Pergamon

Polyhedron Vol. 14, No. 10, pp. 1299–1306, 1995
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0277–5387/95 $9.50+0.00

0277–5387(94)00404–8

KINETICS OF FORMATION AND DISSOCIATION OF TRIAZA-CROWN-ALKANOIC ACID COMPLEXES OF CERIUM(III) AND EUROPIUM(III)

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(*Received* 31 *August* 1994; *accepted* 13 *October* 1994)

Abstract—The formation and dissociation rates of some lanthanide complexes of the 1,4,10-triaza-7,13-dioxacyclopentadecane-*N*,*N*′,*N*″-triacetic acid (**1**) and 1,4,10-triaza-7,13-dioxacyclopentadecane-*N*,*N*′,*N*″-tripropionic acid (**2**) have been measured by using stopped-flow and conventional spectrophotometry. Observations were made at 25.0±0.1°C and at an ionic strength of 0.1 M $NaClO_4$. The complexation of Ce^{3+} and Eu^{3+} ions by ligand **1** proceeds through the formation of an intermediate complex in which the metal ion is incompletely coordinated. This may then proceed to a final product. Between pH 4.57 and 5.61, the monoprotonated (HL^{2-}) form is the kinetically active species despite its low concentration. The dissociation reactions of Ln–**1** and Ln–**2** complexes were investigated with Cu^{2+} ions as scavenger in an acetate buffer. All complexes exhibit acid-independent and acid-catalysed contributions. The buffer and Cu^{2+} concentration dependence of the dissociation rate has also been investigated. The metal and ligand effects on the dissociation rate of some lanthanide complexes are discussed by comparing the rate constants with those of analogous linear and macrocyclic polyaminepolycarboxylate systems.

There has been considerable interest in the coordination chemistry, thermodynamics and kinetics of lanthanide complexes with macrocyclic polyazapolycarboxylate because of their use as aqueous NMR shift reagents,[1,2] magnetic resonance imaging (MRI) contrast agents[3,4] and lanthanide-ion-selective reagents.[5,6] The rates of formation and dissociation of lanthanide complexes with these ligands are affected by several factors,[7,13] including metal ion size, cavity size, steric factors, conformation and preorganization of the free ligand. Formation and dissociation kinetics of lanthanide complexes of NOTA (1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetic acid) have been reported.[14] Formation of the intermediate complex was proposed, followed by rearrangement in the rate-determining step to the final product. The effect of metal ion size on the formation rate of the lanthanide complexes was not as significant as observed for the dissociation reaction of these complexes. Brucher *et al.*[15] also reported the formation and dissociation

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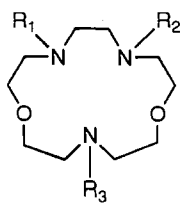
rates of Eu^{3+} complexes of DETA (1,4,7-triazacyclodecane-*N*,*N*′,*N*″-triacetic acid), MeDETA (9-methyl-1,4,7-triazacyclodecane-*N*,*N*′,*N*″-triacetic acid) and Me_2DETA (9,9-dimethyl-1,4,7-triazacyclodecane-*N*,*N*′,*N*″-triacetic acid). Dissociation of the complexes takes place via both acid-independent and acid-catalysed pathways. An increase in cavity size from nine to ten and introduction of a methyl group on a ring carbon of the ligand leads to increased kinetic stabilities of the complexes. Additional studies on the lanthanide complexes of K21DA (1,7,-diaza-4,10,13-trioxacyclopentadecane-*N*′,*N*″-diacetic acid) and K22DA (1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N*′,*N*″-diacetic acid) demonstrated the unusual charge density and cavity size dependence of the thermodynamic stability and dissociation rates.[16,17]

We initiated this kinetic study to understand the effects of metal ion size, number of donor atoms, the cavity and chelate ring size of the macrocycle ligands. We have studied the formation and dissociation kinetics of lanthanide complexes with 1,4,10-triaza-7,13-dioxacyclopentadecane-*N*,*N*′,*N*″-triacetic acid (**1**) and 1,4,10-triaza-7,13-dioxacyclopentadecane-*N*,*N*′,*N*″-tripropionic acid (**2**) (Fig. 1).

