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Study on kinetics and mechanism of dinuclear metal zinc(II) complexes in promoting the hydrolysis of 2-hydroxy-propyl-*p*-nitrophenyl phosphate (HPNP)

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ABSTRACT

Five multi-dentate ligands: *N,N′*-di-(1,10-phenanthroline-2-methylene)-ethylenediamine (L1), *N,N′*-di-(1,10-phenanthroline-2-methylene)-1,3-propanediamine (L2), 1,7-di- (1,10-phenanthroline-2-methylene)-1,4,7-triazaheptane (L3), 1,10-di-(1,10-phenanthroline-2-methylene)-1,4,7,10-tetraazatridecane (L4), 1,13-di-(1,10-phenanthroline-2-methylene)-1,4,7,10,13-pentaazatridecane (L5) have been synthesized and characterized. The hydrolytic kinetics catalyzed by dinuclear complexes of Zn(II) with L1–L5 have been studied in aqueous solution at 298.2 ± 0.1 K, $I = 0.10\,\mathrm{mol\,dm^{-3}}$ KNO_3 at physiological condition (pH 7.0–8.4), respectively. In this study it is found that the catalytic effect of Zn_2L3 was the best one among the five dinuclear complexes for the hydrolysis of 2-hydroxy-propyl-*p*-nitrophenyl phosphate (HPNP). Its $k_{Zn_2L2H_{-1}}$, k_{Zn_2L2} and pK_a are $0.0480\,\mathrm{mol^{-1}\,dm^3\,s^{-1}}$, $0.000043\,\mathrm{mol^{-1}\,dm^3\,s^{-1}}$ and 8.87, respectively. This paper expounds the result from the structure of the ligands and the properties of the metal ions, and deduces the catalysis mechanism.

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1. Introduction

Mimic enzyme is a kind of compound synthesized artificially, which is based on the understanding of the structure of the enzymes, the reaction mechanism and having specific attribute for hydrolysis of biological macromolecular. The characteristic of the mimic enzymes is that the functional molecules are small and their structures are simple. However, they have the active groups and spacial structure similar with the groups that nature enzymes have. There are many hydrolytic enzymes such as Carbonic Anhydras, Carboxypeptidase, Alkalline Phosphatase in the process of organic evolution. These enzymes take part in the hydrolysis of some organic molecules of great importance and play a crucial role in the process of life [1].

The action mechanism of hydrolase and the effect of metal ions on the active center are always important in inorganic biochemistry field [2]. In the past few years more and more research efforts have been devoted to design and synthesize model complexes for promoting the hydrolysis of 2-hydroxy-propyl-*p*-nitrophenyl phosphate (HPNP) [3–6]. Ligands with poly-amino groups and poly-carboxyl groups or ligands bearing multi-ions are potentially useful to achieve more active molecular catalysts.

In this paper, it is studied that hydrolysis property of HPNP catalyzed by the dinuclear complexes of Zn(II) with *N,N′*-di-(1,10-phenanthroline-2-methylene)-ethylenediamine (L1), *N,N′*-di-(1,10-phenanthroline-2-methylene)-1,3-propanediamine (L2), 1,7-di-(1,10-phenanthroline-2-methylene)-1,4,7-triazaheptane (L3), 1,10-di-(1,10-phenanthroline-2-methylene)-1,4,7,10-tetraazatridecane (L4), 1,13-di-(1,10-phenanthroline-2-me-thylene)-1,4,7,10,13-pentaazatridecane (L5), respectively. Our interest was to understand functions of metal ions in biological hydrolysis process and the influence of the structure of complexes Zn_2L1–Zn_2L5 for activity of promoting hydrolysis of HPNP.

2. Experimental

2.1. Materials

All reagents and solvents were of analytical reagent grade and were used without further purification, unless otherwise noted. All aqueous solutions were prepared using redistilled water. Metal ion stock solutions were prepared from their respective salts and were titrated against EDTA following standard procedures. The buffer component tris(hydroxymethyl)aminomethane (Tris) was used as supplied by the manufacturer. The HPNP were prepared and purified as a barium salt following literature methods [7,8]. The ligands (L1–L5) were synthesized following the literature methods [9] as Fig. 1 shown.

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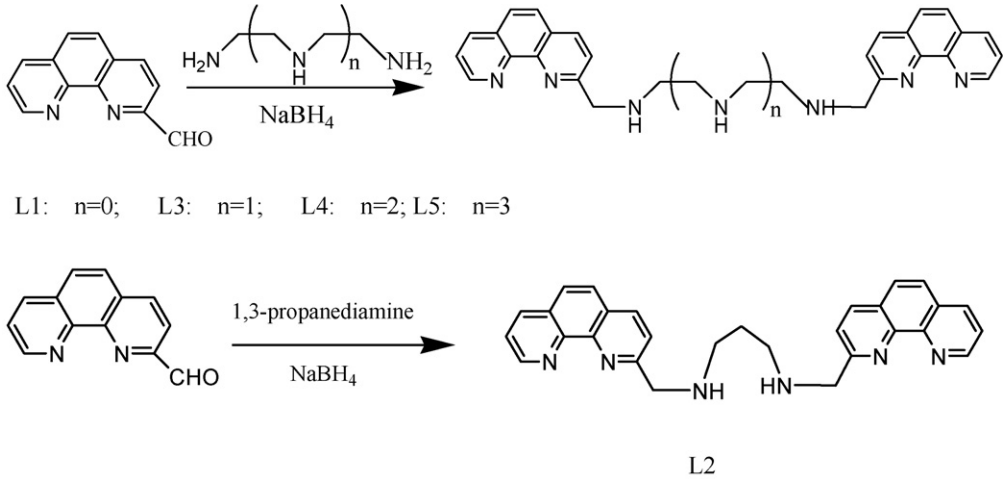

