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SUBSTITUTION REACTIONS OF *trans*-$Co(CN)_4(SO_3)(OH_2)^{3-}$. II. THE RATE OF SUBSTITUTION OF COORDINATED WATER BY AMMONIA, PYRIDINE, AZIDO, THIOCYANATO, AND SULFITO LIGANDS AND THE RATE OF AQUATION OF *trans*-$Co(CN)_4(SO_3)NH_3^{3-}$ AND *trans*-$Co(CN)_4(SO_3)py^{3-}$ *

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* Dedicated to the memory of Wayne Keith Wilmarth.

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A. INTRODUCTION

It is generally agreed that in acidic aqueous solution the substitution reactions of the overwhelming majority of octahedral Co(III) complexes occur by mechanisms which are largely dissociative in nature. However, it has not often been possible to demonstrate that these reactions generate reactive intermediates of reduced coordination number with lifetimes sufficiently long to allow discrimination between various nucleophiles present in the system. In these circumstances the reaction mechanisms are properly designated as S_N1 (or I_d), with the terminology *limiting* S_N1 (or D) being reserved for those cases where competitive scavenger studies provide definite evidence for a reactive intermediate of reduced coordination number [1]. The first well-documented example of a limiting S_N1 mechanism was based on reports [2–5] of kinetic studies of the replacement of H_2O in $Co(CN)_5OH_2^{2-}$ by various nucleophiles:

$$Co(CN)_5OH_2^{2-} + L^{n-} \rightleftarrows Co(CN)_5L^{(2+n)-} + H_2O \qquad (1)$$

where $L^{n-} = N_3^-$, SCN^-, H_2O, I^-, Br^-, Cl^-, I_3^-, py, NH_3, N_2H_4, or $N_2H_5^+$.

In the interval since these reports appeared, evidence in support of a limiting S_N1 mechanism (for complexes other than those with macrocyclic ligands) has been limited primarily to reactions of sulfito complexes of Co(III) [6–9] and low-spin pentacyano complexes of Fe(II) [10]. This mechanism has also been postulated for reactions of spin-paired d^6 bis(diphenylglyoximato) complexes [11] of Fe(II), and bis(dimethylglyoximato) complexes [12,13] of Co(III), in non-aqueous solvents.

The studies of the sulfito complexes of Co(III) include reactions of the amine complexes [6,8], e.g.,

$$trans\text{-}Co(NH_3)_4(SO_3)X^{(1-n)+} + Y^{m-} \rightleftarrows trans\text{-}Co(NH_3)_4(SO_3)Y^{(1-m)+} + X^{n-} \qquad (2)$$

and, as reported in the initial paper in this series, cyanide complexes [7],

$$trans\text{-}Co(CN)_4(SO_3)OH_2^{3-} + CN^- \rightleftarrows Co(CN)_5(SO_3)^{4-} + H_2O \qquad (3)$$

The sulfito complexes of Co(III) are of interest not only because it has been possible to obtain evidence for a limiting S_N1 mechanism, but also because in all cases the reactions proceed with unusual rapidity. Furthermore, the evidence indicates that this rapidity is limited to the ligand *trans* to SO_3^{2-}. Therefore, we shall refer to such labilization as *trans* activation.

In this series of studies, the negatively charged reactants provide the advantage that ion-pair formation is negligible, therefore mechanistic ambiguities arising when oppositely charged reactants are used are not present. The studies presented in this report and the subsequent report have been designed in part to explore the generality of the limiting S_N1 mechanism for the replacement of the ligand water in $Co(CN)_4(SO_3)OH_2^{3-}$ by various nucleophiles. This is rather important since some complexes undergo substitution by different mechanisms depending on the nature of the nucleophiles. For example, the replacement of H_2O in $Co(CN)_5(OH_2)^{2-}$ by either SO_3^{2-} or HSO_3^- is first order in the nucleophile concentration, and the rate of substitution is more rapid than the limiting rate reported for nucleophiles such as Br^- and SCN^- [2,4,14]. Similar behavior has been observed in the substitution of $Co(en)_2(SO_3)(OH_2)^+$ by $Fe(CN)_5(NO)^{2-}$ and SO_3^{2-} [8,15]. A further goal of this study is to gain an understanding of the factors governing the reactivity of the intermediate $Co(CN)_4(SO_3)^{3-}$ towards various nucleophiles and to allow comparison with reactivity profiles for other five-coordinate Co(III) reactive intermediates. This is accomplished by extending the kinetic studies of the ligation of the complex to a wide range of nucleophiles under a variety of conditions.

The present paper is a report of the ligation by neutral molecules such as ammonia and pyridine, uninegative azide ion and thiocyanate ion, and the dinegative sulfite ion as depicted in eqn. 4:

$$trans\text{-}Co(CN)_4(SO_3)OH_2^{3-} + L^{n-} \overset{K_f}{\rightleftarrows} trans\text{-}Co(CN)_4(SO_3)L^{(3+n)-} + H_2O \quad (4)$$

where $L^{n-} = NH_3$, py, N_3^-, SCN^-, or SO_3^{2-}.

These nucleophiles were chosen to extend our understanding of the mechanism of the substitution reactions of Co(III) by ligands of the three different charge types, -2, -1, and 0. In addition, the kinetics of the acid-promoted aquation of the complexes *trans*-$Co(CN)_4(SO_3)NH_3^{3-}$ (eqn. 5) and *trans*-$Co(CN)_4(SO_3)py^{3-}$ have been studied and the results are included herein.

$$trans\text{-}Co(CN)_4(SO_3)NH_3^{3-} + H_2O + H^+ \rightleftarrows trans\text{-}Co(CN)_4(SO_3)(OH_2)^{3-} + NH_4^+ \quad (5)$$

Evidence that $Co(CN)_4(SO_3)OH_2^{3-}$ and the various $Co(CN)_4(SO_3)L^{(3+n)-}$ products have the *trans* geometry has been discussed earlier [7]. We shall, therefore, for simplicity, omit the *trans* prefix in designating the *trans* geometric configuration of the cobalt complexes.

B. EXPERIMENTAL

(i) Reagents

All commercial inorganic chemicals were of reagent grade and were used without further purification. Pyridine was purified by distillation (b.p.

113.8–114.0°C; [lit. 115°C]). The preparation of $Na_5[Co(CN)_4(SO_3)_2]\cdot 3H_2O$ follows the procedure described previously [7]. Stock solutions of sodium perchlorate, for adjustment of the ionic strength of solutions, were prepared by dissolving recrystallized sodium perchlorate (prepared by neutralization of $HClO_4$ with Na_2CO_3) in deionized water. These solutions were analyzed by evaporation of aliquots to dryness and constant weight.

Solutions of $Co(CN)_4(SO_3)OH_2^{3-}$ for kinetic measurements were prepared in two ways. In the first method, $Na_5[Co(CN)_4(SO_3)_2]\cdot 3H_2O$ was dissolved in 0.1M $HClO_4$. At this pH, replacement of one sulfite ligand by water occurs within a matter of seconds and further aquation of $Co(CN)_4(SO_3)OH_2^{3-}$ is very slow [16]. The liberated SO_2 was removed by purging the solution with nitrogen as described previously [7]. The solution was then diluted with sodium hydroxide and sodium perchlorate solutions to adjust the final solution to the desired pH and ionic strength. In order to reduce the possibility of undesirable secondary reactions of $Co(CN)_4(SO_3)OH_2^{3-}$, the second method, a more rapid method, was employed. Solutions of 5×10^{-5} to 1×10^{-3} M $Co(CN)_4(SO_3)_2^{5-}$ were made ~ 0.01 M in perchloric acid. A slightly greater than stoichiometric amount of Ce(IV)-standardized hydrogen peroxide was then added to oxidize the liberated SO_2 to SO_4^{2-}. The negligible effect of the sulfate ion, a relatively poor nucleophile towards Co(III) was verified by control experiments. After ~ 10 min, the solution was adjusted to the desired pH and ionic strength. Spectrophotometric analysis showed this to be sufficient time for complete conversion of $Co(CN)_4(SO_3)_2^{5-}$ to $Co(CN)_4(SO_3)OH_2^{3-}$ [17]. Doubling the concentration of H_2O_2 had no effect on the kinetic results. Solutions of $Co(CN)_4(SO_3)(NH_3)^{3-}$ and $Co(CN)_4(SO_3)py^{3-}$ for aquation studies were prepared by adding a stoichiometric amount of NH_3 and pyridine, respectively, to neutral solutions of $Co(CN)_4(SO_3)OH_2^{3-}$.

(ii) Apparatus

Spectrophotometric measurements were made using a Cary Model 14 recording spectrophotometer and a Beckman DU spectrophotometer. The stopped-flow spectrophotometer was purchased from Atom-Mech Machine Company and has been described elsewhere [18]. A Beckman Research Model pH meter equipped with a well-thermostatted E-3 glass electrode and calomel reference electrode was used for all pH measurements. The saturated KCl solution in the reference electrode was removed and replaced with saturated NaCl solution to prevent clogging due to precipitation of $KClO_4$ when measurements were made in solutions containing perchlorate ion.

