neighbor K^+ ions to Cu^I the contribution to q_{ZZ} is calculated to be 0.05×10^{14} esu cm^{-3}. This is less than 1% of $(q_{ZZ})_{calcd}$. (2) While π bonding between the Cu^I atom and the N_2^{III} atom is unfavorable from the standpoint of the bond angle the effect of its presence was examined. The addition of π bonding to the Cu^I–N_2^{III} bond will sharply lower the asymmetry parameter and hence is considered to be absent. (3) There is the possibility that the amount of π bonding between the Cu^I atom and the carbon atoms is less than that due to the contribution of one electron to each ligand bond. A reduction of the π bonding not only decreases the asymmetry parameter as was indicated earlier but also increases $(q_{ZZ})_{calcd}$. Both of these changes are in opposition to experimental findings and lead to decreased agreement with known Sternheimer factors. (4) If one considers the absence of any π bonding, then it is necessary to decrease the contribution, α, of the ψ_1 orbital to the EFG tensor to 0.38 to have agreement between the experimental and calculated asymmetry parameters. This would also require a value of the Sternheimer factor of -16.1, which is close to that observed for a completely ionic Cu^+ species. In view of the observed Cu^I–N_2^{III} bond distance it is very unlikely that both incomplete overlap and ionic character together could cause that much electron depletion from the ψ_1 orbital.

Summary

The EFG tensor components and asymmetry parameter as calculated on the basis of three sp^2-hybrid σ bonds and two d–π^* bonds from the Cu atom to the three nearest CN groups are in good agreement with experimental values. Consideration of all factors indicates that there must be a large amount of π bonding to lead to this agreement. While the total contribution of the Cu^I–N_2^{III} bonding orbital to the EFG tensor can be determined, it is not possible to say how much is due either to ionic character or to incomplete overlap alone.

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The Rate of Aquation of the Sulfito Ligands in $Co(CN)_4(SO_3)_2^{5-}$ and $Co(CN)_5(SO_3)^{4-}$

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The rates of water displacement of a single SO_3^{2-} ligand in $Co(CN)_5(SO_3)^{4-}$ and in $Co(CN)_4(SO_3)_2^{5-}$ were measured at 25°. Values of the acidity constants of $HCo(CN)_5(SO_3)^{3-}$ and $HCo(CN)_4(SO_3)OH_2^{2-}$ were obtained using conventional acid–base titration and spectrophotometric techniques. The kinetic studies yield values of the acidity quotients of $HCo(CN)_4(SO_3)_2^{4-}$ and $H_2Co(CN)_4(SO_3)_2^{3-}$. Infrared and Raman studies provide evidence that $Co(CN)_4(SO_3)_2^{5-}$ has a *trans* configuration.

Introduction

In the present work we are mainly concerned with the rate of water displacement of the SO_3^{2-} ligands in $Co(CN)_4(SO_3)_2^{5-}$ and $Co(CN)_5(SO_3)^{4-}$. However, acidity quotients are also reported for $HCo(CN)_4(SO_3)OH_2^{2-}$ and $HCo(CN)_5(SO_3)^{3-}$. In addition, infrared and Raman measurements were made to determine the configuration and nature of the bonding of the SO_3^{2-} ligands.

It has been found that the rate of aquation of the first SO_3^{2-} ligand in $Co(CN)_4(SO_3)_2^{5-}$ is very much greater than that of the SO_3^{2-} ligand present in either $Co(CN)_4(SO_3)OH_2^{3-}$ or $Co(CN)_5(SO_3)^{4-}$. This observation combined with our unpublished studies of the rate of ligation of $Co(CN)_4(SO_3)OH_2^{3-}$ strongly suggests that the rapid aquation of $Co(CN)_5(SO_3)_2^{5-}$ represents an unusually large *trans* activation by SO_3^{2-}, a suggestion which has been made by others to explain the steric course of certain preparative reactions.[3,4] The infrared and Raman measurements support the assumption that $Co(CN)_4(SO_3)_2^{5-}$ has a *trans* configuration.

Experimental Section

Reagents.—All inorganic chemicals were of reagent grade. Buffer solutions were prepared using Baker and Adamson reagent grade potassium acid phthalate or acetic acid, or Eastman Kodak phenylacetic acid. Stock solutions of $NaClO_4$ and $LiClO_4$, prepared by dissolving Na_2CO_3 or Li_2CO_3 in $HClO_4$ solutions, were used to adjust the ionic strength.

Preparation of $Na_5[Co(CN)_4(SO_3)_2]\cdot 3H_2O$.—The complex was prepared by the method of Rây and Chackrabarty[5] in which an SO_2-saturated cobalt(II) acetate solution is added slowly to a well-stirred solution of concentrated NaCN at 0°. The solid must be recrystallized to remove at least two known impurities,

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[1] This work was supported by the Atomic Energy Commission.

[2] Taken in part from the M.S. thesis of H. H. Chen submitted in Dec. 1965.

[3] J. C. Bailar and D. F. Peppard, *J. Am. Chem. Soc.*, **62**, 105 (1940).

[4] A. V. Babaeva and I. B. Boranovskii, *Russ. J. Inorg. Chem.*, **7**, 404 (1962).

[5] P. R. Rây and S. Ch. Chackrabarty, *Z. Anorg. Allgem. Chem.*, **211**, 173 (1933).

one an ion of unknown composition which is green in solution but does not seem to discolor the yellow solid phase and a second which is orange and is probably the complex to which Rây[6] assigned the formula $K_6[(NC)_5Co \cdot SO_3 \cdot Co(CN)_5]$. In our experience, the best purification procedure involved dissolving the solid in a solution which is 1.5 *M* in Na_2SO_3 and 1.0 *M* in NaOH at 50–60° and filtering, followed by reprecipitation of the solid by cooling the solution to 0°. The NaOH appears to destroy the green impurity, converting it to an insoluble solid. The Na_2SO_3 converts the orange impurity to the desired product. After the fourth recrystallization, the solid is freed from the last traces of mother liquid by washing twice with 25% ethanol, followed by extensive washing with 40% ethanol until test paper indicates that no more alkali is being removed from the solid. Before vacuum drying the solid is finally washed with 95% ethanol and anhydrous ether.