EXPERIMENTAL

Chemicals and reagents

1,4,10-Triaza-7,13-dioxacyclopentadecane trihydrobromide was prepared by the previous procedure.[18] Ligands **1** and **2** were synthesized according to the method of Martell *et al.*[19] The ligands were characterized by ^{1}H NMR, mass spectrometry and elemental analysis. The concentration of the ligand stock solutions was determined by titration against a standard $Cu(ClO_4)_2$ solution using murexide as an indicator. Stock solutions of Ce^{3+} and Eu^{3+} were prepared from $CeCl_3$ and Eu_2O_3 (Aldrich, 99.9%) and their concentrations determined by complexometric titration using Xylenol Orange as indicator. All other chemicals used were of analytical grades and were used without further purification. All solutions were made in deionized water.



1, $R_1 = R_2 = R_3 = CH_2COOH$

2, $R_1 = R_2 = R_3 = CH_2CH_2COOH$

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

Methods

Solution pH measurements were made using a Beckman Model Φ 71 pH meter fitted with a Beckman combination electrode. The hydrogen ion concentrations were calculated from the measured pH values in acetate buffer solution of 0.1 M ($NaClO_4$) ionic strength by procedures reported previously.[20] Kinetic measurements were made with the use of a UV1DEC-610 spectrophotometer and a Hi-Tech stopped-flow spectrophotometer interfaced with a Scientific data acquisition system. The temperature of the reaction mixture was maintained at 25.0 ± 0.1°C with the use of a Lauda RM 6 circulatory water bath.

The formation reaction of the Eu^{3+} complex was studied in a lightly buffered medium (sodium acetate–acetic acid) by monitoring the decrease in pH ($\Delta pH < 0.2$) with the use of bromocresol green ($4.6 < pH < 5.2$, 615 nm) as indicator.[21] The formation rate of Eu–**1** was monitored as an absorbance decrease due to the release of protons in the complexation reaction [eq. (1)]. The amount of protons released and the

$$Eu^{3+} + H_nL \rightarrow EuL + nH^+ \quad (1)$$

absorbance change in the formation reaction depend on the pH and the ligand protonation constant. The concentration of the indicator was 2.0×10^{-5} M, while that of acetate buffer varied between 5.0×10^{-3} and 2.0×10^{-2} M, independent of the reaction rate. The concentration of **1** was 1.0×10^{-4} M, while that of Ce^{3+} and Eu^{3+} was varied between 2.0×10^{-4} and 2.5×10^{-3} M. The formation reaction of Ce–**1** complex was studied by monitoring the complexation directly at 270 nm, where the kinetic data agreed well with some results obtained by using the indicator method.

The dissociation reaction of Ln–**1** and Ln–**2** complexes was studied in acidic solutions in the presence of excess Cu^{2+} ions. Under these

$$LnL + Cu^{2+} \rightarrow CuL^- + Ln^{3+} \quad (2)$$

conditions, a dissociation reaction takes place and progress of the exchange may be monitored by the formation of CuL^- at 270 nm. Cu^{2+} was used as a scavenger of free ligands. The concentration of LnL was 5×10^{-5} M, while that of exchanging Cu^{2+} was

Table 1. Pseudo-first-order rate constants for the formation reaction of Ln–**1** complexes[a]

