

Dissociation Kinetics of Linear Polyaminopolycarboxylate Complexes of Lanthanides(III)

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The dissociation kinetics of linear polyaminopolycarboxylate complexes of lanthanide ions (Ln^{3+} : Ce^{3+} , Eu^{3+} and Yb^{3+}) has been studied in an aqueous solution of 0.10 M (NaClO_4) at $25.0 \pm 0.1^\circ\text{C}$ using Cu(II) ions as a scavenger. The dissociation rates of acid-catalyzed pathway decrease in the order $\text{Ln(EPDTA)}^- > \text{Ln(DPOT)}^- > \text{Ln(TMDTA)}^- > \text{Ln(MPDTA)}^- > \text{Ln(EDTA)}^- > \text{Ln(PDFTA)}^- > \text{Ln(DCTA)}^-$ according to the present and literature data. An increase in the N-Ln-N chelate ring from 5 to 6 and substitution of two methyl groups, one ethyl and hydroxyl group on a chelate ring carbon of these ligands leads to a decrease in kinetic stabilities of the complexes. The substitution of one methyl group and cyclohexyl ring on a ring carbon, however, results in a significant increase in the kinetic stability of the resulting Ln^{3+} complexes. Individual reaction steps taking place for each system, with different copper, acetate buffer concentration and pH dependence, are also discussed.

Introduction

There has been considerable interest in thermodynamic^{1,2} and kinetic³⁻⁶ studies of lanthanide complexes because of their significant implications in analytical, biological and other chemical application. In general, it is observed that the ligand topology can affect the thermodynamic and kinetic stabilities of lanthanide complexes. Ligand characteristics such as the charge, chelate ring size, the number of donor atoms and stereochemical rigidity imposed are all found to be important. Thus, it is achieved that by varying these factors, one might be able to develop lanthanide ion selective-reagents^{7,8} and magnetic resonance imaging (MRI) contrast agents^{9,10}. The dissociation reactions of lanthanide complexes show strong pH dependence with the rate and mechanism changing upon changes in acid strength. The pH dependence was found to be a linear^{11,12}, quadratic¹³ and saturation³ kinetic dependence. From a mechanistic point of view, there are at least two pathways leading to the dissociation of these complexes. One is the self-dissociation pathway, the rate of which is independent of the concentrations of acid, base or any coordinating anions present in the supporting electrolyte medium. The other is an acid-catalyzed pathway, which may show a first-order or more complex dependence on acid concentration depending on the number of basic sites available for attack, stability of the complex, etc. Certainly other pathways are also found to be catalyzed by the concentration of buffer and attacked by the metal ion.

To further understand the factors involved in chelating kinetics we report herein the systematic dissociation kinetic studies of lanthanides (Ln^{3+} : Ce^{3+} , Eu^{3+} and Yb^{3+}) complexes of 2-methyl-1,2-diaminopropane- N,N,N',N' -tetraacetic acid (MPDFTA), 1-ethyl-1,3-diaminopropane- N,N,N',N' -tetraacetic acid (EPDFTA) and 1,3-diamino-2-propanol- N,N,N',N' -tetraacetic acid (DPOT) (Fig. 1).

Experimental

Reagents and Solutions. The ligands MPDFTA and

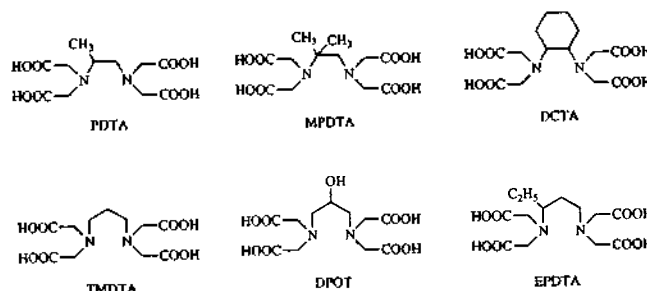


Figure 1. Structures of the linear polyaminopolycarboxylate ligands.

