

- and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1225 (1972). (b) Earlier attempts to prepare phenyl and methyl derivatives resulted in the isolation of products which could not be purified: F. A. Hart, A. G. Massey, and M. S. Saran, *J. Organomet. Chem.*, **21**, 147 (1970).
- (18) R. E. Maginn, S. Manastyrskij, and M. Dubeck, *J. Am. Chem. Soc.*, **85**, 672 (1963).
- (19) M. Schlosser and V. Ladenberger, *J. Organomet. Chem.*, **8**, 193 (1967).
- (20) S. Manastyrskij, R. E. Maginn, and M. Dubeck, *Inorg. Chem.*, **2**, 904 (1963).
- (21) F. A. Cotton and T. J. Marks, *J. Am. Chem. Soc.*, **91**, 7281 (1969).
- (22) In contrast, the $\text{C}\equiv\text{C}$ stretch in free ethynylbenzene occurs at 2085 cm^{-1} (taken from the ir spectrum in the Sadtler Collection of Standard IR Spectra).
- (23) K. Nakamoto in "Characterization of Organometallic Compounds, Part I", M. Tsutsui, Ed., Interscience, New York, N.Y., 1969, Chapter 3.
- (24) J. C. Barnes, *J. Chem. Soc.*, 3880 (1964).
- (25) K. Bukietynska and G. R. Choppin, *J. Chem. Phys.*, **52**, 2875 (1970).
- (26) C. K. Jorgensen and B. R. Judd, *Mol. Phys.*, **8**, 281 (1964).
- (27) B. R. Judd, *J. Chem. Phys.*, **44**, 839 (1966).
- (28) D. G. Karraker, *Inorg. Chem.*, **7**, 473 (1968).
- (29) J. H. Van Vleck and N. Frank, *Phys. Rev.*, **34**, 1494 (1929).
- (30) J. M. Birmingham and G. Wilkinson, *J. Am. Chem. Soc.*, **78**, 42 (1956).
- (31) P. W. Selwood, "Magnetochemistry", Interscience, New York, N.Y., 1956.
- (32) N. E. Topp, "The Chemistry of the Rare Earth Elements", Elsevier, Amsterdam, 1965, pp 9-11.
- (33) H. G. Friedman, Jr., G. R. Choppin, and D. G. Feuerbacher, *J. Chem. Educ.*, **41**, 354 (1964).
- (34) L. J. Nugent, P. G. Laubereau, G. K. Werner, and K. L. Vander Sluis, *J. Organomet. Chem.*, **27**, 365 (1971).
- (35) In compounds containing lanthanide-carbon σ bonds, the electron density (negative charge) of the ligand should be more available for localized interaction with the metal than for π -bonded systems. This could possibly lead to a greater enhancement of f -orbital participation in the bonding than in, for instance, the π -cyclopentadienyl ligand. When cyclopentadiene gains an electron to form the cyclopentadienyl anion, the stability of this anion arises from the ligand being able then to form a delocalized aromatic system. Because of the stability gained by the addition of the electron (and formation of the carbanion), the cyclopentadienyl ligand would be less likely to lose some of its electron density through covalent bonding than would a carbanion which is less stabilized (such as CH_3^-) and has its negative charge more localized.³⁶ This is, of course, certainly not to say that ligands which are π bonded will not form strong covalent bonds by overlap of ligand orbitals with metal orbitals of the proper symmetry. However, this type of enhancement could be especially important in increasing the degree of covalency in compounds where the bonding is primarily ionic, such as the lanthanides.
- (36) For a discussion of carbanions, see J. March "Advanced Organic Chemistry: Reactions, Mechanisms and Structure," McGraw-Hill, New York, N.Y., 1968, pp 141-148.
- (37) J. C. Eisenstein, *J. Chem. Phys.*, **25**, 142 (1956).
- (38) It should be pointed out that in the analogous Cp_3UR complexes (C_{3v} symmetry), where $5f$ -orbital participation in the bonding has been more clearly established,^{12,13} the same symmetry arguments are valid for the uranium and the R moiety. It is, in fact, probably just this overlap responsible for the covalency in the bonding. It should be mentioned, too, that the f_{z^2} orbital of uranium is unoccupied and can accept donation of electron density from the ligand as proposed.

Contribution from the Department of Chemistry,
State University of New York, College at Brockport, Brockport, New York 14420

Competitive Pathways for the Aquation of the (Ethylenediamine)bis(oxalato)chromate(III) Ion in Acidic Media¹

THOMAS W. KALLEN

Received February 7, 1975

AIC50098K

Ion-exchange chromatography has been used to isolate and characterize intermediates in the aquation of the (ethylenediamine)bis(oxalato)chromate(III) ion. The complex $\text{Cr}(\text{C}_2\text{O}_4)_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3)(\text{H}_2\text{O})$ is the major intermediate at pH 1 and aquates in turn to $\text{cis-Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ with a first-order rate constant of $(1.9 \pm 0.1) \times 10^{-5}\text{ sec}^{-1}$ at 25.0°C . Two other intermediates, $\text{Cr}(\text{C}_2\text{O}_4)(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)(\text{H}_2\text{O})_2^+$ and $\text{Cr}(\text{C}_2\text{O}_4)(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3)(\text{H}_2\text{O})_3^{2+}$, result from an oxalate aquation process which is operative at lower pH and leads to the product $\text{Cr}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4^+$. The kinetics of the first step in the aquation of $\text{Cr}(\text{C}_2\text{O}_4)_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)^-$ have been investigated spectrophotometrically at 570 nm, where first-step products are isosbestic with their ultimate reaction products. The rate of change of absorbance with time obeys simple first-order kinetics at hydrogen ion concentrations from 0.50 to 2.00 M . Observed rate constants for the process are described by $k_{\text{obsd}} = k_a + k_b[\text{H}^+] + k_c[\text{H}^+]^2$, where $k_a = 1.7 \times 10^{-5}\text{ sec}^{-1}$, $k_b = (7.69 \pm 0.11) \times 10^{-5}\text{ M}^{-1}\text{ sec}^{-1}$, and $k_c = (6.15 \pm 0.07) \times 10^{-5}\text{ M}^{-2}\text{ sec}^{-1}$ at 25.0°C and $\mu = 2.01\text{ M}$ (KNO_3). Activation enthalpies, ΔH^\ddagger , for k_a , k_b , and k_c , computed from data at 25.0, 35.0, and 45.0°C , are 20.6 ± 0.6 , 17.6 ± 0.2 , and $16.6 \pm 0.6\text{ kcal mol}^{-1}$, respectively, while activation entropies, ΔS^\ddagger , are -11.4 ± 1.9 , -18.3 ± 0.5 , and $-22.0 \pm 1.8\text{ cal mol}^{-1}\text{ deg}^{-1}$. Observed concentrations of mono(oxalato) and bis(oxalato) species at 1 and 10 half-lives are consistent with the aquation rate law if k_a is associated with primary, uncatalyzed ethylenediamine aquation, k_c describes second-order, hydrogen ion catalyzed oxalate aquation, and k_b describes acid-catalyzed aquation of both ethylenediamine (k_b') and oxalate (k_b''). At 25.0°C , $k_b' = (1.7 \pm 0.8) \times 10^{-5}\text{ M}^{-1}\text{ sec}^{-1}$ and $k_b'' = (6.0 \pm 0.9) \times 10^{-5}\text{ M}^{-1}\text{ sec}^{-1}$. A protonated, half-bonded oxalate ligand is proposed to account for hydrogen ion catalysis of the aquation process.

Introduction

Aquation processes of oxalatochromate(III) complexes have clearly been established as pH-dependent processes by past investigators. For example, aquation of $\text{Cr}(\text{ox})_3^{3-}$ to $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ has as its rate law^{2,3} $-d \ln [\text{Cr}(\text{ox})_3^{3-}]/dt = k'[\text{H}^+] + k''[\text{H}^+]^2$. The $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ complex aquates in turn to $\text{Cr}(\text{ox})(\text{H}_2\text{O})_4^+$ with a rate law given by⁴ $-d \ln [\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-]/dt = k[\text{H}^+]$. In both cases, only a single aquation step was noted for the loss of an oxalate ligand, and no evidence was found which would support the existence of large concentrations of monodentate oxalate species.

