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Journal of Molecular Catalysis A: Chemical 187 (2002) 195–200

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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# Phosphodiester hydrolysis by metal ion macrocyclic dioxotetraamine complexes bearing alcohol pendant in comicellar solution

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Received 1 March 2002; received in revised form 9 April 2002; accepted 30 April 2002

**Abstract**

Four new long chain alkyl substituted 2,6-dioxo-1,4,7,10-tetraazacyclododecanes bearing an alcohol pendant has been synthesized. They coordinate with metal ion ($Zn^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$) to yield 1:1 five-coordinate complexes. The catalytic properties of these complexes have been investigated for the hydrolysis of bis(*p*-nitrophenyl) phosphate (BNPP) in comicellar solution. The alcohol pendant has a profound effect on the catalytic properties of macrocyclic complexes, and the nature of transition metal ion, micellar microenvironment, hydrolysis temperature, hydrophobic interactions between the metallocatalyst and substrate are also important factors in the hydrolysis of BNPP. Under the physiological conditions (pH = 7.41, 35±0.1 °C), the complexes exhibit higher catalytic activity (up to over 2–3 orders of magnitude) than metal ion or ligand alone in the hydrolysis of BNPP in comicellar solution with 2 mM Brij 35.


*Keywords:* Synthesis; Macrocyclic polyamine; Hydrolysis; Phosphodiester; Comicelle

## 1. Introduction

Hydrolysis of the activated phosphate diester has been intensively studied as the model of the cleavage of the phosphorus bonds of DNA and RNA [1,2], since the research on the hydrolysis of the phosphate has become extremely important for environmental and biological applications [3]. Although phosphate diester bonds are kinetically stable at physiological pH, many researches have shown that a number of enzymes containing metal ion complex active site can hydrolyze the phosphate diester bond very rapidly [2,4]. The metal ion is proposed to activate the phosphate group and a nucleophilic water molecule and to stabilize the pentacoordinate phosphorus transition state and the possible leaving group by cooperative action in metalloenzymes. Transition metal complexes as metalloenzyme models are applied to the phosphate diester bond hydrolysis. One of these models is the metal ion complex of macrocyclic polyamine which can activate a coordinated water molecule as chemical nuclease to form a metal-ion-hydroxyl complex at physiological pH [2,5].

Kimura et al. demonstrates that the alcohol pendant coordinated with metal ion and the lipophilic long chain pendant are very significant for phosphoryl transfer reaction in micellar or aqueous solutions

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1381-1169/02/$ – see front matter © 2002 Published by Elsevier Science B.V.
PII: S1381-1169(02)00276-5

[1,6]. Other researches also indicate that transition metal complexes of macrocyclic dioxotetraamines show important biological functions as models for metalloporteins and oxygen carriers [7]. There have been numerous studies of phosphatase model systems using simple metal complexes [8]. However, most of these models have been built for the sole M–$OH^-$ systems as nucleophiles, while few were concerned with the net reaction initiated by the metal-bound alcohol, followed by the metal-bound water.

Recently, we discovered that the complexes of chiral lipophilic pyridyl-containing β-amino alcohol and pyridine-containing macrocyclic dioxotetraamines ligands with transition metal ions are very efficient for the enantioselective hydrolysis of α-amino acid ester and the hydrolysis of bis(*p*-nitrophenyl) phosphate (BNPP) in metallomicelles [9]. In this paper, we synthesized four novel long chain macrocyclic dioxotetraamines bearing alcohol pendant **5** and investigated the catalytic hydrolysis for BNPP with transition metal ions (such as $Zn^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$) in comicellar solution.

