The Rate of Aquation of *cis*-Dicyanotetraaquochromium(III) Ion in Acidic Aqueous Solution[1]
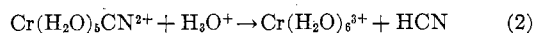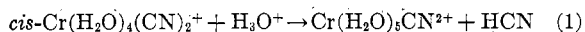
BY DIANE K. WAKEFIELD[2] AND WARD B. SCHAAP

The kinetics of the aquation of the *cis*-dicyanotetraaquochromium (III) ion were studied in acidic aqueous solution. Under these conditions, the aquation proceeds *via* acid-independent and acid-catalyzed pathways. The hydrogen ion dependence of both the kinetic data and the spectrum of the complex indicates that substantial protonation of the complex occurs, especially at higher acidities. The aquation reaction is described by the rate law $-dC_t/dt = (k_0 + kK_1[\text{H}^+])C_t/(1 + K_1[\text{H}^+])$, where C_t is the total concentration of the complex in protonated and nonprotonated forms. At 35° in perchloric acid–sodium perchlorate solutions of ionic strength 2.0, the rate constant for the acid-independent path (k_0) is $(1.8 \pm 0.2) \times 10^{-5}$ sec^{-1}, while for the acid-assisted path the rate constant is $k_1 = (1.0 \pm 0.1) \times 10^{-2}$ sec^{-1}. The equilibrium constant for the protonation reaction (K_1) was calculated from the kinetic data to be $0.26 \pm 0.03 M^{-1}$, and from spectrophotometric data to be 0.7 ± 0.3 M^{-1}. The product $k_1K_1 = (2.65 \pm 0.03) \times 10^{-3}$ sec$^{-1} M^{-1}$. From aquation rate measurements carried out at 15, 25, and 35°, activation parameters were calculated for the product k_1K_1 to be $\triangle H^{\neq} = 19.9 \pm 0.1$ kcal mol^{-1} and $\triangle S^{\neq} = -5.9 \pm 0.3$ eu.

Introduction

In previous studies in this laboratory[3a] and in those by Birk and Espenson, [3b] the kinetics of aquation of the cyanopentaaquochromium(III) ion were investigated in acidic solutions. In the present paper the aquation of its precursor, the dicyanotetraaquochromium(III) ion, is considered. The aquation of the latter species proceeds in acidic aqueous solutions *via* stepwise replacement of the cyanide ligands by water to yield first the cyanopentaaquo complex and then the hexaaquochromium(III) ion as the final product.

$$\text{cis-Cr(H}_2\text{O)}_4\text{(CN)}_2^+ + \text{H}_3\text{O}^+ \rightarrow \text{Cr(H}_2\text{O)}_5\text{CN}^{2+} + \text{HCN} \quad (1)$$

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

The complete aquation of *cis*-dicyanotetraaquochromium(III) ion represents the last two steps in the complete aquation of hexacyanochromate(III) anion, which was first observed by Krishnamurthy in this laboratory[4-6] and which has been shown to proceed *via* a series of stereospecific reactions in which only *cis* isomers are formed; *i.e.*, the incoming water molecule is directed exclusively to positions *cis* to previously substituted water molecules. This stereochemical specificity greatly simplifies the interpretation of the aquation rate data and eliminates complications encountered in some of the other kinetic studies of disubstituted tetraaquochromium(III) complexes.[7-10]

All of the intermediate cyanoaquochromium(III) complexes formed in the complete aquation of the hexacyanochromate(III) ion have been isolated and identified.[4-6] They provide an interesting series of complexes for studying the effects of such factors as charge, number of ligands, stereochemical configurations, and acid–base properties on the rates and parameters of aquation reactions.

Experimental Section

Reagents.—Solutions containing *cis*-dicyanotetraaquochromium(III) ion, Cr(H$_2$O)$_4$(CN)$_2^+$ (hereafter called dicyanochromium(III) ion), 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. Procedures used for preparing the hydrolysis mixture and for the separation and identification of the dicyanochromium(III) ion have been described elsewhere.[3a] The pH of stock solutions of dicyanochromium(III) ion was adjusted to about 2.5 and the solutions were stored in darkness at 0° for no more than 3 days before use.