EPDFTA were synthesized following the method published elsewhere^{14,15} and DPOT (Aldrich) was used as received. The stock solutions of Ce^{3+} , Eu^{3+} and Yb^{3+} were prepared from CeCl_3 , Eu_2O_3 and Yb_2O_3 (Aldrich, 99.99%). The concentration of the stock solutions was determined by EDTA titration using Xylenol Orange as an indicator. The concentration of ligand stock solutions was determined by titration against a standard $\text{Cu(ClO}_4)_2$ solution using murexide as an indicator. Complex solutions were made by mixing appropriate amounts of lanthanide perchlorate and a slight excess of ligand. The complex concentration in the reaction mixtures was 1.0×10^{-4} M, while that of the exchanging Cu^{2+} ion was constant at 1.0×10^{-3} M or it was varied between 2.0×10^{-4} and 1.0×10^{-3} M. The buffer solutions were made by using a constant acetate ion concentration and varying the concentration of acetic acid necessary for attainment of the desired pH. All other chemicals used were of analytical grade and were used without further purification. Distilled water was used for all solutions.

Measurements. The ionic strength was adjusted to 0.10 M with NaClO_4 . The pH measurements were made by a Beckman Model $\Phi 71$ pH meter fitted with a combination electrode. The hydrogen ion concentrations were established from the measured pH value by procedures reported previously⁵. Kinetic measurements were carried out using a Hi-

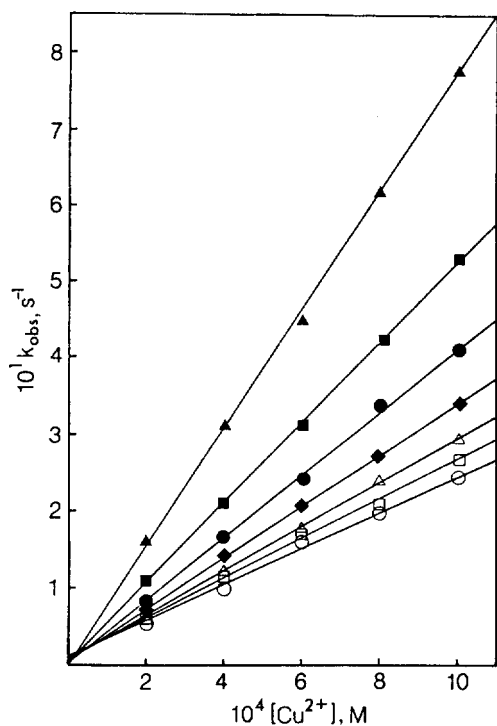
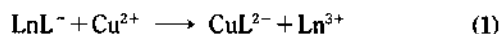


Figure 2. Plots of k_{obs} versus $[Cu^{2+}]$ for the dissociation kinetics of $Ce(MPDTA)^-$ at different pH values ($[Ce(MPDTA)^-] = 1.0 \times 10^{-4}$ M, $[OAc^-] = 0.01$ M, $I = 0.10$ M (NaClO₄), $T = 25 \pm 0.1^\circ C$; pH: \circ , 4.003; \square , 4.072; \triangle , 4.160; \blacklozenge , 4.262; \bullet , 4.401; \blacksquare , 4.565; \blacktriangle , 4.781).

Tech stopped-flow spectrophotometer interfaced with a Scientific data acquisition system. The temperature of the reaction mixture was maintained at $25.0 \pm 0.1^\circ C$ with the use of a Lauda RM 6 circulatory water bath. As the lanthanide complexes do not show appreciable absorption in the UV or visible region, Cu^{2+} was used as the scavenger of free ligand and the reaction kinetics were followed by monitoring the growth in absorbance due to the formation of copper complex at 290 nm.

Results

Since the thermodynamic stabilities of copper polyaminopolycarboxylate complexes are much greater than those of corresponding lanthanide complexes^{15,16} the displacement of Ln^{3+} ions from the complexes is complete in the presence of excess Cu^{2+} ions:



where L is H₄MPDTA, H₄EPDTA and H₄DPOT ligands. The experimental data show excellent pseudo-first-order reaction rates. The standard deviations of the observed rate constants (k_{obs}) were in the range 1-5%. The observed rate constants were calculated from the absorbance versus time data using a first-order kinetic model¹⁷.

