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Equilibrium and Kinetic Studies of the Reactions of N-Substituted Ethylenediamine-*N*,*N'*,*N'*-triacetatoaquachromium(III) with Acetate Ions

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The equilibrium constants of the reactions $CrY(H_2O)^{(n-3)-} + CH_3COO^- \rightleftharpoons Cr(CH_3COO)Y^{(n-2)-} + H_2O$ were determined at 25° and $\mu = 1$ ($NaClO_4$); Y represents ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetate (EDTA), *N*-hydroxyethylethylenediamine-*N*,*N'*,*N'*-triacetate (HEDTRA), ethylenediamine-*N*,*N'*,*N'*-triacetate (EDTRA), and *N*-methylethylenediamine-*N*,*N'*,*N'*-triacetate (MEDTRA); *n* is 4 for EDTA and 3 for HEDTRA, EDTRA, and MEDTRA. The values obtained were 0.62, 17, 18, and 12 M^{-1} for EDTA, HEDTRA, EDTRA, and MEDTRA complexes, respectively. A similar reaction takes place between ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetatoaquachromate(III) and azide ion with the equilibrium constant of 5.9 M^{-1}. The rates of the reactions described above were measured at 25° and $\mu = 1$ ($NaClO_4$). The rate constants for the forward reactions were 3.3, 7.6, 2.9×10^{-2}, and 7.3×10^{-4} M^{-1} sec^{-1} for EDTA, HEDTRA, EDTRA, and MEDTRA complexes, respectively, and those for the backward reactions were 5.4, 0.45, 1.6×10^{-3}, and 5.9×10^{-5} sec^{-1} for EDTA, HEDTRA, EDTRA, and MEDTRA complexes, respectively. The mechanisms of these reactions are discussed.

Introduction

Substitution inertness of chromium(III) complexes is well documented. Recently, it was reported, however, that the equilibrium of the reaction of ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetatoaquachromate(III) ($Cr(edta)(H_2O)^-$) with acetate (OAc^-)

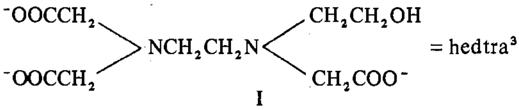
$$Cr(edta)(H_2O)^- + OAc^- \rightleftharpoons Cr(OAc)(edta)^{2-} + H_2O \qquad (1)$$

is established quite rapidly.[1]

In the present work, the equilibrium and kinetic studies of reaction 1 are extended to those of the reactions of complexes $CrY(H_2O)$ containing N-substituted ethylenediamine-*N*,*N'*,*N'*-triacetate (I–III) as Y with acetate in order to learn

$$CrY(H_2O) + OAc^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Cr(OAc)Y^- + H_2O \qquad (2)$$

how the ligand, Y, governs the magnitude of the equilibrium constant of reaction 2 and the lability of the ligand existing at the sixth coordination position of chromium(III) complex.



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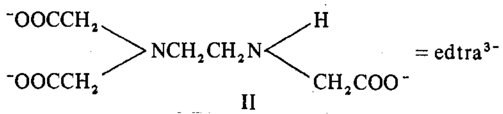

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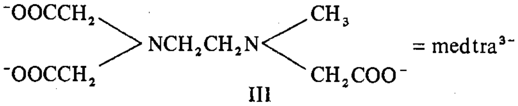

III

Experimental Section

A. Syntheses of Complexes. $[Cr(Hedta)(H_2O)]$. This complex was prepared by the method of Hamm.[2] Crude material was purified by the procedure reported previously.[3]

$[Cr(hedtra)(H_2O)]\cdot H_2O$. Four grams of $H_3hedtra$ (0.015 mol) and 3.6 g of $Cr(CH_3COO)_3\cdot H_2O$ (0.015 mol) were suspended in 200 ml of water. The mixture was heated for 1 hr on a boiling water bath. The pH of the solution was kept at 4.5 by the addition of sodium bicarbonate during the heating. After filtration, the solution was diluted to about 500 ml, passed through a column of Dowex 50W-X8 cation-exchange resin in H^+ form (200 ml) and then through a column of Dowex 1-X4 anion-exchange resin in acetate form (200 ml). After the column of anion-exchange resin was washed with water, the desired complex adsorbed on the column was eluted with a 0.05 *M* acetic acid solution. A trace amount of violet species remained at the top of the column. The eluate was evaporated to small volume under reduced pressure. Violet crystals were deposited on cooling; yield 98%. Anal. Calcd for $[Cr(hedtra)(H_2O)]\cdot H_2O$: C, 33.06; H, 5.27; N, 7.71. Found: C, 33.37; H, 5.24; N, 7.76.

