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Multidentate Ligand Kinetics. II. The Ligand Substitution Reactions of the Triethylenetetraminecadmium(II) Ion and the Tetraethylenepentaminecadmium(II) Ion with the Ethylenediaminetetraacetatocuprate(II) Ion

Tetsuo KATSUYAMA and Toshihiko KUMAI

Department of Basic Technology, Faculty of Engineering, Yamagata University, Yonezawa, Yamagata 992

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The kinetics and mechanism of the ligand-substitution reactions of triethylenetetraminecadmium(II) ion (Cd(II)-trien) and tetraethylenepentaminecadmium(II) ion (Cd(II)-tetren) with ethylenediaminetetraacetatocuprate(II) ion (Cu(II)-edta) were studied spectrophotometrically at $I=0.2$ M (1 M$=$1 mol dm^{-3}) and at 25.0 °C. The ligand-substitution reactions were catalyzed by traces of either edta or the polyamine (triethylenetetramine and tetraethylenepentamine). The substitution reactions were shown to proceed by means of a chain reaction mechanism where the chain-propagating steps are the reactions of the metal complexes with the free ligands. Each chain-propagating step was investigated. The ligand-substitution reactions of Cd(II)-trien and Cd(II)-tetren with edta were studied by the use of the chain reactions in the pH range of 8.8—10.2. The rate law is expressed as: $-\mathrm{d}[\mathrm{CdR}^{2+}]/\mathrm{d}t=k_\mathrm{L}[\mathrm{CdR}^{2+}][\mathrm{edta}^{4-}]+k_\mathrm{HL}[\mathrm{CdR}^{2+}][\mathrm{Hedta}^{3-}]$, where R refers to trien or tetren. The rate constants, k_L and k_HL, were determined at 25.0 °C and $I=0.2$ M as: $k_\mathrm{L}=(1.3\pm0.2)\times10^6$ M^{-1} s^{-1} and $k_\mathrm{HL}=(6.5\pm1.5)\times10^4$ M^{-1} s^{-1} for Cd(II)-trien, and $k_\mathrm{L}=(3.6\pm0.4)\times10^5$ M^{-1} s^{-1} and $k_\mathrm{HL}=(1.0\pm0.2)\times10^4$ M^{-1} s^{-1} for Cd(II)-tetren.

Ligand-substitution reactions between two multidentate ligand complexes have been studied by Margerum *et al.*[1–4] A coordination chain reaction mechanism was proposed for the substitution reactions, where the chain-propagating steps are the reactions of the metal complexes with the free ligands.

These coordination chain reactions are useful for analytical purposes.[5–7] To widen their analytical application, though, it seemed worthwhile to find other coordination chain-reaction systems and to compare them with each other. In a previous paper,[8] the ligand-substitution reaction between the ethylenediaminetetraacetatocuprate(II) ion (Cu(II)-edta) and the triethylenetetraminezinc(II) ion (Zn(II)-trien) was studied; this reaction was found to proceed by means of a coordination chain reaction mechanism. In the present study, the ligand-substitution reaction of Cu(II)-edta with the triethylenetetraminecadmium(II) ion (Cd(II)-trien), and that with the tetraethylenepentaminecadmium(II) ion (Cd(II)-tetren) were investigated:

$$\mathrm{Cuedta}^{2-}+\mathrm{CdR}^{2+}\rightleftarrows\mathrm{CuR}^{2+}+\mathrm{Cdedta}^{2-},\qquad\text{(R1)}$$

where R represents triethylenetetramine (trien) or tetraethylenepentamine (tetren). The results were compared with those of the other systems, which were found to proceed by means of a coordination chain-reaction mechanism. The coordination chain reactions of the present systems provide a useful method for the study of the ligand substitutions of Cd(II)-trien and Cd(II)-tetren with edta.

Experimental

Reagents. Guaranteed reagent-grade cadmium(II) oxide was dissolved in perchloric acid. Twice-recrystallized sodium carbonate was added to the solution to obtain cadmium carbonate. A cadmium(II) perchlorate solution was then prepared by dissolving the cadmium carbonate in a perchloric acid solution. GR grade trien and tetren were purified by distillation under reduced pressure. The polyamine was dissolved in water, and its concentration was determined by the use of a standard copper nitrate solution.

Solutions of Cd(II)-trien and Cd(II)-tetren were prepared by the following procedure. The cadmium(II) perchlorate was added stoichiometrically to a solution containing the ligand, after while a slight excess of the cadmium(II) perchlorate was added to the solution. The excess cadmium(II) of the solutions of Cd(II)-trien and Cd(II)-tetren was precipitated as hydroxide at about pH 9.7 and 10.0 respectively. The precipitate was filtered off, and the solution's pH was then adjusted to about 7 for storage. The concentrations of the Cd(II)-polyamine solutions were determined by a method reported previously.[8]

The way of preparing the Cu(II)-edta solution was described previously.[8] GR-grade sodium perchlorate and sodium chloride were recrystallized from its aqueous solution. The other chemicals used were of a GR grade.