10^4 [Ln^{3+}] (M)		k_{obs} (s^{-1})						
Ce–**1**								
	pH	4.84	5.00	5.20	5.34	5.45	5.55	5.61
2.0		0.25	0.43	0.79	1.23	1.73	2.22	2.60
3.0		0.38	0.62	1.15	1.78	2.49	3.18	3.72
4.0		0.49	0.81	1.51	2.35	3.23	4.17	4.88
6.0		0.71	1.16	2.13	3.28	4.98	6.29	7.14
10.0		1.06	1.82	3.33	5.10	6.71	8.62	10.3
Eu–**1**								
	pH	4.57	4.77	4.94	5.03	5.12	5.20	5.26
5.0		0.48	0.98	1.49	1.75	2.06	2.40	2.82
7.0		0.65	1.30	1.96	2.29	2.65	3.10	3.73
10.0		0.89	1.72	2.56	2.99	3.51	4.13	4.83
15.0		1.24	2.33	3.37	3.91	4.61	5.26	6.33
25.0		1.79	3.18	4.55	5.18	6.02	6.85	7.81

[a] At 25.0±0.1°C, $I = 0.1$ M ($NaClO_4$), [**1**] = 1.0×10^{-4} M, [**2**] = 2.5×10^{-4} M and [acetate] = 1.0×10^{-2} M.

either constant at 5×10^{-4} M or varied between 2.0×10^{-4} and 1.0×10^{-3} M.

RESULTS AND DISCUSSION

Formation kinetics

The formation reaction of Ln–**1** complexes was studied under pseudo-first-order conditions in a lightly buffered medium with Ln^{3+} in large excess. The observed rate constants follow eq. (3), where $[L]_T$

$$d[LnL]/dt = k_{obs}[L]_T \quad (3)$$

is the total concentration of the free ligand. The pseudo-first-order rate constant values, k_{obs}, obtained are shown in Table 1. For all systems at each pH, k_{obs} was found to increase with increasing [Ln^{3+}], and plots of k_{obs} versus [Ln^{3+}] show saturation behaviour. This is characteristic of rapid formation of the intermediate complex, which rearranges to the final product in a rate-determining step. As reported before,[21] the relationship between k_{obs} and Ln^{3+} can be described by

$$k_{obs} = \frac{k_1 K[Ln^{3+}]}{1 + K[Ln^{3+}]}, \quad (4)$$

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. The values of k_1, K and the second-order rate constant, $k_2 = k_1 K$, were obtained from plotting the data according to eq. (5) and are summarized in Table 2. The stability

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{1}{k_1 K[Ln^{3+}]} \quad (5)$$

constants and the rate constants for rearrangement of the intermediate were found to be dependent upon pH over the limited range of 4.57–5.61, as shown in Table 2. The concentrations of the protonated ligand were computed with the use of the ligand protonation constants.† In this pH range, H_2L^- is the major species (53–92%), H_3L is an important contributor (46–47%) and HL^{2-} represents 0.002–0.05% of the total ligand concentration. On the basis of these results, the formation reaction of Ln–**1** complexes may be expressed by eqs (6)–(8).

$$Ln^{3+} + H_2L^- \overset{K}{\rightleftharpoons} (LnH_2L^{2+})^* \quad (6)$$

$$(LnH_2L^{2+})^* \xrightarrow{k_1} LnL + 2H^+ \quad (7)$$

$$Ln^{3+} + H_2L^- \xrightarrow{k_2} LnL + 2H^+ \quad (8)$$

The overall stability constant of the intermediate, $(LnH_2L^{2+})^*$, may be evaluated from K values

† Protonation constants (log K_i) in 0.1 M KCl and at 25.0±0.1°C are 9.55, 9.92, 4.51 and 1.59 for **1**[19] and 8.16, 7.94 and 4.79 for **2**, which were calculated by fitting the potentiometric data to the PKAS program.[22]

Table 2. Rate data for the formation reaction of Ln–**1** complexes[a]

