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Aquation of the Glycinatobis(oxalato)chromate(III) Complex Ion in Acidic Media

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A mixed salt of the (glycinato)bis(oxalato)chromate(III) complex ion has been prepared and characterized with the use of ion-exchange chromatography. In acidic media, this complex has been shown to aquate to the *cis*-diaquabis(oxalato)chromate(III) complex ion; and, an aquation intermediate, characterized as the *cis*-aqua(glycine-*O*)bis(oxalato)chromate(III) ion, has been isolated from partially reacted solutions of the parent complex at pH 0 and 2. The first step of this aquation reaction has been monitored spectrophotometrically at an isosbestic point of the reaction intermediate and the product species. For hydrogen ion concentrations between 0.10 and 0.90 M, the change in absorbance with time was described by a single-step, two-term rate law given by $dA/(A_\infty - A)dt = k'[H^+] + k''$. At 25.0 °C and an ionic strength of 1.00 M, maintained with sodium perchlorate, $k' = (1.57 \pm 0.01) \times 10^{-3}$ M^{-1} s^{-1} and $k'' = (7.9 \pm 0.5) \times 10^{-5}$ s^{-1}. Activation parameters of k', determined between 20.0 and 34.6 °C, were $\Delta H^* = 17.0 \pm 0.2$ kcal/mol and $\Delta S^* = -14.5 \pm 0.7$ cal/(mol K). Activation parameters of k'' were $\Delta H^* = 17.6 \pm 1.1$ kcal/mol and $\Delta S^* = -18.6 \pm 3.8$ cal/(mol K). Analysis of the rate data indicated that they applied to amine terminus aquation of the bidentate glycinato ligand. A detailed mechanism has been proposed for aquation which is initiated by proton transfer from an oxalate ligand to the amine terminus of the bidentate glycinato ligand. Production of a metastable, bidentate glycine-*O*,*O* ligand configuration in the rate-determining step has been proposed to explain the observed preference for amine terminus aquation in the first step of the reaction.

Introduction

Aqua(ethylenediamine)chromium(III) complexes lack basic sites which may effectively interact with hydrogen ions to catalyze the aquation of an amine group. Therefore, the hydrogen ion independence of the aquation rates for $Cr(NH_2CH_2CH_2NH_2)(H_2O)_4^{3+}$ and $Cr(NH_2CH_2CH_2NH_3)(H_2O)_5^{4+}$ [2] is entirely expected, and the activation parameters for these aquation reactions may be interpreted as the enthalpy and entropy changes required to activate essentially dissociative processes.

Recently, it has been demonstrated that partial aquation of an ethylenediamine ligand of $Cr(C_2O_4)_2(NH_2CH_2CH_2NH_2)^-$ occurs via a hydrogen ion dependent pathway in addition to the expected hydrogen ion independent pathway.[3] Furthermore, the activation enthalpies for both pathways are low when compared to those for the stepwise aquation of $Cr(NH_2CH_2CH_2NH_2)(H_2O)_4^{3+}$. Since hydrogen ion catalyzed ethylenediamine aquation occurs in competition with hydrogen ion catalyzed oxalate aquation, it was suggested that ethylenediamine aquation is a consequence of the rotation and rechelation of a half-bonded oxalate ligand present in the oxalate aquation mechanism. In this sense, hydrogen ion catalysis would consist of the increase in stability afforded the half-bonded oxalate by protonation of its free carboxylate group.

In principle, this oxalate-induced aquation mechanism should generalize to any mixed-ligand complex of chromium(III) which contains the oxalate ligand. The effectiveness of the mechanism should depend upon the extent to which the half-bonded oxalate intermediate is generated and the local geometry of the ligand undergoing induced aquation. For the $Cr(C_2O_4)_2$ substrate, in particular, aquation rates and activation parameters should closely parallel those for the trans–cis isomerization of $Cr(C_2O_4)_2(H_2O)_2^-$ since this process incorporates the half-bonded oxalate intermediate and the geometry changes necessary to effect activation of an induced aquation process.[4]

Evidence exists for hydrogen ion catalyzed water exchange of the *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ complex ion.[5] This catalysis is a necessary consequence of the mechanism proposed for oxalate-induced aquation. Also, the $Cr(C_2O_4)_2(O_2CCH_3)(H_2O)^{2-}$ complex aquates via hydrogen ion catalyzed and uncatalyzed pathways with activation parameters which resemble those for the trans–cis isomerization.[6] Here, however, a mechanistic uncertainty is introduced by the proven availability of the acetato ligand as a protonation site.[7,8]

We have examined the aquation kinetics of the glycinato ligand of the $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ complex ion. In this case, protonation of the carboxylate terminus of glycine should not effectively catalyze aquation of the amine terminus, while protonation of an oxalate ligand would lead to aquation of either or both functional groups. Correlation of the results of this investigation with other published results clarifies the role of the oxalate ligand in the induction of aquation processes of adjacent ligands and leads to interesting mechanistic details which may be generalized to complex species that contain carboxylate ligands.

Experimental Section

Preparation of Compounds. *trans*-$KCr(C_2O_4)_2(H_2O)_2 \cdot 3H_2O$ was prepared by Werner's method[9] and was recrystallized once from water. Anal. Calcd for $KCr(C_2O_4)_2(H_2O)_2 \cdot 3H_2O$: Cr, 14.56; $C_2O_4^{2-}$, 49.3. Found: Cr, 14.65 ± 0.01; $C_2O_4^{2-}$, 49.4 ± 0.2. Solutions of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ were obtained by isomerization of the trans complex salt. The visible absorption spectrum of the cis complex was in excellent agreement with previously reported spectra.[3,10]

