Similarly, although a weak $BF_3 \cdot SO_2$ complex reportedly exists below *ca.* −96°,[18] the 1:1 $SbF_5 \cdot SO_2$ adduct is stable above room temperature under a moderate partial pressure of SO_2 and SbF_5.[19] While fragmentary, the evidence suggests that the shift in ν_{CN} is not directly related to acid strength.

Normal-coordinate analysis of $SbF_5 \cdot NCCH_3$ is being deferred until the completion of spectroscopic work on related group V acetonitrile adducts.

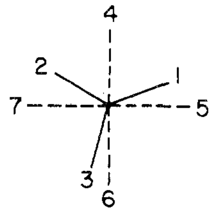
Registry No. $SbF_5 \cdot NCCH_3$, 19106-78-6; $SbF_5 \cdot NCCD_3$, 38894-62-1; $SbF_5 \cdot {}^{15}NCCH_3$, 38894-63-2.

Acknowledgment. We are grateful to the Environmental Protection Agency for a fellowship (U 910143) to D. M. B. and to the NSF for support through Grant GP-28878.

Appendix

Classification of the normal modes of vibration for a nonrigid molecule requires the use of a permutation symmetry group.[20] In the case of $SbF_5 \cdot NCCH_3$ as a nonrigid species in which the methyl group is free to rotate about the *z* axis (containing the FSbNCC backbone), the appropriate permutation symmetry group, which we call E_{24}, is isomorphous with D_{6h}. It has 8 symmetry classes and is of order 24, as shown in Table III. Using the numbering given in Scheme I, the 24 symmetry operations are denoted by standard permutation notation.[20] Table III also gives the reducible representation[21] for the 36 degrees of freedom for the $SbF_5 \cdot NCCH_3$ molecule, as well as the species which contain the translations, rotations, and polizability tensor elements. The reducible representation for the fundamental molecular vibrations consists of $8\ A_1 + 1\ A_2 + 2\ B_1 + 1\ B_2 + 9\ E_3$. The A_1 and E_3 species are Raman and infrared active, while the B_1 and B_2 vibrations are Raman active only. The A_2 mode is inactive.

Scheme I. Viewing down the *z* Axis with the Methyl Group toward the Observer



A direct correlation of E_{24} with C_{3v} and C_{4v} is not possible since the latter are not subgroups of the permutation group. Nevertheless, the similarity between the vibrational representations of the rigid and nonrigid models is immediately apparent.[22]

---

(17) D. A. McCauley and A. P. Lien, *J. Amer. Chem. Soc.*, 73, 2013 (1951); G. A. Olah, *J. Inorg. Nucl. Chem.*, 16, 225 (1961).

(18) H. S. Booth and D. R. Martin, *J. Amer. Chem. Soc.*, 64, 2198 (1942).

(19) E. E. Aynsley, R. D. Peacock, and P. L. Robinson, *Chem. Ind.* (*London*), 1117 (1951).

(20) (a) H. C. Longuet-Higgins, *Mol. Phys.*, 6, 445 (1963); (b) G. Turrell, *J. Mol Struct.*, 5, 245 (1970).

(21) As with Turrell's molecule,[20b] for each permutation on the "heavy" skeletal atoms two at a time [*e.g.*, the operation (46)(57)], each unpermuted atom contributes −1 to the character of that operation. On the other hand, permutations on all four equatorial fluorines in a cyclic fashion [*e.g.*, the operation (4567)] requires that each unpermuted atom contributes +1.

(22) Since all of the degenerate vibrations predicted by the nonrigid model belong to one species, E_3, the subscript 3 has no importance for the purpose of comparing the results of the two models. Hence, for simplicity, throughout the body of the paper we refer to this species as E.

Contribution from the Department of Chemistry,
Dartmouth College, Hanover, New Hampshire 03755

Reaction between Ethylenediaminetetraacetic Acid and Carboxylatopentaaquochromium(III) Complexes

M. V. OLSON

Received September 1, 1972

The kinetics of the reaction between EDTA and three carboxylatopentaaquochromium(III) complexes were studied in the pH range 3.0–3.5. The acetato, formato, and trifluoroacetato complexes all react to form the Cr(III)-EDTA complex substantially faster than does hexaaquochromium(III). Under comparable conditions the acetato complex reacts faster than hexaaquochromium(III) by a factor of 10^3. Simple first-order kinetics were not observed for the carboxylato complexes even under conditions of constant EDTA concentration and pH. The absorbance–time profiles could be analyzed assuming irreversible formation and decay of an intermediate species. Although the intermediate's identity was not established, the reactivity order of the carboxylato complexes (acetato > formato > trifluoroacetato) is the same for both its formation and disappearance. A mechanism is proposed in which the carboxylate's unbound oxygen provides nucleophilic assistance for the replacement of a cis water molecule. The likelihood that this mechanism is responsible for several other cases of unexpected lability in chromium(III)-substitution reactions is discussed.

Introduction

The ligand substitution reactions of acidopentaaquochromium(III) complexes have been the subject of several recent articles.[1-8] They include reports that coordinated iodide[4] as well as O-bonded sulfite[6] and nitrite[7,8] can increase the lability of chromium(III). We have studied another example of labilization by a coordinated ligand: the rate enhancement of EDTA complex formation by a

---

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

(2) D. Thusius, *Inorg. Chem.*, 10, 1106 (1971).

(3) J. H. Espenson, *Inorg. Chem.*, 8, 1554 (1969).

(4) L. R. Carey, W. E. Jones, and T. W. Swaddle, *Inorg. Chem.*, 10, 1566 (1971).

(5) D. R. Stranks and T. W. Swaddle, *J. Amer. Chem. Soc.*, 93, 2783 (1971).

(6) D. W. Carlyle and E. L. King, *Inorg. Chem.*, 9, 2333 (1970).

(7) T. C. Matts and P. Moore, *Chem. Commun.*, 29 (1969).

(8) T. C. Matts and P. Moore, *J. Chem. Soc. A*, 1632 (1971).

bound carboxylate. A kinetic study of this multistep reaction has yielded mechanistic inferences which may apply to other systems as well.

The reaction between EDTA and hexaaquochromium(III) in dilute nitric acid has a time scale of hours below pH 5 at 25°.[9] It proceeds more rapidly in carbon dioxide–bicarbonate[10] and acetic acid–acetate[11] buffers, presumably because of the lability of intermediate bicarbonate and acetate complexes. Deutsch's observation[12] that acetatopentaaquochromium(III) reacts with EDTA in a few minutes in dilute perchloric acid supports this interpretation. Our involvement stems from an attempt to remove maleate from chromium(III) under mild conditions through the reaction of maleatopentaaquochromium(III) with EDTA. The reaction, in surprising contrast to the acetate case, proved to be quite slow. Subsequent experiments revealed that the reactivities of carboxylatopentaaquochromium(III) complexes toward EDTA vary widely. We report here in detail on the acetato case and present more limited data on the formato and trifluoroacetato complexes as well as on hexaaquochromium(III).

Experimental Section

Reagents. Tap distilled water was redistilled from alkaline permanganate. Aqueous solutions of chromium(II) and chromium(III) were prepared as previously described,[13] except that argon was used rather than nitrogen as a blanketing gas for the chromium(II) solutions. All other reagents, with the exceptions described below, were commercial reagent grade chemicals.

