $CrTPPS(H_2O)_2^{3-}$ with NCS^- was undertaken. This paper reports the results of that investigation.

Experimental Section

The materials used and the spectrophotometric methods for the determination of the acidity constant, stability constant, and kinetic data have been described.[5] As in the previous system, $\mu = 1.00$ M

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(2) E. B. Fleischer, S. Jacobs, and L. Mestichelli, *J. Am. Chem. Soc.*, **90**, 2527 (1968).
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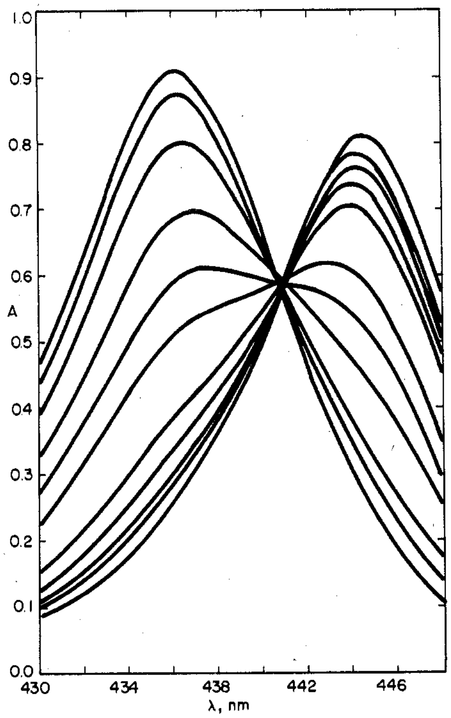

Figure 1. Change in absorbance between pH 6 and pH 9 at 25 °C and μ = 1.00 M (NaClO$_4$).

(NaClO$_4$) for all measurements. The Na$_3$[CrTPPS(H$_2$O)$_2$] was prepared by dissolving 100 mg of Na$_4$TPPS (Man-Win Coordination Chemicals, Washington, D.C.) in 100 mL of dimethylformamide. While the mixture was refluxed and purged with N$_2$, 200 mg of Cr(CO)$_6$ (Ventron Corp.) was added in small portions over a period of about 2 h. The solution was refluxed for an additional 30 min and then filtered.

The solution was cooled to room temperature, and 300 mL of diethyl ether was added. The Na$_3$[CrTPPS(H$_2$O)$_2$] was collected on a fritted disk filter and air-dried. The compound was dissolved in about 20 mL of water, 0.5 mL of acetic acid was added, and the mixture was dried on a water bath. The analyses were performed by Galbraith Laboratories, Inc. Anal. Calcd for Na$_3$[Cr(C$_{44}$H$_{24}$N$_4$S$_4$O$_{12}$)(H$_2$O)$_2$]·14H$_2$O: C, 39.5; H, 4.22; N, 4.19; S, 9.58; Cr, 3.89. Found: C, 39.6; H, 4.15; N, 3.93; S, 8.66; Cr, 4.08.

Results

Spectra. The compounds studied each showed one maxima in the 400–500-nm region. The wavelengths and the molar absorptivities of the maxima are reported in Table I. The molar absorptivities are based on a molecular weight calculated from the percent chromium in the sample.

Acid Dissociation Constant. In 0.100 M HClO$_4$ and μ = 1.00 M (NaClO$_4$), there is only one maxima between 390 and 500 nm. Likewise in 0.100 M NaOH and μ = 1.00 M (NaClO$_4$) the single maxima is at 436 nm. In changing the pH from pH 1 to 14, there is a change in absorbance between about pH 6 and 9 and pH 10 and 13. This change between pH 6 and 9 is shown in Figure 1. Notice the isosbestic point at 441 nm. Figure 2 is a plot of A vs. pH at 444 and 436 nm. The data between pH 10 and 13 were similar to those between pH 6 and 9. However, the change in absorbance at 436 nm was only 0.04 at a total absorbance of 0.7. K_{a1} and K_{a2} are defined in Scheme I.

Considering Beer's law, the mass balance, and the definition of K_{a1}, we can write eq 1, where A is the absorbance at a

$$A = \frac{A_b K_{a1} + A_a[H^+]}{K_{a1} + [H^+]} \qquad (1)$$

particular [H$^+$] ([H$^+$] = 10^{-pH}), A_b is the absorbance of the deprotonated form, and A_a is the absorbance of the protonated form.