Apparatus and Kinetic Measurements. The Cu(II)-polyamines are stronger complexes than Cu(II)-edta, while the opposite is true for cadmium ion, so that the ligand exchange between Cu(II)-edta and Cd(II)-polyamine goes to completion, while the reverse reaction can be neglected in the kinetic study. The kinetics was studied in the presence of a large excess of Cu(II)-edta and small amounts of edta. In the kinetic measurements, a stopped-flow technique was employed with a Hitachi Model RSP2 Rapid Scanning Spectrophotometer. After the two reactant solutions had been mixed, the reaction was followed automatically, the transmittance of the reaction system at 550 nm (in the Cd(II)-trien system) or 575 nm (in the Cd(II)-tetren system) being recorded as a function of the time. The molar absorption coefficients of Cu(II)-trien, Cu(II)-tetren, and Cu(II)-edta are as follows: ε(Cu(II)-trien)$=138$ M^{-1} cm^{-1} (1 M$=$1 mol dm^{-3}), ε(Cu(II)-edta)$=5$ M^{-1} cm^{-1} at 550 nm, ε(Cu(II)-tetren)$=111$ M^{-1} cm^{-1}, ε(Cu(II)-edta)$=11$ M^{-1} cm^{-1} at 575 nm, which were measured with a Hitachi 139 spectrophotometer. Cd(II)-trien, Cd(II)-tetren, and Cd(II)-edta do not absorb light in the visible region.

A mannitol–boric acid–sodium borate or sodium borate–sodium hydroxide buffer system was used to control the pH of the solution. All the pH values were measured with a Toa Electronics Model HM-15A digital pH-meter. The ionic strength was adjusted to 0.2 M with sodium perchlorate or sodium chloride (at pH 9.0—10.2 in the Cd(II)-trien system). All the measurements were made in a thermostated room. The reaction temperature was controlled at 25.0 °C within ±0.1 °C using a thermoelectric circulating bath. Several calculations were performed with the aid of a TOSBAC 40 computer.

Results

Ligand-substitution Reaction between Cu(II)-edta and Cd(II)-trien. At pH's from 9.0 to 10.2 the rate equation can be expressed as

$$-\frac{\mathrm{d}[\mathrm{Cdtrien}^{2+}]}{\mathrm{d}t} = k'_{\mathrm{o},1}[\mathrm{Cdtrien}^{2+}], \qquad (1)$$

where $k'_{\mathrm{o},1}$ is the conditional rate constant involving the concentrations of edta and hydrogen ions. The rate plots of $\log(A_\infty - A)$ *vs.* t, where A and A_∞ denote, respectively, the absorbances at time t and infinity, were linear for over 80% of the reaction. Then the conditional rate constant, $k'_{\mathrm{o},1}$, was determined from the slope of the straight line. The values of the conditional rate constant, $k'_{\mathrm{o},1}$, were found to be linearly related to the added free edta concentration: $[\mathrm{edta}]_\mathrm{a}([\mathrm{edta}]_\mathrm{a} = \sum_{i=0}^{4}[\mathrm{H}_i\mathrm{edta}^{(4-i)-}])$ in the region above a threshold value of b, provided that all the other experimental conditions were kept constant (Fig. 1). Thus, the conditional rate constant, $k'_{\mathrm{o},1}$, is expressed by

$$k'_{\mathrm{o},1} = k_{\mathrm{o},1}([\mathrm{edta}]_\mathrm{a} - b). \qquad (2)$$

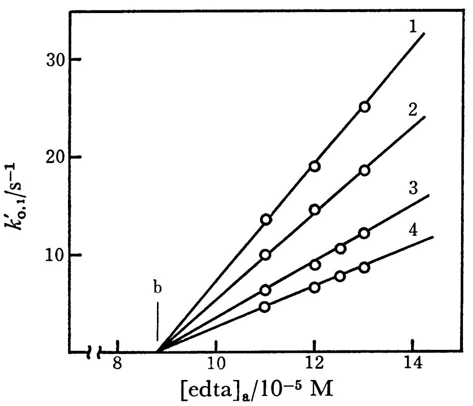


Fig. 1. $k'_{\mathrm{o},1}$ as a function of the concentration of added free edta.
Conditions: $[\mathrm{Cuedta}^{2-}] = 2.50 \times 10^{-2}$ M, $[\mathrm{Cdtrien}^{2+}] = 1.50 \times 10^{-3}$ M, $I = 0.2$ M, 25.0 °C.
1: pH=10.15, 2: pH=9.89, 3: pH=9.70, 4: pH=9.44.

The values of $k_{\mathrm{o},1}$ determined at various pH's are plotted against the pH in Fig. 4.