Fig. 1. The processes of the preparation of ligands L1–L5.

2.2. Potentiometric determination

Potentiometric determination was measured in a 50 cm^3 jacketed cell thermostated at 298.2 ± 0.1 K by a refrigerated circulating water bath. Anaerobic condition were maintained using pre-purified N_2 as an inert atmosphere, and the ionic strengths were maintained by adding KNO_3 to achieve $I = 0.1\ mol\ dm^{-3}$. The calibration of the glass electrode was the same as described in the literature [10]. In a typical experiment, the ligand was dissolved in an adequate amount of dilute HNO_3 and then titrated with 0.1 $mol\ dm^{-3}$ KOH. The values of $k_w = 1.008 \times 10^{-14}$, $\gamma_{H^+} = 0.825$ of water were used for the calculations. The calculations were carried out by SCMAR program [11] based on the improved TITFIT technique [12]. The final results were the averages of three independent titrations, each titration containing about 50 experimental points.

2.3. Kinetics of HPNP hydrolysis

A kinetic study was carried out by the UV–vis spectra method using a Beckman DU-8B spectrophotometer equipped with a thermostated cell holder. The hydrolysis rate of HPNP in aqueous solution was measured by an initial slope method following the increase in absorption at 400 nm due to the release of 4-nitrophenolate. The reaction solution was maintained at 298.2 ± 0.1 K and the ionic strength was adjusted to 0.10 $mol\ dm^{-3}$ with KNO_3. The buffer component tris(hydroxymethyl)aminomethane (Tris) was used to maintain pH, and it do not coordinate with Zn(II) ions under this condition. For the initial rate determination, the following typical procedure was employed:

After HPNP and Zn_2–L complexes solution at the appropriate pH were mixed, the UV absorption increase was recorded immediately (the reference experiment did not contain the catalyst). The increase in concentration of *p*-nitrophenolate was measured every 60 s. The initial slope (<5% conversion) of a plot of the measured absorbance versus time was determined (correlation coefficient >0.99). All the experiments were in triplicate and tabulated data represent the average of these experiments.

3. Results and discussion

3.1. Active nucleophile in Zn_2L complexes systems

The stepwise protonation constants of L1–L5 are shown in Table 1, respectively. Potentiometric titrations indicated that the stoichiometric ratio between Zn(II) ions and the ligands L1–L5 is 2:1 (metal–ligand). The stability constants of dinuclear complexes: Zn_2LH_m ($m = 2$ to -1) are shown in Table 2. Obviously seen from the species percentage distribution diagrams of the Zn_2–L system (Fig. 2), the mode Zn_2LH_{-1} (2,1,−1) having ability to catalyze hydrolysis of HPNP is formed in the solution when pH > 7.0. Therefore the kinetic experiment studied would be carried out in pH 7.0–8.5.

The deprotonation constants of coordination water on Zn_2L (2 1 0) can be obtained according to $pK_a = \mathrm{Log}\,\beta_{Zn_2L} - \mathrm{Log}\,\beta_{Zn_2LH_{-1}}$ shown in Table 3. Zn_2L (2 1 0) can release a proton to give Zn_2LH_{-1} in

Table 1
The protonation constants of ligands L_1–L_5 (pH range 2.5–10.8) (25.0 ± 0.1 °C, $I = 0.1\ mol\ dm^{-3}\ KNO_3$, $C_L = 5 \times 10^{-4}\ mol\ dm^{-3}$)

	LgK_1	LgK_2	LgK_3	LgK_4	LgK_5	LgK_6
L1	8.85	6.27	4.11	2.68	–	–
L2	9.06	7.64	4.17	3.13	–	–
L3	9.45	8.37	4.68	3.20	2.91	–
L4	9.76	8.77	6.05	3.76	2.97	1.31
L5 [16]	9.85	8.79	7.06	4.61	3.72	3.64

Table 2
The stability constants of complexes of ligands L1–L5 with Zn(II) $C_L = C_{Ln} = 5 \times 10^{-4}$ mol/L, $I = 0.1\ mol\ dm^{-3}\ KNO_3$, 25 ± 0.1 °C

