

Europium(III) 및 Ytterbium(III) *N,N'*-Ethylenebis[2-(*o*-hydroxyphenyl)glycine] 착물의 해리 반응속도론

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Dissociation Kinetics of *N,N'*-Ethylenebis[2-(*o*-hydroxyphenyl)glycine] Complexes of Europium(III) and Ytterbium(III)

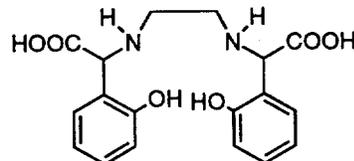
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In recent years the two phenolate-containing multidentate ligand with *N,N'*-ethylenebis[2-(*o*-hydroxyphenyl)glycine] (EHPG), an EDTA-type framework has been developed as ligand having high affinities for Ga³⁺, In³⁺ and Gd³⁺, as well as Fe³⁺, as radiopharmaceuticals, and as magnetic resonance paramagnetic contrast imaging agents.^{1,2} Recently EHPG was also used as an active site model of the iron transport protein transferrin,³ and the stabilities of the complexes with variety of metal ions have been determined.⁴ Studies on the dissociation kinetics of lanthanide complexes of polyaza and polyaminopolycarboxylates demonstrated that the exchange occurs via both acid-dependent and acid-independent pathways.⁵⁻⁹ The rate-determining step in the acid-catalyzed mechanism was assigned either to slow rupture of one of the metal-carboxylate bonds following the protonation of a carboxylate group or to slow transfer of the hydronium ion from the protonated carboxyl oxygen to the neighboring nitrogen site, causing the metal nitrogen bond to break. The acid-independent mode was assumed to proceed via a binuclear intermediate, LnYM, in which the lanthanide and the metal ion are bound to opposite ends of the ligand. The influence of metal ion, ligand topology, buffer anion and electrolyte on



EHPG

Chart 1.

the rate and mechanism of both dissociative and associative pathways has been also reported by our and other research groups.¹⁰⁻¹⁴ However, this effect has not been studied systematically and there is no general explanation.

To further understand the factors involved in the chelating kinetics, we hereby report the result of the dissociation kinetics of Eu(III) and Yb(III) complexes of *N,N'*-ethylenebis[2-(*o*-hydroxyphenyl)glycine] (EHPG) (Chart 1).

EXPERIMENTALS

Stock solutions of Eu³⁺ and Yb³⁺ were prepared from Eu₂O₃ and Yb₂O₃ (Aldrich, 99.99%) and their concentrations were determined by complexometric titration using Xylenol Orange as an indicator. *N,N'*-ethylenebis[2-(*o*-hydroxyphenyl)glycine] (EHPG) was obtained from Aldrich and purified

by successive recrystallization from a hot basic solution by adding perchloric acid and cooling. The concentration of a EHPG stock solution was determined by titration against a standard $\text{Cu}(\text{ClO}_4)_2$ solution using murexide as an indicator. Complex solutions were made by mixing appropriate amount of lanthanide perchlorate and a slight excess of ligand. All other chemicals used were of analytical grade without further purification. Distilled water was used for all solutions.

The ionic strength of the sample solution was adjusted to 0.10 M with NaClO_4 and sodium acetate was used as a buffer. The pH measurements were made by a Beckman Model Φ 71 pH meter fitted with a Beckman combination electrode. The hydronium ion concentrations were established from the measured pH values by procedures previously reported.⁶ Kinetic measurements were carried out on a Hi-Tech stopped-flow spectrophotometer interfaced with Scientific data acquisition system. The temperature of the reaction mixture was maintained at $25.0 \pm 0.1^\circ\text{C}$ with the use of a Lauda RM 6 circulatory water bath. Since the $\text{Ln}(\text{EHPG})^-$ complexes do not show appreciable absorption in the UV or visible region, Cu^{2+} was used as a scavenger of free ligand and the reaction kinetics was followed by monitoring the growth in absorbance due to the formation of $\text{Cu}(\text{EHPG})_2^{2-}$ complex at 285 nm. The concentration of the $\text{Ln}(\text{EHPG})^-$ was 1.0×10^{-4} M, while that of the exchanging Cu^{2+} ion was either constant at 2.0×10^{-3} M or varied between 2.0×10^{-4} and 2.0×10^{-3} M. The reaction was studied over the pH range of 4.03–5.26.