(iii) Kinetic procedures

The rates of reactions with half-lives of $\geqslant 5$ s were measured by following the absorbance changes accompanying the reactions with the Cary Model 14 spectrophotometer equipped with a thermostatted cell compartment. The reactant solutions were always equilibrated at 25.0°C prior to mixing. Those reactions having half-lives of < 5 s were followed using the stopped-flow spectrophotometer. In this apparatus, the reactant solutions and mixing chamber were thermostatted at 25.0 ± 0.2°C. The forward reactions, i.e., formation of $Co(CN)_4(SO_3)NH_3^{3-}$ and $Co(CN)_4(SO_3)_2^{5-}$, were initiated by mixing solutions, adjusted to the desired pH, of $Co(CN)_4(SO_3)OH_2^{3-}$ and the appropriate nucleophile. The reactions of $Co(CN)_4(SO_3)OH_2^{3-}$ with sulfite ion were followed at 313 nm, a wavelength at which $Co(CN)_4(SO_3)_2^{5-}$ exhibits an absorbance maximum ($\xi = 3.2 \times 10^4$ M^{-1} cm^{-1}). At this wavelength, the molar absorbances of $Co(CN)_4(SO_3)OH^{4-}$ and $Co(CN)_4(SO_3)OH_2^{3-}$ are 1.4×10^3 M^{-1} cm^{-1} and 3.0×10^3 M^{-1} cm^{-1}, respectively. The reactions with NH_3 and pyridine were followed in the 280–285 nm region and 300–320 nm region, respectively. The stopped-flow experiments with the SCN^- and N_3^- were performed in the 340–350 nm region.

The pH of the solutions were always measured immediately following completion of the reaction, and hydroxide ion concentration was then calculated with the aid of a calibration curve, generated using solutions of 1.0 M ionic strength and known hydroxide ion concentration. When the $[OH^-]$ was $\leqslant 10^{-3}$ M, the pH was maintained with a sodium borate–sodium hydroxide buffer system. The hydrolysis reactions were initiated by mixing solutions of $Co(CN)_4(SO_3)NH_3^{3-}$ or $Co(CN)_4(SO_3)py^{3-}$ with solutions of the appropriate pH.

(iv) Formation constants

The values for K_f for the formation of $Co(CN)_4(SO_3)SCN^{4-}$ and $Co(CN)_4(SO_3)N_3^{4-}$ from $Co(CN)_4(SO_3)OH_2^{3-}$ were measured by monitoring the absorbance changes accompanying the addition of aliquots of solutions of the sodium salts of either thiocyanate or azide to solutions of $Co(CN)_4(SO_3)OH_2^{3-}$ at 345 nm ($pOH = 4.82$; $\mu = 1.0$ M; 25°C). The formation constants were then determined from linear plots of $\log(A_\infty - A)/(A - A_0)$ vs. $\log[L^{n-}]$. The value of K_f for $Co(CN)_4(SO_3)py^{3-}$ was also determined spectrophotometrically. In order to avoid complications from ligation by pyridinium ion, this reaction was studied in 1.00 M NaOH solution. The K_f was thus calculated as described in the Results Section.

C. RESULTS

All kinetic studies were carried out at 25.0°C. In the NH_3, py, SCN^-, and N_3^- ligation reactions, $NaClO_4$ was added to maintain the ionic strength at unity *. In the SO_3^{2-} studies, it was not possible to maintain both the Na^+ concentration and ionic strength at unity simultaneously, since SO_3^{2-} and ClO_4^- are of different charge types. In these experiments, we chose to keep the $[Na^+]$ at unity, a procedure which should minimize medium effects [19].

Pseudo-first-order kinetic behavior was observed in all experiments, since the nucleophile concentration was always large compared to the total concentration of Co(III). In any given experiment, the rate was characterized by a pseudo-first-order rate constant, k_{obs}, defined by the following equation:

$$\frac{-\mathrm{d}\ln\left(\left[\mathrm{Co(CN)_4(SO_3)OH_2^{3-}}\right]-\left[\mathrm{Co(CN)_4(SO_3)OH_2^{3-}}\right]_{eq}\right)}{\mathrm{d}t}=k_{obs} \qquad (6)$$

Numerical values of k_{obs} were obtained from linear plots of $\log(A_t - A_\infty)$ vs. time, where A_t and A_∞ are the absorbances of the solution at a time t and after a time long enough for the system to reach equilibrium, respectively. These plots were generally linear over three or more half lives and the average deviation in numerical values of k_{obs} obtained in replicate experiments did not exceed ±5%.

For the ligation reactions with each of the nucleophiles which were studied, two series of experiments were carried out. The first series was designed to determine the effect of variable nucleophile concentration and the second the effect of varying alkalinity. The nucleophiles were grouped into charge type and the results are described in the following paragraphs.

(i) The ammonia and pyridine ligation reactions

In several preliminary experiments, it was established that at any given alkalinity, the rate is essentially zero order in $[NH_3]$ at all NH_3 concentrations greater than 0.05 M. Therefore, it was necessary to carry out kinetic studies at very low NH_3 concentrations.

In these experiments, at unit ionic strength and 25.0°C, the OH^- concentration was held constant at one of three alternative values (9.15×10^{-3}, 1.80×10^{-2}, and 1.85×10^{-2} M), and the NH_3 concentration was varied over the range 1.00×10^{-3} to 5×10^{-3} M. The results are presented in Fig. 1 as plots of k_{obs} vs. the NH_3 concentration.

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* Even in experiments involving neutral nucleophiles, the addition of $NaClO_4$ is of importance in that it minimizes changes in the ionization quotients of $Co(CN)_4(SO_3)OH_2^{3-}$.

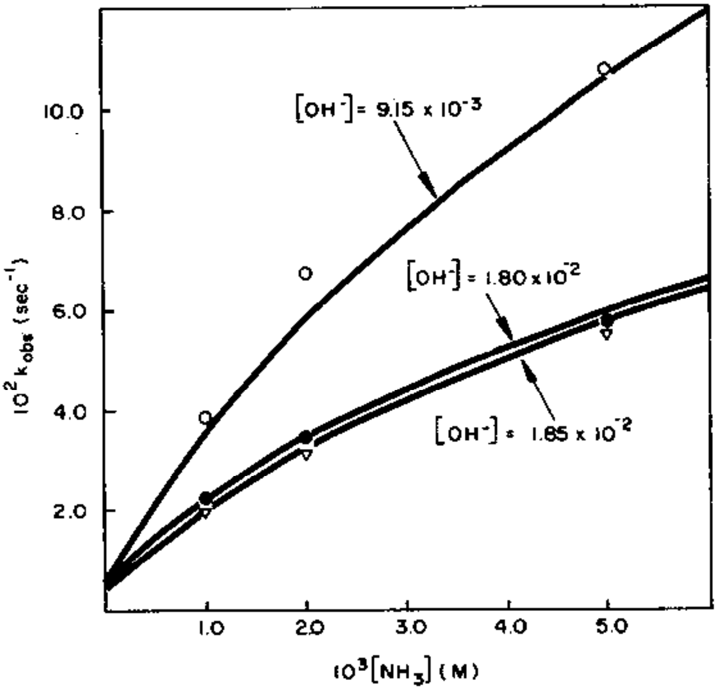


Fig. 1. The dependence of k_{obs} on the ammonia concentration for the reaction of $Co(CN)_4(SO_3)OH_2^{3-}$ at 25.0°C, $\mu = 1.0$ M, and three different $[OH^-]$. The solid lines are theoretical curves.

The lines drawn through the points in Fig. 1 as well as those in the other figures represent calculated values which will be considered in more detail in Section D. However, at this point it may be noted that the rate becomes less than first order in NH_3 even in the millimolar range of concentration and that the deviation from first-order behavior increases with increasing NH_3 concentration. In these experiments, k_{obs} is a measure of the rate of approach to equilibrium, since calculations based on our previously reported value for the equilibrium quotient for reaction 7 indicate that the reaction was far from quantitative.

$$Co(CN)_4(SO_3)OH^{4-} + NH_3 \rightleftharpoons Co(CN)_4(SO_3)NH_3^{3-} + OH^- \ K_1 = 98 \pm 3 \qquad (7)$$

The results of the second series of experiments at variable alkalinity are presented as the upper curve in Fig. 2, a semi-logarithmic plot of k_{obs} vs. $-\log[OH^-]$. In these experiments $[NH_3]$ was kept at 1.0 M so that zero-order dependence in $[NH_3]$ was obeyed and the reaction proceeded to completion.

