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Multidentate Ligand Kinetics. III. The Ligand-substitution Reaction between the Ethylenediaminetetraacetatocuprate(II) Ion and the Tetraethylenepentaminezinc(II) Ion

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The kinetics and mechanism of the ligand-substitution reaction between the ethylenediaminetraacetatocuprate(II) ion (Cu(II)-edta) and the tetraethylenepentaminezinc(II) ion (Zn(II)-tetren) were studied spectrophotometrically over the pH range from 7.0 to 9.0 at $I=0.2$ M (1 M= mol dm^{-3}) and 25.0 °C. The substitution reaction was shown to proceed by means of a chain-reaction mechanism where the chainpropagating steps are the reaction of Cu(II)-edta with tetren and the reaction of Zn(II)-tetren with edta. Each chain-propagating step was investigated. The ligand-substitution reaction of Zn(II)-tetren with edta was studied by the use of the chain reaction. The rate law is expressed as

$$-\frac{\mathrm{d}[\mathrm{Zn(II)\text{-}tetren}]}{\mathrm{d}t}=k_{\mathrm{L}}[\mathrm{Zn(tetren)^{2+}}][\mathrm{edta^{4-}}]+k_{\mathrm{HL}}[\mathrm{Zn(tetren)^{2+}}][\mathrm{Hedta^{3-}}]+k'_{\mathrm{HL}}[\mathrm{Zn(Htetren)^{3+}}][\mathrm{Hedta^{3-}}].$$

The rate constants, k_{L},k_{HL}, and k'_{HL} were determined at 25.0 °C and $I=0.2$ M as: $k_{\mathrm{L}}\approx 3\times 10^2$ M^{-1} s^{-1}, $k_{\mathrm{HL}}=(4.1\pm 0.7)\times 10^2$ M^{-1} s^{-1}, and $k'_{\mathrm{HL}}=(1.7\pm 0.2)\times 10^5$ M^{-1} s^{-1}.

Ligand-substitution reactions between two multidentate ligand complexes often proceed by means of a coordination chain-reaction mechanism, in which two free multidentate ligands are the chain-reaction centers and the chain-propagating steps are the reactions of the metal complexes with the free ligands.[1–7]

In a previous paper,[8] the ligand-substitution reactions of the triethylenetetraminecadmium(II) ion and the tetraethylenepentaminecadmium(II) ion with the ethylenediaminetetraacetatocuprate(II) ion (Cu(II)-edta) were reported. The reactions were found to proceed by means of a coordination chain-reaction mechanism. In the present study, the ligand-substitution reaction between the Cu(II)-edta and tetraethylenepentaminezinc(II) ions (Zn(II)-tetren) was undertaken in order to obtain further understanding of the ligand-substitution reaction between two multidentate ligand complexes:

$$\mathrm{Cu(II)\text{-}edta} + \mathrm{Zn(II)\text{-}tetren} \longrightarrow \mathrm{Cu(II)\text{-}tetren} + \mathrm{Zn(II)\text{-}edta}. \qquad \text{(R1)}$$

The coordination chain reaction of the present system provides a useful method for the study of the ligand substitution of Zn(II)-tetren with edta.

Experimental

Reagents. Reagent-grade zinc(II) and copper perchlorates, and guaranteed reagent-grade sodium perchlorate were recrystallized from their aqueous solutions. GR-grade tetren was purified by distillation under reduced pressure. A standard copper nitrate solution was prepared from copper plate and was subsequently used to standardize the tetren and edta solutions.

Solutions of Cu(II)-edta and Zn(II)-tetren were prepared by the following procedure: a slight excess of the metal perchlorate was added to a solution containing a known quantity of the ligand; the excess metal in the solutions of Cu(II)-edta and Zn(II)-tetren was then precipitated as hydroxide at about pH 9.3 and 9.5 respectively.

Measurements. The reactions were run in the presence of a large excess of Cu(II)-edta and small amounts of edta. The initial Zn(II)-tetren concentration was 1.8×10^{-3} M and the ionic strength was adjusted to 0.2 M with sodium perchlorate. The reaction temperature was controlled at 25.0±0.1 °C. A mannitol–boric acid–sodium borate buffer system was used to control the pH of the solution. The pH values were measured with a Toa Electronics Model HM-15A digital pH-meter. The reaction was followed spectrophotometrically at 575 nm by means of a stopped-flow technique using a Hitachi Model RSP-2 rapidscan spectrophotometer.