Complexes of ligands L1–L5 with Zn(II)	
L1	
$Lg\beta_{2\,1\,0}$	2.67
$Lg\beta_{2,1,-1}$	−7.35
L2	
$Lg\beta_{2\,1\,0}$	3.12
$Lg\beta_{2,1,-1}$	−6.51
L3	
$Lg\beta_{2\,1\,1}$	20.14
$Lg\beta_{2\,1\,0}$	10.18
$Lg\beta_{2,1,-1}$	1.29
L4	
$Lg\beta_{2\,1\,2}$	28.11
$Lg\beta_{2\,1\,1}$	22.78
$Lg\beta_{2\,1\,0}$	14.65
$Lg\beta_{2,1,-1}$	5.27
L5 [16]	
$Lg\beta_{2\,1\,2}$	28.38
$Lg\beta_{2\,1\,1}$	21.76
$Lg\beta_{2\,1\,0}$	12.56
$Lg\beta_{2,1,-1}$	3.20

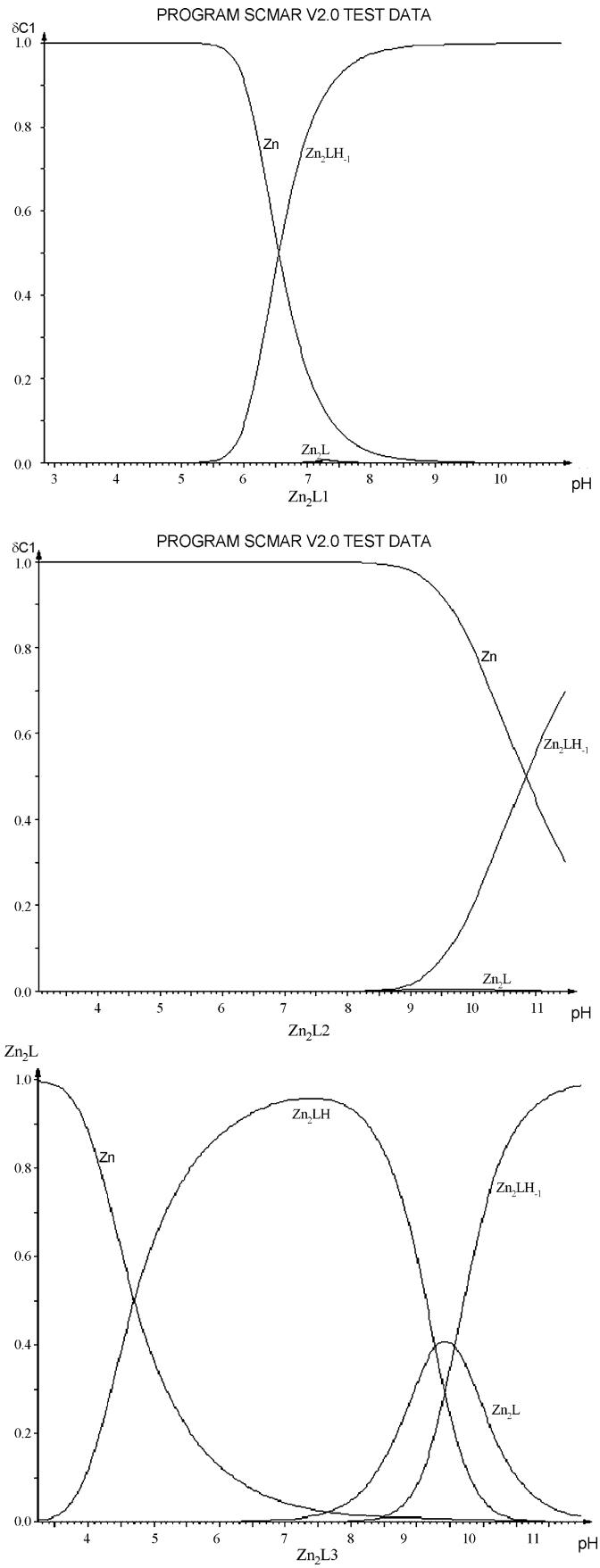

Fig. 2. The species percentage distribution diagrams of Zn_2L1–Zn_2L5 system (298.2 K, $I = 0.1$ mol dm^{-3} KNO_3, $C_L = C_{Zn/2} = 5 \times 10^{-4}$ mol dm^{-3}).