$[Cr(edtra)(H_2O)]\cdot H_2O$. It has been known that manganese(III) in $[Mn(edta)(H_2O)]^-$ is reduced to manganese(II) both in aqueous solution at room temperature[4] and in solid state at elevated temperature[5] and that, upon these decomposition processes, EDTRA and EDDA are produced, where EDDA denotes ethylenediamine-*N*,*N'*-diacetate. The decomposition product of $K[Mn(edta)(H_2O)]\cdot 1.5H_2O$ was used as the source of EDTRA.

Twenty-eight grams of $K[Mn(edta)(H_2O)]\cdot 1.5H_2O$[6] (0.066 mol) taken in a glass tube was heated in an oil bath at 150° for 40 min. The pale yellow decomposition product was dissolved into 150 ml of water. To the solution was added 10 g of sodium hydroxide and air was bubbled through the solution to ensure the precipitation of manganese dioxide. After filtration, the pH of the filtrate was adjusted to 4.5 with acetic acid. To the solution, 16.2 g of $Cr(CH_3COO)_3\cdot H_2O$ (0.066 mol) was added. The mixture was heated on a boiling water bath for 1 hr. After filtration, the filtrate was diluted to 1 l., passed through a column of Dowex 50W-X8 resin in H^+ form (500 ml), and then passed through a column of Dowex 1-X4 in acetate form (500 ml). The desired complex adsorbed on anion-exchange resin was eluted with a 0.5 *M* acetic acid solution. The eluate was evaporated to dryness under the reduced pressure. As the residue contains a small amount of acetic acid, it was dissolved in 50 ml of water and the solutions was evaporated to dryness. This procedure was repeated several times; yield 13%. Anal. Calcd for $[Cr(edtra)(H_2O)]\cdot H_2O$: C, 30.10; H, 4.74; N, 8.78. Found: C, 30.45; H, 4.67; N, 8.82.

$[Cr(medtra)(H_2O)]\cdot 1.5H_2O$. The aqueous solution containing $Na_3medtra$ was prepared from 2 g of *N*-methylethylenediamine (0.028 mol) by the method of Van Saun and Douglas.[7] This solution was used for preparing the chromium(III) complex without isolating the free ligand. The pH of the solution containing $Na_3medtra$ was adjusted to 4.5 with concentrated hydrochloric acid. The solution was concentrated to a small volume and filtered to remove as much sodium chloride as possible. The filtrate was diluted to 200 ml, 5 g of $Cr(CH_3COO)_3\cdot H_2O$ (0.02 mol) was added, and the mixture was heated on a boiling water bath for 1 hr. The pH was kept at 4.5 with sodium bicarbonate during the heating. After filtration, the filtrate was diluted to 500 ml and passed through a column of Dowex 50W-X8 in H^+ form (300 ml). To the resulting solution was added silver acetate to remove chloride ions. After filtration, the filtrate was evaporated to a small volume. Violet crystals were deposited on cooling. The yield, based on the amount of $Cr(CH_3COO)_3\cdot H_2O$, was 55%. Anal. Calcd for $[Cr(medtra)(H_2O)]\cdot 1.5H_2O$: C, 31.59; H, 5.30; N, 8.19. Found: C, 31.85; H, 5.20; N, 8.24.

B. Acid Dissociation Constants of $CrY(H_2O)^{(n-3)-}$. For determining the equilibrium constants of the reaction

$$Cr(Hedta)(H_2O) \rightleftharpoons Cr(edta)(H_2O)^- + H^+ \quad K^H \qquad (3)$$

and of the reaction

$$CrY(H_2O)^{(n-3)-} \rightleftharpoons Cr(OH)Y^{(n-2)-} + H^+ \quad K_a \qquad (4)$$

Table I. p*K* Values of $CrY(H_2O)^{(n-3)-}$ at 25° and $\mu = 0.1$ ($NaClO_4$)[a]

$$Cr(Hedta)(H_2O) \overset{K^H}{\rightleftharpoons} Cr(edta)(H_2O)^- + H^+$$

$$CrY(H_2O)^{(n-3)-} \overset{K_a}{\rightleftharpoons} Cr(OH)Y^{(n-2)-} + H^+$$

Y^{n-}	pK^H	pK_a
$edta^{4-}$	1.8 ± 0.2,[b] 1.95,[c] 2.27[d]	7.39 ± 0.03,[b] 7.39,[c] 7.41[d]
$hedtra^{3-}$		6.13 ± 0.03,[b] 6.02[e]
$edtra^{3-}$		6.25 ± 0.03[b]
$medtra^{3-}$		6.25 ± 0.03[b]

[a] The number *n* denotes the negative charges on Y. [b] This work. [c] G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, **34**, 576 (1951); at 20° and $\mu = 0.1$. [d] C. Furlani, G. Morpurgo, and G. Sartori, *Z. Anorg. Allg. Chem.*, **303**, 1 (1960); at 18° and $\mu = 0.15$. [e] R. K. Wharton and R. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 2404 (1972); at 25° and $\mu = 0.1$.

pH titrations were made with a standard sodium hydroxide solution at 25° and $\mu = 0.1$ ($NaClO_4$), where *n* denotes the number of negative charges on Y. The pH values were measured with a Hitachi F-5 pH meter. The hydrogen ion concentrations were calculated with the activity coefficient of 0.86 for the hydrogen ion.[8] The p*K* values are given in Table I.

