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Volume Changes on the Conversion from Quinquedentate EDTA Complexes of Co(III) and Cr(III) into Sexidentate Complexes

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For the conversion from quinquedentate complexes, $[Co(edtaH)(H_2O)]$ and $[Co(edta)(H_2O)]^-$, into the sexidentate complex, $[Co(edta)]^-$, the respective volume changes were measured from the density data at 25 °C. The volume change was determined as well for the proton dissociation of $[Cr(edtaH)(H_2O)]$. A comparison of the volume changes in the Co(III) system with the corresponding Cr(III) system supports the recent view that edta forms a sexidentate complex with Cr(III) in the pH 3.5—6.5 range.

In the solid state, $[Co(edtaH)(H_2O)]$[1)] and $[Cr(edtaH)(H_2O)]$[2)] have been found to be quinquedentate complexes, in which $Hedta^{3-}$ acts as a quinquedentate ligand with one free carboxyl group.

In aqueous solution, these edta complexes undergo two deprotonation steps in the pH range 1—9.[3—7)] When $[Co(edtaH)(H_2O)]$ is dissolved in solution, quinquedentate complexes, $[Co(edtaH)(H_2O)]$, $[Co(edta)(H_2O)]^-$, and $[Co(edta)(OH)]^{2-}$, are initially present, depending on the pH of the solution.[3)] Shimi and Higginson reported that these quinquedentate complexes are unstable and that they are slowly converted into the sexidentate complex, $[Co(edta)]^-$, at the characteristic rates.[3)] The conversion is complete within one day.

On the other hand, unlike the substitution-inert Co(III)-edta complex, one of the coordination sites of Cr(III)-edta has been found to be unexpectedly substitution-labile.[8—10)] Thus, the interconversion among Cr(III)-edta species present in the pH 1—9 range has been reported to be too rapid to follow, even by the stopped-flow and T-jump methods.[11)] Furthermore, it is difficult to specify the coordination structure for such a substitution labile complex in solution. However, the following acid-base equilibria among quinquedentate species have been considered to account for the rapid interconversion:[5—12)]

$$\begin{aligned}[Cr(edtaH)H_2O)] &\rightleftharpoons [Cr(edta)(H_2O)]^- \\ &\rightleftharpoons [Cr(edta)(OH)]^{2-}.\end{aligned}$$

Therefore, edta in its Cr(III) species has been thought to remain quinquedentate over a wide pH range. While there can be little doubt that quinquedentate complexes predominantly exist as $[Cr(edtaH)(H_2O)]$ below pH 2 and as $[Cr(edta)(OH)]^{2-}$ above pH 7, there must be considerable doubt as to the presence of the quinquedentate complex in a intermediate pH rang.[13—16)] Recent spectroscopic studies have suggested the possibility that the sexidentate edta complex, $[Cr(edta)]^-$, exists in the pH 3.5 to 6.5 region,[14—16)] though there is still room for further investigation.[13)] In addition, the sexidentate coordinate structure of $[Cr(edta)]^-$ has been established in the solid state,[17,18)] though the coordination structure found in the solid state is not always maintained in solution for the substitution-labile complex.

Recently, such volumetric properties as the partial molal volumes and the volume changes on complex formation have been found to be sensitive to the coordination structure of several divalent metal edta complexes in solution.[19)] In this study, the volume changes for Reactions 1 and 2,

$$[Co(edtaH)(H_2O)] \rightarrow [Co(edta)]^- + H^+ + H_2O \qquad (1)$$

and

$$[Co(edta)(H_2O)]^- \rightarrow [Co(edta)]^- + H_2O, \qquad (2)$$

and the volume change for the proton dissociation of quinquedentate Co(III)-edta species,

$$[Co(edtaH)(H_2O)] \rightarrow [Co(edta)(H_2O)]^- + H^+, \qquad (3)$$

have been determined based on the density data. It is therefore interesting to compare these reaction volumes with that of the proton dissociation of $[Cr(edtaH)(H_2O)]$ as to the coordination mode of edta in its Cr(III) complex.