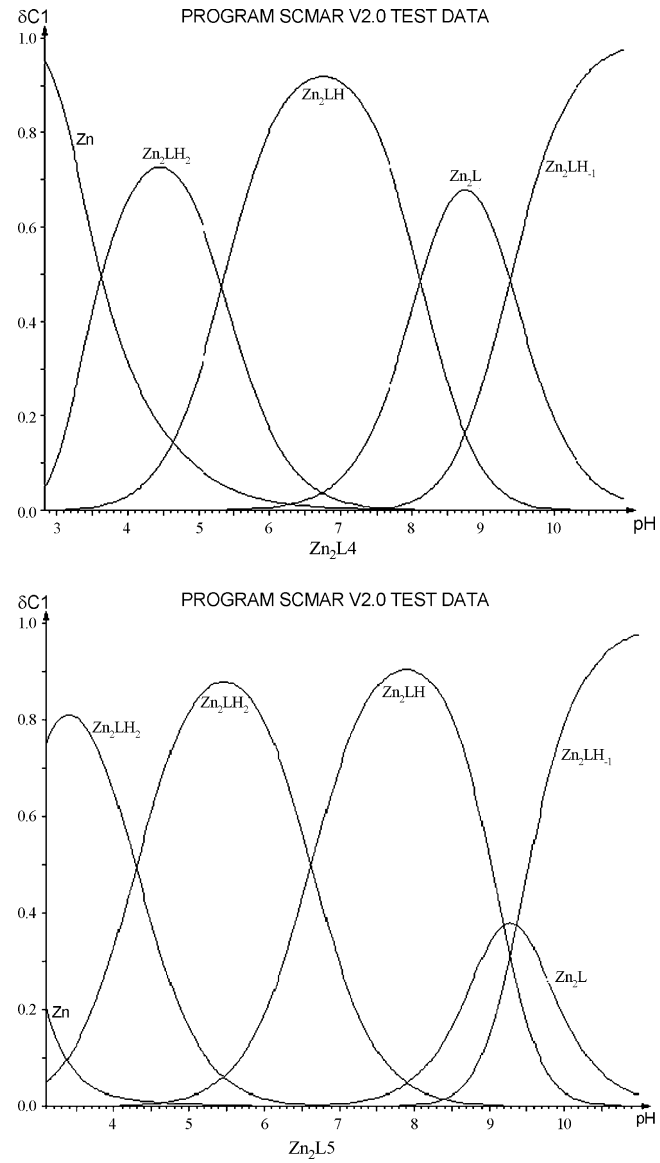

Fig. 2. (*Continued*).

weak basic (pH > 7.0) solution which is a good nucleophilic metal-bond hydroxide species and they can be used as enzyme models for catalyzing the hydrolysis of phosphate diester: HPNP because of their nucleophilic group OH^-.

3.2. Molar extinction coefficient of NP^-

The kinetic study of HPNP hydrolysis was carried out by monitoring changes in absorbance at 400 nm, which is ascribe to UV–vis

Table 3
The apparent rate constants catalyzed hydrolysis of HPNP by Zn_2L1–Zn_2L5 complexes, k_{cat}^{obs}, at different pH values

pH	$[H^+]/10^{-8}$ mol dm^{-3}	k_{cat}^{obs} (mol^{-1} dm^3 s^{-1})				
		Zn_2L1	Zn_2L2	Zn_2L3	Zn_2L4	Zn_2L5 [16]
7.047	10.88	0.00222	0.00288	0.00510	0.00420	0.00326
7.474	4.069	0.00227	0.00279	0.00583	0.00461	0.00354
7.791	1.961	0.00229	0.00301	0.00766	0.00486	0.00379
7.977	1.278	0.00241	0.00306	0.00913	0.00519	0.00433
8.184	0.794	0.00253	0.00357	0.01177	0.00614	0.00523
8.419	0.462	0.00293	0.00435	0.01583	0.00795	0.00688

Table 4
The second-order rate constants k_{Zn_2L}, $k_{Zn_2LH_{-1}}$ and the deprotonation constant of water coordinated on Zn_2L1–Zn_2L5 pK_a^2 in the hydrolysis of HPNP

Complexes	$10^2 k_{Zn_2L}$ ($mol^{-1}\,dm^3\,s^{-1}$)	$k_{Zn_2LH_{-1}}$ ($mol^{-1}\,dm^3\,s^{-1}$)	pK_a (titration)	pK_a
Zn_2L1	0.0022	0.0232	10.02	9.98
Zn_2L2	0.0026	0.0288	9.63	9.60
Zn_2L3	0.0043	0.0480	8.89	8.87
Zn_2L4	0.0038	0.0442	9.38	9.39
Zn_2L5 [16]	0.0031	0.0395	9.36	9.39

absorbance band of *p*-nitrophenolate ion (NP^-) produced in solution. The use of buffer for the studies of hydrolysis kinetics of HPNP was required since the pH value of the solution would have an effect on the concentration of the NP^-. To determine the rate constants one should know the molar extinction coefficient of NP^-, which varies considerably with pH values of the solution. Accordingly, the moler extinction coefficient ε_{NP} and the dissociation constant of *p*-nitrophenol K_a at 400 nm in 0.020 mol dm^{-3} tris solution was obtained according the method reported [4–6] (see supporting information for detailed discussion) with the value of 17,900 $mol^{-1}\,dm^3\,cm^{-1}$ and 7.18×10^{-8} mol dm^{-3}, which is consistent with the reported value [12].