Pentaamminecobalt(III) Complexes. The acetato-,[14] trifluoroacetato-,[14,15] and formatopentaamminecobalt(III)[14,16] complexes are all well characterized in the literature. As a typical case, the acetato complex was prepared by heating the following homogeneous reaction mixture for 2 hr in a covered beaker on a steam bath (*ca.* 80°): 1×10^{-2} mol of aquo complex, 5×10^{-2} mol of HOAc, and 5×10^{-2} mol of NaOAc in 60 ml of H_2O. On cooling in an ice bath, product precipitated in >50% yield. The product was rinsed with ice-cold water, ethanol, and ether and used without further purification. The visible absorption spectra of the complexes were all in satisfactory agreement with the literature.[14-16]

Carboxylatopentaaquochromium(III) Complexes. The carboxylatopentaaquochromium(III) complexes were prepared by the reaction between chromium(II) and the appropriate carboxylatopentaamminecobalt(III) complex followed by a separation of the product solution using cation-exchange chromatography. The detailed procedure for the acetato complex was a scaled-down version of that described by Deutsch and Taube.[1] Straightforward modifications were required for the other two complexes in view of the widely differing rates of the chromium(II)–cobalt(III) reactions[14] and the low solubility of trifluoroacetatopentaamminecobalt(III) perchlorate. The cation-exchange separations of reaction mixtures containing *ca.* 1 mmol of chromium(III) were carried out at 0° on a water-jacketed column with 15-mm i.d. The column contained 10 ml (measured by water displacement) of Bio-Rad AG50W-X2 200–400 mesh resin in the lithium form. Elution was with a 0.50 M sodium perchlorate solution which had been made acidic (0.005–0.05 M) with perchloric acid. Directly after elution, the chromium(III) solutions were frozen until immediately before use. The acetato and formato complexes could be stored without change for 1 day or more at 0° and for at least a few hours at ambient temperature in 10^{-3}–10^{-2} M perchloric acid solutions. The trifluoroacetato complex was less stable toward aquation. It was always rechromatographed in the cold immediately before use. One sample which was analyzed by ion exchange on a small column immediately after rechromatographing was over 96% of 2+ charge. It appeared to be important to keep the perchloric acid concentration at 0.05 M or above to stabilize the trifluoroacetato complex.

The total chromium concentrations of the solutions were determined as described by Deutsch and Taube[1] and assumed equal to the carboxylatopentaaquochromium(III) concentrations. The visible absorption spectra of the acetato[1] and formato[16] complexes were in good agreement with literature reports. The spectrum of trifluoroacetatopentaaquochromium(III) has apparently not been previously published: λ_{max} 410 nm (ϵ 19.6 M^{-1} cm^{-1}) and 575 nm (ϵ 18.6 M^{-1} cm^{-1}).

Planning of Kinetic Runs. The formation of the Cr(III)–EDTA complex at low pH liberates hydrogen ions. The runs were buffered with excess EDTA, but the reagent's low solubility below pH 4 required careful experimental design to minimize the pH change during a run. Reactions were carried out in 10-cm cells to minimize the chromium concentration required for an adequate absorbance change (0.2–0.5). The pH of the EDTA buffers is quite dependent on their concentrations since H_4EDTA, H_3EDTA^-, and H_2EDTA^{2-} are all significant solution components. A set of stepwise dissociation constants for EDTA were measured at 25° by titrating Na_2H_2EDTA solutions at a series of concentrations with perchloric acid. The sodium ion concentration was maintained at a constant 0.25 M with sodium perchlorate. The pH was measured using a sce reference electrode containing a saturated sodium chloride solution rather than potassium chloride to avoid precipitation of potassium perchlorate in the salt bridge; this precaution proved essential for obtaining stable, reproducible pH measurements. A nonlinear least-squares treatment of the titration curves gave the values $K_1 = 7.3 \times 10^{-3}$ and $K_2 = 2.8 \times 10^{-3}$ for the first two stepwise dissociation constants of H_4EDTA. These values are for the mixed constants, expressed in terms of the activity of hydrogen ion and the concentrations of the EDTA species. Schwarzenbach and Ackermann[17] have reported $K_1 = 1.0 \times 10^{-2}$ and $K_2 = 2.1 \times 10^{-3}$ in 0.1 M KCl at 20°. The values measured here were used to design reaction mixtures of the desired initial pH and total EDTA concentration and also to choose a chromium concentration which was low enough to ensure reasonable constancy of the pH during a run.

Measurement of Hydrogen Ion Concentration. The electrode system with the NaCl sce was calibrated to yield the hydrogen ion concentration by measuring the pH of a series of solutions containing perchloric acid concentrations between 10^{-3} and 10^{-4} M as well as 0.25 M sodium perchlorate. As has been true in earlier studies,[6,18] a good linear relationship was obtained between pH and $-\log(H^+)$. In the pH range of prime interest (3.0–3.5), the pH did not differ from $-\log(H^+)$ by more than 0.03 unit.

Methods of Conducting Kinetic Runs. The pH was measured before and after each experiment; the data were rejected if the measured pH drop exceeded 0.1. In most experiments the pH decreased by less than 0.05 unit. The pH dependence of the two rate constants derived from each curve was measured for the acetato complex. A change of 0.1 in the pH never causes more than a 10% change in either rate constant. It is unlikely that pH control was ever the limiting factor in experimental precision since difficulties inherent in the multiparameter curve-fitting techniques account for uncertainties of at least the same magnitude.

The progress of the reactions was followed at the 540-nm absorption maximum[19] of the Cr(III)–EDTA complex on a Cary 14 spectrophotometer. The reaction between hexaaquochromium(III) and EDTA was followed in cells which were thermostated in an external water bath from which they were briefly removed at intervals for absorbance readings. The reactions involving the carboxylato complexes were carried out using stirred 10-cm cells immersed in a water bath with quartz windows which fits inside the cell compartment. The cell and bath design closely follow that devised by Newton.[20] A useful modification was the incorporation of a Neslab Instruments dual-section "Z" pump in the external thermostating bath. This pump allows the maintenance in the open cell compartment bath of a constant level of water which is rapidly circulated from the much larger external constant-temperature bath. It obviates the need for a heat-exchange step between separate fluids in the two baths. Only

---

(9) R. E. Hamm, *J. Amer. Chem. Soc.*, 75, 5670 (1953).

(10) R. M. Agger and C. E. Hedrick, *J. Chem. Educ.*, 43, 541 (1966).

(11) I. Crisan and C. Liteanu, *Stud. Univ. Babes-Bolyai, Ser. Chem.*, 10, 113 (1965); *Chem. Abstr.*, 63, 15825c (1965).

(12) E. A. Deutsch, private communication.

(13) M. V. Olson and H. Taube, *Inorg. Chem.*, 9, 2072 (1970).

(14) M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, 10, 1983 (1971).

(15) R. B. Jordan and H. Taube, *J. Amer. Chem. Soc.*, 88, 4406 (1966).

(16) J. R. Ward and A. Haim, *J. Amer. Chem. Soc.*, 92, 475 (1970).

(17) G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, 30, 1798 (1947).

(18) R. L. Pecsok, L. D. Shields, and W. P. Schaefer, *Inorg. Chem.*, 3, 114 (1964).

(19) V. C. Furlani, G. Morpurgo, and G. Sartori, *Z. Anorg. Allg. Chem.*, 303, 1 (1960).