C. Equilibrium Measurements. Equilibrium measurements were made spectrophotometrically at 25° and $\mu = 1$ ($NaClO_4$). The reactions of chromium(III) complexes with acetate were investigated in acetic acid–sodium acetate buffer solutions (pH 3.7–5.0). For the reaction of $Cr(edta)(H_2O)^-$ with azide, azide buffer solutions (pH 4.9), which were prepared by mixing the solutions of sodium azide and perchloric acid, were used.

In the case of EDTA and HEDTRA complexes, the solution containing chromium(III) complex, sodium perchlorate, and acetate buffer (or azide buffer) was prepared and transferred directly to an optical cell whose temperature was controlled to be 25.0 ± 0.1° by circulating thermostated water through the cell holder. In the case of EDTRA and MEDTRA complexes, the flask containing required components was immersed into thermostated bath for 20 and 30 hr, respectively, before being subjected to the absorbance measurements. The absorbance was recorded with a Hitachi EPS-3 pen-recording spectrophotometer.

D. Kinetic Measurements. Kinetic measurements were made at 25° and $\mu = 1$ ($NaClO_4$). The rate of the reactions of $Cr(edta)(H_2O)^-$ and $Cr(hedtra)(H_2O)$ with acetate was measured by employing the stopped-flow method with a Hitachi RSP-2 rapid-scanning spectrophotometer. The change in the transmittance was monitored at 510 nm for the EDTA complex and at 600 nm for the HEDTRA complex.

The reactions of $Cr(edtra)(H_2O)$ and $Cr(medtra)(H_2O)$ with acetate were followed with a Hitachi EPS-3 spectrophotometer at 420 nm. For the reaction of $Cr(edtra)(H_2O)$ with acetate, the required amounts of acetate buffer and sodium perchlorate solutions were added to an optical cell. Into this solution the solution of $Cr(edtra)(H_2O)$ was injected with a syringe. For the reaction of $Cr(medtra)(H_2O)$ with acetate, a volumetric flask filled with a solution containing the required components was placed in a thermostated bath. The solutions were transferred to an optical cell at appropriate intervals and submitted to the measurement of the absorbance.

The hydrogen ion concentrations of the solutions at $\mu = 1$ were determined with a Hitachi F-5 pH meter, whose meter readings were calibrated against standard perchloric acid solutions.

Results

Determination of the Equilibrium Constants of Reactions 1 and 2. Upon the addition of the acetate buffer solution to the solution of $Cr(hedtra)(H_2O)$, the visible absorption maxima shifted to longer wavelengths spontaneously. When the concentration of the acetate ion was varied, isosbestic points were observed at 393, 460, and 534 nm. Figure 1 shows such spectral changes. Similar spectral changes were observed for $Cr(edta)(H_2O)^-$, $Cr(edtra)(H_2O)$, and $Cr(medtra)(H_2O)$, though the reactions of the latter two complexes with acetate were more sluggish than those of $Cr(edta)(H_2O)^-$ and $Cr(hedtra)(H_2O)$ with acetate.

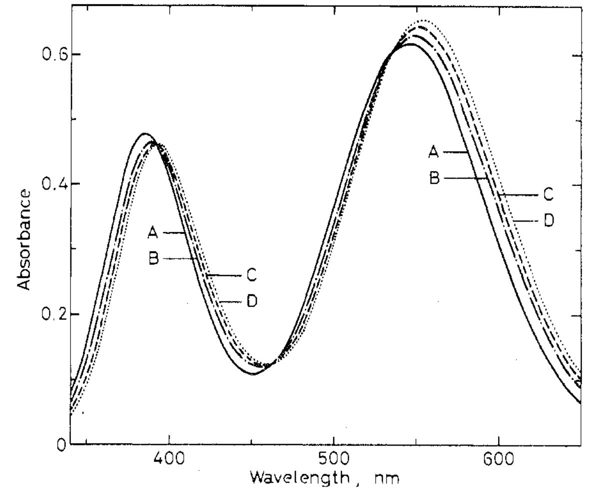

Figure 1. Spectral changes of $Cr(hedtra)(H_2O)$ with the addition of acetate at pH 4.4, 25°, and $\mu = 1$ ($NaClO_4$). $[OAc^-] = 0$ (A), 0.0400 *M* (B), 0.120 *M* (C), and 0.400 *M* (D). $[Cr(III)]_T = 4.08$ m*M*. The optical cell length is 1 cm. The reaction completes practically within the time of mixing.

