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Kinetics of Multidentate Ligand Substitution Reaction. III. Substitution Reactions of BT with Cobalt(II) and Nickel(II) Chelates of *N*-(2-Hydroxyethyl)-ethylenediamine-*N*,*N*′,*N*′-triacetic Acid and 2,2′-Ethylenedioxybis[ethyliminodi(acetic acid)]

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BT can displace EDTA-OH and GEDTA from their cobalt(II) and nickel(II) chelate as in the case of the substitution reaction of BT with cobalt(II)-EDTA chelate or nickel(II)-EDTA chelate. In this paper, kinetics of the substitution reactions of BT with cobalt(II)- and nickel(II)-chelates of EDTA-OH and of GEDTA was studied spectrophotometrically. All substitution reactions were found to be first-order in BT and first-order in metal(II)-chelate of EDTA-OH or GEDTA, and to proceed through two simultaneous reaction paths analogous to those proposed for the substitution reaction of BT with cobalt(II)-EDTA chelate. Although EDTA-OH differs from EDTA by the presence of a hydroxyethyl group in place of one acetate group, its metal(II) chelate behaves in a nearly identical manner with EDTA chelate in the substitution reaction and the cleavage of the metal-nitrogen bond of the glycinate group is considered to be the probable rate-determining step. The substitution reactions of BT with GEDTA chelates are considered to be more favored thermodynamically over the reactions of EDTA-OH chelates, but were found to be less favored kinetically. This fact may suggest that the geometrical structure of metal(II)-GEDTA plays an important role in determining the rate of the substitution reaction of GEDTA.

In the previous papers,[1,2] kinetics of the substitution reactions of Eriochrom Black T (BT) with cobalt(II) and nickel(II) chelates of ethylenediaminetetraacetic acid (EDTA) and of nitrilotriacetic acid (NTA) were studied. Reactions were first-order in BT and first-order in metal(II) chelate of 1 to 1 composition.

BT can also displace *N*-(2-hydroxyethyl)-ethylenediamine-*N*,*N*′,*N*′-triacetate (EDTA-OH) and 2,2′-ethylenedioxybis[ethyliminodi(acetate)] (GEDTA) from their chelates of cobalt(II) and nickel(II). In this paper, the kinetics of the substitution reactions of BT with EDTA-OH and GEDTA chelates of these metal ions were dealt with spectrophotometrically. From comparison of the rate constants of the substitution reactions of EDTA-OH chelates of cobalt(II) and nickel(II) with those of EDTA chelates, the reaction mechanism was assigned in detail.

Experimental

Reagents. The preparation and the standardization of solutions of cobalt(II) and nickel(II) perchlorates were described in the previous papers.[1,2] Reagent grade EDTA-OH and GEDTA were recrystallized from water. The concentration of EDTA-OH solution was standardized against the standard copper(II) solution by a volumetric titration with Murexide as indicator.[3] The standard solution of GEDTA was prepared by dissolving a known amount of GEDTA dried for two hours at 115°C into a diluted alkaline solution. The purification of BT was also described in the previous paper.[4] Other reagents were of guranteed reagent grade and used without further purification.

Apparatus and Procedure. The apparatus and the experimental procedures were the same as described previously.[1] In this study, all measurements were conducted in solutions of ionic strength 0.30 ($NaClO_4$), and no buffer reagent was used, because free EDTA-OH and GEDTA can have enough buffer capacity to maintain the pH values of solutions constant at the pH range from 8.00 to 10.50.

Results and Discussion

All exchange reactions were studied in solutions of pH from 8.00 to 10.50 containing large excesses of complexed and uncomplexed EDTA-OH or GEDTA. Therefore, the exchange reactions can be treated as pseudo first-order reactions. All exchange reactions of BT were found to give invariably the linear relations between $\log (A_D/(A-A_{MD}))$ and time, t, with the intercept identical to $\log (\varepsilon_{BT}/(\varepsilon_{BT}-\varepsilon_{MD}))$, holding the following relation (Fig. 1).

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

[2] M. Kodama, C. Sasaki and M. Murata, *ibid.*, **41**, 1333 (1968).

[3] The same procedure as was proposed for the EDTA titration of copper was employed.

[4] M. Kodama and H. Ebine, This Bulletin, **40**, 1857 (1967).

