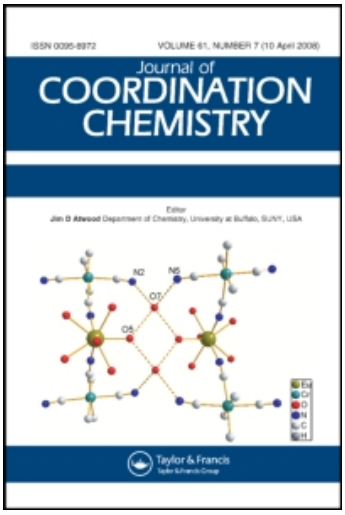

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Choi, Ki-Young , Kim, Ju Chang and Kim, Dong Won(1993) 'DISSOCIATION KINETICS OF 1,4,8,11-TETRAAZACYCLOTETRADECANE-*N,N',N'',N'''*-TETRAACETATE COMPLEXES OF CERIUM(III) AND EUROPIUM(III)', Journal of Coordination Chemistry, 30: 1, 1 — 7
To link to this Article: DOI: 10.1080/00958979308022741
URL: http://dx.doi.org/10.1080/00958979308022741

J. Coord. Chem., 1993, Vol 30, pp. 1–7
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NOTE

DISSOCIATION KINETICS OF 1,4,8,11-TETRAAZACYCLOTETRADECANE-*N*,*N*′,*N*″,*N*‴-TETRAACETATE COMPLEXES OF CERIUM(III) AND EUROPIUM(III)

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(Received 21 September 1992)

KEY WORDS: Lanthanides, TETA, complexes, dissociation, kinetics.

Lanthanide complexes with the macrocyclic polyaza polycarboxylates, NOTA (1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetic acid), DOTA (1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid), and PEPA (1,4,7,10,13-pentaazacyclopentane-*N*,*N*′,*N*″,-*N*‴,*N*⁗-pentaacetic acid) have attracted considerable attention as magnetic resonance imaging (MRI) contrast agents,[1,2] lanthanide ion separations,[3,4] radiopharmaceuticals,[5,6] and models for ion transport in biological systems.[7] Kinetic behaviour of these macrocyclic complexes differs considerably from that of analogous linear polyamine polycarboxylates such as EDTA, TMDTA (trimethylenedinitrilotetraacetic acid), DPTA (diethylenetriaminepentaacetic acid), and TTHA (triethylenetetraaminehexaacetic acid), since the rate of formation and dissociation of lanthanide complexes with DOTA and NOTA are much slower, as reported by Brucher[8] and Sherry.[9] This fact may be attributed to the remarkable rigidity of cyclic aza rings compared to their flexible linear analogues. The rate of complexation of $LnDOTA^-$ is slower than that of the NOTA complex. This probably reflects the thermodynamic stability conferred by the rigidity of the tetraaza ring (DOTA) *versus* the triaza ring (NOTA) cycle.[10] The kinetics of exchange and dissociation of the lanthanide polyaza and polyamine polycarboxylate complexes demonstrate that the exchange of the metal cation occurs *via* both acid-independent and acid-dependent pathways.[11–16] An acid-catalized dissociation path has been described as involving an LnYH intermediate. The acid-independent mode has been assumed to proceed *via* a binuclear intermediate,

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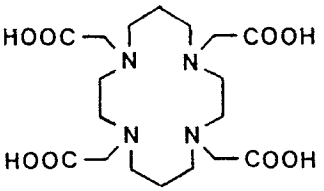
LnYM, in which the lanthanide and the metal ion are bound to opposite ends of the ligand.

In a study of the thermodynamics of complexation of lanthanide with TETA (1,4,8,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid), **1**, stability was found to be less than that of the analogous DOTA complex.[17] The destabilizing effect of the two propylenediamine groups weakens the lanthanide(III) ion-nitrogen donor interaction, even though TETA has an increased internal cavity size (14-membered cycle) comparing to DOTA (12-membered cycle).

To further understand the factors involved in chelating kinetics, we have studied the dissociation of Ce(III) and Eu(III) complexes of TETA.