In contrast, ethylenediamine⁵ and polyamine complexes⁶⁻⁹ of chromium(III) aquate in distinct, stepwise fashion through monodentate or partially "unwrapped" species. These processes seem to be independent of pH in acid solution, or are, at worst, inversely dependent upon the hydrogen ion concentration. In the simplest case, Childers et al⁵ have found

that the $\text{Cr}(\text{en})(\text{H}_2\text{O})_4^{3+}$ ion aquates in two pH-independent steps and have isolated the monodentate ethylenediamine complex intermediate $\text{Cr}(\text{enH})(\text{H}_2\text{O})_5^{4+}$ using ion-exchange chromatography.

When both ethylenediamine and oxalate are coordinated to chromium(III), the question of relative ligand reactivity must ultimately arise and the kinetic interplay of the two, different bidentate ligands must be considered.

Schläfer¹⁰ has determined that the $\text{Cr}(\text{ox})_2(\text{en})^-$ complex ion aquates to $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ in two steps which are essentially pH independent. However, his investigations have been limited to pH values above 1.05 where hydrogen ion catalyzed aquation of the oxalate ligand should not be evident. The magnitude of Schläfer's first-order rate constants, when compared to the second- and third-order rate constants for oxalate aquation processes,¹⁻³ suggests that competitive aquation pathways should exist at lower pH values. Loss of

Table I. Analytical Data for Complexes Obtained Using Ion-Exchange Chromatography

Complex ^{a,b}	Molar ratio	
	C ₂ O ₄ ²⁻ :Cr	C ₂ H ₆ N ₂ :Cr
Cr(ox) ₂ (enH)(H ₂ O)	2.010 ± 0.008 ^c	1.008 ± 0.010 ^c
Cr(ox)(enH)(H ₂ O) ₃ ²⁺	1.009 ± 0.008	1.012 ± 0.015
Cr(ox)(en)(H ₂ O) ₂ ⁺	1.007 ± 0.002	1.006 ± 0.007
<i>cis</i> -Cr(ox) ₂ (H ₂ O) ₂ ⁻	2.000 ± 0.004	
Cr(ox)(H ₂ O) ₄ ⁺	1.000 ± 0.004	

^a Abbreviations: ox, C₂O₄²⁻; en, NH₂CH₂CH₂NH₂; enH, = NH₂CH₂CH₂NH₃⁺. ^b Six normal coordination sites are assumed for Cr(III). ^c Standard deviation of triplicate determinations.

oxalate from Cr(ox)₂(en)⁻ is evident in the presence of heavy metal ions.¹¹

We have therefore examined the aquation of Cr(ox)₂(en)⁻ at higher hydrogen ion concentrations in an attempt to establish the existence and nature of aquation processes which compete with the simple ethylenediamine aquation proposed by Schläfer. We have used chromatographic techniques to isolate reaction intermediates which are indicative of oxalate aquation, and we have determined the kinetic parameters for the oxalate aquation process. Our results, combined with those of Schläfer, should lead to a clearer understanding of mixed polyamine-oxalato complexes of chromium(III).

Experimental Section

Preparation of K[Cr(ox)₂(en)]·1.75H₂O. A 20.0-mmol amount of K₃Cr(ox)₃·3H₂O and 2.5 mmol of oxalic acid dihydrate were heated gently on a steam bath in 20 ml of 0.75 *M* nitric acid until dissolution was complete. Ethylenediamine was then added in three 10-mmol portions at 5-min intervals. The resulting solution was heated on the steam bath for 5 min after the last ethylenediamine addition, and crystallization was then allowed to proceed for 12 hr at 0°C. The crude product was removed by filtration, redissolved in 75 ml of water, and filtered again to remove the insoluble [Cr(en)₂(ox)][Cr(ox)₂(en)] complex salt which had coprecipitated. Finally, the filtrate was treated with acetone (ca. 75 ml) until it became slightly turbid. When the acetone-water mixture was slowly cooled to 0°C, the final product, ca. 2.5 g (35% yield, based on K₃Cr(ox)₃·3H₂O), precipitated as a fine, red, crystalline solid which was separated by filtration, washed with acetone, and air-dried. Anal. Calcd for KCr(C₂O₄)₂(C₂H₆N₂)·1.75H₂O: Cr, 14.49; C₂O₄²⁻, 49.1; N, 7.81; H₂O, 8.79. Found: Cr, 14.52 ± 0.06; C₂O₄²⁻, 49.1 ± 0.1; N, 7.82 ± 0.03; H₂O (as volatile material at 110°C), 8.64 ± 0.09.

The visible absorption spectrum of this complex in 0.1 *M* nitric acid at 25.0°C and $\mu = 1.00$ *M* (KNO₃) is in substantial agreement with previously reported spectra.^{12,13} Our preparation and analyses lead to slightly larger molar absorptivities at the visible absorption maxima than those reported by House and Garner¹³ (see Table II).

Preparation of *trans*-K[Cr(ox)₂(H₂O)₂]·3H₂O. This complex salt

was prepared by the method of Werner¹⁴ and was used in the preparation of the *cis* complex. Anal. Calcd for KCr(C₂O₄)₂(H₂O)₂·3H₂O: Cr, 14.56; C₂O₄²⁻, 49.3. Found: Cr, 14.67 ± 0.02; C₂O₄²⁻, 49.4 ± 0.2.

Isolation of the Cr(ox)(H₂O)₄⁺ Complex Ion. A 0.10-mol sample of potassium oxalate was added to 100 ml of a solution which was 0.1 *M* in chromic perchlorate and 0.1 *M* in perchloric acid. The solution was maintained at 50°C for 12 hr, at which point potassium bicarbonate was added to bring the solution pH to 6.0. After an additional 24 hr at 50°C, the solution was cooled to 5°C and filtered to remove potassium perchlorate. This solution was used to charge a column of 100 ml of Dowex 50W-X8 (50–100 mesh) cation-exchange resin which was in the H⁺ form. The column was then washed with 100 ml of 0.01 *M* perchloric acid to remove neutral and anionic species. Finally, the Cr(ox)(H₂O)₄⁺ complex was eluted at room temperature with a solution 0.1 *M* in nitric acid and 0.9 *M* in potassium nitrate. At a flow rate of 1 ml/min, the Cr(ox)(H₂O)₄⁺ band was symmetrical in appearance and separated cleanly from the other cationic species on the column. A center cut (yield 12% based on chromium(III)) of the band was taken for analysis and characterization. Analytical results are given in Table I and the visible absorption maxima of the complex are given in Table II.

Isolation of the *cis*-Cr(ox)₂(H₂O)₂⁻ Complex Ion. The *cis*-Cr(ox)₂(H₂O)₂⁻ ion was obtained in solution by allowing the *trans* complex to isomerize in 0.1 *M* nitric acid for periods of time computed to be in excess of 10 half-lives for the *trans*-*cis* isomerization.¹⁵ The complex was chromatographed on a column of Dowex 1-X8 (100–200 mesh) resin in the NO₃⁻ form to ensure the absence of mono- and tris(oxalato) complexes. Elution was rapidly accomplished at a rate of 1 ml/min using a solution which was 0.1 *M* in nitric acid and 0.9 *M* in potassium nitrate. A center cut of the intense purple band, containing 80% of the total chromium, was taken for analysis and characterization. Analytical results are given in Table I and the visible absorption maxima of the complex are given in Table II. Spectra of the Cr(ox)(H₂O)₄⁺ ion and *cis*-Cr(ox)₂(H₂O)₂⁻ are in excellent agreement with those of Spinner and Harris,¹⁶ who have also obtained both complexes chromatographically.

Isolation of the Cr(ox)₂(enH)(H₂O) Complex. A 1-mmol sample of KCr(ox)₂(en)·1.75H₂O was treated with 10 ml of 0.1 *M* nitric acid for 12–18 hr at 25°C. The solution was then passed through a 50 ml column of Dowex 50W-X8 resin in the H⁺ form to remove cationic species and a 100 ml column of Dowex 1-X8 resin in the NO₃⁻ form to remove anionic species. The total purple effluent (0.26 ± 0.02 mmol) was taken for analysis. Analytical results are given in Table I.