The line drawn through the filled circle points in Fig. 2 indicates that the

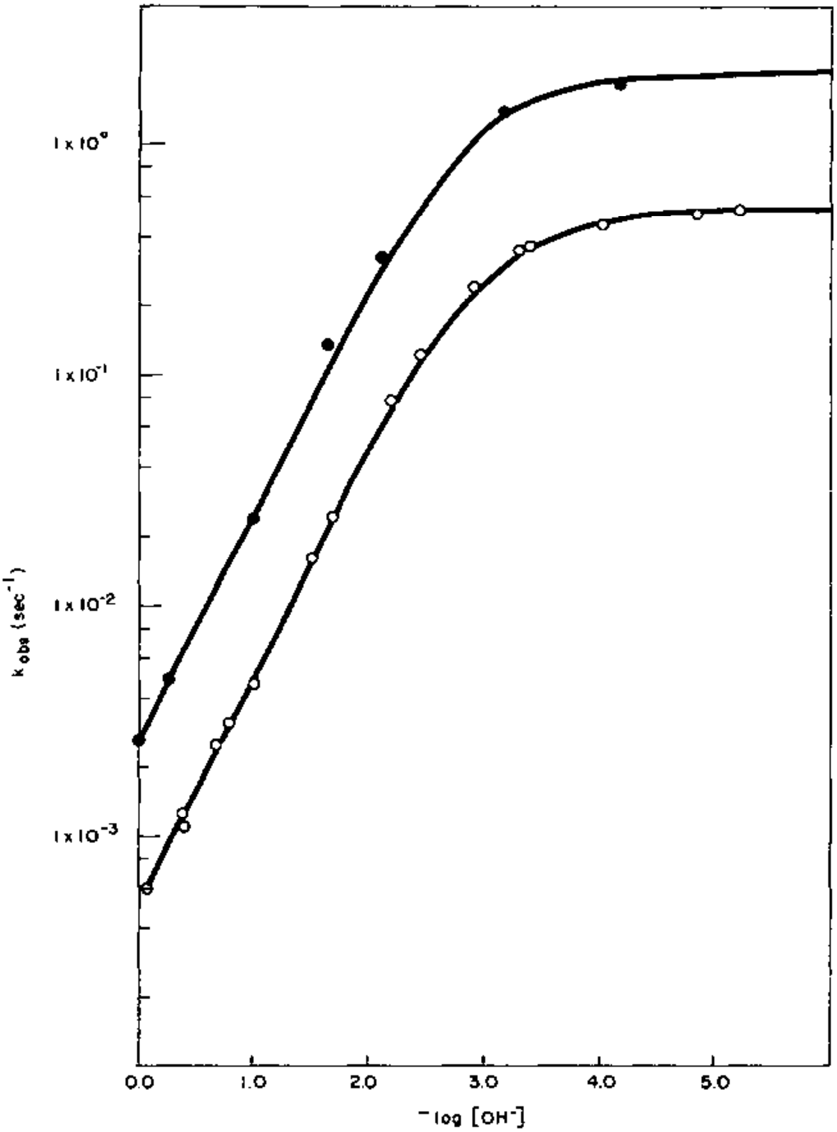


Fig. 2. The dependence of k_{obs} on hydroxide ion concentration for substitution of NH_3 (●) and SO_3^{2-} (○) on $Co(CN)_4(SO_3)OH_2^{3-}$ at 25.0°C and $\mu = 1.0$ M. The concentration of ammonia is kept at 1.0 M and the $[SO_3^{2-}]$ is at 0.10 M.

dependence of k_{obs} upon the OH^- concentration is rather complex, but simple, limiting types of behavior are observable in the ranges of relatively high and low OH^- concentrations. At $[OH^-] > 10^{-2}$ M, the line drawn through the points has unit slope, an indication that under these conditions the rate is inverse first order in $[OH^-]$.

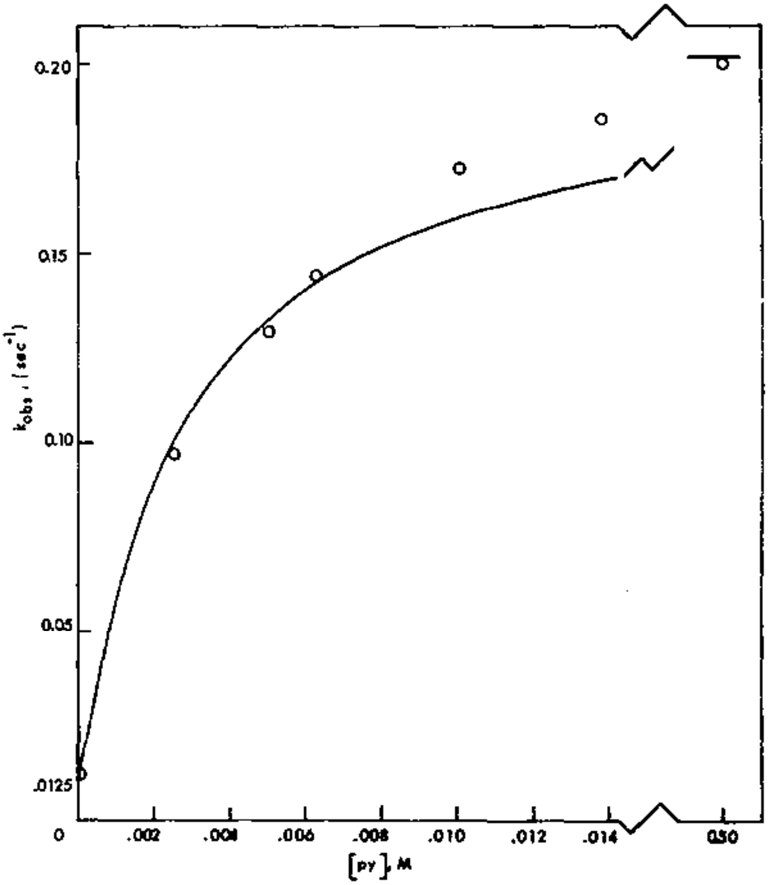


Fig. 3. The dependence of k_{obs} on the pyridine concentration for the reaction of $Co(CN)_4(SO_3)OH_2^{3-}$ with pyridine at 25.0°C, $\mu = 1.0$ M and $[OH^-] = 1.0 \times 10^{-2}$ M. The solid line is the theoretical curve.

The second simple type of kinetic behavior in Fig. 2 is observable at OH^- concentrations of $\leqslant 10^{-3}$ M, where, with decreasing alkalinity, the rate becomes approximately zero order in $[OH^-]$. Unfortunately, it was not possible to decrease the OH^- concentration below 10^{-4} M, since extensive protonation of NH_3 under these conditions complicates the interpretation of the kinetic data.

The pyridine ligation experiments were carried out at 25.0°C and unit ionic strength. In the first series of experiments the pyridine concentration was varied from 2.50×10^{-3} to 0.50 M at $[OH^-] = 1.00 \times 10^{-2}$ M. The results of these runs are depicted in Fig. 3, a plot of k_{obs} vs. [py].

The value of k_{obs} at zero [py] corresponds to the rate of hydrolysis of

$Co(CN)_4(SO_3)py^{3-}$. This was measured as the rate constant for basic hydrolysis of $Co(CN)_4(SO_3)py^{3-}$ in the absence of free pyridine and with $[OH^-] = 1.00$ M. The error bars in this and the other figures represents an uncertainty of ±5%.

In the second series of experiments the pyridine concentration was held constant at 0.50 M and the $[OH^-]$ varied from 1.12×10^{-7} to 1.00 M. The experiments carried out at 1.12×10^{-7} M $[OH^-]$ were buffered with 0.018 M sodium borate. The results of these experiments are illustrated in Fig. 4 (upper curve), a plot of k_{obs} vs. $-\log[OH^-]$.

An additional series of experiments was carried out to determine the

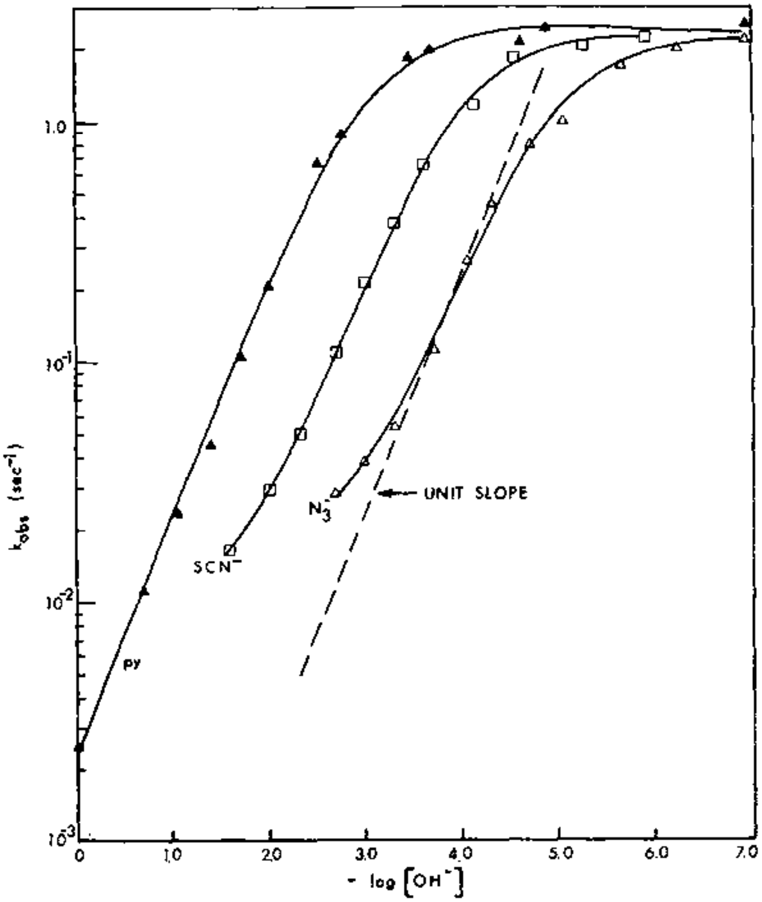


Fig. 4. The dependence of k_{obs} on pOH for the reaction of $Co(CN)_4(SO_3)OH_2^{3-}$ with 0.5 M pyridine, SCN^-, and N_3^- at 25.0°C and $\mu = 1.0$ M. The points for each ligand have been displaced on the pOH scale by $n = 0$ (no displacement for py; displacement by $n = 1$ for SCN^-, and by $n = 2$ for N_3^-). The solid lines are the theoretical curves.