On the other hand, at lower pH's from 7.5 to 8.5 the reaction was of the zeroth-order with respect to Cd(II)-trien. Thus, the rate law is given by

$$-\frac{\mathrm{d}[\mathrm{Cdtrien}^{2+}]}{\mathrm{d}t} = k'_{\mathrm{o},0}, \qquad (3)$$

where $k'_{\mathrm{o},0}$ is the conditional zeroth-order rate constant involving the Cu(II)-edta, the added free edta, and the hydrogen-ion concentration. The plots of A *vs.* t were linear for over 80% of the reaction. Thus, the conditional zeroht-order rate constant, $k'_{\mathrm{o},0}$ was calculated from the slope of the straight line. The values of $k'_{\mathrm{o},0}$ at constant concentrations of the Cu(II)-edta and the hydrogen ion are linearly related to the added free edta concentration $[\mathrm{edta}]_\mathrm{a}$ in the region above the threshold value of b' (Fig. 2). Thus, the conditional rate constant, $k'_{\mathrm{o},0}$, is expressed by

$$k'_{\mathrm{o},0} = k_{\mathrm{o},0}([\mathrm{edta}]_\mathrm{a} - b'). \qquad (4)$$

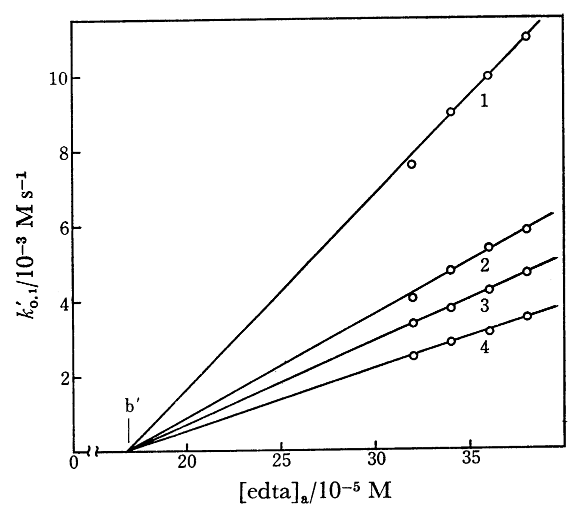


Fig. 2. $k'_{\mathrm{o}.0}$ as a function of the concentration of added free edta.
Conditions: $[\mathrm{Cuedta}^{2-}] = 2.50 \times 10^{-2}$ M, $[\mathrm{Cdtrien}^{2+}] = 1.50 \times 10^{-3}$ M, $I = 0.2$ M, 25.0 °C.
1: pH=8.10, 2: pH=7.81, 3: pH=7.70, 4: pH=7.50.

The values of the $k_{\mathrm{o},0}$ slope were obtained at various pH's.

Ligand-substitution Reaction between Cu(II)-edta and Cd(II)-tetren. At pH's from 8.2 to 9.7 the reaction was of the first-order with respect to Cd(II)-tetren. The rate plots of $\log(A_\infty - A)$ *vs.* t were linear for over 80% of the reaction. Then the conditional first-order rate constant, k'_o, was determined from the slope of the straight line. The conditional rate constant, k'_o, was independent of the concentration of Cu(II)-tetren. From these results, the following rate equation is derived:

$$-\frac{\mathrm{d}[\mathrm{Cdtetren}^{2+}]}{\mathrm{d}t} = k'_\mathrm{o}[\mathrm{Cdtetren}^{2+}]. \qquad (5)$$

In addition, the values of the conditional rate constant, k'_o, at a constant pH are linearly related to the added free edta concentration in the region above the threshold value of b''. Thus, the conditional rate constant, k'_o, is expressed by

$$k'_\mathrm{o} = k_\mathrm{o}([\mathrm{edta}]_\mathrm{a} - b''). \qquad (6)$$

The values of k_o determined at various pH's are plotted against pH in Fig. 5.

Discussion

Reaction Mechanism. The following chain-reaction mechanism was proposed for the ligand-substitution reactions of Cd(II)-trien and Cd(II)-tetren with Cu(II)-edta:

$$\mathrm{Cuedta^{2-} + R' \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} CuR^{2+} + edta'}, \qquad \mathrm{(R2)}$$

$$\mathrm{CdR^{2+} + edta' \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} Cdedta^{2-} + R'}, \qquad \mathrm{(R3)}$$

where edta' and R' represent the sums of the uncomplexed species of edta and polyamine (trien or tetren) respectively. On the basis of the proposed mechanism, the following rate law was derived:

$$-\frac{\mathrm{d[CdR^{2+}]}}{\mathrm{d}t} = \frac{(k_2k_3[\mathrm{Cuedta^{2-}}][\mathrm{CdR^{2+}}] - k_{-2}k_{-3}[\mathrm{Cdedta^{2-}}][\mathrm{CuR^{2+}}])[\mathrm{L'}]}{k_2[\mathrm{Cuedta^{2-}}] + k_{-2}[\mathrm{CuR^{2+}}] + k_3[\mathrm{CdR^{2+}}] + k_{-3}[\mathrm{Cdedta^{2-}}]}, \qquad (7)$$

where [L'] is the total concentration of free ligands, edta and polyamine ([edta']+[R']). The rate law is derived from a steady-state treatment with the assumptions that all of the exchange is carried out by means of Reactions R2 and R3, and that the concentrations of the free ligands, edta and polyamine, remain constant throughout the exchange.