TETA (**1**)

EXPERIMENTAL

Stock solutions of Ce^{3+} and Eu^{3+} were prepared from $CeCl_3$ and Eu_2O_3 (Aldrich, 99.99%) and their concentrations were determined by titration with EDTA using xylenol orange as indicator. H_4TETA (1,4,8,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid) was synthesized by the method of Herlinger *et al.*[18] Stock solutions of the disodium salt of TETA were prepared by dissolving the required amount of the acid in two equivalents of sodium hydroxide. The concentration of a Na_2H_2TETA stock solution was determined by titration against a standard $Cu(ClO_4)_2$ solution using murexide as indicator. The stock solution of $LnTETA^-$ was prepared by mixing equimolar amounts of $Ln(ClO_4)_3$ and Na_2H_2TETA stock solutions. All chemicals used were of analytical grade and were used without further purification. Distilled water was used for all solutions.

The pH measurements were made using a Beckman Model Φ 71 pH meter fitted with a combination electrode. H^+ ion concentrations were calculated from measured pH values in acetate buffer solution of 0.1 M ($NaClO_4$) ionic strength by the expression[13] $-\log[H^+] = pH - 0.109$.

Kinetic measurements were carried out using a UVIDEC-610 spectrophotometer at 25 (± 0.1)°C using thermostatted cells (1 cm). Since the $LnTETA^-$ complexes do not show appreciable absorption in the untraviolet or visible region, Cu^{2+} was used as a scavenger of free ligand and the reaction kinetics were followed by monitoring the growth in absorbance due to the formation of $CuTETA^{2-}$ at 260 nm. The concentration of $LnTETA^-$ was 5.0×10^{-5} M while that of exchanging Cu^{2+} ion was varied between 1.0×10^{-4} and 5.0×10^{-4} M.

RESULTS AND DISCUSSION

Since the stability constant of $CuTETA^{2-}$ [19] (log $\beta_{101}=21.60$) complex is much greater than that of the $CeTETA^{-}$ [20] (log $\beta_{101}=13.12$) and $EuTETA^{-}$ [20] (log $\beta_{101}=14.66$) complexes, the displacement of Ln^{3+} ions from the $LnTETA^{-}$ complexes is complete in the presence of excess Cu^{2+} ions. The experimental data show excellent *pseudo*-first-order reaction rates. The observed rate constant, k_{obs}, is independent of acetate ion concentration. The dependence of k_{obs} on the Cu^{2+} ion concentration is plotted in Figure 1 at different pH values. The standard deviations were in the range 1–5%. In each case, the data fit straight lines with measurable non-zero intercepts, which confirms the exchange reaction as proceeding *vua* both $[Cu^{2+}]$-independent and $[Cu^{2+}]$-dependent pathways. Thus, observed rate constants for the $LnTETA^{-}$ complexes can be expressed as follows,