Kinetic Measurements.—The aquation reactions of the *cis*-dicyanochromium(III) ion were carried out directly in a 10-cm thermostated silica spectrophotometric cell. Procedures used for handling solutions, for taking spectrophotometric measurements, and for performing the chemical analyses were the same as described previously.[3a] Reactions were followed at 447 mμ, where the monocyanochromium(III) and hexaaquochromium(III) ions have an isosbestic point which is independent of the hydrogen ion concentration. At this isosbestic point the molar absorbancy indices of *cis*-dicyanochromium(III) ion and monocyanochromium(III) ion (equal to that of hexaaquochromium(III) ion) are 38.8 and 7.14 M^{-1} cm^{-1}, respectively, in aqueous sodium perchlorate solution at pH 2.5.

In all experiments the aquation reactions eventually went to completion, giving final solutions whose spectra were identical with that of the hexaaquochromium(III) ion. The hydrogen ion concentration remained essentially constant during each reaction because it was at least 50 times the concentration of the *cis*-

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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.

(3) (a) D. K. Wakefield and W. B. Schaap, *Inorg. Chem.*, **8**, 512 (1969); (b) J. P. Birk and J. H. Espenson, *ibid.*, **7**, 991 (1968).

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

(5) R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, **6**, 1338 (1967).

(6) R. Krishnamurthy, Ph.D. Thesis, Indiana University, 1966.

(7) E. Jorgensen and J. Bjerrum, *Acta Chem. Scand.*, **12**, 1047 (1958).

(8) H. G. Johnson and W. L. Reynolds, *Inorg. Chem.*, **2**, 468 (1963).

(9) C. W. Merideth, W. D. Mathew, and E. F. Orlemann, *ibid.*, **3**, 320 (1964).

(10) J. D. Salzman and E. L. King, *ibid.*, **6**, 426 (1967).

dicyanochromium(III) ion, which was $2 \times 10^{-3} M$. All reactions were followed for 3 or 4 half-lives and good pseudo-first-order rate plots of log $(A_t - A \infty)$ vs. time were obtained, where A_t is the absorbancy at time t and $A \infty$ is the absorbancy after more than 8 half-lives. The pseudo-first-order rate constants were obtained with the aid of a computer program[11] from the least-squares best slopes of the straight-line plots of ln $(A_t - A \infty)$ vs. time. The zero-time absorbance obtained by extrapolation of the rate plot was also computed and found to be dependent on the hydrogen ion concentration, decreasing with increasing acidity at 447 mμ. In experiments at high acidities, an instantaneous color change was noted when a solution of the *cis*-dicyanochromium(III) ion was mixed with a solution of perchloric acid and sodium perchlorate, suggesting that an appreciable spectral change occurs as a result of a rapid protonation of the dicyanochromium(III) ion.

Results

Aquation Kinetics.—The aquation of *cis*-dicyanochromium(III) ion was studied over a range of acidities of 0.10–1.6 M perchloric acid and at temperatures of 15.0, 25.0, and 35.0°. The ionic strength was adjusted to 2.0 with sodium perchlorate in all experiments. The pseudo-first-order rate constants for aquation reaction 1 were determined as described in the Experimental Section and are presented in Table I.
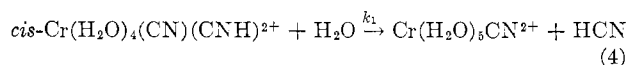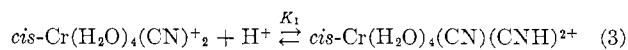
TABLE I

VALUES OF THE PSEUDO-FIRST-ORDER RATE CONSTANT FOR THE ACID-CATALYZED AQUATION OF *cis*-Cr(H$_2$O)$_4$(CN)$_2^+$ [a]