Ligand MPDTA. The observed rate constants for the $Ln(MPDTA)^-$ complexes were found to be independent of acetate ion concentration. The dependence of k_{obs} on the $[Cu^{2+}]$ for $Eu(MPDTA)^-$ complex is plotted in Fig. 2 at different

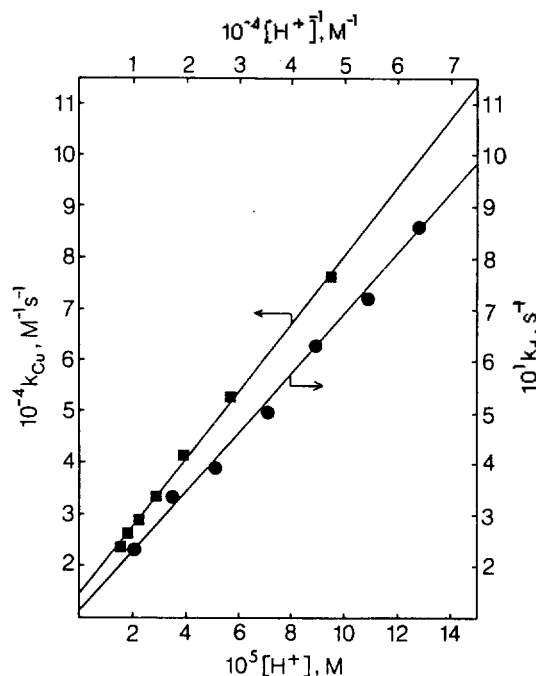


Figure 3. Plots of k_d versus $[H^+]$ and k_{Cu} versus $[H^+]^{-1}$ for the dissociation kinetics of $Ce(MPDTA)^-$ ($[Ce(MPDTA)^-] = 1.0 \times 10^{-4}$ M, $[OAc^-] = 0.01$ M, $I = 0.10$ M (NaClO₄), $T = 25.0 \pm 0.1^\circ C$).

pH values. The variation of k_{obs} with $[Cu^{2+}]$ was linear with significant intercept and slope. The straight line dependence on $[Cu^{2+}]$ indicates a term that is first order in Cu^{2+} , while the intercept indicates a term that give the first-order dissociation of $Ln(MPDTA)^-$ independent of $[Cu^{2+}]$. The observed rate constants can therefore be expressed as:

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

where k_d and k_{Cu} are functions of the acidity, $[H^+]$. Figure 3 shows that k_d is proportional to $[H^+]$ while k_{Cu} is proportional to $[H^+]^{-1}$. Based on these results, the overall rate of reactions can be expressed as:

$$\text{Rate} = k_d [LnL^-] + k_H [LnL^-][H^+] + k_{Cu} [LnL^-][Cu^{2+}] + k_{Cu,H^{-1}} [LnL^-][Cu^{2+}][H^+]^{-1} \quad (3)$$

Values of the specific rate constants (k_d , k_H , k_{Cu} and $k_{Cu,H^{-1}}$) calculated from a weighted least-squares program are listed in Table 1.

Ligands EPDTA and DPOT. The observed rate constants for $Ln(EPDTA)^-$ and $Ln(DPOT)^-$ complexes were found to be independent of $[Cu^{2+}]$ and dependent of [acetate] (except for $Yb(DPOT)^-$). The dependence of k_{obs} on the $[H^+]$ at various acetate buffer concentration for $Eu(EPDTA)^-$ complex is shown in Fig. 4. A linear least-square fit to this plot had a non-zero intercept which is consistent with the exchange reaction proceeding *via* both acid-independent and acid-catalyzed pathways. Thus, the observed rate constants can be expressed as:

$$k_{obs} = k_d + k_H [H^+] \quad (4)$$

where the intercept value of $Yb(DPOT)^-$ system is slightly

Table 1. Summary of Rate Constants for Dissociation Reactions of Lanthanide Complexes of Linear Polyaminopolycarboxylate at $25.0 \pm 0.1^\circ\text{C}$ and $I=0.10\text{ M}$ (NaClO_4)

