CH_3NO_2. A similar ratio of intensities is also found[17] in the reflectance spectra of $Cu(en)_3SO_4$ and the polarized single-crystal spectrum of $Cu(dien)_2Br_2 \cdot H_2O$.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[17] B. J. Hathaway, M. J. Bew, D. E. Billing, R. J. Dudley, and P. Nicholls, *J. Chem. Soc.*, 2312 (1969).

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The Rate of Aquation of 1,2,3-Tricyanotriaquochromium(III) in Acidic Aqueous Solution[1,2]

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The kinetics of aquation of the 1,2,3-tricyanotriaquochromium(III) complex was studied in aqueous perchloric acid–sodium perchlorate solutions at an ionic strength of 2.0. The aquation was found to be acid assisted and to be well described by the rate law

$$\frac{-\mathrm{d}C_{\mathrm{tri}}}{\mathrm{d}t} = \frac{(k_1K_1[\mathrm{H}^+] + k_2K_1K_2[\mathrm{H}^+]^2)C_{\mathrm{tri}}}{1 + K_1[\mathrm{H}^+]}$$

where C_{tri} is the stoichiometric concentration of the complex, K_1 and K_2 are successive protonation constants, and k_1 and k_2 are first-order rate constants for the singly and doubly protonated species. K_1 was evaluated from direct spectrophotometric measurements as well as from the kinetic data. At 15 and 25°, respectively, $K_1 = 0.9 \pm 0.4$ and 1.1 ± 0.4 l. mol^{-1}, $k_1 = 2.2\ (\pm 1.0) \times 10^{-4}$ and $5.8\ (\pm 2.3) \times 10^{-4}$ sec^{-1}, $k_1K_1 = 2.00\ (\pm 0.12) \times 10^{-4}$ and $6.63\ (\pm 0.15) \times 10^{-4}$ sec^{-1} l. mol^{-1}, and $k_2K_2 = 1.5\ (\pm 0.1) \times 10^{-4}$ and $5.6\ (\pm 0.4) \times 10^{-4}$ sec^{-1} l. mol^{-1}. Calculated values of the pseudo-first-order rate constants obtained with these parameters agree with the experimentally observed rate constants with an overall average deviation of 1.5%. Activation parameters calculated for the aquation of the singly protonated species are $\Delta H^{\ddagger} = 16 \pm 6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -19 \pm 9$ eu. The values obtained for the kinetic and activation parameters of the tricyanotriaquo complex are compared with those obtained previously for the cyanopentaaquochromium(III) ion and with recalculated values for the *cis*-dicyanotetraaquochromium(III) ion.

Introduction

Previous work in this laboratory[3–7] has established that in acidic aqueous solutions the hexacyanochromate(III) ion aquates *via* a series of stepwise, stereospecific reactions to give hexaaquochromium(III) cation as the final product. All of the intermediates in this reaction sequence have been isolated.[7]

The complete aquation of the most inert of the intermediate cyanoaquo complexes, the uncharged 1,2,3-tricyanotriaquochromium(III) complex, involves the reactions

$$\text{1,2,3-Cr(H}_2\text{O)}_3\text{(CN)}_3 + \text{H}_3\text{O}^+ \longrightarrow cis\text{-Cr(H}_2\text{O)}_4\text{(CN)}_2{}^+ + \text{HCN} \quad (1)$$

$$cis\text{-Cr(H}_2\text{O)}_4\text{(CN)}_2{}^+ + \text{H}_3\text{O}^+ \longrightarrow \text{Cr(H}_2\text{O)}_5\text{CN}^{2+} + \text{HCN} \quad (2)$$

$$\text{Cr(H}_2\text{O)}_5\text{CN}^{2+} + \text{H}_3\text{O}^+ \longrightarrow \text{Cr(H}_2\text{O)}_6{}^{3+} + \text{HCN} \quad (3)$$

The results of detailed studies of the kinetics of reactions 2 and 3 are discussed elsewhere.[5,6,8] In this paper, the results of a study of the rate of reaction 1 as a function of acidity and temperature at a constant ionic strength are presented and are compared with the results obtained from studies of reactions 2 and 3.

An interesting feature of the overall acid-assisted aquation sequence of the hexacyanochromate(III) ion is that apparently only one isomer of each of the intermediate cyanoaquochromium(III) complexes is formed at each step. On the basis of the relative aquation rates of the anionic complexes, in comparison with those of the uncharged and cationic species, and a consideration of the spectra,[3,7,9] it is concluded that it is the cis isomers which are formed.

The stereospecific nature of the aquation simplifies the kinetic studies and allows a more straightforward interpretation of aquation rates. In the studies involving the thiocyanatoaquochromium(III) complexes,[10–12] the amineaquochromium(III) complexes,[13] and the chloroaquochromium(III) com-

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[2] Taken in part from a thesis submitted by D. K. Wakefield to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree in Chemistry, 1967.

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[4] W. B. Schaap, R. Krishnamurthy, D. K. Wakefield, and J. R. Perumareddi, "Proceedings of the 9th International Conference on Coordination Chemistry," St. Moritz-Bad, Switzerland, 1966, p 351.

[5] D. K. Wakefield and W. B. Schaap, *Inorg. Chem.*, **8**, 512 (1969).

[6] D. K. Wakefield and W. B. Schaap, *ibid.*, **8**, 811 (1969).

[7] W. B. Schaap, R. Krishnamurthy, D. K. Wakefield, and W. F. Coleman, "Coordination Chemistry," S. Kirschner, Ed., Plenum Publishing Co., New York, N. Y., 1969, p 177.

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[9] R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *ibid.*, **6**, 1338 (1967).

[10] N. Bjerrum, *Z. Anorg. Allg. Chem.*, **118**, 131 (1921).

[11] N. Bjerrum, *ibid.*, **119**, 39, 53, 179 (1921).

[12] K. G. Poulsen, J. Bjerrum, and I. Poulsen, *Acta Chem. Scand.*, **18**, 921 (1954).

[13] E. Jorgensen and J. Bjerrum, *ibid.*, **12**, 1047 (1958).

plexes[14-16] the interpretation of the kinetic data is complicated either by cis–trans isomerization and/or aquation of one species to two different geometric isomers.