The $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ ion was isolated as a mixed salt following its ion-exchange separation from other reaction products. In this preparation, 35.7 g of *trans*-$KCr(C_2O_4)_2(H_2O)_2 \cdot 3H_2O$ (0.1 mol) and 25.0 g of glycine (0.33 mol) were dissolved in 100 ml of water at 30 °C. The solution was cooled to room temperature and 6.9 g (0.05 mol) of anhydrous potassium carbonate was slowly added with vigorous stirring. After 1.5 h, the reaction was quenched in 1.5 L of water at 3 °C, and this solution was used to charge a water-cooled, 900-mL column of Dowex 1-X8 (100–200 mesh) chloride-form anion-exchange resin. The charged column was washed with 1.0 L of water and developed with 0.5 M potassium chloride–0.005 M potassium acetate solution at a flow rate of 5 mL/min. Mononegative species were rapidly eluted as diffuse bands, while trinegative species remained at the top of the column. $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ appeared as a well-defined, slow-moving purple band which had a profile skewed in the direction of flow. A total of 2 L, representing the front three-fourths of this band, was collected at 1 °C. After addition of 18.3 g of barium chloride dihydrate (0.075 mol), the cold column effluent was filtered through a medium-porosity sintered-glass filter. An equivalent volume of cold acetone was added to the filtrate to precipitate the complex salt, which was recovered by filtration after 12 h at 1 °C, washed with three portions of 50% acetone, and air-dried in the filter. The product was a finely divided, moderately soluble, purple powder and was free of chloride contamination. Yields ranged from 16 to 23 g (32–46% based on chromium). Anal. Calcd for $K_2Ba_3[Cr(C_2O_4)_2(NH_2CH_2CO_2)]_4 \cdot 18H_2O$: Ba, 20.36; H_2O, 16.03; Cr, 10.28; N, 2.77; K, 3.87. Found: Ba, 20.31 ± 0.04; volatile, 15.99 ± 0.02; Cr, 10.27 ± 0.01; N, 2.76 ± 0.01; K, 3.74 ± 0.07.

An ion-exchange method[11,12] was used to verify the charge of the complex unit in solution. Solutions containing known concentrations of the complex ion (5×10^{-3} M) and potassium chloride (0.5–0.8 M) were stirred with 1.00 g of Dowex 1-X8, chloride-form resin having an exchange capacity of 3.40 equiv/kg. After 10 min, aqueous-phase concentrations of the complex ion and the chloride ion were determined. These data were then used to compute n and K of the distribution coefficient expression $K = [Cr(ox)_2(gly)(resin)_n][Cl^-]^n/[Cr(ox)_2(gly)^{n-}][Cl(resin)]^n$, where bound ion concentrations are expressed in mol/kg of resin. Data at pH 5 and 25 °C lead to $n = 2.10 \pm 0.03$ and $pK = 0.703 \pm 0.004$.

Isolation of $Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^-$. After the reaction of 5 mmol of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ in 5.0 mL of 1.0 M hydrochloric acid for 10 min at room temperature, the aquation reaction was quenched in 200 mL of water at 1 °C. This solution was used to charge a water-jacketed, 18-cm column of Dowex 1-X8 (100–200 mesh) chloride-form resin at 3 °C. The charged column was developed with a solution 0.095 M in sodium chloride and 0.005 M in hydrochloric acid at a flow rate of 3 drops/min, and three sharp bands with relative R_f values of 1:9:18 were observed. These bands were identified in descending order as unreacted $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$, the product *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$, and the $Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^-$ aquation intermediate. When the aquation intermediate band front had descended 12 cm, the resin containing this band was siphoned from the column. The complex intermediate was then removed from the resin by equilibration with cold 0.90 M sodium perchlorate–0.10 M perchloric acid solution. Spectral characterizations and analyses were performed on this solution. The complex was found to have 1.02 ± 0.13 mol of glycine and 2.01 ± 0.02 mol of oxalate per mole of chromium.

Analytical Methods. Analytical methods for chromium[3] and oxalate[13] have been described elsewhere. Nitrogen of solid samples was determined as ammonia, using the Kjeldahl method. Chromatographic fractions were analyzed for amino nitrogen by the method of Yemm and Cocking.[14] Barium was determined as barium sulfate.[15] Chloride was determined by potentiometric titration with standard silver nitrate. The water content of solid salts was determined as the mass loss of 1.0-g samples at 150 °C. Potassium was determined by passing 1.00-mmol samples of the complex salt through columns of Dowex 50W-X8 (100–200 mesh) cation-exchange resin in the ammonium ion form. Ammonia was then distilled from the column effluent into standard hydrochloric acid. The excess acid was then back-titrated to a methyl red end point. A quantity of ammonia, equivalent to the barium present, was deducted from the ammonia found and the balance was computed as potassium. The presence of potassium in the complex salt was verified by flame test.

Lithium and sodium perchlorates were prepared by neutralizing lithium or sodium carbonate with perchloric acid, and their solutions were standardized by precipitation of tetraphenylarsonium perchlorate.

Rate Determinations. Rate determinations were initiated by adding 25.5 ± 0.5 mg of the complex salt to 10.0-mL portions of reactant solutions which had been equilibrated at the reaction temperature for a minimum of 30 min. The reaction mixture was then mixed vigorously for 1 min and was transferred to a 1.00-cm cuvette in the constant-temperature block of a Beckman DU spectrophotometer. The aquation reaction was monitored manually at 545 nm for at least 3 half-lives.

Data points taken in the first portion of the reaction were used to calculate approximate values of the reaction half-life using the initial rate method and the known absorbance change for the complete reaction. Assuming a single first-order reaction, "infinite-time" absorbance measurements were made at the time calculated as 10 half-lives and were checked again at 12 half-lives. In the extreme case of high hydrogen ion concentration and high temperatures, the difference between these values was not significant; but absorbance measurements taken at 20 half-lives showed a slight absorbance decrease.[16]

In all cases, the hydrogen ion concentrations were at least 20 times as large as the "infinite-time" glycine concentration. Pseudo-first-order rate constants, k_{obsd}, were determined by graphic evaluation of the slope of plots of $-\ln (A - A_\infty)$ vs. t. Each reported rate constant is the average of duplicate determinations and is precise to within ±2%.