Complex	k_d (s^{-1})	k_H ($\text{M}^{-1}\text{s}^{-1}$)	k_{Cu} ($\text{M}^{-1}\text{s}^{-1}$)	k_{OAc} ($\text{M}^{-1}\text{s}^{-1}$)	K_{CuOH^+} ($\text{M}^{-1}\text{s}^{-1}$)	$k_{\text{H-OAc}}$ ($\text{M}^{-2}\text{s}^{-1}$)	Ref.
Ce(MPDTA) ⁻	$(1.08 \pm 0.14) \times 10^{-1}$	$(5.76 \pm 0.17) \times 10^3$	$(1.41 \pm 0.04) \times 10^4$	a	$(6.68 \pm 0.11) \times 10^7$	a	
Eu(MPDTA) ⁻	$(6.89 \pm 0.12) \times 10^{-2}$	$(8.84 \pm 0.16) \times 10^2$	$(2.07 \pm 0.06) \times 10^4$	a	$(5.68 \pm 0.14) \times 10^7$	a	
Ce(DPOT) ⁻	2.74 ± 0.10	$(6.06 \pm 0.14) \times 10^6$	a	$(3.87 \pm 0.29) \times 10^1$	a	$(6.67 \pm 0.46) \times 10^7$	
Eu(DPOT) ⁻	$(1.27 \pm 0.14) \times 10^{-1}$	$(6.32 \pm 0.12) \times 10^4$	a	5.52 ± 0.16	a	$(8.02 \pm 0.30) \times 10^5$	
Yb(DPOT) ⁻	a	$(8.88 \pm 0.18) \times 10^2$	a	a	a	a	
Eu(EPDTA) ⁻	3.09 ± 0.12	$(5.02 \pm 0.18) \times 10^5$	a	$(2.40 \pm 0.24) \times 10^1$	a	$(1.88 \pm 0.12) \times 10^7$	
Yb(EPDTA) ⁻	$(3.22 \pm 0.14) \times 10^{-2}$	$(1.77 \pm 0.12) \times 10^4$	a	$(3.85 \pm 0.15) \times 10^{-1}$	a	$(8.27 \pm 0.26) \times 10^5$	
Ce(EDTA) ⁻	2.0×10^{-4}	2.9×10^3	a	a	a	a	21
Eu(EDTA) ⁻	a	6.0×10^2	a	a	a	a	22
Eu(PDTA) ⁻	a	3.5×10^2	a	a	a	a	19
Ce(DCTA) ⁻	$(2.0 \pm 0.5) \times 10^{-4}$	$(6.0 \pm 0.2) \times 10^1$	a	a	a	a	23
Eu(DCTA) ⁻	$(9.8 \pm 3.4) \times 10^{-6}$	2.2 ± 0.2	a	a	a	a	23
Ce(TMDTA) ⁻	$(2.25 \pm 0.30) \times 10^1$	$(3.99 \pm 0.54) \times 10^6$	a	$(5.89 \pm 0.79) \times 10^1$	a	$(1.28 \pm 0.17) \times 10^8$	6
Eu(TMDTA) ⁻	a	$(2.29 \pm 0.13) \times 10^4$	a	a	a	a	5

*Not observed. In this Table k_d and k_H are rate constants of acid-independent and acid-catalyzed dissociation rates of the Ln^{3+} complexes.

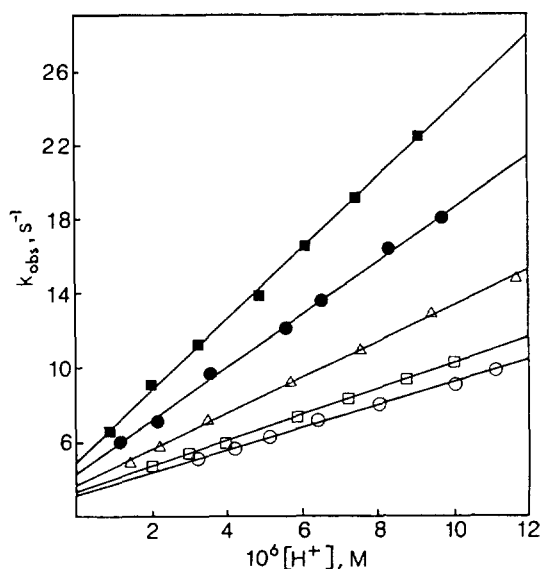


Figure 4. Plots of k_{obs} versus $[\text{H}^+]$ for the dissociation kinetics of $\text{Eu}(\text{EPDTA})^-$ at different buffer concentrations ($[\text{Eu}(\text{EPDTA})^-] = 1.0 \times 10^{-4}\text{ M}$, $[\text{Cu}^{2+}] = 1.0 \times 10^{-3}\text{ M}$, $I = 0.10\text{ M}$ (NaClO_4), $T = 25.0 \pm 0.1^\circ\text{C}$; $[\text{OAc}^-]$: \circ , 5.0 mM; \square , 10.0 mM; \triangle , 25.0 mM; \bullet , 50.0 mM; \blacksquare , 75.0 mM).