Results and Discussion

Rate Equation. The plots of log $(A_\infty-A_t)$ *vs.* t, where A_t and A_∞ denote the absorbances at time t and infinity respectively, were linear over 85% of the reaction. Thus, the reaction was considered to be first-order in Zn(II)-tetren. The conditional first-order rate constant was independent of the concentration of Cu(II)-edta. From these results, it seems that the rate law is given by

$$-\frac{\mathrm{d}[\mathrm{Zn(II)\text{-}tetren}]}{\mathrm{d}t}=k'_{\mathrm{o}}[\mathrm{Zn(II)\text{-}tetren}]. \qquad (1)$$

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 given by

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

The values of k_{o} are plotted against the pH in Fig. 2.

Steady-state Treatment. On the basis of the above results, the ligand-substitution reaction between Cu(II)-edta and Zn(II)-tetren was considered to proceed by means of a chain-reaction mechanism:

$$\mathrm{Cu(II)\text{-}edta} + \mathrm{tetren} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{Cu(II)\text{-}tetren} + \mathrm{edta}, \qquad \text{(R2)}$$

$$\mathrm{Zn(II)\text{-}tetren} + \mathrm{edta} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{Zn(II)\text{-}edta} + \mathrm{tetren}. \qquad \text{(R3)}$$

The conditional equilibrium constants[8] of Reactions R2 and R3 will be useful in the following discussion. The constants were thus calculated from the stability

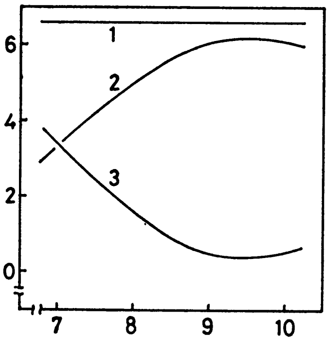


Fig. 1. Dependence of conditional equilibrium constants of reactions R1, R2, and R3 on pH at 25.0 °C and I=0.2 M.
1: R1, 2: R2, 3: R3.

constants of the related complexes and the protonation constants of the related ligands.[9] The calculated values are plotted against the pH in Fig. 1.

According to the proposed mechanism, the following rate law (general equation) is derived from a steady-state treatment reported previously:[8]

$$-\frac{d[\text{Zn(II)-tetren}]}{dt} = \frac{\begin{array}{c}(k_2k_3[\text{Cu(II)-edta}][\text{Zn(II)-tetren}] \\ -k_{-2}k_{-3}[\text{Zn(II)-edta}][\text{Cu(II)-tetren}])[\text{L}]\end{array}}{\begin{array}{c}k_2[\text{Cu(II)-edta}]+k_{-2}[\text{Cu(II)-tetren}] \\ +k_3[\text{Zn(II)-tetren}]+k_{-3}[\text{Zn(II)-edta}]\end{array}}, \qquad (3)$$

where [L] is the total concentration of free ligands, edta and tetren. Since the R2 equilibrium is highly favored to proceed to the right, the $k_2 \gg k_{-2}$ inequality holds. Therefore, Eq. 3 may be simplified to

$$-\frac{d[\text{Zn(II)-tetren}]}{dt} = \frac{k_2k_3[\text{Cu(II)-edta}][\text{Zn(II)-tetren}][\text{L}]}{\begin{array}{c}k_2[\text{Cu(II)-edta}]+k_3[\text{Zn(II)-tetren}] \\ +k_{-3}[\text{Zn(II)-edta}]\end{array}}. \qquad (4)$$

The conditional rate constant, k_2, was calculated from the rate constants of the reaction of Cu(II)-edta with tetren.[10] The values of k_2 are plotted against the pH in Fig. 2.

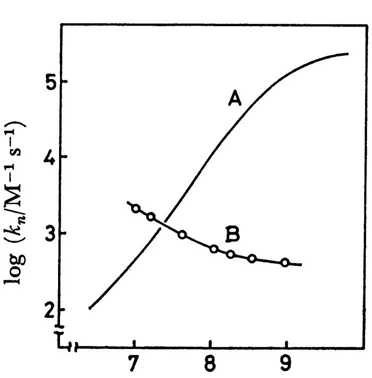


Fig. 2. Dependence of the conditional rate constants of reactions R2 and R3 on pH at 25.0 °C and I=0.2 M (NaClO$_4$).
A: k_2, B: k_3(=k_0). The line A is the curve calculated with the aid of the individual rate constants.[14]

The following approximation seems reasonable from Figs. 1 and 2. In the denominator of Eq. 4, the k_2[Cu(II)-edta] term is predominant, while the other terms may be neglected under the present conditions. Thus, Eq. 4 may be simplified to

$$\frac{d[\text{Zn(II)-tetren}]}{dt} = k_3[\text{Zn(II)-tetren}][\text{L}]. \qquad (5)$$

Since Eq. 5 agrees with the rate equation derived experimentally, k_3 corresponds to the k_0 of Eq. 2. The value of k_3 thus determined is plotted against the pH in Fig. 2.

