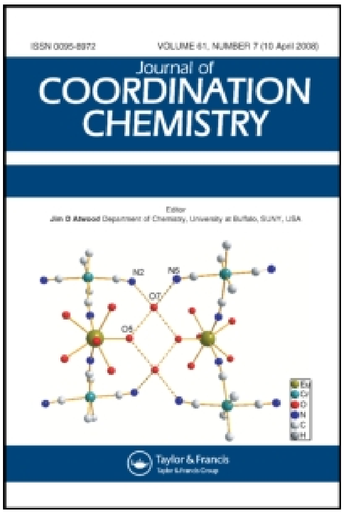

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Rizkalla, E. N. and Choppin, G. R.(1991) 'Dissociation Kinetics of an Ethylene-Dinitrilo-*N,N'*-Diacetato-*N,N'*-DI-3-Propionato Complex of Europium(III)', Journal of Coordination Chemistry, 23: 1, 33 — 41
To link to this Article: DOI: 10.1080/00958979109408240
URL: http://dx.doi.org/10.1080/00958979109408240

J. Coord. Chem. 1991, Vol. 23, pp. 33–41
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DISSOCIATION KINETICS OF AN ETHYLENEDINITRILO-*N*,*N*′-DIACETATO-*N*,*N*′-DI-3-PROPIONATO COMPLEX OF EUROPIUM(III)

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(Received March 12, 1990)

The kinetics of dissociation of EuENDPDA was studied by a stopped-flow technique with a Cu^{2+} scavenger. The dissociation data indicated that EuENDPDA follows a similar dissociative mechanism as EuEDTA and other Eu-aminopolycarboxylate complexes. Both acid-dependent and acid-independent paths are present with a 100-fold increase in the acid catalyzed rate compared to that of EuEDTA. These results are discussed in terms of the relative stability of 5- and 6-membered chelate rings in the complexes.

Keywords: Europium(III), polyaminocarboxylates, dissociation, kinetics

INTRODUCTION

Studies of metal-assisted dissociation of lanthanide-polyaminocarboxylates (LnY) have resulted in a proposed mechanism which includes a proton-catalyzed pathway involving a LnYH intermediate as well as an acid-independent pathway.[1–4] The acid-independent mode was assumed to proceed *via* a binuclear intermediate, LnYM (M is the non-lanthanide metal), in which the lanthanide and the metal are bound to the opposed ends of the ligand.[1] The rate determining step in the acid-catalyzed dissociation path was assigned either to rupture of a second metal–carboxylate bond of the protonated complex or to the slow transfer of the hydrogen ion from the protonated carboxyl–oxygen to the neighbouring nitrogen site, thereby causing rupture of the metal–nitrogen bond. Increasing the alkyl chain length of the carboxylate arm could be expected to reduce the stability of the chelate ring involving Ln bound to a carboxylate oxygen and to a nitrogen; it should also affect the ease of transfer of a proton to a nitrogen.

A study of the thermodynamics of complexation of Ln(III) cations by ethylenedinitrilo-*N*,*N*′-di-3-propionate-diacetate anion (ENDPDA; Fig. 1) showed the stability to be less than for the analogous complexes with ethylenediamino-*N*,*N*′-tetraacetate anion (EDTA).[5] The destabilizing effect of the two propionate arms weakens the lanthanide ion–nitrogen donor interaction. By contrast, an increase was reported in the stability of the protonated HLnENDPDA complexes relative to the protonated HLnEDTA complexes. Thermodynamic parameters for the formation of these protonated species indicated that the proton is associated with the nitrogen donor.

For the reactions (*1*) and (*2*) with EDTA and ENDPDA,

$$Eu^{3+} + Y^{4-} = EuY^- \qquad (1)$$

$$EuY^- + H^+ = EuHY \qquad (2)$$

the respective values of the stability constants are, for EDTA,[6] log $\beta_{101} = 17.32$ and log $\beta_H = 2.0$, and for ENDPDA,[5] log $\beta_{101} = 13.04$ and log $\beta_H = 3.29$. We have extended these studies to measurement of the kinetics of dissociation of EuENDPDA using a stopped-flow technique with Cu^{2+} as scavenger.