The main object of this paper is to specify whether the Cr(III)-edta complex in an intermediate pH range is of the quinquedentate or sexidentate type; however, the formulation $[Cr(edta)]^-$ is provisionally used to represent the uninegative Cr(III)-edta species.

Experimental

Materials and Apparatus. $[Co(edtaH)(H_2O)]\cdot 3H_2O$,[1)] $Na_2[Co(edtaH)(NO_2)]\cdot 3H_2O$,[20)] $Na[Co(edta)]\cdot 4H_2O$,[34)] $[Cr(edtaH)(H_2O)]$,[6)] and $Rb[Cr(edta)]\cdot 2H_2O$[11)] were prepared according to the literature methods. Deionized water (Millipor Milli Q) and Titrisol NaOH solutions (Merck) were used throughout this study.

The densities were measured using a vibrating-tube density meter (Shibayama Scientific Co., Ltd. Model SS-D-200). The temperature of the vibrating-tube chamber was kept constant by completely immersing it in a thermostated bath controlled to within ±0.002°C. The precision of the density, judged by repeated measurements for the same solution at different times, was estimated to be better than $\pm 2\times 10^{-6}$ g cm^{-3}. pH measurements were carried out in a thermostated bath controlled to within ±0.01°C. A digital pH meter (Toa Electronics Ltd. Model HM-60S) having a precision of 0.003 pH unit was used and was calibrated with commercial standard buffers (Merck, for preparation of DIN 19266 standard buffer solution). All of the measurements were carried out at 25.00±0.01°C.

Procedure. A weighted amount of [Co(edtaH)(H_2O)] was dissolved in a reaction medium previously equilibrated at 25 °C in a stoppered flask. An aliquot of the solution was then transferred to the vibrating-tube of the density meter. The remainder was used for the pH measurements. The densities and pH values of the reaction mixture were recorded at constant intervals. The complex concentrations investigated were in the range from 0.01 to 0.05 $\mathrm{mol\,dm^{-3}}$.

Results and Discussion

Determination of pK_a's. The pK_a value for [Co(edtaH)(H_2O)] at 15 °C has been reported by Shimi and Higginson based on the kinetic data (pK_a=3.1).[3] The pK_a value at 25 °C was investigated by the kinetic method. When [Co(edtaH)(H_2O)] was dissolved in pure water, the pH of the solution gradually decreased as the reaction proceeded. Figure 1 shows plots of $\ln([\mathrm{H}^+]_\infty-[\mathrm{H}^+]_t)$ against the time (t), where $[\mathrm{H}^+]_\infty$ and $[\mathrm{H}^+]_t$ represent the value of $10^{-\mathrm{pH}}$ after completion of the reaction, and that at t. It can be seen from Fig. 1 that such a plot gives a straight line. Therefore, $[\mathrm{H}^+]_0$, the value of $[\mathrm{H}^+]$ in the initial solution, can be obtained by extrapolating the linear plots to $t=0$.

It is assumed that the rapid acid dissociation equilibrium, $\mathrm{MHL(OH_2)}\rightleftharpoons\mathrm{ML(OH_2)^-}+\mathrm{H^+}$, is attained in the initial solution, where [Co(edtaH)(H_2O)] and [Co(edta)(H_2O)]$^-$ are abbreviated as MHL(OH_2) and ML(OH_2)$^-$, respectively. The K_a value of [Co(edtaH)(H_2O)] can be calculated using.

$$K_a=\frac{[\mathrm{H^+}]_0[\mathrm{ML(OH_2)^-}]f_\pm}{[\mathrm{MHL(OH_2)}]}=\frac{[\mathrm{H^+}]_0\alpha f_\pm}{(1-\alpha)},$$