Isolation of the Cr(ox)(en)(H₂O)₂⁺ Complex Ion. A 1-mmol sample of KCr(ox)₂(en)·1.75H₂O was treated with 10 ml of 2.0 *M* nitric acid for 2.5 hr at 25°C. The reaction mixture was then used to charge a 50 ml column of Dowex 50W-X8 resin which had been equilibrated with the eluent, a solution of 0.10 *M* nitric acid in 0.90 *M* potassium nitrate. This complex exhibited remarkable stability on the column and was successfully eluted as a single, red band at room temperature. Successive fractions showed no difference in their visible absorption

Table II. Fraction of Product Species Containing One Oxalate Ligand at "Infinite Time" and at 1 Half-Life in the Primary Aquation of Cr(ox)₂(en)⁻

<i>T</i> , °C	[H ⁺], <i>M</i>	<i>f</i> _{Cr(ox)} ^{a,b}	<i>F</i> _{Cr(ox)} ^{a,c}	(<i>f</i> _{Cr(ox)}) _{calcd} ^{a,d}
20.0	2.00	0.93	0.910	
25.0	0.50	0.56	0.587	0.76
25.0	1.00	0.75	0.737	0.89
25.0	1.50	0.87	0.825	0.94
25.0	1.80	0.90		0.95
25.0	2.00	0.90	0.906	0.96
35.0	0.50	0.55	0.579	0.74
35.0	1.00	0.76	0.742	0.88
35.0	1.50	0.85	0.830	0.93
35.0	2.00	0.93	0.895	0.95
45.0	0.50	0.56	0.565	0.69
45.0	1.00	0.78	0.768	0.85
45.0	1.50	0.83	0.832	0.91
45.0	2.00	0.93	0.909	0.94

^a The fraction of product species which contains one oxalate ligand. Species include Cr(ox)(en)(H₂O)⁺, Cr(ox)(enH)(H₂O)₃²⁺, and Cr(ox)(H₂O)₄⁺. ^b Calculated from "infinite-time" absorbance data. $f_{\text{Cr(ox)}} = (\epsilon_1 C_1 - A_\infty) / (\epsilon_1 - \epsilon_2) C_1$, where $\epsilon_1 = 50.2$ *M*⁻¹ *cm*⁻¹ and $\epsilon_2 = 31.6$ *M*⁻¹ *cm*⁻¹. ^c Determined after ion-exchange separation of cationic species at $t = t_{1/2}$. $F_{\text{Cr(ox)}} = 2N_t/N_1$, where N_t is the number of moles of cationic species at 1 half-life and N_1 is the number of moles of Cr(ox)₂(en)⁻ taken. $\mu = 2.0$ *M* (KNO₃). ^d Calculated, using the rate data of Table V and the assumption that ethylenediamine aquation is independent of [H⁺].

spectra, so the entire band (0.38 ± 0.02 mmol) was taken for analysis.¹⁷ Analytical results are given in Table I.

Isolation of the $\text{Cr}(\text{ox})(\text{enH})(\text{H}_2\text{O})_3^{2+}$ Complex Ion. In every chromatographic isolation of $\text{Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$, a small, pale purple band remained at the top of the column during elution. The quantity of material in this band was enhanced by carrying out the reaction for 32 hr in 20 ml of 2.0 M nitric acid and the complex was eluted with a solution 0.1 M in nitric acid and 1.8 M in potassium nitrate after complete elution of $\text{Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$. It was not possible to obtain large quantities (0.10 ± 0.03 mmol) and the complex was not appreciably stable. By careful elution at 15°C we were able to obtain reproducible spectra and analytical results for the complex. Analytical results are given in Table I.

Analytical Methods. All complex salts and solutions of complex ions were analyzed for chromium after oxidation to chromium(VI) with ammonium peroxydisulfate in 1 M sulfuric acid. Chromium(VI) was reduced to chromium(III) with an excess of standard 0.1 N ferrous ammonium sulfate and the excess ferrous ion was back-titrated with standard 0.1 N potassium dichromate to a diphenylaminesulfonate end point.

The amine nitrogen content of solid samples was determined as ammonia using the Kjeldahl method. Solution samples, obtained from chromatographic treatment of reaction mixtures, were analyzed for amine nitrogen using a small-scale modification of the Kjeldahl method. Chromatographed samples for these analyses were eluted with sulfuric acid-potassium sulfate eluents having the same formal cation concentrations as the solutions described above. The amine nitrogen analyses were keyed to chromium analyses on portions of the same solution.

Oxalate was determined by the method of Hamm.¹⁸ Solution oxalate analyses were again keyed to chromium analyses on portions of the same solution.

Volatile materials were determined as the mass loss of 1-g samples of the complex salt at 110°C.

Spectral Measurements. Spectra of the complex ions between 350 and 650 nm and repeated-scan spectra were run on a Beckman DB spectrophotometer. The location of absorption maxima and the values of molar absorptivities were verified using a Guilford Model 240 spectrophotometer. Temperature was maintained in the cell block of both instruments with a Lauda K2/R circulating water bath.

Kinetics Measurements. A survey of the reaction kinetics of the $\text{Cr}(\text{ox})_2(\text{en})^-$ complex was made using the Guilford Model 240 spectrophotometer. Reaction rate constants were evaluated as the slope of plots of $-\ln(A - A_\infty)$ vs. time for absorbance changes at 570 nm. Rate plots were linear for at least 4 half-lives and rate constants were independent of the dwell time of the sample in the light path. At this wavelength, $\text{Cr}(\text{ox})_2(\text{enH})(\text{H}_2\text{O})$ and $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ are isosbestic, with $\epsilon_1 50.2 M^{-1} \text{cm}^{-1}$. In addition, $\text{Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$, $\text{Cr}(\text{ox})(\text{enH})(\text{H}_2\text{O})_3^{2+}$, and $\text{Cr}(\text{ox})(\text{H}_2\text{O})_4^+$ are almost isosbestic, with $\epsilon_2 31.6 \pm 0.6 M^{-1} \text{cm}^{-1}$. An observed, simple first-order process is reasonable if $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ does not aquate to $\text{Cr}(\text{ox})(\text{H}_2\text{O})_4^+$ and if $\text{Cr}(\text{ox})_2(\text{enH})(\text{H}_2\text{O})$ aquates primarily to $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$. If either condition is not valid, a plot of $-\ln(A - A_\infty)$ vs. time would be nonlinear, indicating the presence of two, consecutive first-order processes.

Solutions for the rate determinations were prepared by dilution of standard nitric acid and potassium nitrate solutions at the temperature of the rate determination. Reactions were initiated by adding the complex salt to 25.0 ml of the reagent solution and quickly transferring a portion of this solution to a 1.00-cm cuvette in the cell block of the spectrophotometer. "Infinite-time" absorbance values were taken as the constant value obtained after 10 half-lives of the reaction. Absorbance was checked for constancy at 2-hr intervals until two identical values were obtained.

Infinite-time absorbance measurements at 570 nm are necessarily those of nonequilibrium mixtures of complex ions and depend on the relative abundance of mono(oxalato) complexes and bis(oxalato) complexes which result from the various possible aquation steps. The fraction of the mixture in the form of a mono(oxalato) complex may be calculated as $f_{\text{Cr}(\text{ox})} = (\epsilon_1 C_i - A_\infty) / (\epsilon_1 - \epsilon_2) C_i$, where C_i is the initial concentration of $\text{Cr}(\text{ox})_2(\text{en})^-$ and ϵ_1 and ϵ_2 are the molar absorptivities of the isosbestic points given above. Considering the preconditions for linearity of first-order plots at 570 nm, the fraction $f_{\text{Cr}(\text{ox})}$ should reflect the fraction of $\text{Cr}(\text{ox})_2(\text{en})^-$ which reacts via an initial oxalate aquation step. Values of $f_{\text{Cr}(\text{ox})}$ obtained from the various rate determinations are tabulated in Table II.