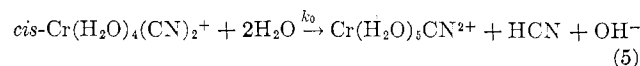| 15.0°		25.0°		35.0°	
[H$^+$], M	$10^4 k$, sec^{-1}	[H$^+$], M	$10^4 k$, sec^{-1}	[H$^+$], M	$10^4 k$, sec^{-1}
0.3970	0.925	0.1046	0.848	0.1069	2.95
0.5855	1.33	0.2123	1.72	0.2156	5.65
0.7947	1.82	0.3926	3.03	0.3058	7.68
0.9925	2.11	0.6026	4.39	0.4079	9.95
1.182	2.50	0.8045	5.84	0.5009	11.9
1.377	2.73	1.003	6.74	0.6092	14.1
1.576	3.09	1.200	7.97	0.8062	18.3
1.947	3.56	1.408	9.36	1.002	21.5

[a] Ionic strength adjusted to 2.0 with sodium perchlorate; initial concentration of Cr(H$_2$O)$_4$(CN)$_2^+$ was $2.0 \times 10^{-3} M$.

Although the reaction is acid catalyzed, the rate of aquation exhibits less than a first-order dependence on the hydrogen ion concentration. This type of hydrogen ion dependence is consistent with a two-step mechanism involving a rapid and reversible equilibrium protonation followed by a rate-limiting aquation of the protonated species, as given by reactions 3 and 4. A

$$cis\text{-Cr(H}_2\text{O})_4(\text{CN})^+{}_2 + \text{H}^+ \overset{K_1}{\rightleftarrows} cis\text{-Cr(H}_2\text{O})_4(\text{CN})(\text{CNH})^{2+} \quad (3)$$

$$cis\text{-Cr(H}_2\text{O})_4(\text{CN})(\text{CNH})^{2+} + \text{H}_2\text{O} \overset{k_1}{\rightarrow} \text{Cr(H}_2\text{O})_5\text{CN}^{2+} + \text{HCN} \quad (4)$$

similar two-step mechanism was postulated for the aquation of the monocyanochromium(III) ion[3a] and for the aquation of the acetatopentaaquochromium-(III) ion at high ionic strengths by Deutsch and Taube.[12]

In addition to the acid-catalyzed aquation pathway, an acid-independent pathway is also evident from the data at 35°. The over-all stoichiometry of this reaction can be represented as

$$cis\text{-Cr(H}_2\text{O})_4(\text{CN})_2{}^+ + 2\text{H}_2\text{O} \overset{k_0}{\rightarrow} \text{Cr(H}_2\text{O})_5\text{CN}^{2+} + \text{HCN} + \text{OH}^- \quad (5)$$

At the other (lower) temperatures involved in this study, this aquation pathway was found to be negligible over the acidity range covered in comparison with the acid-catalyzed pathway.

Under pseudo-first-order conditions of constant hydrogen ion concentration, combination of eq 3–5 leads to the rate law

$$\frac{-\mathrm{d}C_t}{\mathrm{d}t} = \frac{(k_0 + k_1 K_1[\text{H}^+])C_t}{1 + K_1[\text{H}^+]} = k_{\text{obsd}}C_t \quad (6)$$

Equation 6 can be rearranged to give

$$\frac{1}{k_{\text{obsd}} - k_0} = \frac{1}{k_1 - k_0} + \frac{1}{(k_1 - k_0)K_1}\frac{1}{[\text{H}^+]} \quad (7)$$

A plot of $1/(k_{\text{obsd}} - k_0)$ vs. $1/[\text{H}^+]$ should be linear and can be used to evaluate the constants k_0, k_1, and K_1. Once k_0 is estimated, k_1 can be calculated from the intercept and K_1 can be obtained from the ratio of the intercept to the slope. An iterative method of calculation, analogous to that described previously,[3a] was used to obtain the values of the rate parameters which minimized the deviations from eq 7. Excellent linear plots of $1/(k_{\text{obsd}} - k_0)$ vs. $1/[\text{H}^+]$ were obtained using the value of k_0 obtained from the iterative calculations.

