

Zinc(II) Tetraaza-Crown-Alkanoic Acids 착물의 형성 및 해리 반응속도론

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Formation and Dissociation Kinetics of Zinc(II) Complexes of Tetraaza-Crown-Alkanoic Acids

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요 약. 1,4,7,10-tetraaza-13,16-dioxacyclooctadecane-*N,N',N'',N'''*-tetraacetic acid (1), 1,4,7,10-tetraaza-13,16-dioxacyclooctadecane-*N,N',N'',N'''*-tetramethylacetic acid (2), 및 1,4,7,10-tetraaza-13,16-dioxacyclooctadecane-*N,N',N'',N'''*-tetrapropionic acid (3)와 Zn^{2+} 착물의 형성 및 해리 속도를 멈춤-흐름법 및 분광학적 방법으로 측정하였다. 측정 조건은 온도 25.0 ± 0.1 °C 및 이온강도 0.10 M $NaClO_4$ 이었다. Zn^{2+} 이온과 1과 2의 형성 반응은 빠르게 중간 생성물(ZnH_3L^+)*를 형성한다. 여기서 Zn^{2+} 이온은 부분적으로 배위되어 있고 속도 결정 단계는 최종 생성물이었다. pH 범위 4.76-5.76에서, 2가 양성자 (H_2L^{2+}) 형태가 매우 낮은 농도임에도 불구하고 속도론적으로 활성화종임을 알 수 있었다. 또한 중간체 착물의 안정도 상수 ($\log K_{(ZnH_3L^+)}$)와 고유 물분자-보조 속도상수(k_{OH})가 속도론적 자료로부터 계산되었다. Zn^{2+} 이온과 1, 2, 및 3의 해리 반응은 아세테이트 완충 용액 하에서 청소균 Cu^{2+} 이온을 이용하여 측정하였다. 모든 착물의 해리 반응은 산-무관 및 산촉매 반응으로 진행됨을 알 수 있었다. Zn^{2+} 착물의 해리 속도에 영향을 미치는 완충 용액 및 Cu^{2+} 농도의 효과를 알아보았으며, 아울러 리간드 효과를 결과지에 매달려있는 치환기와 킬레이트 고리크기로 논하였다.

ABSTRACT. The formation and dissociation rates of Zn^{2+} Complexes with 1,4,7,10-tetraaza-13,16-dioxacyclooctadecane-*N,N',N'',N'''*-tetraacetic acid (1), 1,4,7,10-tetraaza-13,16-dioxacyclooctadecane-*N,N',N'',N'''*-tetramethylacetic acid (2), and 1,4,7,10-tetraaza-13,16-dioxacyclooctadecane-*N,N',N'',N'''*-tetrapropionic acid (3) have been measured by stopped-flow and conventional spectrophotometry. Observations were made at 25.0 ± 0.1 °C and at an ionic strength of 0.10 M $NaClO_4$. The formation reactions of Zn^{2+} ion with 1 and 2 took place by the rapid formation of an intermediate complex (ZnH_3L^+)* in which the Zn^{2+} ion is incompletely coordinated. This might then lead to be a final product in the rate-determining step. In the pH range 4.76-5.76, the diprotonated (H_2L^{2+}) form is the kinetically active species despite of its low concentration. The stability con-

stants ($\log K_{Zn^{2+}L^{n-}}$) and specific water-assisted rate constants (k_{OH}) of intermediate complexes have been determined from the kinetic data. The dissociation reactions of Zn^{2+} complexes of **1**, **2**, and **3** were investigated with Cu^{2+} ions as a scavenger in acetate buffer. All complexes exhibit acid-independent and acid-catalyzed contributions. The effect of buffer and Cu^{2+} concentration on the dissociation rate has also been investigated. The ligand effect on the dissociation rate of Zn^{2+} complexes is discussed in terms of the side-pendant arms and the chelate ring sizes of the ligands.