Table III. Visible Absorption Maxima of Complex Species in 0.10 M Nitric Acid at 25.0°C^{a,b}

Complex	λ_{max} , nm	ϵ_{max} , $M^{-1} \text{cm}^{-1}$
$\text{Cr}(\text{ox})_2(\text{en})^-$	530	92.5 ± 0.9^c
	394	100.0 ± 1.0
$\text{Cr}(\text{ox})_2(\text{enH})(\text{H}_2\text{O})$	546	59.4 ± 0.4
	405	72.0 ± 0.5
$\text{Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$	522	63.1 ± 0.4
	391	62.0 ± 0.5
$\text{Cr}(\text{ox})(\text{enH})(\text{H}_2\text{O})_3^{2+ d}$	540	39.1 ± 0.5
	403	48.4 ± 0.5
$\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$	562	50.9 ± 0.1
	416	65.8 ± 0.2
$\text{Cr}(\text{ox})(\text{H}_2\text{O})_4^+$	555	34.8 ± 0.1
	417	39.5 ± 0.2

^a Abbreviations: ox, $\text{C}_2\text{O}_4^{2-}$; en, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$; enH, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+$. ^b Ionic strength 1.00 M (KNO_3). ^c Standard deviation of six determinations. ^d Ionic strength 1.90 M (KNO_3).

The fraction of the product species in the form of mono(oxalato) complexes was also determined at 1 half-life of the observed reaction. This was accomplished by allowing 1 mmol of the $\text{Cr}(\text{ox})_2(\text{en})^-$ complex in 25.0 ml of the appropriate reaction medium to react for 1 half-life, quenching the reaction mixture in 225 ml of water at 2°C, and then passing the resulting solution through a 40 ml bed of Dowex 50W-X8 (50-100 mesh) resin in the Na^+ form. Cationic products which result from initial aquation of an oxalate ligand, $\text{Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$, $\text{Cr}(\text{ox})(\text{enH})(\text{H}_2\text{O})_3^{2+}$, and $\text{Cr}(\text{ox})(\text{H}_2\text{O})_4^+$, were retained by the column under these conditions. After the column was washed free of neutral and anionic species, the resin was removed from the column and the cationic species were quantitatively removed from the resin by two successive oxidations with basic solutions of hydrogen peroxide. These solutions were combined and analyzed for chromium content. Results of these determinations are tabulated in Table II as $F_{\text{Cr}(\text{ox})}$, where $F_{\text{Cr}(\text{ox})} = 2N_i/N_t$. Here, N_t represents the number of millimoles of cationic species present in the aquation mixture at $t = t_{1/2}$ and N_i represents the number of millimoles of the $\text{Cr}(\text{ox})_2(\text{en})^-$ complex present at time zero. Unreacted $\text{Cr}(\text{ox})_2(\text{en})^-$ and the neutral or anionic species resulting from partial or complete aquation of the ethylenediamine ligand, $\text{Cr}(\text{ox})_2(\text{enH})(\text{H}_2\text{O})$ and $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$, were not retained by the resin and the sum of their concentrations in the effluent was determined after oxidation with ammonium peroxydisulfate. Recovery of chromium(III)-containing species by these techniques averaged 99.8% of the chromium(III) taken.

Results

Characterization of Reaction Intermediates. The composition of the primary coordination sphere of the reaction intermediates of this study was inferred from analytical data and their ion-exchange chromatographic behavior, which served to define relative charge. The visible absorption spectra of the complexes and, in particular, the location of the low-energy maxima support these assignments. Species postulated as containing monodentate ethylenediamine (one amine chromophore) have low-energy maxima at higher wavelengths than those containing bidentate ethylenediamine (two amine chromophores). This observation is in agreement with the relative locations of low-energy maxima for $\text{Cr}(\text{enH})(\text{H}_2\text{O})_5^{4+}$ ($\lambda 549 \text{ nm}$)⁵ and $\text{Cr}(\text{en})(\text{H}_2\text{O})_4^{3+}$ ($\lambda 517 \text{ nm}$).²⁰ Spectral data are given for the reaction intermediates in Table III.

The rule of average environment²¹ may be used to estimate the location of the low-energy absorption maximum of the parent complex and each of the reaction intermediates. First, it is assumed that the absorption is due to the $4T_{2g}(\text{F}) \leftarrow 4A_{2g}(\text{F})$ octahedral field transition, the transition of energy $10Dq$. Then, it is assumed that the contribution of each bidentate oxalate ligand to $10Dq$ is equal to one-third of the magnitude of $10Dq$ for $\text{Cr}(\text{ox})_3^{3-}$ ($17,600 \text{ cm}^{-1}$),²² and the contribution of each coordinated amine functional group is one-sixth of $10Dq$ for $\text{Cr}(\text{en})_3^{3+}$ ($21,800 \text{ cm}^{-1}$).²³ The field contribution of coordinated water was estimated from the

above data and the position of the low-energy maximum of either *cis*-Cr(ox)₂(H₂O)₂²⁻ or Cr(ox)(H₂O)₄⁺. When the complex field is generated in part by two oxalate ligands, one water molecule contributes 3030 cm⁻¹ to the total field; and, when the complex field is generated in part by one oxalate ligand, one water molecule contributes 3050 cm⁻¹ to the total field. Using these estimating bases, estimates of 10Dq and the wavelength of the low-energy absorption maximum of the species of this investigation are as follows: Cr(ox)₂(en)⁻, 19,000 cm⁻¹, 526 nm; Cr(ox)₂(enH)(H₂O), 18,400 cm⁻¹, 543 nm; Cr(ox)(en)(H₂O)₂⁺, 19,190 cm⁻¹, 521 nm; Cr(ox)(enH)(H₂O)₃²⁺, 18,590 cm⁻¹, 538 nm. The close correspondence of the estimates to the observed positions listed in Table III lends further support to our assignment of groups to the primary coordination sphere of chromium(III).

Although each of the intermediate species could conceivably exist in two isomeric forms, we were unable to obtain chromatographic evidence for isomeric species in the reaction mixtures. We are therefore unable conclusively to deduce the geometry of the isolated species. However, the correlation of predicted low-energy maxima with observed values has an implicit dependence upon symmetry conditions and would seem to forbid high-symmetry, trans arrangements of Cr(ox)₂(enH)(H₂O) and Cr(ox)(en)(H₂O)₂⁺. Of the species isolated, the Cr(ox)₂(enH)(H₂O) complex is the most likely one to consist of a mixture of isomers. The method used in isolation of this complex should not permit differentiation of isomeric, uncharged species.

Aquation at pH 1. Repeated scans at 25°C of the spectrum of a 5.6 × 10⁻³ M solution of Cr(ox)₂(en)⁻ in 0.10 M nitric acid (μ = 1.00 M) duplicated the results of Schäfer.¹⁰ Successive recorder traces gave constant intercepts at 577 and 419 nm, while the intercept of successive traces with the "time-zero" trace varied in a constant progression from 456 to 464 nm. Scans made after 10 hr showed an additional, constant intercept at 476 nm and a shift in the 577-nm intercept to slightly lower wavelength. The "infinite-time" spectrum, taken after 200 hr, closely approximates that of *cis*-Cr(ox)₂(H₂O)₂²⁻. Deviations in this final spectrum could be ascribed to 6% of the product being Cr(ox)(H₂O)₄⁺.

An uncharged reaction intermediate was isolated from 0.10 M nitric acid after 12–18 hr at 25°C. This intermediate contained 1 mol of ethylenediamine and 2 mol of oxalate for every mole of chromium. It was also isosbestic with Cr(ox)₂(en)⁻ at 419, 456, and 577 nm and with *cis*-Cr(ox)₂(H₂O)₂²⁻ at 416, 476, and 570 nm. Since *cis*-Cr(ox)₂(H₂O)₂²⁻ is isosbestic with Cr(ox)₂(en)⁻ at 418, 464, and 575 nm, the observed spectral changes in 0.10 M nitric acid could be rationalized by proposing this single intermediate for the "high-pH" aquation process. In accordance with its stoichiometry and chromatographic behavior, we have formulated the reaction intermediate as Cr(ox)₂(enH)(H₂O), a complex containing a monodentate ethylenediamine ligand. The spectral characteristics of this complex are given in Table III and spectra of the major species in the "high-pH" reaction are shown in Figure 1.

Full chromatographic development of the reaction mixture at 18 hr indicated the presence of Cr(ox)₂(en)⁻, Cr(ox)₂(enH)(H₂O), *cis*-Cr(ox)₂(H₂O)₂²⁻, and a red, cationic complex formulated as Cr(ox)(en)(H₂O)₂⁺ (ca. 5% of the species present). The latter complex constituted our first identification of an oxalate aquation pathway for the reaction. This pathway, operative in 0.10 M nitric acid, may successfully account for the small pH dependencies which Schäfer found¹⁰ and ascribed to Cr(ox)₂(enH)(H₂O).