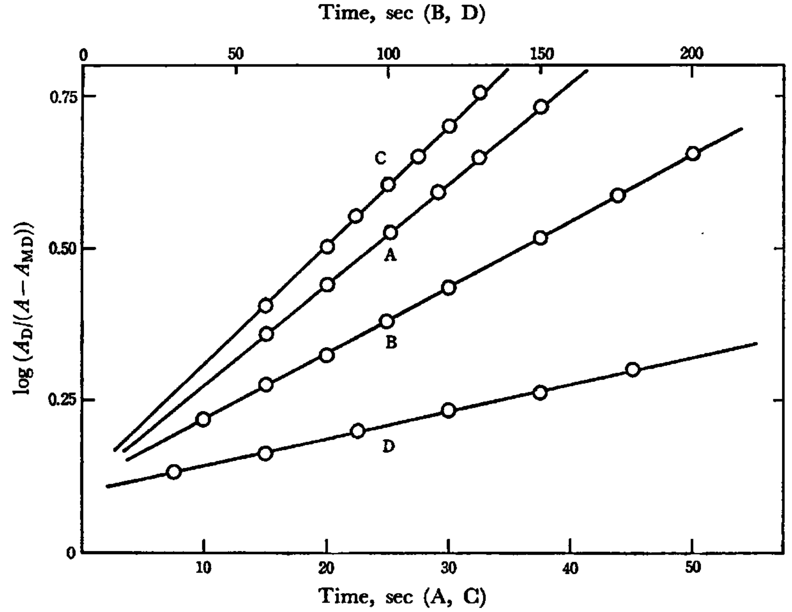

Fig. 1. The plot of $\log[A_D/(A-A_{MD})]$ against t.
$\mu=0.30$, $\lambda=630\,\mathrm{m}\mu$
A: Co(II)EDTA-OH system
$[BT]_0=1.50\times10^{-5}$ M, pH=8.23, $[CoZ^-]=1.0$ mM
Concentration of uncomplexed EDTA-OH=10.0 mM
B: Ni(II)-EDTA-OH system
$[BT]_0=3.05\times10^{-5}$ M, pH=10.17, $[NiZ^-]=8.25_5$ mM
Concentration of uncomplexed EDTA-OH=8.0 mM
C: Co(II)-GEDTA system
$[BT]_0=1.00\times10^{-5}$ M, pH=8.80, $[CoZ^{2-}]=0.30$ mM
Concentration of uncomplexed GEDTA=10.0 mM
D: Ni(II)-GEDTA system
$[BT]_0=2.90\times10^{-5}$ M, pH=10.10, $[NiZ^{2-}]=6.60$ mM
Concentration of uncomplexed GEDTA=10.0 mM

$$\log\frac{A_D}{A-A_{MD}}-\log\frac{\varepsilon_{BT}}{\varepsilon_{BT}-\varepsilon_{MD}}=\frac{k^+}{2.303}\cdot t \tag{1}$$

where simbols, A_D and A, have the same meanings as used in the previous paper[4] and the other notation definitions are as follows. A_{MD}: Absorbance of the solution where all BT ions in the solution is considered to form the complex with nickel(II) or cobalt(II); ε_{BT}: The apparent extinction coefficient of uncomplexed BT at the given pH[2]; ε_{MD}: The true extinction coefficient of metal (II)-BT chelate.

As was stated previously,[1,2] when the stability constants of metal(II)-BT chelate are much greater than those of metal(II)-EDTA-OH or GEDTA chelates, and hence, the concentration of uncomplexed BT at equilibrium, $[BT]_e$, can be neglected as compared with the intial concentration of BT, $[BT]_0$, and with the BT concentration, [BT], at time t, in an early stage of the reaction, the left hand side of Eq. (1) must be equal to $\log([BT]_0-[BT]_e)/([BT]-[BT]_e)$. Therefore, if the above conditions are fulfilled by the systems, the slope of the linear relation between $\log(A_D/(A-A_{MD}))$ and t should correspond to the apparent rate constant of the forward reaction of the pseudo first-order reaction (2).

$$\left\{\begin{matrix}HD^{2-}\\D^{3-}\end{matrix}\right.\ \underset{k^-}{\overset{k^+}{\rightleftharpoons}}\ MD^- \tag{2}$$

where HD^{2-}, D^{3-} and MD^- mean doubly and completely deprotonated BT anion and metal(II)-BT chelate, respectively.

