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The Kinetics of Substitution Reactions Involving Metal Complexes. XIII. Reactions of Zinc(II) with *meso*-Butylenediaminetetraacetatocobaltate(II) and with Propylenediaminetetraacetatocobaltate(II)

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Kinetics of the substitution reactions of zinc(II) with *meso*-butylenediaminetetraacetatocobaltate(II) (cobalt(II)-*meso*-BDTA) and propylenediaminetetraacetatocobaltate(II) (cobalt(II)-PDTA) have been studied. The reaction of zinc(II) with cobalt(II)-*meso*-BDTA complex proceeds through two simultaneous reaction paths involving the acid dissociation reactions of the cobalt(II) complex. On the other hand, the reaction of zinc(II) with cobalt(II)-PDTA proceeds through four simultaneous reaction paths, of which two involve electrophilic substitution reactions and the others, the acid dissociation reactions of the cobalt(II) complex. This kinetic behavior is discussed on the basis of the natures of the ligands.

Kinetic studies of the reactions of zinc(II) with ethylenediaminetetraacetatocobaltate(II) (cobalt(II)-EDTA) and trimethylenediaminetetraacetatocobaltate(II) (cobalt(II)-TRDTA) have been reported.¹⁾ According to the results, the variation of ligands affects the rates of both the electrophilic substitution (S_E) reactions and the acid dissociation reactions of the cobalt(II) complexes. As it seems important to know of the effects of other ligands on both the mechanisms and the rates of the reactions, substitution reactions of zinc(II) with cobalt(II) complexes containing *meso*-butylene-

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1) H. Ogino and N. Tanaka, This Bulletin, **40**, 857 (1967).

diaminetetraacetate (*meso*-BDTA)[*2] and propylenediaminetetraacetate (PDTA)[*3] are investigated at ionic strength 0.2 and 25°C in this study.

Experimental

The preparations and standardizations of the solutions of zinc(II) nitrate, cobalt(II) nitrate and disodium dihydrogen propylenediaminetetraacetate (Na_2H_2pdta) were made by the same method as reported previously.[2,3]

meso-Butylenediaminetetraacetic acid was prepared by the following procedures: *meso*-Butylenediamine was prepared by the method of Dickey *et al.*,[4] and this diamine was converted to the *meso*-BDTA by the method of Dwyer and Garvan.[5] Crude *meso*-BDTA was recrystallized from hot water. Found: C, 40.19; H, 7.00; N, 8.03%. Calcd for $C_{12}H_{20}N_{20}O_8 \cdot 2H_2O$; C, 40.38; H, 6.78; N, 7.83%.

By measuring NMR spectra of *meso*-butylenediamine,[6] *meso*-BDTA[6] and cobalt(III)-*meso*-BDTA complex[7] in aqueous solutions, it was confirmed that *meso*-BDTA thus obtained did not contain *dl*-BDTA as impurity.

The stock solution of disodium dihydrogen *meso*-butylenediaminetetraacetate (Na_2H_2*meso*-bdta) was prepared from equimolar sodium carbonate and H_4*meso*-bdta. The concentration of *meso*-BDTA was determined by amperometric titration with the above-mentioned solutions of metal nitrates. All other chemicals used were analytical reagent grade.

It was reported that cobalt(II)-EDTA, cobalt(II)-TRDTA and cobalt(II)-PDTA give polarographic one-electron oxidation waves in acetate buffer-potassium nitrate media.[8] In this study, it was found that cobalt(II)-*meso*-BDTA gives a similar polarographic one-electron anodic wave with the half-wave potential at +0.099 V *vs.* SCE. The rates of the reactions of zinc(II) with cobalt(II)-*meso*-BDTA and cobalt(II)-PDTA were followed by the measurements of the decrease of the polarographic anodic diffusion current with time.

The measurements of both current-voltage and current-time curves were made with a Yanagimoto GR-103 Galvarecorder and a Yanagimoto AP-1 applying potentiometer. The dropping mercury electrode had an m value of 1.84 mg/sec and a drop time t_d of 4.26 sec at 55 cm of the mercury height in an air-free solution containing 0.1 M acetate buffer and 0.1 M potassium nitrate at 25°C and −0.50 V *vs.* SCE.

The ionic strength was adjusted to be 0.2 with potassium nitrate. Gelatin was added as a maximum suppressor by 0.005% in concentration. The pH of the solution was measured with a Hitachi-Horiba F-5 pH meter.