The air-dried complex was partially dehydrated by vacuum heating at 78° overnight, the weight loss corresponding to the formation of $Na_5Co(CN)_4(SO_3)_2 \cdot 3H_2O$. The latter complex was characterized by elemental analysis. *Anal.* Calcd for $Na_5Co(CN)_4(SO_3)_2 \cdot 3H_2O$: C, 9.76; H, 1.23; N, 11.39; S, 13.03. Found: C, 10.10; H, 1.45; N, 11.26; S, 13.34.

Preparation of $Na_4Co(CN)_5SO_3 \cdot 2H_2O$.—This complex was obtained as a by-product in the preparation of $Na_5Co(CN)_4(SO_3)_2 \cdot 12H_2O$ described above. After separation of the $Na_5Co(CN)_4(SO_3)_2 \cdot 12H_2O$, the mother liquid was allowed to stand at room temperature for 3 days, a period in which the color of the solution changed from reddish orange to light yellow. Addition of ethanol produced an oil which solidified in contact with absolute ethanol. Two recrystallizations were carried out in a procedure which involved dissolving the solid in water, recovery of the oil by addition of ethanol, and solidification of the oil with absolute ethanol. *Anal.* Calcd for $Na_4Co(CN)_5SO_3 \cdot 2H_2O$: C, 15.12; N, 17.62; S, 8.06; H, 1.02. Found: C, 15.22; N, 17.59; S, 8.07; H, 1.13.

Apparatus.—Absorbancy measurements were made using a Cary Model 14 PM recording spectrophotometer and a Beckman Model DU quartz spectrophotometer. A Beckman Model G pH meter equipped with a Beckman Type E (blue) glass electrode was used for pH measurements in the earlier stages of the work. Later pH measurements were made with the more accurate Cambridge Research Model pH meter and electrode. The KCl solution in the reference electrode was replaced by saturated NaCl solution to avoid precipitation of $KClO_4$ when the electrode was immersed in solutions containing ClO_4^-. Infrared measurements were carried out using either a Beckman IR-7 or a Perkin-Elmer Model 137 instrument. The samples were prepared as Nujol mulls. Raman spectra were obtained from concentrated aqueous solutions using a Cary Model 81 spectrometer equipped with a ruby laser source (excitation line 6328 A).[7]

Kinetic Procedures.—In all experiments care was taken to avoid undue exposure to light, since it was found that exposure of the solutions to the full fluorescent lighting of the laboratory produced an appreciable rate of photolytic aquation. Solutions were prepared in a nearly dark room and handled in volumetric flasks wrapped with aluminum foil. It was established that the photolytic aquation produced by the light source of the Beckman DU spectrophotometer during spectrophotometric analysis was inappreciable.

In the study of the aquation of $Co(CN)_4(SO_3)_2^{5-}$, three kinetic procedures were used. In solutions more basic than pH 9, half-life for aquation was approximately 1 day and conventional mixing procedures were used. Under these conditions approximately 30 mg of $Na_5Co(CN)_4(SO_3)_2 \cdot 3H_2O$ was dissolved in 250 ml of a thermostated solution containing the desired amount of $NaClO_4$ and buffer or NaOH. At appropriate time intervals 2.0-ml aliquots of the solution were removed, diluted to 25 ml in a volumetric flask to give the desired order of magnitude of absorbancy, and subjected to spectrophotometric analysis. The absorbancy was measured at 313 mμ, where the molar absorbancy indices of $Co(CN)_4(SO_3)_2^{5-}$, $Co(CN)_4(SO_3)OH_2^{3-}$, and $Co(CN)_4(SO_3)OH^{4-}$ are 3.24×10^4, 2.9×10^3, and 1.6×10^3, respectively.

In the pH range from 9.0 to 4.0, a stock solution containing approximately 5×10^{-3} *M* $Co(CN)_4(SO_3)_2^{5-}$ dissolved in 0.1 *M* NaOH was prepared and used in two or three experiments which were completed within 40 min, a period short compared to the half-life for aquation of the $Co(CN)_4(SO_3)_2^{5-}$ in the stock solution. In a given kinetic experiment, 100 μl of the stock solution was transferred to a 25–100-ml volumetric flask containing the thermostated solution of the buffer and $NaClO_4$. After shaking the solution, an aliquot was transferred to a quartz absorption cell in the cell compartment of a Beckman DU spectrophotometer equipped with thermal spacers. Absorbancy measurements were carried out at appropriate times without removal of the absorption cell from the cell compartment of the spectrophotometer.

In solutions more acidic than pH 3, the freshly prepared alkaline stock solution of $Co(CN)_4(SO_3)_2^{5-}$ was mixed with an acidic solution of the desired composition and the spectrophotometric data were obtained using the stopped-flow technique.[8]

The rate of aquation of $Co(CN)_5SO_3^{4-}$ was slow enough so that the procedure described above for solutions more alkaline than pH 9 could be used.

In the presentation of the rate data in Figure 3, the logarithm of the pseudo-first-order rate constant is plotted *vs.* the logarithm of the hydrogen ion concentration. In solutions more acidic than pH 1.47, the hydrogen ion concentration was calculated from the known amount of $HClO_4$ in the solution. To obtain hydrogen ion concentrations at lower acidities where the $HClO_4$ concentration was not accurately known, hydrogen ion concentrations were obtained from measured pH values by a procedure which involved "calibrating" the pH meter with solutions of known concentrations of $HClO_4$ or NaOH in the range 1.0 to 1.0×10^{-4} *M* in which unit ionic strength was maintained with either $LiClO_4$ or $NaClO_4$.

Measurement of Acidity Quotients.—Acidity quotients were determined spectrophotometrically and by acid–base titration using a pH meter. In both measurements the basic equation relating concentrations of the conjugate acid and its base, HA and A^-, was

$$\log \frac{(A^-)}{(HA)} = \log K_{\text{acid}} - \log (H^+) \qquad (1)$$

Values of H^+ were obtained from pH readings in the manner indicated above. In the spectrophotometric measurements it can be shown that

$$\log \frac{(A^-)}{(HA)} = \log \left[\frac{A - (\text{Co(III)})\epsilon_{\text{HA}}}{(\text{Co(III)})\epsilon_{\text{A}} - A}\right] \qquad (2)$$

In this equation (Co(III)) represents the total concentration of the Co(III) complex, *A* is the measured absorbancy, and ϵ_{HA} and ϵ_A are the molar absorbancy indices of the acid and its conjugate base, respectively. The log *K* values were obtained from the linear plot of the right-hand side of the equation *vs.* $-\log (H^+)$. In the acid–base titrations, the p*K* values were again obtained graphically from the linear plot of $\log [(A^-)/(HA)]$ *vs.* $-\log (H^+)$. The concentrations of HA and A^- were calculated at each point of the titration from the measured pH, the known total Co(III) concentration, and the amount of added $HClO_4$ or NaOH solution.