3.3. Kinetic studies of hydrolysis of HPNP

Under the physiological experimental conditions (pH 7.0–8.4), the hydrolysis rate increases linearly with the increase of HPNP concentration, which indicates that the hydrolysis is first-order with respect to HPNP,

$$V = \frac{dA}{\varepsilon\, dt} = k_{obs}[HPNP] = (k_{cat}^{obs}[complex]^T + k_{OH}[OH] + k_0)[HPNP] \quad (1)$$

Therefore, k_{obs} can be written:

$$k_{obs} = k_{cat}^{obs}[complex]^T + k_{OH}[OH^-] + k_0 \quad (2)$$

At a given pH, when the observed hydrolysis rate constant, k_{obs} was plotted against total concentration of complexes Zn_2–L, the apparent rate constant of complexes, k_{cat}^{obs} can be gotten. Table 4 shows the apparent hydrolysis rate constant, k_{cat}^{obs}, at different pH. As shown in Table 3, k_{cat}^{obs} increases with the increase of the pH value of reaction solution. When k_{cat}^{obs} is plotted against pH, resulting curve indicate the characteristics of a kinetic process controlled by acid–base equilibrium (see Fig. 3). In Eq. (2) $[complex]^T$ is the total concentration of Zn_2–L complexes. The concentrations of Zn_2L and Zn_2LH_{-1} have been controlled by pH value of the reaction solution and can be represented by Eq. (3) and (4).

$$[Zn_2L] = \frac{[complex]^T[H^+]}{(K_a^2 + [H^+])} \quad (3)$$

$$[Zn_2LH_{-1}] = \frac{[complex]^T K_a^2}{(K_a^2 + [H^+])} \quad (4)$$

According to kinetics theory of enzumatic catalysis, Eq. (5) is then obtained.

$$k_{cat}^{obs}[complex]^T = k_{Zn_2L}[Zn_2L] + k_{Zn_2LH_{-1}}[Zn_2LH_{-1}] \quad (5)$$

where k_{Zn_2L} and $k_{Zn_2LH_{-1}}$ stand for the second-order hydrolysis rate constants of HPNP catalyzed by Zn_2L and Zn_2LH_{-1}, respectively. Eq. (6) could be obtained from Eqs. (3)–(5)

$$k_{cat}^{obs} = \frac{(k_{Zn_2L}[H^+] + k_{Zn_2LH_{-1}}K_a^2)}{([H^+] + K_a^2)} = k_{Zn_2L} + \frac{(k_{Zn_2LH_{-1}} - k_{Zn_2L})}{(1 + [H^+]/K_a^2)} \quad (6)$$

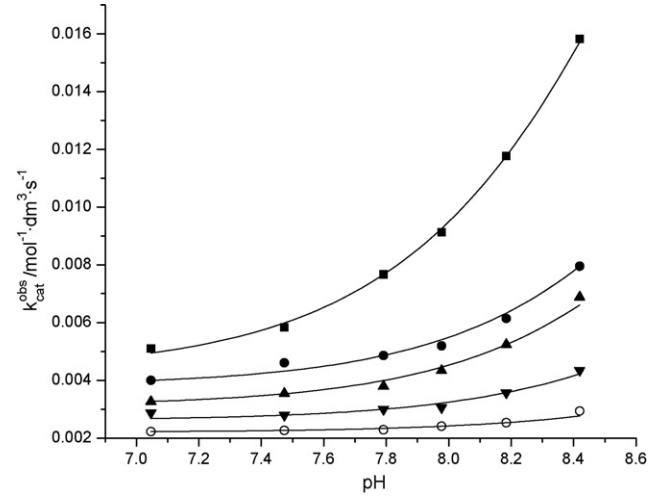

Fig. 3. The curve of relation of apparent hydrolysis rate constant of HPNP, k_{cat}^{obs} versus pH catalyzed by complexes Zn_2L1–Zn_2L5 (○ Zn_2L1, ▼ Zn_2L2, ■ Zn_2L3, ● Zn_2L4, ▲ Zn_2L5).

Thus, by means of non-linear least-squares fit of k_{cat}^{obs} versus $[H^+]$, the values of k_{Zn_2L}, $k_{Zn_2LH_{-1}}$ and K_a^2 could be obtained according to Eq. (6). Table 4 indicated that the dissociation constants of coordination water on the complex Zn_2L (pK_a^2) gotten from the kinetic experiment is consistent with the result gotten from the titration experiment.

From the data in Tables 3 and 4, the mechanism of hydrolysis of HPNP catalyzed by the complexes can be deduced (see Fig. 4). Observed from the data in Table 3, the total apparent rate constants (k_{cat}^{obs}) of hydrolysis of HPNP catalyzed by Zn_2–L system complexes increase with the increase of pH value of reaction solution. This result is consistent with one reported by Richard [13]. It is interesting that ionization of binuclear zinc complex Zn_2L in the weak basic solution was due to loss of a proton from a water coordinated to Zn(II) of the complex Zn_2L, because the pH-rate profiles show that the ionization state of the water bound on Zn(II) of complex Zn_2L is critical for catalytic activity. The pH-rate profiles of the second-order rate constants k_{cat}^{obs} for catalysis of transesterification of HPNP by Zn_2–L dinuclear complexes provide the following important insights into catalytic reaction mechanism.

There is a downward break, which is centered at the pK_a^2 for deprotonation of a bound water molecule to form the monohydroxyl complex Zn_2LH_{-1}, in the pH-rate profiles for the hydrolysis of HPNP catalyzed by the Zn_2–L dinuclear complexes. These pH-rate profiles show that the complex Zn_2L is less active species catalyzing hydrolysis of HPNP than Zn_2LH_{-1}, and is converted to a more active form Zn_2LH_{-1} upon loss of a proton.