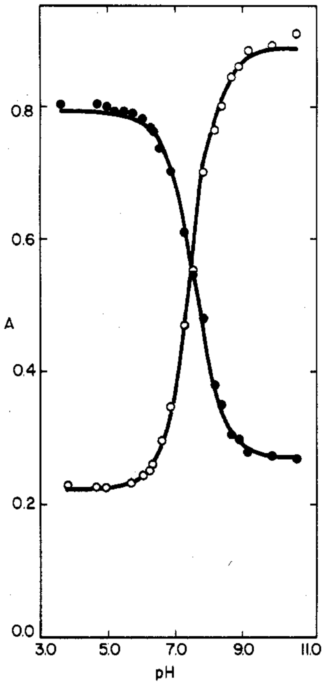

Figure 2. Change in absorbance as a function of pH at 444 (●) and 436 (○) nm at 25 °C and μ = 1.00 (NaClO$_4$). The solid lines are the least-squares fit of the data using eq 1.

The data were fit to eq 1 by using a nonlinear least-squares program.[14] The solid lines in Figure 2 are the computer fit of the data. The values of K_{a1} for this particular run at 444 and 436 nm are (2.31 ± 0.11) × 10^{-8} and (3.09 ± 0.17) × 10^{-8} M, respectively. The uncertainties, and all others reported in this paper, are 1 standard deviation of the parameter. The final values of K_{a1} at 444 and at 15, 25, and 35 °C are (2.00 ± 0.06) × 10^{-8}, (2.33 ± 0.07) × 10^{-8}, and (3.01 ± 0.11) × 10^{-8} M, respectively. The data for K_{a2} were treated similarly. The values of K_{a2} at 436 nm and 15, 25, and 35 °C are (1.96 ± 0.31) × 10^{-12}, (3.53 ± 0.17) × 10^{-12}, and (3.22 ± 0.77) × 10^{-12} respectively.

Stability Constant. The reaction of CrTPPS(H$_2$O)$_2^{3-}$ with Cl$^-$, Br$^-$, I$^-$, and NCS$^-$ was monitored spectrophotometrically at 0.100 M H$^+$. Only NCS$^-$ reacted to a measurable extent, and then only at high concentrations of NCS$^-$. Figure 3 is a plot of A vs. [NCS$^-$] for the reaction. The stability constant K_1^{NCS} is defined in Scheme I. Along with this definition of K_1^{NCS}, Beer's law, and the mass balance, eq 2 can be written.

$$A = \frac{A_r + A_p K_1^{NCS}[NCS^-]}{1 + K_1^{NCS}[NCS^-]} \qquad (2)$$

In eq 2, A is the absorbance at the given [NCS$^-$], A_r is the absorbance of the solution containing only CrTPPS(H$_2$O)$_2^{3-}$, and A_p is the absorbance of the solution containing only CrTPPS(NCS)H$_2$O^{4-}. The value of A_r was fixed and the data were fit to eq 2 by using a nonlinear least-squares program. The line in Figure 3 is the calculated line with the value of K_1^{NCS} being 2.52 ± 0.16 M^{-1} at 25 °C, 0.100 M [H$^+$], and μ = 1.00 M (NaClO$_4$). Note in Table II that the kinetically derived value of K_1^{NCS} is in excellent agreement.

Kinetics. Since pK_{a1} was 7.63 at 25 °C it was anticipated

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Table II. The Values of the Rate Constants and the Derived Equilibrium Constants at μ = 1.00 M ($NaClO_4$)

	k_1^{NCS}, 10^{-3} M^{-1} s^{-1}	k_{-1}^{NCS}, 10^{-3} s^{-1}	k_4^{NCS}, 10^1 M^{-1} s^{-1}	$K_1^{NCS}(k_1^{NCS}/k_{-1}^{NCS})$, M^{-1}
15 °C	1.75 ± 0.03	0.644 ± 0.016	1.03 ± 0.05	2.27 ± 0.05
25 °C	4.67 ± 0.04	1.91 ± 0.10	2.85 ± 0.13	2.45 ± 0.13
35 °C	12.7 ± 0.3	4.08 ± 0.13	7.31 ± 0.35	3.09 ± 0.11
ΔH^*, kcal/mol	16.8 ± 0.4	15.7 ± 1.2	16.7 ± 0.1	
ΔS^*, cal/(deg mol)	−12.8 ± 1.4	−18.5 ± 4.2	4.1 ± 0.2	