Instruments. A Beckman Model DU spectrophotometer and Sargent Thermonitor constant-temperature bath were used in this investigation. A single short-range thermometer was used for all temperature measurements. It was found that the cell block and bath temperatures would be made to coincide within ±0.05 °C by maintaining the room temperature within 1 °C of the bath. Temperatures above 30 °C are block temperatures rather than bath temperatures and are precise to within ±0.1 °C.

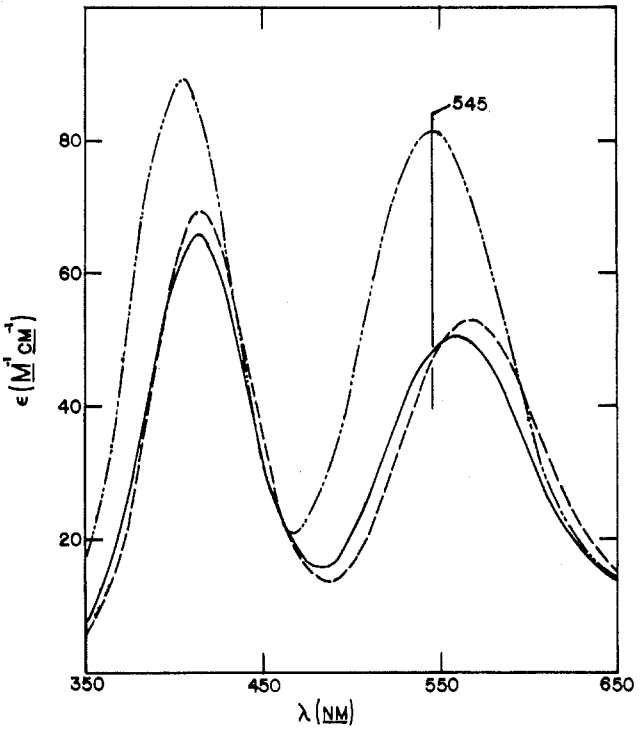


Figure 1. Visible absorption spectra of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ (– ·· –), $Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^-$ (– – –), and *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ (—).

Results

Characterization of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ in Solution. Ion-exchange chromatographic analysis of the product of Werner's preparation of $K_2Cr(C_2O_4)_2(NH_2CH_2CO_2)\cdot 1.5H_2O$[9] revealed that it was actually a complex mixture which contained the $Cr(C_2O_4)_3^{3-}$, $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$, and $Cr(C_2O_4)(NH_2CH_2CO_2)_2^-$ complex ions as major components. Attempts to crystallize the barium salt of the complex ion[9] from concentrated solutions of this mixture led to small yields which were contaminated with barium oxalate. We have modified Werner's preparative methods[9] to include a chromatographic separation step and have isolated a mixed salt of stoichiometry $K_2Ba_3[Cr(C_2O_4)_2(NH_2CH_2CO_2)]_4\cdot 18H_2O$. Fifteen of the 18 mol of water in this empirical formula may be readily removed by drying at 110 °C, while the remaining 3 mol may only be removed by drying at 150 °C. The anhydrous salt, when equilibrated with water vapor at room temperature, reincorporates only 15 mol of water into its crystal lattice. This salt is completely soluble in water and the chromium-containing unit elutes as a single band on Dowex 1-X8 resin. We have verified the dinegative charge of the complex unit in solution at pH 5 by the method of Cady and Connick.[11,12]

Three modes of glycinate coordination are consistent with the dinegative charge of the complex at pH 5: (1) normal bidentate coordination; (2) monodentate coordination through the amine terminus, with the free, unprotonated carboxylate group hydrogen bonded to an adjacent aqua ligand; (3) monodentate coordination through the carboxylate terminus, with the free amine group protonated and in close association with an adjacent hydroxo ligand.[17] The visible absorption spectrum of the complex ion, given in Figure 1, tends to eliminate the last possibility from serious consideration. Absorbance at the absorption maxima, 405 nm (ϵ 89.2 ± 0.3

M^{-1} cm^{-1}) and 545 nm (ϵ 81.6 ± 0.2 M^{-1} cm^{-1}), obeys Beer's law at 25 °C in unbuffered solutions to a complex concentration of 12×10^{-3} M. The position of the low-energy maximum is consistent with that found for other chromium(III) complexes which contain one nitrogen and five oxygen chromophores, such as $Cr(NH_3)(H_2O)_5^{3+}$, 549 nm,[18] $Cr(NH_2CH_2CH_2NH_3)(H_2O)_5^{4+}$, 545 nm,[2] and $Cr(C_2O_4)_2(NH_2CH_2CH_2NH_3)(H_2O)$, 544 nm.[3] Furthermore, the location of the low-energy maximum is in excellent agreement with the value of 546 nm predicted for CrO_5N complexes by application of the rule of average environment[19] to the $Cr(C_2O_4)_3^{3-}$ and $Cr(NH_2CH_2CH_2NH_2)_3^{3+}$ estimating bases.[3] These correlations strongly support coordination of the amine terminus of glycine in solution.

There was no significant difference in the absorption spectrum of the complex in 0.5 M perchloric acid or in 0.05 M sodium hydroxide at 3 °C. The complex also exhibited identical elution rates on Dowex 1-X8 resin at 3 °C whether 0.50 M hydrochloric acid or 0.50 M sodium chloride at pH 5 was used as the eluent. This invariance of absorption spectrum and elution behavior with pH is consistent with neither the amphiprotic aqua(glycinato-*N*) nor the basic hydroxo(glycine-*O*) coordination modes and tends to verify bidentate coordination of the glycinate ligand.

Reaction of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ in Acidic Solution. The aquation reaction was monitored spectrophotometrically at 25 °C in 0.10 M perchloric acid by scanning the visible region of the spectrum of a 5.0 mM solution of the complex at 10-min intervals. In the initial portion of the reaction, points of intersection of successive recorder traces with the "time-zero" trace occurred at 433, 463, and 577 nm. As the rate of change in absorbance decreased, the positions of these points gradually shifted to 437, 465, and 637 nm, indicating the accumulation of at least one metastable intermediate in a multistep aquation reaction. After 24 h, chromatographic analysis of this solution indicated quantitative conversion of the parent complex to the *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ product.