Jencks considers that kinetics provides no information about whether this proton is lost from the catalyst or the substrate [14]. However, Wolfenden and Snider [15] considers that chemical logic demands that a proton be lost from the C2-hydroxyl of HPNP on proceeding from reactant in solution to the transition state for transesterification and that the catalyst functions in some way to facilitate ionization of this hydroxyl. Richard [13] considers that there are two possible pathways for activation of HPNP by directing proton transfer from the C2-hydroxyl to the catalyst: (a) Zn_2(L2O)(OH) and Zn(L1OH)(OH) may serve as the active form of the catalyst and act as Bronsted general base catalysts to deprotonate the C2-hydroxyl of HPNP in reactions where proton transfer to the catalyst is concerted with intramolecular addition of C2-oxygen to the phosphate diester. (b) Proton transfer from substrate to the ionized catalysis Zn_2(L2O)(OH) and

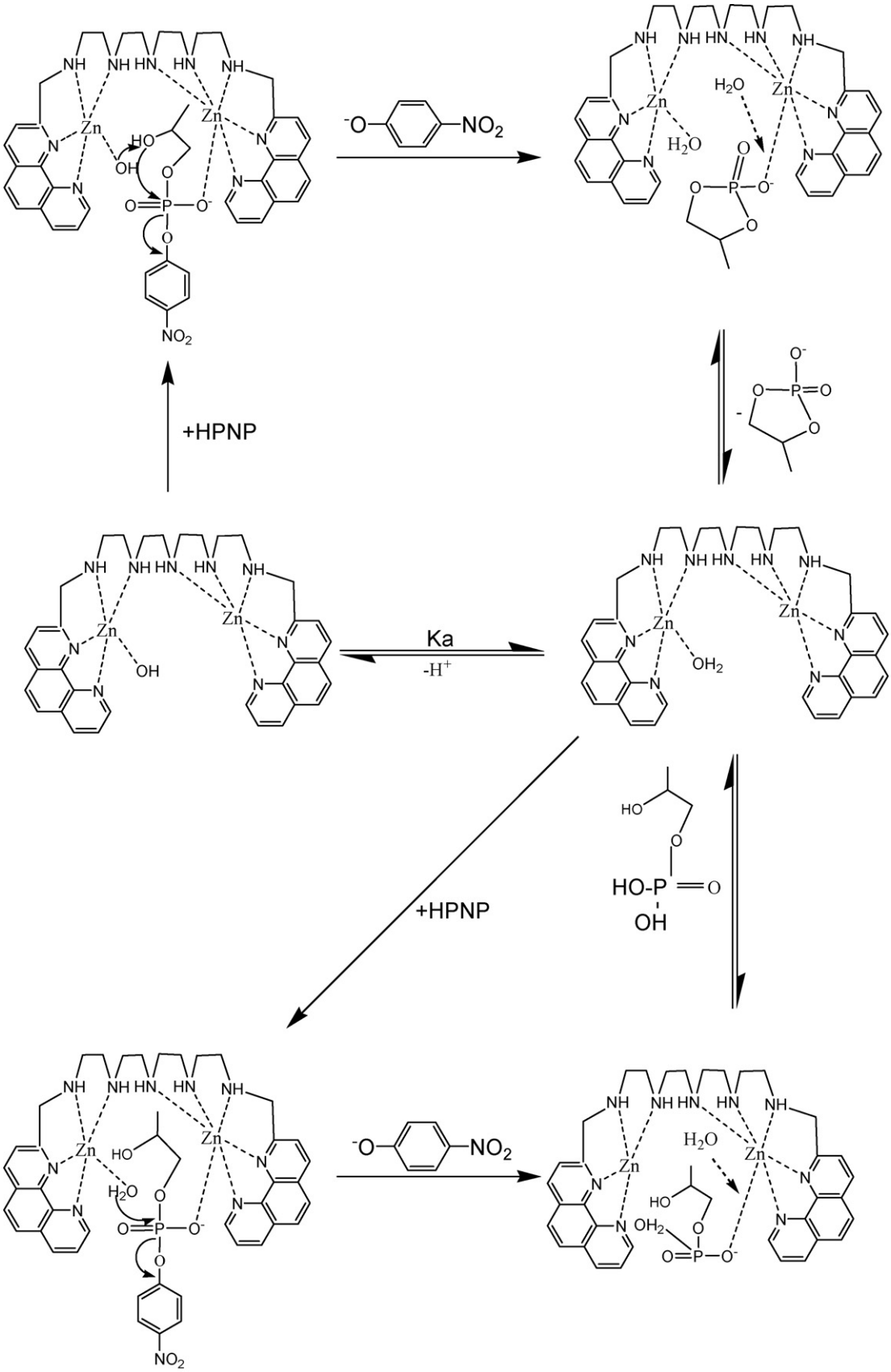

Fig. 4. The proposed mechanism of the hydrolysis of HPNP catalyzed by Zn_2L5.