Reported stability constants of metal(II)-BT chelate, K_{MD},s[1,2] indicate that the requirements are satisfied by the present systems. The following experimental facts were also found in the preliminary experiments where free EDTA-OH or GEDTA ranged from 5.0 mM to 25 mM, and its cobalt(II) or nickel(II) chelate from 0.30 mM to 25.0 mM.

i) In solutions of a given pH, given concentrations of cabalt(II) or nickel(II) chelate of EDTA-OH or GEDTA and the given initial concentration of BT, the slope of $\log(A_D/(A-A_{MD}))$ *vs.* t plot is independent of the concentration of uncomplexed EDTA-OH or GEDTA (Table 1).

TABLE 1. DEPENDENCE OF THE SLOPE ON THE CONCENTRATION OF UNCOMPLEXED CHELATING AGENT

$\mu=0.30$

i) Cobalt(II)-EDTA-OH system

Concentration of EDTA-OH, mM	Slope, $\sec^{-1}$	
10	1.62×10^{-2}	pH=8.23
15	1.68×10^{-2}	$[\mathrm{BT}]_0=1.83\times10^{-5}$ M
20	1.65×10^{-2}	$[\mathrm{CoZ^-}]=1.0$ mM

ii) Nickel(II)-EDTA-OH system

Concentration of EDTA-OH, mM	Slope, $\sec^{-1}$	
8.0	1.90×10^{-3}	pH=10.0
15.0	1.87×10^{-3}	$[\mathrm{BT}]_0=3.05\times10^{-5}$ M
25.0	1.91×10^{-3}	$[\mathrm{NiZ^-}]=8.25_5$ mM

iii) Cobalt(II)-GEDTA system

Concentration of GEDTA, mM	Slope, $\sec^{-1}$	
5	$1.18_2\times10^{-2}$	pH=8.10
10	$1.18_2\times10^{-2}$	$[\mathrm{BT}]_0=1.00\times10^{-5}$ M
15	$1.16_5\times10^{-2}$	$[\mathrm{CoZ^{2-}}]=0.30$ mM

iv) Nickel(II)-GEDTA system

Concentration of GEDTA, mM	Slope, $\sec^{-1}$	
10	1.04×10^{-3}	pH=10.10
15	1.05×10^{-3}	$[\mathrm{BT}]_0=2.90\times10^{-5}$ M
25	1.02×10^{-3}	$[\mathrm{NiZ^{2-}}]=6.60$ mM

TABLE 2. DEPENDENCE OF THE SLOPE ON THE INITIAL CONCENTRATION OF BT

$\mu=0.30$

i) Cobalt(II)-EDTA-OH system

Concentration of BT, M	Slope, $\sec^{-1}$	
7.31×10^{-6}	1.63×10^{-2}	pH=8.23 Concentration of free EDTA-OH=10 mM $[\mathrm{CoZ^-}]=1.0$ mM
1.83×10^{-5}	1.62×10^{-2}	
2.56×10^{-5}	1.61×10^{-2}	

ii) Nickel(II)-EDTA-OH system

Concentration of BT, M	Slope, $\sec^{-1}$	
1.22×10^{-5}	1.45×10^{-3}	pH=9.86 Concentration of free EDTA-OH=8.0 mM $[\mathrm{NiZ^-}]=8.25_5$ mM
2.14×10^{-5}	1.40×10^{-3}	
3.05×10^{-5}	$1.43\times10_{-}{}^{3}$	

iii) Cobalt(II)-GEDTA system

Concentration of BT, M	Slope, $\sec^{-1}$	
8.45×10^{-6}	2.44×10^{-2}	pH=8.16 Concentration of free GEDTA=10 mM $[\mathrm{CoZ^{2-}}]=0.60$ mM
2.11×10^{-5}	2.40×10^{-2}	
2.54×10^{-5}	2.44×10^{-2}	

iv) Nickel(II)-GEDTA system

Concentration of BT, M	Slope, $\sec^{-1}$	
5.80×10^{-6}	1.06×10^{-3}	pH=10.10 Concentration of free GEDTA=10.0 mM $[\mathrm{NiZ^{2-}}]=6.60$ mM
1.45×10^{-5}	1.02×10^{-3}	
2.90×10^{-5}	1.04×10^{-3}	

ii) In solutions of a given pH, given concentrations of uncomplexed EDTA-OH or GEDTA and of cobalt(II)- or nickel(II) chelate of EDTA or GEDTA, the slope of the linear relation is independent of the initial concentration of BT, $[\mathrm{BT}]_0$ (Table 2).