Both of the above techniques were used in determining the acidity constant of $HCo(CN)_5SO_3^{3-}$. In the spectrophotometric studies identical results were obtained using absorbancy measure-

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(6) P. R. Rây, *Z. Anorg. Allgem. Chem.*, **208**, 392 (1932). More recently, it has been suggested by A. A. Vlček and F. Basolo, *Inorg. Chem.*, **5**, 156 (1966), that the correct formula of this complex is $K_6[Co(CN)_5 \cdot SO_2 \cdot Co(CN)_5] \cdot 4H_2O$.

(7) These measurements were obtained through the courtesy of David Nelson and Herbert Haber of Applied Physics Corp., Monrovia, Calif.

(8) The stopped-flow apparatus, obtained from Atom-Mech Machine Co., has been described in detail by G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

ments at 247 and 263 mμ. At 247 mμ, $Co(CN)_5SO_3H^{3-}$ has an absorption maximum and ϵ_{HA} and ϵ_A have numerical values of 14,540 and 7750, respectively. At 263 mμ, $Co(CN)_5SO_3^{4-}$ has an absorption maximum, and ϵ_{HA} and ϵ_A have numerical values of 7330 and 17,250, respectively. In one series of experiments $NaClO_4$ was added to the solutions of $Na_4Co(CN)_5SO_3 \cdot 2H_2O$ and $HClO_4$ to adjust the ionic strength to unity. In a second series of experiments there was no added electrolyte except the $HClO_4$ used to adjust the pH. Titration of 50.0 ml of 2.15×10^{-2} *M* $Co(CN)_5SO_3^{4-}$ was carried out with 0.35 *M* $HClO_4$, the ionic strength at the midpoint of the titration equaling 0.18.

The acidity of $HCo(CN)_4(SO_3)OH_2^{3-}$ was determined spectrophotometrically. The solutions were prepared by converting $Co(CN)_4(SO_3)_2^{5-}$ to $Co(CN)_4(SO_3)OH_2^{3-}$ and its conjugate acid in $HClO_4$ solution. The SO_2 generated in the conversion was removed by bubbling N_2 through the solution for 20 min. Identical results were obtained in measurements made at 245 and at 263 mμ. At 245 mμ the conjugate acid of $Co(CN)_4(SO_3)OH_2^{3-}$ has an absorption maximum, and ϵ_{HA} and ϵ_A have numerical values of 1.09×10^4 and 7.7×10^3, respectively. At 263 mμ, $Co(CN)_4SO_3OH_2^{3-}$ has an absorption maximum, and ϵ_{HA} and ϵ_A have the numerical values of 9.7×10^3 and 1.24×10^4, respectively.

Stoichiometry.—It was established by two methods that the aquation of $Co(CN)_4(SO_3)_2^{5-}$ produced $Co(CN)_4(SO_3)OH_2^{3-}$ and SO_3^{2-} or HSO_3^-.

In one method the free SO_3^{2-} produced by aquation was determined iodometrically.[9] An aliquot of the sulfite-containing solution was slowly pipetted into a stirred solution of 5% acetic acid which contained a known amount of I_3^-. The excess I_3^- was back-titrated with standardized $S_2O_3^{2-}$ to the starch end point.

The ready reversibility of the aquation reaction provides independent evidence that CN^- is not displaced from the complex in the aquation reaction.

Results

Before discussing the kinetic data for the aquation reactions, it is convenient to consider the acidity quotients of the various complex ions under consideration. In the interpretation of the kinetic studies it is important to have accurate values of the acidity quotients of $H_2Co(CN)_4(SO_3)_2^{3-}$, $HCo(CN)_4(SO_3)_2^{4-}$, and $HCo(CN)_5SO_3^{3-}$. Unfortunately, only $HCo(CN)_5SO_3^{3-}$ could be studied by direct acid–base titration, since the other two complexes underwent aquation so rapidly that conventional titration techniques could not be used. However, the kinetic data may be used to obtain estimates of the acidity quotients of the other two complexes. The acidity quotients of $HCo(CN)_4(SO_3)OH_2^{2-}$ and $Co(CN)_4SO_3OH_2^{3-}$ were also determined, since they are of interest for comparative purposes and as a part of other studies being carried out in this laboratory.

Numerical values of the acidity quotients of $HCo(CN)_4(SO_3)OH_2^{2-}$ were evaluated from the data presented in Figure 1 as a plot of log $[(A^-)/(HA)]$ *vs.* $-\log (H^+)$. The lines of unit slope drawn through the open and solid circles correspond to pK_1 values of 1.0_0 and 2.2_6 for unit and 0.006 ionic strength, respectively.

$$HCo(CN)_4(SO_3)OH_2^{2-} \overset{K_1}{\rightleftharpoons} H^+ + Co(CN)_4(SO_3)OH_2^{3-}$$

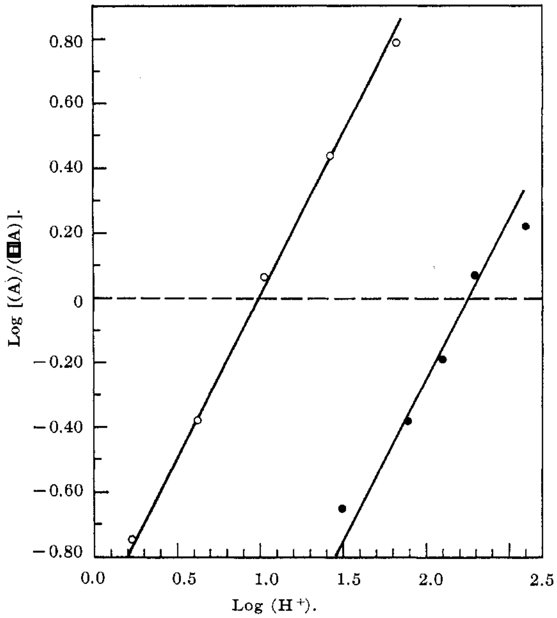

Figure 1.—Evaluation of the acidity quotient of $HCo(CN)_4(SO_3)OH_2^{2-}$. A plot of log [(A)/(HA)] *vs.* $-\log (H^+)$. $NaClO_4$ solutions: ○, $\mu = 1.0$; ●, $\mu = 0.006$.