Experimental Section

Solutions containing the orange 1,2,3-tricyanotriaquochromium(III) complex, $Cr(H_2O)_3(CN)_3$, as the only chromium- or cyanide-containing species were obtained by ion-exchange separation of this species from the various cyanoaquochromium(III) complexes formed during the acid-catalyzed aquation of hexacyanochromate(III) ion. A hydrolysis mixture containing predominantly the 1,2,3-tricyanotriaquochromium(III) complex (hereafter called the tricyano complex) was prepared by dissolving sufficient potassium hexacyanochromate(III) in 0.03 *M* perchloric acid to give a molar ratio of complex to acid of 1:3. Dilute solutions were used to minimize the formation of polymers, which appeared to form at higher concentrations. The hydrolysis mixture was kept in darkness at room temperature with nitrogen bubbling through it until the pH rose to about 3.0, which took about 3 hr. Separation and identification procedures are described elsewhere,[5,7] together with the descriptions of preparations of other reagents and solutions.

Kinetic Measurements.—The aquation of the tricyanochromium(III) complex was followed spectrophotometrically at 447 mμ in a water-jacketed 10-cm silica spectrophotometer cell. A Cary Model 14 recording spectrophotometer was used for all kinetic measurements. The procedures used for obtaining the rate data are described in more detail in previous papers.[5,6] In all kinetic experiments the hydrogen ion concentration was at least 50 times the initial concentration of the tricyanochromium(III) complex, which was held at 8×10^{-4} *M*.

Absorbance measurements at a given wavelength were made continuously during the first 10 min after the sample was transferred to the cell and periodically thereafter. An occasional scan of the visible absorption spectrum was run to check the constancy of the background. In the pH range of 2.5–3.5 and at 447 mμ the molar absorbancy indices of the tricyano-, dicyano-, monocyano-, and hexaaquochromium(III) complexes are 91.3, 38.8, 7.14, and 7.14 l. mol^{-1} cm^{-1}, respectively. The molar absorbancy indices of the tricyano- and dicyanochromium(III) complexes at this wavelength decrease with increasing hydrogen ion concentration, indicating protonation of ligand cyanide in these complexes. The monocyano- and hexaaquochromium(III) ion, however, maintain an isosbestic point at 447 mμ throughout the hydrogen ion concentration range studied. The absorbance measurements are therefore not affected by the aquation of monocyanochromium(III) ion to hexaaquochromium(III), reaction 3. The spectra of these cyanoaquo complexes have been presented in a previous paper.[5]

Spectral Measurement of Protonation Constant.—In order to study the protonation equilibrium of the tricyano complex directly (independently of the kinetic measurements), the molar absorbancy index of solutions of tricyanochromium(III) at 447 mμ was determined as a function of the hydrogen ion concentration using a Zeiss PMQ II spectrophotometer. As a usual procedure aliquots of a stock solution of tricyanochromium(III) and of a solution containing perchloric acid and sodium perchlorate were put in separate arms of a mixing chamber and were brought to the desired reaction temperature in a constant-temperature water bath. The solutions were quickly mixed and transferred directly to the spectrophotometer cell which was held in a thermostated cell compartment. Absorbance measurements were made periodically for as long as 20 min.

The initial (zero-time) absorbance of the solution is due to the sum of the absorbancies of only the protonated and nonprotonated forms of the tricyanochromium(III) complex, and from this initial value the apparent absorbancy index of the equilibrium mixture of tricyano species, ϵ_{tri}, at each acidity may be calculated. The zero-time absorbance was determined from the intercept of plots of log $(A_t - \epsilon_{di}C_i)$ *vs.* *t*, where A_t refers to the absorbance at time *t*, ϵ_{di} is the apparent adsorbancy index of dicyanochromium(III) ion at the wavelength and at the hydrogen ion concentration of the experiment,[6] and C_i is the initial concentration of tricyanochromium(III). These plots are linear during time intervals between 1.5 and 4 min up to 1.5 and 17 min, depending on the acidity of the experiment. The plots were curved after these intervals due to the formation of appreciable amounts of the monocyanochromium(III) ion.

Results

Aquation Kinetics.—The aquation of 1,2,3-tricyanochromium(III) was studied over a range of perchloric acid concentrations at 15.0 and 25.0°. Sodium perchlorate was used to adjust the ionic strength to 2.0. In acidic solutions all reactions went to completion giving final absorption spectra which were identical with that of hexaaquochromium(III) ion. Because the tricyano and dicyano complexes both absorb strongly at 447 mμ, while the monocyano- and hexaaquochromium(III) ions exhibit an isosbestic point,[5] the absorbance data obtained at this wavelength are sensitive to changes in concentration of the former two species and the kinetic data can be treated in terms of two consecutive first-order reactions—the aquation of 1,2,3-tricyanochromium(III) to *cis*-dicyanochromium(III) ion and the aquation of the *cis*-dicyanochromium(III) ion to give the monocyanochromium(III) ion, reactions 1 and 2.

The total absorbance of the solution at 447 mμ is given by

$$A_{obsd} = \epsilon_{tri}C_{tri} + \epsilon_{di}C_{di} + \epsilon_{mono}(C_{mono} + C_{hexa}) \quad (4)$$

where ϵ_{tri}, ϵ_{di}, and ϵ_{mono} refer to the apparent molar absorbancy indices of the tricyano-, dicyano-, and monocyanochromium(III) complexes, respectively, in their equilibrium mixtures of protonated and nonprotonated forms at the hydrogen ion concentration of the experiment. The quantities C_{tri}, C_{di}, C_{mono}, and C_{hexa} refer to the total stoichiometric concentrations of the tricyano-, dicyano-, monocyano-, and hexaaquochromium(III) complexes, whether in their protonated or nonprotonated forms.

