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Multidentate Ligand Substitution Reactions. XI. Substitution Reactions of Nickel(II) Complexes of Diethylenetriamine and Ethylenediaminemonoacetic Acid with Diethylenetriaminepentaacetic Acid and of Nickel(II) Complexes of Diethylenetriamine and Ethylenediamine with Cyclohexane-1,2-diamine-*N*,*N*,*N*′,*N*′-tetraacetic Acid

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The kinetics of substitution reactions of nickel(II) complexes of diethylenetriamine and ethylenediaminemonoacetic acid with diethylenetriaminepentaacetic acid and those of diethylenetriamine and ethylenediamine with cyclohexane-1,2-diamine-*N*,*N*,*N*′,*N*′-tetraacetic acid were studied systematically by using the polarographic technique. All the reactions studied were found to be first-order with respect to the attacking group and also first-order with respect to the nickel(II) complex of diethylenetriamine, ethylenediamine, or ethylenediaminemonoacetic acid with a 1-to-1 composition. From a comparison of the relative rate constants determined experimentally with those calculated on the basis of a postulated reaction intermediate, the reaction mechanism was described in detail. All the reactions were concluded to proceed through the mixed ligand complex reaction intermediates which are characterized as having two nitrogen (amino) groups of displaced ethylenediamine, diethylenetriamine, or ethylenediaminemonoacetate ions bonded to the nickel(II) ion. This finding is contrary to the observation obtained by Rorabacher and Margerum from their kinetic study of the exchange reaction of the ethylenediaminetetraacetate anion with nickel(II) complexes of triethylenetetramine and tetraethylenepentamine.

In previous papers,[1-3] we have studied the kinetics of nucleophilic substitution reactions involving nickel(II) and cobalt(II) complexes of ethylenediaminetetraacetic acid (EDTA) and its related substances. From a comparison of the rate constants, the reaction intermediate for these substitution reactions was characterized as having one

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[1] M. Kodama, This Bulletin, **40**, 2575 (1967).

[2] M. Kodama, C. Sasaki and T. Noda, *ibid.*, **41**, 2033 (1968).

[3] M. Kodama, C. Sasaki and K. Miyamoto, *ibid.*, **42**, 163 (1969).

nitrogen (amino) group and one acetate group of displaced aminopolycarboxylate anions bonded to the metal(II) ion (Glycinate mechanism). The nucleophilic substitution reactions involving nickel(II)-aspartate and iminodiacetate complexes were also found to proceed through a reaction intermediate with a glycinate group bonded to the nickel(II) ion.[4] Rorabacher and Margerum studied the substitution reactions involving nickel(II) complexes of polyamines.[5] In their kinetic studies of the displacement of triethylenetetramine and tetraethylenepentamine by the EDTA anion, they proposed a reaction intermediate in which the released polyamine forms two five-membered rings with the nickel(II) ion through three nitrogen groups. The ethylenediaminemonoacetate (EDMA) ion, in whose complexation reaction with metal ions two nitrogen groups and one acetate group can function as donor groups, was also found to be displaced from its nickel(II) complex by diethylenetriaminepentaacetic acid (DTPA) at a measurable rate. In general, the nickel(II)-nitrogen bond rupture is much slower than the nickel(II)-oxygen bond rupture.

Therefore, the nucleophilic substitution reactions involving the nickel(II)-EDMA complex can hardly be expected to proceed through a glycinate reaction mechanism. On the other hand, if the nucleophilic substitution reaction of the nickel(II)-ethylenediamine (En) complex also proceeds through a mixed ligand complex intermediate, because of steric requirements the reaction intermediate can be expected to have a structure in which a bidentate ethylenediamine occupies two of the six octahedral coordination sites of the nickel(II) ion. Thus, the substitution reaction involving an En complex would have a different reaction intermediate from those of the other polyamine complexes. In the experiments reported in this paper, we studied the kinetics of the substitution reactions of the nickel(II) complexes of diethylenetriamine (Dien) and EDMA with DTPA and of those of Dien and En with cyclohexane-1,2-diamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (CyDTA) and determined the reaction mechanism and rate constants for these reactions. From comparisons of the rate constants determined experimentally and from calculations based on the relative stability of the mixed ligand complex intermediate and the electrostatic interaction between the entering group and the reactant (nickel(II) complex), the structure of the reaction intermediates in the substitution reactions involving nickel(II)-EDMA, Dien, and En complexes were determined.

Experimental

Reagents. A nickel(II) nitrate solution was prepared by dissolving a known amount of metallic nickel (99.99% pure) in dilute nitric acid (1+1) and by then removing the excess nitric acid by distillation under reduced pressure. The preparation and recrystallization of EDMA dihydrochloride have been described previously.[6] The En and Dien were purified by distillation under reduced pressure. The DTPA and CyDTA were recrystallized twice from their aqueous solutions by adding a suitable amount of pure ethanol. The other reagents were of analytical reagent grades and were used without further purification.

