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Synthesis and Aquation Kinetics of *cis*-Bis(oxalato)diazidochromate(III) and *cis*-Bis(oxalato)azidoaquochromate(III)[1]

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The two new ions *cis*-$Cr(C_2O_4)_2(N_3)_2{}^{3-}$ (**1**) and *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$ (**2**) have been isolated by anion-exchange techniques. The visible spectrum of **1** has maxima at 595 and 435 nm with molar absorptivities of 142 and 118 M^{-1} cm^{-1}, respectively. The visible spectrum of **2** displays maxima at 577 and 423 nm with molar absorptivities of 96 and 93 M^{-1} cm^{-1}, respectively. The aquation of **2** to *cis*-$Cr(C_2O_4)_2(OH_2)_2{}^-$ (**3**) occurs with retention of configuration and the observed rate law is $d[\mathbf{3}]/dt = (a + b[H^+])[\mathbf{2}]$ between 0.500 M H^+ and pH 5.0. The values of a and b at 35° are 7.50×10^{-5} sec^{-1} and 4.78×10^{-2} M^{-1} sec^{-1}. For the path associated with a, $\Delta H^* = 18.4 \pm 1.6$ kcal/mol and $\Delta S^* = 18.1 \pm 5.0$ cal/deg mol. The acid-dependent path was interpreted to involve the formation of *cis*-$Cr(C_2O_4)_2(OH_2)(N_3H)^-$ and then the subsequent aquation of this compound. The ΔH^* and ΔS^* values were 17.8 ± 0.4 kcal/mol and −7.0 ± 1.4 cal/deg mol, respectively. The aquation of **1** to **3** occurs with **2** as an intermediate between 0.500 and 0.0500 M H^+. The rate law for the aquation of **1** to **2** is $d[\mathbf{2}]/dt = C[H^+][\mathbf{1}]$. At 35°, $C = 0.29$ M^{-1} sec^{-1} and the values of ΔH^* and ΔS^* are 20.5 ± 0.7 kcal/mol and 5.8 ± 2.3 cal/deg mol, respectively. It was assumed that *cis*-$Cr(C_2O_4)_2N_3(N_3H)^{2-}$ was formed and that it was the reactive species.

Introduction

The chemistry of the oxalato complexes, particularly those of Cr(III), has been reviewed by Krishnamurthy and Harris.[3] Few papers have been published on $Cr(C_2O_4)_2X_2{}^{n-}$ type systems, where X is any monodentate ligand other than water.[4] In general, an I mechanism has been proposed for the aquation of these complexes. The aquation of most Cr(III) complexes is zero or inverse first order in hydrogen ion concentration.[4c] Aquation reactions that are first order in hydrogen ion concentration are less common, being restricted to complexes with ligands of appreciable basicity.[5] Some Cr(III) systems exhibiting acid-catalyzed aquation are *cis*-$Cr(H_2NC_2H_4NH_2)_2(N_3)_2{}^+$,[6] *cis*-α-$Cr(H_2NC_2H_4NHC_2H_4NHC_2H_4NH_2)(N_3)_2{}^+$,[7] $Cr(NH_3)_5N_3{}^{2+}$,[8] $Cr(H_2O)_5N_3{}^{2+}$,[9] and $Cr(H_2O)_5F^{2+}$.[10] This paper presents the results of the synthesis, characterization, and aquation of *cis*-bis(oxalato)diazidochromate(III) and *cis*-bis(oxalato)azidoaquochromate(III) in an acidic medium.

Experimental Details

Chemicals. All chemicals used were reagent, analytical, or primary standard grade depending upon the need. The ion-exchange resin used in the present study was 200–400 mesh Bio-Rad AG 1-X8 anion-exchange resin in the nitrate form.

Instruments. Visible absorption measurements were obtained on a Cary Model 15 recording spectrophotometer or a Beckman Model DU-2 spectrophotometer fitted with constant-temperature cell blocks, maintained to within ±0.1° of the temperature desired. Temperatures of the baths were controlled with a Sargent thermomonitor, Model SW. A Beckman research model pH meter employing calomel and blue glass electrodes was used to measure pH. All of the columns for the ion-exchange chromatography were enclosed in water jackets through which water at 1° from a portable cooling unit was circulated.