The absorbance of the reacting solutions can be expressed as a function of time by substituting standard kinetic expressions for the concentrations of the complexes involved in the two consecutive first-order reactions into eq 4, *i.e.*

$$\begin{aligned} A_{obsd} = {} & \epsilon_{tri}C_i \exp(-k_{tri}t) + \epsilon_{di}C_ik_{tri}[\exp(-k_{tri}t) - \\ & \exp(-k_{di}t)]/(k_{di} - k_{tri}) + \epsilon_{mono}C_i[1 + \\ & k_{tri}\exp(-k_{di}t) - k_{di}\exp(-k_{tri}t)]/(k_{di} - k_{tri}) \quad (5) \end{aligned}$$

where k_{tri} and k_{di} are the pseudo-first-order rate constants at a given hydrogen ion concentration for reactions 1 and 2, respectively, *t* refers to the elapsed time, and C_i represents the initial concentration of the tricyanochromium(III) complex. Trial values for the quantities ϵ_{di}, k_{di}, and ϵ_{mono} were taken from previous experiments.[5,6] Approximate values of ϵ_{tri} at each

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[14] H. B. Johnson and W. L. Reynolds, *Inorg. Chem.*, **2**, 468 (1963).

[15] C. W. Merideth, W. D. Mathews, and E. G. Orlemann, *ibid.*, **3**, 320 (1964).

[16] C. D. Salzman and E. L. King, *ibid.*, **6**, 426 (1967).

acidity were obtained from linear extrapolations to zero time of absorbance measurements made during actual kinetic runs.

Values for k_{tri} were then obtained from eq 5 using a CDC 3600 computer and a modified version of a computer program given by Wiberg.[17] The modified program involves iterative calculations in which first a trial value of k_{tri} is varied and then the trial values of ϵ_{tri}, ϵ_{di}, k_{di}, and ϵ_{mono} are varied in that order until a final set of equation parameters (k_{tri}, ϵ_{tri}, ϵ_{di}, k_{di}, and ϵ_{mono}) is obtained which gives the best fit of the absorbance *vs.* time data. The final values of ϵ_{di}, k_{di}, and ϵ_{mono} obtained by the iterative calculations were in excellent agreement with the trial values used for these parameters. The final values of ϵ_{tri} at each acidity, obtained by varying the parameters of eq 5, were only very slightly (but consistently) lower than the trial values obtained by extrapolation of kinetic data and were also in excellent agreement with the values obtained from the independent spectrophotometric measurements discussed in the next section. The agreement in the values of these parameters obtained in independent experiments substantiates the validity of the iterative calculations.

The values for the observed pseudo-first-order rate constant k_{tri} obtained at 15.0 and 25.0° for a variety of hydrogen ion concentrations are given in Table I.

TABLE I

PSEUDO-FIRST-ORDER RATE CONSTANTS[a] FOR THE ACID-CATALYZED AQUATION OF $Cr(CN)_3(H_2O)_3$ AT 15 AND 25°

15.0°		25.0°	
$[H^+]$, *M*	10^4k_{tri}, sec^{-1}	$[H^+]$, *M*	10^4k_{tri}, sec^{-1}
0.6046	1.13	0.1022	0.682
0.7954	1.40	0.2025	1.29
0.9507	1.66	0.3049	1.94
1.186	2.14	0.4056	2.56
1.389	2.38	0.5051	3.16
1.580	2.76	0.6042	3.78
1.739	2.92	0.8006	4.88
1.981	3.16	1.004	6.09
		1.199	7.37
		1.452	8.71
		1.596	9.31

[a] The initial concentration of $Cr(CN)_3(H_2O)_3$ was 8×10^{-4} *M*; the ionic strength was maintained at 2.0 with sodium perchlorate.

Plots of the pseudo-first-order rate constant *vs.* the hydrogen ion concentration at 15 and 25° are shown in Figure 1 and appear to have zero intercepts, showing that aquation *via* an acid-independent pathway is negligible at these temperatures in the acidity range studied. The plots also exhibit a slight curvature, indicating that the aquation rate has a slightly less than first-order dependence on the hydrogen ion concentration. The curvature in the case of the uncharged tricyano complex appears to be significantly less than the curvature of the corresponding plot made for the positively charged monocyanopentaaquo cation.[5]

Equilibrium Constant for Protonation of 1,2,3-Tricyanotriaquochromium(III).—After the kinetic studies were completed, it became obvious for reasons discussed below that an independent determination of the equilibrium constant for protonation of the tricyano complex was needed. To do this, the apparent molar absorbancy index of the unreacted tricyanochromium(III) complex, ϵ_{tri}, was determined at 447 mμ as a function of perchloric acid concentration, as described in the Experimental Section. As shown in Figure 2

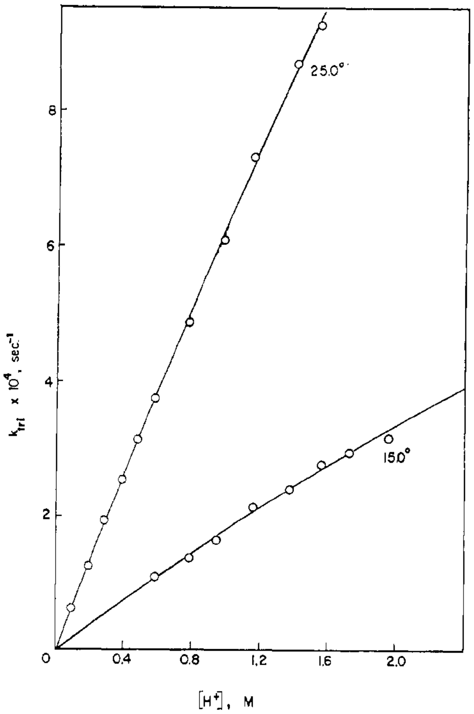

Figure 1.—Dependence of k_{tri}, the pseudo-first-order rate constant for the aquation of $Cr(H_2O)_3(CN)_3$, on hydrogen ion concentration at 15.0 and 25.0° and at an ionic strength of 2.0. The solid curves are calculated with eq 15 using the parameters given in Table II.