Apparatus and Experimental Procedures. All the d.c. polarograms and current-time curves were

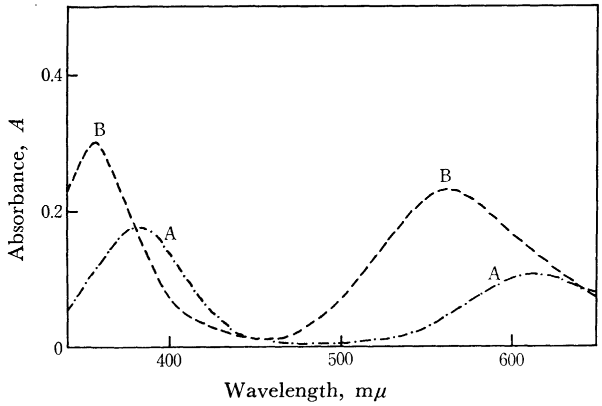

Fig. 1. Absorption curves of nickel(II) ions in the EDMA solution.
$\mu=0.30$, 25°C
Concentration of nickel(II) ion = 30.0 mM
A: Concentration of EDMA = 30.0 mM, pH = 6.0
B: Concentration of EDMA = 80.0 mM, pH = 9.0

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[4] M. Kodama and T. Ueda, This Bulletin, **43**, 419 (1970).

[5] D. B. Borabacher and D. W. Margerum. *Inorg. Chem.*, **3**, 382 (1964).

[6] Fujii, F. Kyuno and R. Tsuchiya, This Bulletin, **43**, 786 (1970).

recorded automatically by means of a Yanagimoto pen-recording polarograph, PA-102, or a Hitachi recorder, QPD-54. The characteristics of the dropping mercury electrode (DME) used in this study have been described previously.7) For all the spectrophotometric measurements, a Hitachi EPS-3 recording spectrophotometer with a pair of 1-cm quartz cells was used. The rate of the substitution reaction was determined by measuring the change in the diffusion current of anodic waves due to the decrease in the uncomplexed DTPA or CyDTA concentration with time. In this study, all the measurements were conducted in solutions with an ionic strength of 0.30. In order to adjust the ionic strength, sodium perchlorate (the EDMA system) or potassium nitrate (the En and Dien systems) was used. In the kinetic study, measurements were made in solutions containing a large excess of complexed and uncomplexed EDMA, En, or Dien over DTPA or CyDTA in the pH range from 8.30 to 10.0 at 25°C. Therefore, all the substitution reactions could be treated as pseudo first-order reactions and no buffer reagent was required to maintain the solution's pH constant over the entire pH range covered. All the experimental procedures employed were the same as had previously been described.7)

Results and Discussion

Spectrophotometric Determination of Formation Constants of the Nickel (II)-Ethylenediaminemonoacetate Complex. As EDMA has two amino groups and one acetate group, it can act as a tridentate ligand in the complexation with metal ions. Therefore, in order to complete the octahedral coordination sphere of a nickel(II) ion, two molecules of EDMA are required. Thus, the nickel(II) ion is expected to form complexes of 1-to-1 and 1-to-2 compositions with EDMA. In Fig. 1, typical absorption curves of the nickel(II) ion in the EDMA solution are reproduced. In this study, we tried to determined the stability constants of the nickel(II)-EDMA complexes spectrophotometrically. If the total concentration of nickel(II) ions is kept constant throughout the experiment, the concentrations of complexed and uncomplexed nickel(II) ions in a solution containing an equimolar EDMA can be represented by the following equations:

$$[\mathrm{NiX}^+] = \frac{A - A_{\mathrm{Ni}}}{\varepsilon_{\mathrm{NiX}} - \varepsilon_{\mathrm{Ni}}} \tag{1}$$

$$[\mathrm{Ni}^{2+}] = \frac{A_{\mathrm{NiX}} - A}{\varepsilon_{\mathrm{NiX}} - \varepsilon_{\mathrm{Ni}}} \tag{2}$$

where ε's denote molar extinction coefficients, where $[\mathrm{Ni}^{2+}]$ and $[\mathrm{NiX}^+]$ are the concentrations of uncomplexed and complexed nickel(II) ions respectively, and where A, A_{NiX} and A_{Ni} are, respectively, the absorbance of the solutions in which complexed and uncomplexed nickel(II) ions coexist, in which all the nickel(II) ions exist in the form of NiX^+, and in which there is no EDMA. Since the concentration of uncomplexed EDMA is identical with that of the uncomplexed nickel(II) ion, the conditional formation constant of the nickel(II)-EDMA complex with a 1-to-1 composition, K'_{NiX}, is given by:

$$K'_{\mathrm{NiX}} = \frac{K_{\mathrm{NiX}}}{(\alpha_{\mathrm{H}})_{\mathrm{X}}} = \frac{(A - A_{\mathrm{Ni}})(\varepsilon_{\mathrm{NiX}} - \varepsilon_{\mathrm{Ni}})}{(A_{\mathrm{NiX}} - A)^2} \tag{3}$$

where $(\alpha_{\mathrm{H}})_{\mathrm{X}}$ is the (α_{H}) value of EDMA, and K_{NiX}, the formation constant of NiX^+.