Aquation at pH 0. Repeated scans at 25°C of the spectrum of a 5.6 × 10⁻³ M solution of Cr(ox)₂(en)⁻ in 1.00 M nitric acid differed greatly from those of the reaction at pH 1. Early

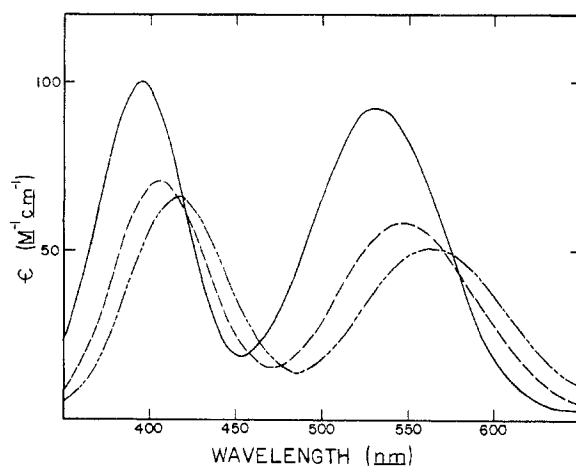


Figure 1. Visible absorption spectra of the dominant species in the aquation of Cr(C₂O₄)₂(NH₂CH₂CH₂NH₂)⁻ at [H⁺] = 0.10 M: Cr(C₂O₄)₂(NH₂CH₂CH₂NH₂)⁻, —; Cr(C₂O₄)₂(NH₂CH₂CH₂NH₃)(H₂O), - -; *cis*-Cr(C₂O₄)₂(H₂O)₂²⁻, - · - ·.

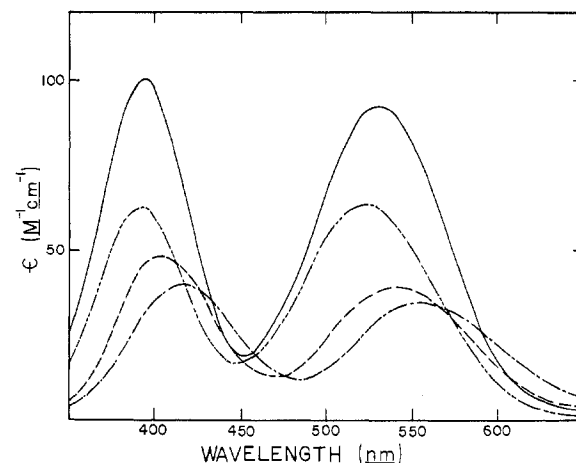


Figure 2. Visible absorption spectra of the dominant species in the aquation of Cr(C₂O₄)₂(NH₂CH₂CH₂NH₂)⁻ at [H⁺] = 1.00 M: Cr(C₂O₄)₂(NH₂CH₂CH₂NH₂)⁻, —; Cr(C₂O₄)(NH₂CH₂CH₂NH₂)(H₂O)₂⁺, - - -; Cr(C₂O₄)(NH₂CH₂CH₂NH₃)(H₂O)₃²⁺, - · - ·; Cr(C₂O₄)(H₂O)₄⁺, - · - ·.

recorder traces had no common points of intersection and the position of the low-energy maximum drifted from 530 to 526 nm before returning to the higher wavelengths characteristic of the anticipated product species. After 26 hr, points of repeated intersection occurred at 419, 458, and 570 nm, indicating that late intermediates and products were isosbestic at these points.

Two new cationic reaction intermediates were isolated by ion-exchange chromatographic separation of the reaction components. On the basis of elution characteristics and analytical results, these intermediates have been assigned the formulas Cr(ox)(en)(H₂O)₂⁺ and Cr(ox)(enH)(H₂O)₃²⁺. The former complex was most easily eluted and had a low-energy absorption maximum at 522 nm (ε 63.1 ± 0.4 M⁻¹ cm⁻¹), while the latter complex was difficult to elute and had a low-energy absorption maximum at 540 nm (ε 39.1 ± 0.5 M⁻¹ cm⁻¹). The spectral characteristics of these ions are given in Table III. Visible absorption spectra of major species involved in the "low-pH" aquation process are shown in Figure 2. The existence of large quantities of Cr(ox)(en)(H₂O)₂⁺ conclusively proves that oxalate aquation competes favorably with ethylenediamine aquation at high hydrogen ion concentrations.

Aquation Kinetics. We have determined the rates of aquation of Cr(ox)₂(en)⁻ spectrophotometrically at 570 nm,

Table IV. Pseudo-First-Order Rate Constants for the Aquation of $\text{Cr}(\text{ox})_2(\text{en})^-$ in Nitrate Media^a

$T, ^\circ\text{C}$	$[\text{H}^+], M$	$10^2 C_1, ^b M$	$10^4 k_{\text{obsd}}, \text{sec}^{-1}$
20.0	2.00	1.07	2.59
25.0	0.50	1.27	0.706
25.0	1.00	1.24	1.56
25.0	1.50	1.15	2.72
25.0	1.80	1.07	3.56
25.0	2.00	1.01	4.14
35.0	0.50	1.13	1.94
35.0	1.00	1.14	4.20
35.0	1.50	1.12	7.26
35.0	2.00	1.02	11.2
45.0	0.50	1.13	5.19
45.0	1.00	1.04	10.7
45.0	1.50	1.11	18.0
45.0	2.00	1.01	27.0

^a $\mu = 2.01 M$ (KNO_3). ^b The initial concentration of $\text{Cr}(\text{ox})_2(\text{en})^-$.

Table V. Derived Rate Constants for the First Step in the Aquation of $\text{Cr}(\text{ox})_2(\text{en})^-$ and Their Activation Parameters^{a,b}

$T, ^\circ\text{C}$	$10^5 k_a, \text{sec}^{-1}$ ^c	$10^5 k_b, M^{-1} \text{sec}^{-1}$	$10^5 k_c, M^{-2} \text{sec}^{-1}$
25.0	1.7	7.69 ± 0.11^d	6.15 ± 0.07^d
35.0	5.1	20.4 ± 0.1	16.5 ± 0.1
45.0	16	52.8 ± 0.5	38.0 ± 0.4
E_a^e	21.2 ± 0.6^d	18.2 ± 0.2^d	17.2 ± 0.5^d
ΔH^\ddagger^e	20.6 ± 0.6	17.6 ± 0.2	16.6 ± 0.6
ΔS^\ddagger^f	-11.4 ± 1.9	-18.3 ± 0.5	-22.0 ± 1.8

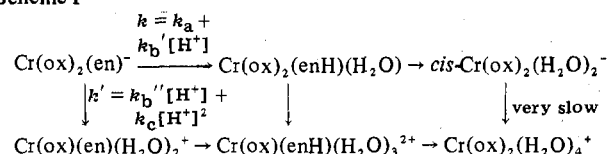
^a $k_{\text{obsd}} = k_a + k_b[\text{H}^+] + k_c[\text{H}^+]^2$. ^b Ionic strength 2.01 M (KNO_3). ^c Curve-fitting parameter, chosen to minimize standard deviation in k_b and k_c . ^d Standard deviation. ^e Units kcal mol^{-1} . ^f Units $\text{cal mol}^{-1} \text{K}^{-1}$.

where $\text{Cr}(\text{ox})_2(\text{enH})(\text{H}_2\text{O})$ is isosbestic with $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$, and $\text{Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$, $\text{Cr}(\text{ox})(\text{enH})(\text{H}_2\text{O})_3^{2+}$, and $\text{Cr}(\text{ox})(\text{H}_2\text{O})_4^+$ are nearly isosbestic. Considering the difference in the molar absorptivities of the isosbestic points for the two series of complexes, a simple first-order rate plot may only be rationalized if two of the following conditions are met: (1) $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ aquates at a rate which is negligibly slow compared to the rate under investigation;¹⁶ and (2a) the $\text{Cr}(\text{ox})_2(\text{enH})(\text{H}_2\text{O})$ complex aquates to $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ alone or (2b) aquation of $\text{Cr}(\text{ox})_2(\text{enH})(\text{H}_2\text{O})$ to $\text{Cr}(\text{ox})(\text{enH})(\text{H}_2\text{O})_3^{2+}$ occurs at an appreciable rate only under conditions which strongly favor primary oxalate aquation of $\text{Cr}(\text{ox})_2(\text{en})^-$. In either case, the observed rate is that of primary aquation—aquation of $\text{Cr}(\text{ox})_2(\text{en})^-$ to a mixture of $\text{Cr}(\text{ox})(\text{enH})(\text{H}_2\text{O})$ and $\text{Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$. Kinetic data are given in Table IV for rate studies at hydrogen ion concentrations from 0.50 to 2.00 M and temperatures from 20 to 45°C. Studies of the first-step product distribution, summarized in Table II, clearly indicate that primary ethylenediamine aquation becomes less important and primary oxalate aquation becomes more important as the hydrogen ion concentration is increased.

