Kinetics of Multidentate Ligand Substitution Reactions. XIII. Substitution Reactions of 1-(Hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic Acid (Calmagite) with Nickel(II)-Glutamate, -Aspartate, -Iminodiacetate, -Nitrilotriacetate and -Diethylenetriamine Complexes and That with the Cobalt(II)-Nitrilotriacetate Complex

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The substitution reactions of calmagite with nickel(II)-glutamate, -aspartate, -iminodiacetate, -nitrilotriacetate, and -diethylenetriamine complexes, and that with the cobalt(II)-nitrilotriacetate complex, were studied by employing the stopped-flow technique. In the calmagite reactions with the nickel(II)-glutamate, -aspartate, and -iminodiacetate complexes, the reaction products were found to be mixed-ligand complexes involving calmagite and glutamate, aspartate, or iminodiacetate anions. In these reactions, the 1: 2 ratio complex dissociates rapidly into the 1: 1 ratio complex first; then, the 1: 1 ratio complex reacts slowly with the calmagite anion to form a mixed-ligand complex. From a comparison of the observed rate constant with that estimated on the basis of the proposed reaction intermediate, it was concluded that the latter step proceeds through the outer-sphere complex between the calmagite anion and a 1: 1 ratio complex, and that the water-loss from the 1: 1 ratio complex is the slowest step. In the cases of the reactions of calmagite with nickel(II)-nitrilotraicetate and -diethylenetriamine complexes, and that with the cobalt(II)-nitrilotriacetate complex, all the reaction invariably gave a metal(II)-calmagite complex with a 1: 1 composition, MD^-. These reactions were found to proceed through the completely-deprotonated and divalent calmagite anions.

We have studied a series of substitution reactions of two *o,o'*-dihydroxyazo dyes, Eriochrome Black T (BT) and calmagite, with cobalt(II) and nickel(II)-aminopolycarboxylate complexes.[1,2] The reactions were invariably first-order in the metal(II)-aminopolycarboxylate complex, and gave a metal(II)-dye complex with a 1: 1 composition, MD^-. In the present paper, the kinetics of the substitution reactions of calmagite with the nickel(II)-glutamate (Glut), -aspartate (Asp), -iminodiacetate (IDA), -nitrilotriacetate (NTA), and -diethylenetriamine (Dien) complexes, and that with the cobalt(II)-NTA complex, will be dealt with spectrophotometrically. From a comparison of the observed rate constant with that calculated on the basis of the reaction intermediate proposed, the detailed reaction mechanism and the structure of the reaction intermediate will also be discussed.

Experimental

Reagents. The preparation and the standardization of cobalt(II) and nickel(II) nitrate solutions were described in a previous paper.[3] Reagent-grade Glut, Asp, IDA, and NTA were recrystallized from their aqueous solutions by adding pure hydrochloric acid and ethanol. The Dien used in this study was purified by distilling it under reduced pressure. The calmagite was recrystallized from its ethanol solution by employing the Lindstrom-Isaac method.[4] The other reagents were of an analytical reagent grade and were used without further purification.

Apparatus and Experimental Procedures. All the absorption spectra were obtained with a Hitachi ESP-3 pen-recording spectrophotometer. For the measurement of the pH of the sample solution, a Hitachi-Horiba glass electrode pH meter F-5 was used. All the measurenmets were conducted in solutions of a constant ionic strength (0.30) ($NaClO_4$ or KNO_3). The reactions of calmagite with nickel(II)-IDA, -NTA, and -Dien complexes were followed spectrophotometrically at 620 mμ using a Hitachi ESP-3 pen-recording spectrophotometer. The kinetic investigation of the reactions of calmagite with nickel(II)-Glut and -Asp complexes and of that with the cobalt(II)-NTA complex were carried out by using a Hitachi Rapid Scanning Spectrophotometer RSP-2 with a stopped-flow mixing chamber. The experimental procedures were the same as those described previously.[3] In this study, no buffer reagent was used, because free Glut, Asp, IDA, NTA, and Dien have enough buffer capacity to maintain the pH values of sample solutions constant over the entire pH range covered. All the exchange reactions were studied in solutions containing large excesses of complexed and uncomplexed Glut, Asp, IDA, NTA, or Dien over calmagite. Therefore, all the exchange reactions could be treated as pseudo-first-order reactions. Thus, the apparent rate constant of the pseudo-first-order reaction, Kap^+, was obtained from the slope of the linear relation between $\log(A_0-A\infty)/(A-A\infty)$ and the time, t.[3] Here, A_0, A, and $A\infty$ indicate the absorbances of solutions at time $=0$, t, and ∞ respectively.