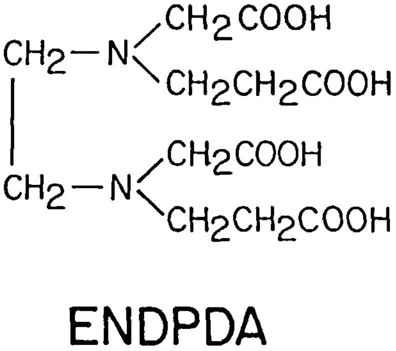


FIGURE 1

EXPERIMENTAL

Reagents and Solutions

A stock solution of europium perchlorate was prepared from Eu_2O_3 (Aldrich 99.99% pure) and standardized by EDTA titration. The disodium salt of ENDPDA, from Sigma Products Co., was recrystallized twice from ethanol-water solutions; its solution was standardized by pH-titration with CO_2-free sodium hydroxide. A stock solution of $EuENDPDA^-$ was prepared by mixing equimolar amounts of $Eu(ClO_4)_3$ and $H_2Na_2ENDPDA$ stock solutions. Solutions of copper(II) perchlorate, acetate buffer and sodium perchlorate (used to maintain constant ionic strength) were prepared from commercially available analytical grade reagents.

Measurements

pH measurements were made with a Radiometer pH M 84 pH meter fitted with a combination glass/saturated NaCl calomel electrode. The H^+ ion concentrations were calculated from the measured pH values at 0.10 M ($NaClO_4$) ionic strength by the expression (*3*).[5]

$$-\log [H^+] = pH - 0.11 \qquad (3)$$

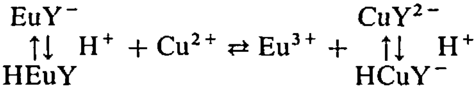
The $CuENDPDA^{2-}$ stability constants were determined by pH-titration of 50.0 cm^3 aliquots of 1.92 mM ENDPDA solution in the presence of equimolar amounts of copper(II) ion using CO_2-free sodium hydroxide. Analysis of the titration data indicated that both CuY^{2-} and $HCuY^-$ complexes were formed in the solution. The details of the method of calculation of the corresponding equilibrium constants have been described previously.[7]

Spectra of the reactants and products in the EuENDPDA$^-$ + Cu^{2+} reaction were obtained using a Milton Roy Spectronic spectrophotometer (model 1201). The kinetic experiments were performed on a Durrum-Gibson D-109 stopped-flow spectrophotometer interfaced with an IBM personal computer. The reaction was initiated by mixing a solution of copper + acetate buffer with a solution of EuENDPDA$^-$ + acetate buffer. The growth in absorbance at 290 nm due to the formation of the ternary copper complex $CuY(Ac)_n^{(2+n)-}$ was monitored. At this wavelength, both $Cu(Ac)_i^{2-i}$ and $EuY(Ac)_j^{(1+j)-}$ have zero absorbance.

The output signals from the spectrometer were fed to a logarithmic amplifier where they were digitized and stored in the buffer memory of the PC computer. For each kinetic run, two sets of data were obtained; each set was an average of at least five consecutive runs stored in the computer memory. The validity of Beer's law at 290 nm over the copper concentration range (0.01–0.20 mM) was confirmed. Log A (A = the molar absorptivity of the ternary copper complex) was found to be 3.48.

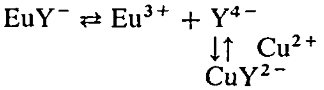
The stability constants for formation of CuENDPDA^{2-} and CuHENDPDA^{1-} by reactions analogous to equations (*1*) and (*2*) at 25°C in solutions of 0.10 M (NaClO$_4$) ionic strength were found to be log β_{101} (CuENDPDA) = 15.59, and log β_H (CuHENDPDA) = 4.03.