Zn(L1OH)(OH) may occur as a pre-equilibrium step to form the protonated catalysis $Zn_2(L2O)(H_2O)$ and $Zn(L1OH)(H_2O)$, respectively, and the C2-oxyanion of the substrate which would then undergo intramolecular nucleophile addition of C2-oxygen to phosphate diester.

We consider that the lost proton related with a downward break in the pH-rate profile come from the water molecule coordinated on Zn(II) of the complex $Zn_2(L2O)(H_2O)$ and $Zn(L1OH)(H_2O)$, because the pK_a of free water at 298.2 K is about 14 and the pK_a of isopropyl alcohol at 298.2 K is about 16. When water molecule coordinated with Zn(II) of the complexes $Zn_2(L2O)$ and Zn(L1OH) to form $Zn_2(L2O)(H_2O)$ and $Zn(L1OH)(H_2O)$, the pK_a of coordinated water, which was affected by Zn(II) ions of the complexes $Zn_2(L2O)$ and Zn(L1OH), markedly decrease but the pK_a of C2-hydroxylpropyl of substrate still is about 16. The complexes $Zn_2(L2O)(H_2O)$ and $Zn(L1OH)(H_2O)$ lost the proton of coordination water on itself and change to the complexes $Zn_2(L2O)(OH)$ and Zn(L1OH)(OH) and then the hydroxyl group of the complexes $Zn_2(L2O)(OH)$ and Zn(L1OH)(OH) attack the C2-hydroxypropyl of the substrate. The proton releasing from the coordination water on the complexes $Zn_2(L2O)(H_2O)$ and $Zn(L1OH)(H_2O)$ decreased the pH value of reaction solution. The proton of C2-hydroxypropyl transfer to the hydroxyl group of complex $Zn_2(L2O)(OH)$ and Zn(L1OH)(OH) with intramolecular attack of C2-oxyanion to the phosphate diester immediately, this transferring proton cannot caused a change of pH value of the reaction solution.

In this paper there are two Zn(II) ions in the dinuclear complexes system (Zn_2L1–Zn_2L5), one Zn(II)(a) combined with water molecule and the water molecule combined on Zn(II)(a) released the proton at action of Zn(II)(a) and changed into OH^-, therefore, there are two species: Zn_2L1–Zn_2L5 and Zn_2L1H_{-1}–Zn_2L5H_{-1} in reaction solution at pH 7.0–8.5, another Zn(II)(b) combined on oxygen anion of P of substrate HPNP. OH^- combined on Zn(II)(a) attacked the C2-hydroxyl of HPNP combined on Zn(II)(b) and H^+ of C2-hydroxyl of HPNP combined on Zn(II)(b) transfer to the hydroxyl group combined on Zn(II)(a), then C2-oxygen anion of HPNP undergo intramolecular addition attack to the P atom of phosphate diester, HPNP, this result load that the lactone was formed and the *p*-nitrophenolate anion was released for complex Zn_2L1H_{-1}–Zn_2L5H_{-1}, and the water molecule combined on Zn(II)(a) direct attacked the P atom of substrate HPNP combined on Zn(II)(b) and *p*-nitrophenolate anion was released for Zn_2L1–Zn_2L5. Then the lactone of phosphonic acid was released by an attack of water molecule and a catalytic cycle is completed for complexes Zn_2L1H_{-1}–Zn_2L5H_{-1} and the 2-hydroxypropyl phosphate anion also was released at an attack of a water molecule and catalytic cycle is completed for complexes Zn_2L1–Zn_2L5. Because the electron cloud density on C2-oxyanion of is large much than one on oxygen atom of H_2O combined on Zn(II)(a) of complex Zn_2L1–Zn_2L5, therefore, $k_{Zn_2LH_{-1}}$ is large much than k_{Zn_2L}.

From Table 4 it is could be found that dissociation constants of coordination water on the complexes Zn_2L1–Zn_2L5 (pK_a^2) obtained from the kinetical experiment were consistent with the results got from the titration experiments, which is a powerful evidence of our viewpoint.