Results and Discussion

Equilibrium Study. In the cases of nickel(II)-glutamate, -aspartate and -iminodiacetate complexes, the absorbances of the equilibrium mixtures with calmagite were found to increase with an increase in the concentration of uncomplexed glutamate, aspartate or iminodiacetate. In considering that the calmagite anion and the aminopolycarboxylate anions used in this study can act as tridentate ligand in the complex-

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[1] M. Kodama, C. Sasaki, and T. Noda, This Bulletin, **41**, 2033 (1968).

[2] M. Kodama, *Nippon Kagaku Zasshi*, **91**, 134 (1970).

[3] a) M. Kodama, This Bulletin, **40**, 2575 (1967). b) M. Kodama, C. Sasaki, and M. Murata, *ibid.*, **41**, 1333 (1968).

[4] F. Lindstrom and R. Isaac, *Talanta*, **13**, 1003 (1966).

formation reaction with the nickel(II) ion, this finiding suggests the possibility of the formation of a mixed-ligand calmagite complex involving the aminopolycarboxylate anion. From the thermodynamic point of view,[5] one can derive Eq. (2) for the following mixed-ligand-complex-formation equilibrium:

$$\mathrm{NiD^-} + \mathrm{X^{2-}} \overset{K^{\mathrm{X}}_{\mathrm{NiD}}}{\rightleftarrows} \mathrm{NiDX^{3-}}$$

$$\log\frac{A-A_{\mathrm{NiD}}}{A_{\mathrm{NiDX}}-A} = \log\frac{K^{\mathrm{X}}_{\mathrm{NiD}}}{(\alpha_{\mathrm{H}})_{\mathrm{X}}} + \log\,[\mathrm{X}]_f \qquad (2)$$

where $\mathrm{NiD^-}$, $\mathrm{X^{2-}}$, and $\mathrm{NiDX^{3-}}$ denote the nickel(II)-calmagite complex, the aminopolycarboxylate anion, and the mixed-ligand complex of the nickel(II) ion respectively, where $(\alpha_{\mathrm{H}})_{\mathrm{X}}$ is the (α_{H}) value of aminopolycarboxylate, and where $[\mathrm{X}]_f$ is the concentration of uncomplexed aminopolycarboxylate, where A_{NiD} is the absorbance of the solution in which all the nickel(II) complex ions are in the form of $\mathrm{NiD^-}$, where A_{NiDX} is that of the solution in which all the nickel(II) complex ions exist in the form of $\mathrm{NiDX^{3-}}$, and where A is that of the solution in which $\mathrm{NiD^-}$ and $\mathrm{NiDX^{3-}}$ coexist. This relation was examined by using some typical experimental data. Typical results obtained for glutamate and aspartate systems are reproduced in Fig. 1. From the $\log\,[\mathrm{X}]_f$ values at $\log\,(A-A_{\mathrm{NiD}})/(A_{\mathrm{NiDX}}-A)=0$, the $\log K^{\mathrm{X}}_{\mathrm{NiD}}$ values were determined to be 2.8_0 and 3.5_0 for the glutamate and aspartate systems respectively. In a similar way, the $K^{\mathrm{X}}_{\mathrm{NiD}}$ value for the IDA system was determined to 4.3_0.

On the other hand, in the cases of the nickel(II)-NTA and Dien systems and of the cobalt(II)-NTA system, the concentrations of uncomplexed NTA and Dien had no effect on the absorption curve of the metal(II)-calmagite complex, disproving the formation of a mixed-ligand complex involving the NTA anion or Dien.

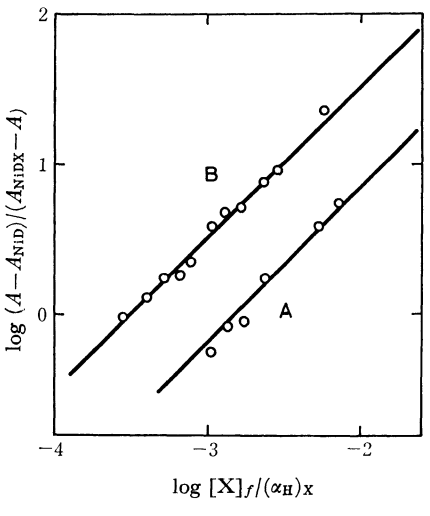

Fig. 1. The plot of log $(A-A_{\mathrm{NiD}})/(A_{\mathrm{NiDX}}-A)$ against log $[\mathrm{X}]_f/(\alpha_{\mathrm{H}})_{\mathrm{X}}$
The concentration of nickel(II) ion=4.0 mM
The concentration of calmagite$=4.0\times10^{-5}$ M
20°C, $\mu=0.30$
A) Glutamate system
The concentration of glutamate ranged from 4.0 to 40.0 mM
pH ranged from 9.70 to 9.86
B) Aspartate system
The concentration of aspartate ranged from 8.0 to 30.0 mM
pH ranged from 9.76 to 9.92