Under the present experimental conditions (pH > 4.2) more than 90% of the europium was present as EuY$^-$. Also, since the stability constants of the europium complexes are much smaller than for the corresponding copper complexes, the exchange reactions (*4*)



$$\begin{array}{ll} \mathrm{EuY^-} & \mathrm{CuY^{2-}} \\ \uparrow\downarrow\ \mathrm{H^+} + \mathrm{Cu^{2+}} \rightleftarrows \mathrm{Eu^{3+}} + & \uparrow\downarrow\ \mathrm{H^+} \\ \mathrm{HEuY} & \mathrm{HCuY^-} \end{array} \qquad (4)$$

goes to completion in the presence of excess Cu^{2+} ions. The data in Table I show that when the experimental conditions are constant except for variable Cu^{2+} concentration, the observed rate constants, k_{obs}, remain constant. This independence of the dissociation kinetics to Cu^{2+} concentration, also observed for other polyaminocarboxylate complexes,[3,8–10] is consistent with a dissociative mechanism,[8] (*5*).



$$\begin{array}{l} \mathrm{EuY^-} \rightleftarrows \mathrm{Eu^{3+}} + \mathrm{Y^{4-}} \\ \qquad\qquad\qquad\quad \downarrow\uparrow\ \mathrm{Cu^{2+}} \\ \qquad\qquad\qquad\quad \mathrm{CuY^{2-}} \end{array} \qquad (5)$$

In all subsequent experiments a 20-fold excess of Cu(ClO$_4$)$_2$ (2.08 mM) was used in the reaction mixtures.

TABLE I

Effect on the dissociation rates of EuENDPDA$^-$ of the concentration of Cu(II); I = 0.10 M (NaClO)$_4$; C_{Buffer} = 0.01 M (acetate); T = 298 K; [EuY$^-$]$_T$ = 0.10 mM.

[Cu(Ac)$_i^{2-i}$] (mM)	pH	K_{obs} (s^{-1})
0.2083	4.588	2.21 ± 0.08
0.4165	4.587	2.17 ± 0.08
0.6245	4.593	2.08 ± 0.08
1.0413	4.593	2.09 ± 0.08
2.0826	4.575	2.23 ± 0.08

Figure 2 reproduces scans of the absorbance changes with time for different pH values at an acetate buffer concentration of 5.88 mM. The corresponding pseudo-first-order plots shown in Figure 3 are linear over at least three or more half-lives. Table II summarizes the results obtained with different experimental conditions. The error limits quoted are the maximum deviations from the average.

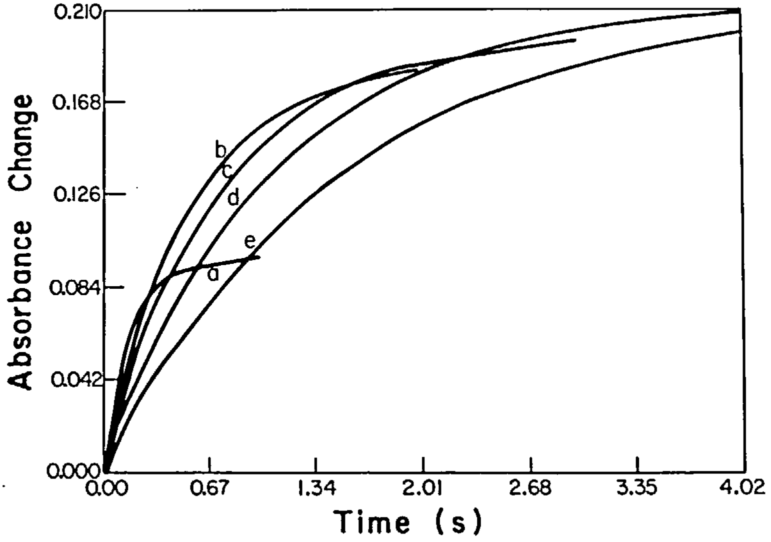


FIGURE 2 Change in absorbance with time for various pH values and [Acetate] = 5.88 mM; the pH values are: a = 3.98; b = 4.63; c = 4.81; d = 4.98; e = 5.20.