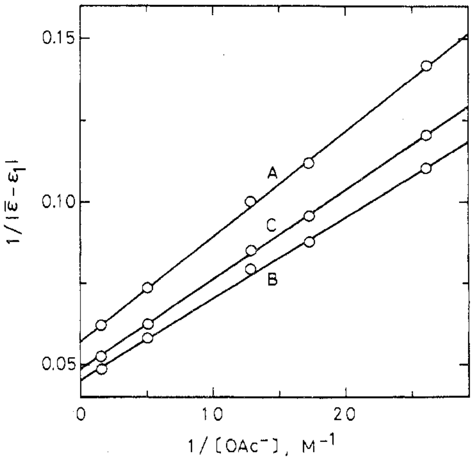

Figure 2. Plots of $1/|\bar{\epsilon} - \epsilon_1|$ vs. $1/[OAc^-]$ for the $Cr(edtra)(H_2O)$–OAc^- system. The measurements were made at pH 4.1. The wavelength employed is 420 nm (A), 590 nm (B), and 600 nm (C), respectively. See the text for the definition of the molar extinction coefficients, $\bar{\epsilon}$ and ϵ_1.

If these spectral changes are attributed to the formation of $Cr(OAc)Y^{(n-2)-}$ given in reactions 1 and 2, the absorbance of $CrY(H_2O)^{(n-3)-}$ in an acetate buffer solution for unit cell length, *D*, is given by

$$D = \epsilon_1[CrY(H_2O)^{(n-3)-}] + \epsilon_2[Cr(OAc)Y^{(n-2)-}] = (\epsilon_1 + \epsilon_2 K[OAc^-])\frac{[Cr(III)]_T}{1 + K[OAc^-]} \tag{5}$$

$$K = \frac{[Cr(OAc)Y^{(n-2)-}]}{[CrY(H_2O)^{(n-3)-}][OAc^-]} \tag{6}$$

where ϵ_1 and ϵ_2 are the molar extinction coefficients of $CrY(H_2O)^{(n-3)-}$ and $Cr(OAc)Y^{(n-2)-}$, respectively, and $[Cr(III)]_T$ is total concentration of chromium(III) complex. Equation 5 is rewritten as

$$\frac{1}{\bar{\epsilon} - \epsilon_1} = \frac{1}{\epsilon_2 - \epsilon_1} + \frac{1}{(\epsilon_2 - \epsilon_1)K[OAc^-]} \tag{7}$$

where $\bar{\epsilon} = D/[Cr(III)]_T$. If the values of the left-hand side of eq 7 are plotted against the reciprocals of acetate ion concentrations, linear plots will be obtained. Figure 2 shows

Table II. Equilibrium Constant (K) at 25° and $\mu = 1$ ($NaClO_4$)

Reaction	K^a
$Cr(edta)(H_2O)^- + OAc^- \rightleftharpoons Cr(OAc)(edta)^{2-} + H_2O$	0.62 ± 0.03^b
$Cr(edta)(H_2O)^- + N_3^- \rightleftharpoons Cr(N_3)(edta)^{2-} + H_2O$	$5.9 \pm 0.3^{c,d}$
$Cr(hedtra)(H_2O) + OAc^- \rightleftharpoons Cr(OAc)(hedtra)^- + H_2O$	16.9 ± 0.9^e
$Cr(edtra)(H_2O) + OAc^- \rightleftharpoons Cr(OAc)(edtra)^- + H_2O$	$17.7 \pm 0.9^{c,f}$
$Cr(medtra)(H_2O) + OAc^- \rightleftharpoons Cr(OAc)(medtra)^- + H_2O$	12.4 ± 0.6^g

[a] Each value is the average of at least two determinations, except as indicated. The uncertainty is the average deviation. [b] At pH 3.7–5.0. [c] This value is that obtained by one determination. The error is assumed to be 5%. [d] At pH 4.9. [e] At pH 3.8–4.4. [f] At pH 4.1. [g] At pH 4.0–4.4.

Table III. Absorption Maxima (λ) and Molar Extinction Coefficients (ε) of Aqua, Acetato, and Azido Complexes of Chromium(III)

Complex	λ, kK (ε)
$Cr(H_2O)_6^{3+}$ [a]	17.5 (13.3), 24.4 (15.8)
$Cr(OAc)(H_2O)_5^{2+}$ [a]	17.5 (24.4), 24.4 (22.2)
$Cr(N_3)(H_2O)_5^{2+}$ [b]	17.1 (67.5), 23.0 (66.4)
$Cr(H_2O)(NH_3)_5^{3+}$ [c]	20.9 (35), 27.8 (29)
$Cr(OAc)(NH_3)_5^{2+}$ [d]	20.2 (52), 27.25 (33)
$Cr(N_3)(NH_3)_5^{2+}$ [e]	20.07 (145), 26.18 (93)
$Cr(edta)(H_2O)^-$	18.4 (213), 25.5 (114)
$Cr(OAc)(edta)^{2-}$	17.7 (147), 25.4 (119)
$Cr(N_3)(edta)^{2-}$	18.15 (213), 24.6 (128)
$Cr(hedtra)(H_2O)$	18.35 (151), 26.0 (117)
$Cr(OAc)(hedtra)^-$	18.0 (162), 25.3 (113)
$Cr(edtra)(H_2O)$	18.5 (133), 25.9 (107)
$Cr(OAc)(edtra)^-$	18.3 (147), 25.45 (108)
$Cr(medtra)(H_2O)$	18.55 (143), 25.9 (113)
$Cr(OAc)(medtra)^-$	18.2 (154), 25.4 (112)

