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The Stability Constants of Complexes of BDBPH-Metals and Species Distributions

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Abstract: The stability constants of the mononuclear complexes of BDBPH-Zn(II), Cd(II) and Mn (II) were determined by the potentiometric equilibrium measurements, and species distributions were also discussed. The metal ions do not combine with the ligand until the first two protons of the ligand have almost been completely neutralized. The main species were mononuclear complexes with the diprotonated ligand, MH_2L. The three metal ions also form mono- and noprotonated (fully deprotonated) complexes, MHL, ML. The relative order of stabilities of the mononuclear complexes, ML, is Zn(II) > Cd(II) > Mn(II). The ligand has strong tendency to form mononuclear complexes with Zn(II), Cd(II) and Mn(II), and it can also form dinuclear complexes at high pH.

Keywords: BDBPH, stability constant, mononuclear complex, species distribution.

The study on the design and synthesis of model compounds for metalloproteins has been a subject of extensive investigation[1]. During the last decade, a number of synthetic structural models for some kinds of metalloproteins with several types of ligands have been reported in literature[2,3,4]. We have recently reported a new 24-membered hexaazadiphenol macrocyclic ligand, 3,6,9,17,20,23-hexaaza-29,30-dihydroxy-13,27-dimethyl-tricyclo [23,3,1,1^{11,15}] triaconta-1 (28),11,13,15 (30),25,26-hexaene, BDBPH[5], and its protonation constants and the species distribution in aqueous solution[6]. Here we present the stability constants of its mononuclear complexes with Zn(II), Cd(II), and Mn(II), as well as the species distribution in aqueous solution.

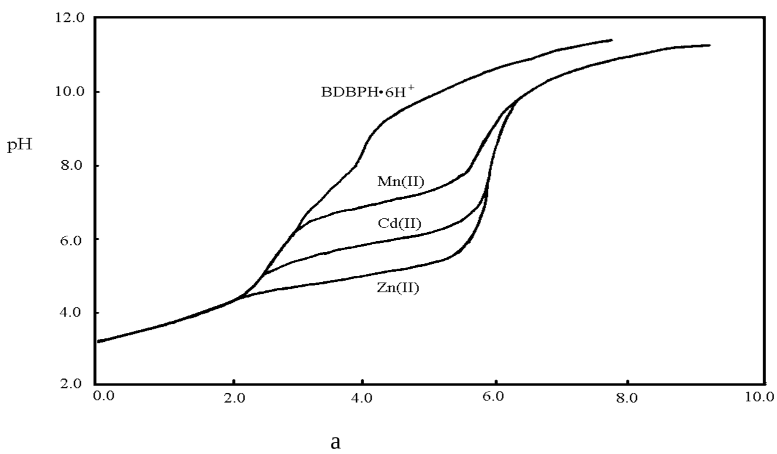
Experimental

BDBPH was synthesized as the hexahydrobromide salt, BDBPH·6HBr·$4H_2O$, by the method described in previous paper[5]. The Stock solution (2.073×10^{-3} mol·L^{-1}) of BDBPH for potentiometric work was prepared with double-distilled water. The stock solution of Zn(II), Cd(II), and Mn(II) 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^{-1} in all cases. A carbonate-free 0.1013 mol·L^{-1} KOH solution was prepared from a dilut-it ampoule and standardized with potassium acid phthalate. The experiments were run in 1:1 (metal: BDBPH). Reagent grade KCl was used as supporting electrolyte for all the experiments. The ionic strengths of the solution were maintained at 0.100 mol · L^{-1} by the addition of KCl solution. The equilibrium constants were determined with the program BEST[7], and the species distribution diagrams were obtained with the program SPE and SPEPLOT[7].