Ln^{3+}	pH	k_1 (s^{-1})	$10^{-2}K$ (M^{-1})	$10^{-3}k_2$ ($M^{-1}s^{-1}$)	$\log K_{(LnH_2L^{2+})^*}$
Ce^{3+}	4.84	6.53	2.12	1.38	2.51
	5.00	9.30	2.34	2.17	2.53
	5.20	15.3	2.72	4.17	2.54
	5.34	22.7	2.86	6.48	2.53
	5.45	30.5	3.00	9.15	2.54
	5.55	38.3	3.06	11.7	2.54
	5.61	44.2	3.11	13.7	2.54
					av. 2.53±0.01
Eu^{3+}	4.57	5.91	1.75	1.04	2.57
	4.77	7.27	3.12	2.26	2.73
	4.94	9.19	3.87	3.56	2.76
	5.03	10.2	4.15	4.23	2.76
	5.12	11.8	4.18	4.96	2.74
	5.20	13.1	4.46	5.86	2.75
	5.26	15.2	4.60	6.99	2.75
					av. 2.72±0.06

[a] At 25.0±0.1°C, I = 0.1 M ($NaClO_4$) and [acetate] = 1.0×10^{-2} M.

obtained at each pH, using known protonation constants of **1** and with the use of eq. (9). The calculated stability

$$K_{(LnH_2L^{2+})^*} = K(1+K_2[H^+]+K_2K_3[H^+]^2) \quad (9)$$

constants of the intermediate complexes are reasonably pH-independent over most of the examined pH range, as shown in Table 2. The stability constants of the intermediate here are about one order of magnitude higher than those for the corresponding monoacetate complexes.[23] This suggests that the Ln^{3+} ion is coordinated with more than a single carboxylate oxygen in the intermediate. Similarly, Brucher and Sherry[14] suggested the coordination of at least two carboxylate oxygens in the intermediate $(LnHNOTA^+)^*$, on the basis of the calculated values of $\log K_{(LnHNOTA^+)^*}$, i.e. 3.2–3.8. The consistent increase in the stability constant of intermediate complexes $(LnH_2L^{2+})^*$ from Ce^{3+} to Eu^{3+} parallels the thermodynamic stability of these complexes with decreasing size of Ln^{3+} ions.

Since eqs (6)–(7) and (6)–(8) account equally well for the kinetic data, the second-order rate constant k_{H_nL} also represents $(k_1K)_{H_nL}$. If one species is markedly more reactive than all the others, the second-order rate constant could be determined from eq. (10), where

$$k_2 = k_{H_nL}(1+K_{H_{(n+1)}L}[H^+])^{-1}; \quad (10)$$

$K_{H_{(n+1)}L}$ are the protonation constants of **1**. From the plots of k_2 against $(1+K_{H_{(n+1)}L}[H^+])^{-1}$, the second-order rate constants for the HL^{2-} and H_2L^- species are $(3.99\pm0.07)\times10^7$ and $(4.14\pm0.79)\times10^4$ M^{-1} s^{-1} for Ce–**1** and $(4.18\pm0.19)\times10^7$ and $(1.62\pm0.17)\times10^4$ M^{-1} s^{-1} for Eu–**1**, respectively. Despite the very low concentration in the pH range, the HL^{2-} species appears to be kinetically much more reactive than the diprotonated species H_2L^-, even though the latter is the predominant species in solution. The same conclusion was reported previously by Kasprzyk and Wilkins.[21] The low reactivity of the H_2L^- form may be assigned to the formation of the dizwitterionic form of **1**. The two N—H^+ groups in the 15-membered cycle of H_2L^- probably hinder the rearrangement of the intermediate complex into the final chelate product due to electrostatic repulsion with the incoming Ln^{3+} ion.

Dissociation kinetics

Since the thermodynamic stabilities‡ of Cu–**1** ($\log K$ = 17.54) and Cu–**2** ($\log K$ = 12.79) are about one or two orders of magnitude higher than those of the corresponding Ln–**1** ($\log K$ = 16.55–17.01) and Ln–**2** ($\log K$ = 10.94–11.66), the displacement of Ln^{3+} ions from the lanthanide complexes is complete in the presence of excess Cu^{2+} ions [eq. (2)].