At each temperature studied the rate parameters were calculated first using the data from only the five lowest acidity points, then from the six lowest points, and so on, until all of the points at each acidity were included. The rate parameters were also calculated from sets of data in which each of the points was omitted one at a time in order to detect the effect of a non-statistical "wild" measurement, but none was found. The values of k_0, k_1, and K_1 obtained from the various calculations were averaged and are presented in Table II, together with their confidence limits corresponding to one unit of standard deviation. The confidence limits of the slopes and intercepts of the reciprocal plots were calculated from standard equations[13] and were used to determine the confidence limits of the rate parameters. The over-all average deviation between the experimental values of k_{obsd} at each temperature and those calculated with eq 6 using the rate parameters given in Table II is 1.5%.

Although the variations in the values of the rate parameters remained within the calculated confidence limits as the number of points included in the calculation increased to include points from a larger acidity range, there appeared to be a slight decreasing trend in the value of K_1 obtained. For example, at 35.0°, as the range of points included increases from 0.1–0.5

(11) K. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1964, p 554.

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

(13) H. A. Laitinen, "Chemical Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 566.

TABLE II

RATE PARAMETERS FOR THE AQUATION OF THE
cis-DICYANOCHROMIUM(III) ION
ACCORDING TO THE RATE LAW

$$\frac{-dC}{dt} = \frac{(k_0 + k_1 K_1[H^+])C_t}{1 + K_1[H^+]}$$

Rate parameter[a]	15.0°	25.0°	35.0
$10^5 k_0$, sec^{-1}	...	$(<0.6)^b$	1.8 ± 0.2
$10^3 k_1$, sec^{-1}	1.3 ± 0.1	4.1 ± 0.6	10 ± 1
K_1, M^{-1}	0.19 ± 0.02	0.21 ± 0.03	0.26 ± 0.03
$10^4 k_1 K_1$, M^{-1} sec^{-1}	2.55 ± 0.05	8.34 ± 0.18	26.5 ± 0.3

a Ionic strength was adjusted to 2.0 with sodium perchlorate.
b This estimated upper limit for k_0 is not included in the calculation of the other parameters and their confidence limits at 25°.

Figure 1.—Dependence of the molar absorbancy index of solutions of the *cis*-dicyanochromium(III) ion, ϵ_s, on the hydrogen ion concentration at 25.0 and 15.0° and at an ionic strength of 2.0. Curves were calculated from $\epsilon_s = (\epsilon_{CN} + \epsilon_{CNH} K_1[H^+])/(1 + K_1[H^+])$, where $\epsilon_{CN} = 38.4$ and 39.2 M^{-1} cm^{-1}, $\epsilon_{CNH} = 27.9$ and 26.7 M^{-1} cm^{-1}, and $K_1 = 0.55$ and 0.37 M^{-1} at 25.0 and 15.0°, respectively.

to 0.1–1.0 *M* perchloric acid, the values of K_1 obtained are 0.297, 0.298, 0.221, and 0.244 M^{-1}. Moreover, when the data were tested for trends by calculating k_1 and K_1 from sets of data in which each set included only four consecutive data points, the value of K_1 decreased slightly as the data included in a set represented higher hydrogen ion concentrations. This suggests that a higher order hydrogen ion term may be detectable at higher acidities which would increase the rate of the reaction and decrease the curvature of the plot of k_{obsd} vs. [H$^+$] and the apparent value of K_1. Such trends in the data were not observed for the aquation of cyanopentaaquochromium(III) ion, which has only one basic ligand group and for which medium effects should have been even more important because of its higher charge.