The rate data of Table IV were fit to a three-term rate law by evaluating the function $(k_{\text{obsd}} - k_a)/[\text{H}^+] = k_b + k_c[\text{H}^+]$. The fitting process was accomplished by varying the parameter k_a to obtain a minimum standard deviation in the intercept k_b and slope k_c of a plot of $(k_{\text{obsd}} - k_a)/[\text{H}^+]$ vs. $[\text{H}^+]$. The values of k_a at which standard deviations were minimized and the resulting derived rate constants, k_b and k_c , are tabulated in Table V for data at 25.0, 35.0, and 45.0°C. Activation parameters for each of the derived constants are also given in Table V.

It is necessary to assume that primary aquation of the ethylenediamine ligand occurs via hydrogen ion independent and hydrogen ion dependent pathways to compute first-step

Scheme I



product compositions which approximate the values obtained for $f_{\text{Cr}(\text{ox})}$ and $F_{\text{Cr}(\text{ox})}$ in Table II. If k_b is partitioned as $k_b = (k_b' + k_b'')$, where $k_b' = (1.7 \pm 0.8) \times 10^{-5} M^{-1} \text{sec}^{-1}$ and $k_b'' = 6.0 \times 10^{-5} M^{-1} \text{sec}^{-1}$ at 25.0°C, a reasonable correspondence is obtained between calculated mono(oxalato) complex abundances and $f_{\text{Cr}(\text{ox})}$. To achieve correlation of rate data to $F_{\text{Cr}(\text{ox})}$, it is necessary to partition k_b as $k_b' = (2.0 \pm 0.6) \times 10^{-5} M^{-1} \text{sec}^{-1}$ and $k_b'' = 5.7 \times 10^{-5} M^{-1} \text{sec}^{-1}$. In this partitioning, the assumption is made that k_a and k_b' are related to primary aquation of the ethylenediamine ligand, k_b'' and k_c are related to oxalate aquation, and the extent of aquation of $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ is negligible in the time scale of the experiment. The lack of substantial variation in either $f_{\text{Cr}(\text{ox})}$ or $F_{\text{Cr}(\text{ox})}$ with temperature suggests that k_b' and k_b'' have the same, or very similar, activation enthalpies.

The full aquation sequence indicated by our chromatographic evidence is given in Scheme I. Our partitioning of the rate constant for primary aquation of $\text{Cr}(\text{ox})_2(\text{en})^-$, derived from kinetic and chromatographic evidence, is included on this diagram. At $[\text{H}^+] = 2.00 M$ and 25°C, the primary aquation step results in oxalate aquation greater than 90% of the time. Primary ethylenediamine aquation, on the other hand, should occur with 90% or greater frequency at pH values above 1.50. At intermediate hydrogen ion concentrations, the true competitive nature of the primary aquation processes is apparent, with roughly equal weight being assigned to each of the alternative aquation modes.

In a separate study, the $\text{Cr}(\text{ox})_2(\text{enH})(\text{H}_2\text{O})$ complex intermediate was allowed to aquate in 0.10 M nitric acid at 25.0°C. The rate of aquation was followed at 545 nm to an equilibrium mixture of $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ (82%) and $\text{Cr}(\text{ox})(\text{H}_2\text{O})_4^+$ (18%). When a calculated infinite-time absorbance value, corresponding to that for complete aquation to $\text{Cr}(\text{ox})(\text{H}_2\text{O})_4^+$, was used, rate constants for two, consecutive processes could be determined. The rate constant corresponding to loss of ethylenediamine was found to be $(1.9 \pm 0.1) \times 10^{-5} \text{sec}^{-1}$, while the rate constant for aquation of $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ was $(4.5 \pm 0.1) \times 10^{-7} \text{sec}^{-1}$. The former constant is in agreement with that obtained using the first 0.5 hr of the rate data, the calculated absorbance interval between $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ and $\text{Cr}(\text{ox})_2(\text{enH})(\text{H}_2\text{O})$, and an "initial-rate" evaluation technique.²⁵ There was no spectrophotometric evidence that aquation of $\text{Cr}(\text{ox})_2(\text{enH})(\text{H}_2\text{O})$ resulted in the production of $\text{Cr}(\text{ox})(\text{enH})(\text{H}_2\text{O})_3^{2+}$ at $[\text{H}^+] = 0.10 M$. Chromatographic separation of the reaction mixture at 2 half-lives on the initial reaction yielded only $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ and traces of the ultimate reaction product, $\text{Cr}(\text{ox})(\text{H}_2\text{O})_4^+$.

Aquation of $\text{Cr}(\text{ox})_2(\text{enH})(\text{H}_2\text{O})$ is accelerated in 2.0 M nitric acid, and a noticeable quantity of the parent complex is aquated to $\text{Cr}(\text{ox})(\text{enH})(\text{H}_2\text{O})_3^{2+}$. We were unable to quantify the first-step product distribution using ion-exchange chromatography under these conditions due to the low concentrations of parent complex available and the high ionic strength of the reaction medium. However, it appears that $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ and $\text{Cr}(\text{ox})(\text{enH})(\text{H}_2\text{O})_3^{2+}$ occur in roughly equal quantities. If $\text{Cr}(\text{ox})_2(\text{enH})(\text{H}_2\text{O})$ and $\text{Cr}(\text{ox})_2(\text{en})^-$ react by parallel mechanisms in acidic solution, the linearity of the first-order plots of this study must be due to the fact that only small quantities of $\text{Cr}(\text{ox})_2(\text{enH})(\text{H}_2\text{O})$ are produced under conditions which would favor second-step oxalate aquation.

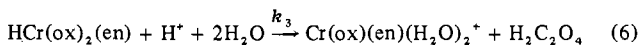
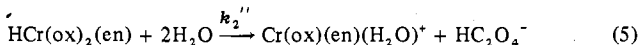
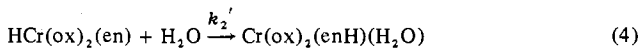
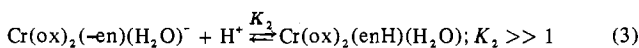
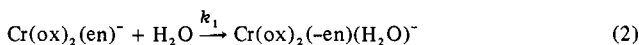
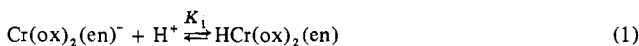
Table VI. Rate-Law Terms for the Aquation of Oxalate and Ethylenediamine Complexes of Chromium(III) at 25°C

Complex ^a	Rate law term, sec ⁻¹	Product ^a	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , cal/(mol deg)
Cr(ox) ₃ ³⁻ ^b	$1.3 \times 10^{-5} [\text{H}^+]$	<i>cis</i> -Cr(ox) ₂ (H ₂ O) ₂ ⁻	21.6	-8.4
Cr(ox) ₃ ³⁻ ^b	$1.3 \times 10^{-5} [\text{H}^+]^2$	<i>cis</i> -Cr(ox) ₂ (H ₂ O) ₂ ⁻	28.5	14.7
<i>cis</i> -Cr(ox) ₂ (H ₂ O) ₂ ^{-c}	$2.0 \times 10^{-6} [\text{H}^+]$	Cr(ox)(H ₂ O) ₄ ⁺	23.9	-4.5
Cr(ox) ₂ (en) ^{-d}	$6.0 \times 10^{-5} [\text{H}^+]^e$	Cr(ox)(en)(H ₂ O) ₂ ⁺	~17.6	
Cr(ox) ₂ (en) ^{-d}	$6.2 \times 10^{-5} [\text{H}^+]^2$	Cr(ox)(en)(H ₂ O) ₂ ⁺	16.6	-22.0
Cr(en)(H ₂ O) ₄ ^{3+f}	2.2×10^{-8}	Cr(enH)(H ₂ O) ₅ ⁴⁺	26.0 ⁱ	-6.0 ⁱ
Cr(enH)(H ₂ O) ₅ ^{4+f}	2.1×10^{-8}	Cr(H ₂ O) ₆ ³⁺	23.3 ⁱ	-15.0 ⁱ
Cr(ox) ₂ (en) ^{-g}	1.8×10^{-5}	<i>cis</i> -Cr(ox) ₂ (H ₂ O) ₂ ⁻	18.9 ⁱ	-16.9 ⁱ
Cr(ox) ₂ (en) ^{-d}	1.7×10^{-5}	Cr(ox) ₂ (enH)(H ₂ O)	20.6	-11.4
Cr(ox) ₂ (en) ^{-d}	$1.7 \times 10^{-5} [\text{H}^+]^e$	Cr(ox) ₂ (enH)(H ₂ O)	~17.6	
Cr(ox) ₂ (enH)(H ₂ O) ^h	1.9×10^{-5}	<i>cis</i> -Cr(ox) ₂ (H ₂ O) ₂ ⁻		