‡ The stability constants in 0.1 M $NaClO_4$ and at 25.0±0.1°C were obtained from the potentiometric data and the ligand protonation constants (see previous footnote) by using the BEST program.[22]

The rates of these exchange reactions have been measured between pH 3.42 and 5.04. In the presence of excess Cu^{2+} ions, the rate of exchange may be expressed as

$$-d[LnL]/dt = k_{obs}[LnL], \quad (11)$$

where k_{obs} is a pseudo-first-order rate constant. The values of k_{obs} for Ln–**1** complexes were found to be independent of $[Cu^{2+}]$, but dependent on [acetate]. The dependence of k_{obs} on $[H^+]$ at various acetate buffer concentrations is shown in Fig. 2. For all systems, a linear least-squares fit to these plots had a non-zero intercept, which is consistent with the exchange reaction proceeding via both acid-independent and acid-catalysed pathways. The observed rate constants for Ln–**1** complexes can be described by

$$k_{obs} = k_d + k_H[H^+]. \quad (12)$$

Figure 3 shows that k_d and k_H are directly proportional to the total acetate buffer concentration. The enhancement in the dissociation rates of Ln–**1** complexes by acetate buffer can be attributed to acetate ion complexation. If a ternary complex, $[Ln–\mathbf{1}–OAc]^-$, is present, it is probably more sensitive than binary [Ln–**1**] to attack by hydrogen ions. Based on these data, the overall rate of reaction may be expressed as

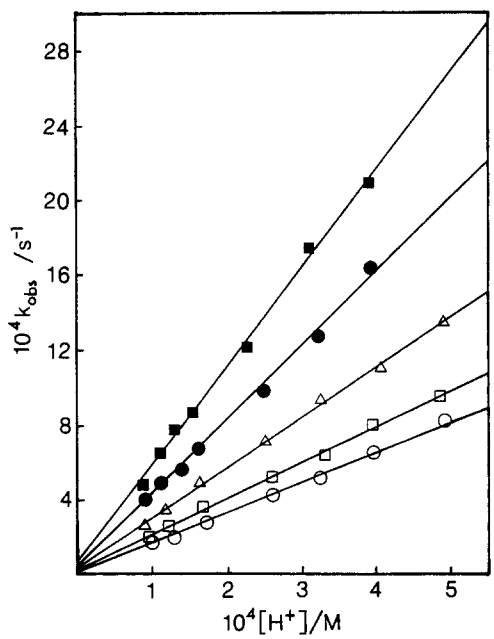


Fig. 2. Plots of k_{obs} vs $[H^+]$ for the dissociation kinetics of Eu–**1** with Cu^{2+} at different buffer concentrations. [Eu–**1**] = 5.0×10^{-5} M, $[Cu^{2+}] = 5.0 \times 10^{-4}$ M, $T = 25.0 \pm 0.1$°C, $I = 0.1$ M ($NaClO_4$). [OAc^-] = 5.0 mM (○), 10.0 mM (□), 25.0 mM (△), 50.0mM (●) and 75.0 mM (■).

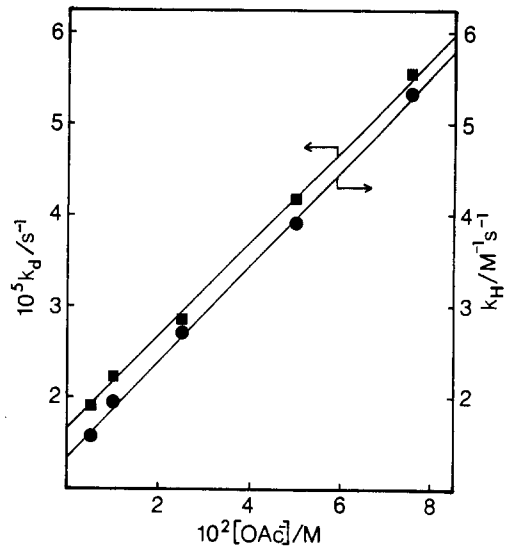


Fig. 3. Plots of k_d and k_H vs [OAc^-] for the dissociation kinetics of Eu–**1** with Cu^{2+}. [Eu–**1**] = 5.0×10^{-5} M, $[Cu^{2+}] = 5.0 \times 10^{-4}$ M, $T = 25.0 \pm 0.1$°C and $I = 0.1$ M ($NaClO_4$).