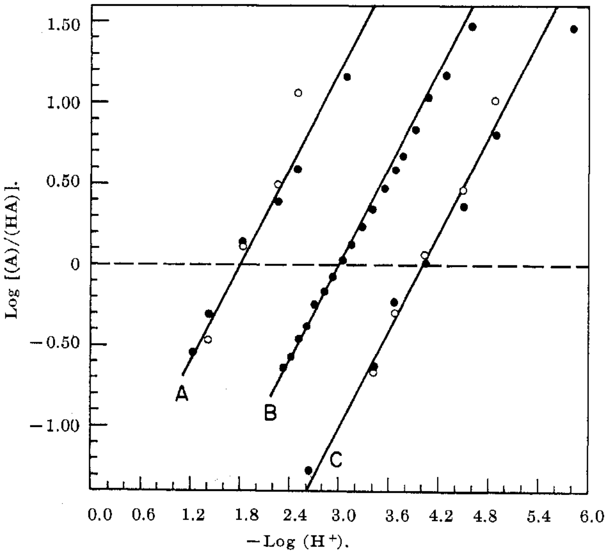

Figure 2.—Evaluation of the acidity quotient of $HCo(CN)_5(SO_3)^{3-}$. A plot of log [(A)/(HA)] *vs.* $-\log (H^+)$. $NaClO_4$ solutions: A, $\mu = 1.0$; B, $\mu = 0.18$; C, $\mu = 2 \times 10^{-4}$. For curves A and C, wavelength: ●, 263 mμ; ○, 247 mμ.

For convenience in use in unpublished kinetic studies, K_2 has been formulated as a neutralization quotient.

$$Co(CN)_4(SO_3)OH_2^{3-} + OH^- \overset{K_2}{\rightleftharpoons} Co(CN)_4(SO_3)OH^{4-} + H_2O$$

K_2 has not yet been determined with high accuracy, but the preliminary experiments, to be presented in detail elsewhere, yield a value of approximately 800.

The lines of unit slope drawn through data presented in Figure 2, a plot entirely analogous to Figure 1, correspond to pK_3 values of 1.8_0, 2.3_0, and 4.0_0 for ionic strengths of 1.0, 0.18, and 2×10^{-4}, respectively.

$$HCo(CN)_5SO_3^{3-} \overset{K_3}{\rightleftharpoons} H^+ + Co(CN)_5SO_3^{4-}$$

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[9] The procedure is described in detail in "Standard Methods for the Examination of Water and Waste Water," 11th ed, American Public Health Association, New York, N. Y., 1960, p 244.

The rate of reaction 3 was studied at 25° at various values of the ionic strength, but the bulk of the measurements were made using $NaClO_4$ to adjust the ionic strength to unity.

$$Co(CN)_4(SO_3)_2^{5-} + H_2O \longrightarrow Co(CN)_4(SO_3)OH_2^{3-} + SO_3^{2-} \quad (3)$$

Equation 3 is oversimplified in that the products undergo reversible acid–base reactions as the pH is changed. In all experiments at this and other ionic strengths, the rate of aquation of the second SO_3^{2-} ligand is negligibly slow compared with the rate of reaction 3.

The solid circles in Figure 3 represent the data obtained at unit ionic strength in solutions containing $NaClO_4$. In this figure and in the plots of the other kinetic data, each circle represents the results of experiments carried out in duplicate or triplicate. In all cases the circle covers the variation in k which was observed in duplicate experiments at any given pH.

In the initial experiments carried out at 10^{-3} to 1.0 M OH^- no attempt was made to exclude air, and the reaction was found to proceed to completion with a half-life of approximately 26 hr. For each of these experiments a pseudo-first-order rate constant k was obtained from the good linear plots of log $(A - A_\infty)$ *vs. t*, where A and A_∞ are the absorbancies at time t and after the reaction had reached equilibrium. In later experiments in weakly acidic solution, where the half-life was less than 30 min, it was observed that the position of the equilibrium after reaction corresponded to only 50–90% aquation. This indicates that quantitative reaction was being achieved in the alkaline solution only because the SO_3^{2-} was being removed by aereal oxidation. In the experiments in weakly acidic solution and in an experiment at pH 12.4 carried out in deaerated solution, the numerical value of k was obtained from the initial slope of the nonlinear plot of log $(A - A_\infty')$ *vs. t*, where A_∞' is the absorbancy calculated for complete aquation. The value of k obtained from the experiment at p- 12.4 was in good agreement with the results obtained without exclusion of air, an indication that the aereal oxidation of SO_3^{2-} was not rate determining. In solutions more acidic than 10^{-3} M H^+, where the stopped-flow technique was used, the reaction proceeded to completion, and k was again obtained from the linear plot of log $(A - A_\infty)$ *vs. t*.

The open circles in Figure 3 represent the somewhat larger pseudo-first-order rate constants obtained at unit ionic strength in solutions containing $LiClO_4$ instead of $NaClO_4$.

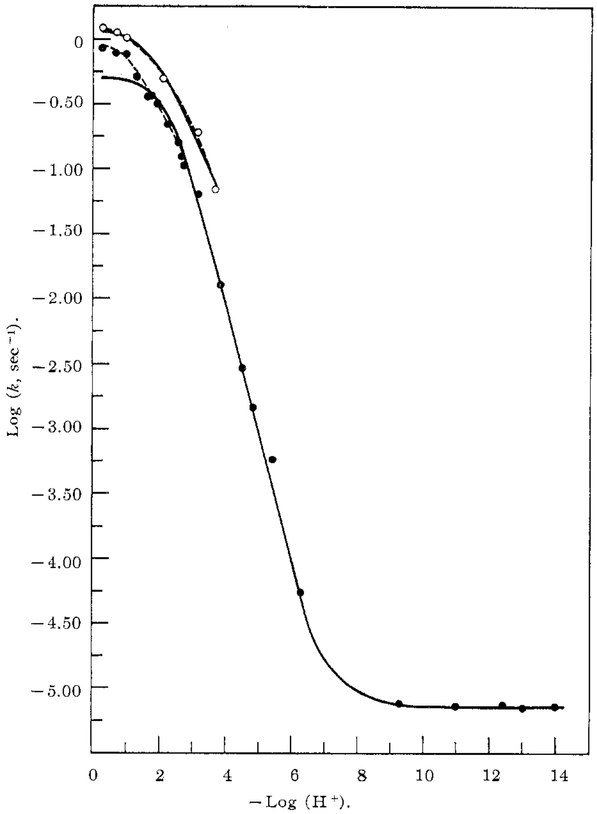

Figure 3.—The rate of $Co(CN)_4(SO_3)_2^{5-}$ at unit ionic strength: ●, $NaClO_4$ solutions; ○, $LiClO_4$ solutions.