Equation (3) clearly indicates that, by plotting $\log[(A-A_{\mathrm{Ni}})(\varepsilon_{\mathrm{NiX}}-\varepsilon_{\mathrm{Ni}})/(A_{\mathrm{NiX}}-A)^2]$ *vs.* $\log(\alpha_{\mathrm{H}})_{\mathrm{X}}$, one can obtain a linear relation with a slope of -1.0 and that the $\log(\alpha_{\mathrm{H}})_{\mathrm{X}}$ value at $\log[(A-A_{\mathrm{Ni}})(\varepsilon_{\mathrm{NiX}}-\varepsilon_{\mathrm{Ni}})/(A_{\mathrm{NiX}}-A)^2]=$zero corresponds to the $\log K_{\mathrm{NiX}}$ value. To prepare an equimolar solution of nickel(II) ions and EDMA, we used a known amount of pure crystals of ethylenediaminemonoacetatotriaquonickel(II) chloride synthesized in our laboratory.*1 With the aid of Eq. (3), the experimental data were analyzed. The results are illustarated in Fig. 2. From the intercept of the linear relation in Fig. 2, the $\log K_{\mathrm{NiX}}$ value was estimated to be 10.44. With an increase in the uncomplexed EDMA concentration and an increased pH value, the absorbance of the nickel (II) solution increases and the absorption curve's maxima shift to shorter wavelengths. This can be ascribed to the formation of a complex with a 1-to-2 ratio. If both the complex with a 1-to-2 ratio and that with a 1-to-1 ratio are formed, and if the uncomplexed nickel(II)-ion concentration can be disregarded as compared with the complexed nickel(II)-ion concentration, the following

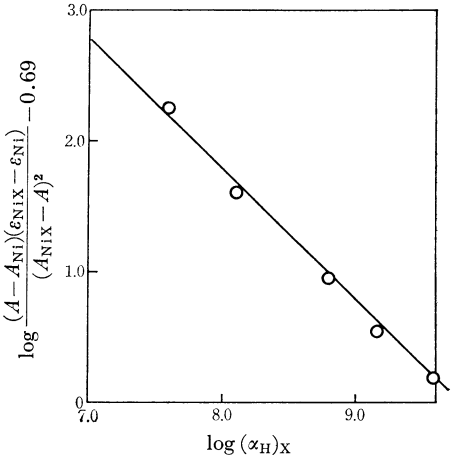

Fig. 2. The plot of $\log(A-A_{\mathrm{Ni}})/(A_{\mathrm{NiX}}-A)^2$ against $\log(\alpha_{\mathrm{H}})_{\mathrm{X}}$.
$\mu=0.30$, 25°C, 360 mμ
Concentration of nickel(II) ion = 30.0 mM
Concentration of EDMA = 30.0 mM

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7) M. Kodama, *ibid.*, **42**, 2532 (1969).

[*1] The preparation of ethylenediaminemonoacetatotriaquonickel(II) chloride will be described elsewhere.

relation can be derived thermodynamically for a solution containing an excess of EDMA over the nickel(II) ion:

$$\log \frac{K_2}{(\alpha_H)_X} = \log \frac{(A-A_{NiX})(\varepsilon_{NiX_2}-\varepsilon_{NiX})}{\left(\begin{array}{l}(A_{NiX_2}-A)\{([X]_t-2[Ni]_t)(\varepsilon_{NiX_2}-\varepsilon_{NiX})\\ \quad +(A_{NiX_2}-A)\}\end{array}\right)} \tag{4}$$

where K_2 is defined as $[NiX_2^0]/[NiX^+]\cdot[X^-]$, where $[X]_t$ and $[Ni]_t$ denote the total concentrations of EDMA and nickel(II) ions respectively, where A_{NiX_2} means the absorbance of a solution where all the nickel(II) ions exist exclusively in the form of NiX_2^0, and where ε_{NiX_2} is the molar extinction coefficient of NiX_2. Equation (4) varified experimentally. As is illustrated in Fig. 3, the plot of the right-hand side of Eq. (4) against $\log(\alpha_H)_X$ gave a linear relation with a slope of -1.0. From this linear relation, the $\log K_2$ value was determined to be 6.34. The presence of chloride ions has no effect on the absorbance or the location of the maximum. This clearly indicates that the nickel(II) ion does not enter into the mixed ligand complex involving the chloride ion under the present experimental conditions. The numerical values determined are given in Table 1.