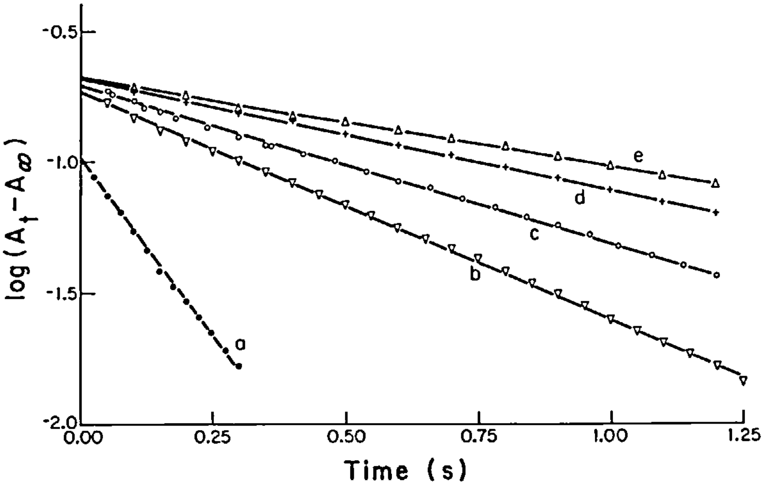


FIGURE 3 Variation of log $(A_t - A_\infty)$ with time where A_t = absorbance at t, A_∞ = absorbance at t = ∞; [Acetate] = 5.88 mM; the pH values are: a = 3.98; b = 4.63; c = 4.81; d = 4.98; e = 5.20.

TABLE II

Variation of the pseudo-first-order rate constants, k_{obs}, with hydrogen ion concentration; $I = 0.10$ M ($NaClO_4$); $[Cu(Ac)_i^{2-i}] = 2.083$ mM; $[EuENDPDA^-] = 0.10$ mM; $T = 298$ K.

C_{Buffer} (mM)	10^5 $[H^+]$ (M)	K_{obs} (s^{-1})
5.88	13.30	6.83 ± 0.65
	10.13	5.44 ± 0.32
	6.41	3.98 ± 0.10
	4.75	2.69 ± 0.02
	3.03	1.91 ± 0.04
	1.98	1.37 ± 0.02
	1.33	0.96 ± 0.05
	0.80	0.71 ± 0.02
10.0	21.87	12.67 ± 0.10
	7.19	4.56 ± 0.15
	5.91	3.58 ± 0.04
	4.45	3.15 ± 0.03
	3.87	2.60 ± 0.02
	3.40	2.23 ± 0.10
	2.86	2.30 ± 0.02
	2.21	1.61 ± 0.02
	1.65	1.28 ± 0.02
	0.05	0.17 ± 0.01
25.0	12.50	8.52 ± 0.10
	8.00	5.15 ± 0.10
	5.65	3.94 ± 0.08
	4.04	2.77 ± 0.10
	2.87	2.37 ± 0.05
	2.06	1.69 ± 0.02
	1.97	1.60 ± 0.03
	0.77	1.00 ± 0.02
50.0	11.14	8.92 ± 0.13
	7.21	7.09 ± 0.08
	5.27	4.96 ± 0.10
	3.51	3.80 ± 0.05
	2.22	2.53 ± 0.03
	1.70	2.18 ± 0.06
	1.22	1.69 ± 0.02
	0.75	1.35 ± 0.02
75.0	7.53	9.44 ± 0.12
	5.13	6.91 ± 0.09
	3.71	5.30 ± 0.08
	2.60	3.80 ± 0.09
	1.79	2.96 ± 0.05
	1.21	2.12 ± 0.02
	0.77	1.57 ± 0.02
100.0	5.06	8.20 ± 0.14
	3.71	6.23 ± 0.13
	2.65	4.98 ± 0.10
	1.84	3.78 ± 0.05
	1.15	2.46 ± 0.02
	0.71	1.84 ± 0.02