Determination of the Protonation Equilibrium Constant K_1 from Spectral Data.—The observed molar absorbancy index ϵ_s of a solution containing dicyanochromium(III) ion at a given acidity was determined from the zero-time intercept of the rate plot. The dependence of ϵ_s on the hydrogen ion concentration at 447 mμ is shown in Figure 1. For the dicyano complex the absorbance of the solution, A_s, is given by

$$A_s = \epsilon_s C_t = \frac{(\epsilon_{CN} + \epsilon_{CNH} K_1[H^+])C_t}{1 + K_1[H^+]} \quad (8)$$

where C_t is the total concentration of *cis*-dicyanochromium(III) ion in both protonated and nonprotonated forms, and ϵ_{CNH} and ϵ_{CN} refer to the molar absorbancy indices of the protonated and the nonprotonated forms, respectively. Equation 8 can be rearranged to give

$$\frac{1}{\epsilon_s - \epsilon_{CN}} = \frac{1}{\epsilon_{CNH} - \epsilon_{CN}} + \frac{1}{(\epsilon_{CNH} - \epsilon_{CN})K_1} \frac{1}{[H^+]} \quad (9)$$

K_1 can be evaluated as the ratio of the intercept to the slope of a plot of $1/(\epsilon_s - \epsilon_{CN})$ vs. $1/[H^+]$. The method of least squares was used to calculate the slopes and intercepts of such plots. The errors in the difference $\epsilon_s - \epsilon_{CN}$ were judged to be proportional to the inverse of the hydrogen ion concentration. This suggests that a weighting factor of [H$^+$]^2 can be used to compensate for the relative errors in $1/(\epsilon_s - \epsilon_{CN})$. An additional weighting factor given approximately by [H$^+$]^2 was

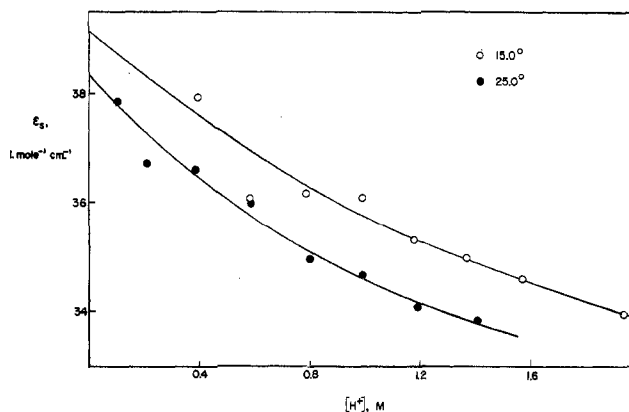introduced to compensate for the least-squares method of calculation. Therefore, the data points were weighted statistically in proportion to the fourth power of their hydrogen ion concentrations. At 25 and 15°, respectively, the values obtained for the equilibrium constant for protonation were 0.55 ± 0.20 and 0.37 ± 0.17 M^{-1}, while the values for the molar absorbancy index of the protonated complex at 447 mμ were found to be 27.9 and 26.7 M^{-1} cm^{-1}. Because the value of ϵ_s varies with temperature (Figure 1) and in order to allow for a reasonable uncertainty in the values of ϵ_{CN}, the confidence limits given include the values obtained from the calculation of K_1 using ϵ_{CN} ranging from 39.0 to 39.5 M^{-1} cm^{-1} at 15° and from 38.3 to 38.8 M^{-1} cm^{-1} at 25°. A meaningful value of K_1 was not obtained at 35.0° by this direct method because of the large error introduced in some experiments due to the appreciable decomposition of the complex (about 1–2%) through the acid-independent pathway during the time taken (over 20 min in some experiments) to warm the solutions for their storage temperature (0°) to 35°. If the difference $\epsilon_{CN} - \epsilon_{CNH}$ which is known from the data at 25° is assumed to be independent of temperature, however, a value of K_1 at 35° can be obtained using eq 8 and an estimated value of ϵ_{CNH}. A value of 0.7 ± 0.3 M^{-1} was calculated by this approach. Using a similar treatment of the spectral data obtained at 15°, a value for K_1 of 0.47 ± 0.2 was obtained, which is in fair agreement which the value of 0.37 obtained by direct calculation.