Results

It is known that zinc(II) and cobalt(II) ions form monoacetato complexes in acetate buffer solutions at ionic strength of 0.2.[9,10] Therefore, the overall reactions of zinc(II) with cobalt(II)-*meso*-BDTA or cobalt(II)-PDTA are expressed by

$$\left\{\begin{matrix}\mathrm{Zn}^{2+}\\ \upharpoonleft\!\downharpoonright\\ \mathrm{ZnOAc}^{+}\end{matrix}\right\} + \left\{\begin{matrix}\mathrm{CoY}^{2-}\\ \upharpoonleft\!\downharpoonright\\ \mathrm{CoHY}^{-}\\ \upharpoonleft\!\downharpoonright\\ \vdots\end{matrix}\right\} \underset{k^-}{\overset{k^+}{\rightleftharpoons}} \left\{\begin{matrix}\mathrm{ZnY}^{2-}\\ \upharpoonleft\!\downharpoonright\\ \mathrm{ZnHY}^{-}\\ \upharpoonleft\!\downharpoonright\\ \vdots\end{matrix}\right\} + \left\{\begin{matrix}\mathrm{Co}^{2+}\\ \upharpoonleft\!\downharpoonright\\ \mathrm{CoOAc}^{+}\end{matrix}\right\} \tag{1}$$

where Y^{4-} means a quadrivalent *meso*-BDTA or PDTA anion. The reactions were initiated by adding a known amount of cobalt(II)-*meso*-BDTA or cobalt(II)-PDTA solution into an acetate buffer-potassium nitrate solution containing zinc(II) ions in a large excess. Considering the anodic current, $\bar{i}$, given by cobalt(II)-*meso*-BDTA or cobalt(II)-PDTA complex, the forward rate constant of Eq. (1), k^+, is written as follows:[1]

$$2.303 \log \frac{\bar{i}_0^2 - \bar{i}_e \bar{i}}{\bar{i}_0(\bar{i} - \bar{i}_e)} = \frac{\bar{i}_0 + \bar{i}_e}{\bar{i}_0 - \bar{i}_e} k^+ t \tag{2}$$

where subscripts e and 0 denote equilibrium and initial conditions, respectively.

It was found that the changes in the initial concentration of cobalt(II) complex did not affect the values of k^+.

Figure 1 shows the values of k^+ which were obtained from the reactions between zinc(II) and cobalt(II)-*meso*-BDTA as a function of the hydrogen ion concentration. The change in concentrations of zinc(II) ions does not affect the values of k^+ as shown in Fig. 1. The plots fit the equation in which the rate is dependent on the

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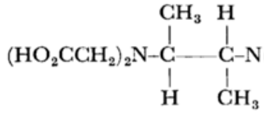
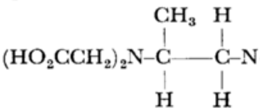
[*2] *meso*-Butylenediaminetetraacetic acid:



$$(\mathrm{HO_2CCH_2})_2\mathrm{N}\text{-}\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\text{—}\underset{\mathrm{CH_3}}{\overset{\mathrm{H}}{\mathrm{C}}}\text{-}\mathrm{N}(\mathrm{CH_2CO_2H})_2$$

[*3] Propylenediaminetetraacetic acid:



$$(\mathrm{HO_2CCH_2})_2\mathrm{N}\text{-}\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\text{—}\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\text{-}\mathrm{N}(\mathrm{CH_2CO_2H})_2$$

2) N. Tanaka and H. Ogino, This Bulletin, **38**, 439 (1965).

3) H. Ogino, *ibid.*, **38**, 771 (1965).

4) F. P. Dickey, W. Fickett and H. J. Lucus, *J. Am. Chem. Soc.*, **74**, 944 (1952).

5) F. P. Dwyer and F. L. Garvan, *ibid.*, **81**, 2955 (1959).

6) J. L. Sudmeier and C. N. Reilley, *Anal. Chem.*, **36**, 1707 (1964).

7) R. J. Day and C. N. Reilley, *ibid.*, **37**, 1326 (1965).

8) N. Tanaka and H. Ogino, This Bulletin, **38**, 1054 (1965).

9) N. Tanaka and K. Kato, *ibid*, **33**, 417 (1960).

10) N. Tanaka, M. Kamada, H. Osawa and G. Sato, *ibid.*, **33**, 1412 (1960).