(20) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, 67, 1425 (1963).

for the acetato complex were the stirred cells necessary to achieve sufficiently rapid mixing (*ca.* 5 sec) although the apparatus was conveniently employed for the slower formato and trifluoroacetato reactions as well.

Analysis of Acetic Acid in Product Solutions. An anion-exchange method was devised for analyzing acetic acid in the product solutions of the acetatopentaaquochromium(III)-EDTA reaction. A solution containing 0.1 mmol of chromium(III) and 0.08 mmol of excess EDTA in a 40-ml volume at pH 2.6 was charged onto a 11-mm i.d. column containing 6 ml (water displacement) of Bio-Rad AG1-X2 200-400 mesh chloride-form resin. The charging effluent, which already contained some acetic acid, was combined with that from elution with 25 ml of 0.02 M hydrochloric acid. This procedure removed all acetic acid but left excess EDTA and the Cr(III)-EDTA complex on the column. The combined effluent was adjusted to pH 10 with sodium hydroxide and then charged onto a second identical column. Absorption of acetate under these conditions was complete. On elution with 0.02 M hydrochloric acid, the first 10 ml of effluent was neutral. At this point, the effluent turned abruptly acidic and the next 10 ml contained all the acetic acid. A potentiometric titration of this undiluted fraction with 0.05 M sodium hydroxide gave an easily observable end point between the titration of the hydrochloric and acetic acid components. The function of the second column was simply to concentrate the acetic acid from a volume of 65 ml to 10 ml, thereby making the stepwise titration of hydrochloric and acetic acids feasible.

Results

Acetatopentaaquochromium(III). All observations suggest that the stoichiometry is straightforward. The participants are shown in eq 1 in their dominant forms for the pH range 3-3.5.

$$2H_2EDTA^{2-} + (H_2O)_5CrOAc^{2+} = H_3EDTA^- + (H_2O)Cr(EDTA)^- + HOAc + 4H_2O \qquad (1)$$

One experiment, which supported this simple stoichiometry, involved a reaction mixture in which $(EDTA)_{tot} = 4.5 \times 10^{-2}\ M$, $((H_2O)_5CrOAc^{2+})_0 = 2.5 \times 10^{-2}\ M$, and $(pH)_0 = 3.4$. It was allowed to stand at ambient temperature for 20 min to allow complete reaction before being analyzed for acetic acid. During the reaction the pH dropped to 2.6 since the low ratio of EDTA to chromium precluded effective buffering. The molar ratio of recovered acetic acid to starting acetatopentaaquochromium(III) complex was 0.97. Further evidence for the stoichiometry in (1) is provided by quantitative agreement between infinite-time spectra of kinetic runs at pH 3.4 and a published spectrum[19] of the Cr(III)-EDTA complex at pH 3.5.

Figure 1 displays an absorbance-time profile for a typical kinetic run. The prominent induction period in Figure 1 was present with all the carboxylato complexes. Its simplest interpretation is that an intermediate with an extinction coefficient comparable to that of the starting complex accumulates during the reaction. Accordingly, the chemical model in eq 2 was used to interpret the kinetic data. The

$$(H_2O)_5CrOAc^{2+} + H_2EDTA^{2-} \underset{\text{rapid}}{\overset{K}{\rightleftarrows}} (H_2O)_5CrOAc^{2+}\cdots H_2EDTA^{2-}$$

$$(H_2O)_5CrOAc^{2+}\cdots H_2EDTA^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} I$$

$$I \xrightarrow{k_2} (H_2O)Cr(EDTA)^- \qquad (2)$$

first step is simply the expected ion-pair association between $(H_2O)_5CrOAc^{2+}$ and H_2EDTA^{2-}. It is a rapid outer-sphere interaction which can be characterized at a particular pH by a conditional formation constant

$$K = \frac{(\text{ion pair})_{tot}}{((H_2O)_5CrOAc^{2+})(EDTA)_{tot}} \qquad (3)$$

The term $(\text{ion pair})_{tot}$ is the sum of the concentrations of all 1:1 ion pairs regardless of the number of associated protons. The quantity $(EDTA)_{tot}$ represents all acid-base forms of free EDTA; it always remained effectively constant during individual runs since $(EDTA)_{tot} \gg (Cr)_{tot}$ in all kinetic experiments. The quantities k_1, k_{-1}, and k_2 are first-order rate constants. Conversion of the intermediate (I) to product is assumed to be irreversible because of the large stability constant for the Cr(III)-EDTA complex.[18]

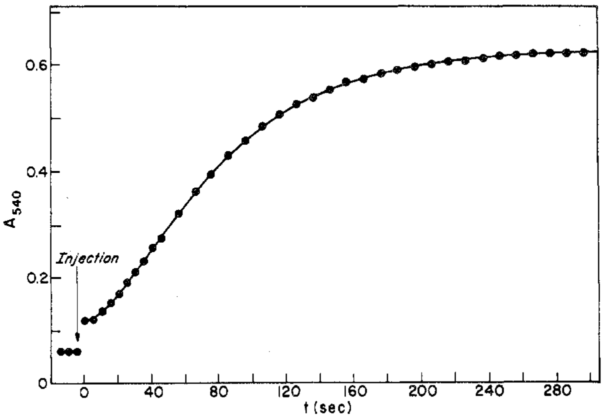


Figure 1. Typical absorbance-time profile for an acetatopentaaquochromium(III)-EDTA kinetic run (no. 15, Table I).

The integrated rate law for the proposed model, which is readily obtained by standard methods,[21] leads to an equation for the spectrophotometrically observable function $(A_\infty - A)/(A_\infty - A_0)$

$$\frac{A_\infty - A}{A_\infty - A_0} = \frac{1}{\lambda_2 - \lambda_1}[(\lambda_2 + \lambda_3)e^{-\lambda_1 t} - (\lambda_1 + \lambda_3)e^{-\lambda_2 t}] \qquad (4)$$

where

$$\lambda_1 = {}^1/_2(p + q)$$

$$\lambda_2 = {}^1/_2(p - q)$$

$$\lambda_3 = \left[\frac{\epsilon_R - \epsilon_I}{\epsilon_P - \epsilon_R}\right]\frac{k_1K(EDTA)_{tot}}{1 + K(EDTA)_{tot}}$$

$$p = \frac{k_1K(EDTA)_{tot}}{1 + K(EDTA)_{tot}} + k_{-1} + k_2$$

$$q = \left[p^2 - \frac{4k_1k_2K(EDTA)_{tot}}{1 + K(EDTA)_{tot}}\right]^{1/2}$$

Equation 4 incorporates the reasonable assumption that a single extinction coefficient, ϵ_R, applies to both the acetato complex and the ion pair. The extinction coefficient ϵ_P is the appropriate value for the Cr(III)-EDTA complex while ϵ_I applies to the intermediate.

Analysis of the data was simplified by the observation that the initial slopes of the absorbance-time traces were always close to zero and sometimes perceptibly negative. This behavior implies that $0 < \epsilon_I < \epsilon_R$. Under typical conditions (pH 3.4) $\epsilon_R = 19\ M^{-1}\ cm^{-1}$ and $\epsilon_P = 200\ M^{-1}\ cm^{-1}$. Evidence will be presented below that the value which ϵ_I assumes within the narrow range 0-19 $M^{-1}\ cm^{-1}$ does not materially affect the results. Consequently, the data reduction will be described for the simplest limiting case: $\epsilon_I = \epsilon_R$ ($\lambda_3 = 0$).