Analytical Methods. The analyses for chromium were performed as described previously.[4e] The azide analysis was performed by modifying a previously known procedure.[11] The modification was in the preparation of the standard curve. Ferric azide was produced *in situ* instead of distilling HN_3 into a flask containing iron(III) nitrate. The slope of the Beer's law plot for this azide analysis was 400 M^{-1} cm^{-1} at 460 nm.

Ion-Exchange Techniques. The ion-exchange analysis of solutions containing *cis*-$Cr(C_2O_4)_2(OH_2)_2{}^-$ and $N_3{}^-$ were performed essentially as described previously.[12] The details of the preparative techniques are described below. The experiments designed to elucidate the composition of the species in solution used a 20 × 1.0 cm column and a flow rate of 0.25 ml/min of 2.0 M sodium nitrate at pH 4. The 10-ml fractions were collected in test tubes immersed in an ice bath and the visible spectrum of each fraction was measured immediately after collection. Analyses for chromium and/or azide were performed after the complete elution from the column.

Preparation of Compounds. The sodium *trans*-bis(oxalato)diaquochromate(III) was prepared by the method described by Werner.[13] The purification and isolation of *cis*-bis(oxalato)diaquochromate(III) were performed as described previously.[14]

***cis*-$Cr(C_2O_4)_2(N_3)_2{}^{3-}$.** The *cis*-bis(oxalato)diazidochromate(III) was isolated from a solution which was 0.1 M in *cis*-$Cr(C_2O_4)_2(OH_2)_2{}^-$ and 1.0 M in NaN_3. The pH was adjusted to about 5.0 with nitric acid. The reaction mixture was left for about 6 hr at room temperature and then introduced onto a 25 × 5.0 cm column.[15] The unreacted *cis*-$Cr(C_2O_4)_2(OH_2)_2{}^-$ was eluted with 0.1 M $NaNO_3$, the band of *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$ (10–15%) was eluted with 1.0 M $NaNO_3$, and *cis*-$Cr(C_2O_4)_2(N_3)_2{}^{3-}$ (70%) was eluted with 2.0 M $NaNO_3$.

***cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$.** The *cis*-bis(oxalato)azidoaquochromate(III) was isolated as described above. However, it was obtained from a solution which was 0.1 M in *cis*-$Cr(C_2O_4)_2(OH_2)_2{}^-$ and 0.2 M in NaN_3. The pH was adjusted to 5.0. The yield of *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$ was about 70% of the total chromium.

Kinetic Measurements. The absorbance changes associated with the aquation reactions of 1×10^{-4} to 1×10^{-3} M *cis*-$Cr(C_2O_4)_2(N_3)_2{}^{3-}$ and *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$ were monitored at 595 nm and at the desired temperature. The ionic strength of all solutions was maintained at 1.00 M ($NaNO_3$). No buffer was used above an analytical hydrogen ion concentration of 0.050 M. Above a pH of 2, a lutidine or an acetate buffer was used, and pH was adjusted with sodium hydroxide or nitric acid using a pH meter. The solutions of the complex ion and the acid or buffer were brought to the desired tempera-

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(1) Taken, in part, from the dissertation of R. S. Lamba for the Ed.D. in the College Teaching of Chemistry degree, presented to East Texas State University, 1973.

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(15) It was observed that at least 6 hr was necessary to establish the equilibrium.

ture, as was the 10.00-cm cuvette used. The solutions were mixed, poured into the cuvette, and placed into the Cary 15 within 40 sec. The reactions were monitored for about 8–10 half-lives.

Results and Discussions

Synthesis. Figure 1 is an elution profile of a solution of *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$ and N_3^- that has reacted for several hours. One can see that there are only two plateaus. The apparent molar absorptivities, $A/l[Cr]_t$ are 96 and 142 M^{-1} cm^{-1}, respectively. The azide and chromium analyses of fractions on the first plateau give a chromium:azide ratio of 1.00:(0.97 ± 0.04). The same ratio for the second plateau was 1.00:(2.06 ± 0.03). These uncertainties and all others, except when explicitly stated, are standard deviations. When these two species are placed in acid solutions, the spectra of the equilibrium solutions are identical with that of *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$ under the same conditions.