In this discussion it is necessary to calculate the conditional equilibrium constants of Reactions R2 and R3, ($[\mathrm{CuR^{2+}}][\mathrm{edta'}]/[\mathrm{Cuedta^{2-}}][\mathrm{R'}]$ and $[\mathrm{Cdedta^{2-}}][\mathrm{R'}]/[\mathrm{CdR^{2+}}][\mathrm{edta'}]$). The conditional equilibrium constants can be calculated from the stability constants of the related complexes and the protonation constants of the related ligands.[9] The conditional equilibrium constants calculated are plotted against the pH in Fig. 3.

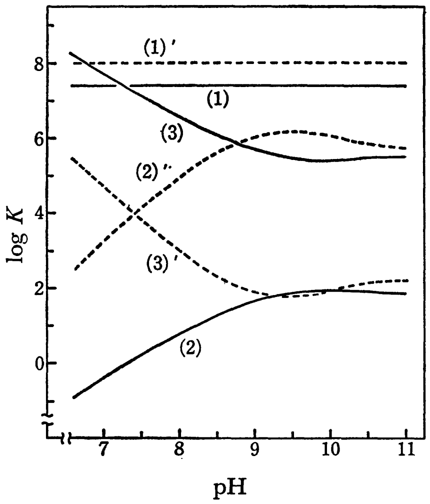


Fig. 3. Dependence of conditional equilibrium constants of reactions (R1), (R2), and (R3) on pH at 25.0 °C and I=0.2 M.
1,1': (R1), 2,2': (R2), 3,3': (R3).
The full lines show the constants of the Cd(II)-trien system and the dotted lines show that of the Cd(II)-tetren system.

Cd(II)-trien System. In the Cd(II)-trien system, Equilibrium R3 much favors the right, so it appears reasonable to assume $k_3 \gg k_{-3}$. Therefore, Eq. 7 can be simplified to

$$-\frac{\mathrm{d[Cdtrien^{2+}]}}{\mathrm{d}t} = \frac{k_2k_3[\mathrm{Cuedta^{2-}}][\mathrm{Cdtrien^{2+}}][\mathrm{L'}]}{k_2[\mathrm{Cuedta^{2-}}] + k_{-2}[\mathrm{Cutrien^{2+}}] + k_3[\mathrm{Cdtrien^{2+}}]}. \qquad (8)$$

The following approximation seems reasonable from Figs. 3 and 4, as will be shown later. In the denominator of Eq. 8, the $k_2[\mathrm{Cuedta^{2-}}]$ term becomes predominant and the other terms may be neglected for the reaction with a large excess of Cu(II)-edta at pH 9.0—10.2. Thus, Eq. 8 becomes

$$-\frac{\mathrm{d[Cdtrien^{2+}]}}{\mathrm{d}t} = k_3[\mathrm{Cdtrien^{2+}}][\mathrm{L'}]. \qquad (9)$$

If free metal ions (*e.g.*, metal impurity) are present in the system, the metal ions will react very rapidly with the added free edta. Consequently, the concentration of free ligands ([L']) in the solution is written as

$$[\mathrm{L'}] = [\mathrm{edta}]_\mathrm{a} - [\mathrm{M}], \qquad (10)$$

where [M] is the concentration of free metal ions (*e.g.*, the metal impurity). Thus, Eq. 9 becomes

$$-\frac{\mathrm{d[Cdtrien^{2+}]}}{\mathrm{d}t} = k_3([\mathrm{edta}]_\mathrm{a} - [\mathrm{M}])[\mathrm{Cdtrien^{2+}}]. \qquad (11)$$

As has been stated above, Eq. 1 can be rewritten as

$$-\frac{\mathrm{d[Cdtrien^{2+}]}}{\mathrm{d}t} = k'_{\mathrm{o},1}[\mathrm{Cdtrien^{2+}}] = k_{\mathrm{o},1}([\mathrm{edta}]_\mathrm{a} - b)[\mathrm{Cdtrien^{2+}}]. \qquad (12)$$

Therefore, k_3 and [M] in Eq. 11 should correspond to $k_{\mathrm{o},1}$ and b respectively. In Fig. 4, the value of k_3 determined at various pH's is plotted against the pH.