## 2. Experimental section

### 2.1. General

Mass spectra were recorded on a Finnigan MAT 4510 spectrometer. IR spectra in $cm^{-1}$ were recorded on a Perkin-Elmer 16 PH spectrometer, $^1$HNMR spectra were recorded at 400 MHz and chemical shifts in ppm are reported relative to internal $Me_4Si$. Melting points were determined by using a micro-melting point apparatus without any corrections. Elemental analysis was performed by using a Carlo Elba 1106 instrument. Kinetic study was carried out using a Perkin-Elmer Lambda 4B UV–VIS spectrophotometer equipped with a thermoelectric cell temperature controller (±0.1 °C). The following compounds were prepared according to literature procedures: diethyl iminodiacetate **2** [10]; 2,6-dioxo-1,4,7,10-tetraazacyclododecane (dioxo[12]$N_4$) **3** [11]; Alkyl epihydrin ether **4** [12]. The Good's buffer [4-(2-hydroxyethyl)-1-piperazineethane-surfonic acid, $pk_a$ = 7.5] and surfactant Brij 35 (polyethylene glycol dodecyl ether; the average number of the ethylene group is 23) were commercially by available. BNPP were purchased and used without further purification. $Zn(ClO_4)_2{\cdot}6H_2O$, $Cu(ClO_4)_2{\cdot}6H_2O$, $Ni(CH_3COO)_2{\cdot}H_2O$, $Co(CH_3COO)_2{\cdot}$ $4H_2O$ were recrystallized from the distilled water. Diethylenetriamine was purified by distilling under reduced pressure. Tetrahydrofuran (THF) was distilled over metalic sodium. All other chemicals and reagents were obtained commercially and used without further purification. All aqueous solutions were prepared by using distilled water.

### 2.2. Procedure for the synthesis of ligand 5

Under $N_2$ atmosphere, to the solution of 2,6-dioxo-1,4,7,10-tetraazacycdodecane **3** (0.4 g, 2.0 mmol) in 30 ml of absolute ethanol, the corresponding alkyl cycloxypropyl ether **4** (2 mmol) dissolved in 30 ml absolute ethanol was added slowly dropwise. After the addition was completed, the reaction mixture was refluxed for 24 h. The organic solvent was evaporated under reduced pressure. The resulting crude product was purified by silica gel chromatography to afford **5**.

10-(1-*n*-Hexyloxy-2-hydroxypropyl)-2,6-dioxo-1,4,7,10-tetraazacycl-ododecane **5a**. The resulting solid was crystallized from $CH_3CN$ to afford **5a** as white crystal 0.22 g (yield 31%); mp 108–110 °C; IR (KBr pellet) 3445, 3324, 2982, 2960, 1634, 1068 $cm^{-1}$; $^1$HNMR (400 MHz, $CDCl_3$) $\delta$ 0.89 (t, $J$ = 7.0 Hz, 3H, *CH*$_3$), 1.30 (m, 6H, (*CH*$_2$)$_3$CH$_3$), 1.56 (m, 2H, OCH$_2$*CH*$_2$(CH$_2$)$_3$), 1.60 (br, s, 1H, *NH*), 2.66 (m, 4H, *CH*$_2$N*CH*$_2$, m, 1H, *CH*OH), 2.74 (m, 2H, NH*CH*$_2$CHOH), 3.38 (br, s, 4H, *CH*$_2$NHCO), 3.44 (s, 4H, *CH*$_2$CO), 3.47 (m, 2H, O*CH*$_2$(CH$_2$)$_4$CH$_3$), 3.49 (m, 2H, HOCH*CH*$_2$O), 3.50 (br, s, 1H,*OH*), 7.90 (br, s, 2H, *CH*$_2$NHCO) ppm. Anal. calcd. for $C_{17}H_{34}N_4O_4$: C, 56.96; H, 9.56; N, 15.63. Found: C, 56.56; H, 9.59; N, 15.14. MS (*m*/*z*): 359 ($M^+$ + 1, 40).

10-(1-*n*-Octyloxy-2-hydroxypropyl)-2,6-dioxo-1,4,7,10-tetraazacyclododecane **5b**. The resulting solid was crystallized from $CH_3CN$ to afford **5b** as white crystal 0.296 g (yield 38%); mp 113–114 °C; IR (KBr pellet) 3446, 3322, 2980, 2928, 1634, 1048 $cm^{-1}$; $^1$HNMR (400 MHz, $CDCl_3$) $\delta$ 0.89 (t, $J$ = 7.1 Hz, 3H, *CH*$_3$), 1.29 (m, 10H, *(CH*$_2$)$_5$CH$_3$), 1.56 (m, 2H, OCH$_2$*CH*$_2$(CH$_2$)$_5$), 1.59 (br, s, 1H, *NH*), 2.63 (m, 4H, *CH*$_2$N*CH*$_2$, m, 1H, *CH*OH), 2.75 (m, 2H, NH*CH*$_2$CHOH), 3.32 (br, s, 4H, *CH*$_2$NHCO), 3.38 (s, 4H, *CH*$_2$CO), 3.42 (m, 2H, O*CH*$_2$(CH$_2$)$_6$CH$_3$),

3.48 (m, 2H, HOCH$CH_2$O), 3.95 (br, s, 1H, *OH*), 7.76 (br, s, 2H, $CH_2$NHCO) ppm. Anal. calcd. for $C_{19}H_{38}N_4O_4$: C, 59.04; H, 9.91; N, 14.49. Found: C, 58.90; H, 9.86; N, 14.65. MS (*m*/*z*): 387 ($M^+$+1, 100).