TABLE 1. NUMERICAL VALUES FOR THE NICKEL(II)-EDMA COMPLEX

i) Formation constants ($\mu=0.30$, 25°C)

$$K_{NiX} = \frac{[NiX^+]}{[Ni^{2+}][X^-]} = 2.75\times10^{10}$$

$$K_2 = \frac{[NiX_2^0]}{[NiX^+][X^-]} = 2.18\times10^6$$

ii) Molar extinction coefficients

	360 mμ	350 mμ
ε_{Ni}	1.07	—
ε_{NiX}	5.98	3.31
ε_{NiX2}	—	9.80

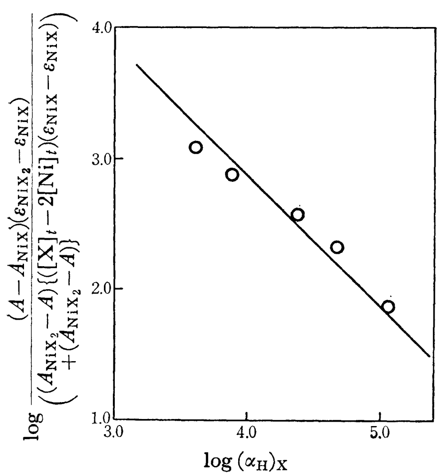

Fig. 3. The plot of $\log[(A-A_{NiX})(\varepsilon_{NiX_2}-\varepsilon_{NiX})/(A_{NiX2}-A)\{([X]_t-2[Ni]_t)(\varepsilon_{NiX_2}-\varepsilon_{NiX})+(A_{NiX_2}-A)\}]$ against $\log(\alpha_H)_X$.
$\mu=0.30$, 25°C, 350 mμ
Concentration of nickel(II) ion = 34.8 mM
Concentration of EDMA = 80.0 mM

Kinetics Study of Substitution Reaction of Nickel(II) Complexes of Dien and EDMA with DTPA and Those of Dien and En with CyDTA. As was found in the substitution reaction of the nickel(II)-NTA complex with DTPA,[7] the linear relations passing through the point of origin could be obtained by plotting the $\log(i_0/i_t)$ against time, t, in all the substitution reactions studied in the present paper (these results are not shown). Here, i_0 and i_t denote the wave heights of DTPA or Cy-DTA wave at time $t=0$ and $t=t$ respectively. When the other experimental conditions were kept constant, the slope of the above linear relation was not influenced by the addition of the nickel(II)-DTPA or CyDTA complex, and it was independent of the initial concentration of DTPA or CyDTA. These facts clearly indicate that the forward reaction is much faster than the backward reaction, and that the dissociation of the nickel(II) complex of Dien, EDMA, or En is not involved in any of the present substitution reactions. Therefore, the log-plot slope multiplied by 2.303 is equal to the apparent rate constant, k_{ap}^+, of the forward reaction. Furthermore, in solutions of a given pH and a given initial concentration of DTPA or CyDTA, the log-plot slope was exactly proportional to the concentration of the nickel(II)-EDMA, En, or Dien complex with a 1-to-1 ratio. The results are given in Table 2. Dien and EDMA act as tridentate

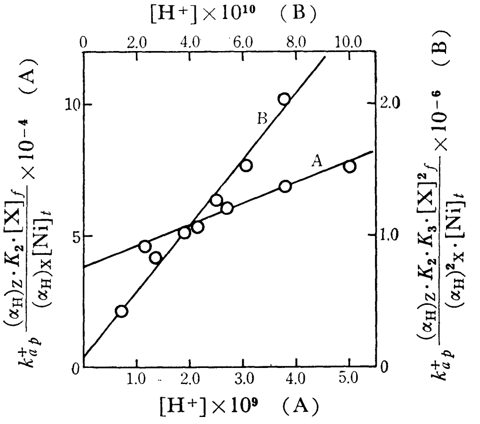

Fig. 4. The plot of $k_{ap}^+(\alpha_H)_Z K_2\cdot[X]_f/(\alpha_H)_X[Ni]_t$ or $k_{ap}^+(\alpha_H)_Z\cdot K_2\cdot K_3[X]^2{}_f/(\alpha_H)^2{}_X[Ni]_t$ against the hydrogen concentration.
$\mu=0.30$, 25°C
Initial concentration of CyDTA = 0.40 mM
Concentration of nickel(II) ion = 10.0 mM
A: Ni(II)-Dien system
Total concentration of Dien = 30.0 mM
B: Ni(II)-En system
Total concentration of En = 40.0 mM

Table 2. The Relation between the log-plot slope and the concentration of nickel(II) complex

A) Nickel(II)-Dien - CyDTA system

Total concentration of nickel(II), $[\mathrm{Ni}]_t$ mM	Concentration of Dien, $[\mathrm{X}]_f$ mM	Slope S sec^{-1}	$\frac{S\times[\mathrm{X}]_f}{[\mathrm{Ni}]_t}$	
10.0	10.0	1.74×10^{-5}	1.74×10^{-5}	pH=8.57 μ=0.30 Initial concentration of CyDTA=0.40 mM
15.0	10.0	2.60×10^{-5}	1.72×10^{-5}	
20.0	10.0	3.50×10^{-5}	1.75×10^{-5}	
10.0	20.0	8.85×10^{-6}	1.77×10^{-5}	
10.0	30.0	5.98×10^{-6}	1.80×10^{-5}	