INTRODUCTION

The metal complexes with the macrocyclic polyoxa- and polyazapolycarboxylate have attracted considerable attention because of their structural, equilibrium, and kinetic behavior, which are often quite different from those of the analogous linear polyaminopolycarboxylates.¹⁻³ Several factors are known to influence the stability and kinetics of the metal complexes with macrocyclic compounds.⁴⁻⁸ These factors include the metal ion size and ligand topology, such as internal cavity size, the number of donor atoms, ligand basicity and rigidity, and side arm substituents. Recently, the studies on the formation and dissociation kinetics of the metal complexes with N-pendant arms N_3O_2 (1,4,10-triaza-7,13-dioxacyclopentadecane)⁹⁻¹¹ and N_5O_3 (1,7,13-triaza-4,10,16-trioxacyclooctadecane)¹² were reported. In these studies, the formation kinetic data of these complexes conformed to the rapid formation of an intermediate, which converted to the final complex. On the other hand, the dissociation of these complexes proceeded via both acid-independent and acid-catalyzed pathways, and dissociation rates varied with the size of metal ions and the ligand topology.

In this paper, we report the formation and dissociation kinetics of Zn^{2+} complexes with macrocyclic tetraaza-

dioxo ligands with acetate, methylacetate, and propionate groups as N-pendant arms (Fig. 1). We intend to investigate the effect of the ring size and rigidity of the macrocycle as well as ring substituent effect on the kinetic properties of these complexes.

EXPERIMENTAL SECTION

Reagents. 1,4,7,10-Tetraaza-13,16-dioxacyclooctadecane tetrahydrobromide was synthesized by previously reported procedures.¹³ The ligands, 1,4,7,10-tetraaza-13,16-dioxacyclooctadecane-*NN'N''N'''*-tetraacetic acid (**1**), 1,4,7,10-tetraaza-13,16-dioxacyclooctadecane-*NN'N''N'''*-tetramethylacetic acid (**2**), and 1,4,7,10-tetraaza-13,16-dioxacyclooctadecane-*NN'N''N'''*-tetrapropionic acid (**3**), were prepared by the literature method.¹⁴ The concentrations of the ligand stock solution were determined by titration against a standardized $Cu(ClO_4)_2$ solution with murexide as an indicator. A stock solution of Zn^{3+} was prepared from $ZnCl_2$ (Aldrich, 99.9%), and its concentration was determined by complexometric titration with xylenol orange as indicator. All chemicals used in the synthesis were of reagent grade and were used without further purification. All solutions were made in deionized water.

Measurements. The ionic strength of the sample solutions was adjusted to 0.10 M with $NaClO_4$. Solution pH values were measured with a Beckman combination electrode and Beckman $\Phi 71$ pH meter. The H^+ ion concentration was established from the measured pH value by the procedures reported previously.³ Kinetic measurements were carried out with a Hi-Tech stopped-flow spectrophotometer interfaced with a scientific data acquisition system and a UVDEB-610 spectrophotometer at 25.0 ± 0.1 °C with the use of a Lauda RM 6 circulatory water bath.

The formation rates of $Zn(L)$ were studied in weakly buffered solutions (0.01 M acetic acid/sodium acetate)

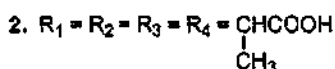
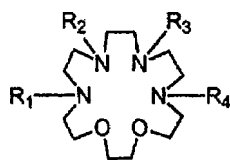


Fig. 1. Structure of the tetraaza-crown-alkanoic acids.

by monitoring the pH decrease with bromocresol green (4.6<pH<5.2, observation wavelength 615 nm) as an indicator.¹⁵ The concentration of the ligands was 2.0×10^{-4} M, while that of Zn^{2+} was varied between 4.0×10^{-4} and 4.0×10^{-3} M.

The dissociation rates of Zn(L) were studied in acidic solutions in the presence of excess Cu^{2+} ions. Under these conditions, the dissociation reaction takes place and the progress of the exchange may be monitored by the formation of Cu(L) at 285 nm. The concentration of Zn(L) was 5.0×10^{-5} M, while that of the Cu^{2+} ion was varied between 2.0×10^{-4} and 1.0×10^{-3} M. The buffer solutions were made by varying the ratio of concentration of acetic acid and sodium acetate necessary for attainment of the desired pH.