10-(1-*n*-Decyloxy-2-hydroxypropyl)-2,6-dioxo-1,4,7,10-tetraazacyclododecane **5c**. The resulting solid was crystallized from $CH_3CN$ to afford **5c** as white crystal 0.397 g (yield 48%); mp 114–115 °C; IR (KBr pellet) 3444, 3323, 2980, 2960, 1633, 1067 $cm^{-1}$; $^1$HNMR (400 MHz, $CDCl_3$) $\delta$ 0.90 (t, 3H, $CH_3$), 1.30 (m, 14H, $(CH_2)_7CH_3$), 1.56 (m, 2H, $OCH_2CH_2(CH_2)_7$), 1.59 (br, s, 1H, *NH*), 2.60 (m, 4H, $CH_2NCH_2$), 2.65 (m, 1H, *CH*OH), 2.72 (m, 2H, $NHCH_2CHOH$), 3.38 (br, s, 4H, $CH_2$NHCO), 3.44 (s, 4H, $CH_2CO$), 3.47 (m, 2H, $OCH_2(CH_2)_8CH_3$), 3.50 (m, 2H, HOCH$CH_2$O), 4.00 (br, s, 1H, *OH*), 7.85 (br, s, 2H, $CH_2$NHCO) ppm. Anal. calcd. for $C_{21}H_{42}N_4O_4$: C, 60.84; H, 10.21; N, 13.51. Found: C, 60.40; H, 10.07; N, 13.23. MS (*m*/*z*): 415 ($M^+$+1, 50).

10-(1-*n*-Dodecyloxy-2-hydroxypropyl)-2,6-dioxo-1,4,7,10-tetraazacyclododecane **5d**. The resulting solid was crystallized from $CH_3CN$ to afford **5d** as white crystal 0.30 g (yield 34%); mp 115–116 °C; IR (KBr pellet) 3444, 3324, 2918, 2852, 1634, 1048 $cm^{-1}$; $^1$HNMR (400 MHz, $CDCl_3$) $\delta$ 0.88 (t, 3H, $CH_3$), 1.26 (m, 18H, $(CH_2)_9CH_3$), 1.57 (m, 2H, $OCH_2CH_2(CH_2)_9$), 1.59 (br, s, 1H, *NH*), 2.61 (m, 4H, $CH_2NCH_2$, m, 1H, *CH*OH), 3.40 (m, 4H, $CH_2$NHCO), 3.45 (s, 4H, $CH_2CO$), 3.48 (m, 2H, $OCH_2(CH_2)_{10}CH_3$), 3.49 (m, 2H, HOCH$CH_2$O), 3.86 (br, s, 1H, *OH*), 7.85 (br, s, 2H, $CH_2$NHCO) ppm. Anal. calcd. for $C_{23}H_{46}N_4O_4$: C, 62.40; H, 10.48; N, 12.66. Found: C, 62.01; H, 9.97; N, 12.38. MS (*m*/*z*): 443 ($M^+$ + 1, 40).

10-(1-*n*-Decyloxy-2-hydroxypropyl)-2,6-dioxo-1,4,7,10-tetraazacyclododecane **5c**-Zn(II) complex. To 10-(1-*n*-decyloxy-2-hydroxypropyl)-2,6- dioxo-1,4,7,10-tetraazacyclododecane **5c** (0.082 g, 0.2 mmol) in 5 ml of dry EtOH, the $Zn(ClO_4)_2{\cdot}6H_2O$ (0.078 g, 0.21 mmol) dissolved in 5 ml EtOH was added dropwise under nitrogen atmosphere. The reaction mixture was kept at 60 °C for 24 h, and then the solvent was evaporated slowly to about 5 ml under reduced pressure, the solid was filtered and washed with cool EtOH, dried in vacuum to obtain Zn(II) complex of 5c as white solid (0.080 g, yield 58%), mp 204 °C (dec.). $^1$HNMR (300 MHz, $D_2O$) $\delta_H$: 0.87 (t, $J$ = 6.70 Hz, 3H, $CH_3$), 1.08 (m, 14H, $(CH_2)_7CH_3$), 1.47 (m, 2H, $OCH_2CH_2(CH_2)_7$), 2.04 (m, 1H, CHOH), 2.52 (s, 4H, $CH_2NHCH_2$), 3.27–3.41 (s, 4H, $CH_2CO$; m, 4H, $CH_2$NHCO; m, 2H, $NHCH_2CH$; br, s, 4H, $CH_2$NHCO; m, 4H, $OCH_2$). Anal. calcd. for $ZnC_{19}H_{44}N_4O_{13}Cl_2$: C,33.92; H,6.59; N,8.33. Found: C,33.95; H,6.57; N, 8.37. FAB-MS (*m*/*z*): ($M^+$ + 1–2$ClO_4$-$H_2O$, 457, 10).