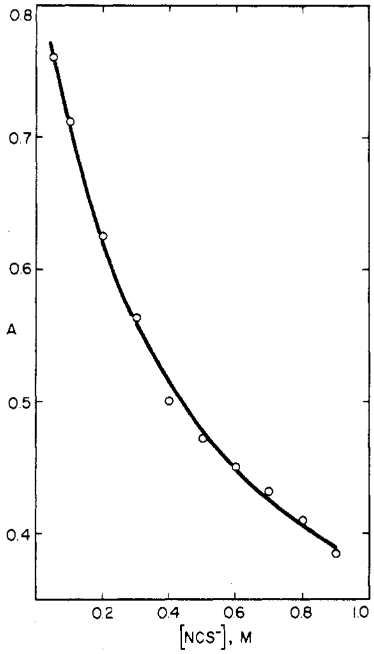

Figure 3. Plot of absorbance vs. [NCS^-] at 25 °C, μ = 1.00 M ($NaClO_4$), and [H^+] = 0.100 M ($HClO_4$). The solid line is the least-squares fit of the data to eq 2.

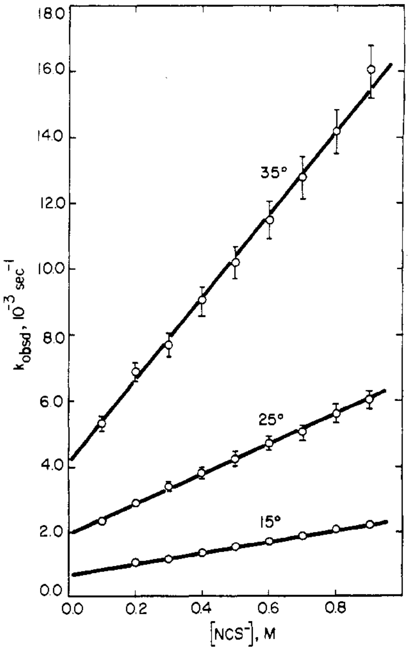

Figure 4. Plot of k_{obsd} vs. [NCS^-] at [H^+] = 0.100 M and μ = 1.00 M ($NaClO_4$). The solid lines are the least-squares fit of the data to eq 4.

that the reactions would be [H^+] independent at low pH values. And, indeed, preliminary experiments confirmed this.

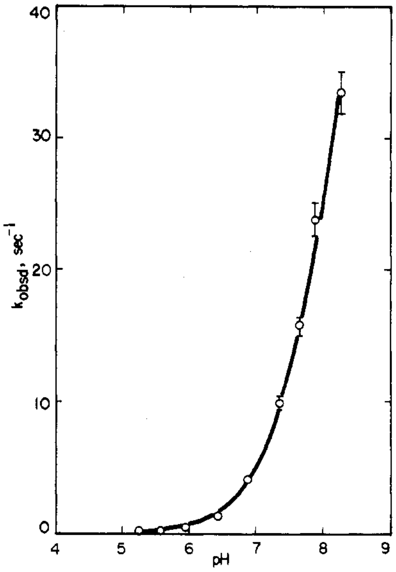

Figure 5. Effect of [H^+] on k_{obsd} at 25 °C, μ = 1.00 M ($NaClO_4$), [NCS^-] = 0.45 M, and 0.02 M phosphate buffer. The solid line is the least-squares fit of the data to eq 8.

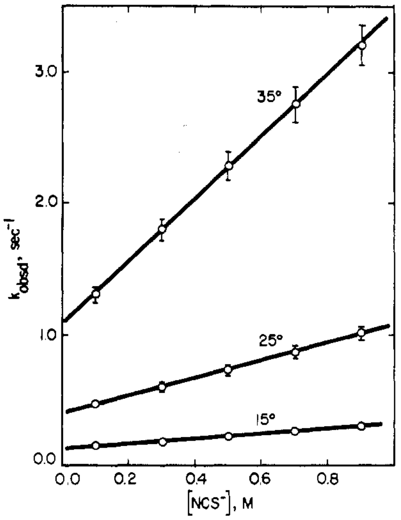

Figure 6. Plot of k_{obsd} vs. [NCS^-] at pH 6.00 ± 0.05, μ = 1.00 M ($NaClO_4$), and 0.02 M phosphate buffer. The solid lines are the least-squares fit of the data to eq 5.