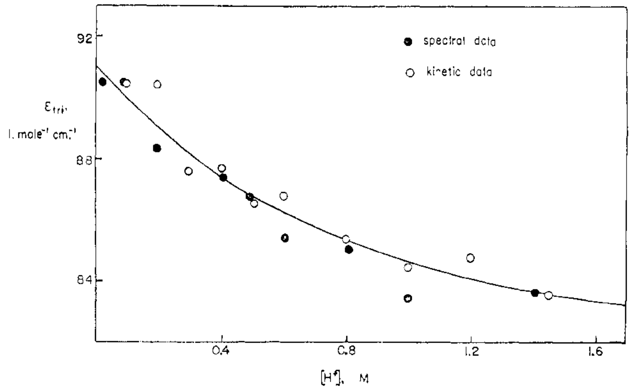

Figure 2.—Dependence of ϵ_{tri}, the apparent molar absorbancy index of solutions of tricyanochromium(III), on the hydrogen ion concentration at 447 mμ, 25.0°, and an ionic strength of 2.0. The curve shown is calculated from the equation $\epsilon_{tri} = (\epsilon_{CN} + \epsilon_{CNH}K_1 \cdot [H^+])/(1 + K_1[H^+])$, where ϵ_{CN} is 91.3 l. mol^{-1} cm^{-1}, ϵ_{CNH} is 79 l. mol^{-1} cm^{-1}, and K_1 = 1.1 l. mol^{-1}. (The open-circle points were obtained by extrapolation of independent spectral measurements to zero time; the solid points were obtained by the iterative treatment of the absorbancy *vs.* time kinetic data.)

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[17] K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, p 567.

(solid points), the values of ϵ_{tri} obtained decrease with increasing hydrogen ion concentration at this wavelength, indicating protonation of the tricyanochromium(III) molecule

$$\text{1,2,3-Cr(H}_2\text{O)}_3\text{(CN)}_3 + \text{H}^+ \xrightleftharpoons{K_1} \text{Cr(H}_2\text{O)}_3\text{(CN)}_2\text{(CNH)}^+ \quad (6)$$

Protonation of a coordinated ligand would be expected to decrease its ligand field strength, causing the spectral bands to shift toward longer wavelengths and the absorbance at 447 mμ to decrease.[5,7]

Assuming that only the nonprotonated and singly protonated tricyanochromium(III) species are present in solution in detectable amounts, the apparent molar absorbancy index, ϵ_{tri}, can be expressed in terms of the protonation equilibrium constant, K_1, and the hydrogen ion concentration, *i.e.*

$$\epsilon_{\text{tri}} = \frac{\epsilon_{\text{CN}} + \epsilon_{\text{CNH}}K_1[\text{H}^+]}{1 + K_1[\text{H}^+]} \quad (7)$$

where ϵ_{CN} and ϵ_{CNH} represent the molar absorbancy indices of the nonprotonated and protonated forms of tricyanochromium(III), respectively. Equation 7 can be rearranged into a more useful linear form

$$\frac{1}{(\epsilon_{\text{CN}} - \epsilon_{\text{tri}})} = \frac{1}{(\epsilon_{\text{CN}} - \epsilon_{\text{CNH}})} + \frac{1}{(\epsilon_{\text{CN}} - \epsilon_{\text{CNH}})K_1}\,\frac{1}{[\text{H}^+]} \quad (8)$$

For the data at 25°, the value of ϵ_{CNH} was calculated from the intercept of a plot of $1/(\epsilon_{\text{CN}} - \epsilon_{\text{tri}})$ *vs.* $1/[\text{H}^+]$, and K_1 was evaluated from the ratio of the intercept to the slope. The value ϵ_{CN} 91.3 l. mol^{-1} cm^{-1} is known from the spectrum of the tricyano complex recorded at pH $\simeq$3. A proton association constant, $K_1 = 1.1 \pm 0.4$ l. mol^{-1}, and a molar absorbancy index for the protonated tricyanochromium(III) complex at 447 mμ, ϵ_{CNH} 79 ± 2 l. mol^{-1} cm^{-1}, were obtained using all the values of ϵ_{tri} shown in Figure 2. The confidence limits reported correspond to one unit of standard deviation. Using these least-squares best values of K_1 and ϵ_{CNH} and the previously known value of ϵ_{CN}, the average difference between the experimental values of ϵ_{tri} at each acidity and the calculated values (eq 7) was 0.5% for all the data points.

There were insufficient spectral data to allow a similar calculation of the protonation equilibrium constant at 15.0°. However, if the temperature dependence of ϵ_{CNH} is assumed to be the same as that of ϵ_{CN} (at 447 mμ, ϵ_{CN} is 93.0 and 91.3 l. mol^{-1} cm^{-1} at 15.0 and 25.0°, respectively), then an ϵ_{CNH} value of 80.3 l. mol^{-1} cm^{-1} at 15.0° can be estimated from the difference $\epsilon_{\text{CN}} - \epsilon_{\text{CNH}}$ obtained from the 25° data. Using this assumption K_1 was calculated with eq 7 using the values of ϵ_{tri} obtained from the iterative treatment of the kinetic data (eq 5). A protonation equilibrium constant of 0.9 ± 0.4 l. mol^{-1} was obtained at 15.0°. A decrease in the value of the proton association constant with decreasing temperature was also observed in the case of the dicyanochromium(III) complex.[6]

Interpretation and Discussion

In acidic aqueous solutions containing the tricyanotriaquochromium(III) complex, the singly protonated and nonprotonated forms of this complex are predominant in solution. These species may undergo aquation to the *cis*-dicyanochromium(III) ion, as illustrated stoichiometrically by the reactions

$$\text{1,2,3-Cr(H}_2\text{O)}_3\text{(CN)}_3 + \text{H}_2\text{O} \xrightarrow{k_0} cis\text{-Cr(H}_2\text{O)}_4\text{(CN)}_2^+ + \text{CN}^- \quad (9)$$

$$\text{Cr(H}_2\text{O)}_3\text{(CN)}_2\text{(CNH)}^+ + \text{H}_2\text{O} \xrightarrow{k_1} cis\text{-Cr(H}_2\text{O)}_4\text{(CN)}_2^+ + \text{HCN} \quad (10)$$

where k_0 and k_1 represent the first-order rate constants for the aquation of the nonprotonated and protonated forms, respectively. Under pseudo-first-order conditions of constant hydrogen ion concentration, consideration of reactions 6, 9, and 10 leads to the rate law

$$\frac{-\mathrm{d}C_{\text{tri}}}{\mathrm{d}t} = \frac{(k_0 + k_1K_1[\text{H}^+])C_{\text{tri}}}{1 + K_1[\text{H}^+]} = k_{\text{tri}}C_{\text{tri}} \quad (11)$$

where C_{tri} refers to the total concentration at time t of the tricyanochromium(III) complex in both protonated and nonprotonated forms and k_{tri} is the observed pseudo-first-order rate constant. The rate law given in eq 11 was found to apply to the aquation reactions of the cyanopentaaquochromium(III),[5] the dicyanotetraaquochromium(III),[6] and the acetatopentaaquochromium(III)[18] ions.