### 2.3. Kinetic studies

Reactions were typically started by injecting an acetonitrile solution (10%, w/v) of substrate BNPP into a 1 cm cuvette containing 3.0 ml of buffered cometallomicellar solution (HEPES, pH = 7.40) formed by 2.00 mM Brij 35. The hydrolysis rate of BNPP catalyzed by the cometallomicellar system was followed by monitoring the release of *p*-nitrophenol at 400 nm, and the reaction temperature was maintained at 35.0 ± 0.1 °C. Pseudo-first-order kinetics was observed for at least five half-lives in all cases. The pseudo-first-order rate constants were obtained from spectrophotometeric data. The rate constants for each reaction were determined three times from three separate runs with an uncertainty of less than 5%.

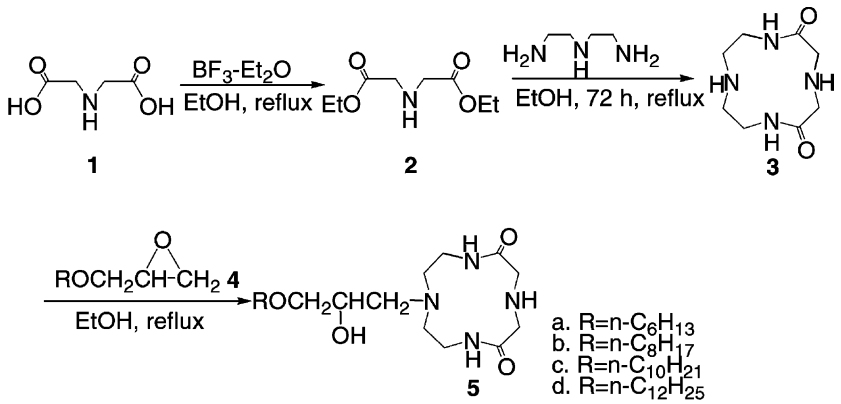
## 3. Results and discussion

The syntheses of ligand **5** were according to the procedure outlined in Scheme 1. The macrocyclic dioxotetraamines **3** [10] and alkyl epihydrin ether **4** [11] were heated to reflux in EtOH for 24 h to obtain ligand **5** in 31–48% yield.

Lipophilic ligand **5** containing lipophilic long alkyl chain and macrocyclic dioxotetraamines can not be dissolved enough in neutral water, but it can be well-dissolved in a micellar solution formed by Brij 35 to yield a comicellar system at 35 °C. The kinetic experiments were carried out by using the mixed micelle composed of a metal ion and a cosurfactant.

### 3.1. Hydrolysis of bis(p-nitrophenyl) phosphate (BNPP) with metal ion (such as $Zn^{2+}$,$Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$) complexes

The rate of hydrolysis was followed under pseudo-first-order conditions by observing the release of




Scheme 1.

*p*-nitrophenol spectrophotometrically. The pseudo-first-order rate constants ($k_{obs}$) for the hydrolysis of BNPP catalyzed by transition metal complexes comicellized with Brij 35 are summarized in Table 1.

The results indicate that large rate enhancement is observed only in the presence of both ligand **5** and metal ion. The catalytic activity is the result of synergistic cooperation between ligand and metal ion, because this depends on the activated degree of the substrate and the nucleophile, the polarized degree of P=6O bond, and the stability of the intermediate. Different metal ion possesses different catalytic activity; the activity deceased in the order of $Ni^{2+} > Zn^{2+} > Co^{2+} > Cu^{2+}$. The large rate enhancement of BNPP hydrolysis by $M^{2+}$-ligand **5** in the micellar system is, thus, explained by the formation of supramolecular assembly.