A important problem is found in Richard's paper that the second-order rate constants, k_{Zn}, for transesterification of HPNP catalyzed by $Zn_2\{L2O\}$ and Zn(L1OH) at 298 K, $I = 0.1\ mol\ dm^{-3}$ $NaNO_3$ and $20\ mmol\ dm^{-3}$ buffer increase with the increase of pH value of reaction solution. As a rule, when the temperature and the medium of reaction solution is confirmed, the rate constant of a reaction is fixed. The reason that the second-order rate constants, k_{Zn}, increase with the increase of pH value of reaction solution is that Richard [13] only obtained apparent second-order rate constants $k_{Zn} = 0.25\ mol^{-1}\ dm^3\ s^{-1}$ for the complex $Zn_2\{L2O\}$ and $k_{Zn} = 0.0013\ mol^{-1}\ dm^3\ s^{-1}$ for the complex Zn(L1OH) at pH 7.6, and do not obtained true second-order rate constants of the complexes $Zn_2(L2O)(OH)$, $Zn_2(L2O)(H_2O)$, Zn(L1OH)(OH) and $Zn(L1OH)(H_2O)$. The values of $k_{Zn_2(L2O)(OH)}$, $k_{Zn_2(L2O)(H_2O)}$, $k_{Zn(L1OH)(OH)}$ and $k_{Zn(L1OH)(H_2O)}$ can be obtained according to the non-linear least-squares fit of k_{Zn} versus $[H^+]$ according to Eq. (6). Though Richard et al. did not obtain the true second-order rate constants of hydrolysis of HPNP catalyzed by the complexes $Zn_2(L2O)(OH)$, $Zn_2(L2O)(H_2O)$, Zn(L1OH)(OH) and $Zn(L1OH)(H_2O)$, the comparison of the activity of hydrolysis of HPNP catalyzed by the complexes Zn_2L1–Zn_2L5 complexes system designed and synthesized in this work with one catalyzed by the complexes $Zn_2(L2O)$, Zn(L1OH) designed and synthesized in Richard's work still can carry out through by the data in Tables 3 and 4. From the data in Table 4, it is found that the activity of hydrolysis of HPNP catalyzed by the complexes Zn_2–L in this work is less than one of the complexes $Zn_2(L2O)$, and larger than one of complexes Zn(L1OH) reported by Richard et al. The true second-order rate constants: k_{Zn_2L3} and $k_{Zn_2L3H_{-1}}$ and the deprotonation constants of coordination water of complex Zn_2L3 in this work are $0.0480\ mol^{-1}\ dm^3\ s^{-1}$, $0.000043\ mol^{-1}\ dm^3\ s^{-1}$ and 8.87, which sufficiently indicated that the complexes Zn_2–L3 are very excellent dinuclear catalyst of hydrolysis of HPNP at physiological condition (pH 7.0–8.4).

3.4. The influencing factors

Obviously shown in Table 4, the order of the second-order rate constants k_{Zn_2L} and $k_{Zn_2LH_{-1}}$ catalyzing hydrolysis of HPNP by the Zn_2–L dinuclear complexes is L1 < L2 < L3 > L4 > L5. So we think that the distance of two zinc cations of the Zn_2–L dinuclear complexes and the number of nitrogen atoms of ligand L coordinated with two zinc cations of Zn_2–L dinuclear complexes are very important factors. When the distance of two zinc cations gradually increased from L1 to L3, the hydrolysis rate constants catalyzing by dinuclear complexes Zn_2L and Zn_2LH_{-1} for HPNP also gradually increased. But while the distance of two zinc cations gradually increased from L3 to L5, the hydrolysis rate constants reversely decreased. This result indicated that the distance of two zinc cations in the complexes Zn_2L3 and Zn_2L3H_{-1} is the most suitable for catalysis of hydrolysis of HPNP in dinuclear complexes Zn_2L1–Zn_2L5 and Zn_2LH_{-1}–Zn_2L5H_{-1}. Of cause, when the complexes have been changed from Zn_2L3 and Zn_2L3H_{-1} to the Zn_2L5 and Zn_2L5H_{-1}, the number of nitrogen atoms coordinated with two zinc cations also gradually increased. Because when nitrogen atoms of ligand L coordinated with zinc cations, the sole pair of electron of nitrogen atom of ligand L enter into the 3d empty orbit of zinc cations and the effective positive charge of zinc cations decreased. The number of nitrogen atoms coordinated with zinc cations is more and the effective positive charge of zinc cation is less. The decrease of the effective positive charge of zinc cation decreased coordination ability of water molecule with zinc cation (a) of dinuclear complexes Zn_2L, this result induced that deprotonation ability of water coordinated on zinc cation of complex Zn_2L decreased (it is found that the deprotonation constants of water coordinated on Zn_2L, pK_a, have been changed from 8.87 to 9.39 when complex has been changed from Zn_2L3 to Zn_2L5, as for increase of deprotonation ability of water coordinated on zinc cation of dinuclear complex Zn_2L when change of complex from Zn_2L1 to Zn_2L3 due to the distance of two zinc cations gradually suit the coordination of water with zinc cation of complex Zn_2L) and also decreased the binding ability of oxygen anion of HPNP with zinc cation (b). This result must decrease the rate constants of catalyzing hydrolysis of HPNP for dinuclear complexes Zn_2L and Zn_2LH_{-1}. Therefore, when the dinuclear metal complexes of catalyzing hydrolysis of HPNP have been

designed and synthesized, ought consider many factors for example the species of metal ion, the distance of two metal ions and the number of coordination atom of ligand with metal ions.

4. Conclusion

The highly efficient catalyzing ability of dinuclear complex Zn_2L3H_{-1} for promoting hydrolysis of HPNP at physiological condition (pH 7.0–8.4). reported in this paper provide the evidence for the importance of distance of two metal cations and the number of coordination atom of ligand with metal cations to the catalyzing hydrolysis of HPNP by comparison of rate constants and by establishing the mechanism of the dinuclear complexes catalysts.

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