^a Abbreviations: ox, C₂O₄²⁻; en, NH₂CH₂CH₂NH₂; enH, = NH₂CH₂CH₂NH₃⁺. ^b Extrapolated from ref 3. $\mu = 2.0 M$ (NaClO₄). ^c Extrapolated from ref 4. $\mu = 2.0 M$ (NaClO₄). ^d This study. $\mu = 2.0 M$ (KNO₃). ^e Derived by partitioning k_b ($=7.7 \times 10^{-5} M^{-1} \text{sec}^{-1}$). ^f Extrapolated from ref 5. $\mu = 3.0 M$ (NaClO₄). ^g Extrapolated from spectrophotometric data of ref 10. $\mu = 0.16 M$ (NaClO₄). ^h This study. $\mu = 0.10 M$ (HNO₃). ⁱ Recalculated from original data.

Discussion

A mechanism consistent with our chromatographic evidence and the kinetic survey is given in eq 1-6. This mechanism



yields a rate law for the disappearance of Cr(ox)₂(en)⁻ and appearance of first-step aquation products which has an observed rate constant given by eq 7. When $K_1[\text{H}^+] \ll 1$,

$$k_{\text{obsd}} = \frac{k_1 + (k_2' + k_2'')K_1[\text{H}^+] + k_3K_1[\text{H}^+]^2}{1 + K_1[\text{H}^+]} \quad (7)$$

eq 7 reduces to our experimental form, given by $k_{\text{obsd}} = k_1 + (k_2' + k_2'')K_1[\text{H}^+] + k_3K_1[\text{H}^+]^2$, where $k_1 = k_a$, $(k_2' + k_2'')K_1 = k_b$ and $k_3K_1 = k_c$ of our curve-fitting treatment. If eq 1 is considered to be an oxalate dechelation-protonation equilibrium, then it would be reasonable to expect a magnitude of K_1 which is less than or equal to $5 \times 10^{-2} M^{-1}$.²⁶

The data of Table VI indicate that both ethylenediamine and oxalate aquations of Cr(ox)₂(en)⁻ proceed at unusually rapid rates when compared to rates for similar species under the same conditions. First-step aquation of ethylenediamine is a factor of 10³ more rapid than either aquation step of Cr(en)(H₂O)₄³⁺ at 25°C and is further distinguished by having a hydrogen ion dependent pathway. The difference in rates might be rationalized on the basis of relative complex charge, but there is little difference between aquation rates or activation parameters for Cr(en)(H₂O)₄³⁺ and Cr(enH)(H₂O)₅⁴⁺; and, Cr(ox)₂(en)⁻ and Cr(ox)₂(enH)(H₂O) show similar uncatalyzed ethylenediamine aquation rates as well. The activation enthalpy for primary ethylenediamine aquation of Cr(ox)₂(en)⁻ bears little resemblance to that for aquation of Cr(en)(H₂O)₄³⁺ or Cr(enH)(H₂O)₅⁴⁺. Instead, activation parameters most closely resemble those for aquation processes of polyamine complexes which involve concurrent isomerization,⁷⁻⁹ in spite of large complex charge differences and different, apparent strain features for the various species.

Acid-catalyzed aquation of an oxalate ligand from Cr(ox)₂(en)⁻ is 30 times more rapid at 25°C than aquation of *cis*-Cr(ox)₂(H₂O)₂⁻ and 7 times more rapid than Cr(ox)₃³⁻ aquation when the rate constants are statistically corrected. Activation enthalpies of the oxalate aquation terms are

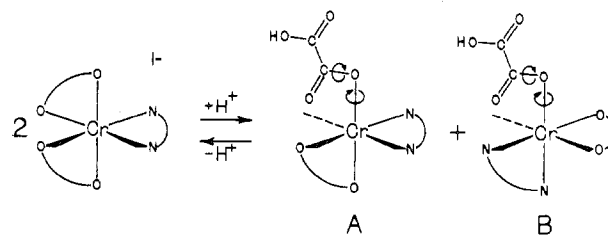


Figure 3. Proposed half-bonded oxalate intermediates in the hydrogen ion catalyzed aquation of Cr(C₂O₄)₂(NH₂CH₂CH₂NH₂).

substantially less than those for Cr(ox)₃³⁻ or *cis*-Cr(ox)₂(H₂O)₂⁻. Instead, the activation parameters strongly resemble those for racemization of Cr(ox)₂(bpy)⁻ and Cr(ox)₂(phen)⁻²⁷ and those for catalyzed isomerization processes of *trans*-Cr(ox)₂(H₂O)₂⁻.^{28,29}

Correlation of both the ethylenediamine and the oxalate aquation processes to systems undergoing isomerization or racemization strongly suggests that both occur during basic isomerization or racemization steps. In the case of uncatalyzed ethylenediamine aquation (k_a), a tetragonal twist along either of two O-Cr-N axes could be imagined to lead to occasional loss of one end of an ethylenediamine ligand and entry of one water molecule into the coordination sphere of chromium. The activation energy for this twisting mode should be greater than that for racemization by trigonal or rhombic twists,^{30,31} where ligand interaction is minimized, but less than that for an unassisted, dissociative aquation. Since the same tetragonal twisting motion could lead to combined isomerization and aquation of complexes like 1,2,3-Cr(trienH)(H₂O)₃⁴⁺ ($E_a = 21.2 \pm 2.2$ kcal/mol),⁸ 1,2,6-Cr(trienH)(H₂O)₃⁴⁺ ($E_a = 18.0 \pm 2.6$ kcal/mol),⁸ and 1,2,6-Cr(dien)(H₂O)₃³⁺ ($E_a = 19.6 \pm 0.6$ kcal/mol),⁷ the activation energy we have determined, 21.2 kcal/mol, would seem to be entirely reasonable.

Acid-catalyzed aquation (k_b) is most reasonably discussed in terms of half-bonded oxalate intermediates in view of the existing literature. These intermediates must necessarily exclude water from entry into the coordination sphere of chromium(III) during racemization or isomerization reactions of oxalato or aquooxalato species.³²⁻³⁴ Intermediates consistent with our observations are shown in Figure 3. Either intermediate, A or B, could lead to racemization by rotation and rechelation of the half-bonded oxalate. However, intermediate A would also tend to lead to aquation of oxalate or one end of the ethylenediamine ligand during rotation, due to the steric interference between the half-bonded oxalate and the "puckered" backbone of the ethylenediamine ligand. Our results at 25°C indicate that activation by a single hydrogen ion leads to 78% oxalate aquation and 22% primary ethylenediamine aquation.