Table 1
Pseudo-first-order rate constants ($k_{obs}$, $s^{-1}$) for the hydrolysis of BNPP by ligand **5** and $M^{2+}$ comicellized with Brij 35

| Entry | Ligand | $M^{2+}$ | $k_{obs}/10^{-3}(s^{-1})$ |
|---|---|---|---|
| 1 | None | $Cu^{2+}$ | 8.09 |
| 2 | None | $Zn^{2+}$ | 6.90 |
| 3 | 5a | $Cu^{2+}$ | 336 |
| 4 | 5a | $Zn^{2+}$ | 374 |
| 5 | 5a | $Ni^{2+}$ | 513 |
| 6 | 5a | $Co^{2+}$ | 473 |
| 7 | 5b | None | 1.95 |
| 8 | 5b | $Cu^{2+}$ | 352 |
| 9 | 5b | $Zn^{2+}$ | 535 |
| 10 | 5b | $Ni^{2+}$ | 783 |
| 11 | 5b | $Co^{2+}$ | 398 |
| 12 | 5c | $Cu^{2+}$ | 307 |
| 13 | 5d | None | 3.08 |
| 14 | 5d | $Cu^{2+}$ | 537 |
| 15 | 5d | $Zn^{2+}$ | 750 |
| 16 | 5d | $Ni^{2+}$ | 4500 |
| 17 | 5d | $Co^{2+}$ | 433 |

Conditions: 35 ± 0.1 °C, pH = 7.41 (HEPES buffer), [ligand] = $2.5 \times 10^{-4}$ mol dm$^{-3}$, [substrate]= $2.5 \times 10^{-3}$ mol dm$^{-3}$, [$M^{2+}$]= $2.5 \times 10^{-4}$ mol dm$^{-3}$, [Brij 35]= $2.0 \times 10^{-3}$ mol dm$^{-3}$.

The influence of reaction temperature on the pseudo-first-order rate constants ($k_{obs}$) for the hydrolysis of BNPP catalyzed by ligand **5a** and $Cu^{2+}$ comicellized with Brij 35 are summarized in Table 2.

Table 2 shows that the reaction rate constants observed for the hydrolysis of BNPP increase along with the increase of the reaction temperature in the comicellar system.

### 3.2. Stoichiometry of the reactive complexes

In order to determine the stoichiometry of kinetically reactive complexes, the kinetic version of Job plots was examined by plotting $k_{obs}$ as a function of molar fraction of ligand (ϒ), with keeping the total

Table 2
Influence of temperature on the hydrolysis of BNPP by ligand **5a** and $Cu^{2+}$ comicellized with Brij 35

| Temperature (±0.1 °C) | Ligand | $k_{obs}/10^{-2}$ ($s^{-1}$) |
|---|---|---|
| 30 | 5a | 9.67 |
| 35 | 5a | 32.0 |
| 40 | 5a | 76.2 |

Conditions: pH 7.40 (HEPES buffer), see Table 1 for other conditions.