TABLE 1

Temperature dependence of the rate constants for the reaction *trans*-$Co(CN)_4(SO_3)OH_2^{3-}$ + py $\rightleftharpoons$ *trans*-$Co(CN)_4(SO_3)py^{3-} + H_2O$ [a]

T (°C)	k_{obs} (s^{-1})
15.1	0.693
20.5	1.36
25.0	2.54
30.7	4.62
35.3	10.50

[a] $\mu = 1.0$ M; $[OH^-] = 1.12 \times 10^{-7}$ M, maintained by addition of 0.10 M pyH^+ buffer; [py] = 0.50 M.

activation parameters. In this series [py] = 0.50 M and $[OH^-] > 1.12 \times 10^{-7}$ M, and the temperature was varied from 15.1 to 35.3°C. The results are listed in Table 1. A plot of log k_{obs} vs. T^{-1}, which shows excellent linearity, was used to obtain the activation parameters, $\Delta H^\ddagger$ (22.0 kcal/mole) and $\Delta S^\ddagger$ (+17.4 eu).

(ii) *The thiocyanate and azide ion ligations*

The ligations by SCN^- and N_3^- were carried out in the same manner as the NH_3 and py experiments. In one series of experiments, the $[OH^-]$ was held constant at 1.30×10^{-5} M while the $[SCN^-]$ was varied from 5.00×10^{-3} to 0.50 M. The value for the reverse reaction rate constant, i.e., k_{obs} for hydrolysis of the complex $Co(CN)_4(SO_3)SCN^{4-}$, was obtained in 0.10 M OH^-. In another series the $[SCN^-]$ was held constant at 0.50 M and the $[OH^-]$ was varied. The results for the SCN^- experiments are depicted in Figs. 4 and 5. Again, the solid lines are theoretical.

The kinetic behavior for the ligation by azide ion was studied by varying the $[N_3^-]$ from 5.0×10^{-3} to 0.50 M at constant $[OH^-]$ (1.30×10^{-5} M; buffered with sodium borate), and by varying $[OH^-]$ at constant $[N_3^-]$ ($[OH^-] = 1.3 \times 10^{-5}$ to 0.20 M; $[N_3^-] = 0.50$ M). The results are plotted also in Figs. 4 and 5.

(iii) *The SO_3^{2-} ligation reaction*

The SO_3^{2-} ligation studies again consisted of two series of experiments which were analogous to those performed earlier. In addition, in a third series of experiments it was shown that k_{obs} was independent of the initial Co(III) concentration.

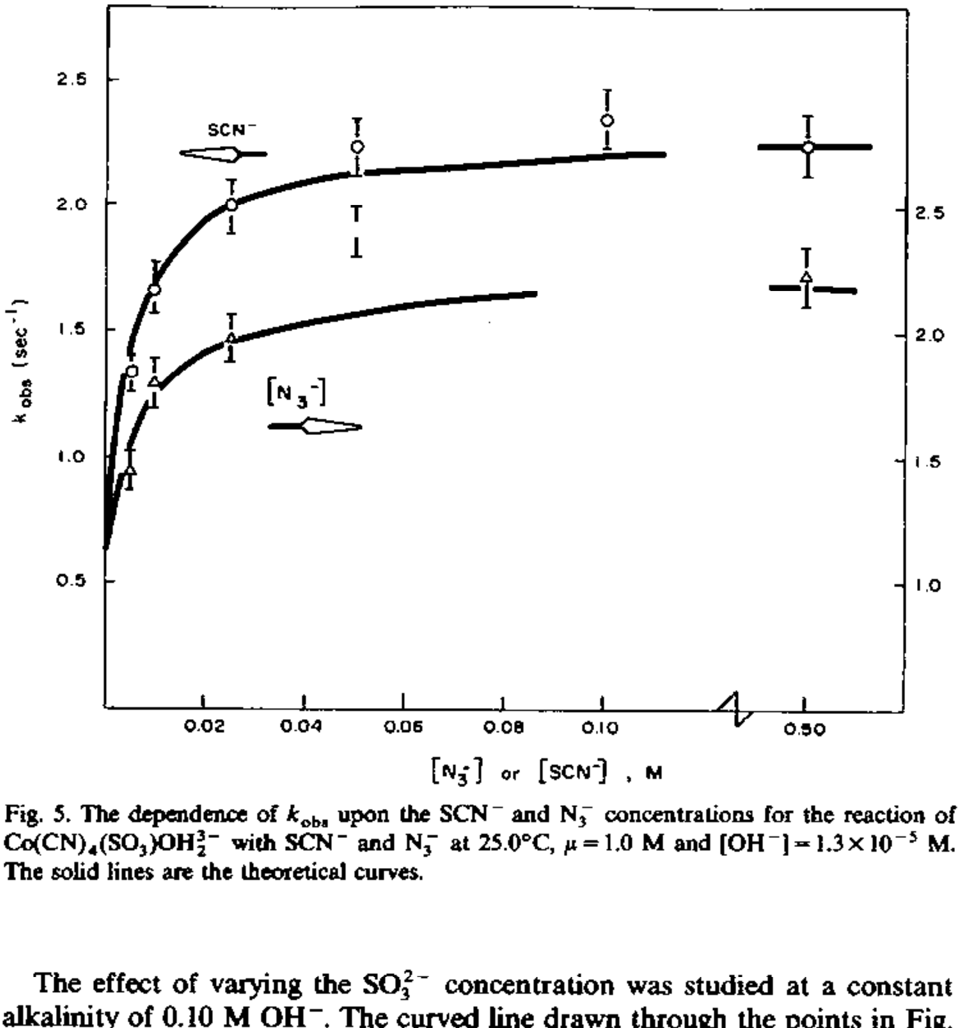


Fig. 5. The dependence of k_{obs} upon the SCN$^-$ and N$_3^-$ concentrations for the reaction of Co(CN)$_4$(SO$_3$)OH$_2^{3-}$ with SCN$^-$ and N$_3^-$ at 25.0°C, $\mu = 1.0$ M and [OH$^-$] = 1.3×10^{-5} M. The solid lines are the theoretical curves.

The effect of varying the SO$_3^{2-}$ concentration was studied at a constant alkalinity of 0.10 M OH$^-$. The curved line drawn through the points in Fig. 6, a plot of k_{obs} vs. [SO$_3^{2-}$], indicates that the rate is less than first order in [SO$_3^{2-}$]. However, the deviation from first order in much less than that observed for the NH$_3$ and pyridine ligation reactions. Even at 0.40 M, the maximum concentration which could be employed at unit Na$^+$ concentration, the slope of the line corresponds to an order with respect to [SO$_3^{2-}$] of ~ 0.7.

The open circle points in the lower curve in Fig. 2 represent data obtained at a fixed SO$_3^{2-}$ concentration of 0.10 M and variable alkalinity. It may be seen that the line drawn through the points is essentially parallel to the line drawn through the NH$_3$ data points. However, the k_{obs} values for the SO$_3^{2-}$ ligation at any OH$^-$ concentration are lower by a factor of ~ 0.2 than those for the NH$_3$ ligation. This difference in values of k_{obs} is not unexpected,

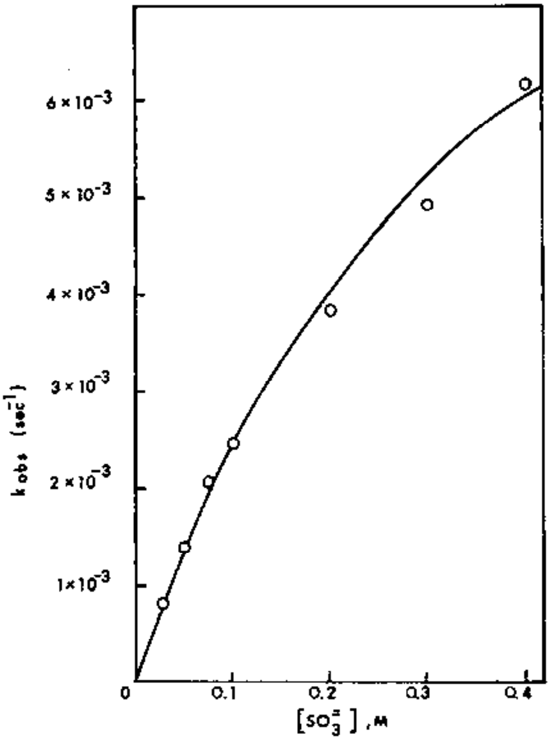


Fig. 6. The dependence of k_{obs} on $[SO_3^{2-}]$ for the reaction of $Co(CN)_4(SO_3)OH_2^{3-}$ with SO_3^{2-} at 25.0°C, $\mu = 1.0$ M and $[OH^-] = 0.10$ M.

since an examination of Fig. 5 indicates that at 0.10 M SO_3^{2-}, the rate is far from zero order in $[SO_3^{2-}]$, and larger values of k_{obs} would have been observed for each alkalinity if the SO_3^{2-} concentration could have been increased.

In the final series of experiments the $[OH^-]$ and $[SO_3^{2-}]$ were held constant at 0.400 and 0.100 M, respectively, and the pseudo-first-order rate constants were measured with the [Co(III)] fixed at 6.9×10^{-6}, 1.4×10^{-5}, and 1.4×10^{-3} M. The corresponding values of k_{obs} were 1.09×10^{-3}, 1.10×10^{-3}, and 1.14×10^{-3} s^{-1} showing independence of k_{obs} on [Co(III)].