RESULTS AND DISCUSSION

Formation kinetics. The formation rates of the complexes were studied at different pH values as a function of excess $[Zn^{2+}]$ to ensure first-order kinetics. At a given pH, the measured pseudo-first-order rate constant (k_{obs}) values increased with increasing $[Zn^{2+}]$, and plots of k_{obs} versus $[Zn^{2+}]$ show saturation behavior. This is characteristic of rapid formation of the intermediate complex that rearranges to the final product in a rate-determining step. A similar behavior was also observed for the formation of $M(N_3O_2Ac)$ ($M=Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, N_3O_2Ac=1,4,10$ -triaza-7,13-dioxacyclopentadecane- N, N', N'' -tri-acetic acid).¹⁰ The dependence of k_{obs} values on $[Zn^{2+}]$ can be expressed as¹⁶.

$$k_{obs} = \frac{k_1 K [Zn^{2+}]}{1 + K [Zn^{2+}]} \quad (1)$$

where K is the equilibrium constant for the formation of the intermediate complex and k_1 is the rate constant for the rearrangement of the intermediate to the final product. Plots of $1/k_{obs}$ against $1/[Zn^{2+}]$ lead to straight lines as shown in Fig. 2. The values of k_1 , K , and the second-order rate constant $k_2=k_1K$ were obtained from eq 1 and are summarized in Table 1. The protonated forms of 1 and 2 could contribute to the kinetics of complex formation of Zn^{2+} ion between pH 4.77 and 5.79. The concentrations of protonated ligands were calculated with the use of ligand protonation constants.¹⁴ For example, 1,

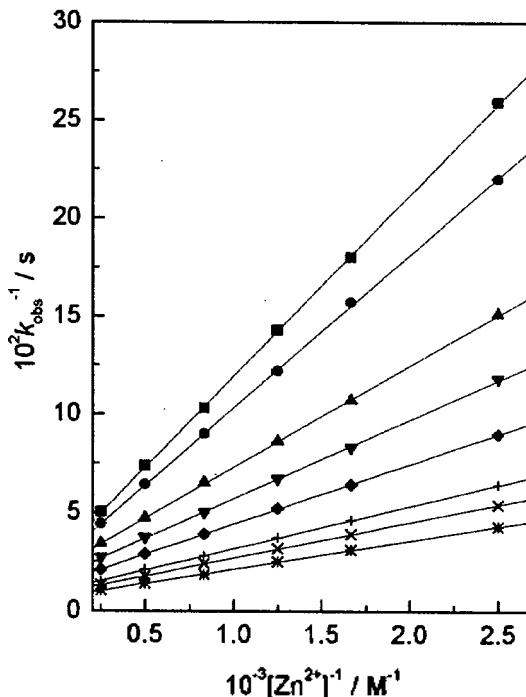
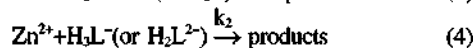
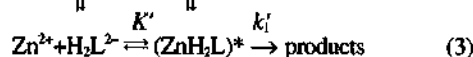
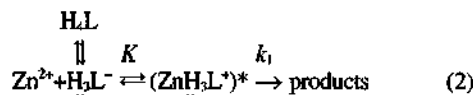


Fig. 2. Plots of k_{obs}^{-1} vs $[Zn^{2+}]^{-1}$ for the formation kinetics of Zn(L) at different pH values. $[L]=2.0 \times 10^{-4}$ M; $[OAc^-]=0.01$ M; $T=25.0 \pm 0.1$ °C; $I=0.10$ M ($NaClO_4$); pH=4.79 (*), 4.91 (x), 5.12 (+), 5.27 (◆), 5.41 (▼), 5.58 (▲), 5.66 (●), 5.79 (■).

H_3L^- is major species in this pH range (from 60.57 to 93.42%), H_2L is an important contributor (from 38.67 to 5.89%), and H_2L^{2-} represents from 0.043 to 0.68% of the total ligand concentration. On the basis of these results, the formation reaction of Zn^{2+} ion with ligands may be expressed by eqs 2-4.