Solutions of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ which had been allowed to aquate for 1–2 half-lives at pH 0 and 2 were chromatographed on Dowex 1-X8 resin to determine the number and nature of the intermediates in the reaction. In each case, three discrete bands were obtained which were identified as unreacted $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$, the *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ product, and a green complex which contained one molecule of glycine per $Cr(C_2O_4)_2$ unit. The relative R_f values of these bands at 3 °C was 1:9:18 when 0.1 M chloride ion was used as the eluent at pH 1, 2.3, and 5.0. Neutral eluents caused slow decomposition of the band which contained the reaction intermediate.

The high elution rate of the reaction intermediate relative to the *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ complex ion is consistent with a mononegative ion which has a lower dipole moment than the cis complex. The pH invariance of the relative R_f values suggests that it has a very small acid dissociation constant. These criteria would be met by an intermediate which included a monodentate glycine molecule bonded to chromium through its carboxylate group.

The visible absorption spectrum of the reaction intermediate is given in Figure 1. The absorption maxima of this complex, 415 and 567 nm, have molar absorptivities of 70 ± 3 and 53 ± 2 M^{-1} cm^{-1} in a pH 1 solution at 3 °C. Close correspondence of the reaction intermediate spectrum to that of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$, which has maxima at 415 and 560 nm, and to that of $Cr(C_2O_4)_3^{3-}$, which has maxima at 417 and 569 nm, supports the contention that glycine is bonded to chromium through its carboxylate group. The spectrum of the reaction intermediate bears no resemblance to that of *trans*-$Cr(C_2O_4)_2(O_2CCH_3)(H_2O)^{2-}$ which has maxima at 410 nm (ϵ 22.2 M^{-1} cm^{-1}) and 545 nm (ϵ 20.0 M^{-1} cm^{-1}).[6] It is therefore probable that the reaction intermediate is the *cis*-$Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^-$ complex ion.

The $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ complex is isosbestic with the isolated reaction intermediate at 430, 465, and 578 nm and is isosbestic with *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ at 438, 465, and 638 nm. The excellent correlation between these isosbestic points and the points of intersection of repeated scans with the "time-zero" scan of a solution undergoing aquation verifies the accumulation of only a single, long-lived intermediate during the aquation reaction. The overall aquation sequence is therefore represented by eq 1 and 2.

$$Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-} + H_3O^+ \rightarrow Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^- \quad (1)$$

$$Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^- + H_2O \rightarrow \textit{cis}\text{-}Cr(C_2O_4)_2(H_2O)_2^- + NH_3CH_2CO_2 \quad (2)$$

$Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ Aquation Kinetics. The rate of aquation of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ was followed spectrophotometrically at 545 nm by measuring the decrease in absorbance with time. At this wavelength, the isolated intermediate and the product species are virtually isosbestic. Therefore, the only steps which result in an observed change in absorbance with time are those which are related to the formation of $Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^-$ from the chelated glycinate complex (eq 1). If an effective parallel pathway involving carboxylate terminus aquation exists, it must operate without significant accumulation of the $Cr(C_2O_4)_2(NH_2CH_2CO_2H)(H_2O)^-$ intermediate. At low hydrogen ion concentrations, plots of $-\ln (A - A_\infty)$ vs. time exhibited excellent linearity for periods up to 4 half-lives. This result establishes the first-order dependence of the rate upon the concentration of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$. At high hydrogen ion concentrations and low temperature, the plots showed a slight curvature for the first 5–8 min but then assumed a linear configuration and remained linear for periods up to 4 half-lives. In these cases, rate constants were evaluated as the slope of the final, linear portion of the plot. This curvature could be due to the slight increase in absorbance at 545 nm which would accompany the aquation of the reaction intermediate to *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$, if this step is more rapid at high hydrogen ion concentrations than the initial aquation step. $Cr(C_2O_4)_2(O_2CCH_3)(H_2O)^{2-}$, which is similar to our intermediate, aquates at slightly greater hydrogen ion dependent rates than the rate of the process which we have observed.[6] Curvature of the first-order rate plots was not observed for runs between 27.5 and 34.6 °C or at hydrogen ion concentrations below 0.7 M.

When the reaction rate is monitored at a wavelength where the intermediate and product are not isosbestic (i.e., 415 or 570 nm), the influence of the second process is seen as a continuous curvature of first-order semilogarithmic plots. There was no good possibility of determining the rate constant for the second process because the absorbances of the intermediate and final product were quite similar at all wavelengths.

The variation of the pseudo-first-order rate constant with hydrogen ion concentration was studied over the temperature range from 20.0 to 34.6 °C. Hydrogen ion concentration was varied from 0.10 to 0.90 M, while the ionic strength was maintained at 1.00 M with sodium perchlorate. Lithium perchlorate was used to maintain the ionic strength for one series of rate determinations at 25.0 °C. The results of this series of rate determinations are given in Table I.

The data of Table I specify a two-term rate law involving one hydrogen ion dependent, second-order rate constant and one hydrogen ion independent, first-order rate constant. These data were fit to eq 3 by use of the least-squares method of

Table I. Pseudo-First-Order Rate Constants for the First Aquation Step of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ in Sodium Perchlorate Media[a]

	$10^4 k_{obsd}$,[b] s^{-1}								
T, °C	[H⁺] = 0.10 M	[H⁺] = 0.20 M	[H⁺] = 0.30 M	[H⁺] = 0.40 M	[H⁺] = 0.50 M	[H⁺] = 0.60 M	[H⁺] = 0.70 M	[H⁺] = 0.80 M	[H⁺] = 0.90 M
20.0	1.27	2.26	3.19	4.15	5.03	5.90	6.86	7.73	8.75
22.5	1.71	2.99	4.20	5.39	6.59	7.70	9.12	10.3	11.3
25.0	2.26	3.96	5.53	7.17	8.69	10.3	11.8	13.3	14.0
25.0[c]	2.32	4.04	5.69	7.11	8.71	10.2	11.9	13.2	14.8
27.5	2.84	4.96	7.04	9.06	11.1	13.0	15.1	17.2	18.9
30.0	3.62	6.18	8.91	11.5	14.2	16.5	19.3	21.9	
32.5	4.50	8.06	11.3	14.5	17.6	20.4			
34.6	5.72	10.0	13.9	17.9	21.7				

[a] μ = 1.00 M; $[Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}]_0 = 5.0 \times 10^{-3}$ M. [b] Average of duplicate rate determinations. [c] Ionic strength maintained with $LiClO_4$.