$$-d[Ln–\mathbf{1}]/dt = k_1[Ln–\mathbf{1}] + k_2[Ln–\mathbf{1}][OAc^-] + k_3[Ln–\mathbf{1}][H^+] + k_4[Ln–\mathbf{1}][H^+][OAc^-]. \quad (13)$$

Values of the specific rate constants, $k_n (n = 1–4)$, calculated from a weighted least-squares program, are listed in Table 3. Similar behaviour has been reported for the dissociation reaction of Ln^{3+} complexes with other polyazapolycarboxylates.[12,14] In these mechanisms, the Ln–carboxylate bonds are rapidly forming and breaking, allowing the attachment of H^+ or Cu^{2+} to a dissociated carboxylate. Presumably, the slow step involves the rupture of a Ln–N bond subsequent to the formation of Ce–**1**–H or Ce–**1**–Cu intermediates.

On the other hand, the observed rate constants, k_{obs}, for Ln–**2** complexes were found to be independent of [acetate] but dependent on $[Cu^{2+}]$. The dependence of k_{obs} on $[Cu^{2+}]$ is plotted in Fig. 4 at different pH values. In each case, the data fit straight lines with measurable non-zero intercepts, which confirms the exchange reaction as proceeding via both Cu^{2+}-independent and Cu^{2+}-dependent pathways. The observed rate constants can be expressed as

$$k_{obs} = k_d + k_{Cu}[Cu^{2+}], \quad (14)$$

where k_d and k_{Cu} are functions of the acidity, $[H^+]$. Figure 5 shows that k_d is proportional to $[H^+]$, while k_{Cu} is proportional to $[H^+]^{-1}$. Based on these results, the overall rate of reaction can be expressed as

Table 3. Rate constants for the dissociation reaction of lanthanide complexes of linear and macrocyclic polyaminopolycarboxylates[a]

Complexes	k_d (s^{-1})	k_H ($M^{-1}s^{-1}$)	$k_{d\cdot OAc}$ ($M^{-1}s^{-1}$)	$k_{H\cdot OAc}$ ($M^{-2}s^{-1}$)	k_{Cu} ($M^{-1}s^{-1}$)	k_{CuOH^+} ($M^{-1}s^{-1}$)
Ce–**1**	$(1.07\pm0.04)\times10^{-4}$	$(2.00\pm0.16)\times10^{1}$	$(2.26\pm0.06)\times10^{-3}$	$(1.18\pm0.04)\times10^{3}$	[b]	[b]
Eu–**1**	$(1.62\pm0.03)\times10^{-5}$	(1.38 ± 0.06)	$(5.15\pm0.05)\times10^{-4}$	$(5.26\pm0.07)\times10^{1}$	[b]	[b]
Ce–**2**	$(1.38\pm0.05)\times10^{-2}$	$(3.02\pm0.09)\times10^{2}$	[b]	[b]	$(1.23\pm0.08)\times10^{2}$	$(5.75\pm0.11)\times10^{5}$
Eu–**2**	$(8.97\pm0.04)\times10^{-3}$	$(2.18\pm0.10)\times10^{2}$	[b]	[b]	$(6.59\pm0.07)\times10^{1}$	$(4.72\pm0.10)\times10^{5}$
Eu(K21DA)$^{+c}$	$(1.76\pm0.06)\times10^{-3}$	$(3.11\pm0.04)\times10^{1}$	$(8.09\pm0.23)\times10^{-2}$	[b]	[b]	[b]
Eu(K22DA)$^{+d}$	$(4.31\pm1.47)\times10^{-4}$	$(5.70\pm0.96)\times10^{-1}$	[b]	[b]	[b]	[b]
Eu(ENDPDA)$^{-e}$	$(3.60\pm0.50)\times10^{-1}$	$(4.26\pm0.10)\times10^{4}$	(5.80 ± 0.60)	$(1.03\pm0.21)\times10^{6}$	[b]	[b]
Eu(EDTA)$^{-f}$	[b]	(2.28×10^{2})	[b]	[b]	[b]	[b]

[a] At 25.0 ± 0.1°C, $I = 0.1$ M ($NaClO_4$).
[b] Not observed.
[c] Ref. 16.
[d] Ref. 17.
[e] Ref. 24.
[f] Ref. 26.