Discussion

Careful ion-exchange separations[3a] show that only the *cis* isomer of the dicyanochromium(III) complex is formed during the complete aquation of the hexacyanochromate(III) ion to give the hexaaquochromium(III) ion. Reactions involving *cis–trans* isomerization and/or the aquation of the *trans*-dicyanochromium(III) ion

therefore were not considered in the over-all reaction scheme for the aquation of the *cis*-dicyanochromium(III) ion.

The acid-catalyzed aquation pathway of the dicyano complex is interpreted most simply in terms of the protonation of the complex and the subsequent aquation of the singly protonated species, reactions 3 and 4. This interpretation is supported by the nonlinear hydrogen ion dependence of the aquation rate and in general by the instantaneous spectral changes observed upon addition of acid. On the other hand, at 25.0° the value of the protonation equilibrium constant, K_1, calculated from the spectral data ($0.55 \pm 0.20 M^{-1}$) is higher at the 85% confidence level, based on the precision of the two sets of results, than the value from the kinetic data ($0.21 \pm 0.03 M^{-1}$). A similar, though smaller, discrepancy was noted by Deutsch and Taube[12] in the protonation equilibrium constant for acetatopentaaquochromium(III) ion evaluated by the two methods. They suggested that their difference might be due to the nonconstancy of the activity quotient term relevant to one or both of the methods.

In the case of the dicyano complex, however, the presence of two basic ligands makes it possible that a reaction pathway involving the addition of a second proton might contribute to the aquation rate at higher acidities. This additional pathway can account for the decreasing trend in the values calculated for K_1 at higher acidities and for the discrepancy in the kinetic and spectrophotometric values of K_1. (We believe that the spectrophotometric value for K_1 is a better estimate of the true value than is the kinetic value, since the latter would be depressed by a contribution of a higher order pathway.) This additional pathway will be discussed in detail in a subsequent paper dealing with the acid-assisted aquation of the 1,2,3-tricyanotriaquo-chromium(III) complex. The significance of this pathway in the present study is too slight and tenuous to warrant its inclusion here.

The activation parameters corresponding to the product $k_1 K_1$ were determined using the Eyring transition-state equation ($\kappa = 1$). For the aquation of the *cis*-dicyanochromium(III) ion the activation parameters for $k_1 K_1$ are $\Delta H^{\ddagger} = 19.9 \pm 0.1$ kcal mol⁻¹ and $\Delta S^{\ddagger} = -5.9 \pm 0.3$ eu. These values are very similar to the corresponding values for the aquation reaction of monocyanochromium(III) ion, *i.e.*, 20.2 ± 0.1 kcal mol⁻¹ for $\Delta H^{\ddagger}$ and -5.5 ± 0.3 eu for $\Delta S^{\ddagger}$.

At 15.0 and 25.0° a negligible amount of the aquation of the *cis*-dicyanochromium(III) ion proceeds *via* the acid-independent pathway (reaction 5) under the experimental conditions employed; therefore, the activation parameters for the k_0 pathway could not be calculated. If the activation parameters for the k_0 pathway are similar to the corresponding ones for the monocyanochromium(III) ions,[3] one would expect this pathway to be negligible at these lower temperatures under the conditions studied.

An experimental value of k_0 was obtained from

measurements at 35.0°, where a larger portion of the reaction proceeds *via* the acid-independent pathway. This value of k_0 for the *cis*-dicyanochromium(III) ion is compared with that of the monocyanochromium(III) ion and other chromium(III) complexes[10,14-16] of interest in Table III. In general, the values of k_0 for disubstituted complexes with nonbasic ligands in a *cis* configuration and an over-all charge of 1+ are larger by a factor of at least 10 than the corresponding values for the monosubstituted complexes with a charge of 2+. In contrast to this, the k_0 value for the *cis*-dicyano complex is smaller by a factor of 2 than the value for the monocyanochromium(III) complex, indicating that with this strongly basic ligand a different mechanism may be operative.