If the values of k_{tri} calculated from eq 5 for the tricyano complex are treated in terms of this rate law in the usual manner, a protonation equilibrium constant, $K_1 = 0.07$ l. mol^{-1}, is obtained from the data at 25.0°. This value is unreasonably small in comparison with the constants calculated from kinetic data for the dicyano complex (0.21 l. mol^{-1}) and for the monocyano complex (0.19 l. mol^{-1}), both of which have a higher positive charge and should protonate less readily. This kinetic value of K_1 also clearly disagrees with the more reasonable value of 1.1 l. mol^{-1} obtained for K_1 in independent spectrophotometric measurements of the dependence of the molar absorbancy index of the tricyano complex upon hydrogen ion concentration. Possible explanations for the unexpectedly small value of K_1 obtained from the kinetic data include medium effects and the presence of another reaction pathway with a higher order dependence upon hydrogen ion.

Medium effects do not appear to be responsible for the comparatively small value of K_1 obtained for the tricyano complex (in comparison with the values for the dicyano and monocyano complexes) because the kinetic data were obtained in the same acid–salt medium at the same ionic strength and over approximately the same range of acid concentrations in all three cases. Furthermore, the spectrophotometric value of K_1 measured in the same solutions is reasonable. Deutsch and Taube[18] found only a small difference in the values of K_1 evaluated by the same two methods for the acetatopentaaquochromium(III) ion, *i.e.*, 0.20 l. mol^{-1} from kinetic data and 0.33 l. mol^{-1} from spectral data, and suggested that the K_1 values obtained by the two methods should be expected to agree within an order of magnitude. In our previous study of the dicyano com-

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(18) E. Deutsch and H. Taube, *Inorg. Chem.*, **7**, 1532 (1968).

plex under the same conditions used in the present study, a much smaller difference was also observed: 0.21 l. mol^{-1} for the kinetic value and 0.55 l. mol^{-1} for the spectral value. For these reasons we conclude that the large discrepancy in the value of K_1 of the tricyano complex obtained by the two methods (a factor of 16) cannot be attributed to medium effects. We believe, rather, that reactions 6, 9, and 10 do not represent all the significant aquation pathways for the tricyano complex and that a pathway with a higher order dependence upon hydrogen ion becomes important at higher acidities. Such a pathway would tend to accelerate the aquation at higher acidities, thereby decreasing the curvature of a plot of k_{tri} *vs.* $[H^+]$ and causing the apparent value of K_1 evaluated from the kinetic data to be too low.

The equilibrium constants for the protonation of the tricyano- (spectrophotometric value), dicyano-, and monocyanochromium(III) complexes appear to change by a factor of not more than 2 or 3 with each increase of one unit of positive charge as cyanide ligands are replaced by water molecules. Because additional proton-acceptor sites are available on the tricyano complex and because addition of a second proton to the tricyano complex would still result in a protonated species with a positive charge no larger than that of the singly protonated dicyanochromium(III) ion, a reasonable additional aquation pathway could involve a doubly protonated form of the tricyano complex.

Addition of more than one proton to complexes containing more than one cyanide ligand has been proposed previously. In their studies of the acid-catalyzed aquation of cyanonitrosylchromium(III) complexes, Burgess, *et al.*,[19] concluded that the kinetic data indicated only single protonation in the case of the monocyano complex $Cr(CN)(H_2O)_4NO^+$, but supported double protonation in the case of the dicyano species $Cr(CN)_2(H_2O)_3NO^0$. Esr studies on these complexes indicated that the protonation occurred on the cyanide ligands rather than on the nitrosyl group. In other studies of protonation of cyano complexes, Schilt[20] reported evidence for the addition of two protons to both Fe(*o*-phen)$_2$(CN)$_2$ and Fe(dipy)$_2$(CN)$_2$ and concluded from infrared evidence that the protonation occurs on the nitrogen atom of the cyanide ligand.

Adding a reaction for the second protonation of the tricyano complex and another for the subsequent aquation of the doubly protonated species, reactions 12 and 13, to reactions 6, 9, and 10 leads to the general rate law (eq 14) for the three paths, where K_2 refers to the second protonation equilibrium constant and k_2 is the first-order rate constant for aquation of the doubly protonated complex.

$$Cr(H_2O)_3(CN)_2(CNH)^+ + H^+ \overset{K_2}{\rightleftharpoons} Cr(H_2O)_3(CN)(CNH)_2{}^{2+} \qquad (12)$$

$$Cr(H_2O)_3(CN)(CNH)_2{}^{2+} + H_2O \xrightarrow{k_2} cis\text{-}Cr(H_2O)_4(CN)(CNH)^{2+} + HCN \qquad (13)$$

$$\frac{-dC_{tri}}{dt} = \frac{(k_0 + k_1K_1[H^+] + k_2K_1K_2[H^+]^2)C_{tri}}{1 + K_1[H^+] + K_1K_2[H^+]^2} = k_{tri}C_{tri} \qquad (14)$$

In the acidity range studied, the aquation of the tricyanochromium(III) molecule *via* the acid-independent pathway, reaction 9, is negligible and therefore k_0 can be omitted from the rate law. Also, if $(1 + K_1[H^+]) \gg K_1K_2[H^+]^2$, which seems likely, eq 14 reduces to the more simple form

$$\frac{-dC_{tri}}{dt} \cong \frac{(k_1K_1[H^+] + k_2K_1K_2[H^+]^2)C_{tri}}{1 + K_1[H^+]} \cong k_{tri}C_{tri} \qquad (15)$$

which describes the case in which the doubly protonated species is important kinetically but is never present in the solution in appreciable stoichiometric amounts.

It should be noted that the postulated reactions giving rise to the rate law represented by eq 14 or 15 are not the only possibilities. For example, eq 15 can also be derived from reactions in which the rate-determining steps are proton attacks on the unprotonated species $Cr(CN)_3(H_2O)_3$ and the singly protonated species $Cr(CN)_2(CNH)(H_2O)_3{}^+$. Although the data do not allow a choice to be made between these alternate sets of reactions, we feel that the reactions proposed above are to be preferred in view of the evidence cited for the possible addition of more than one proton to other polycyanochromium(III) complexes[19,20] and in view of the differences in the kinetic behavior of the tricyano complex compared to that of the monocyano and dicyano complexes, where the protonation should be much less.