Ligand-substitution Reaction of Zn(II)-tetren with edta. Acid Complex of Zn(II)-tetren: When the successive formation constants of the ammine copper(II) complex, K_n, are compared with those of the ammine zinc(II) complex, K'_n, the constants, K_n and K'_n, differ at n=1,2,3; however, they are equal at n=4 ($K^{\text{NH}_3}_{\text{Cu(NH}_3)_4}$=10$^{2.1}$, $K^{\text{NH}_3}_{\text{Zn(NH}_3)_4}$=10$^{2.1}$), and the constants over n=4 are extremely small in both complexes.

The successive formation constant, K_1, of the dien (diethylenetriamine : tridentate ligand) copper(II) complex and that of the dien zinc(II) complex differ from one another (K_{Cudien}=10$^{16.0}$, K_{7ndien}=10$^{8.9}$); however, the successive formation constant, K_2, of the copper(II) complex is approximately equal to that of the zinc(II) complex ($K^{\text{dien}}_{\text{Cu(dien)}_2}$=10$^{5.3}$, $K^{\text{dien}}_{\text{Zn(dien)}_2}$=10$^{5.5}$).

Therefore, in hexadentate polyamine complexes of copper(II) and zinc(II), it may be said that the fifth and sixth nitrogen atoms (which dissociate secondarily and firstly respectively in the dissociation reaction) are weakly bonded to the central metal, and that the intensities of the fifth and sixth Cu–N bonds in the copper(II) complex are approxinately equal to those of the fifth and sixth Zn–N bonds respectively in the zinc(II) complex. Consequently, the protonation constant of the hexadentate polyamine copper(II) complex is expected to be close to that of the zinc(II) complex; in practice, the protonation constant of the penten (tetrakis(2-aminoethyl)ethylenediamine : hexadentate ligand) copper(II) complex is equal to that of the penten zinc(II) complex ($K^{\text{H}}_{\text{CuHpenten}}$=10$^{8.16}$, $K^{\text{H}}_{\text{ZnHpenten}}$=10$^{8.16}$).

If the above considerations can be applied to the pentadentate polyamine complex, it can be assumed that the protonation constant of Cu(II)-tetren ([Cu(H$_2$O)tetren]$^{2+}$) is approximatly equal to that of Zn(II)-tetren ([Zn(H$_2$O)tetren]$^{2+}$). Thus, the protonation constant of Zn(II)-tetren may be estimated as follows: $K^{\text{H}}_{\text{ZnHtetren}}$=$K^{\text{H}}_{\text{CuHtetren}}$=10$^{5.18}$. The protonation constant of Zn(II)-tetren has been reported[11] as $K^{\text{H}}_{\text{ZnHtetren}}K^{\text{H}}_{\text{ZnH}_2\text{tetren}}$=10$^{9.4}$($K^{\text{H}}_{\text{ZnH}_2\text{tetren}}$=[Zn(H$_2$tetren)$^{4+}$]/[Zn(Htetren)$^{3+}$][H$^+$]). Then, $K^{\text{H}}_{\text{ZnH}_2\text{tetren}}$ can be calculated to be 10$^{4.2}$

Resolution of the Conditional Rate Constant, k_3: B in Fig. 2 shows the pH dependence of the conditional rate constant for the ligand-substitution reaction of Zn(II)-tetren with edta. The pH dependence of the conditional rate constant was analyzed in the pH range of 7.5—9.0. In this pH range, the dominant species of edta are Hedta^{3-} and edta^{4-}, while the dominant species of acid complex of Zn(II)-tetren is [Zn(Htetren)]$^{3+}$.[12]

Thus, the rate equation for the ligand substitution of Zn(II)-tetren with edta is given by

$$-\frac{d[\text{Zn(II)-tetren}]}{dt} = k_3[\text{Zn(II)-tetren}][\text{edta}]$$

$$= k_L[\text{Zn(tetren)}^{2+}][\text{edta}^{4-}] + k_{HL}[\text{Zn(tetren)}^{2+}][\text{Hedta}^{3-}] + k'_{HL}[\text{Zn(Htetren)}^{3+}][\text{Hedta}^{3-}], \quad (6)$$

where k_L, k_{HL}, and k'_{HL} are defined as follows:[13)]

$$\begin{tikzcd}
 & \text{edta}^{4-} \arrow[dr, "k_L"] & \\
\text{Zn(tetren)}^{2+} + & \text{Hedta}^{3-} \arrow[r, "k_{HL}"'] & \text{Zn(edta)}^{2-}. \\
\text{Zn(Htetren)}^{3+} + & \text{Hedta}^{3-} \arrow[ur, "k'_{HL}"'] &
\end{tikzcd} \quad (7)$$