(iv) Formation constants for ligation reactions

It is convenient to measure the formation quotients for the py, SCN^-, and N_3^- ligated complexes under limiting conditions at high or low alkalinity. Under these conditions, the predominant form of the complex is either $Co(CN)_4(SO_3)OH^{4-}$ or $Co(CN)_4(SO_3)OH_2^{3-}$. The formation constants for

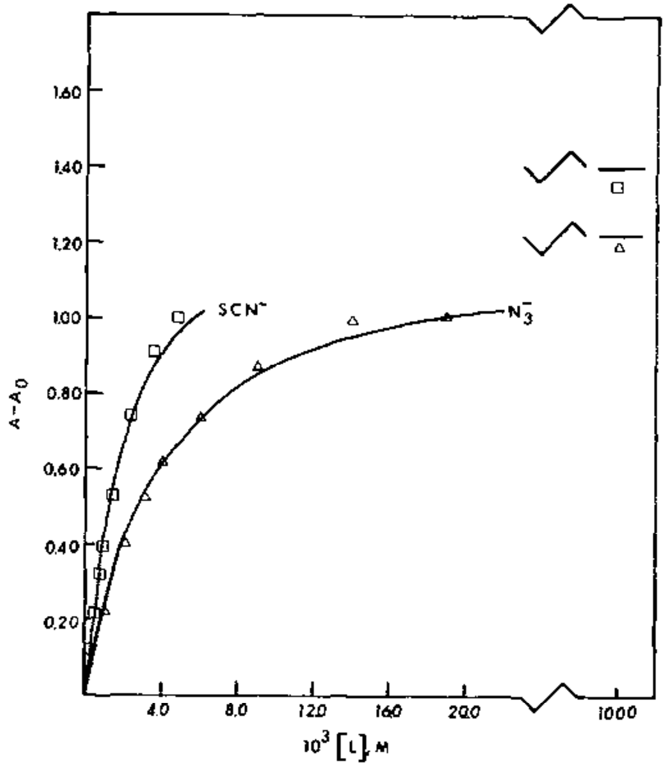


Fig. 7. The variation of absorbance with concentration of N_3^- and SCN^- for the complex $Co(CN)_4(SO_3)OH_2^{3-}$ at 25.0°C, $\mu = 1.0$ M and $\lambda = 315$ nm.

$Co(CN)_4(SO_3)SCN^{4-}$ and $Co(CN)_4(SO_3)N_3^{4-}$, as depicted in eqn. 4, were determined at $[OH^-] = 1.50 \times 10^{-5}$ M. The results of these experiments are illustrated in Fig. 7, a plot of $(A - A_0)$ vs. $[L^{n-}]$. The equilibrium constants can be evaluated using these data and eqn. 8:

$$\frac{A - A_0}{[Co(III)]l} = \frac{\Delta\xi K_f [L^{n-}]}{1 + K_f [L^{n-}]} \tag{8}$$

where l is the path length and $\Delta\xi$ represents the differences in extinction coefficients between $Co(CN)_4(SO_3)OH_2^{3-}$ and $Co(CN)_4(SO_3)L^{(3+n)-}$. Thus, plots of $l[Co^{III}](A - A_0)^{-1}$ vs. $[L^{n-}]^{-1}$ were linear with slopes of $(\Delta\xi K_f)^{-1}$ and intercepts of $\Delta\xi^{-1}$. The values of K_f, which are listed in Table 2, were then used together with eqn. 8 to generate the solid curve in Fig. 7. This illustrates the close fit between theory and experiment.

The equilibrium quotient for the formation of $Co(CN)_4(SO_3)py^{3-}$ was determined in 0.10 M NaOH solution with the ionic strength adjusted to

TABLE 2

Summary of the kinetic and thermodynamic parameters for the reaction *trans*-$Co(CN)_4(SO_3)OH_2^{3-} + L^{n-} \rightleftharpoons$ *trans*-$Co(CN)_4(SO_3)L^{(n+3)-} + H_2O$ at 25.0°C and unit ionic strength

L	k_1 (s^{-1})	$10^3\,k_2/k_3$ (M)	$10^2\,k_4$ (s^{-1})	K_n (M^{-1})	K_f (calc.)[a] (M^{-1})	K_f (measured)[d] (M^{-1})
SO_3^{2-}	2.5±0.3[b]	380±50	(7.2±0.4)×10^{-4}	1062±30	7×10^5	—
CN^-[c]	1.73±0.07	28.4	0	776±34	large	—
N_3^-	2.2±0.1	7.5±1.3	115±10	1000±95	(2.55±0.35)×10^2	(2.5±0.3)×10^2
NH_3	2.1±0.1	7.0±0.4	0.51±0.04	807±54	(5.9±0.5)×10^4	(7.9±0.5)×10^4
SCN^-	2.3±0.1	5.9±1.0	78±8	1093±85	(5.1±0.8)×10^2	(5.0±0.3)×10^2
py	2.5±0.1	2.9±0.4	1.25±0.10	1114±58	(6.9±0.6)×10^4	(4.5±0.5)×10^4

[a] $K_f = k_1k_3/k_2k_4$. [b] Indicated uncertainties are the standard deviations of the parameters. [c] Data from ref. 7. [d] Measured as K_1 and converted to K_f using the expression $K_f = K_1K_n$.

unity with $NaClO_4$. Under these conditions the equilibrium observed is

$$Co(CN)_4(SO_3)OH^{4-} + py \overset{K_1}{\rightleftarrows} Co(CN)_4(SO_3)py^{3-} + OH^- \qquad (9)$$

The value for K_1 was determined in the same manner as K_f for the SCN^- and N_3^- ligations. The measurements were made at 285 and 395 nm and the results are shown in Fig. 8. In this figure, the solid lines represent the theoretical curves and correspond to a quotient of 40 ± 2. The uncertainty

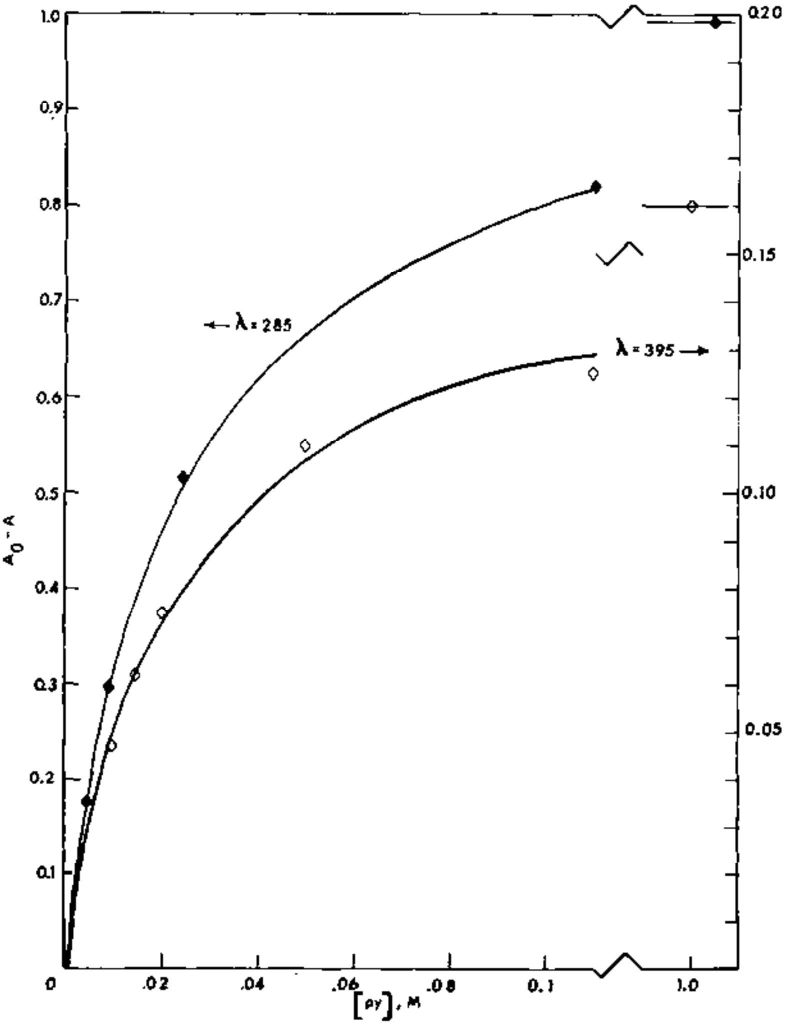


Fig. 8. The variation of absorbance with concentration of pyridine for the ligation of $Co(CN)_4(SO_3)OH_2^{3-}$ at 25.0°C, $\mu = 1.0$ M, and $\lambda = 285$ and 395 nm.

represents the standard deviation obtained from the least-squares computation.

The equilibrium quotient for the reaction

$$Co(CN)_4(SO_3)OH_2^{3-} + OH^- \overset{K_n}{\rightleftarrows} Co(CN)_4(SO_3)OH^{4-} + H_2O \qquad (10)$$

was determined from the kinetic experiments for the various ligations as described earlier. The value of K_n obtained for the py reaction was then used together with the expression $K_f = K_1 K_n$ to calculate the formation constant K_f.