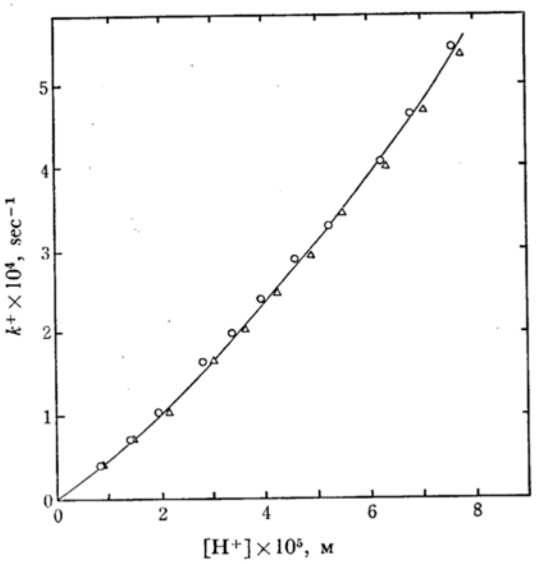


Fig. 1. k^+ for the reaction between zinc(II) and cobalt(II)-*meso*-BDTA as a function of hydrogen ion concentration. $[Zn^{2+}]_{0,app}$'s are 10.3 mM for ○ and 20.6 mM for △. Acetate ion concentrations are 0.096_8 M for ○ and 0.093_8 M for △.

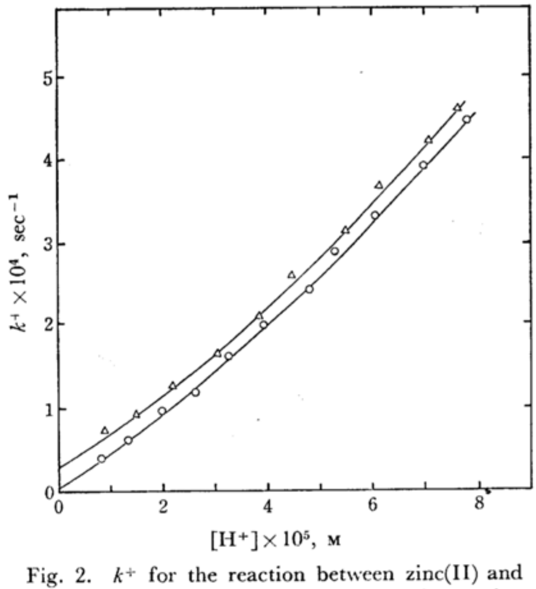


Fig. 2. k^+ for the reaction between zinc(II) and cobalt(II)-PDTA as a function of hydrogen ion concentration. $[Zn^{2+}]_{0,app}$'s are 5.15 mM for ○ and 25.8 mM for △. Acetate ion concentrations are 0.098_4 M for ○ and 0.092_4 M for △.

second power of the hydrogen ion concentration. From Fig. 1, the equation,

$$k^+ = 0.51_0 \times 10[H^+] + 0.02_7 \times 10^6[H^+]^2 \qquad (3)$$

was obtained at $[Zn^{2+}]_{0,app}$ equal to both 10.3 mM and 20.6 mM.

In Fig. 2, the values of k^+ which were obtained from the reactions between zinc(II) and cobalt(II)-PDTA are plotted against the hydrogen ion concentration. In this case, the values of k^+ increase with the concentration of zinc(II) ions. From Fig. 2, the following equations were obtained:

At $[Zn^{2+}]_{0,app} = 5.15$ mM,

$$k^+ = 0.05 \times 10^{-4} + 0.40_8 \times 10[H^+] + 0.02_0 \times 10^6[H^+]^2 \qquad (4)$$

At $[Zn^{2+}]_{0,app} = 25.8$ mM,

$$k^+ = 0.33 \times 10^{-4} + 0.43_3 \times 10[H^+] + 0.01_7 \times 10^6[H^+]^2 \qquad (5)$$