At 0.100 M [H^+] and μ = 1.00 M ($NaClO_4$) the rate law for the anation reaction is

$$-d[CrTPPS(H_2O)_2^{3-}]/dt = k_1^{NCS}[NCS^-] \times [CrTPPS(H_2O)_2^{3-}] - k_{-1}^{NCS}[CrTPPS(NCS)H_2O^{4-}] \quad (3)$$

The pseudo-first-order rate constant, k_{obsd}, is defined by eq 4. The rate constants are defined in Scheme I. Figure 4 is

$$k_{obsd} = k_1^{NCS}[NCS^-] + k_{-1}^{NCS} \quad (4)$$

a plot of k_{obsd} vs. [NCS^-] at 15, 25, and 35 °C at 0.100 M [H^+] and μ = 1.00 M ($NaClO_4$). The lines are the computer fit of the data. The values of k_1^{NCS} and k_{-1}^{NCS} are contained in Table II. Also in Table II are the activation parameters calculated by a least-squares fit of the data to the Erying–Polanyi equation.

As the pH was increased at a constant NCS^- concentration it was anticipated by analogy to other Cr(III) reactions that the pseudo-first-order rate constant, k_{obsd}, would increase.[12] Figure 5 represents the data at 25 °C $[NCS^-] = 0.45$ M, and $\mu = 1.00$ M ($NaClO_4$). Higher pH values could not be investigated due to the small changes in absorbance. Clearly there is some sort of inverse $[H^+]$ dependence. Figure 6 depicts the dependence of k_{obsd} upon $[NCS^-]$ at pH 6.00 ± 0.05 and $\mu = 1.00$ M ($NaClO_4$). The lines in Figure 6 are the least-squares fit of the data to eq 5. The values of a and b respectively are 0.131 ± 0.001 s^{-1} and 0.185 ± 0.003 $M^{-1}\ s^{-1}$, 0.400 ± 0.004 s^{-1} and 0.669 ± 0.010 $M^{-1}\ s^{-1}$, and 1.07 ± 0.01 s^{-1} and 2.40 ± 0.03 $M^{-1}\ s^{-1}$ at 15, 25, and 35 °C, respectively.

$$k_{obsd} = a + b[NCS^-] \tag{5}$$

From an examination of Scheme I, it is apparent that as the pH is increased the concentration of $CrTPPS(H_2O)OH^{4-}$ increases ($pK_{a1} = 7.63$). If $CrTPPS(H_2O)OH^{4-}$ were a reactive species, then the rate expression for the first-order approach to equilibrium would be

$$\begin{aligned}-d[CrTPPS(H_2O)_2^{3-}]_{total}/dt = {} & k_1^{NCS}[CrTPPS(H_2O)_2^{3-}][NCS^-] - \\ & k_{-1}^{NCS}[CrTPPS(H_2O)NCS^{4-}] + \\ & k_4^{NCS}[CrTPPS(OH)H_2O^{4-}][NCS^-] - \\ & k_{-4}^{NCS}[CrTPPS(OH)NCS^{5-}]\end{aligned} \tag{6}$$

Upon notation of the definitions of K_{a1} and K_{a1}^{NCS}, notation of the mass balances, and performance of the integration, the pseudo-first-order rate constant can be written as eq 7. Notice

$$k_{obsd} = \frac{(k_1^{NCS}[H^+] + k_4^{NCS}K_{a1})[NCS^-]}{K_{a1} + [H^+]} + \frac{k_{-1}^{NCS}[H^+] + k_{-4}^{NCS}K_{a1}^{NCS}}{K_{a1}^{NCS} + [H^+]} \tag{7}$$

that at high $[H^+]$, eq 7 reduces to eq 4. Under conditions of constant $[H^+]$ and variable $[NCS^-]$, eq 7 is equivalent to eq 5 with $a = (k_{-1}^{NCS}[H^+] + k_{-4}^{NCS}K_{a1}^{NCS})/(K_{a1}^{NCS} + [H^+])$ and $b = (k_1^{NCS}[H^+] + k_4^{NCS}K_{a1})[NCS^-]/(K_{a1} + [H^+])$. Since b, k_1^{NCS}, $[H^+]$, $[NCS^-]$, and K_{a1} are known, the values of k_4^{NCS} at 15, 25, and 35 °C can be calculated. The values along with the activation parameters are reported in Table II.