From these observations one can conclude that pure solutions of $Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$ and $Cr(C_2O_4)_2(N_3)_2^{3-}$ have been isolated. In Table I are reported some pertinent molar absorptivities. The cis configuration is assigned to the two azide complexes, because of their ion-exchange behavior, because of the relatively large values for the molar absorptivities, and because of the shapes of the visible bands.[16,17] This is in agreement with previous conclusions.[4]

From the data in this report and in ref 4, the spectrochemical series for the *cis*-$Cr(C_2O_4)_2^-$ moiety can be stated. For *cis*-$Cr(C_2O_4)_2X_2^{n-}$, the series is $N_3^- < (CH_3)_2SO \simeq {}^-OOCCH_3 < H_2O$ and for *cis*-$Cr(C_2O_4)_2X(OH_2)^{n-}$, the series is $N_3^- \simeq (CH_3)_2SO < H_2O < \text{-NCS}^-$. This is consistent with the normal ordering of these ligands.

Aquation of *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$. The aquation was studied over the range $[H^+] = 0.0500$–$0.892\ M$ and between pH 2 and 5. The aquation product of *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$ was *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$. The observed reaction was thus

$$cis\text{-}Cr(C_2O_4)_2(N_3)(OH_2)^{2-} + H_2O \xrightarrow{k_{obsd}} cis\text{-}Cr(C_2O_4)_2(OH_2)_2^- + N_3^- \quad (1)$$

Of course, N_3^- and H_2O are in equilibrium with HN_3 and H_3O^+. The rate law was $d[cis\text{-}Cr(C_2O_4)_2(OH_2)_2^-]/dt = k_{obsd}[cis\text{-}Cr(C_2O_4)_2(N_3)(OH_2)^{2-}]$. The pseudo-first-order rate constant, k_{obsd}, was calculated by fitting the absorbance-time data to the equation $A = A_\infty + (A_0 - A_\infty)e^{-tk_{obsd}}$, where A is the absorbance at time t, A_0 is the absorbance at time zero, and A_∞ is the absorbance at 10 half-lives, using a generalized nonlinear least-squares program and a weighting of $1/A^2$ for the dependent variable. The parameters A_∞, $(A_0 - A_\infty)$, and k_{obsd} were allowed to vary to produce the best fit. The derived values of A_∞ and $(A_0 - A_\infty)$ were within experimental error of the measured values.

It was observed that the equation $k_{obsd} = k_0 + k_1[H^+]$ was obeyed from pH 5 to $[H^+] = 0.500\ M$. However, between $[H^+] = 0.0500\ M$ and $[H^+] = 0.500\ M$, the equation reduced to $k_{obsd} = k_1[H^+]$. The values of k_1 were derived by the least-squares fit of the equation $k_{obsd} = k_1[H^+]$ using a weighting of $1/k_{obsd}^2$ and ten different $[H^+]$ values. These data are reported in Table II. The activation parameters were calculated by using the Eyring-Polanyi equation, the assumption that the transmission coefficient is unity, and a least-squares program.[18] These are reported also in Table II.

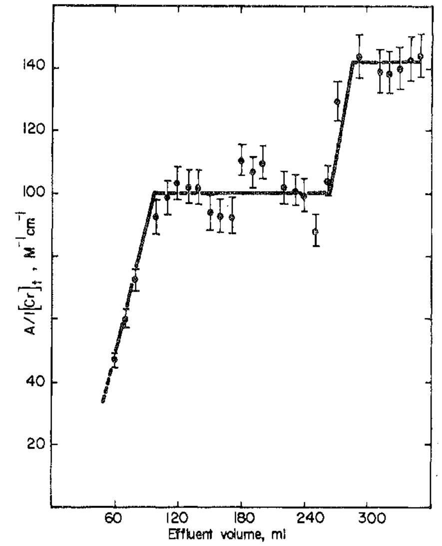

Figure 1. A plot of apparent molar absorptivity at 595 nm *vs.* effluent volume for the anion-exchange chromatographic separation of *cis*-$Cr(C_2O_4)_2(N_3)_2^{3-}$ and *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$. The error bars are ±5%.