Under these circumstances the absorbance-time traces are ideally determined by the two parameters λ_1 and λ_2. The mixing time of the apparatus, however, was not infinitely fast compared to the length of the induction period, so it

---

(21) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, pp 173-177.

was necessary to introduce a third adjustable parameter, Δt, to reflect the time lag between chromium injection and the true $t = 0$. Runs were rejected in the rare cases when the curve-fitting procedure yielded a value of Δt which lay outside the range 0-12 sec. The average value for the 27 acceptable runs was 6 sec, in good agreement with the independently measured mixing characteristics of the apparatus.

Absorbance-time traces were fit to eq 4 by a standard nonlinear least-squares routine[22] using the three adjustable parameters λ_1, λ_2, and Δt. The solid line in Figure 1 is typical of the good fits obtained. Table I lists optimized values of λ_1 and λ_2 for experiments carried out at 25° and $(Na^+) = 0.25\ M$. The sodium ion concentration rather than the ionic strength was held constant because of the significant and varying concentrations of multiply charged anions present. The ionic strengths of all experiments remained within the range 0.25-0.30 M; comparison of runs 17, 18, and 19 illustrates that no significant changes in rate occur when the ionic strength is varied from 0.20 to 0.30 M.

The data from several representative runs were fit using a value of λ_3 which corresponds to $\epsilon_I = 0$ rather than $\epsilon_I = \epsilon_R$. The quality of the fits invariably decreased somewhat while the optimized values of Δt often became unreasonable. More significantly the optimum value of λ_2 was quite insensitive to the choice of λ_3, never changing by more than 2%. The less well-defined λ_1 changed by as much as 20%, a margin which is not appreciably greater than experimental error.

In Figure 2, λ_1 and λ_2 are plotted *vs.* $(EDTA)_{tot}$ for runs 1-17, all of which were carried out at pH 3.4. Despite the large scatter in the values, it is apparent that λ_1 is substantially independent of $(EDTA)_{tot}$. The variance of the 17 points from the constant value $4.0 \times 10^{-2}\ sec^{-1}$ is $0.5 \times 10^{-2}\ sec^{-1}$. Comparison of duplicate runs such as 2 and 3 or 11 and 12 shows that the reproducibility of repeated measurements of λ_1 is often only comparable to this overall variance. It was assumed, therefore, that λ_1, which is related to the length of the induction period, is independent of $(EDTA)_{tot}$.

Examination of eq 4 reveals that λ_1 becomes independent of $(EDTA)_{tot}$ only when $k_{-1} = 0$. When this condition holds $\lambda_1 = k_2$ and $\lambda_2 = k_1K(EDTA)_{tot}/(1 + K(EDTA)_{tot})$. The solid line in Figure 2 illustrates the good fit of λ_2 to the latter equation; it was obtained with $k_1 = 3.4 \times 10^{-2}$ sec and $K = 19\ M^{-1}$. Because only about half of the starting complex is converted to the ion pair at the highest EDTA concentration studied, the quantities k_1 and K are not independently well-determined by the data in Figure 2. Reasonable uncertainty estimates are $K = 19 \pm 6\ M^{-1}$ and $k = (3.4 \pm 0.8) \times 10^{-2}\ sec^{-1}$. The product is much better defined: $k_1K = 0.65 \pm 0.08\ M^{-1}\ sec^{-1}$.

The dependences of λ_1 and λ_2 on $(EDTA)_{tot}$, therefore, are consistent with irreversible formation of the intermediate. If some reversibility is assumed, a situation which cannot be ruled out by the low quality of the data, λ_1 is predicted to increase somewhat with increasing $(EDTA)_{tot}$.

The pH range that is accessible for kinetic investigation is quite small. On the low side it is limited by the slight solubility of EDTA. Even at pH 3.4, reaction mixtures with $(EDTA)_{tot} \gtrsim 0.04\ M$ are supersaturated at 25°. Precipitation, however, does not set in for many hours under these conditions. On the high side, Deutsch and Taube[1] reported rapid condensation of acetatopentaaquochromium(III) to polynuclear species once a significant fraction of the complex is converted to its conjugate base. For that reason, all experiments were performed a full pH unit below the reported pK_a of 4.5. In Table I, data are reported for a limited series of experiments at pH 3.0 (runs 20-24). The pattern of dependence of λ_1 and λ_2 on $(EDTA)_{tot}$ is unchanged from the more extensive measurements at pH 3.4. Also significant is the relatively low sensitivity of λ_1 and λ_2 to changes in pH. For instance, although the hydrogen ion concentration increases by a factor of almost 3 from pH 3.5 to 3.0, the decreases in both λ_1 and λ_2 are only on the order of 40% at $(EDTA)_{tot} = 1.8 \times 10^{-2}\ M$.

Table I. Kinetic Data on the EDTA-Acetatopentaaquochromium(III) Reaction[a]

Run no.	pH	$10^2(EDTA)_{tot}$, M	$10^4(Cr)_{tot}$,[b] M	$10^2\lambda_1$, sec^{-1}	$10^3\lambda_2$, sec^{-1}
1	3.4	0.6	1.5	3.0	3.7
2	3.4	1.0	1.5	4.2	5.3
3	3.4	1.0	1.5	3.8	5.5
4	3.4	1.4	1.5	4.4	7.3
5	3.4	1.8	2.0	3.3	9.0
6	3.4	2.2	2.0	4.2	9.8
7	3.4	2.6	2.0	3.6	11.9
8	3.4	2.6	2.0	3.5	11.8
9	3.4	3.0	2.5	4.5	12.3
10	3.4	3.4	2.5	4.5	13.3
11	3.4	3.8	2.5	5.0	13.9
12	3.4	3.8	2.5	4.7	14.0
13	3.4	4.2	3.0	4.2	15.0
14	3.4	4.2	3.0	4.0	15.2
15	3.4	4.6	3.0	3.8	16.9
16	3.4	4.6	3.0	3.7	15.9
17[c]	3.4	5.0	3.0	3.8	16.9
18[c]	3.4	5.0	3.0	4.2	17.2
19[c]	3.4	5.0	3.0	4.0	17.7
20	3.0	0.6	2.0	3.0	2.4
21	3.0	0.6	2.0	2.0	2.6
22	3.0	1.0	2.0	2.8	4.0
23	3.0	1.4	2.5	2.6	5.0
24	3.0	1.8	3.0	3.1	6.1
25	3.1	1.8	2.5	3.1	7.2
26	3.5	1.8	1.5	4.8	9.3
27	3.5	1.8	1.5	4.5	8.8

[a] Experimental conditions were 25.0°, $(Na^+) = 0.25\ M$; the parameter λ_3 in eq 4 was held fixed at zero. [b] The value of $(Cr)_{tot}$ generally reflects the highest concentration consistent with adequate pH control; see Experimental Section. [c] In run 17 $(Na^+) = 0.25\ M$ and $I = 0.30\ M$; in runs 18 and 19 the sodium ion concentration was adjusted to give ionic strengths of 0.25 and 0.20 M, respectively.