where the brackets indicate the molar concentration of substances in $\mathrm{mol\,dm^{-3}}$ units, α is the degree of dissociation, $\alpha=[\mathrm{ML(OH_2)^-}]/([\mathrm{MHL(OH_2)}]+[\mathrm{ML(OH_2)^-}])$, and $f_\pm$ is the mean activity coefficient of the monovalent ion. The value of α could be estimated by the following iteration procedure. First, the activity coefficient was assumed to be unity; an approximate α value was obtained from $\alpha=[\mathrm{H^+}]_0/[\mathrm{C}]$, where [C] is the sum of the molar concentration of the substances, $[\mathrm{C}]=[\mathrm{MHL(OH_2)}]+[\mathrm{ML(OH_2)^-}]$, in $\mathrm{mol\,dm^{-3}}$ units. By means of these estimated values for α and [C], the activity coefficient of the ion was calculated according to $\log f_\pm=-A\sqrt{I}/(1+\sqrt{I})$.[22] A more accurate α could then be obtained from $\alpha=[\mathrm{H^+}]_0/f_\pm[\mathrm{C}]$. The iteration process was repeated until a consistent α value was obtained. The thus-obtained pK_a value was 3.02±0.02.

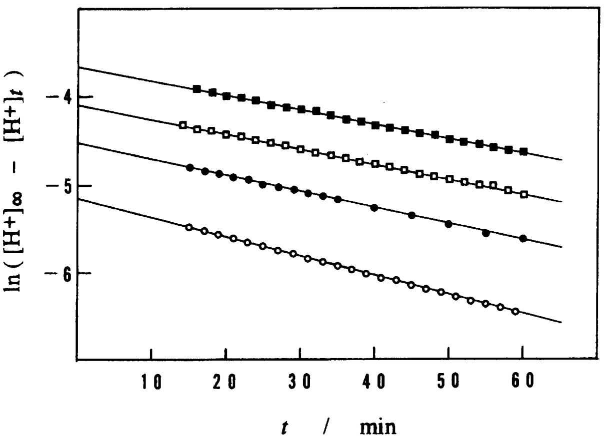

Fig. 1. Plots of $\ln([\mathrm{H}^+]_\infty-[\mathrm{H}^+]_t)$ in water against t. Total concentration of complexes, $[\mathrm{C}]/\mathrm{mol\,dm^{-3}}$: ■, 0.05221; □, 0.03445; ●, 0.02250; ○, 0.01252.

Higginson et al. investigated the conversion from [Co(edtaH)(H_2O)], [Co(edta)(H_2O)]$^-$ and [Co(edta)(OH)]$^{2-}$ to [Co(edta)]$^-$ in various pH regions.[3] They reported that the conversion reactions into [Co(edta)]$^-$ in constant-pH media were pseudo first-order reactions, and estimated the individual rate constants and pK_a values from the pH dependence of the pseudo first-order rate constants.[3] In an acidic solution, [Co(edtaH)(H_2O)] and [Co(edta)(H_2O)]$^-$ initially coexist and individually transform into [Co(edta)]$^-$ at characteristic rates denoted, respectively, as k_1 and k_2; then, the pseudo first-order rate constants for the formation of [Co(edta)]$^-$ in well buffered media may be expressed as $k=(k_1[\mathrm{H^+}]+k_2K_a)/([\mathrm{H^+}]+K_a)$.[3]

$$\begin{tikzcd}
\mathrm{MHL(OH_2)} \arrow[rr, rightleftharpoons, "K_a"] \arrow[dr, "k_1"'] & & \mathrm{ML(OH_2)^-}+\mathrm{H^+} \arrow[dl, "k_2"] \\
& \mathrm{ML^-}+\mathrm{H^+}+\mathrm{H_2O} &
\end{tikzcd}$$

It follows that, at high $[\mathrm{H^+}]$ (pH≦1), k reduces to $k=k_1$. However, in the present study, such a stationary state approximation is not the case, because the route via [Co(edta)(H_2O)]$^-$ is estimated to contribute to about 20% to the total rate at the initial time. Furthermore, good first-order rate plots were obtained even when [Co(edtaH)(H_2O)] was neutralized to the extent of 80% by dissolving it in an aqueous NaOH solution. Since this study was not carried out in well buffered media, it is difficult to solve the rate expressions accurately. However, it has at least been found that the rate of the increase in $[\mathrm{H^+}]$, or the decrease in the activity of [Co(edtaH)(H_2O)], obeys good pseudo first-order kinetics. A complete treatment of this subject involves a somewhat detailed study of kinetics.