B) Nickel(II)-En - CyDTA system

Total concentration of nickel(II), $[\mathrm{Ni}]_t$ mM	Concentration of En, $[\mathrm{X}]_f$ mM	Slope S sec^{-1}	$\frac{S\times[\mathrm{X}]^2{}_f}{[\mathrm{Ni}]_t}$	
10.0	10.0	2.00×10^{-3}	2.00×10^{-5}	25°C pH=9.46 μ=0.30 Initial concentration of CyDTA=0.40 mM
16.0	10.0	3.19×10^{-3}	2.00×10^{-5}	
20.0	10.0	4.10×10^{-3}	2.05×10^{-5}	
10.0	10.0	3.32×10^{-3}	3.32×10^{-5}	pH=9.30 μ=0.30 Initial concentration of CyDTA=0.50 mM 25°C
10.0	20.0	8.00×10^{-4}	3.20×10^{-5}	
10.0	35.0	2.59×10^{-4}	3.18×10^{-5}	
10.0	50.0	1.32×10^{-4}	3.30×10^{-5}	
10.0	70.0	6.72×10^{-5}	3.29×10^{-5}	

C) Nickel(II)-Dien - DTPA system

Total concentration of nickel(II), $[\mathrm{Ni}]_t$ mM	Concentration of Dien, $[\mathrm{X}]_f$ mM	Slope S sec^{-1}	$\frac{S\times[\mathrm{X}]_f}{[\mathrm{Ni}]_t}$	
10.0	10.0	4.00×10^{-3}	4.00×10^{-3}	25°C pH=9.80 μ=0.30 Initial concentration of DTPA=0.40 mM
15.0	10.0	6.20×10^{-3}	4.13×10^{-3}	
20.0	10.0	8.00×10^{-3}	4.00×10^{-3}	
10.0	20.0	2.10×10^{-3}	4.20×10^{-3}	
10.0	30.0	1.33×10^{-3}	4.00×10^{-3}	

D Nickel(II)-EDMA - DTPA system

Total concentration of nickel(II), $[\mathrm{Ni}]_t$ mM	Concentration of EDMA, $[\mathrm{X}]_f$ mM	Slope S sec^{-1}	$\frac{S\times[\mathrm{X}]_f}{[\mathrm{Ni}]_t}$	
10.0	10.0	4.16×10^{-4}	4.16×10^{-4}	25°C μ=0.30 Initial concentration of DTPA=0.50 mM
15.0	10.0	6.22×10^{-4}	4.16×10^{-4}	
20.0	10.0	8.35×10^{-4}	4.17×10^{-4}	
10.0	15.0	2.75×10^{-4}	4.15×10^{-4}	
10.0	20.0	2.06×10^{-4}	4.13×10^{-4}	

ligands in the complex formation reaction. Therefore, the concentration of the nickel(II) complex of Dien or EDMA with a 1-to-1 ratio can be expressed by $[\mathrm{Ni}]_t/[1+K_2[\mathrm{X}]_f/(\alpha_\mathrm{H})_\mathrm{X}]$. Here, $[\mathrm{X}]_f$ and $(\alpha_\mathrm{H})_\mathrm{X}$ denote the concentration of uncomplexed Dien or EDMA and the (α_H) value of Dien or EDMA, and K_2 is the second successive formation constant of the nickel(II)-EDMA or Dien complex. On the other hand, in the nickel(II)-En system, the concentration of the nickel(II)-En complex with a 1-to-1 ratio is given by $[\mathrm{Ni}]_t/[1+K_2\cdot[\mathrm{X}]_f/(\alpha_\mathrm{H})_\mathrm{X}+K_2\cdot K_3\cdot[\mathrm{X}]_f{}^2/(\alpha_\mathrm{H})_\mathrm{X}{}^2]$. Here, K_2 and K_3 are the second and third successive formation constants of the nickel(II)-En complexes. As is illustrated in Figs. 4 and 5, the product of the apparent rate constant, k^{+}_{ap}, and $(\alpha_\mathrm{H})_\mathrm{Z}(1+K_2\cdot[\mathrm{X}]_f/(\alpha_\mathrm{H})_\mathrm{X})/[\mathrm{Ni}]_t$ (Dien and EDMA systems) or $(\alpha_\mathrm{H})_\mathrm{Z}(1+K_2[\mathrm{X}]_f/(\alpha_\mathrm{H})_\mathrm{X}+K_2\cdot K_3\cdot[\mathrm{X}]^2{}_f/(\alpha_\mathrm{H})^2{}_\mathrm{X})/[\mathrm{Ni}]_t$ (En system) was found to be a linear function of the hydrogen ion concentration and is given by