Equation 15 can be rearranged to give an equation linear in $[H^+]$

$$k_{tri}\left(\frac{1}{[H^+]} + K_1\right) = k_1K_1 + k_2K_1K_2[H^+] \qquad (16)$$

Very good straight lines were obtained for plots of $k_{tri} \cdot (1/[H^+] + K_1)$ *vs.* $[H^+]$ using the experimental data at 15.0 and 25.0° and using the values of K_1 obtained spectrophotometrically, as shown in Figure 3. The rate parameters k_1 and k_1K_1 were evaluated from the intercepts and the product k_2K_2 was calculated from the slopes of these plots using the method of least squares. All data points were weighted according to the inverse squares of the quantity $k_{tri}(1/[H^+] + K_1)$. The values of k_1, k_1K_1, and k_2K_2 obtained are shown in Table II and were used to calculate the solid lines in Figure 1.

The values of k_{tri} calculated with these rate parameters using the rate law given in eq 15 are in excellent agreement with the experimental values (Table I) over the entire range of acidity. The average difference between the experimental and calculated values is 1.1% for the data at 25° and 1.9% for the data at 15°. Because the rate law which includes a $[H^+]^2$ term (eq 15) agrees somewhat better with the experimental data than the simpler rate law which takes into account only the singly protonated complex (eq 11) and, in addition, because it incorporates a value of K_1 consistent with that obtained by an independent spectrophotometric method, we believe that the rate law for the aquation of the tricyano complex is described better by eq 15 than by eq 11.

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[19] J. Burgess, G. Goodman, and J. Raynor, *J. Chem. Soc. A*, 501 (1968).

[20] A. A. Schilt, *J. Amer. Chem. Soc.*, **85**, 904 (1963).

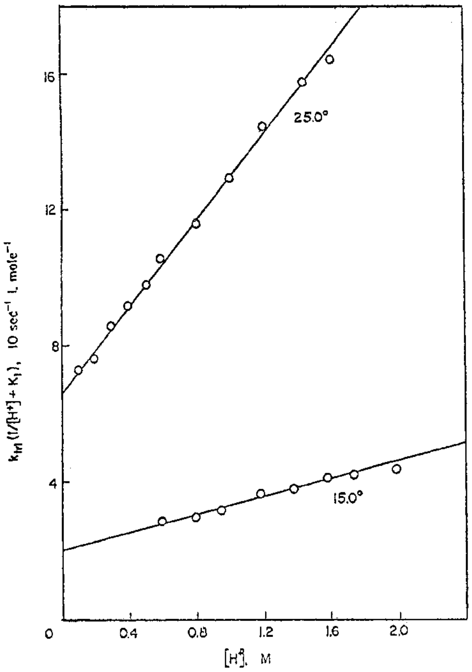

Figure 3.—Plots of $k_{tri}(1/H^+] + K_1)$ *vs.* hydrogen ion concentration for data obtained at 15.0 and 25.0° and at an ionic strength of 2.0 (sodium perchlorate). The straight lines are calculated with the equation $k_{tri}(1/[H^+] + K_1) = k_1K_1 + k_2K_1K_2[H^+]$, where at 15.0° $k_1 = 2.2 \times 10^{-4}$ sec^{-1}, $K_1 = 0.9$ l. mol^{-1}, and $k_2K_2 = 1.5 \times 10^{-4}$ sec^{-1} l. mol^{-1}, while at 25.0° $k_1 = 5.8 \times 10^{-4}$ sec^{-1}, $K_1 = 1.1$ l. mol^{-1}, and $k_2K_2 = 5.6 \times 10^{-4}$ sec^{-1} l. mol^{-1}.

TABLE II

RATE PARAMETERS FOR THE AQUATION OF 1,2,3-TRICYANOTRIAQUOCHROMIUM(III) AND *cis*-DICYANOTETRAAQUOCHROMIUM(III) ION ACCORDING TO THE RATE LAW

$$\frac{-\mathrm{d(complex)}}{\mathrm{d}t} = \frac{(k_0 + k_1K_1[H^+] + k_2K_1K_2[H^+]^2)C_t}{1 + K_1[H^+]}$$

1,2,3-Tricyanotriaquochromium(III)

Rate paramteer	15.0°	25.0°
10^4k_1, sec^{-1}	2.2 ± 1.0	5.8 ± 2.3
K_1, l. mol^{-1}	0.9 ± 0.4	1.1 ± 0.4
$10^4k_1K_1$, sec^{-1} l. mol^{-1}	2.00 ± 0.12	6.63 ± 0.15
$10^4k_2K_2$, sec^{-1} l. mol^{-1}	1.5 ± 0.1	5.6 ± 0.4

cis-Dicyanotetraaquochromium(III) ion

Rate parameter	15.0°	25.0°	35.0°
10^4k_0, sec^{-1}	...	...	0.18 ± 0.2
10^4k_1, sec^{-1}	5.6 ± 2.2	15 ± 6	38 ± 15
K_1, l. mol.$^{-1}$	0.47 ± 0.2	0.55 ± 0.22	0.72 ± 0.3
$10^4k_1K_1$, sec^{-1} l. mol^{-1}	2.63 ± 0.05	8.44 ± 0.17	27.0 ± 0.5
$10^4k_2K_2$, sec^{-1} l. mol^{-1}	1.0 ± 0.3	4.1 ± 0.1	14 ± 3

TABLE III

RATE AND ACTIVATION PARAMETERS FOR THE AQUATION OF CYANOAQUOCHROMIUM(III) COMPLEXES ACCORDING TO THE RATE LAW

$$\frac{-\mathrm{d(complex)}}{\mathrm{d}t} = \frac{(k_0 + k_1K_1[H^+] + k_2K_2[H^+]^2)C_t}{1 + K_1[H^+]}$$