The stability constants of the intermediates $(ZnH_3L^+)^*$ may be evaluated from K values at a given pH, the ligand protonation constants, and with the use of eq 5.

$$K_{(ZnH_3L^+)^*} = K(1 + K_4[H^+] + K_4K_5[H^+]^2) \quad (5)$$

The calculated stability constants of the intermediate complexes of 1 and 2 are summarized in Table 2. The

Table 1. Rate data for Zn²⁺ complex formation with 1 and 2 at 25.0±0.1 °C, I=0.10 M (NaClO₄), and [OAc⁻]=1.0×10⁻² M

Ligands	pH	$k_1(s^{-1})$	$K(M^{-1})$	$k_2(M^{-1}s^{-1})$
1	4.79	$(3.36±0.11)×10^1$	$(2.99±0.14)×10^2$	$(1.09±0.10)×10^4$
	4.91	$(3.99±0.06)×10^1$	$(3.22±0.10)×10^2$	$(1.28±0.08)×10^4$
	5.12	$(4.83±0.12)×10^1$	$(3.94±0.16)×10^2$	$(1.91±0.15)×10^4$
	5.27	$(5.91±0.15)×10^1$	$(4.23±0.17)×10^2$	$(2.50±0.16)×10^4$
	5.41	$(7.49±0.07)×10^1$	$(4.36±0.05)×10^2$	$(3.27±0.06)×10^4$
	5.58	$(11.2±0.12)×10^1$	$(4.54±0.15)×10^2$	$(4.61±0.12)×10^4$
	5.66	$(11.6±0.13)×10^1$	$(4.70±0.18)×10^2$	$(5.47±0.18)×10^4$
	5.79	$(15.2±0.17)×10^1$	$(4.53±0.19)×10^2$	$(6.86±0.21)×10^4$
2	4.77	$1.10±0.05$	$(1.01±0.05)×10^2$	$(1.10±0.06)×10^2$
	4.89	$1.13±0.07$	$(1.45±0.08)×10^2$	$(1.64±0.14)×10^2$
	5.11	$1.41±0.08$	$(1.86±0.10)×10^2$	$(2.61±0.17)×10^2$
	5.26	$1.68±0.05$	$(2.21±0.07)×10^2$	$(3.70±0.15)×10^2$
	5.40	$2.13±0.09$	$(2.26±0.11)×10^2$	$(4.80±0.18)×10^2$
	5.58	$3.00±0.07$	$(2.39±0.08)×10^2$	$(7.17±0.20)×10^2$
	5.65	$3.46±0.14$	$(2.79±0.15)×10^2$	$(9.64±0.27)×10^2$
	5.78	$4.27±0.12$	$(2.91±0.16)×10^2$	$(12.4±0.29)×10^2$

Table 2. Stability constants ($\log K_{(ZnH_3L^+)^*}$), second-order rate constants ($k_{H_2L^2}$), and water-assisted rate constants (k_{OH}) of the intermediate complexes at 25.0±0.1 °C and I=0.10 M (NaClO₄)

Complexes	$\log K_{(ZnH_3L^+)^*}$	$k_{H_2L^2}(M^{-1}s^{-1})$	$k_{H_3L^+}(M^{-1}s^{-1})$	$k_{OH}(M^{-1}s^{-1})$
Zn(1)	$2.70±0.04$	$(1.19±0.04)×10^8$	$(9.05±0.16)×10^6$	$(1.61±0.06)×10^{10}$
Zn(2)	$3.24±0.06$	$(8.95±0.25)×10^6$	$(7.47±0.25)×10^5$	$(4.71±0.08)×10^8$

stability constants of the intermediates obtained here are larger than those for the corresponding monoacetate and monomethylacetate complexes.¹⁷ This suggests that the Zn²⁺ ion is coordinated to more than one carboxylate group in the intermediate. The stability constant for the intermediate of Zn(2) is somewhat larger than that of Zn(1). This fact may be attributed to the thermodynamic stability ($\log \beta_{Zn(1)}=13.00$ versus $\log \beta_{Zn(2)}=14.53$).¹⁴ From the kinetic data, the second-order rate constant $k_{H_2L^2}$ also represents $(k_1K)_{H_2L^2}$. If one species is markedly more reactive than all the others, the second-order rate constant could be obtained from the following expression.¹⁸