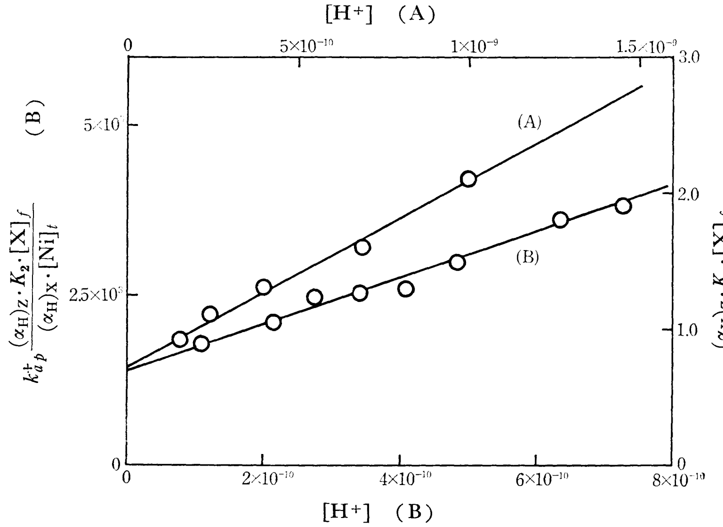

Fig. 5. The plot of $k^{+}_{ap}(\alpha_H)_Z K_2\cdot[X]_f/(\alpha_H)_X[Ni]_t$ against the hydrogen ion concentration.
$\mu=0.30$, 25°C
Initial concentration of DTPA=0.40 mM
Concentration of nickel(II) ion=10.0 mM
A: Ni(II)-Dien system
Total concentration of Dien=30.0 mM
B: Ni(II)-EDMA system
Total concentration of EDMA=30.0 mM

Eq. (5a) or (5b):

$$k^{+}_{ap}(\alpha_H)_Z\cdot\left(1+\frac{K_2\cdot[X]_f}{(\alpha_H)_X}\right)\frac{1}{[Ni]_t}=k_{\alpha}{}^{+}+k_{\beta}{}^{+}[H^+] \tag{5a}$$

$$k^{+}_{ap}(\alpha_H)_Z\cdot\left(1+\frac{K_2\cdot[X]_f}{(\alpha_H)_X}+\frac{K_2\cdot K_3\cdot[X]_f{}^2}{(\alpha_H)_X{}^2}\right)\cdot\frac{1}{[Ni]_t}=k_a{}^{+}+k_b{}^{+}[H^+] \tag{5b}$$

Here, $(\alpha_H)_Z$ in Eqs. (5a) and (5b) is the (α_H) value of DTPA or CyDTA, and $1+K_2\cdot[X]_f/(\alpha_H)_X$ in Eq. (5a) and $1+K_2\cdot[X]_f/(\alpha_H)_X+K_2\cdot K_3\cdot[X]_f{}^2/(\alpha_H)^2{}_X$ in Eq. (5b) are practically identical with $K_2\cdot[X]_f/(\alpha_H)_X$ and $K_2\cdot K_3\cdot[X]_f{}^2/(\alpha_H)_X{}^2$ respectively under the present experimental conditions. From the above data, we may conclude that the mechanism of the substitution reactions of the nickel(II)-EDMA or Dien complex and that involving the nickel(II)-En complex can be expressed by (A) and (B) respectively:

$$\text{(A)}\quad \text{i)}\quad \begin{array}{l} NiX^{2-a}+Z^{m-}\overset{k_1{}^{+}}{\rightleftharpoons}NiZ^{2-m}+X^{a-}\\ \quad\Big\Updownarrow\text{rapid}\\ NiX_2{}^{2-2a}\end{array}$$

$$\text{ii)}\quad \begin{array}{l} NiX^{2-a}+HZ^{1-m}\overset{k_2{}^{+}}{\rightleftharpoons}NiZ^{2-m}+HX^{1-a}\\ \quad\Big\Updownarrow\text{rapid}\\ NiX_2{}^{2-2a}\end{array}$$

where $NiX_2{}^{2-2a}$ denotes 1-to-2 complex of Dien or EDMA and where Z^{m-} means a completely-deprotonated DTPA or CyDTA anion.

$$\text{(B)}\quad \text{i)}\quad \begin{array}{l} NiX^{2+}+Z^{4-}\overset{k_1{}^{+}}{\rightleftharpoons}NiZ^{2-}+X^{0}\\ \quad\Big\Updownarrow\text{rapid}\\ NiX_2{}^{2+}\overset{\text{rapid}}{\rightleftharpoons}NiX_3{}^{2+}\end{array}$$

$$\text{ii)}\quad \begin{array}{l} NiX^{2+}+HZ^{3-}\overset{k_2{}^{+}}{\rightleftharpoons}NiZ^{2-}+HX^{+}\\ \quad\Big\Updownarrow\text{rapid}\\ NiX_2{}^{2+}\\ \quad\Big\Updownarrow\text{rapid}\\ NiX_3{}^{2+}\end{array}$$

From the above reaction mechanisms, it is very clear that $k_{\alpha}{}^{+}$ and $k_a{}^{+}$ can be equated with $k_1{}^{+}$, and $k_{\beta}{}^{+}$ and $k_b{}^{+}$ with $k_2{}^{+}/K_d$. Here, K_d denotes the K_4 of CyDTA or the K_5 of DTPA. The possibility of the formation of a mixed ligand complex of nickel(II) ions involving the CyDTA anion and En can be eliminated, because the addition of En had no effect on the absorption curve of the nickel(II)-CyDTA complex. The rate constant, $k_1{}^{+}$ and $k_2{}^{+}$, were determined from the linear relations shown in Figs. 4 and 5: they are listed, together with the $k_2{}^{+}$ value determined for the substitution reaction of the nickel(II)-iminodiacetate (IDA) complex with DTPA, in Table 3.