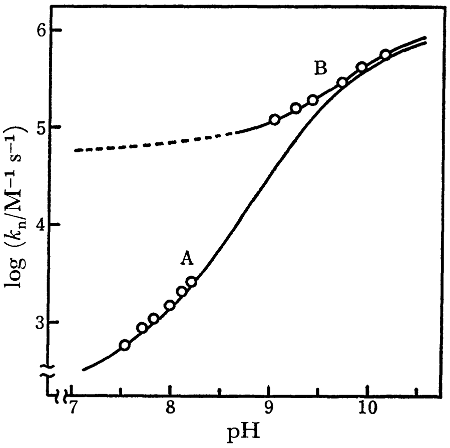


Fig. 4. Dependence of the conditional rate constants k_2 and k_3 ($=k_{\mathrm{o},1}$) of the Cd(II)-trien system on pH at 25.0 °C and I=0.2 M.
A: k_2, B: k_3 ($=k_{\mathrm{o},1}$). The lines A and B are the curves calculated with the aid of the individual rate constants. ----: Extrapolated by Eq. 21.

On the other hand, in the denominator of Eq. 8, the $k_3[\mathrm{Cdtrien^{2+}}]$ term becomes predominant and the other terms may be neglected for pH 7.5—8.5; this can be shown to be valid from Figs. 3 and 4. Thus, Eq. 8 becomes

$$-\frac{\mathrm{d[Cdtrien^{2+}]}}{\mathrm{d}t} = k_2[\mathrm{Cuedta^{2-}}][\mathrm{L'}]. \qquad (13)$$

For a large excess of Cu(II)-edta, $k_2[\text{Cuedta}^{2-}]$ is constant during the reaction, so that Eq. 13 becomes

$$-\frac{d[\text{Cdtrien}^{2+}]}{dt} = (\text{const})([\text{edta}]_a - [\text{M}]). \tag{14}$$

Equation 3 can be rewritten as

$$-\frac{d[\text{Cdtrien}^{2+}]}{dt} = k_{o,0}([\text{edta}]_a - b'). \tag{15}$$

Therefore, Eq. 14 agrees with the rate equation derived experimentally at lower pH's. Thus, k_2 can be calculated from the value of $k_{o,0}$. The value of k_2 thus obtained is plotted against the pH in Fig. 4. The conditional rate constant, k_2, thus obtained agrees with the conditional rate constant of the reaction of Cu(II)-edta with trien which was determined previously.[8)]

Cd(II)-tetren System. In the Cd(II)-tetren system, the R2 equilibrium much favors the right, so that the $k_2 \gg k_{-2}$ inequality can be considered to hold. Therefore, Eq. 7 can be simplified to

$$-\frac{d[\text{Cdtetren}^{2+}]}{dt} = \frac{k_2 k_3[\text{Cuedta}^{2-}][\text{Cdtetren}^{2+}][\text{L}']}{k_2[\text{Cuedta}^{2-}] + k_3[\text{Cdtetren}^{2+}] + k_{-3}[\text{Cdedta}^{2-}]}. \tag{16}$$

The conditional rate constant, k_2, was calculated from the rate constants of the reaction of Cu(II)-edta with tetren which had been determined by Margerum *et al.*[10)] The value of k_2 thus calculated is plotted against the pH in Fig. 5. The following approximation seems reasonable from Figs. 3 and 5. In the denominator of Eq. 16, the $k_2[\text{Cuedta}^{2-}]$ term becomes predominant and the other terms may be neglected under the present experimental conditions. Consequently, Eq. 16 becomes

$$\begin{aligned}-\frac{d[\text{Cdtetren}^{2+}]}{dt} &= k_3[\text{Cdtetren}^{2+}][\text{L}'] \\ &= k_3([\text{edta}]_a - [\text{M}])[\text{Cdtetren}^{2+}]. \end{aligned} \tag{17}$$

Equation 5 can be rewritten as

$$-\frac{d[\text{Cdtetren}^{2+}]}{dt} = k_o([\text{edta}]_a - b'')[\text{Cdtetren}^{2+}]. \tag{18}$$

Therefore, Eq. 17 agrees with the rate equation derived experimentally. Then k_3 is equal to k_o. The value of k_3 thus determined is plotted against the pH in Fig. 5.

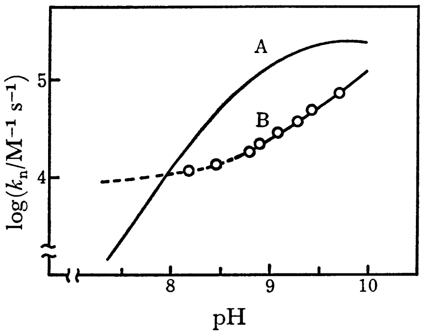


Fig. 5. Dependence of the conditional rate constants k_2 and k_3 ($=k_o$) of the Cd(II)-tetren system on pH at 25.0 °C and $I=0.2$ M.
A: k_2, B: k_3 ($=k_o$). The lines A and B are the curves calculated with the aid of the individual rate constants.
----: Extrapolated by Eq. 21.