From the results mentioned above and those reported in the previous paper,[1] the reaction of zinc(II) with cobalt(II)-*meso*-BDTA and that of zinc(II) with cobalt(II)-PDTA are considered to proceed through the following reaction paths:

$$\text{(i)} \quad Zn^{2+} + CoY^{2-} \overset{k_{Zn}^{CoY}}{\rightleftharpoons} ZnY^{2-} + Co^{2+} \qquad (6)$$

$$\text{(ii)} \quad CoY^{2-} + H^+ \rightleftharpoons CoHY^- \qquad (7a)$$

$$Zn^{2+} + CoHY^- \overset{k_{Zn}^{CoHY}}{\rightleftharpoons} ZnHY^- + Co^{2+} \qquad (7b)$$

$$\text{(iii)} \quad CoY^{2-} + H^+ \overset{k_{H}^{CoY}}{\rightleftharpoons} Co^{2+} + HY^{3-} \qquad (8a)$$

$$Zn^{2+} + HY^{3-} \rightleftharpoons ZnY^{2-} + H^+ \qquad (8b)$$

$$\text{(iv)} \quad CoY^{2-} + 2H^+ \overset{k_{2H}^{CoY}}{\rightleftharpoons} Co^{2+} + H_2Y^{2-} \qquad (9a)$$

$$Zn^{2+} + H_2Y^{2-} \rightleftharpoons ZnY^{2-} + 2H^+ \qquad (9b)$$

Equation (10) was obtained on the basis of these reaction mechanisms.

$$k^+ \alpha_{CoY(H)} = k_{Zn}^{CoY} \frac{[Zn^{2+}]_{0,app}}{\alpha_{Zn(OAc)}} + \left(k_{Zn}^{CoHY} K_{CoHY}^{H} \frac{[Zn^{2+}]_{0,app}}{\alpha_{Zn(OAc)}} + k_{H}^{CoY}\right)[H^+] + k_{2H}^{CoY}[H^+]^2 \qquad (10)$$

where

$$\alpha_{CoY(H)} = 1 + K_{CoHY}^{H}[H^+]$$

$$\alpha_{Zn(OAc)} = 1 + \beta_{ZnOAc}[OAc^-]$$

$$[Zn^{2+}]_{0,app} = [Zn^{2+}]_0 + [ZnOAc^+]_0$$

$$K_{CoHY}^{H} = [CoHY^-]/[CoY^{2-}][H^+]$$

β_{ZnOAc} represents the formation constant of acetatozinc(II) complex reported in the previous paper.[9] It has been shown that the values of K_{CoHY}^{H} are $10^{3.0}$ and $10^{2.4}$ for cobalt(II)-EDTA and cobalt(II)-TRDTA complexes, respectively.[11] Since it is unlikely that the values of K_{CoHY}^{H} for cobalt(II)-*meso*-BDTA and cobalt(II)-PDTA complexes are very different in magnitude from those for Co(II)-EDTA and cobalt(II)-TRDTA complexes and all measurements were carried out

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11) G. Anderegg, *Helv. Chim. Acta*, **47**, 1801 (1964).

at pH range from 4.2 to 5.0, it is reasonable to assume that the values of $\alpha_{\mathrm{CoY(H)}}$ do not differ significantly from unity.

The rate constants for the reaction between zinc(II) and cobalt(II)-*meso*-BDTA were obtained from the analysis of Eq. (3) with the aid of Eq. (10), and are given in Table 1. It should be noted that reaction paths (i) and (ii) were not observed in this reaction.

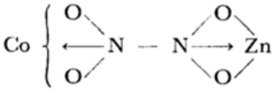
The rate constants for the reaction between zinc(II) and cobalt(II)-PDTA were obtained from the analysis of Eqs. (4), (5) and (10), and are also given in Table 1.

TABLE 1. RATE CONSTANTS AT IONIC STRENGTH 0.2 AND 25°C

Rate constant	*meso*-BDTA	PDTA
$k_{\mathrm{Zn}}^{\mathrm{CoY}}$ ($l\,\mathrm{mol^{-1}\,sec^{-1}}$)	$<7\times10^{-4}$	2×10^{-3}
$k_{\mathrm{Zn}}^{\mathrm{CoHY}}$ ($l\,\mathrm{mol^{-1}\,sec^{-1}}$)	—	$\sim2\times10^{-2}$
$k_{\mathrm{H}}^{\mathrm{CoY}}$ ($l\,\mathrm{mol^{-1}\,sec^{-1}}$)	$5._1$	$4._3$
$k_{\mathrm{2H}}^{\mathrm{CoY}}$ ($l^2\,\mathrm{mol^{-2}\,sec^{-1}}$)	3×10^4	2×10^4

Discussion

By the application of the treatment of Bydalek *et al.*,[12-14] it was proposed previously[1] that the binuclear intermediate,