Kinetic Study. In the kinetic study, although the results will not be shown here, the following facts were found in preliminary experiments:

i) In solutions of a given pH, a given concentration of a metal(II) complex of Glut, Asp, IDA, NTA, or Dien, and a given initial concentration of calmagite, k^{+}_{ap} is inversely proportional to the concentration of uncomplexed Glut, Asp, IDA, NTA, or Dien.

ii) In solutions of a given pH, a given concentration of uncomplexed Glut, Asp, IDA, NTA, or Dien, and a given initial concentration of calmagite, k^{+}_{ap} is exactly proportional to the total concentration of a metal(II)-Glut, -Asp, -IDA, -NTA, or -Dien complex.

iii) In solutions of a given pH and given concentrations of uncomplexed and complexed Glut, Asp, IDA, NTA, or Dien, k^{+}_{ap} is independent of the initial concentration of calmagite.

iv) As is shown in Figs. 2 and 3, in solutions of a given initial concentration of calmagite, and given concentrations of a free Glut, Asp, IDA, NTA, or Dien and its metal(II) complex, k^{+}_{ap} multiplied by $K_2\cdot[\mathrm{X}]_f\cdot(\alpha_{\mathrm{H}})_{\mathrm{D}}/(\alpha_{\mathrm{H}})_{\mathrm{X}}$ is a linear function of the concentration of the hydrogen ion and is given by:

$$\frac{k^{+}_{ap}\cdot K_2[\mathrm{X}]_f\cdot(\alpha_{\mathrm{H}})_{\mathrm{D}}}{(\alpha_{\mathrm{H}})_{\mathrm{X}}} = k_\alpha + k_\beta\cdot[\mathrm{H^+}] \qquad (3)$$

where K_2 and $(\alpha_{\mathrm{H}})_{\mathrm{D}}$ are the second successive formation constant of a metal(II)-Asp, -Glut, -IDA, -NTA, or -Dien complex and the (α_{H}) value of calmagite respec-

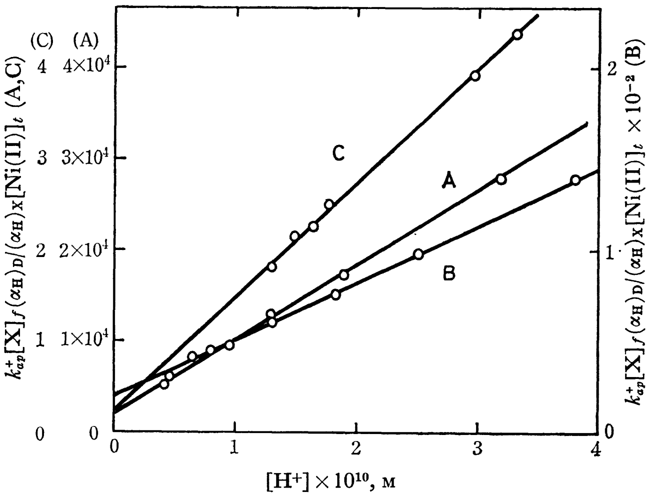

Fig. 2. The plot of $k^{+}_{ap}\,[\mathrm{X}]_f\,(\alpha_{\mathrm{H}})_{\mathrm{D}}/(\alpha_{\mathrm{H}})_{\mathrm{X}}\,[\mathrm{Ni(II)}]_t$ against the hydrogen ion concentration
The concentration of calmagite$=4.0\times10^{-5}$ M
$\mu=0.30$, 20°C
A) Glutamate system
The concentration of nickel(II) ion=80.0 mM
The concentration of uncomplexed Glut=6.0 mM
B) Aspartate system
The concentration of nickel(II) ion=8.0 mM
The concentration of uncomplexed Asp=32 mM
C) Iminodiacetate system
The concentration of nickel(II) ion=8.0 mM
The concentration of uncomplexed IDA=6.0 mM

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[5] M. Kodama and K. Miyamoto, This Bulletin, **42**, 1596 (1969).