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[8] D. W. Margerum, D. B. Rorabacher and J. F. Clarke, Jr., *Inorg. Chem.*, **2**, 667 (1963).

Table 3. Rate constants

System	k_1^+ $\mathrm{M^{-1}\,sec^{-1}}$	k_2^+ $\mathrm{M^{-1}\,sec^{-1}}$
Ni(II)-IDA - DTPA	3.8×10^4	6.13×10^3
Ni(II)-EDMA - DTPA	$1.3_6\times10^3$	2.58×10^2
Ni(II)-Dien - DTPA	7.2×10^5	9.80×10^4
Ni(II)-En - CyDTA	7.2×10^4	1.23×10^4
Ni(II)-Dien - CyDTA	3.8×10^4	2.97×10^1

The substitution reactions of the nickel(II)-Dien and -En complexes are much faster than their dissolication rates.[8)] This clearly indicates that the presence of DTPA or CyDTA in a solution effectively aids in the removal of the Dien and En from the coordination sphere of the nickel(II) ion. To perform this function, DTPA and CyDTA may form coordination bonds with the nickel(II) ion prior to the complete dissociation of the Dien or En from the nickel(II) ion. As in the case of the reactions of Eriochrom Black T (BT) with nickel(II) and cobalt(II)-aminopolycarboxylic acids, this mechanism indicates the formation of mixed ligand intermediate complexes involving Dien or En, and DTPA or CyDTA, anion. If the substitution reaction of CyDTA with the nickel(II)-Dien complex has a reaction intermediate quite different from that of the reaction with the nickel(II)-En complex, the rate constants of the former reaction can not reasonably be compared with those for the latter reaction. However, if the reaction with the nickel(II)-Dien complex proceeds through a reaction intermediate quite similar to that through which the reaction with the nickel(II)-En complex proceeds, the relative rate constant determined experimentally can be compared with that estimated on the basis of the proposed reaction intermediate.

In Fig. 6, the structures of some possible reaction intermediates are shown. As in the cases of the reactions of BT with the nickel(II) and cobalt(II)-EDTA and -EDTA-OH complexes,[2)] the rate-

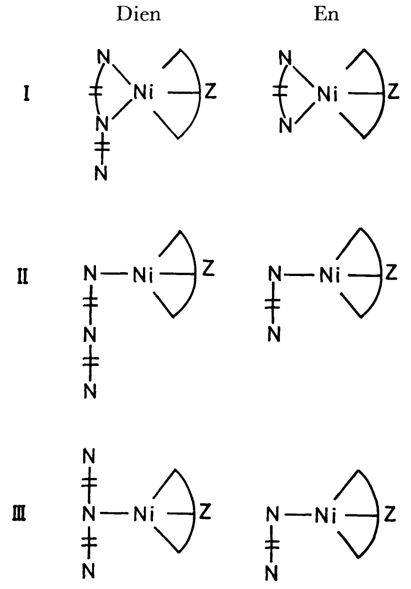

Fig. 6. Reaction intermediates for the substitutions reactions of nickel(II)-Dien and En complexes.

Table 4. Rate constant ratios

A) The reactions of CyDTA with nickel(I)-En and -Dien complexes.

System	Ratio for the elementary reaction (ii)					
	Structure I		Structure II		Structure III	
	calcd	obsd	calcd	obsd	calcd	obsd
En	7.55×10^2	4.15×10^2	1.51×10^3	4.15×10^2	3.02×10^3	4.15×10^2
Dien	1.00	1.00	1.00	1.00	1.00	1.00

B) The reactions of DTPA with nickel(II)-IDA and -EDMA complexes

System	Ratio				
	Elementary reaction (i)		Elementary reaction (ii)		
	calcd$_2$**	obsd	calcd$_1$*	calcd$_2$**	obsd
IDA	1.00	2.79×10^1	$1.34_6\times10^3$	4.27	2.38×10^1
EDMA	1.00	1.00	1.00	1.00	1.00

* Electrostatic interaction between reactants was not taken into consideration.