RESULTS AND DISCUSSION

Since the stability constants of $\text{Ln}(\text{EHPG})^-$ complexes are much lower than that of the corresponding $\text{Cu}(\text{EHPG})_2^{2-}$ complex,⁴ the displacement of Ln^{3+} ions from the $\text{Ln}(\text{EHPG})^-$ complexes is complete in the presence of excess Cu^{2+} ions



The experimental data show excellent pseudo-first-order reaction rates. The rate of dissociation

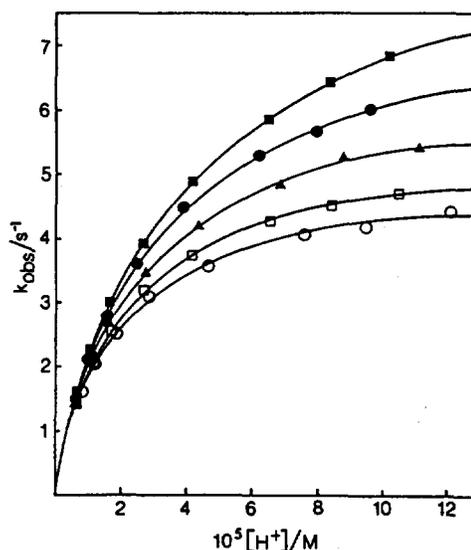


Fig. 1. Plots of k_{obs} versus $[\text{H}^+]$ for the dissociation kinetics of $\text{Eu}(\text{EHPG})^-$ at different acetate buffer concentrations ($[\text{Eu}(\text{EHPG})^-] = 1.0 \times 10^{-4}$ M, $[\text{Cu}^{2+}] = 2.0 \times 10^{-3}$ M, $T = 25.0 \pm 0.1^\circ\text{C}$, $I = 0.10$ M (NaClO_4); $[\text{Acetate}] = 10$ mM (\circ); 25 mM (\square); 50 mM (\triangle); 75 mM (\bullet); 100 mM (\blacksquare)).

of $\text{Ln}(\text{EHPG})^-$ was independent of $[\text{Cu}^{2+}]$, suggesting no appreciable Cu^{2+} ion attack on the Ln^{3+} complex. The concentration of Cu^{2+} ion was varied by a factor of 10, and the observed rate constant (k_{obs}) values were within 5% of the average value of k_{obs} at a given pH. Such independence of $[\text{Cu}^{2+}]$ in the dissociation kinetics of lanthanide complexes has been observed by other workers.^{5,7,12,13} Plots of k_{obs} versus $[\text{H}^+]$ at various acetate buffer concentrations as shown in Fig. 1 always deviated from linearity. The proton dependence upon the rate decreased reaching a saturation condition with a shift from first- to zero-order dependence. Eq. (2) accounts

$$k_{\text{obs}} = \frac{a[\text{H}^+]}{1 + b[\text{H}^+]} \quad (2)$$

for the experimental behavior which reduce to zero-order dependence when $1 \ll b[\text{H}^+]$. The experimental data fitted with the linear functional form as shown in Fig. 2. The terms a and a/b from Eq. (3) could be obtained. In analogy with previous