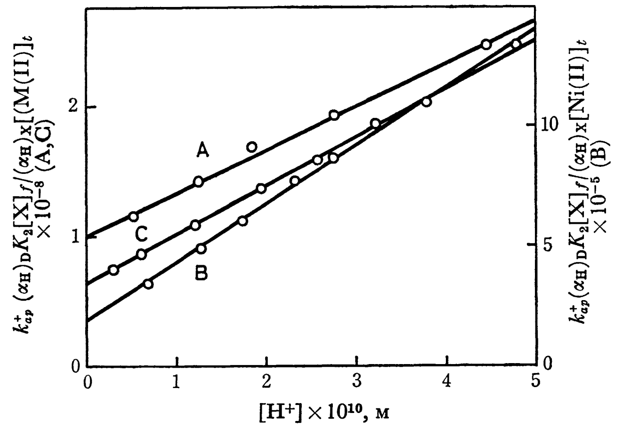

Fig. 3. The plot of $k_{ap}^{+}K_2\ [X]_f(\alpha_H)_D/(\alpha_H)_X\ [M(II)]_t$ against the hydrogen ion concentration
$\mu=0.30$, 25°C
The concentration of calmagite=3.78×10^{-5} M
A) Ni(II)-Dien system
The concentration of nickel(II) ion=5.0 mM
The concentration of uncomplexed Dien=30.0 mM
B) Ni(II)-NTA system
The concentration of nickel(II) ion=5.0 mM
The concentration of uncomplexed NTA=30.0 mM
C) Co(II)-NTA system
The concentration of coblat(II) ion=2.0 mM
The concentration of uncomplexed NTA=40.0 mM

tively. In considering that, under the present experimental conditions, all the metal(II) ions are considered to exist in the form of MX_2^{2-2m}, the above experimental findings suggest that all the substitution reactions are first-order with respect to the concentration of a metal(II)-Glut, -Asp, -IDA, -NTA, or -Dien complex with a 1 : 1 composition, and first-order with respect to the concentration of calmagite, and also that the reactions invariably proceed through the completely-deprotonated and divalent calmagite anions, D^{3-} and HD^{2-}. The K_{NiD}^{X} values obtained show that the reaction products in the substitution reactions of calmagite with the nickel(II)-Glut, -Asp, and -IDA complexes under the present experimental conditions are given by $NiDX^{3-}$. Therefore, the reaction mechanism for the exchange reactions of calmagite with nickel(II)-Glut, -Asp, and -IDA complexes can be depicted as:

$$NiX_2^{2-} \rightleftharpoons NiX^0 + X^{2-} \quad \text{in a rapid equilibrium}$$

$$NiX^0 + \begin{cases} HD^{2-} \overset{k_{HD}}{\rightleftharpoons} NiDX^{3-} + H^+ \\ D^{3-} \overset{k_D}{\rightleftharpoons} NiDX^{3-} \end{cases} \qquad \text{r.d.s. I}$$

For the above reaction, Eq. (3) can be rewritten as:

$$k_{ap}^{+} = 2.303\times \text{log-plot slope}$$

$$= \frac{[Ni(II)]_t}{(1+K_2'\cdot[X]_f)\cdot(\alpha_H)_D}\left(k_D + \frac{k_{HD}\cdot[H^+]}{K_3^D}\right) \qquad (4)$$

From the slopes and intercepts of the straight lines in Fig. 2, the k_{HD} and k_D values for the substitution reactions of calmagite with the nickel(II)-Glut, -Asp, and -IDA complexes were determined; they are listed in Table 1. On the other hand, in the cases of the exchange reactions of calmagite with the nickel(II)-NTA and -Dien complexes, and that with the cobalt(II)-NTA complex, in connection with the experimental facts given above, it can be concluded that the reaction mechanism for these reactions can be formulated as:

$$MX_2^{2-2m} \rightleftharpoons MX^{2-m} + X^{m-} \quad \text{in a rapid equilibrium}$$

$$MX^{2-m} + \begin{cases} HD^{2-} \overset{k_{HD}}{\rightleftharpoons} MD^- + HX^{1-m} \\ D^{3-} \overset{k_D}{\rightleftharpoons} MD^- + X^{m-} \end{cases} \qquad \text{r.d.s. II}$$

where X^{m-} means the tervalent NTA anion or completely-deprotonated Dien.