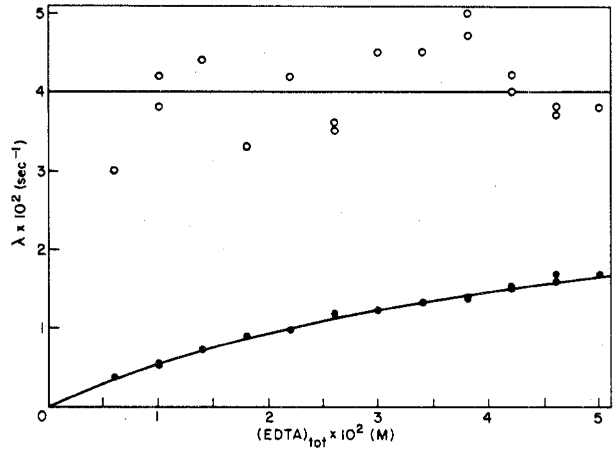


Figure 2. Dependence of λ_1 (open circles) and λ_2 (solid circles) on $(EDTA)_{tot}$ for the acetato complex at pH 3.4.

Formatopentaaquochromium(III). A series of kinetic runs was carried out at pH 3.4 on the formatopentaaquochromium(III)-EDTA reaction. The general time scale is about $^1/_{50}$th as fast as that for the acetato case, but the

---

(22) D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, 11, 431 (1963).

qualitative behavior of the two complexes is remarkably similar. The shapes of the absorbance-time profiles, for instance, are the same; eq 4, therefore, provides a good representation of the data for both complexes. Because the formato reaction is much slower, it was unnecessary to introduce Δt as an adjustable parameter. The ratio of λ_1 to λ_2 is somewhat smaller for the formato reaction. The intermediate, therefore, accumulates to higher concentrations, and the determination of λ_1 and λ_2 is more sensitive to the assumed value of ϵ_I. The initial slopes of the absorbance-time curves showed a consistent tendency to be slightly negative in the formato experiments. In fact, if λ_3 was allowed to remain an adjustable parameter (along with λ_1 and λ_2), values were obtained which corresponded to $\epsilon_I < 0$. The quality of the fits remained good, however, if ϵ_I was held constant anywhere in the range 0 to ϵ_R (15 M^{-1} cm^{-1}). In Table II, the optimized values of λ_1 and λ_2 are reported assuming that $\lambda_3 = 0$ ($\epsilon_I = \epsilon_R$) as was done for the acetato case. With $\lambda_3 = 0$, typical fits of the absorbance-time curves had a root-mean-square deviation between the calculated and observed absorbance of 0.004 absorbance unit for 40 points covering a total absorbance change of 0.4. In Figure 3 the values of λ_1 and λ_2 are plotted *vs.* $(\mathrm{EDTA})_{\mathrm{tot}}$. The pattern closely resembles that observed for the acetato complex. Once again, λ_1 remains essentially constant as $(\mathrm{EDTA})_{\mathrm{tot}}$ is varied while λ_2 shows a weakly saturating first-order dependence on the chelate concentration. The intermediate, therefore, appears to form irreversibly in this case as well. Because of the lower ratio of λ_1 to λ_2 the values of λ_2 are considerably less precise than was true for the acetate data. Consequently, the lower curve in Figure 3 cannot be analyzed for meaningful independent values of k_1 and K. The product k_1K is reasonably well defined as $(2.5 \pm 1) \times 10^{-2}\ M^{-1}\ \mathrm{sec}^{-1}$. If a value of $K = 19\ M^{-1}$ is assumed, by analogy with the acetate case, the optimum value of k_1 is $1.3 \times 10^{-3}\ \mathrm{sec}^{-1}$ and the solid curve in Figure 3 is obtained. The mean value of the λ_1 points (which defines k_2) is $(6.4 \pm 0.2) \times 10^{-4}\ \mathrm{sec}^{-1}$.

The absorbance-time curves were also analyzed holding λ_3 fixed at a value which corresponds to $\epsilon_I = 0$. This exercise provided a quantitative estimate of the sensitivity of the derived λ_1 and λ_2 values to the assumed extinction coefficient of the intermediate. The qualitative appearance of the plots of the λ's against $(\mathrm{EDTA})_{\mathrm{tot}}$ was unchanged from those in Figure 3. The optimum value of k_1K did not change significantly while k_2 increased to $7.7 \pm 0.2 \times 10^{-4}\ \mathrm{sec}^{-1}$.

Trifluoroacetatopentaaquochromium(III). Two kinetic runs were carried out at pH 3.4 on the trifluoroacetatopentaaquochromium(III)-EDTA reaction. The shape of the absorbance-time profiles closely resembled that observed for the other two carboxylato complexes, but the time scale was the slowest of the three (on the order of $^1/_{100}$th as fast as the acetato case). The data were analyzed as described for the formato system. When λ_3 was held fixed at 0, optimum values of λ_1 and λ_2 at $(\mathrm{EDTA})_{\mathrm{tot}} = 0.05\ M$ were $5.2 \times 10^{-4}\ \mathrm{sec}^{-1}$ and $9.0 \times 10^{-5}\ \mathrm{sec}^{-1}$, respectively. At $(\mathrm{EDTA})_{\mathrm{tot}} = 0.04\ M$ the corresponding values were $4.6 \times 10^{-4}\ \mathrm{sec}^{-1}$ and $8.0 \times 10^{-5}\ \mathrm{sec}^{-1}$.

On the assumption that λ_1 and λ_2 have the same interpretation as in the previous cases, the λ_2 results can be used to estimate k_1. The conditional ion-pair constant $K = 19\ M^{-1}$ (from the acetato data) leads to k_1 values of 1.83×10^{-4} and $1.86 \times 10^{-4}\ \mathrm{sec}^{-1}$ at $(\mathrm{EDTA})_{\mathrm{tot}}$ levels of 0.05 and 0.04 M, respectively. In view of the expected imprecision in the λ_1 determinations it is reasonable to ascribe the difference between 5.2×10^{-4} and $4.6 \times 10^{-4}\ \mathrm{sec}^{-1}$ to experimental error and use $5 \times 10^{-4}\ \mathrm{sec}^{-1}$ as an estimate for k_2.

Table II. Kinetic Data on the EDTA–Formatopentaaquochromium(III) Reaction[a]

$10^2(\mathrm{EDTA})_{\mathrm{tot}}$, M	$10^4(\mathrm{Cr})_{\mathrm{tot}}$,[b] M	$10^4\lambda_1$, sec^{-1}	$10^4\lambda_2$, sec^{-1}
1.0	1.5	7.0	1.9
1.5	2.0	6.8	2.4
2.0	2.5	5.8	3.5
2.5	2.5	7.2	3.4
3.0	2.5	6.1	4.6
3.5[c]	2.5	5.9	5.8
4.0[c]	3.0	6.0	5.9
4.5	3.0	6.4	5.8
5.0[c]	3.0	6.6	6.5
5.0[c]	3.0	6.4	6.4

[a] Experimental conditions were 25.0°, pH 3.4, and $(\mathrm{Na}^+) = 0.25\ M$; the parameter λ_3 in eq 4 was held fixed at 0. [b] See footnote *b*, Table I. [c] In some runs the optimized values of λ_1 and λ_2 were equal or nearly equal; this situation causes difficulty with eq 4 since it has a singularity at $\lambda_1 = \lambda_2$. When necessary the following limiting form of eq 4 was applied: $(A_\infty - A)/(A_\infty - A_0) = [(\lambda + \lambda_3)t + 1]e^{-\lambda t}$ (assumes $\lambda_1 = \lambda_2 = \lambda$).