A. Rate Parameters at 25.0[a]

Complex	10^5k_0, sec^{-1}	10^4k_1, sec^{-1}	K_1, l. mol^{-1}	$10^4k_1K_1$, sec^{-1} l. mol^{-1}	$10^4k_2K_2$, sec^{-1} l. mol^{-1}
$Cr(H_2O)_3(CN)_3$	(<0.3)	5.8 ± 2.3	1.1 ± 0.4	6.6 ± 0.2	5.6 ± 0.4
$Cr(H_2O)_4(CN)_2^+$	(<0.6)	15 ± 6	0.55 ± 0.22	8.4 ± 0.2	4.1 ± 1
$Cr(H_2O)_5CN^{2+}$	1.1 ± 0.1	32 ± 1	0.19 ± 0.01	5.90 ± 0.05	0.00

B. Activation Parameters[a]

Complex	Rate parameter	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}
$Cr(H_2O)_5CN^{2+}$	k_0	26.9 ± 0.3	+8.9 ± 1.1
$Cr(H_2O)_3(CN)_3$	k_1	16 ± 6	−19 ± 9
$Cr(H_2O)_4(CN)_2^+$	k_1	16 ± 5	−18 ± 7
$Cr(H_2O)_5CN^{2+}$	k_1	16 ± 2	−16 ± 4
$Cr(H_2O)_3(CN)_3$	k_1K_1	19.0 ± 0.8	−6.4 ± 1.1
$Cr(H_2O)_4(CN)_2^+$	k_1K_1	20.0 ± 0.2	−5.5 ± 0.7
$Cr(H_2O)_5CN^{2+}$	k_1K_1	20.2 ± 0.1	−5.5 ± 0.3
$Cr(H_2O)_3(CN)_3$	k_2K_2	22 ± 1	+0.4 ± 1.3
$Cr(H_2O)_4(CN)_2^+$	k_2K_2	22 ± 1	+1.4 ± 3

[a] The ionic strengths of the perchloric acid–sodium perchlorate solutions were adjusted to 2.0 in all cases; the uncertainties given correspond to one unit of standard deviation.

The aquation of the tricyano complex is an interesting example of a reaction for which a plausible, well-fitting rate law involving a simple first-order concentration dependence has to be rejected because the values of the parameters involved are considered to be unreasonable in comparison with those of other closely related members of the series of complexes.

The activation parameters for the aquation of tricyanochromium(III) corresponding to the individual rate parameters k_1, k_1K_1, and k_2K_2 were calculated using Eyring's transition-state equation ($\kappa = 1$) and are in Table III.

Recalculation of Data for *cis*-Cr(CN)$_2$(H$_2$O)$_4$$^+$.—In the previous paper in this series concerning the aquation of *cis*-dicyanochromium(III) ion,[6] a small difference, significant at the 85% confidence level, was noted in the values for the protonation equilibrium constant determined at 25° from the dependence on hydrogen ion concentration of the kinetic data (0.21 ± 0.03 l. mol^{-1}) and of the spectral data (0.55 ± 0.2 l. mol^{-1}). Because this discrepancy could possibly arise for the same reason postulated for the much larger discrepancy in the case of the tricyano complex, the kinetic data for the aquation of the dicyano complex were reinterpreted to take into account a [H$^+$]^2 term according to the rate law given in eq 15. A procedure similar to that used for tricyanochromium(III) (eq 16) was used to obtain the rate parameters k_1, k_1K_1, and k_2K_2 for the aquation of *cis*-dicyanochromium(III) at 15.0 and 25.0°. At 35.0° the acid-independent pathway is not negligible and the rate parameters were obtained from plots of $k_{di}(1/[H^+] + K_1) - k_0/[H^+]$ *vs.* $[H^+]$. The spectrophotometric values of K_1 used to recalculate the rate parameters for the aquation of the dicyano complex were 0.47 ± 0.2, 0.55 ± 0.2, and 0.7 ± 0.3 l. mol^{-1} for the data at 15, 25, and 35°, respectively.[6] The value of k_0 used was that obtained from the treatment of the data assuming a single protonation. The rate parameters obtained by this approach for the dicyano complex are included in Table II. Recalculated values for the activation parameters for the dicyano complex are included in Table III, together with the rate and activation parameters for the monocyano and tricyano complexes.

The pseudo-first-order rate constants calculated from these new rate parameters for the aquation of the dicyano complex at 15 and at 25° agree somewhat better with the experimental values (1.2% average deviation) than the rate constants calculated from the parameters obtained by treating the kinetic data in terms of only a single protonation step (1.5% average deviation).[6] For the data at 35°, the average deviation between calculated and observed k_{di} values decreased from 1.24 to 0.54% when a $[H^+]^2$ term was included in the rate law. Similar values for the product k_1K_1 are obtained regardless of which of the two rate laws is used (eq 11 or 15). The recalculated values for the rate parameters for the dicyano complex seem very reasonable when compared to the corresponding values for the monocyano and tricyano species.

Comparison of Results for Mono-, Di-, and Tricyano Complexes.—Aquation *via* an acid-independent pathway was observed to be significant only for the monocyanochromium(III) ion[5,8] and for the *cis*-dicyanochromium(III) ion[6] at 35.0°. Because of its positive entropy of activation, this pathway is thought to proceed *via* a mechanism which involves an intramolecular proton transfer from a coordinated water molecule to the cyanide ligand, yielding a hydroxo ligand and a protonated cyanide ligand in the transition state.[5,8] The rate of an aquation reaction involving such a proton-transfer mechanism should depend upon both the acidity and the number of water molecules coordinated at positions cis to the cyanide ligand and should depend upon the basicity of the ligand involved. Although the basicity of the cyanide ligands decreases only gradually as the number of coordinated cyanide groups decreases and the positive charge on the complex increases (see values of K_1 in Table III), the acidity of the coordinated water molecules increases sharply in this series of complexes.[21] Because the changes in proton-donating ability in this series of complexes are greater than the changes in proton-accepting ability, aquation *via* an intramolecular proton-transfer mechanism should become more important as the number of coordinated cyanide groups decreases and the positive charge increases, which is in agreement with the observed results. This increasing rate for the acid-independent aquation reaction with decreasing number of ligands is unusual. In most other similar series, the rate of aquation increases by at least an order of magnitude with each additional substituted anionic ligand.[6]

All the cyanoaquochromium(III) complexes studied exhibit an acid-assisted aquation pathway which is thought to involve first the protonation of a cyanide ligand, described by the equilibrium constant K_1, and then the aquation of the singly protonated species, described by the rate constant k_1. The protonated intermediates are relatively stable and can be detected in appreciable amounts in solution by spectrophotometric measurements. The values of K_1 decrease regularly with an increase in the positive charge of the complex, but the rate of decrease between successive complexes is surprisingly small. If this initial protonation involves the nitrogen atom of the bound cyanide, as has been suggested for other similar cyano complexes,[19,20] these small changes in K_1 may be due to a strengthening of the Cr–C bond and concomitant weakening of the C–N bond as the overall positive charge on the complexes increases, thus rendering the nitrogen more basic than would be predicted on the basis of the relative overall charges of the complexes.