If the rigid, planar ligand 1,10-phenanthroline (phen) is

substituted for ethylenediamine, there would be no steric barrier to rotation of oxalate in either intermediate and aquation would not be a consequence of catalyzed racemization. If the more flexible, planar ligand 2,2'-bipyridine (bpy) is substituted for ethylenediamine, oxalate aquation would be more substantial during acid-catalyzed racemization. These projections, based on our mechanism, are confirmed by Broomhead's observations.²⁷

We have chosen to draw the half-bonded oxalate intermediates as quasioctahedral species, with the carbonyl group of the rotated oxalate ligand shielding, or stabilizing, the sixth coordination position of chromium(III). This arrangement has great potential for rationalizing the remarkable similarity in the ^{18}O exchange parameters of oxalate complexes of chromium(III)³⁵ and for explaining the similarity of exchange parameters to the kinetic parameters for racemization and aquation of related bis(oxalato) species. The latter processes require an additional change in geometry of intermediates A or B, while ^{18}O exchange presumably requires attack of water at carbon. Therefore, the similarity between ^{18}O exchange and racemization-aquation parameters is in all probability coincidental. However, ^{18}O exchange may occur via intermediates like A or B at a point distant from the chromium(III) center with rates and activation parameters which are essentially independent of the nature of the complex ion.

A consequence of the application of our mechanism to other mixed-ligand complexes containing oxalate is that hydrogen ion catalyzed aquation of simple, monodentate ligands should also occur through rotation of half-bonded oxalate. Carbon dioxide³⁶ and the nitrate ion³⁷ are believed to catalyze simple aquation processes by a similar mechanism. Hydrogen ion catalysis of $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ water exchange³⁸ and aquation of acetatobis(oxalato)chromate(III) complexes³⁹ have been reported. A more complete examination of other, simple systems should lead to additional examples which correlate with our observations.

Acknowledgment. This research was initiated with the support of a SUNY Research Foundation, Faculty Research Fellowship during the summer of 1971. We wish to thank Edward L. Byde for his assistance during the early stages of the investigation.

Registry No. $\text{Cr}(\text{ox})_2(\text{en})^-$, 21827-84-9; $\text{Cr}(\text{ox})_2(\text{enH})(\text{H}_2\text{O})$, 56377-01-6; $\text{Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$, 21748-29-8; $\text{Cr}(\text{ox})(\text{enH})(\text{H}_2\text{O})_3^{2+}$, 56348-62-0; $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$, 15489-30-2; $\text{Cr}(\text{ox})(\text{H}_2\text{O})_4^+$, 24777-95-5.

References and Notes

- (1) Abbreviations used for ligands in this study: ox, $\text{C}_2\text{O}_4^{2-}$; en, $\text{NH}_2\text{C}-\text{H}_2\text{CH}_2\text{NH}_2$; enH, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+$.
- (2) K. V. Krishnamurthy and G. M. Harris, *J. Phys. Chem.*, **64**, 346 (1960).
- (3) D. Banerjee and M. S. Mohan, *J. Inorg. Nucl. Chem.*, **27**, 1643 (1965).

- (4) D. Banerjee and M. S. Mohan, *J. Inorg. Nucl. Chem.*, **26**, 613 (1964).
- (5) R. F. Childers, Jr., K. G. Vander Zyl, Jr., D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, **7**, 749, 2678 (1968).
- (6) T. J. Williams and C. S. Garner, *Inorg. Chem.*, **8**, 1639 (1969).
- (7) D. K. Lin and C. S. Garner, *J. Am. Chem. Soc.*, **91**, 6637 (1969).
- (8) D. A. Kamp, R. L. Wilder, S. C. Tang, and C. S. Garner, *Inorg. Chem.*, **10**, 1396 (1971).
- (9) S. J. Ranney and C. S. Garner, *Inorg. Chem.*, **10**, 2437 (1971).
- (10) H. L. Schläfer, *J. Inorg. Nucl. Chem.*, **13**, 101 (1960).
- (11) E. Bushra and C. H. Johnson, *J. Chem. Soc.*, 1937 (1939).
- (12) H. L. Schläfer, O. Kling, L. Mahler, and H. P. Opitz, *Z. Phys. Chem. (Frankfurt am Main)*, **24**, 307 (1960).
- (13) D. A. House and C. S. Garner, *Inorg. Chem.*, **5**, 840 (1966).
- (14) A. Werner, *Justus Liebigs Ann. Chem.*, **406**, 216 (1914).
- (15) K. R. Ashley and R. E. Hamm, *Inorg. Chem.*, **4**, 1120 (1965).
- (16) T. Spinner and G. M. Harris, *Inorg. Chem.*, **11**, 1067 (1972).
- (17) When the column was initially in the H^+ form, slight differentiation of the band took place. Again, there was no difference in the absorption spectra of successive fractions however.
- (18) R. E. Hamm, *J. Am. Chem. Soc.*, **75**, 609 (1953).
- (19) The second-order, hydrogen ion dependent rate constant for aquation of $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ may be extrapolated as $2.0 \times 10^{-6} \text{ M}^{-1} \text{ sec}^{-1}$ at 25°C .⁴ Rates for this aquation are ca. 100 times slower than the rates we have determined for $\text{Cr}(\text{ox})_2(\text{en})^-$ aquation.
- (20) D. A. House and C. S. Garner, *Inorg. Chem.*, **5**, 840 (1966).
- (21) B. N. Figgis, "Introduction to Ligand Fields", Interscience, New York, N.Y., 1966, pp 236-237.
- (22) A. Mead, *Trans. Faraday Soc.*, **30**, 1052 (1934).
- (23) H. L. Schläfer and O. Kling, *Z. Anorg. Allg. Chem.*, **287**, 296 (1956).
- (24) G. M. Harris, "Chemical Kinetics", D. C. Heath, Boston, Mass., 1966, pp 57-58. We have used $(1/\Delta\epsilon)(\Delta A/\Delta t) = k_{\text{obsd}}$, where $\Delta\epsilon$ is the difference in molar absorptivities and $\Delta A/\Delta t$ is the initial rate of change of absorbance with time.
- (25) Aquation of $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ has a pseudo-first-order rate constant of $2.0 \times 10^{-7} \text{ sec}^{-1}$ at $[\text{H}^+] = 0.10 \text{ M}$ and an ionic strength of 2.0 M according to the data of ref 4.
- (26) A value of $5 \times 10^{-2} \text{ M}^{-1}$ has been estimated for the magnitude of the dechelation-protonation equilibrium of $\text{Cr}(\text{ox})_3^{3-}$: H. Kelm and G. M. Harris, *Inorg. Chem.*, **6**, 1743 (1967).
- (27) J. A. Broomhead, N. Kane-Maguire, and I. Lauder, *Inorg. Chem.*, **9**, 1243 (1970).
- (28) H. Kelm, H. Stieger, and G. M. Harris, *Z. Phys. Chem. (Frankfurt am Main)*, **67**, 98 (1969).
- (29) H. Kelm, H. Stieger, and G. M. Harris, *Ber. Bunsenges. Phys. Chem.*, **73**, 939 (1969).
- (30) Twist mechanisms are summarized by F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions. A study of Metal Complexes in Solution", 2nd ed, Wiley, New York, N.Y., 1968, Chapter 4.
- (31) E_a for uncatalyzed racemization is 15.8 kcal/mol .¹¹
- (32) C. A. Bunton, J. H. Carter, D. R. Llewellyn, C. O'Connor, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 4615 (1964).
- (33) C. A. Bunton, J. H. Carter, D. R. Llewellyn, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 4622 (1964).
- (34) D. R. Llewellyn, C. O'Connor, A. L. Odell, and R. W. Olliff, *J. Chem. Soc.*, 4627 (1964).
- (35) ^{18}O -exchange parameters have been summarized in ref 27, with the exception of those for exchange of $\text{Cr}(\text{ox})(\text{H}_2\text{O})_2^+$ [S. G. Gourley and R. M. Milburn, *Inorg. Chem.*, **11**, 2262 (1972)] and those for exchange of $\text{Cr}(\text{ox})(\text{bpy})_2^+$, $\text{Cr}(\text{ox})(\text{phen})_2^+$, and $\text{Cr}(\text{ox})(\text{en})_2^+$ [J. A. Broomhead, N. Kane-Maguire, and I. Lauder, *ibid.*, **10**, 955 (1971)].
- (36) J. E. Earley, D. J. Surd, L. Crone, and D. Quane, *Chem. Commun.*, 1401 (1970).
- (37) G. Guastalla and T. W. Swaddle, *Inorg. Chem.*, **13**, 61 (1974).
- (38) H. Stieger, G. M. Harris, and H. Kelm, *Ber. Bunsenges. Phys. Chem.*, **74**, 262 (1970).
- (39) M. Casula, G. Illuminati, and G. Ortaggi, *Inorg. Chem.*, **11**, 1062 (1972).