Results and Discussion

The titration curves for BDBPH · $6H^+$ and the complexes of Zn(II), Cd(II), and Mn(II) with BDBPH (**Figure 1)** show that the three metal ions do not combine with BDBPH until the first two protons of the ligand have almost been completely neutralized. It can be seen from the **Figure 1** that for the three metal ions, the curves have inflections at a=6 (where a = moles of KOH/mole of BDBPH), revealing that the three metal ions readily form complexes with the six-deprotonated ligand. The species distributions of the complexes of each metal ion with the ligand are presented in **Figure 2**, **Figure 3**, and **Figure 4**, respectively. In addition to the main complexes of LMH_2, the three metal ions can also form 1:1 complexes with mono- or fully deprotonated ligand, LMH and LM. Besides, Mn (II) can form a little amount of 1:1 complex with tripronated ligand, $LMnH_3$. With the increase of pH, the LCd is hydrolized to form LCd(OH) (or $LCdH_{-1}$) , whereas the LZn and LMn are hydrolized to form $LZn(OH)_2$ (or $LZnH_{-2}$) and $LMn(OH)_2$ (or $LMnH_{-2}$). Under alkaline conditions, the three metal ions also have tendency to form dinuclear complexes to some extent, such as LZn_2H_{-2}, LCd_2H_{-2}, LMn_2H_{-1}, and LMn_2H_{-2}.

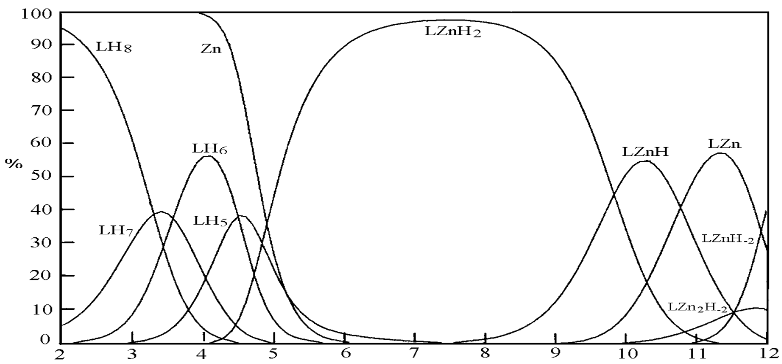
Figure 1 Potentiometric equilibrium curves for BDBPH · $6H^+$ and 1:1 metal-BDBPH systems



(I=0.100MKCl, t=25.0°C, a=moles of KOH added per mole of BDBPH, $T_{Zn}=1.34\times10^{-3}$ M, $T_{Cd}=1.25\times10^{-3}$ M, $T_{Mn}=1.34\times10^{-3}$ M, $T_L=T_M$)

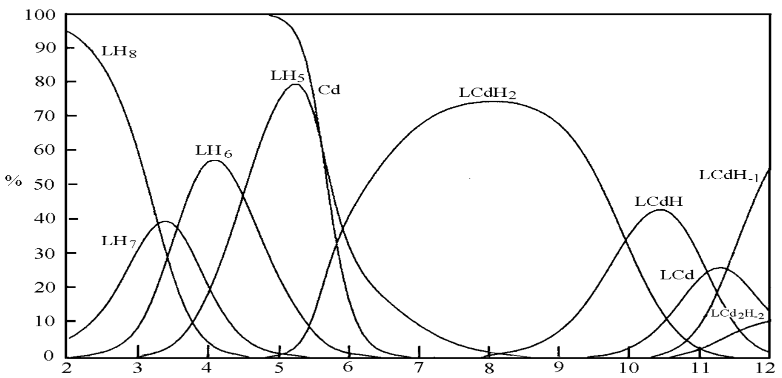
The stability constants of the complexes of Zn (II), Cd (II), and Mn (II) with BDBPH are listed in **Table 1**. All the metal ions were found to combine with BDBPH to form deprotonated (LM), monoprotonated (LMH), diprotonated (LMH_2), as well as hydroxo-