Table II. Derived Rate Constants for the Aquation of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ in Sodium Perchlorate Media[a]

T, °C	$10^3 k'$,[d] M^{-1} s^{-1}	$10^5 k''$,[e] s^{-1}
20.0	0.92 ± 0.01[b]	4.0 ± 0.3[b]
22.5	1.20 ± 0.01	5.6 ± 0.6
25.0	1.57 ± 0.01	7.9 ± 0.5
25.0[c]	1.55 ± 0.01	9.2 ± 0.7
27.5	2.01 ± 0.01	9.5 ± 0.8
30.0	2.61 ± 0.02	10.3 ± 0.9
32.5	3.17 ± 0.05	16.0 ± 1.9
34.6	3.97 ± 0.05	19.2 ± 1.7

[a] μ = 1.00 M; $k_{obsd} = k'[H^+] + k''$. [b] Standard deviation. [c] Ionic strength maintained with $LiClO_4$. [d] For k' in $NaClO_4$, $\Delta H^{\ddagger}$ = 17.0 ± 0.2 kcal/mol and $\Delta S^{\ddagger}$ = −14.5 ± 0.7 cal/(mol K). [e] For k'' in $NaClO_4$, $\Delta H^{\ddagger}$ = 17.6 ± 1.1 kcal/mol and $\Delta S^{\ddagger}$ = −18.6 ± 3.8 cal/(mol K).

$$k_{obsd} = k'[H^+] + k'' \quad (3)$$

evaluation. Values of k' and k'' derived through this fitting process are given in Table II. It was found that the second-order rate constant, k', was independent of specific cation effects, but the first-order rate constant differed somewhat with the nature of the electrolyte. This difference was just outside the limits of experimental uncertainty and cannot be construed as strong evidence for a specific cation effect upon the hydrogen ion independent pathway.

The activation enthalpies for k' and k'' were determined to be 17.0 ± 0.2 and 17.6 ± 1.1 kcal/mol, respectively, while activation entropies were found to be −14.5 ± 0.7 and −18.6 ± 3.8 cal/(mol K), respectively. An increase in the activation entropy is consistent with entry of a hydrogen ion into the activated complex. However, the activation enthalpy *and* activation entropy uncertainty limits of the catalyzed and uncatalyzed pathways overlap, and it is not possible to conclude that catalysis is an entropy effect.

Since barium(II) is present in the complex salt used in the rate determinations, we have briefly examined its effect upon the rate. For rate determinations at 27.5 °C, μ = 1.00 M ($NaClO_4$), and a hydrogen ion concentration of 0.10 M, the pseudo-first-order rate constant was found to be independent of the barium(II) concentration ($(2.82 \pm 0.03) \times 10^{-4}$ s^{-1}) for barium(II) concentrations as high as 1.88×10^{-2} M.

The variation of the pseudo-first-order rate constant with ionic strength was studied at two different hydrogen ion concentrations to determine whether the increase in the rate of aquation was a real function of the hydrogen ion concentration or merely a function of a change in the activity of water which accompanied the systematic substitution of hydrogen ions for sodium ions. The results of this study are given in Table III. Although all values of the ionic strength were above the upper limit of the region of applicability of the extended Debye–Hückel limiting law, the trend of the data clearly indicates different limiting rates for the process at

Table III. Variation of the Pseudo-First-Order Aquation Rate Constant with Ionic Strength and Hydrogen Ion Concentration

	$10^4 k_{obsd}$,[a] s^{-1}	
μ, M	[H⁺] = 0.10 M	[H⁺] = 0.30 M
1.00	2.26	5.53
0.70	2.28	5.61
0.50	2.39	5.94
0.32	2.63	6.57
0.12	3.12	

[a] T = 25.0 °C; ionic strength maintained with $NaClO_4$.

hydrogen ion concentrations of 0.10 and 0.30 M. These data allow us to conclude that hydrogen ion catalysis is not simply an activity effect.

Discussion

Any reaction mechanism which is proposed for the aquation of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ must be consistent with three major observations: (1) a single, pseudo-first-order step is observed for its aquation to $Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^-$ and *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ at the isosbestic point for these "product" species; (2) $Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^-$ concentrations increase to isolable quantities during the aquation process; (3) $Cr(C_2O_4)_2(NH_2CH_2CO_2H)(H_2O)^-$ is not present in isolable quantities during the aquation process. The reaction scheme shown in eq 4–9 may be used in analysis

$$Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-} + H_3O^+ \xrightarrow{k_1} Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^- \quad (4)$$

$$Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-} + H_3O^+ \overset{k_2}{\rightleftharpoons} Cr(C_2O_4)_2(NH_2CH_2CO_2H)(H_2O)^- \quad (5)$$

$$Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^- + H_3O^+ \xrightarrow{k_4} Cr(C_2O_4)_2(H_2O)_2^- + NH_3CH_2CO_2H^+ \quad (6)$$

$$Cr(C_2O_4)_2(NH_2CH_2CO_2H)(H_2O)^- + H_3O^+ \xrightarrow{k_5} Cr(C_2O_4)_2(H_2O)_2^- + NH_3CH_2CO_2H^+ \quad (7)$$

$$Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-} + H_2O \xrightarrow{k_6} Cr(C_2O_4)_2(O_2CCH_2NH_3)(OH)^{2-} \quad (8)$$

$$Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^- \overset{K_a}{\rightleftharpoons} Cr(C_2O_4)_2(O_2CCH_2NH_3)(OH)^{2-} + H^+ \quad (9)$$

of the kinetic data and qualitative observations.