The pK_a values of [Cr(edtaH)(H_2O)] and [Co(edtaH)(NO_2)]$^-$ were determined from the pH titration curve up to the first pH inflection. The detailed method of the calculation was essentially the same as those described in the literature.[23] The alkalimetric titration of the [Cr(edtaH)(H_2O)] solution gave pK_a=2.10±0.02 and the acidimetric titration of the $\mathrm{Na_2[Co(edta)(NO_2)]}$ solution gave pK_a=3.27±0.02. Although the pK_a value for [Cr(edtaH)(H_2O)] has been reported by Ogino et al. (pK_a=1.8±0.2 at I=0.1),[8] a somewhat larger value was obtained in this study. The value is considerably lower than might be expected for the dissociation of a free carboxyl group, as in [Co(edtaH)(H_2O)] and [Co(edtaH)(NO_2)]$^-$.

Determination of ΔV^{∞}'s. The conversion reaction of quinquedentate Co(III)-edta complexes into the sexidentate complex at 25 °C is sufficiently slow to measure any change in the density of the reaction mixture at appropriate intervals. The respective reaction volumes, ΔV_1^{∞} and ΔV_2^{∞}, for Reactions 1 and 2 can be estimated from the density data. Furthermore, the difference between ΔV_1^{∞} and ΔV_2^{∞} gives a reaction volume (ΔV_3^{∞}) for the ionization of the free carboxyl group in [Co(edtaH)(H_2O)].

When [Co(edtaH)(H_2O)] was dissolved in pure water, a significant decrease in the density with time was observed. Figure 2 illustrates some plots of $\ln(\Delta V_t)=\ln(1000/d_{\infty}-1000/d_t)$ against t, where d_{∞} and d_t are the density of the final solution and that of the solution at t. The experimental data also gave linear plots. The slopes of these plots indicate the observed pseudo first-order rate constants. The difference in the volume between the final and initial solutions in cm^3 (kg of solution)$^{-1}$ units, $\Delta V=1000/d_{\infty}-1000/d_0$, were obtained from the intercept of the linear plot, where d_0 is the density of the initial solution. The reaction volume at a finite concentration is given by $\Delta V_{\mathrm{obsd}}=\Delta V/\{\mathrm{M}\}$, where {M} means the total concentration of complexes in the initial solution, $\{\mathrm{M}\}=\{\mathrm{MHL(OH_2)}\}+\{\mathrm{ML(OH_2)^-}\}$, and is expressed in mol (kg of solution)$^{-1}$ units.

When [Co(edtaH)(H_2O)] was partially neutralized by dissolving it in an aqueous NaOH solution, as can be seen in Fig. 3, the plot of $\ln(\Delta V_t)$ against t was concave. However, the expression $\Delta V_t=(A\exp(-Ct)+(B\exp(-Dt))$ represented the data quite satisfactorily, where A, B, C, and D are fitting parameters determined by a method of non-linear least squares. Consequently, plots of $\ln(\Delta V_{\mathrm{A}})=\ln(\Delta V_t-B\exp(-Dt))$ and $\ln(\Delta V_{\mathrm{B}})=\ln(\Delta V_t-A\exp(-Ct))$ versus t should give straight lines. Such plots are also given in Fig. 3, where the open circles indicate the experimental points for $\ln(\Delta V_t)$, and the triangles and squares indicate the calculated points for $\ln(\Delta V_{\mathrm{A}})$ and $\ln(\Delta V_{\mathrm{B}})$, respectively. Thus, the difference in the volume between the final and initial solutions in cm^3 (kg of solution)$^{-1}$ units, $\Delta V=1000/d_{\infty}-1000/d_0$, could be obtained from empirical parameters.

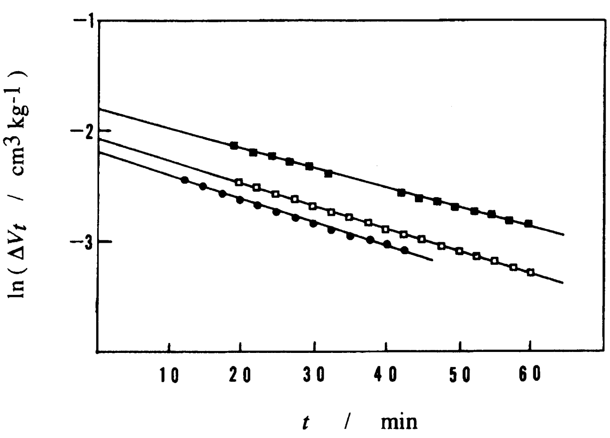

Fig. 2. Plots of $\ln(\Delta V_t)$ in water against t. Total concentration of complexes, {M}/mol kg^{-1}: ■, 0.05188; □, 0.03784; ●, 0.02986.