Resolution of the Conditional Rate Constant, k_3. The following relation can be derived from a steady-state consideration of Reactions R2 and R3 on the assumption that the concentrations of the free ligands remain constant:

$$\begin{aligned}\frac{[\text{edta}']}{[\text{R}']} &= \frac{k_2[\text{Cuedta}^{2-}] + k_{-3}[\text{Cdedta}^{2-}]}{k_{-2}[\text{CuR}^{2+}] + k_3[\text{CdR}^{2+}]} \\ &\approx \frac{k_2[\text{Cuedta}^{2-}]}{k_{-2}[\text{CuR}^{2+}] + k_3[\text{CdR}^{2+}]}. \end{aligned} \tag{19}$$

The inequality $k_2[\text{Cuedta}^{2-}] \gg k_{-2}[\text{CuR}^{2+}] + k_3[\text{CdR}^{2+}]$ holds under the present experimental conditions in the Cd(II)-trien and Cd(II)-tetren systems. Consequently, $[\text{edta}'] \gg [\text{R}']$. Thus, $[\text{L}'] = [\text{edta}'] + [\text{R}'] \approx [\text{edta}']$. In the pH 8.8—10.2 range, the dominant species of edta are Hedta^{3-} and edta^{4-}. Thus, the following relationship can be derived:

$$\begin{aligned} k_3[\text{L}'][\text{CdR}^{2+}] &= k_3[\text{edta}'][\text{CuR}^{2+}] \\ &= k_\text{L}[\text{edta}^{4-}][\text{CdR}^{2+}] \\ &\quad + k_\text{HL}[\text{Hedta}^{3-}][\text{CdR}^{2+}], \end{aligned} \tag{20}$$

where k_L and k_HL are the rate constants for the following reactions

$$\text{CdR}^{2+} + \begin{array}{l} \text{edta}^{4-} \xrightarrow{k_\text{L}} \text{Cdedta}^{2-} + \text{R} \\ \quad\Updownarrow \\ \text{Hedta}^{3-} \xrightarrow{k_\text{HL}} \text{Cdedta}^{2-} + \text{HR}^+ \end{array} \tag{R4}$$

With the protonation constant of Hedta^{3-}, Eq. 20 is rewritten as

$$k_3(K_1[\text{H}^+] + 1) = k_\text{HL}K_1[\text{H}^+] + k_\text{L}, \tag{21}$$

where K_1 is the protonation constant. The plots of the left-hand side of Eq. 21 *vs.* $K_1[\text{H}^+]$ give a straight line in the Cd(II)-trien and Cd(II)-tetren systems, as is shown in Figs. 6 and 7. The slopes and intercepts correspond to the k_HL and k_L rate constants respectively. The rate constants obtained in the two systems are summarized in Table 1.

The concentrations of the hydrogen and hydroxide complexes[9)] of CdR^{2+} are negligibly small at high pH values (9—10); for example, the concentration of CdHtrien^{3+} is 0.06% of $[\text{Cd(II)-trien}]_\text{total}$ at pH 9.6. It seems reasonable to neglect the contribution of the hydrogen and hydroxide complexes of CdR^{2+} to the total reaction in the present pH region. Using the

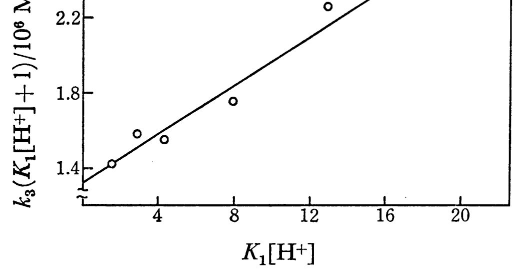


Fig. 6. Relation between $k_3(K_1[\text{H}^+]+1)$ and $K_1[\text{H}^+]$ in the Cd(II)-trien system.

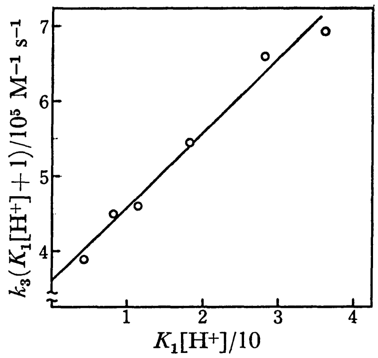


Fig. 7. Relation between $k_3(K_1[\mathrm{H^+}]+1)$ and $K_1[\mathrm{H^+}]$ in the Cd(II)-tetren system.

