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The Study on the Stability Constant and Species Distribution of Eu (III) and Tb (III) Complexes with BDBPH

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Abstract: The stability constants and species distributions of complexes of two lanthanide ions, Eu(III) and Tb(III), with a macrocyclic ligand, BDBPH, in 1:1 and 2:1system, were determined potentiometrically at 25.0 ºC and I=0.100 mol L^{-1}. The two metal ions could form deprotonated mono- or dinuclear complexes with BDBPH after the first two protons of the ligand completely neutralized. At higher pH values, Eu(III) could not form hydroxy complexes with BDBPH, while Tb(III) could form hydroxy complexes in the type of $M_2L(OH)$, $M_2L(OH)_2$, and $M_2L(OH)_3$.

Keywords: BDBPH, Eu(III), Tb(III), stability constant, species distribution.

Biomimetic hydrolysis of DNA or RNA is of increasing importance in biotechnology and medicine. The ability to cleave nucleic acids efficiently, in a non-degradative manner, and with high levels of selectivity for site or structure will be required by many applications for the manipulation of genes, the design of structural probes and the development of novel therapeutics[1]. There has been much interest in the development of lanthanide complexes as nucleic acid cleavage agents. It has been found that some macrocyclic lanthanide complexes have ability to promote Lewis acid cleavage of the phosphate backbone of DNA[2-4]. We have reported a 24-membered hexaazadiphenol macrocyclic ligand, 3,6,9,17,20,23-hexaaza-29,30-dihydroxy-13,27-dimethyltricyclo [23,3,1,$1^{11,15}$] triaconta-1(28),11,13,15(30),25,26-hexaene, BDBPH[5-7], and the stability constants of its transition metal complexes[8]. In this paper we used a direct potentiometric titration to determine the stability constants of the complexes formed by BDBPH and two lanthanide ions, Eu(III) and Tb(III), as well as species distribution in aqueous solution at pH 2-12. The results provided some information for the further research of the nucleic acid cleavage.

Experimental

BDBPH was synthesized as the hexahydrobromide salt, $BDBPH{\cdot}6HBr{\cdot}4H_2O$, by the

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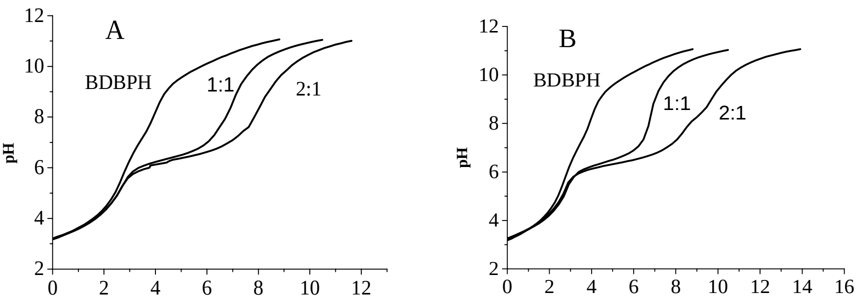
method described in the previous paper[5, 6]. The Stock solution (2.500×10^{-3} mol/L) of BDBPH for potentiometric work was prepared with double-distilled water. The stock solution of Eu(III) and Tb(III) chlorides were prepared also with double-distilled water, the concentrations of metal ions determined by titration with EDTA were close to 0.02 mol/L in the two cases. A carbonate-free 0.0839 mol/L KOH solution was standardized with potassium acid phthalate. The experiments were run in 1:1 (metal:BDBPH) and 2:1 systems. Reagent grade KCl was used as supporting electrolyte for all the experiments. The ionic strength of the solution was maintained at 0.1000 mol/L by the addition of KCl solution. The equilibrium constants were determined with the program BEST[9], and the species distribution diagrams were obtained with the program SPE and SPEPLOT[9].

Results and Discussion

The titration curves for the complexes of Eu(III) and Tb(III) with BDBPH in 1:1 and in 2:1 systems are presented in **Figure 1**.

It can be seen from **Figure 1** that the two metal ions do not combine with BDBPH until the first two protons of the ligand have almost been completely neutralized. For the two metal ions in 1:1 system, the curves have inflections at a=7(where a=moles of KOH / per mole of BDBPH), revealing that the two metal ions readily form complexes with the seven-deprotonated ligand. In 2:1 systems, the curve of Eu(III) complexes has inflection at a=8, while the curve inflection of Tb(III) complexes appears, when a=8-11, reflecting that Eu(III) could easily form dinuclear complex with fully deprotonated ligand, LM_2, and Tb(III) could form hydroxy dinuclear complexes, $LM_2(OH)_n$, as well as LM_2. The species distributions of the complexes of two metal ions with the ligand in 1:1 and 2:1 systems are presented in **Figure 2**, **3**, **4**, and **5**, respectively. In 1:1 and 2:1 Eu(III)-BDBPH system, many kinds of mono and dinuclear Eu(III)-BDBPH complexes existed, no hydroxy complexes were found, even at high pH condition, as shown in **Figure 2**, **3**. **Figure 4**, **5** showed that the dinuclear complexes $LTb_2(OH)$, $LTb_2(OH)_2$, and $LTb_2(OH)_3$ were formed under alkaline conditions, no mononuclear hydroxy complex was found. In both the 1:1 system, existed many kinds of dinuclear complexes, showing that the two metal ions have a strong tendency to form the dinuclear complexes.