negative, which means that the acid-independent dissociation process may be negligible. Figure 5 shows that k_d and k_H are directly proportional to the total acetate buffer concentration. The enhanced rates in the presence of higher acetate buffer concentration may be attributed to the acetate ion complexation. If a ternary complex, LnLOAc^{2-} is present, it is probably more sensitive than binary LnL^- to be attacked by the hydrogen ions. Based on the data, the overall rate of reaction may be expressed as:

$$\text{Rate} = k_d [\text{LnL}^-] + k_{\text{OAc}} [\text{LnL}^-][\text{OAc}^-] + k_H [\text{LnL}^-][\text{H}^+]$$

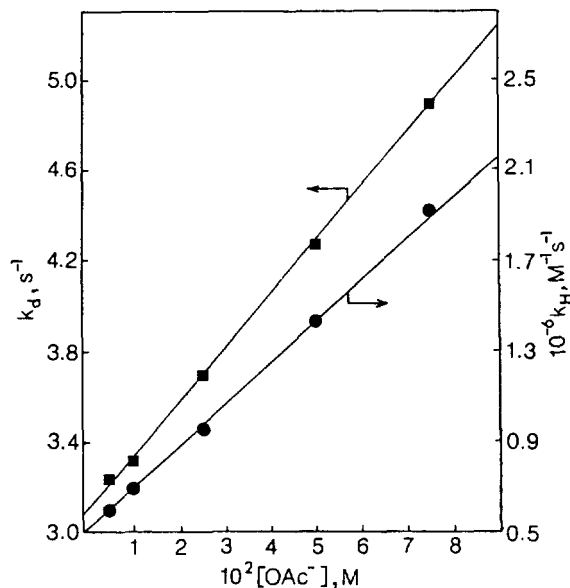


Figure 5. Plots of k_d and k_H versus $[\text{OAc}^-]$ for the dissociation kinetics of $\text{Eu}(\text{EPDTA})^-$ ($[\text{Eu}(\text{EPDTA})^-] = 1.0 \times 10^{-4}\text{ M}$, $[\text{Cu}^{2+}] = 1.0 \times 10^{-3}\text{ M}$, $I = 0.10\text{ M}$ (NaClO_4), $T = 25.0 \pm 0.1^\circ\text{C}$).



Values of the specific rate constants (k_d , k_{OAc} , k_H and $k_{\text{H-OAc}}$) calculated from a weighted least-squares program are listed in Table 1.

Discussion

The reaction between $\text{Ln}(\text{MPDTA})^-$ complex and Cu^{2+} ion proceeds by reaction pathway that is similar to those reported in the displacement of lanthanide ions in their polyaminopolycarboxylate complexes^{12,18}. Both dissociative pathway,

which obviously shows an acid-independent and an acid-catalyzed contribution, and associative pathways take place. The first and the second terms in eq. (3) are responsible for the dissociative pathway of the $[\text{Cu}^{2+}]$ -independent mode. The rate-determining step involves the loss of Ln^{3+} from the complex and a rapid reaction of the released ligand with Cu^{2+} . Equation (3) also represents the associative pathway of the $[\text{Cu}^{2+}]$ -dependent mode which is composed of the direct attack route of Cu^{2+} on partially dissociated $\text{Ln}(\text{MPD}\text{T}\text{A})^-$ and the $[\text{H}^+]^{-1}$ dependence. The $[\text{H}^+]^{-1}$ dependence could be explained by the existence of the attack of hydrolyzed copper species (CuOH^+) on $\text{Ln}(\text{MPD}\text{T}\text{A})^-$, even though investigated pH is not higher. Thus, k_{CuOH^+} is obtained by the expression $k_{\text{Cu-H}^{-1}} = k_{\text{CuOH}^+} \beta_{\text{CuOH}^+}$ where β_{CuOH^+} ($=K_{\text{CuOH}^+} K_w$) is a stability constant (i.e., 2.0×10^{-8})¹².

On the other hand, the dissociation of $\text{Ln}(\text{EPD}\text{T}\text{A})^-$ and $\text{Ln}(\text{DPOT})^-$ complexes follows a mechanism similar to that of the dissociation of other lanthanide polyaminopolycarboxylate complexes^{6,18}. In these mechanisms, the Ln-carboxylate bonds are rapidly formed and broken, allowing attachment of H^+ or Cu^{2+} to dissociated carboxylate. Presumably, the slow step involves the rupture of a Ln-N bond subsequent to the formation of a protonated CeLH or a ternary LnLCu^+ intermediate.