iii) In solutions of a given pH, given concentrations of uncomplexed EDTA-OH or GEDTA, and of the given initial concentration of BT, the slope of the linear relation is proportional to the concentration of metal(II) chelate of EDTA-OH or GEDTA (Table 3).

iv) In solutions of a given initial concentration of BT, given concentrations of uncomplexed EDTA-OH or GEDTA, and of cobalt(II) or nickel(II) chelate of EDTA-OH or GEDTA, the slope of the linear relation is a linear function of the reciprocal of the concentration of hydrogen ion (Fig. 2), and given by

$$\text{slope} = k_\alpha + k_\beta/[\mathrm{H^+}] \tag{3}$$

These facts clearly indicate that the present substitution reactions of BT have the same reaction mechanism as was proposed for the substitution reaction of BT with cobalt(II)-EDTA chelate.[1] Consequently, k^+ in Eq. (1) or (2) should be given by

$$k^+ = (k_1{}^+ + k_2{}^+\cdot k_2/[\mathrm{H^+}])\cdot[\mathrm{MZ}] \tag{4}$$

where k_2 refers to the dissociation of the second phenolic group of BT,[5] and [MZ] to the concentration of cobalt(II) or nickel(II) chelate of EDTA-OH or of GEDTA. Here, $k_1{}^+$ and $k_2{}^+$ in Eq. (4) are the second-order rate constants of the following reactions

i) $\mathrm{HD^{2-}} + \mathrm{MZ^{2-\mathit{n}}} \underset{k_1^-}{\overset{k_1^+}{\rightleftarrows}} \mathrm{MD^-} + \mathrm{HZ^{1-\mathit{n}}}$

ii) $\mathrm{HD^{2-}} \xrightleftharpoons{\text{rapid}} \mathrm{H^+} + \mathrm{D^{3-}}$

$\mathrm{D^{3-}} + \mathrm{MZ^{2-\mathit{n}}} \underset{k_2^-}{\overset{k_2^+}{\rightleftarrows}} \mathrm{MD^-} + \mathrm{Z^{\mathit{n}-}}$

rate determining step

where $\mathrm{MZ^{2-\mathit{n}}}$ means metal(II)-EDTA-OH or -GEDTA chelate and $\mathrm{Z^{\mathit{n}-}}$, completely deprotonated EDTA-OH or GEDTA anion.

From slopes of the linear relation between $k^+/[\mathrm{MZ}]$ and $1/[\mathrm{H^+}]$ and the intercepts, $k_1{}^+$'s and $k_2{}^+$'s

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[5] G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 678 (1948).

TABLE 3. DEPENDENCE OF THE SLOPE ON THE CONCENTRATION OF METAL(II) CHELATE

$\mu=0.30$

i) Cobalt(II)-EDTA-OH system

Concentration of Co(II)-EDTA-OH, mM	Slope, sec^{-1}	Slope ratio		
		calcd	obsd	
0.40	$6.6_6\times10^{-3}$	1.00	1.00	pH=8.23 Concentration of free EDTA-OH=10 mM $[BT]_0=1.83\times10^{-5}$ M
1.00	1.68×10^{-2}	2.50	2.54	
1.40	2.34×10^{-2}	3.50	3.52	
2.00	3.33×10^{-2}	5.00	5.00	

ii) Nickel(II)-EDTA-OH system

Concentration of Ni(II)-EDTA-OH, mM	Slope, sec^{-1}	Slope ratio		
		calcd	obsd	
8.25_5	1.90×10^{-3}	1.00	1.00	pH=10.0 Concentration of free EDTA-OH=8.0 mM $[BT]_0=3.05\times10^{-5}$ M
16.51	3.74×10^{-3}	2.00	1.97	
24.77	5.70×10^{-3}	3.00	3.00	

iii) Cobalt(II)-GEDTA system

Concentration of Co(II)-GEDTA, mM	Slope, sec^{-1}	Slope ratio		
		calcd	obsd	
0.15	5.66×10^{-3}	1.00	1.00	pH=8.00 Concentration of free GEDTA=10 mM $[BT]_0=1.40\times10^{-5}$ M
0.30	$1.13_5\times10^{-2}$	2.00	1.95	
0.45	$1.72_0\times10^{-2}$	3.00	2.94	
0.60	$2.26_5\times10^{-2}$	4.00	3.88	

iv) Nickel(II)-GEDTA system

Concentration of Ni(II)-GEDTA, mM	Slope, sec^{-1}	Slope ratio		
		calcd	obsd	
3.30	5.18×10^{-4}	1.00	1.00	pH=10.10 Concentration of free GEDTA=10.0 mM $[BT]_0=2.90\times10^{-5}$ M
6.60	1.04×10^{-3}	2.00	1.97	
13.20	2.07×10^{-3}	4.00	3.99	

were determined (Fig. 2). These values are listed in Table 4 together with those for the substitution reactions of BT with EDTA chelates reported previously.[1,2]