Hence, the following relationship is derived from Eq. 6:

$$k_3(1+K_1[\text{H}^+])(1+K^{\text{H}}_{\text{ZnHtetren}}[\text{H}^+]) = k_L + [\text{H}^+]K_1k_{HL} + [\text{H}^+]^2K_1K^{\text{H}}_{\text{ZnHtetren}}k'_{HL}, \quad (8)$$

where K_1 is the formation constant of Hedta^{3-}. The rate constant, k_3, was resolved into individual rate constants, k_L, k_{HL}, and k'_{HL}, to fit Eq. 8. The calculation of the resolved rate constants was performed with the aid of an electronic computer. The resolved rate constants are shown in Table 1.

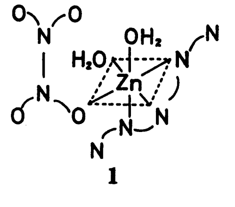
TABLE 1. RATE CONSTANTS FOR THE LIGAND-SUBSTITUTION REACTION OF Zn(II)-tetren WITH edta AT 25.0 °C AND I=0.2 M (NaClO$_4$)

$\frac{k_L}{\text{M}^{-1}\text{s}^{-1}}$	$\frac{k_{HL}}{\text{M}^{-1}\text{s}^{-1}}$	$\frac{k'_{HL}}{\text{M}^{-1}\text{s}^{-1}}$
$\approx 3\times10^2$	$(4.1\pm0.7)\times10^2$	$(1.7\pm0.2)\times10^5$

Mechanism of the Substitution Reaction of Zn(tetren)$^{2+}$ with edta: The reaction scheme can be described as

$$\begin{tikzcd}
 & \text{ZnL-(edta)}^{2-} \arrow[r, shift left, "K_w"] \arrow[d, shift left] & \text{ZnL(edta)}^{2-} \arrow[l, shift left] \arrow[d, "k"] \\
\text{ZnL}^{2+} \arrow[r, shift left, "K_d"] & \text{ZnL}_d^{2+} \arrow[l, shift left] \arrow[u, shift left, "K_{os}"'] \arrow[d, shift left, "K'_{os}"] & \text{Zn(edta)}^{2-}, \\
 & \text{ZnL-(Hedta)}^{-1} \arrow[u, shift left] \arrow[r, shift left, "K'_w"] & \text{ZnL(Hedta)}^{-1} \arrow[l, shift left] \arrow[u, "k'"']
\end{tikzcd} \quad (9)$$

where K_d is the dissociation constant of ZnL^{2+} to the partially dissociated complex ZnL$_d{}^{2+}$, K_{os} is the formation constant of the outer-sphere conplex ZnL-(edta)$^{2-}$, K_w is the equilibrium constant between [ZnL-(edta)]$^{2-}$ and the mixed-ligand intermediate ZnL(edta)$^{2-}$, and L refers to the ligand tetren. Since the structure for the mixed-ligand intermidiate is considered to be the same as that of the nickel system,[14)] the structure for the mixed-ligand intermediate (for edta^{4-}) seems to be as follows:



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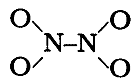
where edta^{4-} and tetren are symbolized as  and N–N–N–N–N respectively and where the charges are omitted; the rate-determining step for the formation of [Zn(edta)]$^{4-}$ is considered to be the loss of a water molecule from the intermediate **1**, as in the nickel system.

According to the proposed mechanism, the following equation is obtained:

$$k[\text{ZnL(edta)}^{2-}] + k'[\text{ZnL(Hedta)}^{-1}]$$

$$= K_dK_{os}K_wk[\text{edta}^{4-}][\text{ZnL}^{2+}] + K_dK'_{os}K'_wk'[\text{Hedta}^{3-}][\text{ZnL}^{2+}]$$

$$= k_L[\text{edta}^{4-}][\text{ZnL}^{2+}] + k_{HL}[\text{Hedta}^{3-}][\text{ZnL}^{2+}]. \quad (10)$$

from Eq. 10, the k_L/k_{HL} ratio is given by

$$\frac{k_L}{k_{HL}} = \frac{K_{os}K_wk}{K'_{os}K'_wk'} \quad (11)$$

Since k_L is approximately equal to k_{HL} (Table 1), Eq. 11 becomes

$$\frac{K_{os}K_wk}{K'_{os}K'_wk'} \approx 1. \quad (12)$$

The release of a water molecule from the outer-sphere complex is the rate-determining step in the formation of the inner-sphere complex,[15)] and the loss of a water molecule from the mixed-ligand intermediate seems to be the rate-determining step in the formation of [Zn(edta)]$^{2-}$. Therefore, it appears reasonable to assume that $K_w \approx K'_w$ and that $k \approx k'$. Thus, K_{os} is nearly equal to K'_{os}.