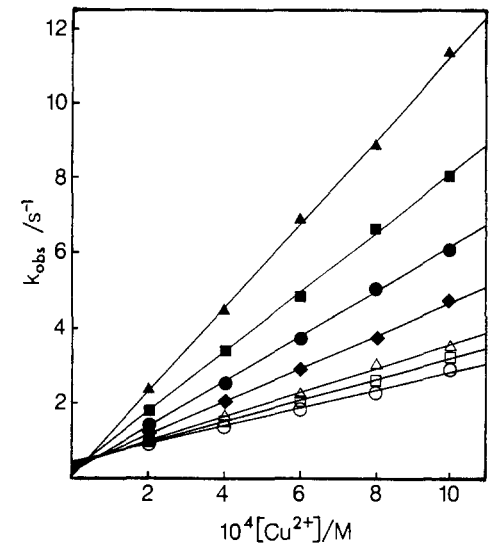


Fig. 4. Plots of k_{obs} vs $[Cu^{2+}]$ for the dissociation kinetics of Ce–**2** at different pH values. [Ce–**2**] = 5.0×10^{-5} M, $[OAc^-] = 0.01$ M, $T = 25.0\pm0.1$°C, $I = 0.1$ M ($NaClO_4$); pH = 4.18 (○), 4.26 (□), 4.39 (△), 4.54 (◆), 4.71 (●), 4.88 (■) and 5.04 (▲).

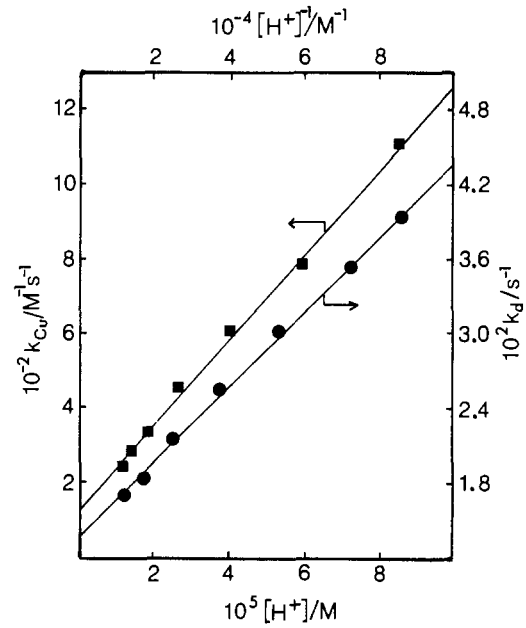


Fig. 5. Plots of k_d vs $[H^+]$ and k_{Cu} vs $[H^+]^{-1}$ for the dissociation kinetics of Ce–**2**. [Ce–**2**] = 5.0×10^{-5} M, $[OAc^-] = 0.01$ M, $T = 25.0\pm0.1$°C, $I = 0.1$ M ($NaClO_4$).

$$-d[Ln\text{–}\mathbf{2}]/dt = k_1[Ln\text{–}\mathbf{2}] + k_2[Ln\text{–}\mathbf{2}][H^+] + k_3[Ln\text{–}\mathbf{2}][Cu^{2+}] + k_4[Ln\text{–}\mathbf{2}][Cu^{2+}][H^+]^{-1}. \quad (15)$$