(v) Acid-promoted aquation of $Co(CN)_4(SO_3)NH_3^{3-}$ *and* $Co(CN)_4(SO_3)py^{3-}$

Microscopic reversibility requires that the hydrolysis of $Co(CN)_4(SO_3)L^{(3+n)-}$ (eqn. 11), be by a dissociative mechanism:

$$Co(CN)_4(SO_3)L^{(3+n)-} + H_2O \rightleftharpoons Co(CN)_4(SO_3)OH_2^{3-} + L^{n-} \qquad (11)$$

In addition to the simple loss of L^{n-} from the complex, acid-promoted

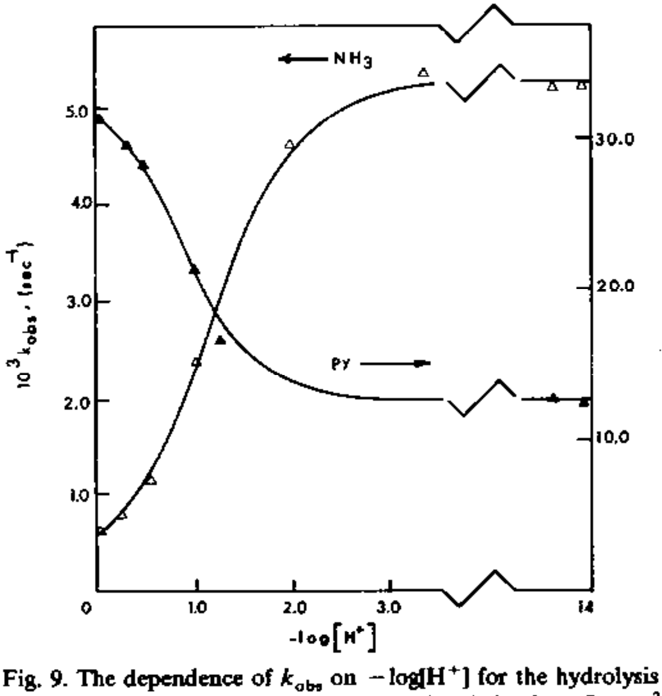


Fig. 9. The dependence of k_{obs} on $-\log[H^+]$ for the hydrolysis of $Co(CN)_4(SO_3)NH_3^{3-}$ (△) and left ordinate; and for the hydrolysis of $Co(CN)_4SO_3py^{3-}$ (▲) and right ordinate at 25.0°C and $\mu = 1.0$ M. The solid lines are theoretical curves.

dissociation also occurs. Consequently, we have studied the hydrogen ion dependence for the aquation reactions with $L^{n-} = NH_3$ and py.

The aquation of $Co(CN)_4(SO_3)py^{3-}$ was studied at two concentrations of complex (3.75×10^{-4} and 7.5×10^{-5} M), with the $[H^+]$ varied from 1.0×10^{-14} to 1.00 M. The aquation of $Co(CN)_4SO_3NH_3^{3-}$ was studied with the complex concentration at 7.0×10^{-5} and the $[H^+]$ was likewise varied from 1.0×10^{-14} to 1.00 M. The results of these experiments are depicted in Fig. 9.

D. DISCUSSION

(i) Rate laws and mechanism

The present results and those obtained in previous work on the CN^- ligation reaction exhibit kinetic behavior consistent with the limiting S_N1 mechanism [7]:

$$Co(CN)_4(SO_3)OH_2^{3-} + OH^- \overset{K_n}{\rightleftharpoons} Co(CN)_4(SO_3)OH^{4-} + H_2O \tag{12}$$

$$Co(CN)_4(SO_3)OH_2^{3-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Co(CN)_4(SO_3)^{3-} + H_2O \tag{13}$$

$$Co(CN)_4(SO_3)^{3-} + L^{n-} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Co(CN)_4(SO_3)L^{(3+n)-} \tag{14}$$

In this mechanism k_1 and k_4 are the rate constants for the loss of ligand water and the nucleophile L^{n-} from their respective complexes. The rate constant ratio of k_2/k_3 corresponds to the relative reactivity of the five-coordinated reactive intermediate, $Co(CN)_4SO_3^{3-}$, towards water and the nucleophile L^{n-}. Other reactions pertinent to the above substitution reaction are

$$Co(CN)_4(SO_3)OH^{4-} + L^{n-} \overset{K_1}{\rightleftharpoons} Co(CN)_4(SO_3)L^{(3+n)-} + OH^- \tag{15}$$

$$Co(CN)_4(SO_3)OH_2^{3-} + L^{n-} \overset{K_f}{\rightleftharpoons} Co(CN)_4(SO_3)L^{(3+n)-} + H_2O \tag{16}$$

$$Co(CN)_4(SO_3)OH_2^{3-} + H_2O \overset{K_a}{\rightleftharpoons} Co(CN)_4(SO_3)OH^{4-} + H_3O^+ \tag{17}$$

In order to explain the kinetic results, it is necessary to assume that the reactive intermediate, $Co(CN)_4SO_3^{3-}$, generated in reaction 12 has a lifetime long enough for it to exhibit a reactivity pattern towards the various nucleophiles in the system.

The reaction mechanism derived based on eqns. 12–14 with the usual steady-state approximation gives the following relationship between k_{obs} and the various kinetic parameters:

$$k_{obs} = \frac{\alpha k_1[L^{n-}]}{k_2/k_3 + [L^{n-}]} + \frac{k_4 k_2/k_3}{k_2/k_3 + [L^{n-}]} \tag{18}$$

where

$$\alpha = \frac{1}{1 + K_n[OH^-]}$$

The factor α is a measure of the position of the equilibrium in reaction 12 and is the only term in the rate expression which is dependent on hydroxide ion concentration.

Equation 18, the derived k_{obs} expression, is the most general form of the rate law and is analogous to that for a simple reversible reaction in that it consists of the sum of the forward and reverse rate constants. The overall equation is complex but under most experimental conditions it can be replaced by simpler approximations whose physical significance is more easily visualized. However, the numerical values of k_1, k_2/k_3, and k_4, that are listed in Table 2, were obtained using eqn. 18 in a computer-assisted non-linear least-squares analysis of all of the data.

Before considering the experimental data in detail, it should be noted that there are several equations which provide relationships between the kinetic parameters and the various equilibrium quotients defined by eqns. 15–17. Based on the restriction of microscopic reversibility, eqn. 19 is derived and will be used in this discussion.

$$K_f = \frac{k_1 k_3}{k_2 k_4} \tag{19}$$

(ii) Ligation reactions of the uncharged nucleophiles

The kinetic parameters for the NH_3 and pyridine ligation reactions are listed in Table 2. They were obtained in a computer-assisted non-linear least-squares fit of all experimental values of k_{obs} using eqn. 18. For the NH_3 experiment, 33 k_{obs} values were analyzed. Some of these values are not observable in Figs. 1 or 2 because they overlap and become indistinguishable from other points at the same alkalinity or NH_3 concentration. The average discrepancy between the experimental and calculated values of k_{obs} for the 33 experiments is 7.4%, a figure which is compatible with the errors inherent in the measurement. The deviations are random and show no particular trends which would suggest that some important feature has been omitted from the proposed mechanism. The agreement between eqn. 18 and the experiment is shown in Figs. 1 and 2. The solid lines in these figures are theoretical curves calculated using the least-squares parameters listed in Table 2.

In the analysis of the data of Fig. 1 it is necessary to use the exact form of the rate law, eqn. 18, since in these experiments the reaction did not proceed to completion and the NH_3 concentrations were of the same order of magnitude as k_2/k_3. By contrast, the data of Fig. 2 were carried out at a higher NH_3 concentration where the second term of eqn. 18 could be neglected because the reaction was essentially quantitative. When these conditions exist and when $[NH_3] \gg k_2/k_3$, eqn. 18 may be replaced by a much simplified approximate expression:

$$k_{obs} = \frac{k_1}{1 + K_n[OH^-]} \tag{20}$$

Under these circumstances reaction 13 is rate determining and the reverse of reaction 13 does not compete effectively with the forward reaction of reaction 14.

The upper curve of Fig. 2 shows that there are two limiting behaviors of NH_3 ligation reaction with $Co(CN)_4(SO_3)OH_2^{3-}$. The first limiting situation is observed at $[OH^-] \geqslant 10^{-2}$ M, where the slope of unity indicates that the rate is inversely dependent on $[OH^-]$. In this region of alkalinity, $K_n[OH^-] \gg 1.0$ and eqn. 20 may be replaced with an even simpler approximate expression:

$$k_{obs} = \frac{k_1}{K_n[OH^-]} \tag{21}$$

In the other limiting region, $[OH^-] \ll 10^{-3}$ M and $K_n[OH^-] \ll 1.0$, the rate approaches and becomes zero order in $[OH^-]$. Thus, eqn. 20 is replaced by $k_{obs} = k_1$. At extremely low hydroxide ion concentration, the curve approaches, but does not quite reach this latter limiting behavior.

The internal consistency of the kinetic and equilibrium parameters for the NH_3 ligation reaction may be determined using eqn. 20. From the values of k_1, k_2/k_3, and k_4 a value for K_f of 5.9×10^4 M^{-1} is calculated. This result is consistent and in satisfactory agreement with 7.9×10^4 M^{-1}, a value calculated using the measured value of K_1 and the least-squares value of K_n from the kinetic studies and the expression $K_f = K_1K_n$.

A very interesting aspect of the NH_3 ligation reaction is the observed remarkable efficiency with which NH_3 competes against ligand water in their competition for the reactive intermediate. In quantitative terms, NH_3 is more reactive than ligand water by a factor of 7900, a result which may be obtained by evaluating the quantity $(55)/(k_2/k_3)$, where 55 M is the assumed formal concentration of water in the solution. In terms of the experimental observation, this large difference in relative reactivity is responsible for the curvature of the curves in Fig. 1. This type of curvature is observable even in the millimolar concentration range.

For the pyridine ligation studies as a function of hydroxide ion dependence the concentration of the added pyridine is kept at 0.5 M which is sufficiently high that the reaction goes to completion. Non-linear least-squares computer-assisted analysis was carried out using eqn. 18 on the experimental results and the values of the kinetic and thermodynamic parameters are listed in Table 2 with the other ligands. The average relative deviation of the values of k_{obs} from the theoretical values for 20 experiments is 5.1%. Similar to the case in the ammonia experiment where $[L^{n-}] \gg k_2/k_3$, the observed first-order rate constant becomes independent of the concentration of the nucleophiles and thus obeys the simplified expression, eqn. 20. This plot is depicted in Fig. 4 with the SCN^- and N_3^- data. As demonstrated earlier [9], the ammonia and pyridine data when plotted together give identical results. This is to be expected since in the absence of medium effects, k_1 and K_n, the parameters defining the $[OH^-]$ dependence curves are independent of the nature of L^{n-}.