At constant $[NCS^-]$ and variable $[H^+]$, eq 7 can be rearranged to eq 8. The left-hand side of eq 8 can be calculated for each $[H^+]$. Then eq 8 can be fit by the computer, with k_{-1}^{NCS} held constant, to give k_{-4}^{NCS} and K_{a1}^{NCS}. The solid line in Figure 5 is the computer fit of the data. The value at 25 °C of k_{-4}^{NCS} is 41.3 ± 4.9 s^{-1} and K_{a1}^{NCS} is (7.34 ± 1.01) × 10^{-9} M. The calculated value of K_4^{NCS} is 0.69 ± 0.09 M^{-1}.

$$k_{obsd} - \left[\frac{(k_1^{NCS}[H^+] + k_4^{NCS}K_{a1})[NCS^-]}{K_{a1} + [H^+]}\right] = \frac{k_{-1}^{NCS}[H^+] + k_{-4}^{NCS}K_{a1}^{NCS}}{K_{a1}^{NCS} + [H^+]} \tag{8}$$

Discussion

Acid Dissociation Constant. Fleischer and Krishnamurthy reported values of pK_{a1} and pK_{a2} of 4.8 and 7.9.[11] Taniguchi has published the spectrum of the sample of $Cr(TPPS)(H_2O)_2^{3-}$ that was used for these pK_a determinations.[15] Between 400 and 500 nm there was one maximum at 444 nm in 0.01 M $HClO_4$ and two maxima in 0.10 M NaOH at 414 and 434 nm. The maximum at 444 nm was wide enough to enclose a peak at 435 nm. The free TPPS has a maximum at 435 nm in 0.01 M $HClO_4$ and a maximum at 414 nm in 10^{-4}M NaOH.[16] This could be interpreted to imply that the sample had free TPPS in it. This would give rise to an erroneous pK_a. The pK_a of TPPS is 4.8.[16] This is the reported value of pK_{a1} for $Cr(TPPS)(H_2O)_2^{3-}$. The conclusion is that the pK_{a1} of $Cr(TPPS)(H_2O)_2^{3-}$ is 7.6 not 4.8 as reported by Fleischer and Krishnamurthy. This value of 7.6 compares favorably with the value of 7.9 reported for pK_{a2} by Fleischer and Krishnamurthy.

Table III. Kinetic Parameters for Anation by NCS^- for Selected Compounds

reactant	μ, M	k, $M^{-1}\ s^{-1}$	ΔH^*, kcal/mol	ΔS^*, cal/(deg mol)
$Cr(H_2O)_6^{3+}$ [a]	0.16	3.5×10^{-6}	25.1	0.63[d]
	1.0	1.8×10^{-6}		
$Cr(NH_3)_5H_2O^{3+}$ [b]	0.106	4.6×10^{-5}	24.2	3.0
	1.70	3.0×10^{-5}		
cis-$Cr(C_2O_4)_2(H_2O)_2^-$ [c]	1.0	7.25×10^{-5}	18.9	−20.4
$CrTPPS(H_2O)_2^{3-}$ [e]	1.0	4.67×10^{-3}	16.8	−12.8
$CrTPPS(OH)H_2O^{4-}$ [e]	1.0	2.88×10	16.7	4.1

[a] Reference 12. [b] Reference 21. [c] Reference 20. [d] Calculated from the data in ref 12 by using the equation $\Delta S^* = R(\ln PZ - \ln \kappa T/h - 1)$ and $T = 298$ K. [e] This work.

The higher value for pK_{a2} was expected. However, an increase in pK_{a2} by 4 is greater than usually observed. For comparison, the pK_{a1} of *trans*-$Cr(H_2NC_2H_4NH_2)_2(H_2O)_2^{3+}$ is 4.1 and pK_{a2} is 7.5.[17] The pK_{a1} of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ is 7.1 and pK_{a2} is 9.3.[18] In $CoTPPS(H_2O)_2^{3-}$ the values of pK_{a1} and pK_{a2} are 7.02 and 9.76.[6] Clearly, the pK_{a2} is always higher by several units and the substitution of a negatively charged ligand for a neutral one increases the pK_a. This is what is expected. However, the K_{a1} decreases by only a factor of 3.2 in going from $CrTPPS(H_2O)_2^{3-}$ to $CrTPPS(NCS)H_2O^{4-}$.