$$LnTETA^{-}+Cu^{2+}\rightarrow CuTETA^{2-}+Ln^{3+} \quad (1)$$

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

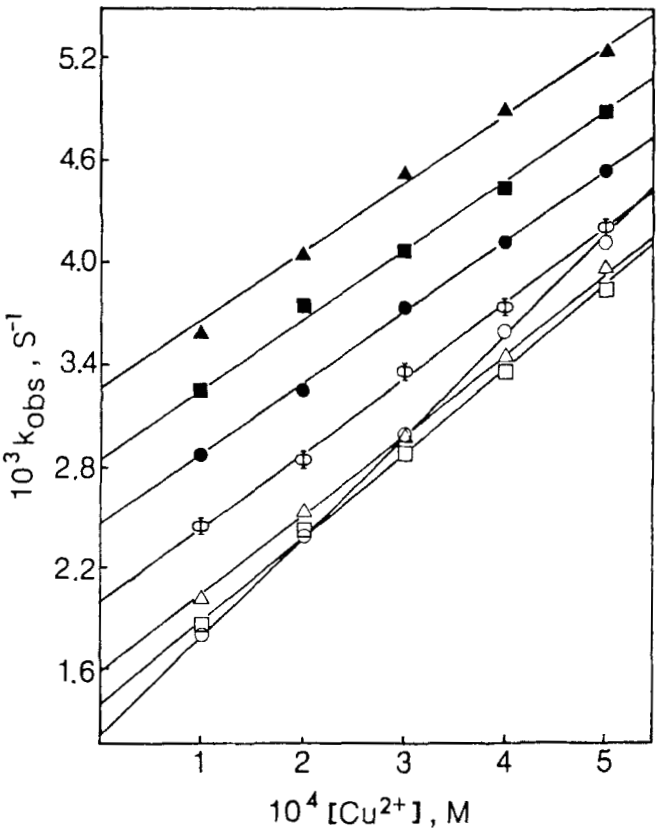


Figure 1 Plots of k_{obs} *vs* $[Cu^{2+}]$ for the dissociation kinetics of $CeTETA^{-}$ at different pH values ([acetate] = 0.01 M, μ = 0.1 M ($NaClO_4$), T = 25°C); pH: (▲) 3.088; (■) 3.170; (●) 3.274; (Φ) 3.422; (△) 3.644; (□) 3.766; (○) 3.983.

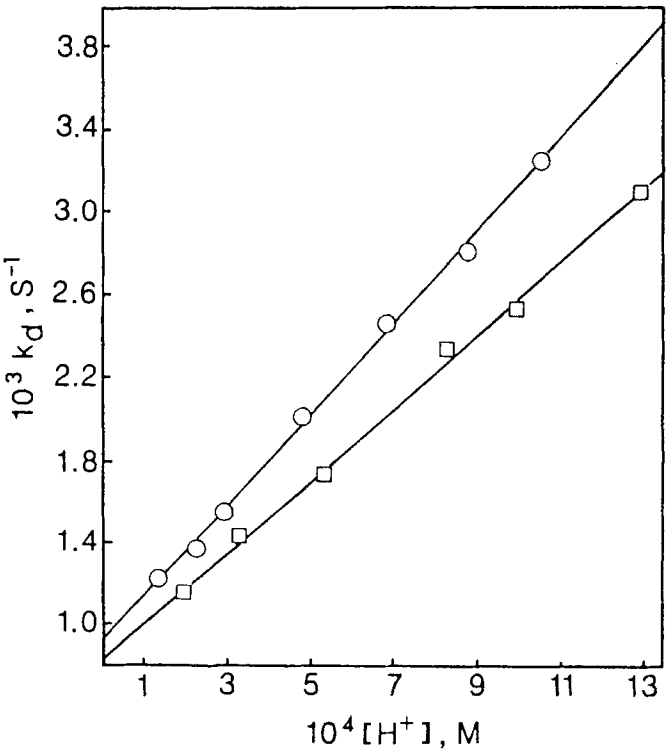


Figure 2 Plots of k_d *vs* $[H^+]$ for the dissociation kinetics of $CeTETA^-$ (○) and $EuTETA^-$ (□) ([acetate] = 0.01 M, μ = 0.1 M ($NaClO_4$), T = 25°C).

where k_d and k_{cu} are functions of the acidity, $[H^+]$. Figure 2 shows that k_d is proportional to $[H^+]$ while k_{cu} is proportional to $1/[H^+]$ as shown in Figure 3. Based on these results, the overall rate of reaction can be expressed as follows.

$$\text{Rate} = k_1[LnY^-] + k_2[LnY^-][H^+] + k_3[LnY^-][Cu^{2+}] + k_4[LnY^-][Cu^{2+}][H^+]^{-1} \quad (3)$$

Values of the specific rate constants, k_n (n = 1–4), calculated from a weighted least-squares program, are listed in Table 1.

The reaction between LnY^- complexes and Cu^{2+} ions proceeds by reaction paths that are similar to those reported for the exchange of metal ions in their polyamino polycarboxylate complexes.[21] In both cases, the $[Cu^{2+}]$-independent pathway clearly shows acid-independent and an acid-catalyzed modes while the $[Cu^{2+}]$-dependent pathway is simultaneous. The reaction sequence (4)–(10) can account for the observed results. Equations (4) and (6) are responsible for the dissociative pathway of the $[Cu^{2+}]$ independent mode,