** Electrostatic interaction between reactants was taken into consideration.

C) The reactions of DTPA with nickel(II)-Dien and EDMA complexes

System	Ratio			
	Elementary reaction (i)		Elementary reaction (ii)	
	calcd	obsd	calcd	obsd
EDMA	1.00	1.00	1.00	1.00
Dien	6.63×10^2	5.30×10^2	1.55×10^2	3.80×10^2

constant ratios between the reaction of CyDTA with the nickel(II)-Dien complex and that with the nickel(II)-En complex were calculated on the assumption that the rates for breaking Dien and En from their mixed ligand complex intermediates are the same. In the calculation of the rate constant ratio, the stability constants of 2.34×10^7 and 3.55×10^{10} ($\mu=0.30$) were used for the nickel(II)-En and -Dien complexes respectively, with a 1-to-1 ratio. The additional stability due to the statistical effect was also taken into account.[9] These results are listed in Table 4, together with those obtained experimentally. The calculated ratio based on structure I agrees best with the observed ratio. This finding is contrary to the observation of Rorabacher and Margerum obtained in their kinetics study of the displacement of polyamine from its nickel(II) complex by the EDTA anion.[5]

In the case of the reaction of the nickel(II)-EDMA complex, the following are considered to be possible reaction intermediates (Fig. 7). The one in which only the acetate group of the displaced EDMA anion is bonded to the nickel(II) ion can be eliminated, because the nickel(II)-oxygen(acetate) bond rupture is much faster than the nickel(II)-nitrogen (amino) bond rupture[9]; hence, at least one nickel(II)-nitrogen bond rupture should be involved in the rate-determining step. Furthermore, in considering the conclusion that the reactions of the nickel(II)-aspartate and -IDA complexes with CyDTA and DTPA proceed through glycinate intermediates, the reaction intermediate having only one nitrogen group of displaced EDMA bonded to the nickel(II) ion seems unlikely. If the substitution reaction of the nickel(II)-EDMA complex with DTPA also has a glycinate mechanism, a comparison of its rate constant with that of the reaction of nickel(II)-IDA complex should be possible. The rate-constant ratio calculated on the basis of a glycinate reaction intermediate occurring between the reaction of DTPA with the nickel(II)-EDMA complex and that with the nickel(II)-IDA complex is 1 : $1.34_6\times10^3$. In a calculation of the relative stability of the reaction intermediate, stability constants of 1.29×10^8 and 2.75×10^{10} ($\mu=0.30$) were used for the nickel(II)-IDA and -EDMA complexes respectively, with a 1-to-1 ratio. Here, additional stabilities due to statistical and electrostatic factors were also taken into account.[9] As is clear from the data in Table 4, there is no close agreement between the calculated ratio and the observed ratio for either elementary reaction pathway, i) or ii). As was mentioned by Margerum *et al.* in their kinetic study of the formation reactions of nickel(II)-triethylenetetramine and tetraethylenepentamine complexes,[8] the electrostatic interaction between the entering group and the reactant (the nickel(II) complex) should also be taken into consideration. If the above electrostatic contribution to the rates of the reactions of nickel(II)-IDA and -EDMA complexes can be evaluated by means of Eq. (27) in Ref. (7), the rate-constant ratios for the two elementary reaction pathways, i) and ii), can be calculated to be 1 : 4.27 and 1 : 1, respectively. Even when the electrostatic interaction between the DTPA anion and the nickel(II)-IDA or -EDMA complex is taken into consideration, there is no close agreement between the calculated rate-constant ratio and the observed ratio. This disagreement clearly eliminates the possibility of a glycinate reaction mechanism (Structure II). As in the case of reactions of CyDTA with the nickel(II)-Dien and En complexes, if the reaction of DTPA with the nickel(II)-EDMA complex proceed through reaction intermediate I, the rate-constant ratios for $k_1{}^+$ and $k_2{}^+$ between the reaction of DTPA with the nickel(II)-Dien complex and that with the nickel(II)-EDMA complex can be estimated to be 6.63×10^2 : 1 and 1.55×10^2 : 1 respectively. Of course, the additional stability of the reaction intermediate due to the statistical and electrostatic effects and the contribution of electrostatic interaction between the attacking group and the nickel(II)-EDMA or -Dien complex were also taken into consideration. The agreement between the observed ratio and the calculated ratio can be regarded as satisfactory. From the results discussed in this paper, it can safely be concluded that the nucleophilic substitution reaction involving the nickel(II)-EDMA complex proceeds through a reaction intermediate in which the displaced EDMA anion is bonded to the nickel(II) ion through two nitrogen groups. This is a reasonable conclusion, because the nickel(II)-oxygen (acetate) bond cleavage is much faster than the nickel(II)-nitrogen (amino) bond cleavage.

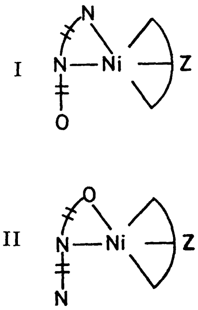

Fig. 7. Reaction intermediates for the substitution reaction of nickel-EDMA complex.

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[9] T. J. Bydalek and D. W. Margerum, *Inorg. Chem.*, **2**, 678 (1963).