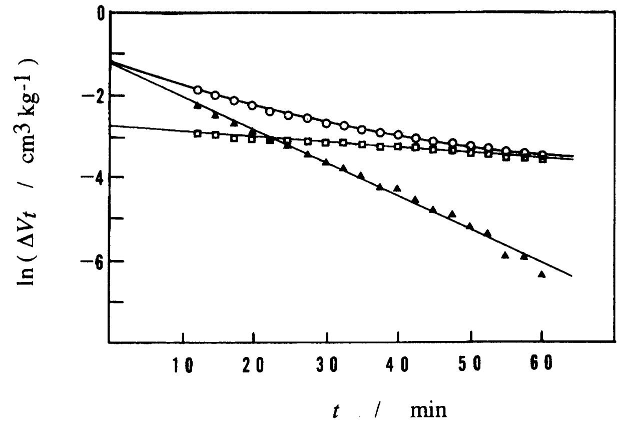

Fig. 3. Plots of $\ln(\Delta V_t)$ (○), $\ln(\Delta V_{\mathrm{A}})$ (△), and $\ln(\Delta V_{\mathrm{B}})$ (□) against t. The total concentration of complexes, {M}=0.04945 mol kg^{-1}; the concentration ratio in the initial solution, $\{\mathrm{ML(OH_2)^-}\}/\{\mathrm{M}\}$= 0.6117.

All of the ΔV were first corrected for the contribution attributable to the ionic interactions, ΔV_{corr}.[24,25] This contribution can be calculated by assuming the Debye–Hückel limiting behavior for the apparent molal volume of the ion.[24,25] The observed volume change per mole of product at infinite dilution ($\Delta V_{\mathrm{obsd}}^{\infty}$) is given by the equation $\Delta V_{\mathrm{obsd}}^{\infty}=(\Delta V-\Delta V_{\mathrm{corr}})/\{\mathrm{M}\}$. Because [Co(edtaH)($H_2O$)] and [Co(edta)($H_2O$)]$^-$ coexist in the initial solution,[3] the relation $\Delta V_{\mathrm{obsd}}^{\infty}=(1-\alpha)\Delta V_1^{\infty}+\alpha\Delta V_2^{\infty}$ holds, where α is the degree of dissociation of [Co(edtaH)(H_2O)] in the initial solution, and ΔV_1^{∞} and ΔV_2^{∞} are the volume changes for Reactions 1 and 2, respectively. The values of α were calculated from the pK_a value. The estimated values of α varied over a wide range (0.2—0.8), depending on the concentration of NaOH in the solution used as the solvent. Consequently, the plot of $\Delta V_{\mathrm{obsd}}^{\infty}$ against α gives a straight line with ΔV_1^{∞} as the intercept at α=0 and ΔV_2^{∞} as the intercept at α=1. Such a plot is shown in Fig. 4. A least-squares fit of the data gave $\Delta V_{\mathrm{obsd}}^{\infty}=(2.6\pm0.2)+(6.9\pm0.3)\alpha$ cm^3 mol^{-1}, so that $\Delta V_1^{\infty}=2.6\pm0.2$ cm^3 mol^{-1} and $\Delta V_2^{\infty}=9.5\pm0.4$ cm^3 mol^{-1} were obtained.