TABLE III

ACID-INDEPENDENT RATE CONSTANTS FOR THE
AQUATION OF MONO- AND DISUBSTITUTED
BISETHYLENEDIAMINE AND AQUO COMPLEXES
OF CHROMIUM(III)

Complex	Temp, °C	$10^5 k_0$, sec⁻¹	Ref
cis-Cr(en)$_2$Br$_2$⁺	25	280	14
cis-Cr(en)$_2$(H$_2$O)Br²⁺	25	11.8	14
cis-Cr(en)$_2$Cl$_2$⁺	25	33	16
cis-Cr(en)$_2$(H$_2$O)Cl²⁺	25	2.8	16
cis-Cr(H$_2$O)$_4$Cl$_2$⁺	35	~8.2	10
Cr(H$_2$O)$_5$Cl²⁺	35	0.1	15
cis-Cr(H$_2$O)$_4$(CN)$_2$⁺	35	1.8	This study
Cr(H$_2$O)$_5$CN²⁺	35	4.0	3a

It has been postulated[3] on the basis of kinetic evidence that the aquation of the monocyanochromium(III) ion *via* the acid-independent pathway involves an intramolecular proton transfer from a coordinated water molecule to the ligand cyanide.

The acid-independent aquation of the dicyano complex appears to follow a similar mechanism. In the proton-transfer mechanism the leaving group is neutral and hence the rate of the reaction would not be as sensitive to the over-all charge of the complex as it would be if the leaving group were anionic. Moreover, the rate of an aquation reaction involving an intramolecular proton transfer should depend upon the acidity of the coordinated water molecules (the proton donors), as well as on the basicity of the ligands (proton acceptors) and a statistical factor involving the number of water molecules coordinated at positions *cis* to the basic ligand. There is apparently little difference in the basicities of the cyanide ligands in the mono and dicyano complexes, judging from the protonation equilibrium constants of 0.19 and 0.55 M^{-1} obtained for these complexes, respectively, at 25°. On the other hand, the acidity of coordinated water molecules is known to increase sharply with increasing positive charge of a complex and is estimated from some preliminary measurements with these cyanoaquo com-

(14) L. P. Quinn and C. S. Garner, *Inorg. Chem.*, **3**, 1348 (1964).
(15) T. W. Swaddle and E. L. King, *ibid.*, **4**, 532 (1965).
(16) J. Selbin and J. C. Bailar, *J. Am. Chem. Soc.*, **79**, 4285 (1957).

plexes to change by a factor of about 10 for a unit change in charge. Acid-independent aquation *via* an intramolecular proton-transfer mechanism, therefore, may be expected to occur less readily with the singly charged dicyanotetraaquochromium(III) cation than with the doubly charged monocyano cation, with its

much more strongly acidic coordinated water molecules. This expectation is in agreement with experiment and is in contrast to the relative rates observed for singly and doubly substituted aquo complexes containing less basic ligands which do not aquate *via* a mechanism involving proton transfer.

Electrochemical Investigation of Molybdenum(III)–Chloro Complexes with Pyridine, 2,2'-Bipyridine, and 1,10-Phenanthroline in Acetonitrile

BY DONALD W. DU BOIS, REYNOLD T. IWAMOTO, AND JACOB KLEINBERG

A series of molybdenum(III)–chloro complexes with pyridine, 2,2'-bipyridine, and 1,10-phenanthroline were prepared and their electrochemistry in acetonitrile was studied. The compounds investigated included $MoCl_3(py)_3$, $MoCl_3(py)bipy$, $MoCl_3(py)phen$, $(C_2H_5)_4N[MoCl_4(py)_2]$, $(C_2H_5)_4N[MoCl_4bipy]$, $(C_2H_5)_4N[MoCl_4phen]$, $[MoCl_2(bipy)_2][MoCl_4bipy]$, $[MoCl_2(phen)_2][MoCl_4phen]$, and $[MoCl_2(phen)_2]Cl$. Current–voltage curves of acetonitrile solutions of all of the compounds exhibited at least one reversible one-electron reduction step. In addition, a second reversible one-electron reduction step was observed for the compounds containing the $MoCl_2(phen)_2^+$ and $MoCl_2(bipy)_2^+$ cations. These steps are attributed to the reduction of the metal. At potentials more negative than those required for metal reduction, cathodic waves were found which, on the basis of the electrochemical evidence, have been ascribed to reduction of the ligands. Compounds containing $MoCl_4$–amine anions gave reversible one-electron oxidation steps involving the conversion of the metal in the anion to the tetrapositive state. Anodic steps, at more positive potentials than for the $MoCl_4$–amine anions, occur for the other molybdenum complex species. Of the complexes studied, $(C_2H_5)_4N[MoCl_4(py)_2]$, $[MoCl_2(phen)_2][MoCl_4phen]$, and $[MoCl_2(phen)_2]Cl$ were prepared for the first time.