We have mentioned previously[2] the importance of mixed ligand complexes as reaction intermediates in the proposed mechanism of the substitution reactions of BT with cobalt(II) and nickel(II)-EDTA chelates; prior to the complete dissociation of EDTA anion (Y^{4-}) from metal ion, BT may form coordinate bonds with metal ions, block the reformation of metal-EDTA bonds, and, thus, greatly increase the rate of dissociation of EDTA anion from the metal ion.

Electrostatically, the incompletely deprotonated BT anion (HD^{2-}) would have less repulsion against the negatively charged metal(II)-EDTA chelate. Therefore, kinetically, the reaction which proceeds through incompletely deprotonated BT anion can be expected to have an advantage over that proceeds through compltely deprotonated BT anion (D^{3-}). However, rate constants for the reactions through compltely deprotonated BT anion were much greater than those for the reactions through doubly deprotonated BT anion (HD^{2-}). This may suggest the need for the second phenolic oxygen to form the second metal(II)-oxygen bond prior to the rate determining step. Thus, the structure of a mixed ligand chelate as a reaction intermediate in the substitution reaction of BT with EDTA chelate should have metal-D^{3-} segment where two metal-oxygen bonds and one metal-nitrogen bond are included. Therefore, in this structure, at least, one half of Y^{4-} must be unwrapped.

Although EDTA-OH differs from EDTA by the presence of a hydroxyethyl group in place of one acetate group, its metal(II) chelate behaves kinetically in a nearly identical manner with EDTA chelate. Therefore, the structure of the reaction intermediate in the substitution reaction involving EDTA-OH chelate may be identical with that in the reaction of EDTA chelate.

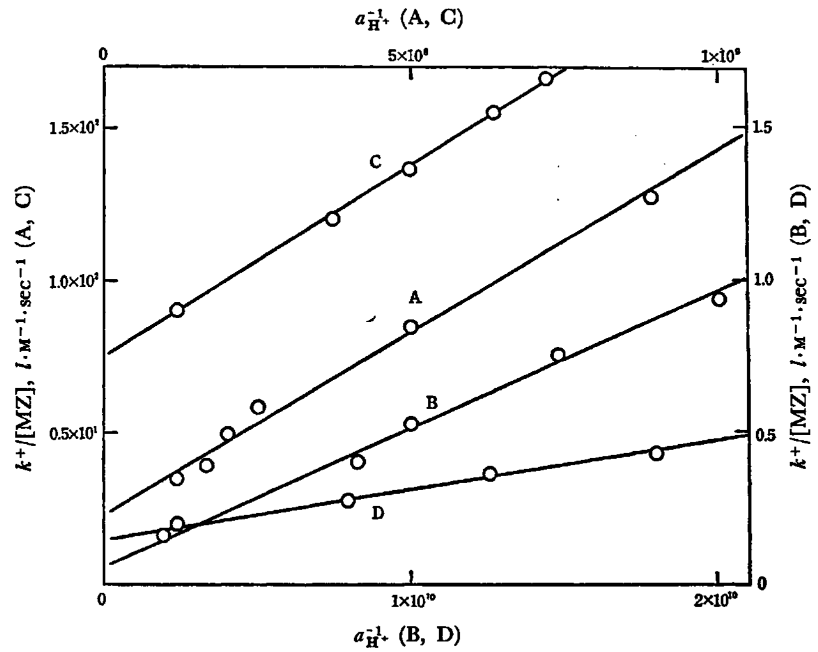

Fig. 2. Relation between k^+/[MZ] and the concentration of hydrogen ion.
$\mu=0.30$, $\lambda=630$ mμ
A: Co(II)-EDTA-OH system
$[BT]_0=1.50\times10^{-5}$ M, $[CoZ^-]=1.00$ mM
Concentration of uncomplexed EDTA-OH = 10.0 mM
B: Ni(II)-EDTA-OH system
$[BT]_0=3.05\times10^{-5}$ M, $[NiZ^-]=8.25_5$ mM
Concentration of uncomplexed EDTA-OH = 8.0 mM
C: Co(II)-GEDTA system
$[BT]_0=2.00\times10^{-5}$ M, $[CoZ^{2-}]=0.60$ mM
Concentration of uncomplexed GEDTA = 10.0 mM
D: Ni(II)-GEDTA system
$[BT]_0=2.90\times10^{-5}$ M, $[NiZ^{2-}]=6.60$ mM
Concentration of uncomplexed GEDTA = 10.0 mM