[a] E. Deutsch and H. Taube, *Inorg. Chem.*, 7, 1532 (1968). [b] T. W. Swaddle and E. K. King, *ibid.*, 3, 234 (1964). [c] M. A. Levine, J. P. Jones, W. E. Harris, and W. J. Wallace, *J. Am. Chem. Soc.*, 83, 2453 (1961). [d] D. Zinato, P. Lindholm, and A. W. Adamson, *J. Inorg. Nucl. Chem.*, 31, 449 (1969). [e] M. Linhard, H. Siebert, and M. Weigel, *Z. Anorg. Allg. Chem.*, **278**, 287 (1955).

the plots obtained for the $Cr(edtra)(H_2O)$ system. The linear plots are consistent with the occurrence of reaction 2. The K values obtained at various wavelengths for $Cr(edtra)(H_2O)$ were 17.6 at 420 nm, 18.1 at 590 nm, and 17.5 at 600 nm, which are essentially identical. Similar results were obtained for other systems and the K values are summarized in Table II. The K value of each system was independent of pH, even for EDTA system, within the range shown in Table II.

The addition of azide buffer solutions to the solution of $Cr(edta)(H_2O)^-$ yielded spectral changes similar to those observed for the addition of acetate buffer solutions. This phenomenon was found to be compatible with the formation of $Cr(N_3)(edta)^{2-}$. The equilibrium constant of this reaction is also given in Table II.

The value of ϵ_2 at any wavelength can be determined by using the values of ϵ_1 and K. Table III summarizes the numerical data of the absorption spectra for the chromium(III) complexes concerned in the present work.

Determination of Rate Constants for the Reactions 1 and 2. The kinetics of the reaction of $CrY(H_2O)^{(n-3)-}$ with acetate were studied under the pseudo-first-order conditions; concentrations of acetate greatly exceeded those of $CrY(H_2O)^{(n-3)-}$. The rate law for reaction 2 can be expressed as

$$-\frac{d[CrY(H_2O)^{(n-3)-}]}{dt} = k_f[CrY(H_2O)^{(n-3)-}][OAc^-] - k_b[Cr(OAc)Y^{(n-2)-}] \tag{8}$$

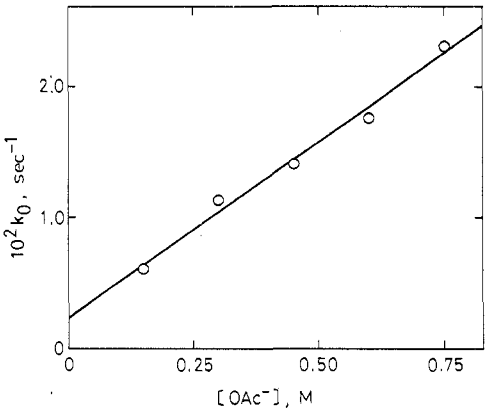

Figure 3. Plot of the pseudo-first-order rate constant of reaction 2 (k_0) vs. $[OAc^-]$ for the $Cr(edtra)(H_2O)$–OAc^- system.

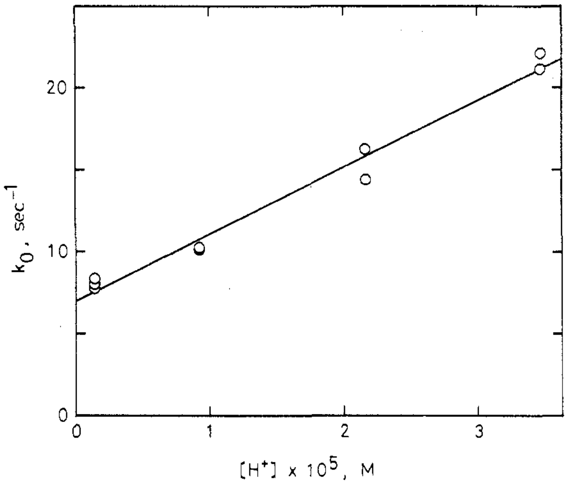

Figure 4. Plot of the pseudo-first-order rate constant of reaction 1 (k_0) vs. $[H^+]$ for the $Cr(edta)(H_2O)^-$–OAc^- system. $[OAc^-] = 0.500\ M$.