Introduction

It is generally recognized that low oxidation states of transition metals may be stabilized by coordination with ligands which permit back-donation of d electrons from the metal to the π system of the ligands.[1,2] However, few quantitative data, in terms of redox potentials, which reflect the effect of systematic changes in the aromatic π system of the coordination sphere are available. The present communication describes a study in acetonitrile as the solvent of a series of tetrachloro-, trichloro-, and dichloromolybdenum(III) complexes containing as ligands with π character pyridine, 2,2'-bipyridine, 1,10-phenanthroline, and mixtures thereof. In connection with the investigation, several of the complexes were prepared for the first time.

Experimental Section

Materials.—Acetonitrile (Baker Analyzed reagent) was purified by distillation first from sodium hydride and then from phosphorus(V) oxide. Pyridine (Baker Analyzed reagent) and 2,2'-bipyridine and 1,10-phenanthroline, both obtained from Aldrich Chemical Co., were used without further purification. Tetraethylammonium perchlorate was precipitated by mixing

aqueous solutions of tetraethylammonium bromide and sodium perchlorate. The precipitate was recrystallized six times from water and then vacuum dried under an infrared lamp. Tetraethylammonium perchlorate, from Eastman Chemical Co., was also found to be suitable for electrochemical work after one or two recrystallizations from water and appropriate drying.

Preparation of Compounds. Pyridinium Perchlorate.—A solution of pyridine in absolute ethanol was made just acidic by the addition of 60% perchloric acid. The white precipitate was filtered, washed with ethanol, recrystallized from hot ethanol, and dried in air. *Anal.* Calcd for $C_6H_5N \cdot HClO_4$: equiv wt, 180. Found: equiv wt, 186.

Phenanthrolinium Perchlorate.—This compound was prepared by a procedure similar to that given above. *Anal.* Calcd for $C_{12}H_8N_2 \cdot HClO_4$: equiv wt, 281. Found: equiv wt, 292.

Ammonium Hexachloromolybdate(III) Monohydrate, Ammonium Pentachloroaquomolybdate(III), and Potassium Hexachloromolybdate(III).—These substances were made according to published procedures.[3,4] *Anal.* Calcd for $(NH_4)_3MoCl_6 \cdot H_2O$: Cl, 56.0. Found: Cl, 56.3. Calcd for $(NH_4)_2MoCl_5 \cdot H_2O$: Cl, 54.2. Found: Cl, 54.3. Calcd for K_3MoCl_6: Cl, 49.9. Found: Cl, 47.4.

Tetraethylammonium Tetrachlorodiaquomolybdate(III).—A modification of the procedure for the synthesis of the hexachloromolybdate complexes listed above was used to prepare this compound. This consisted of substituting tetraethylammonium chloride for ammonium or potassium chloride. The infrared spectrum confirmed the presence of water and the tetraethyl-

(1) J. Chatt, *J. Inorg. Nucl. Chem.*, **8**, 515 (1958).
(2) R. S. Nyholm and M. L. Tobe, *Advan. Inorg. Chem. Radiochem.*, **5**, 1 (1963).

(3) W. R. Bucknall, S. R. Carter, and W. Wardlaw, *J. Chem. Soc.*, 512 (1927).
(4) K. H. Lohmann and R. C. Young, *Inorg. Syn.*, **4**, 97 (1953).