In the formation of a metal complex, a charged group removed from the eventual coordination site is relatively unimportant.[16)] The negative charge removed from the coordination site in edta thus seems unimportant in the formation of the above mixed-ligand intermediate. Consequently, K_{os} can be expected to be equal to K'_{so}.

Mechanism of the Substitution Reaction of Zn(II)-tetren with Hedta^{3-}: The following reaction mechanism was proposed:

$$\begin{tikzcd}
\text{ZnL}_d^{2+} \arrow[r, shift left, "K_{os}"] \arrow[d, shift left, "K_d"] & \text{ZnL-(Hedta)}^{-1} \arrow[l, shift left] \arrow[r, shift left, "K_w"] & \text{ZnL(Hedta)}^{-1} \arrow[l, shift left] \arrow[dd, "k"] \\
\text{ZnL}^{2+} \arrow[u, shift left] \arrow[d, shift left] & & \\
\text{ZnHL}^{3+} \arrow[u, shift left] \arrow[d, shift left, "K'_d"] & & \text{Zn(edta)}^{2-}. \\
 & & \\
\text{ZnHL}_d^{3+} \arrow[u, shift left] \arrow[r, shift left, "K'_{os}"] & \text{ZnHL-(Hedta)} \arrow[l, shift left] \arrow[r, shift left, "K'_w"] & \text{ZnHL(Hedta)} \arrow[l, shift left] \arrow[uu, "k'"']
\end{tikzcd} \quad (13)$$

On the basis of the reaction mechanism, the following equation is derived:

$$k[\text{ZnL(Hedta)}^{-1}] + k'[\text{ZnHL(Hedta)}]$$

$$= K_dK_{os}K_wk[\text{Hedta}^{3-}][\text{ZnL}^{2+}] + K'_dK'_{os}K'_wk'[\text{Hedta}^{3-}][\text{ZnHL}^{3+}]$$

$$= k_{HL}[\text{Hedta}^{3-}][\text{ZnL}^{2+}] + k'_{HL}[\text{Hedta}^{3-}][\text{ZnHL}^{3+}]. \quad (14)$$

From Eq. 14, the k_{HL}/k'_{HL} ratio is given by

$$\frac{k_{\mathrm{HL}}}{k'_{\mathrm{HL}}}=\frac{K_{\mathrm{d}}K_{\mathrm{os}}K_{\mathrm{w}}k}{K'_{\mathrm{d}}K'_{\mathrm{os}}K'_{\mathrm{w}}k'}. \tag{15}$$

Since it appears reasonable to assume that $K_{\mathrm{os}}\approx K'_{\mathrm{os}}$, $K_{\mathrm{w}}\approx K'_{\mathrm{w}}$, and that $k\approx k'$, Eq. 15 can be simplified to

$$\frac{k_{\mathrm{HL}}}{k'_{\mathrm{HL}}}\approx\frac{k_{\mathrm{d}}}{k'_{\mathrm{d}}}. \tag{16}$$

The difference between k_{HL} and k'_{HL} is mostly determined by the difference between K_{d} and K'_{d}. Since the $k'_{\mathrm{HI}}/k_{\mathrm{HL}}$ ratio is about 400 : 1, the partial dissociation rate of the Zn(Htetren)$^{3+}$ complex is 400 times faster than that of the Zn(tetren)$^{2+}$ complex; the proton bonded to the tetren facilitates the partial dissociation.

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12) For example, at pH 8.0, the concentrations of [Zn(Htetren)]$^{3+}$ and [Zn(H$_2$tetren)]$^{4+}$ are 0.2 and 0.00003% respectively of the total concentration of Zn(II)-tetren.

13) In the pH range of 7.5—9.0, edta^{4-} is negligible at a low pH and [Zn(Htetren)]$^{3+}$ is negligible at a high pH; therefore, the reaction of [Zn(Htetren)]$^{3+}$ with edta^{4-} can be omitted in the reaction scheme.

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