(A)

was formed for the acid-independent electrophilic substitution ($\mathrm{S_E}$) reaction,

$$\mathrm{Zn^{2+} + CoY^{2-} \xrightarrow{k_{Zn}^{CoY}} ZnY^{2-} + Co^{2+}} \qquad (11)$$

where $\mathrm{Y^{4-}}$ denotes a quadrivalent EDTA or TRDTA anion. Furthermore, it was shown that the change of the rate constants of reaction (11) can be related to the equation,[1]

$$\frac{k_{\mathrm{Zn}}^{\mathrm{Cotrdta}}}{k_{\mathrm{Zn}}^{\mathrm{Coedta}}} = \frac{K_{\mathrm{Coedta}}}{K_{\mathrm{Cotrdta}}} \qquad (12)$$

It is shown in Table 2 that the order of the observed rates of $\mathrm{S_E}$ reactions is given as

$$\mathrm{TRDTA > EDTA > PDTA > \mathit{meso}\text{-}BDTA \approx 0}$$

Table 2 gives also the comparisons of the observed rate constant ratios of various $\mathrm{S_E}$ reactions, $k_{\mathrm{Zn}}^{\mathrm{CoY'}}/k_{\mathrm{Zn}}^{\mathrm{CoY}}$, and the stability constant ratios, $K_{\mathrm{CoY}}/K_{\mathrm{CoY'}}$. The observed values of PDTA system and especially *meso*-BDTA system are not in agreement with the calculated values. These disagreements are considered to be due to the following reasons: The formation of binuclear intermediate (A) is accompanied necessarily by the rotation about the ethylenic carbon-carbon bond. PDTA and *meso*-BDTA complexes contain one and two methyl groups on the ethylenic carbon-carbon bond, respectively. Hence, the rotational barrier about the ethylenic bond increases with the order,

$$\mathrm{EDTA < PDTA < \mathit{meso}\text{-}BDTA}$$

This steric hindrance of methyl groups leads to the decrease in the rate of reaction (11), so that the acid-independent $\mathrm{S_E}$ reaction of zinc(II) with cobalt(II)-*meso*-BDTA could not be observed. In addition, the inductive effect of the methyl groups increases the basicity of nitrogen in ligands and strengthens the cobalt-nitrogen bonds. This effect may assist also the decrease of reaction rate because the $\mathrm{S_E}$ reaction is accompanied by breaking of a cobalt-nitrogen bond.

TABLE 2. COMPARISONS OF RATIOS OF OBSERVED RATE CONSTANTS WITH THOSE OF STABILITY CONSTANTS

Obsd*		Calcd**
$k_{\mathrm{Zn}}^{\mathrm{Cotrdta}}/k_{\mathrm{Zn}}^{\mathrm{Coedta}}$	1.1×10	$K_{\mathrm{Coedta}}/K_{\mathrm{Cotrdta}} = 1.7\times10$
$k_{\mathrm{H}}^{\mathrm{Cotrdta}}/k_{\mathrm{H}}^{\mathrm{Coedta}}$	1.7×10	
$k_{\mathrm{Zn}}^{\mathrm{Copdta}}/k_{\mathrm{Zn}}^{\mathrm{Coedta}}$	9×10^{-3}	$K_{\mathrm{Coedta}}/K_{\mathrm{Copdta}} = 4.4\times10^{-2}$
$k_{\mathrm{H}}^{\mathrm{Copdta}}/k_{\mathrm{H}}^{\mathrm{Coedta}}$	1.4×10^{-1}	
$k_{\mathrm{Zn}}^{\mathrm{Co\mathit{meso}\text{-}bdta}}/k_{\mathrm{Zn}}^{\mathrm{Coedta}}$	$<3\times10^{-3}$	$K_{\mathrm{Coedta}}/K_{\mathrm{Co\mathit{meso}\text{-}bdta}} = 3.8\times10^{-2}$
$k_{\mathrm{H}}^{\mathrm{Co\mathit{meso}\text{-}bdta}}/k_{\mathrm{H}}^{\mathrm{Coedta}}$	1.7×10^{-1}	

* The values[1] ($l\,\mathrm{mol^{-1}\,sec^{-1}}$) used in this calculation are: 0.23 for $k_{\mathrm{Zn}}^{\mathrm{Coedta}}$, 3×10 for $k_{\mathrm{H}}^{\mathrm{Coedta}}$, $2._5$ for $k_{\mathrm{Zn}}^{\mathrm{Cotrdta}}$ and 5×10^2 for $k_{\mathrm{H}}^{\mathrm{Cotrdta}}$.