$$LnY^- \overset{k_1}{\rightleftharpoons} Ln^{3+} + Y^{4-} \quad (4)$$

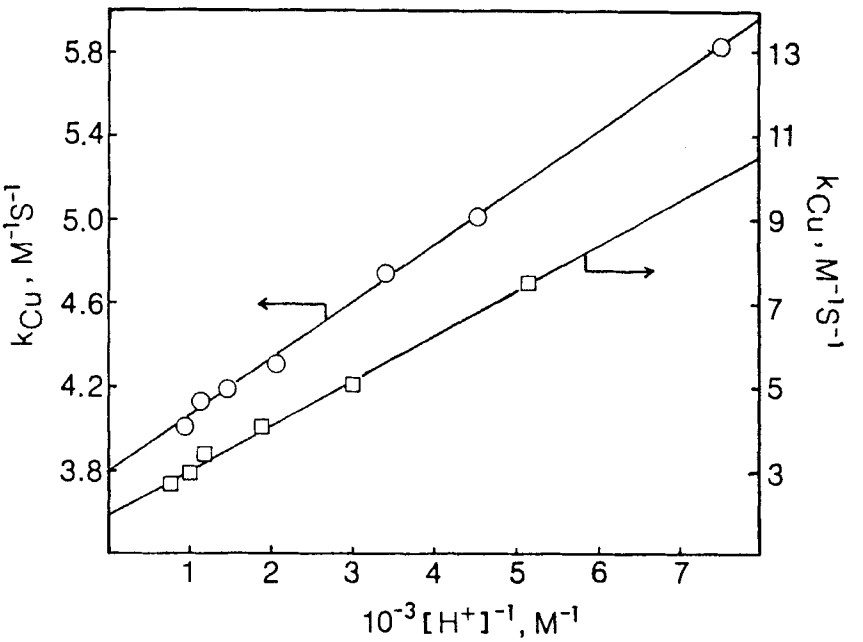


Figure 3 Plots of k_{Cu} *vs* $[H^+]^{-1}$ for the dissociation kinetics of $CeTETA^-$ (○) and $EuTETA^-$ (□) ([acetate] = 0.01 M, μ = 0.1 M ($NaClO_4$), T = 25°C).

Table 1 Rate constants for the exchange reaction of LnY/M; μ = 0.1 M ($NaClO_4$), T = 25°C

Exchange reaction	Rate term	Rate constant	Ref.
$CeTETA^-$/Cu(II)	$k_1[CeY^-]$	$(9.13 \pm 0.12) \times 10^{-4}\ s^{-1}$	this work
	$k_2[CeY^-][H^+]$	$(2.22 \pm 0.19)\ M^{-1}\ s^{-1}$	"
	$k_3[CeY^-][Cu^{2+}]$	$(3.79 \pm 0.10)\ M^{-1}\ s^{-1}$	"
	$k_{CuOH^+}[CeY^-][CuOH^+]$	$(2.72 \pm 0.27) \times 10^4\ M^{-1}\ s^{-1}$	"
$EuTETA^-$/Cu(II)	$k_1[EuY^-]$	$(8.32 \pm 0.28) \times 10^{-4}\ s^{-1}$	this work
	$k_2[EuY^-][H^+]$	$(1.76 \pm 0.35)\ M^{-1}\ s^{-1}$	"
	$k_3[EuY^-][CU^{2+}]$	$(1.95 \pm 0.16)\ M^{-1}\ s^{-1}$	"
	$k_{CuOH^+}[EuY^-][CuOH^+]$	$(1.06 \pm 0.06) \times 10^5\ M^{-1}\ s^{-1}$	"
$CeDOTA^-$/Cu(II)	$k_1[CeY^-][H^+]$	$(8 \pm 2) \times 10^{-4}\ M^{-1}\ s^{-1}$	8
	$k_2[CeY^-][H^+]^2$	$(2 \pm 0.5) \times 10^{-3}\ M^{-2}\ s^{-1}$	8
CeNOTA/Cu(II)	$k_1[CeY]$	$(2.5 \pm 0.3) \times 10^{-5}\ s^{-1}$	9
	$k_2[CeY][H^+]$	$(4.3 \pm 0.5) \times 10^{-2}\ M^{-1}\ s^{-1}$	9
$CeEDTA^-$/Ce(III)	$k_1[CeY^-][H^+]$	$1.38 \times 10^3\ M^{-1}\ s^{-1}$	11
	$k_2[CeY^-][H^+][Ac^-]$	$3.85 \times 10^5\ M^{-2}\ s^{-1}$	11
$CeDCTA^-$/Cu(II)	$k_1[CeY^-]$	$(2.0 \pm 0.5) \times 10^{-4}\ s^{-1}$	12
	$k_2[CeY^-][H^+]$	$(6.0 \pm 0.2) \times 10^1\ M^{-1}\ s^{-1}$	12