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



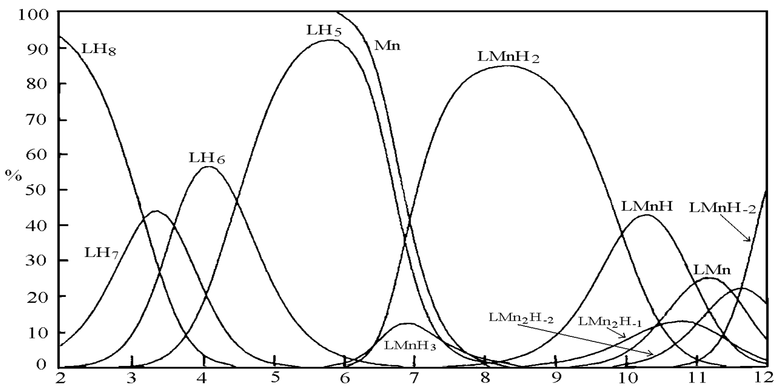
pH
(I=0.100MKCl, t=25.0°C, T_{Zn}=T_L=1.34×10^{-3} M)

Figure 3 Species distribution diagram for Cd(II)-BDBPH system in 1:1 molar ratio



pH
(I=0.100MKCl, t=25.0°C, T_{Cd}=T_L=1.25×10^{-3} M)

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



pH
(I=0.100MKCl, t=25.0°C, T_{Mn}=T_L=1.34×10^{-3} M)

bridged (LMH_{-1}, LMH_{-2}) complexes in the solutions of pH ranges of 2-12. The successive stability constants of the mononuclear complexes are relatively close to each other, because the complexes contain the metal ions with the same number of positive charges and adopt the similar conformation. The order of stability constants of the mononuclear complexes, LM, is Zn(II) > Cd(II) > Mn(II).

Table 1 Logarithms of the stability constants of metal complexes of BDBPH-Zn(II), Cd(II) and Mn(II) (I=0.100 mol·L^{-1} KCl, t=25.0°C)

Equilibrium Quotient, K	logK*		
	Zn(II)	Cd(II)	Mn(II)
$[LMH_3]/[LMH_2]$ [H]			6.43
$[LMH_2]$/[LMH] [H]	9.83	9.96	9.96
[LMH]/[LM] [H]	10.77	11.11	10.65
[LM]/[M] [L]	17.72	14.28	11.58
[LMOH] [H]/[LM]	-12.70	-11.39	-12.42
$[LM(OH)_2]$ [H]/[LMOH]	-11.12		-10.74
$[LM_2OH]$ [H]/$[LM_2]$			-10.76
$[LM_2(OH)_2]$ [H]/$[LM_2OH]$	-10.64	-11.52	-13.83

* Estimated error = ± 0.02~0.04

Compared with the work of Motekaitis[8] on the stability constants of Zn(II)-OBOSDIEN complexes, the result above shows that the phenolic oxygens in BDBPH take part in the coordination with metal ions in 1:1 system.

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References

1. P. K. Coughlin, S. J. Lippard, *J. Am. Chem. Soc.*, **1984**, *106*, 2328.
2. Z. Wang, J. Reibenspies, A. E. Martell, *Inorg. Chem.*, **1997**, *36*, 629.
3. D. Chen, A. E. Martell, *Tetrahedron*, **1991**, *47*, 6895.
4. Q. Lu, R. Carroll, J. Reibenspies,A. E Martell, *J. Mol. Struc.*, **1998**, *469*, 121.
5. G. Q. Shangguan, A. E. Martell, Z. R. Zhang, *Chin. Chem. Lett.*, **2000**, *11* (7), 573.
6. G. Q. Shangguan, N. Wang, H. E. Wang, *Chin. Chem. Lett.*, **2001**, *12* (2), 171.
7. A. E. Martell, R. J. Motekaitis, *The Determination and Use of Stability Constants*, 2nd Ed., VCH Publishers Inc., New York, **1992,** p.143-194.
8. J. Reibenspies, A. E. Martell, J. P. Lecomte, *Inorg. Chem.*, **1983**, *22*, 609.

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