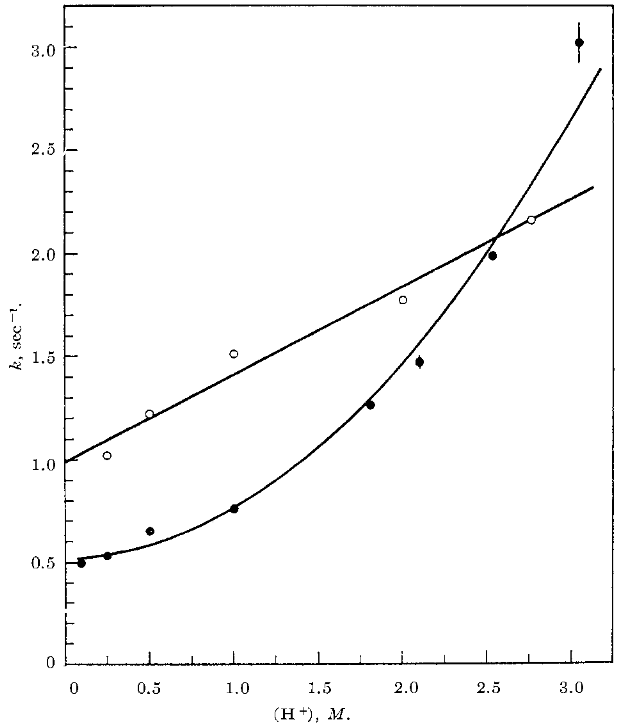

Figure 4.—The rate of aquation of $Co(CN)_4(SO_3)_2^{5-}$ in highly acidic solutions: ●, $NaClO_4$ solutions of ionic strength 4.0; ○, $LiClO_4$ solutions of ionic strength 3.5.

Figure 4 is a plot of data obtained at higher ionic strength. The solid circles represent data in which $NaClO_4$ was used to adjust the ionic strength to 4.0. Open circles are used to represent data in $LiClO_4$ solutions at ionic strength 3.5, the lower value being chosen because of solubility limitations. In experiments at acidities greater than 2.0 M, it was necessary to mix solutions which differed considerably in ionic strength in the stopped-flow apparatus, a procedure which is known to lead to difficulties in achieving complete mixing. In approximately 50% of the experiments attempted under these conditions, the oscilloscope traces clearly indicated incomplete mixing, and the data were discarded. In the remaining 50% of the experiments, the oscilloscope traces appeared to be normal and yielded the appropriate linear plots for a pseudo-first-order reaction, with the same value of k being obtained in duplicate experiments. Despite the reproducibility and lack of evidence for incomplete mixing in these latter experiments, it is possible that rate constants under consideration are in error by amounts which are difficult to estimate.

The aquation of $Co(CN)_5SO_3^{4-}$ was studied at unit ionic strength and 40°, the conditions employed in earlier studies of the aquation of pentacyanocobalt(III) derivatives.[10]

$$Co(CN)_5SO_3^{4-} + 2H^+ \longrightarrow Co(CN)_5OH_2^{3-} + SO_2 \qquad (4)$$

At pH 12.6 no appreciable reaction was observed in 11 days. In the same period of time a detectable change in absorbancy was observed at pH 6.2, but the change was too small to use in a quantitative calculation of the rate constant. In acidic solution appreciable reaction occurred in the 11-day period, and values of k of 1.00×10^{-6}, 2.14×10^{-6}, and 3.55×10^{-6} sec^{-1} were obtained at 0.01, 0.1, and 1.0 M hydrogen ion concentration from the initial slopes of a plot of log $(A - A_\infty')$ *vs.* time.

The results of the infrared and Raman spectra are summarized in Table I and Figure 5. Figure 5 illustrates the nature of the fine structure observed in the CN^- stretching region in the infrared spectra of $Na_5Co(CN)_4(SO_3)_2 \cdot 3H_2O$ and $Na_4Co(CN)_5SO_3 \cdot 2H_2O$. In the spectrum at the left side of the figure, the bands occur at 2155, 2145, 2134 sh, 2130, 2127, and 2117 cm^{-1}. In the spectrum to the right, the two bands are at 2113 and 2118 cm^{-1}.

The Raman spectrum of $Na_5Co(CN)_4(SO_3)_2 \cdot 2H_2O$ was studied in its saturated solution at approximately 0.1 M, a concentration high enough so that the per cent aquation at equilibrium would have been negligible. The spectrum in the CN^- stretching region[11] was found to consist of bands at 2145 s and 2135 sh cm^{-1}. The Raman spectrum of 0.4 M $Co(CN)_5SO_3^{4-}$ in the CN^- stretching region consisted of bands at 2152 s, 2140 w, and 2133 sh cm^{-1}.

The remaining Raman and infrared data are collected in Table I. In the Raman studies higher concentrations would have been desirable, since some of the bands were quite weak and others may have been too weak to detect.

Discussion

Aquation of $Co(CN)_4(SO_3)_2^{5-}$ at Unit Ionic Strength.—Most of the details of the mechanism of aquation of $Co(CN)_4(SO_3)_2^{5-}$ at unit ionic strength may be deduced from an examination of the data obtained in $NaClO_4$ solutions and presented in Figure 3. In strongly alkaline solution where the rate is pH independent, the reactive species is obviously $Co(CN)_4(SO_3)_2^{5-}$. In the range of hydrogen ion concentration of 10^{-4}–10^{-1} M the rate is first order in H^+, an indication that the reactive species, present only at low concentration, has the chemical composition $HCo(CN)_4(SO_3)_2^{4-}$. Formation of one or more protonated species at appreciable concentration evidently occurs over the range of hydrogen ion concentration 10^{-1}–10^{-4} M where the rate is less than first order in H^+. Above 0.10 M H^+, protonation is complete, and the rate is again pH independent.