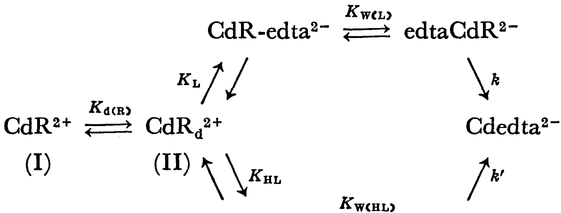
TABLE 1. RATE CONSTANTS FOR THE LIGAND-SUBSTITUTION REACTION OF THE Cd(II)-POLYAMINE COMPLEX WITH edta AT 25.0 °C AND $I=0.2$ M

	$\frac{k_\mathrm{L}}{\mathrm{M^{-1}\,s^{-1}}}$	$\frac{k_\mathrm{HL}}{\mathrm{M^{-1}\,s^{-1}}}$
Cd(II)-trien[a]	$(1.3\pm0.2)\times10^6$	$(6.5\pm1.5)\times10^4$
Cd(II)-tetren[b]	$(3.6\pm0.4)\times10^5$	$(1.0\pm0.2)\times10^4$

a) $I=0.2$ M(NaCl), b) $I=0.2$ M(NaClO$_4$).

resolved rate constants, the conditional rate constant, k_3, can be calculated from Eq. 21 at pH 8.8—10.2. The values calculated for the Cd(II)-trien and Cd(II)-tetren systems are shown in Figs. 4 and 5 respectively. In Figs. 4 and 5, the dotted lines show the estimates calculated from Eq. 21.

Mechanism of the Substitution Reactions of Cd(II)-polyamine Complexes with edta. The following reaction mechanism was proposed for the ligand-substitution reactions of Cd(II)-trien and Cd(II)-tetren with edta



(R5)

where $K_{\mathrm{d(R)}}$ refers to the dissociation constant of the complex CdR^{2+} to the partially dissociated complex CdR$_\mathrm{d}{}^{2+}$, K_L and K_HL are the formation constants of the outer-sphere complexes, CdR-edta^{2-} and CdR-Hedta$^-$ respectively, and $K_{\mathrm{W(L)}}$, the equilibrium constant between CdR-edta^{2-} and the mixed ligand intermediate edtaCdR^{2-} (inner-sphere complex). According to the proposed mechanism, the rate equation of the substitution of the Cd(II)-polyamine complexes with edta can be written as

$$\begin{aligned}\frac{\mathrm{d[Cdedta^{2-}]}}{\mathrm{d}t} &= k[\mathrm{edtaCdR^{2-}}] + k'[\mathrm{HedtaCdR^-}] \\ &= K_\mathrm{d}K_\mathrm{L}K_{\mathrm{W(L)}}k[\mathrm{CdR^{2+}}][\mathrm{edta^{4-}}] \\ &\quad + K_\mathrm{d}K_\mathrm{HL}K_{\mathrm{W(HL)}}k'[\mathrm{CdR^{2+}}][\mathrm{Hedta^{3-}}] \\ &= k_\mathrm{L}[\mathrm{CdR^{2+}}][\mathrm{edta^{4-}}] \\ &\quad + k_\mathrm{HL}[\mathrm{CdR^{2+}}][\mathrm{Hedta^{3-}}]. \qquad (22)\end{aligned}$$

The estimation of the k/k' ratio is interesting. From Eq. 22 the following relationship is derived

$$\frac{k_\mathrm{L}}{k_\mathrm{HL}} = \frac{K_\mathrm{L}K_{\mathrm{W(L)}}k}{K_\mathrm{HL}K_{\mathrm{W(HL)}}k'} \qquad (23)$$

The release of a water molecule from the outer-sphere complex is the rate-determining step in the formation of a metal complex.[11] Therefore, the rate of the formation of edtaCdR^{2-} from CdR-edta^{2-} is expected to be equal to that of HedtaCdR$^-$ from CdR-Hedta$^-$. Further, the rate of the dissociation of edta^{4-} from edtaCdR^{2-} to the outer-sphere complex does not seem to differ from that of Hedta^{3-} from HedtaCdR$^-$. Thus, it appears reasonable to assume that $K_{\mathrm{W(L)}}\approx K_{\mathrm{W(HL)}}$. K_L and K_HL can be calculated according to the Fuoss equation.[12,13] Then, with the calculated values of K_L and K_HL, and the rate constants of k_L and k_HL, the k/k' ratio can be estimated. The ratios obtained at $I=0.2$ M and 25 °C are 3.1 and 5.6 for the Cd(II)-trien and Cd(II)-tetren systems respectively. In other words, the formation rate of Cdedta^{2-} from edtaCdR^{2-} is larger than that from HedtaCdR$^-$. The dipolar-ion (zwitter-ion) form of edta is known to be unreactive in the formation of many metal complexes because the NH$^+$ group of edta prevents chelation.[14] Therefore, in the formation of Cdedta^{2-} from HedtaCdR$^-$, the NH$^+$ group of the edta seems to prevent the chelation. Consequently, k' can be expected to be less than k. Thus, the coordination of the second nitrogen atom to the central metal in the mixed ligand intermediates, HedtaCdR$^-$ and edtaCdR^{2-}, is probably rate-determining.