Table I. Molar Absorptivities of Some Chromate(III) Complexes[a]

Complex	λ_{max}, nm
cis-$Cr(C_2O_4)_2(OH_2)_2^-$ [b]	560 (51.0), 415 (66.2)
trans-$Cr(C_2O_4)_2(OH_2)_2^-$ [c]	533 (16.7), 398 (17.0)
cis-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$ [d]	577 (96.0), 423 (93.0)
cis-$Cr(C_2O_4)_2(N_3)_2^{3-}$ [e]	595 (142), 435 (118)

[a] Values in parentheses are molar absorptivities; units are M^{-1} cm^{-1}. [b] $\mu = 0.10\ M$ ($NaNO_3$), pH 5.0. [c] D. H. Huchital, *Inorg. Chem.*, 9, 486 (1970). [d] $\mu = 1.0\ M$ ($NaNO_3$), 2°, pH 5.0. [e] $\mu = 2.0\ M$ ($NaNO_3$), 2°, pH 5.0.

Even though retention of configuration is observed, it is conceivable that the reaction sequence might be *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$ to *trans*-$Cr(C_2O_4)_2(OH_2)_2^-$ to *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$. This possibility now can be excluded definitely because at 25° and these acidities k_1 is only 7 times the second-order rate constant for isomerization, and, hence, a second step would have been observed.[19] It was not.

The usual mechanism invoked to explain a first-order dependence upon $[H^+]$ for an aquation reaction is[9]

$$cis\text{-}Cr(C_2O_4)_2(N_3)(OH_2)^{2-} + H^+ \overset{K_1}{\rightleftharpoons} cis\text{-}Cr(C_2O_4)_2(OH_2)(N_3H)^- \quad (2)$$

$$H_2O + cis\text{-}Cr(C_2O_4)_2(OH_2)(N_3H)^- \xrightarrow{k} cis\text{-}Cr(C_2O_4)_2(OH_2)_2^- + HN_3 \quad (3)$$

The rate law for such a mechanism would be

$$d[cis\text{-}Cr(C_2O_4)_2(OH_2)_2^-]/dt = \{kK_1[H^+]/(1 + K_1[H^+])\}[cis\text{-}Cr(C_2O_4)_2(N_3)(OH_2)^{2-}]_{total}$$

where K_1 and k are defined by reactions 2 and 3 and $[cis\text{-}Cr(C_2O_4)_2(N_3)(OH_2)^{2-}]_{total}$ represents the concentration of the unreacted complex, regardless of form. If $K_1[H^+] \ll 1.00$, then the rate law becomes equivalent to that observed between 0.50 and 0.050 M H^+ with $k_1 = kK_1$.

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Table II. Kinetic Data for the Acid-Assisted Aquation of *cis*-$Cr(C_2O_4)_2(N_3)_2^{3-}$ and of *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$

Temp, °C	10^2k_1,[a] M^{-1} sec^{-1}	$10^2k_1'$,[b] M^{-1} sec^{-1}	$10k_2$,[c] M^{-1} sec^{-1}
5		0.180 ± 0.015	0.126 ± 0.067
15	0.688 ± 0.084	0.605 ± 0.031	0.377 ± 0.096
25	1.77 ± 0.11	1.73 ± 0.08	1.11 ± 0.15
35	4.78 ± 0.25	4.72 ± 0.32	2.89 ± 0.13
ΔH^*, kcal/mol	17.1 ± 0.5	17.9 ± 0.2	20.5 ± 0.7
ΔS^*, cal/deg mol	−9.1 ± 1.7	−6.5 ± 0.7	5.8 ± 2.3

[a] Observed second-order rate constant for aquation of *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$. [b] Observed second-order rate constant for aquation of *cis*-$Cr(C_2O_4)_2(N_3)_2^{3-}$; slow step. [c] Observed second-order rate constant for aquation of *cis*-$Cr(C_2O_4)_2(N_3)_2^{3-}$; fast step.

Table III. Activation Parameters for the Aquation of Various Chromate(III) Complexes

Reactants	ΔH^*, kcal/mol	ΔS^*, cal/deg mol	Ref
cis-$Cr(C_2O_4)_2\{(CH_3)_2SO\}(OH_2)^-$ [c,e]	17.8 ± 0.8	−17.6 ± 2.6	4a
trans-$Cr(C_2O_4)_2(O_2C_2H_3)(OH_2)^{2-}$ [d,g]	16.3 ± 1	−18.8 ± 2	4c
cis-$Cr(C_2O_4)_2(NCS)(OH_2)^{2-}$ [b,h]	20.1 ± 0.4	−13.1 ± 1.2	4b
cis-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$ [b,i]	18.4 ± 1.6	−18.1 ± 5.0	This work
cis-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$ [b] + H^+	17.8 ± 0.4[k]	−7.0 ± 1.4[k]	This work
trans-$Cr(C_2O_4)_2(O_2C_2H_3)(OH)^{3-}$ [d]	8.4 ± 1	−38.8 ± 2	4c
trans-$Cr(C_2O_4)_2(C_5H_5N)_2^+$ [a,f,l]	22.6 ± 0.4	−5.3 ± 1.2	4d
trans-$Cr(C_2O_4)_2(C_5H_5N)_2^-$ [d,j,l]	27.7 ± 1	10.0 ± 2	4c
cis-$Cr(C_2O_4)_2\{(CH_3)_2SO\}_2^-$ [c,e,l]	12.3 ± 0.6	−30.6 ± 1.9	4a
cis-$Cr(C_2O_4)_2(N_3)_2^{3-}$ [b,l] + H^+	20.5 ± 0.7	5.8 ± 2.3	This work