TABLE I

INFRARED AND RAMAN SPECTRA[a]

Compound	Ligand assignment: SO_3^{2-}	H_2O	Unidentified
$Na_5Co(CN)_4(SO_3)_2 \cdot 3H_2O$			
(1) Infrared	1129 s, 1072 s,	1613	
	970 s, 636 s		
	1111 sh	3512	
		3560	
(2) Raman	1067 w, 1004 w,		
	647 s		417 s
$Na_4Co(CN)_5SO_3 \cdot 2H_2O$			
(1) Infrared	1118 s, 1085 sh,		
	977 s, 652 m	1631	
	1068 s, 989 s	3543	
	1050 sh		
(2) Raman	1066 w, 985 m,		
	636 m		564 w
			410 s

[a] The infrared studies covered only the range 600–4000 cm^{-1} and would not detect the ν_4 absorption of SO_3^{2-}, which probably occurs in the region below 500 cm^{-1}.

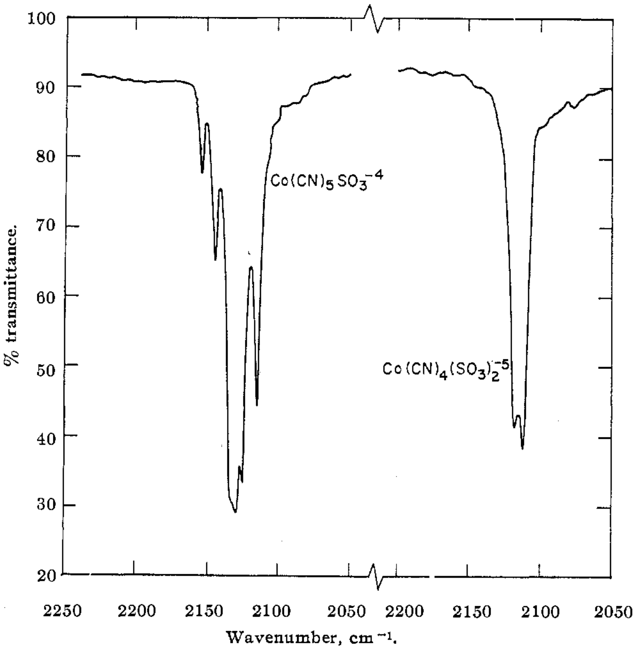

Figure 5.—Infrared spectrum in the CN^- stretching region.

The major point of uncertainty in the above mechanism is the number of protons which are added to the complex in the region where extensive protonation occurs. A recent study of the basicity of $Fe(CN)_6^{4-}$ indicates that at least two protons might be added over a rather narrow range of pH. The numerical values

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[10] For a review of this data, see Advances in Chemistry Series, No. 41, American Chemical Society, Washington, D. C., 1965, p 31.

[11] On one occasion, working with a supersaturated solution, the band at 2135 cm^{-1} was clearly resolved, but later attempts to repeat this only produced a shoulder on the side of the 2145-cm^{-1} band.

of the acidity quotients[12] of $H_2Fe(CN)_6^{2-}$ and $HFe(CN)_6^{3-}$ at ionic strength 0.5 are $(1.2 \pm 0.5) \times 10^{-2}$ and $(1.9 \pm 0.1) \times 10^{-3}$, respectively. As the calculations presented below will indicate, both mono- and diprotonation of $Co(CN)_4(SO_3)_2^{5-}$ apparently occur in the pH range covered in our study.

Attempts were first made to interpret the kinetic data in terms of a mechanism involving only a single protonation.

$$Co(CN)_4(SO_3)_2^{5-} + H_2O \xrightarrow{k_1} Co(CN)_4(SO_3)OH_2^{3-} + SO_3^{2-} \quad (5)$$

$$HCo(CN)_4(SO_3)_2^{4-} \overset{K_4}{\rightleftharpoons} H^+ + Co(CN)_4(SO_3)_2^{5-} \quad (6)$$

$$HCo(CN)_4(SO_3)_2^{4-} + H_2O \xrightarrow{k_2} Co(CN)_4(SO_3)OH_2^{3-} + HSO_3^- \quad (7)$$

This mechanism would require that the pseudo-first-order rate constants be related to the kinetic parameters by

$$k = \frac{k_1K_4 + k_2(H^+)}{(H^+) + K_4} \quad (8)$$

When reactions 9 and 10 are added to this oversimplified mechanism, the corresponding relationship is given by

$$H_2Co(CN)_4(SO_3)_2^{3-} \overset{K_5}{\rightleftharpoons} H^+ + HCo(CN)_4(SO_3)_2^{4-} \quad (9)$$

$$H_2Co(CN)_4(SO_3)_2 \xrightarrow{k_3} Co(CN)_4(SO_3)OH_2^{3-} + SO_2 \quad (10)$$

$$k = \frac{k_1K_4K_5 + k_2K_5(H^+) + k_3(H^+)^2}{K_4K_5 + K_5(H^+) + (H^+)^2} \quad (11)$$

The nonlinear least-square calculations now to be considered show that eq 8 does not adequately represent the data. In this and in the other least-square calculations presented below individual k values were weighted by the factor $1/k^2$, a procedure which assumes that the per cent error in all experiments is the same. Use of eq 8 yields the numerical values of $k_1 = (7.29 \pm 0.69) \times 10^{-6}$, $k_2 = 0.499 \pm 0.040$, and $K_4 = (5.35 \pm 0.63) \times 10^{-3}$, where the uncertainties listed are the standard deviations. The solid line in Figure 3 represents the values of k calculated for the data obtained in $NaClO_4$ solutions using these parameters. The calculated values of k differ from the experimental values by amounts which are believed to be considerably greater than the experimental error.

For the 38 data points, the average per cent deviation between the calculated and observed values of k is 15.7, and the maximum deviation is 48%. Further, when the nature of the deviations is examined, it is found that they are not random, particularly in solution more acidic than 2.0×10^{-3} M, the region where protonation of $Co(CN)_4(SO_3)_2^{5-}$ becomes thermodynamically important. In solutions more acidic than 5×10^{-2} M, the calculated values of k are 15–40% too small, a feature observable in Figure 3. By contrast, the calculated values are too large by 5–29% over the acidity range of 5×10^{-2} to 2×10^{-3} M. The discrepancies here are not so readily seen in Figure 3 because of the condensed ordinate scale. An alternate mechanistic description of the nonrandom nature of the deviation is that protonation of $Co(CN)_4(SO_3)_2^{5-}$ is occurring over a greater range of pH than that predicted by a single equilibrium of the form of reaction 6.