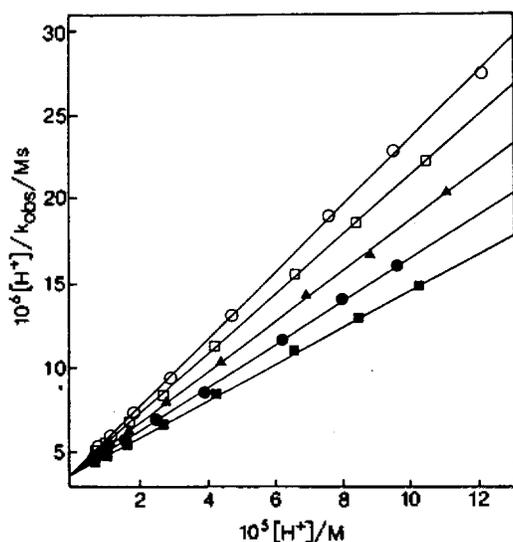


Fig. 2. Plots of $[H^+]/k_{obs}$ versus $[H^+]$ for the dissociation kinetics of $\text{Eu}(\text{EHPG})^-$ at different acetate buffer concentrations ($[\text{Eu}(\text{EHPG})^-] = 1.0 \times 10^{-4} \text{ M}$, $[\text{Cu}^{2+}] = 2.0 \times 10^{-3} \text{ M}$, $T = 25.0 \pm 0.1 \text{ }^\circ\text{C}$, $I = 0.10 \text{ M}$ (NaClO_4); [Acetate] = 10 mM (\circ); 25 mM (\square); 50 mM (\triangle); 75 mM (\bullet); 100 mM (\blacksquare)).

Table 1. Values of k_d and k_H for dissociation reactions of $\text{Ln}(\text{EHPG})^-$ at $25.0 \pm 0.1 \text{ }^\circ\text{C}$ and $I = 0.10 \text{ M}$ (NaClO_4).

Ln^{3+}	$10^2[\text{OAc}^-], \text{ M}$	$k_d, \text{ s}^{-1}$	$k_H, \text{ M}^{-1}\text{s}^{-1}$
Eu^{3+}	1.0	5.02	2.73×10^5
	2.5	5.59	2.74×10^5
	5.0	6.60	2.71×10^5
	7.5	7.70	2.76×10^5
	10.0	8.96	2.69×10^5
Yb^{3+}	1.0	2.46×10^{-1}	5.93×10^3
	2.5	2.52×10^{-1}	6.01×10^3
	5.0	2.42×10^{-1}	5.86×10^3
	10.0	2.48×10^{-1}	5.97×10^3

$$\frac{[H^+]}{k_{obs}} = \frac{1}{a} + \frac{b}{a} [H^+] \quad (3)$$

investigation,¹⁵ the terms a/b and a represent k_d and k_H respectively. Where k_d and k_H are acid-independent and acid-catalyzed rate constant. These values are listed in Table 1. Both k_d and k_H of $\text{Yb}(\text{EHPG})^-$ are independent of acetate buffer concentration and k_H of $\text{Eu}(\text{EHPG})^-$ is also independent whereas k_d of $\text{Eu}(\text{EHPG})^-$ shows a linear

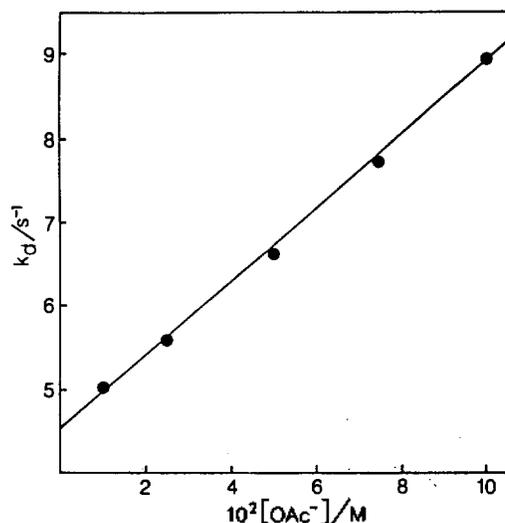


Fig. 3. Plots of k_d versus $[\text{OAc}^-]$ for the dissociation kinetics of $\text{Eu}(\text{EHPG})^-$ ($[\text{Eu}(\text{EHPG})^-] = 1.0 \times 10^{-4} \text{ M}$, $[\text{Cu}^{2+}] = 2.0 \times 10^{-3} \text{ M}$, $T = 25.0 \pm 0.1 \text{ }^\circ\text{C}$, $I = 0.10 \text{ M}$ (NaClO_4)).