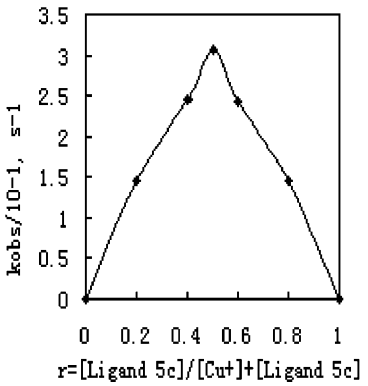
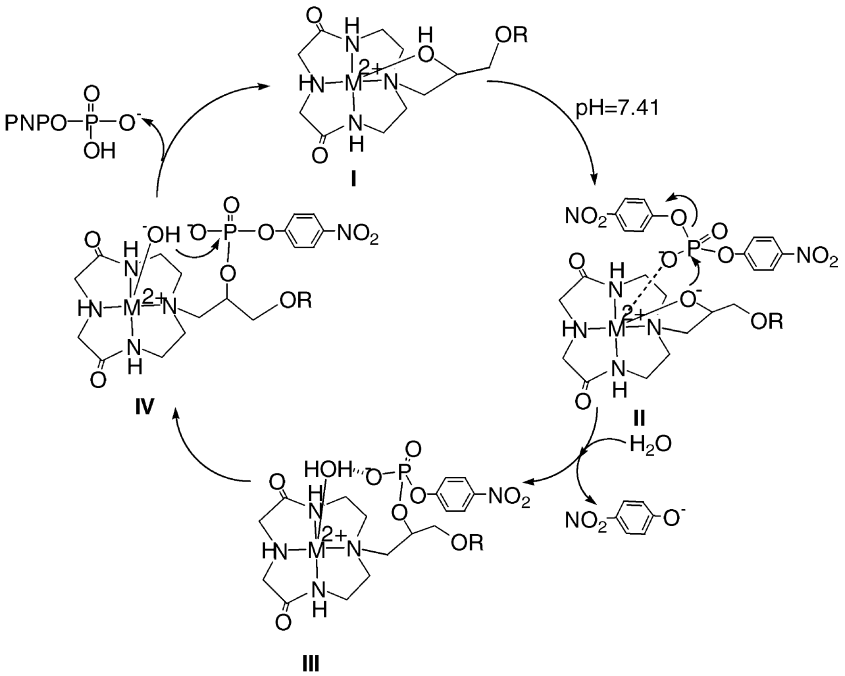



Fig. 1. Kinetic Job plots for the hydrolysis of BNPP by ligand **5c** and $Cu^{2+}$ in HEPES buffer (0.02 mol dm$^{-3}$), pH = 7.41, $T = 35\pm0.1\,^{\circ}$C, [5] + [$Cu^{2+}$] = $5.0\times10^{-3}$ mol dm$^{-3}$, see Table 1 for other conditions.

concentration of the ligand and metal ion constant. As shown in Fig. 1. in the case of $Cu^{2+}$ and ligand **5c** the rate maximum is observed at $\gamma = 0.5$. The results also show that the ratio of $Cu^{2+}$ to ligand for active species is 1:1. Ligand **5c** forms stable complexes with $Cu^{2+}$ as indicated by the sharp maximum in the Job plots.

### 3.3. Mechanism

The proposed mechanism for the hydrolysis of BNPP catalyzed by **5**-$M^{2+}$ is outlined in Scheme 2 on the basis of previous reports [2,13] and p$K_a$ values of complexes (Cu(II)-**5a**, Cu(II)-**5c**, Zn(II)-**5c** are 7.35, 7.73, 7.25, respectively). We previously demonstrated the formation of a ternary complex in the analogical system involving ligand/metal ion/substrate, and established the ternary complex kinetic model. The kinetics evidence that the micellar aggregation may fully stimulate catalytic effects as a likely consequence of change in the coordination geometry of the complex [14]. When $M^{2+}$ coordinates with the hydroxyl group which is located on the alkyl long chain, the formation of the metal complex represented as I is possible in a slightly alkaline solution. The hydroxyl group is firstly activated by the metal ion to form oxygen anion that provides the effective nucleophile at near neutral pH. Kimura [1] has demonstrated that the $Zn^{2+}$-alkoxide anion catalyzes the nucleophilic reaction faster than the $Zn^{2+}$-hydroxide anion. It is understood that the $Zn^{2+}$-alkoxide anion is a better nucleophile than $Zn^{2+}$-hydroxide anion




Scheme 2. Proposed Mechanism of the hydrolysis of BNPP by macrocyclic polyamine metallomicelles.

toward the phosphate substrate. It should be noted, however, that the reaction with $Zn^{2+}$-alkoxide is a phosphoryl transfer to form a phosphoryl intermediate II, as the previously found acyl transfer with $Zn^{2+}$-(*N*-hydroxyethyl-[12]aneN$_3$ complex [15]. This is the key step for this hydrolysis reaction, and a pseudo-intramolecular nucleophilic attack of the oxygen anion on the P=O of the substrate results in the release of *p*-nitrophenol. After water coordinates with the metal ion, the intermediate II release the *p*-nitrophenol and the intramolecular hydrogen bond is formed between the hydrogen of the coordinated water and the oxygen anion of P–O bond as intermediate III, simultaneously. Lastly, the intermediate IV is hydrolyzed by the intramolecular nucleophilic attack of metal-bound $^{-}$OH on the phosphorus atom of coordinated ester group, and thus, completing the catalytic cycle.

## Acknowledgements

This project was supported by the National Natural Science Foundation of China.

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