When the mechanism consisting of reactions 5, 6, 7, 9, and 10 is assumed and the least-square calculation is based upon eq 11, the values of the kinetic parameters obtained are $k_1 = (7.25 \pm 0.39) \times 10^{-6}$, $k_2 = (1.98 \pm 0.35) \times 10^{-1}$, $k_3 = (9.83 \pm 1.26) \times 10^{-1}$, $K_4 = (1.81 \pm 0.35) \times 10^{-3}$, and $K_5 = (5.96 \pm 2.27) \times 10^{-2}$. The values of k calculated from eq 11 are represented by the dashed line in Figure 3 in those regions of pH where overlap of the solid and dashed lines does not occur.

It would appear that the revised mechanism which includes eq 9 and 10 is much more satisfactory. The average per cent deviation is now 8.4% and the maximum per cent deviation is now 14.9%, except for the points at a hydrogen ion concentration of 3.55×10^{-6} M, where the average per cent deviations of 25–39% suggest that some error occurred in these experiments.

The average per cent deviation of 8.4%, which is rather large for good kinetic work, probably arises in part from medium effects and in part from experimental error. The error in the present experiments may be unusually large for two reasons. First, it might be noted that the work was carried out by two different experimentalists working at different times and using different experimental techniques, a feature which tends to enhance experimental error when the data are considered as a whole. Second, the errors in measurement of pH and the conversion of this quantity to H^+ concentration may equal in importance the errors in the measured values of the rate constants.

Medium effects associated with the replacement of one cation by another are expected to be present when at least one of the reactants is a highly charged negative ion, as in the present studies. They probably arise not only from long-range electrostatic interaction but also from ion pairing.[13] In the data obtained in $NaClO_4$ solutions they are expected to be of major importance at acidities above 0.1 M, the region where the per cent change in the Na^+ concentration becomes large. A comparison of the average values of the rate constants of 0.76, 0.78, 0.85, and 1.19 obtained at 0.1, 0.2, 0.5, and 1.0 M H^+, respectively, suggests that the anomalously high value obtained at 1.0 M H^+ probably represents only a medium effect, although the possibility of further acid catalysis at high acidities exists and will be considered in more detail later.

A least-square calculation using the data at unit ionic strength in the $LiClO_4$ solutions was made using both eq 8 and 11. Equation 8 yielded the values $k_1 = (5.47 \pm 0.94) \times 10^{-2}$, $k_2 = 1.15 \pm 0.07$, $K_4 = (9.14 \pm 1.82) \times 10^{-3}$, and rate constants given by the solid line in Figure 3. For the 17 experiments the average per cent deviation was 11.0 and the maximum devia-

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(12) J. Jordan and G. J. Ewing, *Inorg. Chem.*, **1**, 587 (1962).

(13) Ion pairing of K^+ and $Fe(CN)_6^{4-}$ has been reported by S. R. Cohen and R. A. Plane, *J. Phys. Chem.*, **61**, 1096 (1957).

tion was 31%, with the trends in the deviations being analogous to those observed in $NaClO_4$ solution. In these experiments reaction 5 does not contribute significantly to the aquation reaction, and the evaluation of the corresponding rate constant k_1 is therefore subject to very large errors, a factor which makes understandable the otherwise incomprehensible change in k_1 by a factor of 10^4 by changing the medium from $NaClO_4$ to $LiClO_4$.

To minimize this error when carrying out the least-square calculation using eq 11, k_1 was assigned the value 7.2×10^{-6}, the experimental result obtained in $NaClO_4$ solutions. The calculation yielded the results $k_2 = (4.24 \pm 0.27) \times 10^{-1}$, $k_3 = 1.29 \pm 0.03$, $K_4 = (1.05 \pm 0.09) \times 10^{-3}$, $K_5 = (4.50 \pm 0.76) \times 10^{-2}$, an average per cent deviation of 1.5, and a maximum deviation of 7.6%. For the reasons given above these parameters are believed to have greater mechanistic significance than those obtained using eq 8.

Aquation of $Co(CN)_4(SO_3)_2^{5-}$ in Solutions More Acidic than 1.0 *M*.—In the above discussion of the data obtained in $NaClO_4$ solutions, it was suggested that the 40% increase in rate in going from 0.50 to 1.0 *M* H^+ was a medium effect. However, as an alternate explanation the possibility existed that further acid catalysis might be observed in solutions more acidic than 1.0 *M*.

As the results presented in Figure 4 indicate, acid catalysis was observed in the more acidic solution, but the catalysis quite possibly is merely a medium effect operative. This interpretation is strengthened by the observation that the rate laws in the two solutions differ considerably in their H^+ dependence. In the $NaClO_4$ solutions a rate law containing terms zero, first, and second order in H^+ was assumed, and the least-square computation yielded the result given by

$$k = 0.520 \pm 0.024 + (8 \pm 62) \times 10^{-3}(H^+) + (0.233 \pm 0.025)(H^+)^2 \quad (12)$$

In eq 12 the linear term in H^+ is poorly defined and is negligible in its contribution to the rate compared to the term which is second order in H^+. By contrast, the rate in $LiClO_4$ solution seems to show only a linear dependence on H^+. The least-square calculation based on a two-term rate law yielded the kinetic parameters given by

$$k = 1.00 + 0.42(H^+) \quad (13)$$

The solid lines in Figure 4 were calculated using eq 12 and 13.