$$k_2 = k_{H_2L^2} (1 + K_{H(OH)L}^{-1} [H^+])^{-1} \quad (6)$$

where $K_{H(OH)L}$ is the protonation constants of 1 and 2. From the plots of k_2 against $(1 + K_{H(OH)L}^{-1} [H^+])^{-1}$, the second-order rate constants for the H₂L²⁻ and H₃L⁻ species are collected in Table 2. Despite of their very low concentration in the pH range observed, the H₂L²⁻ species appears to be kinetically much more reactive than the H₃L⁻ species, even though the latter is the predominant

species in solution. The same conclusion was reported previously by Kasprzyk and Wilkins.¹⁵ The low reactivity of the H₃L⁻ form may be assigned to the formation of trizwitterionic form of 1 and 2. The three N-H⁺ groups in the 18-membered cycle of H₃L⁻ probably hinder the rearrangement of the intermediate complex into the final chelate product due to the electrostatic repulsion with the incoming Zn²⁺ ion.

The values of k_1 increased with increasing pH as shown in Table 1. This indicates that the rearrangement of the intermediate complex into the final chelate product is catalyzed by the hydroxide ion. A plot of k_1 vs $[H^+]^{-1}$ is expected to be a straight line as shown in Fig. 3. This observation is consistent with the previously reported works.^{9,10,12,19} An expression consistent with this functional dependence is given by eq 7.¹⁹

$$k_1 = k_{H_2O} + k_{OH} K_w [H^+]^{-1} \quad (7)$$

where k_{H_2O} and k_{OH} are the water and hydroxide-catalyzed rate constants of the rearrangement of the intermediate. The k_{OH} values calculated from the slope of the straight

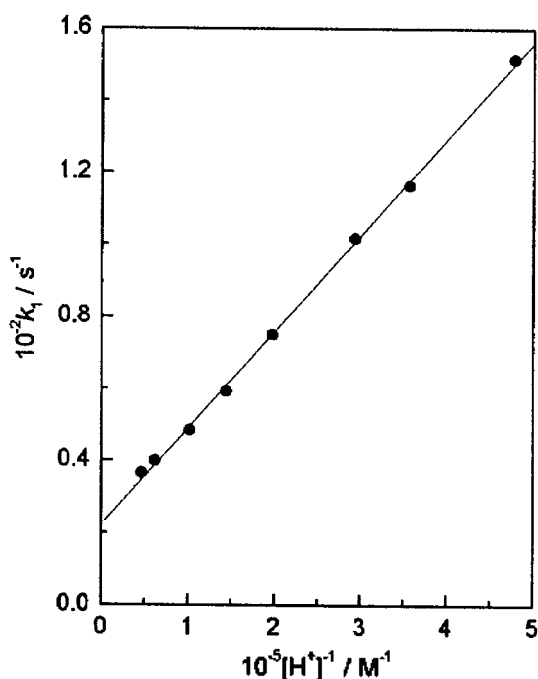


Fig. 3. Plots of k_1 vs $[H^+]^{-1}$ for the formation kinetics of Zn(1) at 25.0 ± 0.1 °C and $I=0.10$ M (NaClO₄).

line in Fig. 3 and eq 7 ($\log K_a=13.78$) are listed in Table 2. A significant contribution from the base form of the buffer is not expected, since the concentration of buffer used in the present work is low. The k_{off} value of Zn(2) is about 30 times smaller than that of Zn(1). This indicates that the substitution of four methyl groups on the acetate pendant arms of **1** makes the ligand more rigid.²⁰

Dissociation kinetics. Since the stability constants of Cu²⁺ complexes are much greater than those of corresponding Zn²⁺ complexes,¹⁴ the exchange reaction is driven to completion in the presence of excess Cu²⁺ ions



where L is the H₃L⁻ form under the pH range 4.37-5.58. The experimental data show excellent pseudo-first-order reaction rates. The observed rate constants (k_{obs}) were found to be independent of [OAc⁻] but dependent on [Cu²⁺]. The dependence of k_{obs} on [Cu²⁺] is plotted in Fig. 4 for different pH values. In each case, the data fit straight lines with measurable nonzero intercepts which is the evidence that the exchange reaction proceeds via both of [Cu²⁺]-independent and [Cu²⁺]-dependent path-