The reaction mechanisms of the two systems (Cd(II)-trien and Cd(II)-tetren) seem to be similar except that the dissociation of the (I) complex to the partially dissociated complex (II) is different. Further, the $K_{\mathrm{d(Cdtrien)}} > K_{\mathrm{d(Cdtetren)}}$ inequality can be expected to hold, because the formation constant of Cd(II)-tetren is greater than that of Cd(II)-trien. Therefore, the rate of the reaction of Cd(II)-trien with edta can be expected to be faster than that of the Cd(II)-tetren system. This agrees with the experimental results.

Comparison of Chain-reaction Systems. The coordination chain-reaction systems use Cu(II)-edta as one reactant, while the other reactant consists of metal(II)-polyamine complexes. It is interesting to compare the reaction rates of the coordination chain-reaction systems. The reaction rates under the same conditions can be compared by means of the conditional rate constant, k_3, when the reaction is of the first-order with respect to the metal(II)-polyamine complex. The conditional

TABLE 2. CONDITIONAL RATE CONSTANTS FOR THE LIGAND-SUBSTITUTION REACTIONS OF THE METAL(II)-POLYAMINE COMPLEXES WITH edta AT A CERTAIN pH AT 25.0 °C AND AT $I=0.2$ M

	$\frac{k_3}{\mathrm{M^{-1}\,s^{-1}}}$	pH		$\frac{k_3}{\mathrm{M^{-1}\,s^{-1}}}$	pH
Cd(II)-trien	2.14×10^5	9.5	Cd(II)-tetren	2.52×10^4	9.0
Zn(II)-trien[8]	9.33×10^5		Zn(II)-tetren[15]	5.13×10^2	
Ni(II)-trien[5]	1.6×10^{3}[a]		Ni(II)-tetren[3]	1.2[a]	

a) $I=0.1$ M

TABLE 3. THE LOWER LIMIT OF THE pH REGION WHERE THE FIRST-ORDER REACTION PROCEEDS IN THE PRESENCE OF A 15-FOLD EXCESS OF Cu(II)-edta

	pH		pH
Cd(II)-trien	9.44	Cd(II)-tetren	7.80
Zn(II)-trien	9.90	Zn(II)-tetren	7.30
Ni(II)-trien	7.8	Ni(II)-tetren	5.9

rate constants, k_3, of various systems at a certain pH are summarized in Table 2. Table 2 shows that the reaction rates of the cadmium and zinc systems are greater than that of the nickel system, and that the reaction rate of the trien system is greater than that of the tetren system. In fast reactions, kinetic measurements can be easily repeated using the stopped-flow technique. Therefore, in analytical applications, using the fast-coordination chain reaction, rapid analysis may be achieved by handling the results statistically with an on-line computer.

The pH region where the first-order reaction takes place can be estimated approximately from the conditional rate constants and the experimental conditions. In Table 3, the lower limits of the pH region in the presence of a 15-fold excess of Cu(II)-edta are tabulated. It may be seen from Tables 2 and 3 that the greater the value of k_3, the greater is the lower limit of the pH region. In general, the first-order reaction takes place without an excess of Cu(II)-edta when $k_2 \gg k_3$. However, a large excess of Cu(II)-edta is required for the first-order reaction when the $k_2 \gg k_3$ inequality is not satisfied.

References

1) D. C. Olson and D. W. Margerum, *J. Am. Chem. Soc.*, **84**, 680 (1962).

2) D. C. Olson and D. W. Margerum, *J. Am. Chem. Soc.*, **85**, 297 (1963).

3) D. W. Margerum and J. D. Carr, *J. Am. Chem. Soc.*, **88**, 1639 (1966).

4) J. D. Carr and D. W. Margerum, *J. Am. Chem. Soc.*, **88**, 1645 (1966).

5) D. W. Margerum and R. K. Steinhaus, *Anal. Chem.*, **37**, 222 (1965).

6) R. H. Stehl, D. W. Margerum, and J. J. Latterll, *Anal. Chem.*, **39**, 1346 (1967).

7) D. W. Margerum and R. H. Stehl, *Anal. Chem.*, **39**, 1351 (1967).

8) T. Katsuyama and T. Kumai, *Bull. Chem. Soc. Jpn.*, **48**, 3581 (1975).

9) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-ion Complexes," The Chemical Society, London (1964).

10) J. D. Carr, R. A. Libby, and D. W. Margerum, *Inorg. Chem.*, **6**, 1083 (1967).

11) M. Eigen and K. Tamm, *Z. Electrochem.*, **66**, 107 (1962).

12) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

13) G. G. Hammes and M. L. Morell, *J. Am. Chem. Soc.*, **86**, 1497 (1964).

14) J. C. Cassatt and R. G. Wilkins, *J. Am. Chem. Soc.*, **90**, 6045 (1968).

15) T. Katsuyama and T. Kumai, Abstr. No. 3M13, 32th National Meeting of the Chemical Society of Japan, Tokyo, April 1975.