Within this scheme, aquation by dissociation and protonation of an amine group of glycine is given as an unidirectional step (eq 4) due to the tendency of the monodentate glycine-*O* ligand to remain monodentate in acidic solution.[20] Dissociation and protonation of the carboxylate terminus (eq 5) are written

in a reversible form to allow analysis of steady-state or equilibrium conditions placed on this process. Hydrogen ion dependent aquation steps have been assigned to the first step products (eq 6 and 7) in view of the observed instability of $Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^-$ in acidic solution. Hydrogen ion independent aquation has been depicted in the simplest fashion consistent with a product which is unlikely to undergo chelation (eq 8 and 9).[20] The acid dissociation constant, K_a of eq 9, should have a magnitude greater than K_{a1} for *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ ($pK_{a1} = 7.1$[21]) due to hydrogen-bonding possibilities between the hydroxo ligand and the free, protonated amine group of the glycine-*O* ligand. However, we would still anticipate $K_a << 1$.

Application of the steady-state condition to the concentration of the glycine-*N* intermediate, $Cr(C_2O_4)_2(NH_2CH_2CO_2H)(H_2O)^-$, of this reaction sequence leads to an equation for the rate of absorbance change, dA/dt, which is given by eq 10. This equation reverts to our observed rate law when

$$dA/(A_\infty - A)dt = k_1[H^+] + k_2k_5[H^+]^2/(k_3 + k_5[H^+]) + k_6 \quad (10)$$

$k_5[H^+] >> k_3$. However, it is then necessary that $k_5 >> k_2$ in order that the steady-state condition be preserved. If similar magnitudes are assumed for k_1, k_4, and k_5, then we must conclude that $k_1 >> k_2$, and the rate of change of absorbance will be given by eq 11.

$$dA/(A_\infty - A)dt = (k_1 + k_2)[H^+] + k_6 \simeq k_1[H^+] + k_6 \quad (11)$$

If the hydrogen ion dependence of eq 7 is removed and the steady-state condition is again applied to the concentration of $Cr(C_2O_4)_2(NH_2CH_2CO_2H)(H_2O)^-$, then the rate of change of absorbance is given by eq 12. In the absence of hydrogen

$$dA/(A_\infty - A)dt = k_1[H^+] + k_2k_5[H^+]/(k_3 + k_5) + k_6 \quad (12)$$

ion catalysis, it is likely that k_5 would have the small magnitude characteristic of the rate constants for uncatalyzed aquation of an amine group of $Cr(C_2O_4)_2(NH_2CH_2CH_2NH_2)^-$.[3] Now, to preserve the steady-state condition, k_3 must be much larger than k_2, and the rate of change of absorbance would be given by eq 13.

$$dA/(A_\infty - A)dt = (k_1 + k_2k_5/k_3)[H^+] + k_6 \simeq k_1[H^+] + k_6 \quad (13)$$

Finally, if it is assumed that eq 5 represents an equilibrium condition and that eq 7 has no hydrogen ion dependence, eq 14 may be derived for the rate of change of absorbance. Here

$$dA/(A_\infty - A)dt = \{(k_1 + k_5K)[H^+] + k_6\}/(1 + K[H^+]) \quad (14)$$

it is necessary that $K = k_2/k_3 << 1$ due to the linearity of our hydrogen ion dependence and the need for small concentrations of $Cr(C_2O_4)_2(NH_2CH_2CO_2H)(H_2O)^-$. It is also probable that k_5 for uncatalyzed amine terminus aquation is small.[3] Therefore, the rate of change of absorbance would reduce to eq 15.

$$dA/(A_\infty - A)dt = (k_1 + k_5K)[H^+] + k_6 \simeq k_1[H^+] + k_6 \quad (15)$$

It is clear from the preceding analysis that our data represent the parameters for aquation of the amine terminus of the bidentate glycinate ligand. Primary aquation of the carboxylate terminus cannot be considered as a significant factor in any of the reasonable aquation mechanisms. Two major questions are posed by these conclusions. First, how is amine terminus aquation catalyzed by the hydrogen ion? Then, why is the aquation of the amine terminus favored as the primary step?

The mechanism proposed for hydrogen ion catalysis of $Fe(bpy)_3^{2+}$ aquation[22] has been generalized to a "special mechanism for chelates"[23] and may certainly be applied to the problem of hydrogen ion catalyzed amine terminus aquation. Within the context of this mechanism (see eq 16) protonation

$$L_nM\begin{matrix}A\\ \diagup\\ \diagdown\\ B\end{matrix} \underset{k_b}{\overset{k_a}{\rightleftarrows}} L_nM\begin{matrix}A\\ \diagup\\ \diagdown\\ B\end{matrix} \xrightarrow[+H_3O^+]{k_c} L_n(H_2O)M\text{-}A\text{-}BH \quad (16)$$

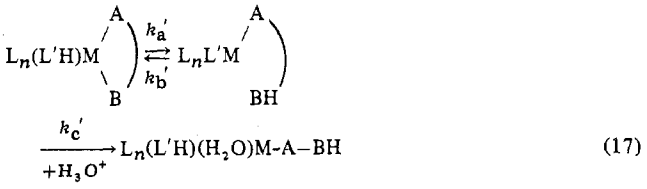
and water entry (k_c) must compete with chelation (k_b) of the half-bonded bidentate ligand generated by a dissociation step (k_a). When $k_b > k_c[H^+]$, the overall reaction will be observed to be hydrogen ion dependent. When $k_b < k_c[H^+]$, the observed reaction will be independent of the hydrogen ion concentration. Ligand-specified steric conditions, operating on k_c, tend to cause the observed reaction to be hydrogen ion dependent.[22,24,25]

Application of this mechanism to $Cr(H_2O)_4(NH_2CH_2CH_2NH_2)^{3+}$ specifies that $k_c[H^+] >> k_b$ for amine terminus aquation. Its first and second aquation steps are independent of the hydrogen ion concentration above $[H^+] = 0.10$ M.[2] The same condition must apply to the "unwrapping" steps of polyamine complexes of chromium(III), where the unbound portion of the ligand must represent a more severe impediment to protonation and water molecule entry.[26-29] If the steric considerations of these species present no noticeable limitation to k_c, then it must be considered unusual that amine terminus aquation rates of $Cr(C_2O_4)_2(NH_2CH_2CH_2NH_2)^-$ [3] and $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ have a first-order hydrogen ion dependence.