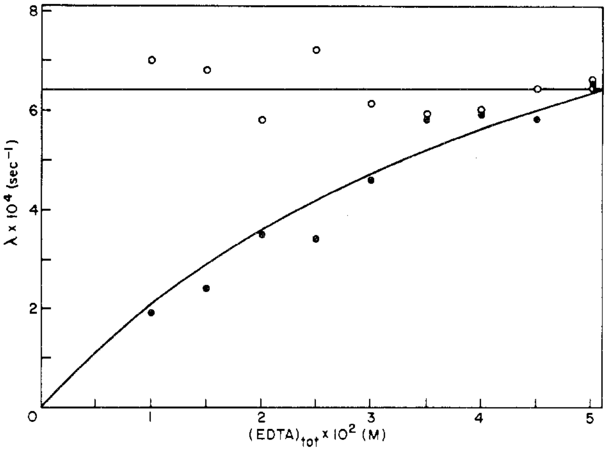


Figure 3. Dependence of λ_1 (open circles) and λ_2 (solid circles) on $(\mathrm{EDTA})_{\mathrm{tot}}$ for the formato complex.

The ratio of λ_2 to λ_1 is sufficiently high that calculated absorbance-time profiles are quite insensitive to the choice of ϵ_I. If a value of λ_3 is chosen which corresponds to $\epsilon_I = 0$, the data could be fit slightly better than with $\epsilon_I = \epsilon_R$ but there was no significant change in the optimum values of λ_1 or λ_2.

The trifluoroacetato case is a poor candidate for a thorough investigation of the dependence of the λ's on $(\mathrm{EDTA})_{\mathrm{tot}}$. The stoichiometry in eq 1 for the acetato reaction shows acetate picking up one of the protons lost by $\mathrm{H_2EDTA^{2-}}$. Since trifluoroacetic acid is a strong acid, trifluoroacetate does not play an analogous role. The difficulty of achieving good pH control is already considerable in the acetate system; for the trifluoroacetato reaction a sensibly constant pH could be maintained only at low chromium and high EDTA concentrations. The problem of pH control is exactly the same for the trifluoroacetato and hexaaquo complexes. In the latter case, however, simple first-order kinetics were observed and it was possible to define the corresponding single rate constant adequately with a smaller absorbance change (lower $(\mathrm{Cr})_{\mathrm{tot}}$) than was required for proper analysis of the trifluoroacetato data.

Hexaaquochromium(III). Four kinetic runs were carried out on the hexaaquochromium(III)-EDTA reaction under the same conditions used most extensively with the carboxylato complexes: pH 3.4, 25.0°, $(\mathrm{Na}^+) = 0.25\ M$. The reaction obeyed good pseudo-first-order kinetics for over 90% of the observed absorbance change. The ratio $(\mathrm{EDTA})_{\mathrm{tot}}/$

$(Cr)_{tot}$ always exceeded 65. At $(EDTA)_{tot}$ values of 1.0×10^{-2}, 2.0×10^{-2}, 3.0×10^{-2}, and 4.0×10^{-2} *M*, pseudo-first-order rate constants of 0.74×10^{-5}, 1.12×10^{-5}, 1.29×10^{-5}, and 1.42×10^{-5} sec^{-1} were obtained. Assuming that the mechanism simply involves reversible formation of an ion pair followed by rate-determining anation, the dependence of the pseudo-first-order rate constants (k) on $(EDTA)_{tot}$ is described by eq 5. The conditional formation constant, K, is defined in a manner analogous to that for the equilibrium constant in eq 3. The first-order rate constant k_A applies to the rate-determining complexation step within the 1:1 complex. The four data points are plotted in Figure 4 along with the best fit to eq 5, which was obtained with $K = 59\ M^{-1}$ and $k_A = 2.0 \times 10^{-5}$ sec^{-1}.

$$k = \frac{Kk_A(EDTA)_{tot}}{1 + K(EDTA)_{tot}} \qquad (5)$$

These results contrast somewhat with those of Hamm,[9] although the conditions are not fully comparable. He observed no dependence of the rate on $(EDTA)_{tot}$; the range of concentrations investigated, however, was not specified. Presumably, the experiments were carried out at very high EDTA concentrations using extensively supersaturated solutions at the higher acidities studied. Also, although Hamm reported good first-order kinetics for an initial, major part of the absorbance change, he observed subsequent slower absorbance increases leading to the final spectrum of the Cr(III)-EDTA complex. No comparable phenomenon was observed here; the values of A_∞ used in the good-quality pseudo-first-order kinetic plots corresponded to complete reaction. It is possible that the complications in the earlier study were associated with the nitrate medium employed.

The first-order kinetic plots invariably extrapolated to an absorbance at zero time which was slightly less (*ca.* 0.01 absorbance unit) than the observed initial absorbance. This effect, which was too small to analyze quantitatively, suggested the presence of an induction period with a time scale on the order of 20 min.

Discussion

The skeletal mechanism outlined in eq 2 will be used as the basis for discussion. Alternate possibilities exist, but eq 2 appears to be the simplest reasonable model that is consistent with the kinetic data. It assumes that only one partially complexed intermediate accumulates and that this intermediate is on the reaction path for all the material. The intermediate's identity, as well as the detailed nature of the rate-determining steps involved in its formation and disappearance, is uncertain. There is a little known[23-25] about the behavior of partially complexed Cr(III)-EDTA complexes, but not enough to reach definite conclusions on these points.

It will be argued below that not only is the foreign carboxylate still present in the intermediate but that it is not lost in the rate-determining step for its disappearance. It may not leave until the last step, which is likely to involve a rapid SN2 ring closing by an EDTA carboxylate.[25] In any event, the foreign carboxylate is unlikely to persist in a species such as $(EDTA)CrOAc^{2-}$. No complexes are known in which the residual water molecule in $(EDTA)Cr(OH_2)^-$ is replaced.[24] Furthermore, the final spectrum of the product obtained in the EDTA-acetatopentaaquochromium(III) reaction corresponds exactly with that for $(EDTA)Cr(OH_2)^-$; free acetic acid can also be recovered chromatographically from the product solutions under relatively mild conditions.

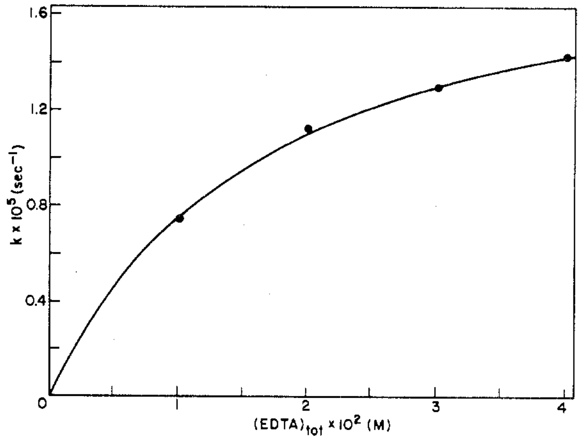


Figure 4. Dependence of k on $(EDTA)_{tot}$ for hexaaquochromium(III).

The kinetic parameters obtained for the mechanism in eq 2 are summarized for the four complexes in Table III. At pH 3.4, 88% of the EDTA is present as H_2EDTA^{2-}, while H_3EDTA^- accounts for most of the balance. The ion-pair formation constants, therefore, should essentially reflect the interaction between the cations and a dinegative anion. There are few meaningful comparisons to be made with literature data. The value obtained for K for hexaaquochromium(III) is somewhat high compared to an ion-pair association constant of 12 measured for hexaaquochromium(III) and sulfate[26] although the sulfate value was obtained at unit ionic strength. The $(en)_2Co(H_2O)(OH)^{2+}$-HPO_4^{2-} system gives an ion-pair association constant of 60 (22.5°, $I = 1.0\ M$)[27] while $(en)_2Co(H_2O)(OH)^{2+}$-$C_2O_4^{2-}$ gives a value of 6 (25°, $I = 0.3\ M$).[28] Obviously more than simple electrostatic interactions are involved; all that can be said is that the order of magnitude of the values reported for K in Table III is reasonable.