Stability Constant. The stability constants for $Cr(H_2O)_5NCS^{2+}$ and *cis*-$Cr(C_2O_4)_2NCS(H_2O)^{2-}$ are 182 and 4.50 M^{-1} at $\mu = 1.00$ M.[19,20] The value of 2.52 M^{-1} for $CrTPPS(NCS)(H_2O)^{5-}$ compares favorably with these values. However, it is substantially smaller than the value of 2640 M^{-1} for $CoTPPS(NCS)H_2O^{4-}$.[6] Until more stability constant data become available, not much more can be said. However, the low value of the stability constant could be interpreted to mean than the electron density on Cr(III) in the porphine complex is greater than in the aquo complex.

Kinetics of Anation. The value of 25 °C for k_1^{NCS} of 4.7 × 10^{-3} $M^{-1}\ s^{-1}$ clearly indicates that labilization of Cr(III) has been effected. The extent of labilization is dependent upon the comparison reaction. For example, using the data in Table III one can see that the $CrTPPS(H_2O)_2^{3-}$ has been labilized by factors of 2700, 100, and 60 compared to $Cr(H_2O)_6^{3+}$, $Cr(NH_3)_5H_2O^{3+}$, and *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$, respectively. Clearly this is not as great as the increase of 1.12 × 10^9 in the rate constant for anation by NCS^- of $CoTPPS(H_2O)_2^{3-}$ compared to $Co(NH_3)_5H_2O^{3+}$.[6]

It is thought that the labilization effect of the porphines is due to their ability to donate electron density to the metal ions. In these d^3 and d^6 metal cases this would tend to produce d^4-

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and d^7-like labile metal ions. If this is the case, either the Cr(III) is not as efficient in accepting the electron density from the TPPS^{6-} or the TPPS^{6-} is not as able to efficiently donate the electron density to the Cr(III).

The activation parameters for the anation of several Cr(III) compounds show a surprising trend. Table III shows that as the anation rate constant increases, ΔH^* decreases and ΔS^* becomes negative. In the reactions with cobalt(III) porphines, the labilization effect is accompanied with a positive ΔS^* and a somewhat smaller ΔH^* than usual for anation reactions.[6] This positive entropy has been interpreted to imply dissociative activation for Co(III) anation reactions.[5] It is uncertain as to what would be the activation parameters for dissociative activation for anation reactions of Cr(III). One would expect them to be similar to those of Co(III). Until more data are acquired, additional discussion is inappropriate at this time.

The anation of $\mathrm{CrTPPS(OH)H_2O^{4-}}$ is 6.1×10^3 times faster than of $\mathrm{CrTPPS(H_2O)_2^{3-}}$ and 9.5×10^5 faster than of $\mathrm{Cr(NH_3)_5H_2O^{3+}}$.[21] This is indeed a labilization effect! The ability of $\mathrm{OH^-}$ to labilize substitution has been reported before.[12] For the anation of $\mathrm{Cr(H_2O)_5OH^{2+}}$ by $\mathrm{NCS^-}$, $\mathrm{NO_3^-}$, HF, $\mathrm{Cl^-}$, $\mathrm{SCN^-}$, $\mathrm{Br^-}$, and $\mathrm{I^-}$, the rate constant is from 27 to 3250 times greater than for $\mathrm{Cr(H_2O)_6^{3+}}$.[12] This is accompanied by a decrease in the value of ΔH^* from 2 to 6 kcal/mol and also a decrease in the value of ΔS^* from 1 to 11 cal/(deg mol), with the exception of $\mathrm{I^-}$ which has a ΔS^* increase of 4.6 cal/(deg mol). In the anation reaction of $\mathrm{CrTPPS(OH)H_2O^{4-}}$, ΔH^* is not changed but ΔS^* has increased by about 12 cal/(deg mol) and is positive. This would seem to imply dissociative activation for the anation of $\mathrm{CrTPPS(OH)H_2O^{4-}}$ by $\mathrm{NCS^-}$.