** Stability constants used in this calculation are: 15.71[3] for $\log K_{\mathrm{Coedta}}$, 14.48[3] for $\log K_{\mathrm{Cotrdta}}$, 17.07[3] for $\log K_{\mathrm{Copdta}}$ and 17.13[15] for $\log K_{\mathrm{Co\mathit{meso}\text{-}bdta}}$.

In the previous paper,[1] the value of $k_{\mathrm{H}}^{\mathrm{CoY}}/k_{\mathrm{Zn}}^{\mathrm{CoY}}$ for both EDTA and TRDTA matched best with the calculated intermediate stability constant ratio of $K_{\mathrm{Himda}}\times K_{\mathrm{el}}/K_{\mathrm{Znimda}}$, where imda denotes iminodiacetate segment and K_{el} implies a correction for an electrostatic attraction. This fact suggests that the intermediate formed in the reac-

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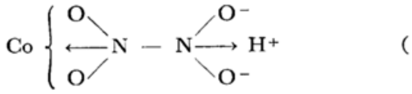
[12] T. J. Bydalek and D. W. Margerum, *Inorg. Chem.*, **2**, 678 (1963).

[13] T. J. Bydalek and M. L. Blomster, *ibid.*, **3**, 667 (1964).

[14] T. J. Bydalek and A. H. Constant, *ibid.*, **4**, 833 (1965).

[15] H. Ogino, T. Baba and N. Tanaka, unpublished results.

tion between CoY^{2-} ion and hydrogen ion corresponds to the structure,


(B)

If the basicities and steric environments of ligands are similar, it is expected that the rate constant of the reaction of CoY^{2-} with a hydrogen ion, $k_{\mathrm{H}}^{\mathrm{CoY}}$, can be related to Eq. (13), which is analogous to Eq. (12):

$$\frac{k_{\mathrm{H}}^{\mathrm{CoY'}}}{k_{\mathrm{H}}^{\mathrm{CoY}}} \fallingdotseq \frac{K_{\mathrm{CoY}}}{K_{\mathrm{CoY'}}} \qquad (13)$$

In Table 2, are also given the comparison of the ratios of observed rate constants, $k_{\mathrm{H}}^{\mathrm{CoY}}/k_{\mathrm{H}}^{\mathrm{CoY}}$, and those of the stability constants, $K_{\mathrm{CoY}}/K_{\mathrm{CoY'}}$. Although the value of $k_{\mathrm{H}}^{\mathrm{Cotrdta}}/k_{\mathrm{H}}^{\mathrm{Coedta}}$ is in good agreement with the value of $K_{\mathrm{Coedta}}/K_{\mathrm{Cotrdta}}$, the observed values of $k_{\mathrm{H}}^{\mathrm{Copdta}}/k_{\mathrm{H}}^{\mathrm{Coedta}}$ and $k_{\mathrm{H}}^{\mathrm{Co}meso\text{-}\mathrm{bdta}}/k_{\mathrm{H}}^{\mathrm{Coedta}}$ do not agree with the ratios of the stability constant. However, these disagreements are not so marked as those in the values of $k_{\mathrm{Zn}}^{\mathrm{CoY'}}/k_{\mathrm{Zn}}^{\mathrm{Coedta}}$. This seems to be attributable to the fact that the complete rotation about the ethylenic carbon-carbon bond is not required for the reaction between CoY^{2-} and a hydrogen ion taking place. In fact, molecular models show that both hydrogen and cobalt ions can coordinate simultaneously to each nitrogen atom in a ligand without complete rotation about the ethylenic bond. An extreme case is the reaction between cyclohexanediaminetetraacetato complex (CyDTA complex) ions and hydrogen ions. Although cyclohexane ring in CyDTA forbids the rotation of the two iminodiacetate groups, the reaction of CyDTA complex ions with hydrogen ions proceeds.[16,17]

TABLE 3. VALUES OF $k_{\mathrm{H}}^{\mathrm{CoY}}$ AND $k_{\mathrm{Co}}^{\mathrm{HY}}$ AT IONIC STRENGTH 0.2 AND 25°C