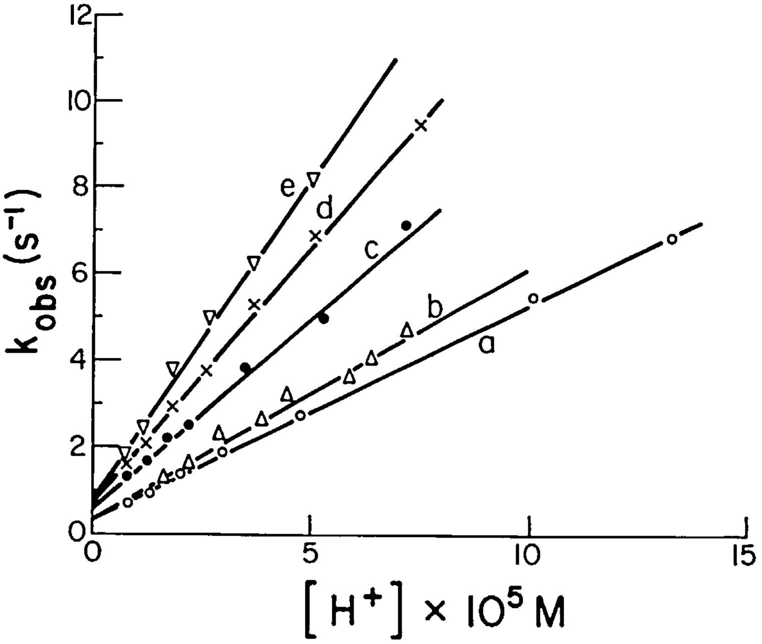


FIGURE 4 Dependence of k_{obs} on [H^+] for different buffer concentrations. The concentrations of acetate are: a = 5.9 mM; b = 10 mM; c = 50 mM; d = 75 mM; e = 100 mM.

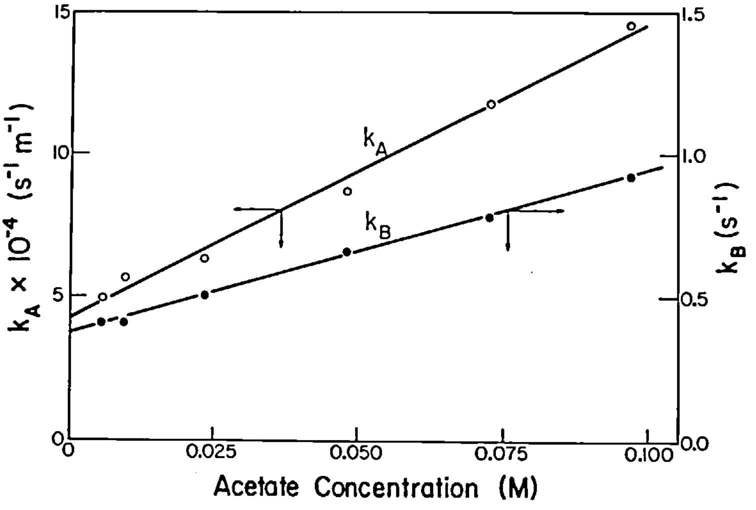


FIGURE 5 Depedence of k_A, the acid dependent rate constant, and k_B, the acid independent rate constant on acetate buffer concentration.