$$LnY^- + H^+ \rightleftharpoons LnYH \tag{5}$$

$$LnYH \overset{k_2}{\rightleftharpoons} Ln^{3+} + HY^{3-} \tag{6}$$

$$Y^{4-} \text{ (or } HY^{3-}) + Cu^{2+} \xrightarrow{\text{fast}} CuY^{2-} \text{ (or } +H^+) \tag{7}$$

$$LnY^- + Cu^{2+} \rightleftharpoons LnYCu^+ \tag{8}$$

$$LnYCu^+ \xrightarrow{k_3} CuY^{2-} + Ln^{3+} \tag{9}$$

$$LnY^- + CuOH^+ \xrightarrow{k_{CuOH^+}} CuY^{2-}. + Ln^{3+} + OH^- \tag{10}$$

where k_1 and k_2 are the acid-independent and acid-catalyzed rate constants, respectively. The free ligand released from the complex reacts rapidly with Cu^{2+} (7). Equations (8) and (10) represent the associative pathway by the direct attack of Cu^{2+} on LnY^-. The $[H^+]^{-1}$ dependence in equation (3) suggests that the $CuOH^+$ species is active as shown in equation (10). Higher hydrolyzed species can be neglected. Thus, k_{CuOH^+} is obtained from the following equation,

$$k_4 = k_{CuOH^+} \beta_{CuOH^+} \tag{11}$$

where β_{CuOH^+} ($= K_{CuOH^+} K_w$) is a stability constant (i.e., 10^{-8}).[19] In these reactions, the Ln-carboxylate bonds are rapidly forming and breaking and the slow step involves the rupture of a Ln-N bond subsequent to the formation of ternary LnYH or $LnYCu^+$ intermediates. Two amine groups in TETA are very basic with log K values of 11.5 and 10.3, while the remaining two amines are almost neutral (log K < 2).[20] This fact would suggest that at least two nitrogen donors do not participate in bonding to Ln^{3+}.

The effect of the ligand on the dissociation rate constant can be seen by comparing the values in Table 1 along with the other lanthanide polyaza and polyamino polycarboxylate complexes. The consistent decrease in the acid-independent and acid-catalyzed dissociation rates of the $LnTETA^-$ complexes from Ce^{3+} to Eu^{3+} parallels the thermodynamic stability of these complexes with decreasing ionic size. In the study of $CeDOTA^-$ dissociation, the rate constant for the acid-ctalyzed pathway was found to be about fifty times smaller than that for the CeNOTA complex. This may be interpreted as reflecting the thermodynamic stability[10] (log $\beta_{CeNOTA} = 13.24$ *versus* log $\beta_{CeDOTA^-} = 23.43$) by increasing ring size from 9 (NOTA) to 12 (DOTA). The acid-catalyzed rate constant for $CeTETA^-$ is about three orders of magnitude larger than that for $CeDOTA^-$. Meanwhile, CeNOTA dissociates about fifty times more slowly than $CeTETA^-$, even though the difference in log β between $CeTETA^-$ and CeNOTA is not significant. This fact may be attributed to the destabilizing effect of the 6-membered nitrogen-Ce-nitrogen chelate ring involving the propylene-diamine group of the TETA ligand. A similar argument has been used to explain the fact that the dissociation rate of $CeTMDTA^-$ (TMDTA = trimetylenedinitrilotetraacetic acid) is much faster than $CeEDTA^-$.[15] On the other hand, the acid-catalyzed rate constant for the dissociation of $CeTETA^-$ is about 10^3 and 10 times smaller than those of $CeEDTA^-$ and $CeDCTA^-$, respectively, even though the stability of

$CeTETA^-$ is considerably smaller than $CeEDTA^-$ and $CeDCTA^-$ ($\log \beta_{101} = 17.67$) complexes. This fact can be explained by the rigidity of the tetraaza ring in TETA cycle as compared with the flexibility of the linear ligand complexes.

Acknowledgements

This work was supported by the research fund of Mokwon University, 1992.

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