The kinetic data obtained at unit ionic strength define the chemical composition of the three activated complexes generated in reactions 5, 7, and 10, but do not provide information about the possible formation of reactive intermediates which might be generated in the reactions. Our unpublished data provide evidence that reactions 5, 7, and 10 involve limiting types of SN1 mechanisms, with the initial generation of the reactive intermediate $Co(CN)_4(SO_3)^{3-}$ and the subsequent addition of a water molecule to form $Co(CN)_4(SO_3)OH_2^{3-}$. This conclusion is reached on the basis of the restrictions imposed by the microscopic reversibility requirement. The displacement of H_2O in $Co(CN)_4(SO_3)OH_2^{3-}$ by various ligands including SO_3^{2-} has been found to proceed by a limiting type of SN1 mechanism.[14] Consequently, the aquation of $Co(CN)_4(SO_3)_2^{5-}$, the reverse of the reaction of $Co(CN)_4(SO_3)OH_2^{3-}$ with SO_3^{2-}, must proceed through the same sequence of activated complexes and reactive intermediates. At this point it might be noted that the zero-order dependence of rate on OH^- concentration in strongly alkaline solution implies that direct displacement of the SO_3^{2-} ligand in $Co(CN)_4(SO_3)_2^{5-}$ by OH^- is unimportant, an additional mechanistic feature consistent with an SN1 mechanism of aquation.

The Aquation of $Co(CN)_5(SO_3)^{4-}$.—Only three experiments were carried out in the aquation of $Co(CN)_5(SO_3)^{4-}$, since our major objective was merely to show that the rate was orders of magnitude slower than that observed for $Co(CN)_4(SO_3)_2^{5-}$. On the basis of this limited amount of data, it would appear that the rate law is analogous to that observed for $Co(CN)_4(SO_3)_2^{5-}$, except for the path zero order in H^+ which is immeasurably slow. In addition, there is no evidence that diprotonation of $Co(CN)_5(SO_3)^{4-}$ occurs in the acidity range of interest.

The data conform to a rate law of the form of eq 14 and the relationship between the kinetic parameters given by eq 15.

$$-\frac{d\{[Co(CN)_5SO_3{}^{4-}] + [Co(CN)_5SO_3H]\}}{dt} = k_4[Co(CN)_5SO_3H^{3-}] + k_5[Co(CN)_5SO_3H^{3-}][H^+] \quad (14)$$

$$k = \frac{k_4(H^+) + k_5(H^+)^2}{(H^+) + K_3} \quad (15)$$

Values of $k_4 = 2.52\ M^{-1}\ sec^{-1}$ and $k_5 = 1.10\ M^{-2}\ sec^{-1}$ were calculated using eq 15, the rate constants obtained at 10^{-2} and 1.0 *M* H^+, and the value of K_3 listed above. Use of these parameters leads to a calculated value of k at 0.10 *M* H^+ of $2.27 \times 10^{-6}\ sec^{-1}$, a result in satisfactory agreement with the experimental value of $2.14 \times 10^{-6}\ sec^{-1}$.

It is of interest to consider why the rate of aquation of $Co(CN)_4(SO_3)_2^{5-}$ should be so much greater than that of $Co(CN)_5(SO_3)^{4-}$. In this connection it is pertinent to note that our unpublished experiments indicate that the anation reactions of $Co(CN)_4(SO_3)OH_2^{3-}$ are also orders of magnitude faster than those of $Co(CN)_5OH_2^{2-}$. It has been suggested on the basis of preparative studies[3,4] that the presence of an SO_3^{2-} ligand in a Co(III) complex greatly enhances the rate of substitution in the ligand position *trans* to itself. The infrared and Raman studies now to be considered provide support for this suggestion in that they indicate that $Co(CN)_4(SO_3)_2^{5-}$ does have a *trans* configuration.

Infrared and Raman Spectra.—The splitting of the absorption band in either the infrared or Raman spectrum in the region of the CN^- stretching frequency can

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[14] Unpublished work carried out in this laboratory.

be predicted from symmetry considerations. Not many infrared spectra of octahedral CN^- complexes have been reported, but the predictions[15] have been found to be in agreement with experiment for a large number of the analogous carbonyl complexes. In general, the infrared spectra of complexes having the general formula $M(CO)_5X$ have been found to consist of four bands, in agreement with theory. In order of increasing wavenumber, there is a weak band, a second weak band lying fairly close to the strong band, a strong band, and a fourth weak band which sometimes appears as a shoulder on the strong band. The infrared spectra of CN^- complexes of analogous structure should also contain four bands. It can be seen in Figure 5 that this type of spectrum is observed for $Na_4Co(CN)_5SO_3 \cdot 2H_2O$, apart from the minor addition splitting of the strong band over a range of 7 cm^{-1}. This latter splitting is not unexpected, since it is frequently observed in the infrared spectrum of solids. The agreement between experiment and theory for $Co(CN)_5SO_3^{4-}$, where the configuration is known, thus lends support to the applicability of this approach to determination of configuration.

Four bands are predicted for the infrared spectrum of the *cis* isomer of $Na_5Co(CN)_4(SO_3)_2 \cdot 3H_2O$ and only one band for the *trans* isomer.[15] The close-lying doublet observable in Figure 5, with a separation of only 5 cm^{-1}, is not in agreement with the four-band spectrum expected for the *cis* isomer. Solid-state splitting of a single band arising from a *trans* configuration would seem to represent a much more plausible explanation of the spectrum.

The Raman spectra in the CN^- stretching region are compatible with the above interpretation, but they do not provide much additional evidence because of inadequate resolution. In the spectrum of $Co(CN)_5(SO_3)^{4-}$, where four bands are predicted, only a strong band with two shoulders was detected. The spectrum of $Co(CN)_4(SO_3)_2^{5-}$ consisting of a strong band with a single shoulder is in agreement with the two bands predicted for a *trans* configuration. However, the four bands predicted for a *cis* configuration could conceivably have been present and escaped detection because of lack of resolution.

Attempts have been made to use the infrared spectrum in the region of 450–1200 cm^{-1} to distinguish[16,17] Co–SO_3 and Co–OSO_2 bonding. However, conclusive experimental support of the attempted distinction has not yet been achieved, in part because the spectrum of a compound known to contain an M–OSO_2 bond does not seem to have been reported. In addition, solid-state splitting of these bonds commonly occurs and complicates the comparison of theory and experiment. However, the spectra of $Na_4Co(CN)_5(SO_3) \cdot 2H_2O$ and $Na_5Co(CN)_4(SO_3)_2 \cdot 3H_2O$ are quite similar and analogous to those of compounds[16–19] believed to contain an M–SO_3 bond. The relative simplicity of the spectrum of $Na_5Co(CN)_4(SO_3)_2 \cdot 3H_2O$ makes it hard to believe that the complex contains both a Co–SO_3 and a Co–OSO_2 bond, a possible but rather unlikely explanation for the very different rates of aquation of the two SO_3^{2-} ligands.

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