The dependence of the observed rate constants on the hydrogen ion concentration at variable total buffer concentration is shown in Figure 4. In each case, the data fit straight lines with measurable non-zero intercepts which is consistent with the exchange reaction proceeding *via* both an acid-independent and an acid-dependent pathway. The latter has a first-order hydrogen ion dependency. Accordingly, (*6*) is obtained.

$$k_{obs} = k_A[H^+] + k_B \qquad (6)$$

Both k_A and k_B are directly proportional to the total acetate concentration corrected for the formation of copper acetate complexes as shown in Figure 5. Based on these results, the overall rate of reaction can be expressed as shown in (*7*).

$$\text{Rate} = k_1[EuY^-] + k_2[EuY^-][Ac^-] + k_3[EuY^-][H^+] + k_4[EuY^-][H^+][Ac^-] \qquad (7)$$

The values of the specific rate constants, k_n (n = 1–4), calculated with a weighted least-squares program, are listed in Table III. This Table also gives analogous rate constants for the dissociation of other lanthanide-polyaminocarboxylates.

TABLE III

Rate constants for the exchange reaction M/LnY; T = 25°C; I = 0.10 M.

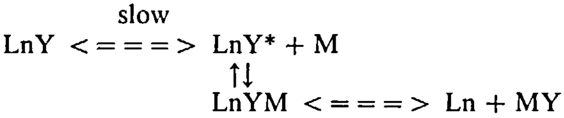
Exchange Reaction	Rate Term	Rate Constant	Ref.
Cu(II)/EuENDPDA$^-$	$k_1[EuY^-]$	$0.36 \pm 0.05\,s^{-1}$	p.w.
	$k_2[EuY^-][Ac^-]$	$5.80 \pm 0.60\,M^{-1} \times s^{-1}$	p.w.
	$k_3[EuY^-][H^+]$	$4.26 \pm 0.10 \times 10^4\,M^{-1} \times s^{-1}$	p.w.
	$k_4[EuY^-][Ac^-][H^+]$	$1.03 \pm 0.21 \times 10^6\,M^{-2} \times s^{-1}$	p.w.
Ce(III)/CeHEDTA	$k_1[CeY][H^+]$	$1.01 \times 10^3\,M^{-1}s^{-1}$	4
	$k_2[CeY][Ac^-][H^+]$	$3.85 \times 10^5\,M^{-2}s^{-1}$	4
Ce(III)/CeEDTA$^-$	$k_1[CeY^-][H^+]$	$1.38 \times 10^3\,M^{-1}s^{-1}$	4
	$k_2[CeY^-][Ac^-][H^+]$	$4.22 \times 10^4\,M^{-2}s^{-1}$	4
Eu(III)/EuEDTA$^-$	$k_1(EuY)(H^+)$	$2.28 \times 10^2\,M^{-1}s^{-1}$	1
Ce(III)/CeCDTA$^-$	$k_1[CeY^-][H^+]$	$6.3\,M^{-1}s^{-1}$	4
	$k_2[CeY^-][H^+][Ac^-]$	$400\,M^{-2}s^{-1}$	4
Eu(III)/EuTMDTA$^-$	$k_1[EuY][H^+]$	$2.29 \times 10^4\,M^{-1}s^{-1}$	11
Cu(II)/EuK22DA^{2+*}	$k_1[EuY^+]$	$4.31 \times 10^{-4}\,s^{-1}$	10
	$k_2[EuY^+][H^+]$	$0.57\,M^{-1}s^{-1}$	10

* K22DA = 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N*,*N'*-diacetic acid.