One explanation for the increased labilization by $\mathrm{OH^-}$ would be that the $\mathrm{OH^-}$ ligand is able to donate additional electron density to Cr(III) and hence labilize it more. The proposition is as follows. A 3+ metal ion (d^6 or d^3) can accept a certain amount of electron density. The more is accepts the more labile the metal ion becomes. If the porphine is unable, for some reason, to donate as much electron density to the metal ion as it is inherently able to accept, then those ligands that are able to donate more electron density to the metal ion will labilize it even more. This proposition is supported by the data for the anation of $\mathrm{CoTMPpy(H_2O)_2^{5+}}$.[22] The rate constant for the addition of $\mathrm{NCS^-}$ to $\mathrm{CoTMPpy(OH)H_2O^{4+}}$ is increased 52 times over that of $\mathrm{CoTMPpy(H_2O)_2^{5+}}$ and $\mathrm{NCS^-}$ to $\mathrm{CoTMPpy(NCS)H_2O^{4+}}$ is increased 10^4 times over that of $\mathrm{CoTMPpy(H_2O)_2^{5+}}$.[4]

The aquation rate constant (k_{-1}^{NCS}) is very similar to that for anation. This is expected from the value of the formation quotient. The activation parameters are similar also, although the entropy is somewhat more negative. It is interesting to note that these activation parameters are similar to those for the aquation of *cis*-$\mathrm{Cr(C_2O_4)_2(X)H_2O^{n-}}$, where X = $\mathrm{(CH_3)_2SO}$, $\mathrm{HCON(CH_3)_2}$, $\mathrm{CH_3COO^-}$, $\mathrm{NCS^-}$, and $\mathrm{N_3^-}$.[23]

Some comparisons to the previous work are possible.[11] The acid dissociation constant has already been discussed. The comparison of the equilibrium constants and the rate constants will have to be semiquantitative since the previous work was performed at pH 7. The $\mathrm{CrTPPS(H_2O)_2^{3-}}$ is 21% in the form of $\mathrm{CrTPPS(OH)(H_2O)^{4-}}$ at this pH. The reported values of K_1^{L} for $\mathrm{F^-}$ and $\mathrm{C_5H_5N}$ are 27 and 150 $\mathrm{M^{-1}}$. This compares to the calculated value of 2.0 $\mathrm{M^{-1}}$ for $\mathrm{NCS^-}$ at pH 7. Generally the value of K_1^{L} for $\mathrm{C_5H_5N}$ is higher than for $\mathrm{NCS^-}$.[7] No comparisons can be made for $\mathrm{F^-}$. The second-order rate constants for anation at pH 7.0 are 5.5×10^{-4}, 3.8, and 8.2 $\mathrm{M^{-1}\ s^{-1}}$ for $\mathrm{F^-}$, $\mathrm{C_5H_5N}$, and $\mathrm{NCS^-}$, respectively. It is tempting to suggest that an I_d mechanism is occurring in these reactions. However, the fact that two different Cr(III) species are reacting makes this interpretation unclear. The investigations of the reactions with $\mathrm{F^-}$ and $\mathrm{C_5H_5N}$ are currently underway.

The compound $\mathrm{CrTPPS(H_2O)_2^{3-}}$ has two observable acid dissociation constants. The porphine has labilized the Cr(III) to anation by $\mathrm{NCS^-}$, although not as much as in the Co(III) case. The compound $\mathrm{CrTPPS(OH)H_2O^{4-}}$ has been labilized even more than $\mathrm{CrTPPS(H_2O)^{3-}}$. The labilization has been interpreted to occur by electron donation to Cr(III) from the porphine and $\mathrm{OH^-}$.

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Registry No. $\mathrm{Na_3[CrTPPS(H_2O)_2]}$, 73090-55-8; $\mathrm{CrTPPS(H_2O)_2^{3+}}$, 33339-70-7; $\mathrm{CrTPPS(H_2O)OH^{4-}}$, 73090-56-9; $\mathrm{CrTPPS(OH)_2^{5-}}$, 73104-82-2; $\mathrm{CrTPPS(H_2O)NCS^{4-}}$, 73090-57-0; $\mathrm{CrTPPS(OH)NCS^{5-}}$, 73090-58-1.

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