The volume change for the proton dissociation of [Cr(edtaH)(H_2O)] may be estimated from the volume change upon the neutralization. However, it was convenient to measure the volume change upon the pro-

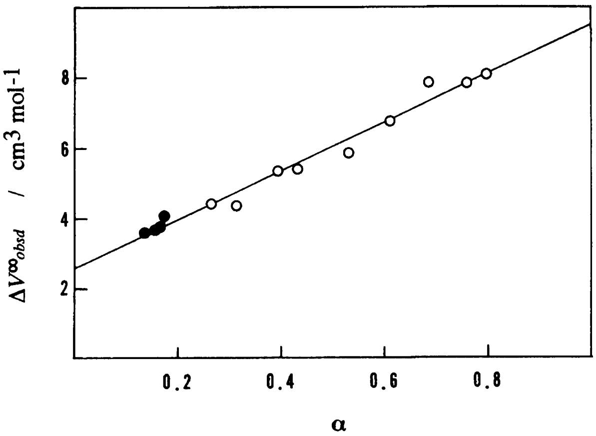

Fig. 4. The relation between $\Delta V^{\infty}_{\mathrm{obsd}}$ and α. The complex was dissolved in water (●) and in aqueous NaOH solutions (○).

tonation of $[Cr(edta)]^-$ because the solubility of $[Cr(edtaH)(H_2O)]$ was too low to accurately measure the volume change. This volume change was estimated in the following manner.

An aqueous solution of $Rb[Cr(edta)]\cdot 2H_2O$ was mixed with an aqueous $HClO_4$ solution. The observed volume change was calculated using

$$\Delta V_{\mathrm{expl}} = \frac{1000d}{w_1 + w_2}\left(\frac{w_1 + w_2}{d} - \frac{w_1}{d_1} - \frac{w_2}{d_2}\right),$$

where ΔV_{expl} is the volume change upon making up of 1 kg of the mixed solution from the respective solutions; w_1, w_2, d_1, and d_2 are the weights and densities of the chelate and the $HClO_4$ solutions before mixing, and d is the density of the mixed solution. The volume change for the protonation of the complex anion is given by

$$\Delta V^{\infty}_{\mathrm{pro}} = (\Delta V_{\mathrm{expl}} - \Delta V_{\mathrm{corr}})/\{\mathrm{M}\}(1 - \alpha) = -\Delta V^{\infty}_4,$$

where $\{M\}$ means the total concentration of the Cr(III)-edta complexes in the mixed solution, and is expressed in mol (kg of solution)$^{-1}$ units. The results are listed in Table 1. Furthermore, the same results for the typical quinquedentate edta complex, $[Co(edta)(NO_2)]^{2-}$, are also listed in Table 1. Since these reactions are reversible, the volume change for the reverse process is equal in magnitude, though opposite in sign.

Comparison between ΔV^{∞}'s. Positive volume changes were observed for the conversion from quinquedentate Co(III)-edta complexes to the sexidentate one. The fairly large positive value (9.5 ± 0.4 cm^3 mol^{-1}) for ΔV^{∞}_2 can be explained by the electrostriction effect. Firstly, the negative charge originally situated in the free carboxylate group in $[Co(edta)(H_2O)]^-$ can be regarded as being spread over the larger complex ion, $[Co(edta)]^-$. Secondly, one coordinated water is released from the first coordination site of the complex. The smaller value (2.6 ± 0.2 cm^3 mol^{-1}) of ΔV^{∞}_1 than that of ΔV^{∞}_2 is due to the negative volume change for the ionization of the free carboxyl group in $[Co(edtaH)(H_2O)]$. This volume change can be obtained as follows.

The above two reaction volumes, ΔV^{∞}_1 and ΔV^{∞}_2, can be expressed as the following expressions:

$$\Delta V^{\infty}_1 = V^{\infty}([Co(edta)]^-) + V^{\infty}(H_2O) + V^{\infty}(H^+) - V^{\infty}([Co(edtaH)(H_2O)])$$

and

$$\Delta V^{\infty}_2 = V^{\infty}([Co(edta)]^-) + V^{\infty}(H_2O) - V^{\infty}([Co(edta)(H_2O)]^-),$$

were V^{∞} means the partial molal volume at infinite dilution of the species described in the parenthesis.[26] Consequently, the volume change (ΔV^{∞}_3) for the ionization, $[Co(edtaH)(H_2O)] \rightarrow [Co(edta)(H_2O)]^- + H^+$, is estimated to be $\Delta V^{\infty}_3 = \Delta V^{\infty}_1 - \Delta V^{\infty}_2 = -6.9\pm0.4$ cm^3 mol^{-1}, which can not be obtained by the usual method due to the conversion reaction.