As in the cases of the nickel(II)-Glut, -Asp, and -IDA systems, the k_{HD} and k_D values for these reactions were determined from the slopes and intercepts of the straight lines in Fig. 3. The k_{HD} and k_D values determined are also listed in Table 1.

TABLE 1. RATE CONSTANTS (μ=0.30,25°C)

System	Rate constants, M^{-1} sec^{-1}	
	k_D	k_{HD}
Ni(II)-glutamate	4.9×10^7	$1.5_8\times 10^6$
Ni(II)-aspartate	3.5×10^6	$4.0_5\times 10^5$
Ni(II)-iminodiacetate	4.8×10^5	$1.5_2\times 10^4$
Ni(II)-nitrilotriacetate	2.5×10^5	$1.6_7\times 10^3$
Ni(II)-diethylenetriamine	9.8×10^7	$2.5_0\times 10^5$
Co(II)-nitrilotriacetate	6.5×10^5	$2.6_4\times 10^5$

We can propose the common water-loss mechanism for the substitution reactions of calmagite with nickel(II)-Glut, -Asp, and -IDA complexes. A nickel(II)-Glut, -Asp, or -IDA complex with a 1 : 2 composition diffuses first and dissociates rapidly to form an outer-sphere complex with the calmagite anion. Then, a coordinated water molecule dissociates from the nickel(II) complex, NiX^0, and a donor group of the calmagite anion coordinates with the nickel(II) ion at the vacated coordination site. In the above reaction mechanism, the water loss from the nickel(II) complex, NiX^0, is considered to be the rate-determining step. In the above water-loss mechanism, if, in the nickel(II)-Glut, -Asp, and -IDA complex segments of the outer-sphere complexes, the Glut, Asp, and IDA anions are bonded to the nickel(II) ion through two oxygen and one nitrogen atoms, all the rate constants (k_D or k_{HD} values) should be identical, because the difference in the electrostatic and steric effects among these three systems are considered to be negligible. On the other hand, if the outer-sphere complexes have the structure shown by I or II in Fig. 4, the rate constants, k_D and k_{HD},

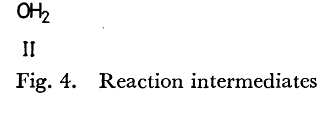

Fig. 4. Reaction intermediates

must be given by Eq. (5):

$$k[6] = k^{-\mathrm{H_2O}} \frac{K_{\mathrm{Ni\text{-}gly}} \cdot K_{as} \cdot K_{ele} \cdot K_{st}}{K_{\mathrm{NiX}}} \qquad (5)$$

where $k^{-\mathrm{H_2O}}$ is the rate constant of water-loss from the nickel(II) ion; K_{as}, the association constant of the outer-sphere complex, and $K_{\mathrm{Ni-gly}}$, the stability constant of the nickel(II)-glycinate segment, and where K_{ele} and K_{st} are the electrostatic contribution to the stability of the reaction intermediate and the statistical factor respectively. This relation was examined experimentally. The k_{D} and k_{HD} values for the glutamate system were calculated to be 1.1×10^7 and $1.1 \times 10^6 \mathrm{M^{-1}sec^{-1}}$ respectively by using $k^{-\mathrm{H_2O}} = 10^{5.30}$,[7] $K_{\mathrm{Ni-gly}} = 10^{4.71}$,[8] $K_{as} = 10^{1.7}$ or $10^{0.7}$,[9] $K_{ele} = 10^{0.5}$, and $K_{st} = 1.0$. In consideration of the assumption made in the above calculation, the agreement between the calculated and observed rate constants can be regarded as satisfactory. Equation (5) also shows that k_{D} and k_{HD} values should be proportioanl to the reciprocal of the stability constant, K_{MX}^{-1}. In Table 2, the relative rate constants and the ratio of K_{MX} are compared. The K_{MX} values used in the estimation of the K_{MX}^{-1} ratio were calculated from the related stability constants in a solution with an ionic strength of 0.10 by using the activity coefficients calculated by means of the Davies equation.[10] Generally, the stability constants reported in the literature are of widely varying accuracy, differing from each other by several tenths of log K units. Considering this, and also the assumption made in the calculation of the activity coefficients, it can be said that the observed ratio agrees, at least semi-quantitatively, with the K_{MX}^{-1} ratio. These findings lend strong support to the above water-loss mechanism proposed for the substitution reactions of the nickel(II)-Glut, -Asp, and -IDA complexes with calmagite.