The variations in reactivity toward EDTA which the acetato, formato, trifluoroacetato, and aquo complexes display pose a challenging mechanistic problem. Three general possibilities were considered for the role of a bound carboxylate in facilitating the reaction with EDTA: (1) participation as a better leaving group than water in an associative mechanism, (2) labilization of the trans water molecule, and (3) labilization of the cis water molecules. The first possibility is safely excluded. Trifluoroacetate, formate, and acetate exhibit a reactivity trend which is strongly inverted from that which would be expected if they functioned as leaving groups. Furthermore, both the rates of formation and disappearance of the intermediate depend markedly on the identity of the carboxylate. Loss of the carboxylate, therefore, cannot accompany the intermediate's formation.

The extent to which k_1 and k_2 parallel one another as the carboxylate is varied is striking. The ratio k_2/k_1 has values of about 1, 0.5, and 3 for acetate, formate, and trifluoroacetate while k_2 varies monotonically by an overall factor of

---

(23) A. G. Sykes and R. N. F. Thorneley, *J. Chem. Soc. A*, 655 (1969).

(24) A. G. Sykes and R. N. F. Thorneley, *J. Chem. Soc. A*, 742 (1969).

(25) R. N. F. Thorneley, A. G. Sykes, and P. Gans, *J. Chem. Soc. A*, 1494 (1971).

(26) N. Fogel, J. M. J. Tai, and J. Yarborough, *J. Amer. Chem. Soc.*, **84**, 1145 (1962).

(27) S. F. Lincoln and D. R. Stranks, *Aust. J. Chem.*, **21**, 1745 (1968).

(28) S. C. Chan and G. M. Harris, *Inorg. Chem.*, **10**, 1317 (1971).

Table III. Summary of Kinetic Parameters for the Reactions of $(H_2O)_5CrL^{n+}$ Complexes with EDTA[a]

L	K, M^{-1}	k_1, sec^{-1}	k_2, sec^{-1}
Acetate	19	3.4×10^{-2}	4.0×10^{-2}
Formate	*b*	1.3×10^{-3}	6.4×10^{-4}
Trifluoroacetate	*b*	1.8×10^{-4}	5×10^{-4}
Water	59	*c*	*c*

[a] Conditions: pH 3.4, 25.0°, $(Na^+) = 0.25\ M$. [b] An independent value of K could not be extracted from the data; the value obtained for acetate was used to calculate k_1. [c] Simple first-order kinetics were observed; the resulting rate constant for conversion of the ion pair to product was 2.0×10^{-5} sec^{-1}.

80. This behavior suggests that the carboxylate performs a similar function both in facilitating formation and disappearance of the intermediate.

The second possibility, that of a marked kinetic trans effect for the carboxylate, also seems inconsistent with available observations. A simple objection is that if the carboxylate is trans to the water molecule which is replaced to form the intermediate, it should be cis to whatever water molecule is replaced in the rate-determining step for the intermediate's disappearance. This requirement is not absolute since the complex could rearrange in conjunction with the first substitution step; nonetheless, mechanisms which explain the enhancement of both steps by a trans effect appear contrived. A more telling argument is the absence of any other evidence that carboxylates exert strong kinetic trans effects either in chromium(III) chemistry or in that of other metal centers. A concrete indication to the contrary is provided by the measured rate of water exchange for *cis*-$(H_2O)_2Cr(ox)_2^-$. Both water molecules are trans to one oxalate linkage and cis to two others, yet the water-exchange rate is slower than that for hexaaquochromium(III).[29]

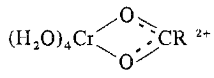
The simplest explanation for the EDTA reactions is a mechanism in which the bound carboxylate assists attack on chromium(III) at cis positions. This conclusion finds strong support in a study which was just published on the aquation of substituted acetatopentaamminechromium(III) complexes.[30] While trichloroacetatopentaamminechromium(III) undergoes normal acid-catalyzed aquation to trichloroacetic acid and aquopentaamminechromium(III), the initial step in the aquation of the dichloroacetato, chloroacetato, and acetato complexes is loss of a cis ammonia. The rate of ammonia loss increases as the carboxylate becomes more basic; for the acetato complex, decomposition sets in within minutes at ambient temperatures. Zinato, Furlani, Lanna, and Riccieri tentatively explained these results in terms of ground-state weakening of the chromium–nitrogen bond by hydrogen bonding between the carboxylate's unbound oxygen and a cis ammonia.

The details of this explanation seem dubious on theoretical grounds. Hydrogen bonding between a carboxylate oxygen and a hydrogen on an adjacent ammonia would weaken the chromium–carboxylate linkage but should strengthen the chromium–nitrogen bond. By effecting partial transfer of the proton from the ammonia (acting as an acid) to the carboxylate (acting as a base) the electron density on nitrogen would increase. The analogy which the authors draw with Adamson's SN2 FS mechanism[31] is not apt. In the case of Adamson's mechanism, the departure of a basic group such as chloride or thiocyanate is being assisted by partial protonation through hydrogen bonding to a solvent water molecule acting as an acid.

Similarly, in the reactions studied here, hydrogen bonding between the carboxylate and a cis water molecule should strengthen the bond between chromium and the cis water. In the limiting case of complete transfer of a proton from a cis water to the carboxylate, a hydroxo group would be left bound to the metal. Certainly the lability of a coordinated hydroxo group is expected to be less than that of a water molecule. For instance, the solvent-exchange rate of hydroxopentaamminecobalt(III) is much slower than that of aquopentaamminecobalt(III).[32] Although the hydrogen bonding in these systems certainly falls far short of complete proton transfer, the direction of the effect on the lability of the cis water or ammonia should be the same.

Hydrogen bonding between the carboxylate and a cis acidic group *could* conceivably enhance the lability of a *third* ligand. The hydrogen-bonded interaction leads to partial formation of a hydroxide-like (or amide-like) ligand cis to the carboxylate. Since coordinated hydroxides (or amides) are known to labilize other coordination positions in conjugate base mechanisms, presumably an analogous effect could operate with coordinated waters (or ammines) which are functioning as the acids in hydrogen bonds. Essentially, the resulting mechanism would represent intramolecular general base catalysis of the substitution process.

Without discounting the possibility of such an intramolecular general base mechanism, we prefer a simpler explanation of the carboxylate's role. It retains the notion that the labilization results from the interaction of the carboxylate's unbound oxygen with a cis position. The intimate role envisioned for the carboxylate is analogous to acetate's common function as a neighboring group in substitutions at carbon.[33] The limiting case for this assistance would involve rate-determining formation of an unstable intermediate or transition state of the structure shown as II. This species would be presumed to react rapidly with an entering group. Alternately, a concerted associative mechanism is plausible in which both the free carboxylate oxygen and the entering group assist the departure of the leaving water molecule.



$$(H_2O)_4Cr\begin{smallmatrix}O\\ \\ O\end{smallmatrix}CR^{2+}$$

II

The structure represented as II entails a substantial deviation from ideal octahedral geometry. It has been pointed out that two adjacent oxygens coordinated to a strictly octahedral chromium(III) center must be about 2.8 Å apart.[34] In contrast, the two oxygens of carboxylate functions are typically separated by 2.2 ± 0.1 Å.[35] This argument weighs against the likelihood of II as an intermediate but does not vitiate a concerted mechanism in which the entering group, the leaving group, and the free carboxylate oxygen all figure significantly in the energetics of the transition state.