Other interesting features of the acid-assisted pathway are the great similarity in the values of k_1K_1 for these three complexes, due to the canceling effect of opposing trends, and the increasing trend in the values of k_1 with increasing overall positive charge on the complexes. Since the leaving group is a neutral molecule, in this case protonated cyanide, the reaction rate would not be expected to show as much dependence on charge as is usually observed for the loss of an anionic ligand.[22] Nevertheless, the rate of replacement of a strongly coordinated ligand would normally be expected to decrease with an increase in the positive charge of the complex. The explanation for this unusual increasing trend may be similar to that advanced above to account for the trends in the values of k_0 and may lie in the possible involvement of coordinated water molecules in the intimate aquation mechanism of the protonated complex. As the positive charge on the complex increases, there is also an increase in the number and the acidity of the coordinated water molecules, and the fact that the values of k_1 parallel the number and acidity of the water molecules rather than the expected decreasing strength of the Cr–C bond argues for an important role for the water molecules in the transition state. It is possible that water molecules coordinated cis to a protonated cyanide ligand could aid, *via* hydrogen bonding, either in the stabilization of an entering water molecule or in

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(21) Preliminary work by G. D. Jimerson in this laboratory on the acid-base properties of these cyanoaquo complexes indicates that the first deprotonation (acidity) equilibrium constants of the successive complexes in the series are as follows: pK_1 = 6.8, 5.9, 5.4, and 3.9, respectively, for $Cr(CN)_3(H_2O)_3$, *cis*-$Cr(CN)_2(H_2O)_4^+$, $Cr(CN)(H_2O)_5^{2+}$, and $Cr(H_2O)_6^{3+}$.

(22) N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966).

the stabilization of the protonated configuration of the cyanide ligand in the transition state. Although the initial protonation of the cyanide ligand is thought to occur on the nitrogen atom,[20] it is possible that the proton is transferred to the carbon atom in the activated complex and that in this configuration the proton is stabilized by an adjacent water molecule.

The activation parameters for k_1 are subject to rather large uncertainties and it is difficult to draw definite conclusions from them. If it is assumed that the trends in Table III are valid, then it is seen that $\Delta H^{\ddagger}$ is approximately constant for this series of complexes and $\Delta S^{\ddagger}$ becomes more negative in going from the monocyano to the tricyano complex. Since the Cr–C bond strength should increase with the increase in positive charge in going from the tricyano to the monocyano complex, a compensating factor must be involved which keeps the $\Delta H^{\ddagger}$ values for these complexes constant. This factor may be the involvement of coordinated water molecules in stabilizing the protonated cyanide ligand in its transition state, referred to above. This process should be more favorable for the monocyano complex than for the others and should act to decrease the activation energy.

Because of its greater positive charge, the solvent water molecules should be drawn closest and should be most highly ordered in the case of the monocyano complex, and the least amount of additional ordering would be needed to bring an incoming (substituting) water molecule into its transition-state position (whatever that may be). The value of $\Delta S^{\ddagger}$ for the aquation of the monocyano complex should therefore be less negative than for the dicyano complex and, similarly, the value of $\Delta S^{\ddagger}$ for the dicyano aquation reaction should be less negative than the value for the tricyano reaction, in agreement with experiment.

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Hydrogen and Metal Complexes of Some 3-Cyanoformazans

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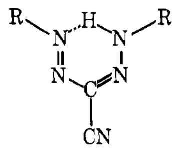
1,5-Bis(2-hydroxyphenyl) (I), 1,5-bis(2-hydroxy-4-nitrophenyl) (II), 1,5-bis(2-hydroxy-5-sulfophenyl) (III), 1,5-bis(2-carboxyphenyl) (IV), 1,5-bis(2-arsonophenyl) (V), 1,5-bis(8-quinolyl) (VI), 1,5-bis(8-quinaldyl) (VII), and 1,5-bis(4-antipyrinyl) (VIII) derivatives of 3-cyanoformazan were prepared and their hydrogen and metal complexes were investigated. The investigation involved the following metals: calcium, scandium, lanthanum, thorium, vanadium(V), molybdenum(VI), manganese(II), iron(II), iron(III), cobalt(II), nickel, copper(II), palladium(II), zinc, cadmium, mercury(II), lead(II), and bismuth. Complex ZnH_2L of compound VI and complexes CuL and PdL of compound VIII are of unusual stability. The values of logarithmic overall stability constants are 32.4, 28.2, and 28.1, respectively.

Introduction

The formazan skeleton is a good carrier of π-bonding and chelating properties. Wizinger with coworkers[1,2] prepared several derivatives of 1,5-bis(2-hydroxyphenyl)formazan and 1,5-bis(2-carboxyphenyl)formazan and investigated the composition of the solid chromium(III), copper(II), and nickel complexes. Hunter and Roberts[3] pointed out the symmetry of the formazan molecule as a basic requirement for its good chelating and chromogenic properties. Recently, Dziomko and his coworkers[4,5] investigated 1,5-bis(2-hydroxyphenyl)formazan and some of its derivatives as extractants for metals.

The interesting metallochromic properties and ease of preparation were why we investigated the complexation of some 3-cyanoformazans; see formula A.



A

I, R = 2-hydroxyphenyl
II, R = 2-hydroxy-4-nitrophenyl
III, R = 2-hydroxy-5-sulfophenyl
IV, R = 2-carboxyphenyl
V, R = 2-arsonophenyl
VI, R = 8-quinolyl
VII, R = 8-quinaldyl
VIII, R = 4-antipyrinyl

Experimental Section

Apparatus.—All photometric measurements were made with a double-beam Unicam 800B recording spectrophotometer. Quartz cells (1 cm) were used throughout. An Orion Model 801 pH

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