DISCUSSION

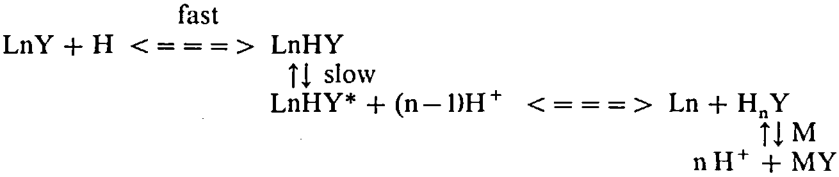
Recent luminescence measurements of hydration[11] showed that the mode of bonding for all Eu-diaminotetracarboxylate complexes is the same, *i.e.*, the metal ion is coordinated to the six donor sites of the ligand with approximately 2.5 additional water molecules to saturate the coordination sphere. This was the mode for LnENDPDA$^-$, also.[11] The kinetic data further support the common nature of these complexes as the dissociation of LnENDPDA$^-$ follows a similar mechanism to that observed for the dissociation of other lanthanide complexes containing polyaminocarboxylate ligands.[1-4,12] This mechanism can be shown schematically as follows.

a. acid-independent



$$\begin{tikzcd}
LnY \arrow[r, leftrightarrow, "slow"] & LnY^* + M \arrow[d, leftrightarrow] & \\
 & LnYM \arrow[r, leftrightarrow] & Ln + MY
\end{tikzcd}$$

b. acid-dependent



$$\begin{tikzcd}
LnY + H \arrow[r, leftrightarrow, "fast"] & LnHY \arrow[d, leftrightarrow, "slow"] & \\
 & LnHY^* + (n-1)H^+ \arrow[r, leftrightarrow] & Ln + H_nY \arrow[d, leftrightarrow, "M"] \\
 & & nH^+ + MY
\end{tikzcd}$$

The lanthanide-carboxylate bonds are rapidly breaking and forming, allowing the attachment of H^+ or M to a dissociated carboxylate. The slow step for the acid-independent pathway is considered to be due to the formation of a (LnY*) complex in which the bonding to the lanthanide cation of one of the nitrilodiacetate segments is broken. This is sequentially followed by a rapid attachment of Cu^{2+} ion to the free iminodiacetate arm. The reaction proceeds to completion by breaking the remaining LnY bonds. The enhancement observed for the acid-dependent dissociation pathway may be explained in terms of a rapid protonation of one of the free carboxylate arms, followed by a slow transference of this carboxylate bound proton to the associated nitrogen of the nitrilodiacetate segment to form (LnHY*). As with Cu^{2+} reaction, this protonation retards the reformation of the stable LnY complex and leads to complete dissociation of that species.

Essentially, the mechanisms proposed for the two pathways are similar. The enhancement observed for the acid-dependent pathway reflects the differences in binding ability of the free donor sites toward Cu^{2+} *vs* H^+ as well as the effective concentration of each in the immediate vicinity of the breaking bonds.

In the study of the $EuTMDTA^-$ dissociation, the rate constant for the acid catalyzed path was found to be about a hundred times greater than that for the analogous dissociation of the $EuEDTA^-$ complex. This was interpreted as reflecting the greater strain (and, therefore, decreased stability) in the 6-membered chelate ring of the Eu and the two nitrogen donors in TMDTA compared to that of the 5-membered ring for $EuEDTA^-$. In this study, the Eu chelate ring with the two nitrogen sites is 5-membered but the propionate arms lead to 6-membered rings for chelation of Eu to a carboxylate of the propionate groups and the neighbouring nitrogen. The values in Table III show that the effect on the acid catalyzed dissociation rate is about the same as in the TMDTA complex. It is noteworthy that the LnHEDTA complex, which involves only 3 carboxylate groups (but only 5-membered chelate rings), is more stable than the TMDTA or the ENDPDA complex. Obviously, the stabilizing effect of the 5-membered chelate rings is a major factor in the dissociation kinetics of these multidentate ligand complexes. The stabilizing structural effects are particularly evident in the very small dissociation rate constants for the EuK22DA complex (K22DA = 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N*,*N*′-diacetate). The aza ring with its multiple 5-membered chelation to Eu(III) is about 400 times slower to dissociate (by the acid catalyzed path) than EuEDTA.

ACKNOWLEDGMENTS

This research was supported by a grant from the Division of Chemical Sciences, OBES-USDOE.

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