TABLE 4. RATE CONSTANTS FOR THE SUBSTITUTION REACTIONS OF BT WITH COBALT(II) AND NICKEL(II) CHELATES OF EDTA, EDTA-OH AND GEDTA

	EDTA chelates[1,2]		EDTA-OH chelates		GEDTA chelates	
	k_1^+	k_2^+	k_1^+	k_2^+	k_1^+	k_2^+
Co(II)	0.40	3.28×10^3 [a]	2.20×10^1	3.24×10^4 [b]	7.37×10^1	2.28×10^4 [c]
Ni(II)	0	1.25 [d]	0.08	6.93 [d]	0.16	3.30 [d]

Rate constants, M$^{-1}\cdot$sec^{-1}, $\mu=0.30$: a) 24.5°C b) 26°C c) 25°C d) 15°C.

In the kinetic studies of the electrophilic and the nucleophilic substitution reactions involving multidentate ligands, Margerum *et al.*[6,7] determined the detailed reaction mechanism by relating the experimental rate constant of the substitution reaction to the stability of the proposed reaction intermediate (a dinuclear complex or a mixed ligand complex). As was discussed above, the reaction intermediate in the present substitution reaction of BT may have one of these four structures listed in Fig. 3. To assign the detailed reaction mechanism, the treatment proposed by Rorabacher and Margerum[7] for the nucleophilic substitution reaction between EDTA and nickel(II)-polyamine complexes was applied directly to the present substitution reactions of BT with cobalt(II) and nickel(II) chelates of EDTA and of EDTA-OH. The direct application of their treatment leads to the conclusion that

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

[7] D. B. Rorabacher and D. W. Margerum, *ibid.*, **3**, 382 (1964).

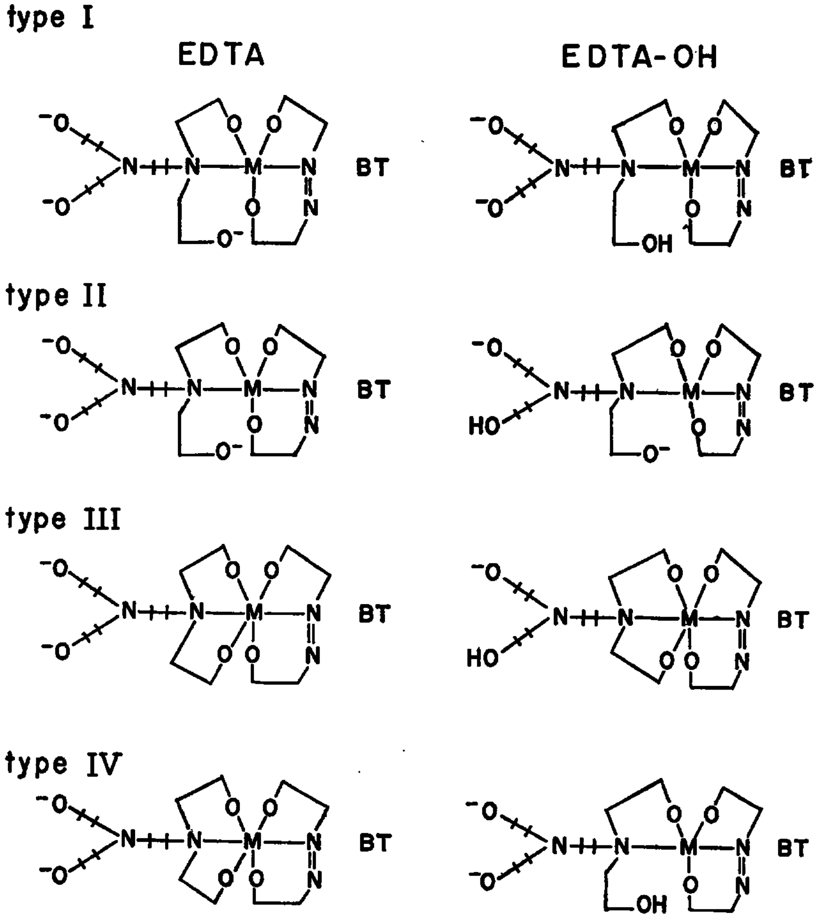

Fig. 3. Reaction intermediates.