It is found that the volume changes for the ionization of unbound carboxyl groups in $[Co(edtaH)(H_2O)]$ and $[Co(edtaH)(NO_2)]^-$ are fairly large negative values. However, the absolute value for ΔV^{∞}_3 is significantly smaller compared with those of simple carboxylic acids. The volume change for the ionization of the simple carboxylic acid is generally about -14 cm^3 mol^{-1}, except for those of formic acid and acetic acid (-8.5 and -11.3 cm^3 mol^{-1}, respectively).[29,30] It thus appears that the volume change for the ionization of the carboxyl group depends quite strongly on the nature of its adjacent group.[31]

The volume change (-9.0 ± 0.1 cm^3 mol^{-1}) for the process, $[Co(edtaH)(NO_2)]^- \rightarrow [Co(edta)(NO_2)]^{2-} + H^+$, has a larger negative value than that of ΔV^{∞}_3 as a result of the cooperative action of the ionized carboxylate moiety in $[Co(edta)(NO_2)]^{2-}$ and the uninegative charge on the complex body. A similar phenomenon can be seen with the volume changes for the ionization of straight chained dicarboxyl acids. In the lower homologues, such as oxalic acid and malonic acid, the volume change of the second dissociation has a larger negative value than that of the first one.[32] In addition, the difference between the first and the second volume changes for higher homologues up to adipic acid decreases with an increase in the carbon chain length.[32]

Now, one can compare the volume change for the proton dissociation of $[Cr(edtaH)(H_2O)]$ with those of Co(III)-edta:

$$[Cr(edtaH)(H_2O)] \rightarrow [Cr(edta)]^- + H^+ + H_2O \qquad (4)$$

$$\Delta V^{\infty}_4 = 2.0 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$$

Although the formulation, $[Cr(edta)]^-$, is provisional, it is apparent that the value of ΔV^{∞}_4 is small positive and that the magnitude is almost the same as that of ΔV^{∞}_1 (2.6 ± 0.2 cm^3 mol^{-1}), which is the reaction volume for the formation of the sexidentate $[Co(edta)]^-$ from the quinquedentate $[Co(edtaH)(H_2O)]$. If the widely

Table 1. Volume Changes on the Protonation of $[Cr(edta)]^-$ and $[Co(edta)(NO_2)]^{2-}$

$\{M\}\times10^2$ / $mol\,kg^{-1}$ a)	$\{A\}\times10^2$ / $mol\,kg^{-1}$ b)	$(1-\alpha)$ c)	$\Delta V_{expl}\times10^2$ / $cm^3\,kg^{-1}$	$\Delta V_{corr}\times10^2$ / $cm^3\,kg^{-1}$	ΔV^{∞}_{pro} / $cm^3\,mol^{-1}$
		Rb[Cr(edta)]			
2.489	2.525	0.5167	−3.6	−0.8	−2.2
2.487	2.528	0.5173	−3.6	−0.8	−2.2
2.488	5.045	0.7226	−4.7	−1.5	−1.8
2.487	5.047	0.7228	−5.0	−1.5	−2.0
2.673	5.046	0.7151	−4.7	−1.5	−1.8
2.977	5.045	0.7022	−5.6	−1.7	−1.9
2.978	3.055	0.5459	−4.6	−1.0	−2.2
2.975	3.058	0.5464	−4.5	−1.0	−2.2
		$Na_2[Co(edta)(NO_2)]$			
0.5007	0.5127	0.6692	2.7	−0.3	9.0
0.5009	0.5126	0.6694	2.7	−0.3	9.0
1.000	1.024	0.7366	5.6	−0.9	8.8
0.9996	1.025	0.7371	5.8	−0.9	9.1
1.495	1.533	0.7693	8.5	−1.7	8.9
1.495	1.534	0.7695	8.7	−1.7	9.0
1.994	2.044	0.7891	11.6	−2.6	9.0
1.996	2.042	0.7884	11.7	−2.6	9.1

a) {M} means $\{M\}=\{MHL(X)^n\}+\{ML(X)^{n-1}\}$ ($X=H_2O$ or NO_2) in the mixed solution and is expressed in mol (kg of solution)$^{-1}$ units. b) {A} means $\{A\}=\{H^+\}+\{MHL(X)^n\}$ in the mixed solution and is expressed in mol (kg of solution)$^{-1}$ units. c) The fraction of the protonated species.