Equation 8 is rewritten as

$$2.303 \log \frac{D_0 - D_\infty}{D_t - D_\infty} = k_0 t \tag{9}$$

$$k_0 = k_f[OAc^-] + k_b \tag{10}$$

where D_0, D_t, and D_∞ represent absorbancies at time 0, t, and infinity, respectively. The conventional plots of $\log |D_t - D_\infty|$ vs. time gave straight lines for all the systems studied in the present work and the values of k_0 were determined from these straight lines.

The values of k_0 for the reaction of $Cr(edtra)(H_2O)$ with acetate were determined at various concentrations of acetate. Figure 3 shows the plots of k_0 thus obtained vs. $[OAc^-]$ which give a good linear relation. The values of k_f were calculated from the relation

$$k_f = \frac{k_0}{[OAc^-] + K^{-1}} \tag{11}$$

The values thus obtained were independent of $[OAc^-]$. This fact supports the validity of the mechanism shown in eq 2. Then, the value of k_b was calculated from the values of k_f and K. The values of k_0 were independent of both the change in pH within the range of 3.8–4.6 and that in the initial concentration of $Cr(edtra)(H_2O)$ within the range of 1.6–6.6 mM. The individual rate constants, k_f and k_b, for HEDTRA and MEDTRA complexes were determined by the same procedures as for the EDTRA system.

The k_0 values of the reaction of $Cr(edta)(H_2O)^-$ with acetate

Table IV. Rate Constants at 25° and $\mu = 1$ ($NaClO_4$)[a]

Reaction	k_f, M^{-1} sec^{-1}	k_b, sec^{-1}
$Cr(edta)(H_2O)^- + OAc^- \rightleftharpoons Cr(OAc)(edta)^{2-} + H_2O$[b,c]	3.3 ± 0.4	5.4 ± 0.6
$Cr(Hedta)(H_2O) + OAc^- \rightleftharpoons Cr(OAc)(Hedta)^- + H_2O$[b,c]	$(3.3 \pm 0.4) \times 10^3$	$(3.1 \pm 0.4) \times 10^5 \times K^H{}_{Cr(OAc)Y}$[d]
$Cr(hedtra)(H_2O) + OAc^- \rightleftharpoons Cr(OAc)(hedtra)^- + H_2O$[e]	7.60 ± 0.61	0.450 ± 0.030
$Cr(edtra)(H_2O) + OAc^- \rightleftharpoons Cr(OAc)(edtra)^- + H_2O$[f]	$(2.88 \pm 0.14) \times 10^{-2}$	$(1.63 \pm 0.13) \times 10^{-3}$
$Cr(medtra)(H_2O) + OAc^- \rightleftharpoons Cr(OAc)(medtra)^- + H_2O$[g]	$(7.31 \pm 0.35) \times 10^{-4}$	$(5.89 \pm 0.28) \times 10^{-5}$

[a] Each value is the average of at least five determinations. The uncertainty is the average deviation, except as indicated. [b] At pH 4.4–5.9 and at 0.500–1.00 *M* acetate. [c] The error is estimated from the standard deviation at the 95% confidence level. [d] $K^H{}_{Cr(OAc)Y} = [Cr(OAc)(edta)^{2-}][H^+]/[Cr(OAc)(Hedta)^-]$. [e] At pH 4.0–4.6 and at 0.100–0.400 *M* acetate. [f] At pH 3.8–4.6 and at 0.150–0.750 *M* acetate. [g] At pH 4.0–4.4 and at 0.100–0.400 *M* acetate.

were dependent on the hydrogen ion concentrations, as shown in Figure 4. If the reaction proceeds through the two simultaneous reaction paths

$$Cr(edta)(H_2O)^- + OAc^- \underset{k_{1b}}{\overset{k_{1f}}{\rightleftharpoons}} Cr(OAc)(edta)^{2-} + H_2O \qquad (12)$$

$$Cr(Hedta)(H_2O) + OAc^- \underset{k_{2b}}{\overset{k_{2f}}{\rightleftharpoons}} Cr(OAc)(Hedta)^- + H_2O \qquad (13)$$

and if the concentration of $Cr(OAc)(Hedta)^-$ is negligibly small under the experimental conditions, k_f and k_b in eq 10 can be expressed by the relations

$$k_f = k_{1f} + \frac{k_{2f}}{K^H}[H^+] \qquad (14)$$

$$k_b = k_{1b} + \frac{k_{2b}}{K^H{}_{Cr(OAc)Y}}[H^+] \qquad (15)$$

$$K^H{}_{Cr(OAc)Y} = \frac{[Cr(OAc)(edta)^{2-}][H^+]}{[Cr(OAc)(Hedta)^-]} \qquad (16)$$

The individual rate constants, k_{1f}, k_{2f}, k_{1b}, and k_{2b}, were determined by analyzing the data with eq 14 and 15 and are given in Table IV. The reaction of $Cr(edta)(H_2O)^-$ with azide ion completes within 2 sec.