The dependence of k_{obs} vs. [py] at $[OH^-] = 0.010$ M, 25.0°, and unit ionic strength is shown in Fig. 3. In this plot it is clear that k_{obs} increases in a less than first-order manner, curving towards a limiting value at high pyridine concentration ($\gg 0.1$ M). The intercept k_4 is the hydrolysis rate constant of $Co(CN)_4(SO_3)L^{(3+n)-}$. This relationship is evident from consideration of the full rate expression since at the intercept [L or py] = 0 and $k_{obs} = k_4$.

The discriminating reactivity pattern of the five-coordinated intermediate is again towards the uncharged nucleophile, in this case the pyridine over the ligand water, by a factor of 1.9×10^4. The calculated value of K_f (6.9×10^4 M^{-1}) agrees, within the experimental errors, with the measured K_f listed in Table 2.

(iii) Ligation reaction of the uninegative nucleophiles, SCN^- and N_3^-

For the SCN^- and N_3^- experiments, average relative deviation between experimental data and the theoretical solid lines obtained with non-linear least-squares fit using eqn. 18 is 5.5% for 17 experiments. The theoretical curves are the solid lines in Figs. 4 and 5. The appearance of the plots in Fig. 4 for the ligation reaction of SCN^- and N_3^- deserves some comments. The slope of the curve is essentially unity at intermediate hydroxide ion concentration. However, they differ from the ammonia and pyridine plots at high hydroxide ion concentration. The cause or origin of this type of behavior comes, not in the introduction of more complex $[OH^-]$ dependency, but, rather, from the reverse reaction of reaction 14. When the reaction does not go to completion, i.e., when K_f is relatively small as in the cases of SCN^- and N_3^-, the data do not obey the simple inverse first-order dependence on hydroxide ion concentration as occurs when it is very high. The rate expression at high $[L^-]$ then corresponds to replacing eqn. 18 by eqn. 22:

$$k_{obs} = \frac{k_1}{1 + K_n[OH^-]} + \frac{k_4 k_2/k_3}{[L^{n-}]} \tag{22}$$

Thus, there will always be a constant contribution to the rate constant from the second term which becomes relatively more significant as $[OH^-]$ is increased. This results in the curvature or deviation from the unit slope when log k_{obs} vs. pOH is plotted.

Consideration of the full rate law will also help in understanding these observations. The observed first-order rate constant is composed of the sum of the contributions from the forward and reverse reactions, k_f and k_r, respectively, where

$$k_f = \frac{k_1[L^{n-}]}{k_2/k_3 + [L^{n-}]} \cdot \frac{1}{1 + K_n[OH^-]} \tag{23}$$

and

$$k_r = \frac{k_4(k_2/k_3)}{k_2/k_3 + [L^{n-}]} = \frac{k_1/K_f}{k_2/k_3 + [L^{n-}]} \tag{24}$$

When K_f becomes small, k_r can become large relative to k_f. This is especially true at large $[OH^-]$ ($\geqslant 10^{-2}$ M) since in this region k_f is inversely proportional to $[OH^-]$, whereas k_r is independent of $[OH^-]$. It then follows that when $K_n[OH^-] \gg 1$, the expression from k_{obs} will consist of a sum of a term which is inverse first order in $[OH^-]$ and a term which is constant. Therefore, it is expected from a log k_{obs} vs. pOH plot that at high $[OH^-]$ the plot will curve in the positive direction from the unit slope which would be observed when $k_f \ll k_r$.

The dependence of k_{obs} as a function of the anion concentration was studied at $[OH^-] = 1.3 \times 10^{-5}$ M, 25.0° and $\mu = 1.0$ M. The data are plotted in Fig. 5. The rate of reaction increases again in a less than first-order manner, curving towards a limiting value ($\gg 0.04$ M) which is similar to the situation observed for the pyridine reaction. The intercepts at $[L^{n-}] = 0$ M give the hydrolysis rate constant for the complexes or $k_{obs} = k_4$.

As a check on the kinetic parameters the formation constant K_f is calculated from eqn. 19 and compared with the measured K_f. In this series the K_f agrees extremely well as shown in Table 2. A further illustration of the discriminating ability of the reactive intermediate shows that ligation with SCN^- and N_3^- is 9.3×10^3 and 7.3×10^3, respectively, greater than water.

(iv) Ligation reaction of dinegative nucleophile, sulfite ion

Computer-assisted non-linear least-squares analysis of 40 observed first-order rate constants gives the resulting kinetic parameters listed in Table 1. In these studies the average deviation between calculated and experimental values of k_{obs} is $\pm 12\%$, a value somewhat larger than that observed in most of our ligation studies. However, the discrepancies again appear to be random and do not seem to be of mechanistic significance. It is possible that the discrepancies were introduced, at least in part, in the interconversion of pH measurement and OH^- concentrations in the procedure which involved calibration of the pH meter. The sulfito ligation study was one of the first systems which was investigated and was carried out at a time when the importance of the errors in the calibration of the pH meter may not have been fully appreciated.

A comparison of the plots in Figs. 1 and 6 indicates that in the ammonia and sulfito systems the order of the reaction with respect to $[L^{n-}]$ decreases with increasing L^{n-} concentration. However, the sulfite ion is much less efficient than ammonia as a nucleophile in competing with ligand water for the reactive intermediate. The relative reactivity of sulfite ion to water is 145. Figure 6 is a consequence of the inability to make $[L^{n-}$ or $SO_3^{2-}] \gg k_2/k_3$, although under conditions such that the reaction goes to completion. The result is a plot of the sulfite dependence of k_{obs} showing little curvature when compared to the other systems investigated. Another consequence is that k_{obs} cannot approximate to k_1, but is simply reduced by the factor $[L^{n-}]/(k_2/k_3 + [L^{n-}])$. Therefore, the numerical values of k_{obs} for the sulfito reaction at any pH are all less than the ammonia system by a factor of 0.2. At a sulfite ion concentration of 0.10 M and $k_2/k_3 = 0.38$ the factor has a numerical value evaluated to be 0.21 which agrees with the difference in k_{obs} determined between ammonia and sulfite ion ligation reactions.

(v) Reactivity pattern of the nucleophiles

Since the rate constant for attack on the reactive intermediate by water must be independent of the added nucleophile, L^{n-}, and assuming medium effects are negligible, the values of k_2/k_3 are a measure of the relative reactivity of the various nucleophiles towards $Co(CN)_4(SO_3)^{3-}$. The resulting order is $py > SCN^- \sim NH_3 \sim N_3^- > CN^- > SO_3^{2-} > H_2O$. It has usually been assumed that differences in nucleophilicity of various ligands arise from differences in charge, basicity, and polarizability. The above observed reactivity pattern, however, indicates that such a simple correlation with either basicity or polarizability is not correct. For example, the order of the pK_a values for the conjugate acid of the following nucleophiles is $NH_3 > CN^- > SO_3^{2-} > py > N_3^- > SCN^-$, and the order of stability constants for the complex formation with the soft acid CH_3Hg^+ is $CN^- > SO_3^{2-} > NH_3 > SCN^- > N_3^- > py$ [1]. These orders certainly do not match the observed relative reactivities towards $Co(CN)_4SO_3^{3-}$ by the same nucleophiles. However, the reactivity pattern does show a rough correlation with charge on the nucleophile. Although SCN^- is slightly more reactive than ammonia, the difference is very small when the error limits of the experiments are taken into account: k_2/k_3 for SCN^- is $(5.9 \pm 1.0) \times 10^{-3}$ M while for NH_3 it is $(7.0 \pm 0.4) \times 10^{-3}$ M. Therefore, thiocyanate ion, ammonia, and azide ion can probably be considered as having nearly the same reactivity under these experimental conditions.

The very low reactivity of water towards the intermediate, $Co(CN)_4SO_3^{3-}$, is of some interest when attempting to understand the factors affecting the reactivity pattern of the various nucleophiles. The values of k_2/k_3 obtained from the kinetic studies should include the concentration of the solvent water. A correction factor of 55 M can be used to obtain the relative reactivity of the nucleophile to water. The results of this calculation for the reactions reported here indicate low reactivity of water. For example, water is approximately 10^4 less reactive than thiocyanate ion towards $Co(CN)_4SO_3^{3-}$. This result is clearly not consistent with the above interpretation of the reactivity pattern, but may instead reflect a special role of water as solvent.

The orders of reactivity of several nucleophiles towards the intermediates $Co(NH_3)_4(SO_3)^+$ and $Co(CN)_5^{2-}$ have been reported [1 – 5,20]. With respect to the intermediate $Co(CN)_5^{2-}$, no simple pattern is apparent; however, CN^- and SO_3^{2-}, the two poorest nucleophiles towards $Co(CN)_4(SO_3)^{3-}$, were not studied. The reactivities relative to NH_3 are: N_3^-, 3.5; py, 2.9; SCN^-, 2.3; I^-, 1.3; NH_3, 1.0; and Br^-, 0.68. The pattern of reactivity of several nucleophiles towards the positively charged intermediate $Co(NH_3)_4(SO_3)^+$ is approximately the reverse of that for $Co(CN)_4(SO_3)^{3-}$; $SO_3^{2-} > CN^- \sim SCN^- > NH_3$. Such a reversal in the order is consistent with the charge of the nucleophile playing a significant role in the reactivity pattern.