Ligand	$k_{\mathrm{H}}^{\mathrm{CoY}}$ $l\ \mathrm{mol}^{-1}\ \mathrm{sec}^{-1}$	$k_{\mathrm{Co}}^{\mathrm{HY}}$ $l\ \mathrm{mol}^{-1}\ \mathrm{sec}^{-1}$	Ref.
TRDTA	5×10^2	8×10^6	1
EDTA	3×10	8×10^6	1
meso-BDTA	$5._1$	4×10^6	This work
PDTA	$4._3$	7×10^6	This work

In Table 3, are shown the values of $k_{\mathrm{H}}^{\mathrm{CoY}}$ for various ligands. The values of $k_{\mathrm{H}}^{\mathrm{CoY}}$ can be related to the rate constants, $k_{\mathrm{Co}}^{\mathrm{HY}}$ of the complex-forming reactions,

$$\mathrm{Co}^{2+} + \mathrm{HY}^{3-} \underset{k_{\mathrm{H}}^{\mathrm{CoY}}}{\overset{k_{\mathrm{Co}}^{\mathrm{HY}}}{\rightleftharpoons}} \mathrm{CoY}^{2-} + \mathrm{H}^{+} \qquad (14)$$

with the equation,

$$k_{\mathrm{H}}^{\mathrm{CoY}} = \frac{k_{\mathrm{Co}}^{\mathrm{HY}}}{K_{\mathrm{CoY}}K_{\mathrm{HY}}} \qquad (15)$$

where K_{HY} denotes the fourth dissociation constant of $\mathrm{H_4Y}$. The values of $k_{\mathrm{Co}}^{\mathrm{HY}}$ calculated by Eq. (15) are also given in Table 3. In accord with the previous conclusion that the second-order rate constants of the complex-forming reactions of a metal ion with related ligands (with the same charge and a similar size) are almost the same,[1,18] the values of $k_{\mathrm{Co}}^{\mathrm{HY}}$ given in Table 3 are essentially identical for various ligands. Hence, the nature of ligands may reflect predominantly to the values of $k_{\mathrm{H}}^{\mathrm{CoY}}$.

It may be seen in Table 3 that the order of the values of $k_{\mathrm{H}}^{\mathrm{CoY}}$ is as follows:

$$\mathrm{TRDTA} > \mathrm{EDTA} > meso\text{-}\mathrm{BDTA} > \mathrm{PDTA}$$

The increase in basicities of PDTA and *meso*-BDTA by the presence of methyl groups may cause the decrease in the value of $k_{\mathrm{H}}^{\mathrm{CoY}}$ with the following order:

$$k_{\mathrm{H}}^{\mathrm{Coedta}} > k_{\mathrm{H}}^{\mathrm{Copdta}} > k_{\mathrm{H}}^{\mathrm{Co}meso\text{-}\mathrm{bdta}}$$

However, as is seen in Table 3, the value of $k_{\mathrm{H}}^{\mathrm{Co}meso\text{-}\mathrm{bdta}}$ is larger than the value of $k_{\mathrm{H}}^{\mathrm{Copdta}}$ in spite of the increase of the number of methyl groups in the ligand. This can be understood by considering the conformation of methyl groups in the coordinated ligands. There are two possibilities of the orientation of a methyl group on the N–C–C–N chelate ring of the coordinated PDTA; that is, an equatorial and an axial orientations. The complex with a methyl group of equatorial orientation is strainless as in the EDTA complex, while the complex with a methyl group of axial orientation is more crowded on the chelate and is strained. In fact, it is known that the orientation of a methyl group of the coordinated PDTA is equatorial.[19–22] In the *meso*-BDTA complex, there are two methyl groups on the N–C–C–N chelate ring. Molecular models reveal that the orientation of one methyl group in the coordinated *meso*-

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[16] D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, **2**, 683 (1963).

[17] D. W. Margerum, P. J. Menardi and D. L. Janes, *ibid.*, **6**, 283 (1967).

[18] H. Ogino and N. Tanaka, This Bulletin, **40**, 852 (1967).

[19] D. H. Busch and D. W. Cooke, *J. Inorg. Nucl. Chem.*, **23**, 145 (1961).

[20] F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **83**, 2610 (1961).

[21] F. P. Dwyer and T. E. MacDermatt, *ibid.*, **85**, 2916 (1963).

[22] R. J. Day and C. N. Reilley, *Anal. Chem.*, **37**, 1326 (1965).

BDTA is equatorial and the orientation of another methyl group is necessarily axial. Therefore, it is considered that the *meso*-BDTA complex is not more stable than the PDTA complex due to the presence of axial methyl group.

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