In the substitution reactions of calmagite with the nickel(II)-NTA and -Dien complexes, and that with the cobalt(II)-NTA complex, the fact that the rate constants are larger than the corresponding dissociation constants can be explained by assuming a reaction mechanism where the reaction proceeds through a mixed-ligand reaction intermediate involving leaving and attacking groups. Here, the dissociation of the leaving group from the reaction intermediate is the rate-determining step. As was discussed in connection with the substituion reaction of diethylenetriaminepentaacetic acid (DTPA) with the nickel(II)-NTA complex in the presence of ethylenediamine,[11] when the calmagite segments in the reaction intermediates of nickel(II)-NTA and -Dien complexes have the same structures, and when the leaving NTA anion and Dien are bonded to the nickel(II) ion through glycinate and ethylenediamine chelate rings respectively, the rate-constant ratio between the nickel(II)-NTA and -Dien complex systems should be 2.2×10^2. As is clear from the data in Table 1, the observed k_{D} and k_{HD} ratios are 3.9×10^2 and 1.5×10^2 respectively. The agreement between observed and calculated ratios can thus be regarded as satisfactory. Furthermore, if the calmagite reactions of both nickel(II)- and cobalt(II)-NTA complexes have as the reaction intermediate, (III), the rate constant ratio, $k_{\mathrm{Co}}/k_{\mathrm{Ni}}$, between the cobalt(II) and Nickel(II) systems should be given by:

$$\frac{k_{\mathrm{Co}}}{k_{\mathrm{Ni}}} = \frac{k_{\mathrm{Co}}^{-\mathrm{gly}}}{k_{\mathrm{Ni}}^{-\mathrm{gly}}} \times \frac{K_{\mathrm{Co\text{-}gly}}}{K_{\mathrm{Ni\text{-}gly}}} \times \frac{K_{\mathrm{NiX}}}{K_{\mathrm{CoX}}} \times \frac{K_{\mathrm{Co\text{-}D}}}{K_{\mathrm{Ni\text{-}D}}} \qquad (6)$$

where $k_{\mathrm{M}}^{-\mathrm{gly}}$, $K_{\mathrm{M-gly}}$, $K_{\mathrm{M-D}}$, and K_{MX} are the dissociation rate constant of the metal(II)-glycinate complex of a 1:1 ratio, the stability constant of the metal(II)-glycinate complex, the stability constant of the metal(II)-calmagite segment, and the stability constant of the 1:1 ratio metal(II)-NTA complex respectively. From the above relation, the $k_{\mathrm{Co}}/k_{\mathrm{Ni}}$ value was calculated to be 1.0×10^2, by using the $k_{\mathrm{Co}}^{-\mathrm{gly}}/k_{\mathrm{Ni}}^{-\mathrm{gly}}$ value reported by Hammes and Steinfeld[12] and the reported K values ($\mu = 0.30$).[13] Here, the cobalt(II)- and nickel(II)-4-(*p*-arsonaphenylazo)-3-hydroxynaphthalene-2,7-disulfonic acid complexes were used as models of the metal(II)-calmagite segments of the mixed-ligand reaction intermediates.[13] The rate constant ratios for the k_{D} and k_{HD} were 2.5×10^2 and 1.6×10^2 respectively. The calculated ratio is in good agreement with the observed ratio. This agreement also supports the present authors' explanation that the calmagite reactions of cobalt(II)- and nickel(II)-NTA complexes proceed through the reaction intermediate III.

TABLE 2. RATE CONSTANT RATIOS

System	Rate constant ratio		K_{MX}^{-1} ratio
	k_{D}	k_{HD}	
Ni(II)-glutamate	1.04×10^2	1.04×10^2	5.9×10^2
Ni(II)-aspartate	7.3	26.6	14.1
Ni(II)-iminodiacetate	1.0	1.0	1.0

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

[7] D. W. Margerum and H. M. Rosen, *J. Amer. Chem. Soc.*, **89**, 1088 (1967).

[8] The nickel(II)-*N*-ethylglycinate complex was used as a model.

[9] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd Ed., John Wiley and Sons (1967), p. 37.

[10] J. N. Butler, "Ionic Equilibrium," Addison-Wesley Publishing Co., Reading, Massachusetts (1964), p. 437.

[11] M. Kodama, S. Karasawa, and T. Watanabe, This Bulletin, **44**, 1815 (1971).

[12] G. G. Hammes and J. I. Steinfeld, *J. Amer. Chem. Soc.*, **84**, 4639 (1962).

[13] L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," 2nd Ed., The Chemical Society, London (1964).