[a] $\mu = 1.00\ M$ ($NaClO_4$). [b] $\mu = 1.00\ M$ ($NaNO_3$). [c] No added inert electrolyte. [d] μ was unspecified but implied to be 2.00 M ($NaClO_4$). [e] pH 1–4. [f] pH 2–4. [g] pH 3–5. [h] pH 3–4. [i] pH 4–5. [j] $[H^+] = 2.0$ to $1 \times 10^{-3}\ M$. [k] Calculated using all data for k_1 and k_1' in Table II. [l] The product is the $Cr(C_2O_4)_2(\text{ligand})(OH_2)^{n-}$ complex.

The observation that both *cis*-$Cr(C_2O_4)_2[(CH_3)_2SO](OH_2)^-$ and *cis*-$Cr(C_2O_4)_2(NCS)(OH_2)^{2-}$ do not have a first-order hydrogen ion dependent aquation pathway supports the suggestion that the azide ligand is protonated.[4a,b]

Since no deviation from first-order $[H^+]$ dependence up to 0.50 M $[H^+]$ was observed, $K_1 < 0.1\ M^{-1}$. For the protonation of N_3^-, the acid association constant at 26° is 4.4×10^4 M^{-1}.[20] This greater than 10^5 change in basicity is consistent with what has been observed for $Cr(NH_3)_5N_3^{2+}$, $Co(NH_3)_5N_3^{2+}$, $Rh(NH_3)_5N_3^{2+}$, and $Cr(OH_2)_5N_3^{2+}$.[8,9] However, $Co(CN)_5N_3^{3-}$ has a proton association constant of 4.7 M^{-1}.[21] This might be rationalized on the basis of the 3− charge of the complex. If this is the case, then a proton association constant for *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$ of <0.1 M^{-1} is reasonable.

The ΔH° and ΔS° for the protonation of N_3^- are −3.8 kcal/mol and 8.6 cal/deg mol, respectively.[20] Since both reaction 2 and the protonation of N_3^- involve the removal of a proton from solution and the reduction in the magnitude of the charge on the species, the entropies of both reactions should be positive. The observed ΔS^*, assuming that reactions 2 and 3 are operative, is the sum of the ΔS° for reaction 2 and ΔS^* for reaction 3. Since ΔS° should be positive, the ΔS^* for the aquation of *cis*-$Cr(C_2O_4)_2(OH_2)(NH_3)^-$, reaction 3, would be smaller than the observed ΔS^* for the overall reaction, reaction 1.

The ΔH° for reaction 2 should be close to zero or slightly positive. This implies that the value of ΔH^* for the aquation of *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$ is probably close to the observed ΔH^*. This value of 17.8 kcal/mol can be compared to the values of ΔH^* for similar compounds in Table III, as well as the ΔS^* value of 7.0 cal/deg mol.

The zero-order hydrogen ion dependent aquation of *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$ was studied at 35, 45, and 55° in 0.10 M lutidine or 0.10 M acetate buffer and $\mu = 1.00\ M$ ($NaNO_3$) between pH 4 and 5. The values of the first-order rate constants, k_0, at 35, 45, and 55° are 7.50×10^{-5}, 1.52×10^{-4}, and 4.09×10^{-4} sec^{-1}, respectively. The activation parameters are reported in Table III. At pH 4 and 35°, the rate constant for trans-cis isomerization is about 22 times that for aquation.[19] Even if retention of configuration during aquation were not occurring, it would not have been observed. Hence, the stereochemistry of this reaction cannot be specified. In general, retention of configuration does occur in these types of reactions.[4]