Discussion

Acid Dissociation Constants of the Chromium(III) Complexes. As shown in Table I, the pK_a value of $Cr(edta)(H_2O)^-$ is larger than those of the chromium(III) complexes containing HEDTRA, EDTRA, and MEDTRA by 1–1.5 pK units. These may be attributed to the difference of the total charge of the complexes. The removal of a proton from the negatively charged complex is more difficult than that from the neutral complex.

Equilibrium Constants. The reaction of $CrY(H_2O)^{(n-3)-}$ with acetate to give $Cr(OAc)Y^{(n-2)-}$ was demonstrated by the following facts. (i) Spectral changes of $CrY(H_2O)^{(n-3)-}$ with acetate concentrations show isosbestic points as exemplified in Figure 1. (ii) The application of eq 7 to each system yields a linear relationship. (iii) The equilibrium constants determined at various wavelengths are essentially identical. As shown in Table II, the equilibrium constants of the reaction of $CrY(H_2O)$ with acetate are 20–30 times larger than that of $Cr(edta)(H_2O)^-$. Although $Cr(hedtra)(H_2O)$ has a free $-CH_2CH_2OH$ group, which is comparable in bulkiness to free $-CH_2COO^-$ in $Cr(edta)(H_2O)^-$, the equilibrium constant of $Cr(hedtra)(H_2O)$ is essentially the same as those of $Cr(edtra)(H_2O)$ and $Cr(medtra)(H_2O)$. Therefore, the smaller K value of $Cr(edta)(H_2O)^-$ may not be regarded as the steric hindrance exerted by a free $-CH_2COO^-$ group in this complex ion. The difference would be attributable to that of the total charges of the complex. The reaction of negatively charged $Cr(edta)(H_2O)^-$ ion with acetate is more difficult than those of neutral $CrY(H_2O)$ complexes because of the electrostatic repulsion.

An azide ion can form $Cr(N_3)(edta)^{2-}$ with an equilibrium constant 10 times larger than that of $Cr(OAc)(edta)^{2-}$. Preliminary experiments revealed that chloride, bromide, and pyridine could not form the (mixed-ligand)chromium(III) complexes of EDTA at pH 4–6.[9] On the other hand, cobalt(III) complexes containing EDTA,[10,11] HEDTRA,[12,13] EDTRA,[14] and MEDTRA[7] can form the stable $[Co(X)Y]^{m-}$-type complexes where ligand X is H_2O, Cl^-, Br^-, and NO_2^-, respectively, and where $m = 1$ (X = H_2O) or 2 (X = an anion) for EDTA and 0 (X = H_2O) or 1 (X = an anion) for HEDTRA, EDTRA, and MEDTRA, respectively.

Table III shows that when a water molecule coordinated to the Cr^{III}–Y complex is replaced by an acetate or an azide ion, the absorption maxima shift to smaller wave numbers. This is a trend similar to those of absorption spectra of other aqua- and acidochromium(III) complexes. The geometric configurations of $CrY(H_2O)^{(n-3)-}$ and $Cr(OAc)Y^{(n-2)-}$ are not known. Recent studies, however, revealed that $[Co(X)Y]^{m-}$ takes the equatorial form exclusively in which the monodentate ligand X is in the plane containing the metal ion and two amino nitrogen atoms.[15,16] The complexes $CrY(H_2O)^{(n-3)-}$ and $Cr(OAc)Y^{(n-2)-}$ may also take the equatorial form from the similarity of stereochemical situation between chromium(III) and cobalt(III) complexes.

Rate Constants. The usual substitution reactions of chromium(III) complexes have time scales of hours, days, or months at room temperature. For instance, the aquation and the anation rate constants at 25° have been reported to be smaller than 10^{-3} sec^{-1} and 10^{-4} M^{-1} sec^{-1}, respectively, for both acidopentaaquachromium(III) and acidopentaamminechromium(III) complexes.[17-19] However, the substitution reactions of the chromium(III) complexes investigated in this work are very rapid. Especially, the rate constants for Cr^{III}–EDTA and Cr^{III}–HEDTRA complexes are the largest among those for various chromium(III) complexes which have been reported so far. Although the value of p$K^H{}_{Cr(OAc)Y}$ is not known, it may be estimated to be 2.5 ± 1 from the corresponding values of the related complexes, e.g., 1.8 for $Cr(Hedta)(H_2O)$ and 3.0 for $Co(Br)(Hedta)^-$.[20] Hence, the k_{2b} value may be in a range of 1×10^2–1×10^4 sec^{-1}.