(vi) Aquation reactions of $Co(CN)_4(SO_3)py^{3-}$ and $Co(CN)_4(SO_3)NH_3^{3-}$

Microscopic reversibility requires that the hydrolysis or aquation (i.e., reverse) reactions of these complexes occur by a dissociative mechanism. Kinetic studies of the base hydrolysis of $Co(CN)_4(SO_3)py^{3-}$ and

$Co(CN)_4(SO_3)NH_3^{3-}$ are in accord with this requirement. Experimentally, one observes acid-catalyzed paths as well, so the aquation studies were carried out with the $[H^+]$ varied from 1.0×10^{-14} to 1.00 M. The results of these studies are consistent with the mechanism given below in eqns. 25–28 [7,9]. Therefore, for the hydrolysis of $Co(CN)_4SO_3py^{3-}$ and $Co(CN)_4(SO_3)NH_3^{3-}$:

$$Co(CN)_4SO_3L^{(3+n)-} + H_3O^+ \overset{K_p}{\rightleftharpoons} HCo(CN)_4SO_3L^{(2+n)-} + H_2O \tag{25}$$

$$Co(CN)_4SO_3L^{(3+n)-} \xrightarrow{k_4} Co(CN)_4SO_3^{3-} + L^{n-} \tag{26}$$

$$HCo(CN)_4SO_3L^{(2+n)-} \xrightarrow{k_7} Co(CN)_4SO_3^{3-} + HL^{(1-n)} \tag{27}$$

$$Co(CN)_4SO_3^{3-} + H_2O \xrightarrow{\text{fast}} Co(CN)_4SO_3OH_2^{3-} \tag{28}$$

These kinetic studies yield the rate expression

$$\frac{-\mathrm{d}\ln\left(\left[Co(CN)_4SO_3L^{(3+n)-}\right] + \left[HCo(CN)_4SO_3L^{(2+n)-}\right]\right)}{\mathrm{d}t} = k_{obs} \tag{29}$$

where

$$k_{obs} = \frac{k_4 K_p^{-1} + k_7[H^+]}{K_p^{-1} + [H^+]} \tag{30}$$

The observed pH dependence of k_{obs} for these reactions is shown in Fig. 9. A non-linear least-squares analysis of the data of these experiments yields the parameters listed in Table 3. There were then used in eqn. 30 to obtain the solid lines in the figure. The excellent correspondence between theory and experiment is evident.

The hydrolysis of $Co(CN)_4(SO_3)_2^{5-}$ exhibits the same kinetic behavior as that described above with an added equilibrium involving a diprotonated species in solution of high $[H^+]$ (10^{-2} M) [16]. The values of K_p for these

TABLE 3

Summary of rate and equilibrium constants obtained for the hydrolysis reactions [a]

L	k_4 (s^{-1})	k_7 (s^{-1})	K_p^{-1} (M)
NH_3	$(5.3 \pm 0.1) \times 10^{-3}$	$(3.4 \pm 0.5) \times 10^{-4}$	$(6.2 \pm 0.6) \times 10^{-2}$
py	$(1.25 \pm 0.03) \times 10^{-2}$	$(3.6 \pm 0.1) \times 10^{-2}$	$(1.8 \pm 0.3) \times 10^{-1}$

[a] Indicated uncertainties are standard deviations. T = 25.0°C; $\mu = 1.0$ M.

three systems are 5.55, 16.1, and 550 M^{-1}, respectively, for L^{n-} = py, NH_3 and SO_3^{2-}. The kinetic data for the disulfite complex yield a relatively small value for k_4 (7.2×10^{-6} s^{-1}) when compared to the ammonia and pyridine complexes (Table 3).

A major point of interest in these results is that protonation of the NH_3 complex decreases the aquation rate while protonation of the pyridine complex increases the rate of aquation. The implication in these results is that protonation must be occurring at different sites on the complexes. In the protonated complexes, $HCo(CN)_4(SO_3)L^{2-}$, the proton may, in principle, be bonded to the *trans* SO_3^{2-} ligand, to a *cis* CN^- ligand, to a pair of t_{2g} electrons, or in the case of the pyridine complex, to the π-electrons of the pyridine ring. In fact, all of these protonated species must exist in a series of tautomeric equilibria, but in terms of concentration, the predominant species is almost certainly the one in which the proton is bonded to the SO_3^{2-} ligands. Evidence in support of this latter postulation is based on the observed protonation of the SO_3^{2-} complexes cited above, and the failure to observe protonation of CN^- ligands in $Co(CN)_6^{3-}$ or $Fe(CN)_6^{3-}$ in the range of acidity under consideration. Protonation of a CN^- ligand could thus seem to be energetically less favorable than protonation of SO_3^{2-}. However, in view of the fact that anhydrous $H_3Co(CN)_6$ is a known compound, there is a distinct possibility that the cyano-protonated complexes are present at low concentration in 1.0 M H^+ solution.

In unpublished experiments performed in this laboratory we have found that the rate of formation of $Co(CN)_4(SO_3)SCN^{4-}$, by reaction of SCN^- with $Co(CN)_4(SO_3H)OH_2^{2-}$, is slower than the corresponding reaction with $Co(CN)_4(SO_3)OH_2^{3-}$ by a factor of 0.20. The mechanism of the reaction has not been studied in great detail, but it seems likely that the rate-determining step involves a limiting S_N1 mechanism which is initiated by loss of H_2O ligand from the protonated complex. The decrease in rate upon protonation of the complex is probably a result of the inductive withdrawal of electrons from the Co(III) ion and strengthening of the $Co-OH_2$ bond. By analogy it would appear that the decrease in rate of aquation of the NH_3 ligand in $Co(CN)_4(SO_3)NH_3^{3-}$ upon protonation of the complex is a direct result of protonation of the SO_3^{2-} ligand.

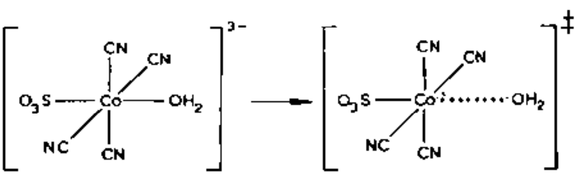
A reasonable explanation for the contrasting increase in aquation rate observed on increasing the $[H^+]$ for the complex $Co(CN)_4(SO_3)py^{3-}$ is that a site different from that in $Co(CN)_4(SO_3)NH_3^{3-}$ is protonated. However, there are several arguments against this explanation. The leveling of the reaction rate at high $[H^+]$ suggests that the reactive protonated species is present in an equilibrium which is being saturated. The protonated sulfito ligand would be the likely major contributor to this equilibrium as in the ammine complex. The similarity between the values of K_f for the two complexes would imply that the protonation site is the same.

Isied and Taube [21] have recently shown that the protonation of the sulfito ligand in $[Ru(NH_3)_4(SO_3)OH_2]^{2+}$ reduces the rate of loss of water ligand in ligation by pyrazine. The protonation of the complexes $[Ru(NH_3)_4(SO_3)(OH_2)]^{2+}$ and $[Ru(NH_3)_4(SO_3)(pyrazine)]$ has been reported to involve protonation at the sulfito ligand in both cases. From the equilibrium constants reported, Isied and Taube [21] conclude that addition of a π acid ligand increases the acidity of the coordinated S(IV) by a factor of ~ 2.5. Identical behavior is observed for the cobalt(III) complexes studied here. Replacement of the ammonia ligand by the π acid pyridine in the complex $Co(CN)_4(SO_3)NH_3^{3-}$ increases the acidity of the complex by a factor of ~ 2.9. It is interesting to note, however, that the rate of aquation of $[Ru(NH_3)_4(SO_3)(pyrazine)]$ decreases by a factor of ~ 6 as the concentration of hydrogen ion is increased from 10^{-5} to 1.0 M.

The results reported here do not rule out a contribution to the equilibrium mixture from a labile tautomer of $Co(CN)_4(SO_3H)py^{2-}$ in which, for example, the π cloud of the pyridine ring or a pair of t_{2g} electrons on one face of the complex was protonated. Such a species would presumably not be the major contributor to the equilibrium. If such a reactive complex was the only species, then the rate would not level off, but would continue to increase as the $[H^+]$ was increased as observed for the acid-catalyzed aquation of $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_5py^{2+}$ in acidic aqueous solutions [22].

(vii) Activation parameters

The temperature dependence of the ligation by pyridine was measured at $[py] \gg k_2/k_3$ and $K_n[OH^-] \ll 1$. Thus, the activation parameters obtained are for the forward reaction of reaction 13 with the rate constant k_1, the loss of ligand water from the complex. The values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ calculated from the temperature-dependence studies are +22.0 kcal/mole and +17.4 e.u., respectively. The observed positive $\Delta S^\ddagger$ value is consistent with the dissociative mechanism and implies that bond breaking is more important than bond making in the transition state. This large kinetic *trans*-labilizing effect of sulfite is rather remarkable and a process corresponding to



is suggested.

Perhaps additional evidence can be provided from the crystal structure studies of several Co(III) ammine complexes of *cis* and *trans* geometries and containing sulfito ligand. For example, in $[Co(NH_3)_5SO_3]Cl \cdot H_2O$, the difference between the *cis* and *trans* Co–N distance is a significant 0.089 Å, showing large structural sulfur *trans* effect [23].

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