TABLE 5. STABILITY CONSTANTS ($\mu=0.30$)*

1)	Co(II)-EDTA chelate[8]	$K_{\mathrm{CoY}}=10^{15.71}$
2)	Ni(II)-EDTA chelate[8]	$K_{\mathrm{NiY}}=10^{18.02}$
3)	Co(II)-EDTA-OH chelate[9]	$K_{\mathrm{CoZ}}=10^{13.95}$
4)	Ni(II)-EDTA-OH chelate[9]	$K_{\mathrm{NiZ}}=10^{16.55}$
5)	Ni(II)-EDTP chelate[10]	$K_{\mathrm{NiZ}}=10^{9.10}$
6)	Ni(II)-NTA chelate[11]	$K_{\mathrm{NiX}}=10^{11.09}$
7)	α-Amino, α-methylpropionate[12]	
	Co(II) chelate	$K_{\mathrm{CoX}}=10^{3.51}$
	Ni(II) chelate	$K_{\mathrm{NiX}}=10^{4.56}$
8)	*N*-Methyliminodiacetate[13]	
	Co(II) chelate	$K_{\mathrm{CoX}}=10^{7.32}$
	Ni(II) chelate	$K_{\mathrm{NiX}}=10^{8.43}$
9)	BT chelates[1,2]	
		$K_{\mathrm{CoD}}=10^{20.0}$
		$K_{\mathrm{NiD}}=10^{20.8}$
10)	Co(II)-GEDTA chelate[14]	
		$K_{\mathrm{CoZ}}=10^{11.70}$
11)	Ni(II)-GEDTA chelate[14]	
		$K_{\mathrm{NiZ}}=10^{13.00}$

* These values are calculated from the related stability constants in solutions of ionic strength 0.10 and the activity constants of the ions calculated by means of Davies equation.[1]

experimental rate constant ratio between EDTA and EDTA-OH systems should be equal to the ratio of the reaction intermediate stability, provided that the rate of the dissociation of tervalent EDTA-OH anion Z^{3-} from the reaction intermediate can be equated with that of Y^{4-}. As suggested by Margerum *et al.*,[7] the relative stability for the reaction intermediate given by the following relation was used in place of the actual one.

$$K_r{}^{7)} = \frac{K_{\mathrm{chelon-segment}} \cdot K_{\mathrm{BT-segment}}}{K_{\mathrm{MZ}}} \tag{5}$$

Where $K_{\mathrm{chelon-segment}}$ corresponds to the stability

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8) G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

9) S. Chaberek, Jr., and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 1477 (1955).

10) R. C. Courtney, S. Chaberek, Jr., and A. E. Martell, *ibid.*, **75**, 4814 (1953).

11) G. Schwarzenbach and R. Gut, *Helv. Chim. Acta*, **39**, 1583 (1956).

12) H. Irving and L. D. Pettit, *J. Chem. Soc.*, **1963**, 1946.

13) G. Schwarzenbach, G, Anderagg, W. Schneider and H. Senn, *Helv. Chim. Acta*, **38**, 1147 (1955).

14) J. H. Holloway and C. N. Reilley, *Anal. Chem.*, **32**, 249 (1960).

TABLE 6. REACTION INTERMEDIATES AND RATE CONSTANT RATIOS

			EDTA	EDTA-OH	Rate constant ratio	
					Calcd	Obsd
Type I	Ni(II)	log K_r	7.34	8.81		
		log K_{elcc}	0.50	—	2.35	5.54
		statistical factor	4.0	1.0		
	Co(II)	log K_r	7.80	9.56		
		log K_{elec}	0.50	—	4.57	9.85
		statistical factor	4.0	1.0		
Type II	Ni(II)	log K_r	7.34	8.81		
		log K_{elec}	0.50	0.50	14.8	5.54
		statistical factor	4.0	2.0		
	Co(II)	log K_r	7.80	9.56		
		log K_{elec}	0.50	0.50	28.9	9.85
		statistical factor	4.0	2.0		
Type III	Ni(II)	log K_r	11.24	12.71		
		log K_{elec}	—	—	14.8	5.54
		statistical factor	2.0	1.0		
	Co(II)	log K_r	11.61	13.37		
		log K_{elec}	—	—	28.9	9.85
		statistical factor	2.0	1.0		
Type IV	Ni(II)	log K_r	11.11	9.56		
		log K_{elec}	—	—	1/317	5.54
		statistical factor	2.0	1.0		
	Co(II)	log K_r	11.41	8.81		
		log K_{elec}	—	—	1/224	9.85
		statistical factor	2.0	1.0		

constant of metal(II)-glycinate or -iminodiacetate chelate, $K_{BT-segment}$, to the stability constant of metal(II)-BT chelate, and K_{MZ}, the stability constant of metal(II)-EDTA or -EDTA-OH chelate.