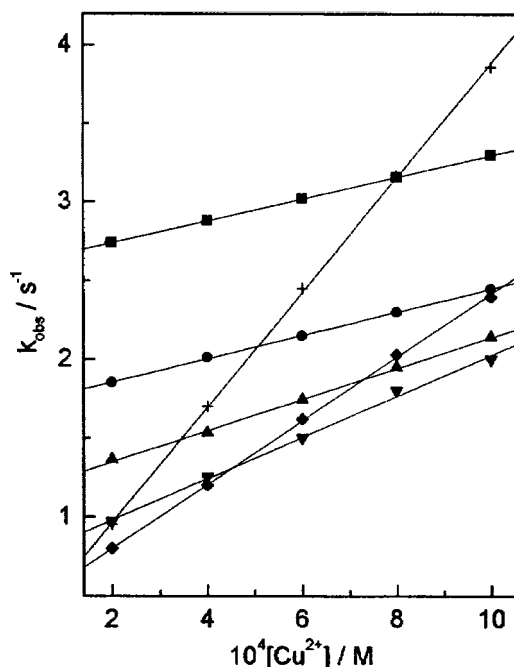


Fig. 4. Plots of k_{obs} vs $[Cu^{2+}]$ for the dissociation kinetics of Zn(1) at different pH values. $[Zn(1)]=5.0 \times 10^{-5}$ M; $[OAc^-]=0.01$ M; $T=25.0 \pm 0.1$ °C; $I=0.10$ M (NaClO₄); pH=4.43 (■), 4.63 (●), 4.80 (▲), 5.00 (▼), 5.31 (◆), 5.60 (+).

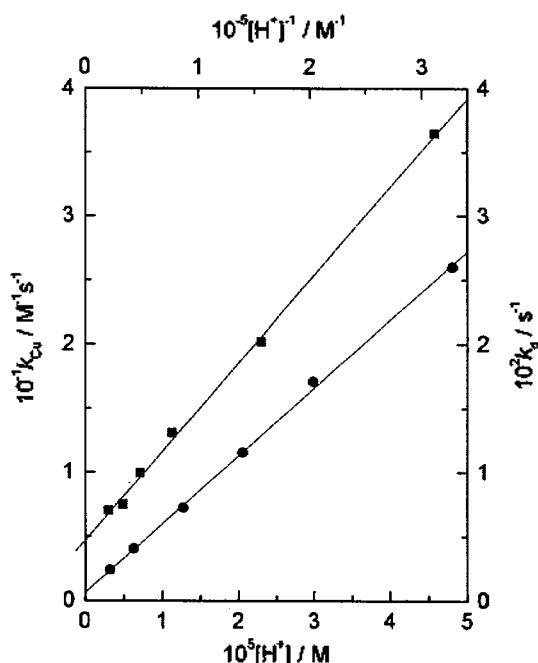


Fig. 5. Plots of k_d vs $[H^+]^{-1}$ and k_{cu} vs $[H^+]^{-1}$ for the dissociation kinetics of Zn(1). $[Zn(1)]=5.0 \times 10^{-5}$ M; $[OAc^-]=0.01$ M; $T=25.0 \pm 0.1$ °C; $I=0.10$ M (NaClO₄).

Table 3. Rate constants for the dissociation reactions of Zn²⁺ complexes of macrocyclic ligands at 25.0±0.1 °C and I=0.10 M (NaClO₄)

Complexes	k_d (s ⁻¹)	k_H (M ⁻¹ s ⁻¹)	k_{Cu} (M ⁻¹ s ⁻¹)	k_{CuOH^+} (M ⁻¹ s ⁻¹)
Zn(1)	(6.43±0.21)×10 ⁻⁴	(5.31±0.08)×10 ²	4.69±0.29	(5.07±0.10)×10 ³
Zn(2)	(4.59±0.32)×10 ⁻⁴	(4.37±0.13)×10 ²	4.28±0.07	(4.53±0.06)×10 ³
Zn(3)	(6.06±0.23)×10 ⁻³	(1.29±0.09)×10 ³	(1.28±0.31)×10 ²	(8.64±0.11)×10 ⁵
Zn(DTPA) ^b	1.8×10 ¹	3.0×10 ⁵	2.0×10 ⁴	a