dependence. This fact may be attributed to the increase in coordination site of Eu^{3+} compared to that of Yb^{3+} .¹⁶ The dependence of k_d on the acetate buffer concentration can be given by

$$k_d = k_d' + k_{d \cdot \text{OAc}} [\text{OAc}^-] \quad (4)$$

Fig. 3 shows that the straight line was obtained by plotting k_d versus $[\text{OAc}^-]$, which indicates a first-power dependence on acetate buffer concentration. The values of the specific rate constant (k_d' , $k_{d \cdot \text{OAc}}$ and k_H) calculated from the data are given in Table 2. The mechanism of the dissociation of $\text{Ln}(\text{EHPG})^-$ complexes seems to be similar to that of the dissociation of other polyaminopolycarboxylate complexes previously reported.¹⁵ 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 LnLH intermediate.

The effect of the metal and ligand on the dissociation rate constant can be considered by comparing the values in Table 2 along with the other lanthanide polyaminopolycarboxylate complexes.¹⁷⁻¹⁹

Table 2. Rate constants for dissociation reactions of lanthanide complexes of polyaminopolycarboxylate at 25.0±0.1 °C and I=0.10 M (NaClO₄)

Complex	k_d' , s ⁻¹	$k_{d, \text{acc}}$, M ⁻¹ s ⁻¹	k_H , M ⁻¹ s ⁻¹	Ref.
Eu(EHPG) ⁻	4.51±0.08	(4.35±0.13)×10 ¹	(2.73±0.03)×10 ⁵	
Yb(EHPG) ⁻	(2.47±0.04)×10 ⁻¹	"	(5.94±0.06)×10 ³	
Eu(EDTA) ⁻	"	"	(2.28±0.05)×10 ²	17
Yb(EDTA) ⁻	"	"	7.60±0.80	18
Eu(ENDPDA) ⁻	(3.60±0.50)×10 ⁻¹	5.80±0.60	(4.26±0.10)×10 ⁴	19

*Not observed. In this Table k_d' and k_H are rate constants of acid-independent and acid-catalyzed dissociation rates of the Ln³⁺ complexes.

The consistent decrease in the acid-independent and acid-catalyzed dissociation rates of the Ln (EHPG)⁻ complexes from Eu³⁺ to Yb³⁺ parallels the thermodynamic stability of these complexes with decreasing ionic size or increasing charge density of Ln³⁺ ion. This fact may be attributed to decreasing metal-nitrogen bond lability. The acid-catalyzed rate constant of Eu(EHPG)⁻ was found to be about two orders of magnitude larger than that for the analogous dissociation of the Eu (EDTA)⁻ complex. This fact may be interpreted as reflecting the 6-membered rings for chelation of Eu³⁺ to an oxygen of the phenolate groups and the neighboring nitrogen in EHPG. Meanwhile, the acid-catalyzed rate of Eu(EHPG)⁻ dissociates about six times faster than that of Eu(ENDPDA)⁻ (ethylenedinitrilo-*N,N'*-di(3-propanoic)-*N,N'*-diacetic acid), even though EHPG as well as ENDPDA has the same 6-membered chelate ring size (O-Eu-N). This indicates that the chelate ring conformation of the 6-membered phenolate in Eu (EHPG)⁻ may be somewhat different from that of Eu(ENDPDA)⁻. This conformation may allow easier dissociation of one of the phenolate oxygens from the Eu³⁺ coordination sphere.

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