The rate constants for both aquation and anation reactions given in Table IV show a marked variation with the nature of Y coordinated to the chromium(III) ions and decrease in the order $Cr(Hedta)(H_2O) \gg Cr(hedtra)(H_2O) > Cr(edta)(H_2O)^- \gg Cr(edtra)(H_2O) > Cr(medtra)(H_2O)$ for the anation reaction and $Cr(OAc)(Hedta)^- > Cr(OAc)(edta)^{2-} > Cr(OAc)(hedtra)^- \gg Cr(OAc)(edtra)^- > Cr(OAc)(medtra)^-$ for the aquation reaction. These results can be explained reasonably by considering the associative nature of the chromium(III) substitution reactions. Recent investigations reveal that the substitution reactions of chromium(III) belong to an associative interchange mechanism.[18,19,21] The Cr^{III}–EDTA complex contains a free $-CH_2COOH$ or $-CH_2COO^-$ group, and the Cr^{III}–HEDTRA complex, a free $-CH_2CH_2OH$ group. Even $-CH_2COOH$ and $-CH_2CH_2OH$ groups have been believed to have coordinating ability for several metal ions.[22-26] On the other hand, Cr^{III}–EDTRA and –MEDTRA complexes have none of such free coordinating groups. Therefore, the rapid reactions observed for Cr^{III}–EDTA and

–HEDTRA complexes may suggest that the reactions proceed through seven-coordinate intermediates in which the free $-CH_2COOH$, $-CH_2COO^-$, or $-CH_2CH_2OH$ group coordinates to the chromium(III) ion and assists the elimination of the coordinated water molecule or acetate ion.

Several recent papers reported that chromium(III) substitution reactions were catalyzed by the presence of oxy anions such as nitrite,[27-29] sulfite,[28,30,31] nitrate,[30-32] and carboxylates.[33,34] These reactions were interpreted recently in terms of an anchimeric mechanism[30,31,33,35] in which the reaction proceeds through the intermediate formed by the chelation of the oxy anion. In the present system, however, it is postulated that free $-CH_2COOH$, $-CH_2COO^-$, or $-CH_2CH_2OH$ existing in the complex ion inherently acts as a nucleophile and catalyzes the substitution. This would have a primary importance for the unexpectedly rapid substitution rate of Cr^{III}–EDTA and –HEDTRA complexes.

Although the reaction rates for Cr^{III}–EDTRA and –MEDTRA complexes are much smaller than those of Cr^{III}–EDTA and –HEDTRA complexes, the rates are still much larger than those of the usual substitution reactions of chromium(III) complexes. Deutsch and Taube reported that the rate constant of the aquation reaction of $Cr(OAc)(H_2O)_5^{2+}$ is 4.1×10^{-7} sec^{-1} at 25° and $\mu = 1$.[36] Therefore, the replacement of five water ligands by $edtra^{3-}$ and $medtra^{3-}$ brings about 4400 and 140 times increase in the rate, respectively. It is known that the exchange reaction of a water molecule coordinated to $Cr(H_2O)(NH_3)_5^{3+}$ with a solvent water molecule is faster than the corresponding reaction of $Cr(H_2O)_6^{3+}$.[37] This is attributable to the fact that the $Cr-OH_2$ bonding is weakened owing to the electron donation from the nitrogen ligands to chromium ion. In the present system, the coordination of Y involving nitrogen atoms reduces the electron density of the central chromium(III) ion. This may lead to loosening of the $Cr-OH_2$ or –OAc bond and labilizing the ligand existing in the sixth coordination position. The faster aquation rate of $Cr(OAc)Y^{(n-2)-}$ than of $Cr(OAc)(H_2O)_5^{2+}$ may also come from the difference of the charge type.

The position of bond breaking in reactions 1 and 2 should be considered. Though the aquation reaction of $Cr(OAc)(H_2O)_5^{2+}$ is much slower than those for $Cr(OAc)Y^{(n-2)-}$ complexes, it was suggested that the Cr–O cleavage competed with the O–C cleavage.[36] As mentioned above, the reaction of $Cr(edta)(H_2O)^-$ with azide ion to yield $Cr(N_3)(edta)^{2-}$ is reversible and completes within the time of mixing. This observation indicates that the cleavage of the $Cr-OH_2$ or $Cr-N_3$ bond occurs very rapidly. Hence, the reactions of $Cr(OAc)Y^{(n-2)-}$ complexes are considered to proceed through the cleavage of chromium(III)–oxygen bond.

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Registry No. $Cr(edta)(H_2O)^-$, 19610-17-4; $Cr(OAc)(edta)^{2-}$, 52676-80-9; $Cr(N_3)(edta)^{2-}$, 55622-32-7; $Cr(hedtra)(H_2O)$, 15955-78-9; $Cr(OAc)(hedtra)^-$, 55622-33-8; $Cr(edtra)(H_2O)$, 55622-34-9; $Cr(OAc)(edtra)^-$, 55622-35-0; $Cr(medtra)(H_2O)$, 55622-36-1; $Cr(OAc)(medtra)^-$, 55622-37-2; $Cr(Hedta)(H_2O)$, 55637-94-0; $Cr(OAc)(Hedta)^-$, 55637-95-1; OAc^-, 71-50-1; N_3^-, 14343-69-2.

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