^aNot observed. ^bReference 23.

way. The latter is first-order in Cu²⁺ ion concentration. Accordingly,

$$k_{obs} = k_d + k_{Cu}[Cu^{2+}] \quad (9)$$

where k_d and k_{Cu} are the functions of acidity, [H⁺]. Fig. 5 shows that k_d is proportional to [H⁺], while k_{Cu} is proportional to [H⁺]⁻¹. Based on these data, the overall rate of dissociation reaction can be expressed by:

$$\text{Rate} = k_d[Zn(L)] + k_H[Zn(L)][H^+] + k_{Cu}[Zn(L)][Cu^{2+}] + k_{CuOH^+} \frac{[Zn(L)][Cu^{2+}][H^+]^{-1}}{[H^+]^{-1}} \quad (10)$$

The rate constants (k_d , k_H , k_{Cu} , and k_{CuOH^+}) calculated from the experimental data are listed in Table 3. The reaction between Zn(L) complexes and Cu²⁺ ion proceeds by reaction pathways that are similar to those reported for the exchange of the metal ions in their macrocyclic complexes.¹² As can be seen, the first and second terms in eq 10 are responsible for the dissociative pathway of the Cu²⁺-independent mode. The rate-determining step involves the loss of Zn²⁺ ion from the complexes and the rapid reaction of the released ligand with Cu²⁺ ion. Equation 10 also represents the associative pathway of the Cu²⁺-dependent mode, which is composed of the direct attack of the Cu²⁺ ion on the partially dissociated Zn-L and the [H⁺]⁻¹ dependence. [H⁺]⁻¹ behavior can be interpreted by the existence of the attack of hydrolyzed copper species (CuOH⁺) on Zn-L, even though the investigated pH is not higher. k_{CuOH^+} is therefore calculated by the expression.

$$k_{CuOH^+} = k_{CuOH^+} \beta_{1CuOH^+} \quad (11)$$

where $\beta_{1CuOH^+} (=K_{CuOH^+}/K_w)$ is a stability constant (i.e. 2.0×10^{-8}).²¹

The effect of ligand on the dissociation rate constants of dissociation reactions of Zn²⁺ complexes can be seen by comparing the values in Table 3 along with other lin-

ear DTPA (diethylenetriaminepentaacetic acid). A comparison of the dissociation rate constants of Zn²⁺ complexes indicates that the rates of the dissociative pathway decrease in the order Zn(3) > Zn(1) > Zn(2). Both rate constants are significantly affected by the side arm substituents and chelate ring sizes of the ligands. The dissociation rate of Zn(2) complex was found to be slower than that of Zn(1) complex. This indicates that the substitution of four methyl groups on the acetate pendant arms of **1** increases the rigidity of the macrocycle, yielding a complex with even greater kinetic stability. A methyl substitution in other triaza-crown-alkanoic acid has also been observed to increase the inertness of their resulting complexes.¹² The rate constant of both the acid-independent and acid-catalyzed pathway of the Zn(3) complex is about one order of magnitude larger than that of the corresponding Zn(1). This fact may be attributed to the destabilizing effect of the six-membered N-Zn-O chelate ring involving the four propionate group of **3**. A similar result has been used to explain the fact that the dissociation rate of Eu(ENDPDA) (ethylenedinitrilo-N,N'-di(3-propanoic)-N,N'-diacetic acid)²² is much faster than that of Eu(EDTA)⁻. On the other hand, the acid-independent and acid-catalyzed rate constants of Zn(1) are much smaller than those of Zn(DTPA)²³, even though the stability constant of Zn(1) ($\log \beta = 13.0$)¹⁴ is much smaller than that of Zn(DTPA) ($\log \beta = 18.29$).¹⁷ This may be due to the remarkable rigidity of cyclic tetraazadioxo ring of **1** compared to flexibility of linear DTPA.

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