In addition to this unusual hydrogen ion dependence, the catalyzed and uncatalyzed amine terminus aquation rate constants are 3–5 orders of magnitude greater and activation enthalpies are lower in the presence of the oxalate ligand.[3] These data imply that the oxalate ligand labilizes the amine group and increases k_a relative to k_c. Labilization is possible through $(L \rightarrow M)\pi$ interactions between the π molecular orbitals of the oxalate ligand and the T_{2g} orbital sets of the metal center. This interaction would weaken the $(L \rightarrow M)\sigma$ interactions of both the oxalate ligand and the amine terminus, lower the activation enthalpy for amine terminus aquation, and effectively increase k_a. However, this argument makes it more difficult to rationalize the necessary increase in the relative rate of k_b.

Addition of two parallel pathways to the "special mechanism" may successfully resolve the problems presented by these similar systems. The parallel pathways include the effect of adjacent ligands upon the protonation step and specify eq 16 as the mechanism for reaction when the adjacent ligands are neither effective Bronsted acids nor effective Bronsted bases.

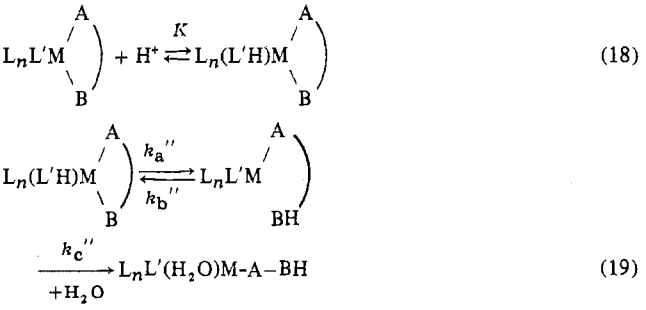
When a ligand adjacent to the leaving group is a Bronsted acid, the leaving group may abstract a hydrogen ion during its dissociation. Subsequent reprotonation of the donor ligand by a bulk solvent hydrogen ion, at a point somewhat removed from the leaving group, would then represent the rapid protonation step required for hydrogen ion independent rates ($k_b' << k_c'[H^+]$ of eq 17). The efficiency of this pathway would depend, of course, on the relative acidity of the donor ligand and the protonated leaving group. If the donor ligand is substantially less acidic than the protonated leaving group, this parallel pathway cannot exist. $Ni(NH_2CH_2CH_2NH_2)^{2+}$, which has a hydrogen ion dependent rate,[22] may fall into this category. However, the enhanced acidity of coordinated water



(17)

would almost guarantee acid-independent aquation rates for aquaethylenediamine and aquapolyamine complexes of trivalent cations via the mechanism of eq 17.

If an adjacent ligand is a Bronsted base, protonation of this site may precede the dissociation step (eq 18 and 19). The



(18)

(19)

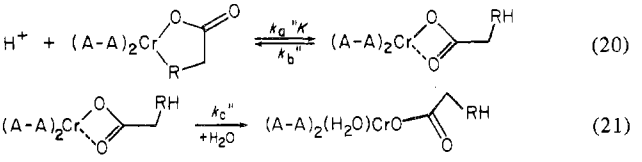
protonated base would then act as a proton donor during the dissociation of the leaving group. The efficiency of this pathway is dependent on the relative basicity of the adjacent ligand and the leaving group. Bases, L′, of weak to intermediate strength will lead to hydrogen ion dependent aquation rates. Strong bases, L′, will lead to hydrogen ion independent rates or rates which become independent at relatively low values of the hydrogen ion concentration. When L′ is a much stronger base than the leaving group or when L′ is an extremely weak base, the reaction must again proceed by the mechanism of eq 16.

Partial aquation of an ethylenediamine ligand of $Cr(NH_2CH_2CH_2NH_2)_2X_2^+$ ($X^- = F^-$, Cl^-, Br^-, and SCN^-) during the aquation of X in acidic solution may be rationalized by the mechanism of eq 18 and 19. This process becomes increasingly important as the basicity of X increases and is virtually the only first-step process when[30] $X^- = F^-$. The observed hydrogen ion independence of the reaction when $X^- = F^-$ is reasonable if $K[H^+] >> 1$ for protonation of a fluoro ligand. Rechelation of the free ethylenediamine terminus and displacement of a fluoro ligand[30] may be taken as evidence of the high order of basicity of the fluoro ligands of this complex. We propose that amine terminus aquation of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ also proceeds via the mechanism of eq 18 and 19, as do the amine group aquation reactions of $Cr(C_2O_4)_2(NH_2CH_2CH_2NH_2)^-$ [3] and $Cr(C_2O_4)(trien)^+$.[31] The coordinated oxalate ligand has been shown to have the low but crucial order of basicity necessary for this mechanism to operate and generate an observed hydrogen ion dependence.[4]

We have found no evidence for competitive, hydrogen ion catalyzed oxalate aquation of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$, although oxalate aquation is a major pathway for the decomposition of $Cr(C_2O_4)_2(NH_2CH_2CH_2NH_2)^-$ in our pH range.[3] Oxalate aquation is typically 2 orders of magnitude slower than the process we have observed,[3,16,32] and its absence in this case would tend to rule out physical displacement of the amine terminus of the glycinato-*N,O* ligand by the free end of a half-bonded oxalate ligand.