The first four entries in Table III are for similar reactions. One can see that the values of ΔH^* and ΔS^* are similar and somewhat intermediate to usual values for activation parameters of aquation reactions. The rate constants for the aquation of the dimethyl sulfoxide, acetato, isothiocyanato and azido complexes at 25° are 30.3×10^{-5}, 51.0×10^{-5}, 1.61×10^{-5}, and 2.19×10^{-5} sec^{-1}, respectively. This is a 32-fold change. For $Co(NH_3)_5X^{2+}$ where $X^- = {}^-O_2CCH_3$, N_3^-, or NCS^-, there is a 4200-fold change in the aquation rate constant.[22] The aquation of $Co(NH_3)_5X^{2+}$ has been concluded to occur by an I_d mechanism.[23] The apparent insensitiveness of the rate constant for aquation of $Cr(C_2O_4)_2X(OH_2)^{2-}$ to the leaving group implies that associative activation is occurring. However, to be more certain that this is the case, the equilibrium constants for the reactions should be known. Unfortunately, only the value of 4.5 M^{-1} for the isothiocyanato complex is known.[4b] Since no intermediate was observed, the reactions tentatively are suggested to occur by an I_a mechanism.[24]

It has been reported that the difference in ΔS^* of aquation between $Cr(H_2O)_5N_3^{2+}$ and $Cr(H_2O)_5NCS^{2+}$ is 19.7 cal/deg mol.[9] Similarly, the difference in ΔS^* between $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_5NCS^{2+}$ is 22.9 cal/deg mol.[9] It reasonably was suggested that these differences implied that HN_3 was

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[24] Reference 4b. In this reference the same arguments were used apparently to support an I_d mechanism. The d subscript was a typographical error and should have been an a. The rest of the statements in the argument are applicable here.

produced in the transition state instead of N_3^-. However, in the system reported here, this is not apparently the case and N_3^- is being produced in the transition state.

Above 0.50 *M* H$^+$, the aquation reactions were no longer first order in [H$^+$]. Figure 2 is a plot of k_{obsd} *vs.* [H$^+$] for the aquation of *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$ to *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$ beginning with either the *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$ or the *cis*-$Cr(C_2O_4)_2(N_3)_2{}^{3-}$ ions. A very similar plot was obtained for the aquation for *cis*-$Cr(C_2O_4)_2(N_3)_2{}^{3-}$ to *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$. It should be noted that the hydrogen ion concentrations are analytical and are not calculated from a glass electrode measurement. Hence the deviation is not a result of an erroneous measurement of hydrogen ion concentration. One can see that by plotting $k_{obsd}/[H^+]$ *vs.* [H$^+$] the positive deviation cannot be explained by simply adding a term to the rate law that is second order in hydrogen ion concentration. Attempts to fit the data to more complicated rate laws were unsuccessful. Apparently this unusual behavior is due to some specific activity coefficient effect.[25]

Aquation of *cis*-$Cr(C_2O_4)_2(N_3)_2{}^{3-}$. The proton-assisted aquation of *cis*-$(Cr(C_2O_4)_2(N_3)_2{}^{3-}$ did not follow simple first-order kinetics. The plots of log $(A - A_\infty)$ *vs.* time were initially curved and then linear. Since there were two azide ions to be replaced, it was anticipated that the consecutive aquation of the azido ions was occurring. If this were the case, the following scheme might be applicable

$$cis\text{-}Cr(C_2O_4)_2(N_3)_2{}^{3-} + H_3O^+ \xrightarrow{k_2} cis\text{-}Cr(C_2O_4)_2(N_3)(OH_2)^{2-} + HN_3$$

$$cis\text{-}Cr(C_2O_4)_2(N_3)H_2O^{2-} + H_3O^+ \xrightarrow{k_1'} cis\text{-}Cr(C_2O_4)_2(OH_2)_2{}^- + HN_3$$

To test this scheme, the absorbance-time data were fit to the equation

$$A = A_\infty + ae^{-k_1't} + be^{-k_2t}$$

using a nonlinear least-squares program with *A* weighted as $1/A^2$. The parameters *a* and *b* are composed of the molar absorptivities of all three complex ions, the cuvette length, the total chromium concentration, k_1', and k_2. In the fit of the data, A_∞, *a*, k_1', *b*, and k_2 were treated as variable parameters. Initial values of k' and k were obtained by plotting log $(A - A_\infty)$ *vs.* time and extracting the two rate constants in the usual manner.[4a] The calculated value of A_∞ agreed, within experimental error, with the observed value, and the fit to the equation was good. Generally the aquation reaction was studied at from five to eight different hydrogen ion concentrations between 0.050 and 0.50 *M*. The two steps were found to be first order in hydrogen ion concentration and the pseudo-first-order rate constant k_{obsd} was fit by the computer to the equation

$$k_{obsd} = k_i[H^+]$$

The data are tabulated in Table II.