The relative stability of the proposed reaction intermediate calculated from the numerical values given in Table 5 are listed in Table 6 together with the rate constants. In the evaluation of the stability, the additional stability due to the electrostatic attraction of acetate group, K_{elec} (3.17),[6] and the statistical factor[6] were also taken into consideration. Here, *N*-methyl iminodiacetate and α-amino, α-methylpropionate were chosen as intermediate models.[6] Clearly, the structures type I fit the observed data best and are considered to be the preferred intermediates.

If the rupture of the second (EDTA or EDTA-OH anion) nitrogen-nickel bond accompanied by the rotation around a C–N or C–C bond and the formation of nickel-water bond is the rate determining step, the products of the rate constant for the rupture of nickel-nitrogen bond corrected for the rotational barrier involved[7] and K_r values must be equal to the experimental rate constants. However, K_r values in Table 6 clearly show that the experimental rate constants are much smaller than these products. Generally, it is very hard to consider that the rupture of the last nickel-oxygen bond is involved in the rate determining step, because the nickel-acetate cleavage is much faster than the nickel-amine cleavage.[6] Consequently, the above fact may indicate that the BT anion coordinated to the nickel(II) ion gives a serious effect on the rupture of nickel-nitrogen bond, the accompanied rotation around the C–N or the C–C bond of the leaving EDTA or EDTA-OH anion, other structural transformation or the formation of nickel(II)-water bond. To get additional information about this effect, further systematic investigations should be conducted.

As was tried in the substitution reaction of BT with EDTA-OH chelate, if the same reaction mechanism (glycinate intermediate) also fits the substitution reaction with GEDTA chelate, the rate of the reaction of BT with GEDTA chelate can be compared with that of EDTA chelate theoretically on the basis of the reaction intermediates.

Stability constant ratios of reaction intermediates between reactions with GEDTA chelates and those with EDTA chelates were also calculated by choosing α-amino, α-methylpropionate as an intermediate model and using stability constants listed in Table 5. Calculated values for cobalt(II) and nickel(II) systems were 1.02×10^4 and 1.07×10^5, respectively. This may suggest that the substitution reactions of BT with GEDTA chelates must be much favored thermodynamically over the reactions of BT with

EDTA chelates. However, rate constant ratios experimentally found for cobalt(II) and nickel(II) systems were 6.80 and 2.64, in a remarkable disagreement with the theoretically predicted ones. This probably means that the substitution reaction of BT with GEDTA chelate involves the reaction intermediate quite different from that for the reaction of EDTA chelate, or that the substitution reaction of BT with GEDTA chelate may have the same reaction intermediate as the reaction with EDTA, but, the steric effect due to the $-O-CH_2-CH_2-O-CH_2-CH_2-N-(CH_2COO^-)_2$ segment in GEDTA makes the reaction intermediate less stable to make the reaction less favorable kinetically. The latter explanation may be probable, because the rate constant ratio for the reaction of cobalt(II) chelate is not diffrent considerably from that for the reaction of nickel(II)-chelate.

If the glycinate mechanism also fits the reaction of BT with nickel(II)-NTA chelates, the stability constant ratio of reaction intermediates between the reaction with nickel(II)-NTA chelate and that with nickel(II)-EDTA chelate can be calculated to be 6.30×10^6. This result clearly suggests that if the reaction of BT with nickel(II)-NTA chelate had the same reaction mechanism as that with EDTA chelate had, the reaction of nickel(II)-NTA chelate would proceed very rapidly as compared with that of nickel(II)-EDTA chelate. As was reported previously,[2)] the reaction was found to proceed rapidly in accordance with the above prediction.

Finally, we can mention that the kinetic study of substitution reactions of metal chelates with dyes other than BT would provide the additional information about the mechanism of multidentate ligand substitution reactions.