Figure 1 Potentiometric equilibrium curve for Eu(III)-BDBPH (A) and Tb(III)-BDBPH (B) in 1:1 and 2:1 system.



a = moles of KOH / per mole of BDBPH

Figure 2 Species distribution diagram for Eu(III)-BDBPH system in 1:1 molar ratio

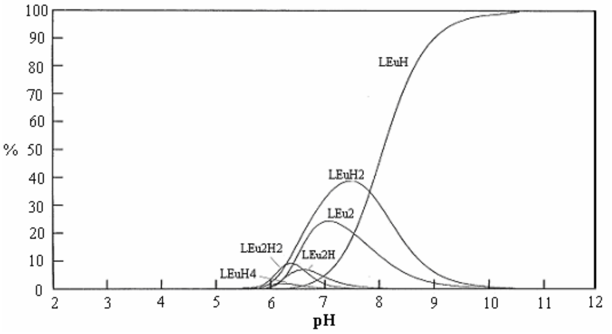


Figure 3 Species distribution diagram for Eu(III)-BDBPH system in 2:1 molar ratio

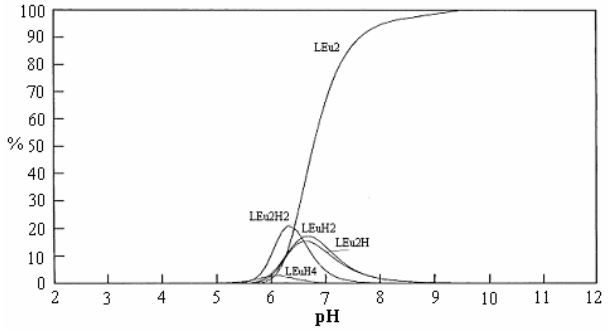


Figure 4 Species distribution diagram for Tb(III)-BDBPH system in 1:1 molar ratio

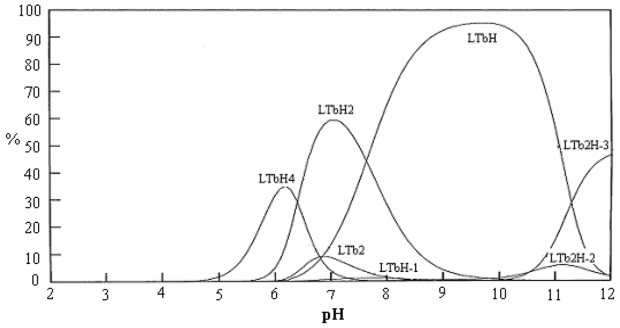
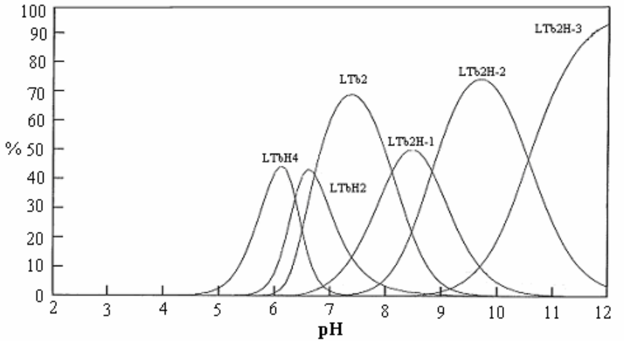


Figure 5 Species distribution diagram for Tb(III)-BDBPH system in 2:1 molar ratio



Logarithms of the stability constants of the complexes of Eu(III) and Tb(III) with BDBPH are listed in **Table 1**. For complexes of LMH_4, LMH_2, LMH, and LM_2, the Log K values of Eu(III)-BDBPH system are relatively close to those of Tb(III)-BDBPH system, the possible reason is that, the complexes containing the lanthanide ions have the same number of positive charges and adopt the similar conformation. The stability constants of the same type of mononuclear complexes, LMH_n, and dinuclear complexes, LM_2, is in the order of Tb(III)> Eu(III).

The LogK values of $LTb(III)_2(OH)$, $LTb(III)_2(OH)_2$ are 19.30 and 21.63, respectively, indicating strong stability of the complexes. $LTb(III)_2(OH)_2$ is not easy to form $LTb(III)_2(OH)_3$ further. All the complexes except LMH_4 have high kinetic and thermodynamic stability, and contain different positive charges. So it is possible that they could promote Lewis acid cleavage of phosphate backbone of DNA efficiently. The study on the cleavage of phosphate ester and selected DNA is in progress.

Table 1 Logarithms of the stability constants of metal complexes of Eu(III) and Tb(III) with BDBPH (I = 0.100 mol/L KCl, t=25.0°C)

Equilibrium Quotient, K	LogK*	
	Eu(III)	Tb(III)
$[LMH_4]/[LH_4][M]$	3.47	5.12
$5.12[LMH_2]/[LH_2][M]$	11.27	12.00
$[LMH]/[LH][M]$	14.48	15.39
$[LM_2]/[LM][M]$	12.74	16.71
$[LM_2H_2]/ [LH_2][M]^2$	14.67	
$[LM_2H]/[LH][M]^2$	19.11	
$[LM_2(OH)]/[LMOH][M]$		19.30
$[LM_2(OH)_2]/[LM(OH)_2][M]$		21.63
$[LM_2(OH)_2][OH]/[LM_2(OH)_3]$		10.56

* Estimated error = ± 0.02-0.04

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