The values of k and k_1' agree remarkably well, thus showing that they are identical. Also the activation parameters for this step are the same. This confirms that the second step is indeed the aquation of *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)_2{}^{2-}$ to *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$. The stereochemical details of the first step are not that clear-cut. It is possible that *cis*-$Cr(C_2O_4)_2(N_3)_2{}^{3-}$ aquates to *trans*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$ which very rapidly isomerizes to *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$. The rate constant for isomerization would have to be larger than 1.1·[H$^+$] M^{-1} sec^{-1} at 25° or it would have been observed. At present there is no way to decide the stereochemistry of the first aquation step. However, the aquation reactions of the *cis*-$Cr(C_2O_4)_2^-$ derivatives have been reported usually to occur with retention of configuration.[4]

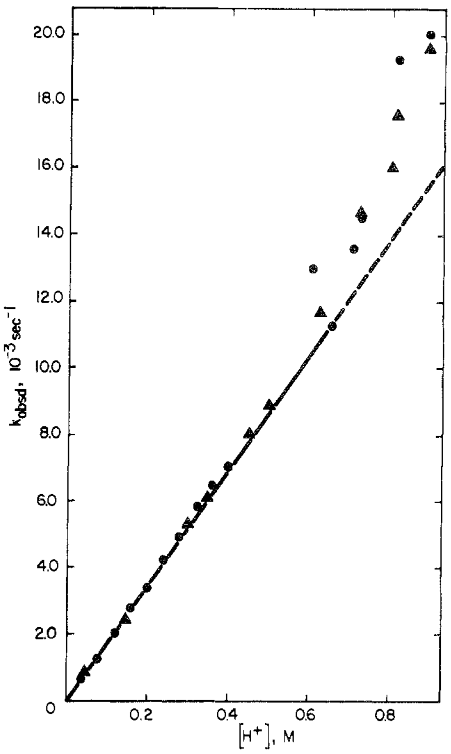

Figure 2. The hydrogen ion dependence of k_{obsd}, the pseudo-first-order rate constant for aquation of *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$ to *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$ + HN_3: ●, *cis*-$Cr(C_2O_4)_2(N_3)_2{}^{3-}$ was the initial ion; ▲, *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$ was the initial ion. Conditions: 25° and $\mu = 1.00\,M$ ($NaNO_3$).

The mechanism of the acid-assisted aquation of *cis*-$Cr(C_2O_4)_2(N_3)_2{}^{3-}$ to *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$ is suggested to be directly analogous to that proposed for the acid-assisted aquation of *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$; that is, $k_2 = k'K_2$, where K_2 is the formation constant for *cis*-$Cr(C_2O_4)_2(N_3)(N_3H)^{2-}$ and k' is the first-order rate constant for aquation of this species. The low positive ΔS^* is consistent with loss of solvent structure about the ions due to protonation. However, the value of 20.5 kcal/mol for ΔH^* is surprisingly large, especially since it is thought that N_3H is the leaving group. It might be that the lowering of the charge on the complex ion severely destabilizes the activated complex by loss of hydration enthalpy. Without more information and the realization that k_2 might be a composite constant ($k_2 = k'K_2$) a more detailed mechanism justifiably cannot be presented.

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Registry No. *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$, 15489-30-2; *cis*-$Cr(C_2O_4)_2(N_3)(OH_2)^{2-}$, 51830-75-2; *cis*-$Cr(C_2O_4)_2(N_3)_2{}^{3-}$, 51830-76-3.

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[25] Attempts to study the reactions in $LiNO_3$-HNO_3 solutions resulted in an unexpected observation. *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$ aquates abnormally rapidly in this solution, much faster than in $NaClO_4$-$HClO_4$ or $NaNO_3$-HNO_3 solutions. This is now being investigated.