The effect of the metal and ligand on the dissociation rate can be seen by comparing the values in Table 1 along with the other lanthanide polyaminopolycarboxylate complexes. The consistent decrease in the acid-independent and acid-catalyzed dissociation rates of the Ln^{3+} complexes from Ce^{3+} to Yb^{3+} parallels the thermodynamic stability of these complexes with decreasing ionic size or increasing charge density of Ln^{3+} . A comparison of the dissociation rate constants of Ln^{3+} complexes of linear polyaminopolycarboxylates demonstrates the order $\text{Ln}(\text{EPD}\text{T}\text{A})^- > \text{Ln}(\text{DPOT})^- > \text{Ln}(\text{TMD}\text{T}\text{A})^- > \text{Ln}(\text{MPD}\text{T}\text{A})^- > \text{Ln}(\text{EDT}\text{A})^- > \text{Ln}(\text{PD}\text{T}\text{A})^- > \text{Ln}(\text{DCT}\text{A})^-$. Both rate constants are significantly affected by chelate ring size and the substituent group between two nitrogen atoms of ligands. The dissociation rates of the EPDTA, DPOT and TMDTA (trimethylenedinitrilotetraacetic acid) complexes were found to be much faster than those of the MPDTA, EDTA, PDTA (propylenedinitrilotetraacetic acid) and DCTA (cyclohexylenedinitrilotetraacetic acid) complexes.²³ This probably reflects the lower stability of the complexes as the chelate ring size of the N-Ln-N ring increases from 5 to 6. The much slower rate of dissociation of DCTA complex compared to that of EDTA and PDTA complexes may be attributed to the stereochemical rigidity imposed by the cyclohexyl ring⁵. The acid-catalyzed rate constant of $\text{Eu}(\text{PD}\text{T}\text{A})^-$ ¹⁹ was found to be about twice smaller than that of $\text{Eu}(\text{EDT}\text{A})^-$, while $\text{Eu}(\text{MPD}\text{T}\text{A})^-$ dissociates about three times faster than $\text{Eu}(\text{EDT}\text{A})^-$. Substitution of a single methyl group on the ethylene chelate ring of PDTA increases the thermodynamic stability ($\log \beta_{\text{Eu}(\text{MPD}\text{T}\text{A})^-} = 18.09$ versus $\log \beta_{\text{Eu}(\text{EDT}\text{A})^-} = 17.51$)¹⁶ by steric rigidity, yielding a complex with somewhat greater kinetic inertness. Substitution of two methyl groups on the ethylene chelate ring carbon of MPDTA, however, has a detrimental effect upon the dissociation rate and upon the resulting thermodynamic stability of $\text{Eu}(\text{MPD}\text{T}\text{A})^-$ ($\log \beta_{\text{Eu}(\text{MPD}\text{T}\text{A})^-} = 17.14$)¹⁶. A similar argument has been used to explain the dissociation rate of $\text{Gd}(\text{MeDETA})$ (MeDETA = 9-methyl-1,4,7-triazacyclodecane-N,N',N''-triacetic acid) and Gd

(Me_2DETA) (Me_2DETA = 9,9-dimethyl-1,4,7-triazacyclodecane-N,N',N''-triacetic acid)²⁰. On the other hand, the acid-catalyzed rate of $\text{Eu}(\text{DPOT})^-$ is about twice faster than that of $\text{Eu}(\text{TMD}\text{T}\text{A})^-$. This probably may be attributed to the decrease of nitrogen donor basicity by the hydroxyl group of DPOT compared to that of TMDTA ($pK_{\text{a}(\text{DPOT})} = 9.49$ versus $pK_{\text{a}(\text{TMD}\text{T}\text{A})} = 10.30$)¹⁶, and in addition presumably the hydroxyl group of the DPOT ligand does not participate in metal ion coordination. However, $\text{Eu}(\text{EPD}\text{T}\text{A})^-$ dissociates about ten or twenty times much faster than $\text{Eu}(\text{DPOT})^-$ and $\text{Eu}(\text{TMD}\text{T}\text{A})^-$, although EPDTA has the same chelate ring as well as DPOT and TMDTA. It is likely that the 6-membered propylene chelate ring conformation in $\text{Eu}(\text{EPD}\text{T}\text{A})^-$ is substantially different from that in $\text{Eu}(\text{DPOT})^-$ and $\text{Eu}(\text{TMD}\text{T}\text{A})^-$. This difference in conformation due to the possible repulsion between the ethyl group and the complex may cause the easier dissociation of one of the nitrogen atoms from the Eu^{3+} ion.

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