Values of the specific rate constants, $k_n (n = 1\text{–}4)$, calculated from a weighted least-squares program, are also listed in Table 3. The reaction of Ln–**2**

complexes with Cu^{2+} ion proceeds by a reaction pathway that is similar to those reported for the exchange of Ln^{3+} ions in their polyaza-polycarboxylate complexes.[10,11] Both the dissociative pathway, which obviously shows an acid-independent and an acid-catalysed contribution, and the associative pathway take place. The first and second terms in eq. (15) are responsible for the dissociative pathway of the Cu^{2+}-independent mode. The rate-determining step involves the loss of Ln^{3+} from the complex and rapid reaction of the released ligand with Cu^{2+}. Equation (15) also represents the associative pathway of the Cu^{2+}-dependent mode, which is composed of the direct attack route of Cu^{2+} on partially dissociated Ln–**2** and the $[H^+]^{-1}$ dependence. The $[H^+]^{-1}$ dependence can be explained by the existence of the attack of hydrolysed copper species ($CuOH^+$) on Ln–**2**, even though the investigated pH is not higher. k_{CuOH^+} is therefore calculated from the following equation:

$$k_{CuH^{-1}} = k_{CuOH^+}\beta_{CuOH^+}, \qquad (16)$$

where β_{CuOH^+} ($=K_{CuOH^+}K_w$) is a stability constant (i.e. 2.0×10^{-8}).[10]

The effect of the metal ion and the ligand on the dissociation rate can be seen by comparing the values in Table 3 with other linear and macrocyclic complexes. The consistent decrease in the acid-independent and acid-catalysed dissociation rates of **1** and **2** complexes from Ce^{3+} to Eu^{3+} parallels the thermodynamic stability of these complexes with decreasing ionic size or increasing charge density of Ln^{3+} ions. The rate constant of both the acid-independent and acid-catalysed pathway of the Ce–**2** complex is about one order of magnitude larger than that of the corresponding Ce–**1**. This fact may be attributed to the decrease of thermodynamic stability due to the destabilizing effect of the six-membered N—Ce—O chelate ring involving the three propionate groups of **2**. A similar argument has been used to explain the fact that the dissociation rate of Eu(ENDPDA)$^-$ [ethylenedinitrilo-*N*,*N*′-di(3-propanoic)-*N*,*N*′-diacetic acid][24] is much faster than that of Eu(EDTA)$^-$. The acid-catalysed rate constant of Eu–**1** is about one order of magnitude larger than that of Eu(K21DA)$^+$, even though **1** has the same cavity size (15-membered cycle) as K21DA. This may be due to the increase of thermodynamic stability ($\log K_{Eu\text{-}1} = 17.01$ versus $\log K_{Eu(K21DA)^+} = 11.85$)[25] by the increase in nitrogen donor basicity ($pK_{3(1)} = 9.55$ versus $pK_{3(K21DA)} = 9.02$, see earlier footnote and ref. 25), the difference in the type of cyclic donor atoms and the number of acetate pendant arms of ligands. In contrast, although Eu–**1** has an increased thermodynamic stability compared with Eu(K22DA) ($\log K = 12.02$)[25], the acid-catalysed rate of Eu–**1** dissociates about twice as fast as that of Eu(K22DA)$^+$. An increase in cavity size from 15–(**1**) to 18-membered cycles (K22DA) leads to an increase in kinetic stability because of the rigidity of the triazadioxa–**1** compared with the diazatetraoxa (K22DA) macrocycles. On the other hand, the acid-catalysed rate constant of Eu–**1** is about 100 times smaller than that of Eu(EDTA)$^-$, even though the difference in thermodynamic stability between Eu–**1** and Eu(EDTA)$^-$ ($\log K = 17.29$)[23] is not significant. This fact can be explained by the remarkable rigidity of the macrocyclic triazadioxa ring in **1** compared to the flexibility of the linear EDTA.

Acknowledgement—The present studies were supported by the Basic Science Research Institute Program, Ministry of Education of Korea, 1994, Project No. BSRI-94-3435.

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