accepted formulation, $[Cr(edta)(H_2O)]^-$,[5—12] for the complex anion is correct, a larger negative volume change, as can be seen in ΔV^{∞}_3 (about $-7\ cm^3\,mol^{-1}$), would be expected. Further, it seems that the volume change is almost independent of the nature of the central metal ion, (Cr(III) or Co(III)). For example, the volume changes for the formation of M(II)-edta chelates, $M^{2+}+edta^{4-}\rightarrow M(edta)^{2-}$ (M(II) = Co(II), Ni(II), Cu(II), and Zn(II)) have been reported to be almost the same (about 44—46 $cm^3\,mol^{-1}$).[19] However, a rather smaller volume change (32.8 $cm^3\,mol^{-1}$) has been observed for the formation of the Mn(II)-edta chelate.[19] This phenomenon can be explained by assuming that the Mn(II)-edta adopts a seven-coordinate structure[19,33] similar to that proposed in the solid state.[34] Thus, it is clear that the proton dissociation of $[Cr(edtaH)(H_2O)]$ is not a simple ionization of the free carboxyl group. The process can be viewed as being a deprotonation of the unbound carboxyl arm to form an anionic quinquedentate complex, which rapidly transforms to the sexidentate complex, followed by losing one coordinated water.[14—16]

The results of this study are in complete agreement with those of ^2H NMR,[14] CD and MCD[15] and Raman[16] studies concerning the coordination structure of the Cr(III)-edta complex as well as closely related complexes. The results of spectroscopic studies indicated that edta forms a complex with C_2 symmetry over the pH 3.5—6.5 range, and suggested the possibility that edta forms a sexidentate complex with Cr(III).[14—16] However, as has been pointed out by Ogino and Shimura, these results may also be explained by two other possibilities for the coordination structure of the complex anion.[13] One possibility is to assume a substitution-labile quasi-quinquedentate coordinate structure in which a coordination site of a water molecule rapidly alternates with that of the G-ring carboxylate.[13] Another possibility is to assume a pentagonal-bipyramidal seven-coordinate structure with one coordinated water,[13] though there is neither a precedent in the Cr(III) complexes nor any direct evidence in the Cr(III)-edta complex.[14] In either case, at least one coordinated water might remain in the first coordination sphere of the complex anion. However, the results from this study suggest that the proton dissociation of $[Cr(edtaH)(H_2O)]$ is followed not only by coordination of the carboxylate group to the metal, but also by the release of one coordinated water at the same time. Since these two other possibilities may be ruled out, it is reasonable to suppose that the complex anion, $[Cr(edta)]^-$, is the six-coordinate sexidentate edta complex, which is a predominant species in the pH 3.5—6.5 range.

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26) The partial molal volume, V^{∞}, of $[Co(edta)]^-$ was estimated as follows. The apparent molal volumes, ϕ_v, of the electrolytes, H[Co(edta)] and Na[Co(edta)], were calculated from density data. The partial molal volumes of electrolytes were obtained with the aid of the Redlich–Meyer equation[27] using the ϕ_v's below 0.05 mol dm^{-3},

$$\phi_v = V^{\infty} + S_v\sqrt{C} + b_vC,$$

where S_v is the theoretical slope and b_v is a fitting parameter.[27] The partial molal volume V^{∞} of the anion $[Co(edta)]^-$, was estimated by subtracting the V^{∞} of the cation[28] from that of the electrolyte. When apparent molal volumes were calculated from d_{∞}'s of the final solutions of $[Co(edtaH)(H_2O)]$ in pure water, the V^{∞} of $[Co(edta)]^-$ was estimated to be 174.9±0.2 cm^3 mol^{-1}. This value is in good agreement with the value of 175.1±0.1 cm^3 mol^{-1} estimated from the apparent molal volumes of Na[Co(edta)].

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