The idea of labilization of the cis positions through the nucleophilic action of the carboxylate's unbound oxygen is consistent with the observed reactivity trend in the EDTA

---

(29) H. Stieger, G. M. Harris, and H. Kelm, *Ber. Bunsenges. Phys. Chem.*, **74**, 262 (1970).

(30) E. Zinato, C. Furlani, G. Lanna, and P. Riccieri, *Inorg. Chem.*, **11**, 1746 (1972).

(31) A. W. Adamson, *J. Amer. Chem. Soc.*, **80**, 3183 (1958).

(32) H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, **80**, 2642 (1958).

(33) B. Capon, *Quart. Rev., Chem. Soc.*, **18**, 45 (1964).

(34) J. E. Finholt and S. N. Deming, *Inorg. Chem.*, **6**, 1533 (1967).

(35) R. W. G. Wyckoff, "Crystal Structures," Vol. 5, 2nd ed, Interscience, New York, N. Y., 1966, p 311 ff.

reactions since the effectiveness of the carboxylates increases with their basicities. The mechanism also allows the initially bound carboxylate to perform the same role in both the formation and disappearance of the observed intermediate.

An intriguing corollary to the mechanism is the prediction that bound carboxylates which are members of existing small chelate rings should be ineffective at labilizing cis positions. The unbound oxygen of a carboxylate in a small chelate ring cannot attack a cis position without major stretching of the bond to the coordinated oxygen. Similarly, in the stepwise formation of a chelate ring in which a carboxylate forms the first bond to the metal, the initially bound carboxylate is unable to assist the completion of the ring through cis labilization. Configurations of the bound carboxylate which even remotely resemble II leave the second functionality in an inchoate five- or six-membered ring far from the metal. In short, the cis positions are predicted to be labilized in such a monodentate complex but the ring formation process is geometrically barred from benefiting. The special features of carboxylate groups in existing or incipient chelate rings explain why the first EDTA carboxylate to bind to chromium does not ensure rapid consummation of the chelation, while a foreign carboxylate is effective not only in facilitating the initial attack by EDTA but also in assisting one or more of the subsequent steps. Similarly, these arguments show that the proposed role for coordinated carboxylates is consistent with the low rates reported for water exchange in *cis*-$(H_2O)_2Cr(ox)_2^-$ and for ring-closing in malonatopentaaquochromium(III).[36,37] On the other hand, it would be difficult to rationalize these two observations with our results if the carboxylate's labilizing function simply involved a π interaction between the coordinated oxygen's unshared electron pairs and the metal, since it is unclear why such an interaction would be sensitive to incorporation of the carboxylate into a chelate ring.

The literature provides other examples, in addition to the carboxylatopentaamminechromium(III) aquations, of substitution processes which may be mechanistically related to the EDTA–carboxylatopentaaquochromium(III) reactions. Two prime candidates are the recently discovered *O*-sulfite-[6] and *O*-nitrite-enhanced[7,8] aquations of chromium(III) complexes. In both cases the free oxy anion is in labile equilibrium with the first coordination sphere of chromium(III) *via* a substitution process which does not disrupt chromium–oxygen bonds. When coordinated, the two anions greatly facilitate loss of other ligands. In both cases cis labilization is strongly implicated.

Matts and Moore[8] have suggested a mechanism for labilization by *O*-nitrite which is similar to that advanced here for carboxylates. They proposed cis nucleophilic attack by the nitrogen's lone pair. In view of the similar behavior of chromium(III)-coordinated *O*-sulfite, *O*-nitrite, bicarbonate, and carboxylates, it is tempting to hypothesize that an unbound oxygen is the nucleophile in all cases. Certainly steric factors favor attack by oxygen rather than the nitrogen in nitrite or the sulfur in sulfite.

Regardless of the atom involved, however, the basic mechanism, as pointed out by Matts and Moore, is an inorganic example of anchimeric assistance. Although conclusive evidence for the mechanism is lacking in any one system, it provides an attractive hypothetical umbrella for several systems which have not until now been mechanistically linked. We propose the name anchimeric cis effect as a general term for the labilization of cis positions through the nucleophilic action of an unshared electron pair on a ligand's unbound atom.

Extreme caution is required in using the results reported here to predict the behavior of other metal centers. Margerum, *et al.*,[38] observed, for example, that $CuOAc^+$ reacts much more slowly with EDTA than does $Cu^{2+}(aq)$. The contrasting behavior of chromium(III) and copper(II) is consistent with the hypothesized anchimeric cis effect. Since it involves rate-determining nucleophilic attack at the metal, the mechanism is presumably most favorable for metal centers with a proclivity for associative substitution mechanisms. There is now considerable evidence that chromium(III) is in this category. The systematics of its substitution kinetics,[2,3] the relative facility of linkage isomerization,[39,40] and the pressure dependence of its water-exchange rate[5] all support a significant role for the entering group in the transition state.

The anchimeric cis effect involves σ donation to the metal by the assisting group. This feature distinguishes it from the well-established participation of ligand electrons with π symmetry in substitution processes. There are many examples in cobalt(III) chemistry of donor atoms with nonbonding electron pairs which assist the departure of cis groups by stabilizing the incipient intermediate through π donation.[41] Even coordinated amido groups in conjugate base mechanisms for base hydrolysis may function in this way although there remains a controversy over whether the amido group forms cis[42] or trans[43] to the leaving group. Similarly, in the chemistry of chromium(III) aquo ions, such ligands as hydroxide[2,3] and iodide[4] may labilize cis positions by π donation.

Registry No. H_4EDTA, 60-00-4; $(H_2O)_5CrO_2CCH_3^{2+}$, 18894-45-6; $(H_2O)_5CrO_2CH^{2+}$, 38673-73-3; $(H_2O)_5CrO_2CCF_3^{2+}$, 38656-83-6; $Cr(H_2O)_6^{3+}$, 14873-01-9.

Acknowledgment. The author especially acknowledges Professor E. A. Deutsch, who first called his attention to the reaction between EDTA and acetatopentaaquochromium(III), for helpful discussions during the course of the work. Dr. T. W. Newton kindly supplied details of the construction of the internal thermostating bath for the spectrophotometer. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

---

(36) D. H. Huchital and H. Taube, *Inorg. Chem.*, 4, 1660 (1965).

(37) M. J. Frank and D. H. Huchital, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, No. INOR 42.

(38) D. W. Margerum, B. A. Zabin, and D. L. Jones, *Inorg. Chem.*, 5, 250 (1966).

(39) J. A. Broomhead, N. Kane-Maguire, and I. Lauder, *Inorg. Chem.*, 10, 955 (1971).

(40) J. E. Earley and W. Alexander, *J. Amer. Chem. Soc.*, 92, 2294 (1970).

(41) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 170–177.

(42) F. R. Nordmeyer, *Inorg. Chem.*, 8, 2780 (1969).

(43) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 89, 5129 (1967).