General metal ion catalysis must also be viewed as an inefficient and minor process. While metal ions catalyze the trans–cis isomerization of $Cr(C_2O_4)_2(H_2O)_2^-$ by association with the oxalate ligands,[33-35] catalysis of amine terminus aquation of the glycinato-*N,O* ligand must involve transfer of the cation to the leaving group by our mechanism. This transfer would only be effective for small cations of high charge density and a special affinity for the leaving group as well as the oxalate ligand.

Rate constants for the catalyzed and uncatalyzed amine terminus aquation of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ are 2 orders of magnitude greater than those for amine terminus aquation of $Cr(C_2O_4)_2(NH_2CH_2CH_2NH_2)^-$.[3] In a similar fashion, rate constants for the catalyzed and uncatalyzed thio terminus aquation of $Cr(NH_2CH_2CH_2NH_2)_2(SCH_2CO_2)^+$ are 2 orders of magnitude greater than those for thio terminus aquation of $Cr(NH_2CH_2CH_2NH_2)_2(SCH_2CH_2NH_2)^{2+}$.[36] In addition, the 2-thioacetato-*O,S* complex shows a preference for thio terminus aquation that is analogous to the amine terminus aquation preference of our glycinato-*N,O* complex. This parallel aquation behavior suggests general carboxylate terminus acceleration of the aquation of the amine or thio terminus of the bidentate ligand. Since this effect is not mirrored by amine or thio terminus acceleration of carboxylate terminus aquation processes and cannot be simply explained as an inductive effect, the most reasonable source of the acceleration is the geometry and bifunctional nature of the carboxylate group. We therefore propose the mechanism of eq 20 and 21 for the acceleration (R = S or NH_2).



(20)

(21)

We propose that the protonation and dissociation steps of the amine or thio terminus are followed by rapid rotation of the ligand to a carboxylato-*O,O* bonding configuration (the overall process is abbreviated as $k_a''K$). Temporary blocking of the vacated site by the carbonyl group would then allow migration of the protonated amine or thio group from its vicinity. Entry of a water molecule at the carbonyl group coordination site would follow in a rapid step of low activation enthalpy. A similar mechanism may be imagined for the uncatalyzed process. However, an equivalent stabilization of the vacated coordination site is not possible during carboxylate terminus aquation, nor is it possible in the aquation mechanism of ethylenediamine or the 2-mercaptoethylamine-*N,S* ligand.

The free energy of activation is virtually the same for amine terminus aquation of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ and thio terminus aquation of $Cr(NH_2CH_2CH_2NH_2)_2(SCH_2CO_2)^+$. The glycinato-*N,O* complex has a slightly higher activation enthalpy (17.0 vs. 16.2 kcal/mol[36]) and entropy (−14.5 vs. −17.6 cal/(mol K)[36]), but it is clear that the parameters show little dependence on the nature of the leaving group or complex charge and type. Activation free energies are also similar for $Cr(C_2O_4)_2(NH_2CH_2CH_2NH_2)^-$ and $Cr(NH_2CH_2CH_2NH_2)_2(SCH_2CH_2NH_2)^{2+}$. Here, however, the drastic difference in the enthalpy and entropy components more clearly denotes a dissociative process. Thio terminus aquation occurs with a greater activation enthalpy (22.3 vs. ca. 18 kcal/mol[3,36]) and activation entropy (−7.2 vs. ca. −22 cal/(mol K)[3,36]). Differences in $\Delta S^\ddagger$ may be explained by large differences in solvation of the protonated leaving groups in the transition state. Differences in $\Delta H^\ddagger$ could stem from the presence of π-bonding interactions between the thio group and the metal that are partially replicated by the coordinated carbonyl group of the hypothetical 2-mercaptoacetato-*O,O* intermediate.

It should be noted that the (glycine-*O,O*)bis(oxalato)chromate(III) intermediate would tend to lead to retention of the cis configuration of the oxalate ligands in either the

hydrogen ion catalyzed process or the uncatalyzed process. We have isolated only one product of each aquation step, and each has a cis configuration. Weschler and Deutsch[36] have also isolated only a cis isomer of $Cr(NH_2CH_2CH_2NH_2)_2(O_2CCH_2SH)(H_2O)^{2+}$ from their reaction mixtures. However, we would expect rapid isomerization rates that would make isolation of the trans isomers difficult by ion-exchange chromatography. While the spectral changes which accompany trans–cis isomerizations tend to be ruled out by the linearity of our first-order kinetic plots, we cannot conclude with absolute certainty that the cis configuration is retained during aquation.

Features of the mechanism of eq 20 and 21 may be generalized to other mixed-ligand complexes that contain carboxylato ligands. An oxalato-*O,O* analogue of the glycine-*O,O* and 2-mercaptoacetato-*O,O* bonding configurations has been proposed[4] as a feature common to the anation mechanism of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ and the aquation mechanism of $Cr(C_2O_4)_3^{3-}$. Also, monodentate carboxylate ligands have been observed to induce aquation of ammonia from $Cr(NH_3)_5X^{2+}$. The monodentate hydrogen oxalate ligand ($X^- = O_2CCO_2H^-$) displaces ammonia less rapidly than the monodentate oxalate ligand;[37] and ammonia is displaced by substituted acetato ligands ($X^- = O_2CCH_3^-$, $O_2CCH_2Cl^-$, $O_2CCHCl_2^-$) with rate constants which increase with ligand basicity.[8] Increases in ligand basicity would both stabilize the carboxylato-*O,O* configuration and facilitate protonation. The absence of hydrogen ion catalysis in these cases tends to specify that formation of the carboxylato-*O,O* configuration is far more important than the mechanism by which the leaving group is protonated. Indeed, the potential which carboxylato ligands possess to assume a metastable, bidentate carboxylato-*O,O* configuration in aquation processes may be a cardinal feature in determining the reactivity of mixed-ligand complexes of chromium(III).

Registry No. *trans*-$KCr(C_2O_4)_2(H_2O)_2$, 14639-33-9; $K_2Ba_3[Cr(C_2O_4)_2(NH_2CH_2CO_2)]_4$, 61544-11-4; *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$, 15489-30-2; $Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^-$, 61544-12-5.

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