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Studies of artificial hydrolytic metalloenzymes: the catalytic carboxyester hydrolysis by new macrocyclic polyamine zinc(II) complexes with a phenolic-pendant as novel nucleophile

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Abstract—Zinc(II) complexes of new macrocyclic tetraamines (cyclam derivatives) having a strategically appended phenolic group, 6-(2′-hydroxy)-benzyl-1,4,8,11-tetraazacyclotetradecane (L_A), 6-(2′-hydroxy-5′-bromo)-benzyl-1,4,8,11-tetraazacyclotetradecane (L_B) and 6-(2′-hydroxy-3′,5′-dibromo)-benzyl-1,4,8,11-tetraazacyclotetradecane (L_C), have been examined as catalysts for the hydrolyses of 4-nitrophenylacetate (NA). The phenolic functionalized macrocycles form 1 : 1 ZnL complexes at pH *ca* 5. The potentiometric pH titration of L_A, L_B and L_C-Zn^{II} complexes showed dissociation of a phenolic proton with pKa values of 8, 8, 8.7 and 8.5 at 298 K and $I = 0.10$ mol.l^{-1} KNO_3 for L_A, L_B and L_C–Zn^{II} complexes respectively. In the kinetic studies using the zinc complex in 10% (v/v) CH_3CN at 298 K, $I = 0.10$ mol.l^{-1} KNO_3 and pH 7.0–9.5, we proved that the coordinated phenolate can serve as a good nucleophile that effectively catalyzes NA hydrolysis. The hydrolysis rate follows the law $v = (k_{cat}[\text{complex}] + k_{OH}[OH^-] + k_0)[NA]$. The pH rate profile gave a sigmoidal curve with inflection points at pH 8.8, 8.7 and 8.6 for L_A, L_B and L_C, respectively, which correspond to the pKa value of the complex. The second-order (first-order each in complex and NA) rate constants are 0.056, 0.084 and 0.127 mol.l^{-1}.s^{-1} for L_A, L_B and L_C are obviously larger than the corresponding value of 0.047 mol.l^{-1}.s^{-1} for N-methylcyclen-Zn(II)-OH^- complex catalyst. This is, to our knowledge, the first phenolate coordinated zinc complex that efficiently catalyses the hydrolysis of 4-nitrophenyl acetate (NA). The present study also proves that solvolysis of NA (*i.e.* water attack on the ester) does exist, but the reaction rate ($k_0 = 1.12 \times 10^{-5}$ s^{-1}) is rather small. © 1997 Elsevier Science Ltd

Keywords: catalytic hydrolysis; carboxyester; macrocyclic polyamine; zinc(II) complex; biomimics; metalloenzyme.

Nature has developed many hydrolytic metalloenzymes which are involved in the hydrolysis of some of the most important molecules of life including proteins, phospholipids, and DNA. Over the years numerous hydrolytic metalloenzyme models have been designed and studied. Much has been learned through elegant designs and careful analyses of simple enzyme models [1–7].

Among trace essential elements, zinc is second to iron in terms of the quantity found in the human body or in virtually any other organism. The most numerous of zinc enzymes are classified as hydrolases; they catalyze the hydrolysis of such condensed bonds as those in pyrophosphate, in esters (both phosphate and carboxylate), and in various types of peptides. Reaction mechanisms of hydrolytic metalloenzymes (such as carbonic anhydrase (CA) carboxypeptidase and phosphatase) and the role of metal ions in their active centers have constantly been interesting bioinorganic subjects [8–10]. As one of the approaches, various types of metal complexes have been designed to account for or mimic the functions played by the central zinc(II) ions. Thus far, most successful model complexes have employed cobalt(III) [2,11–13] or copper(II) [14–16] ions, which how-

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ever, are not common in those enzymes. Recently, zinc(II) complexes as metalloenzyme models have been reported [17–21]. Hydrolytic zinc enzymes often use external H_2O or internal alcoholic residues as nucleophiles to react with electrophilic substrates (carboxyesters, phosphates, and amides), wherein the prior activation of the nucleophiles is essential [8,22]. For example, in carbonic anhydrase(CA) the Zn^{II}-bound water at the active center deprotonates to yield the good nucleophile Zn^{II}—OH^- which attacks the electrophilic center of the substrate CO_2 as shown in Scheme 1 [23].

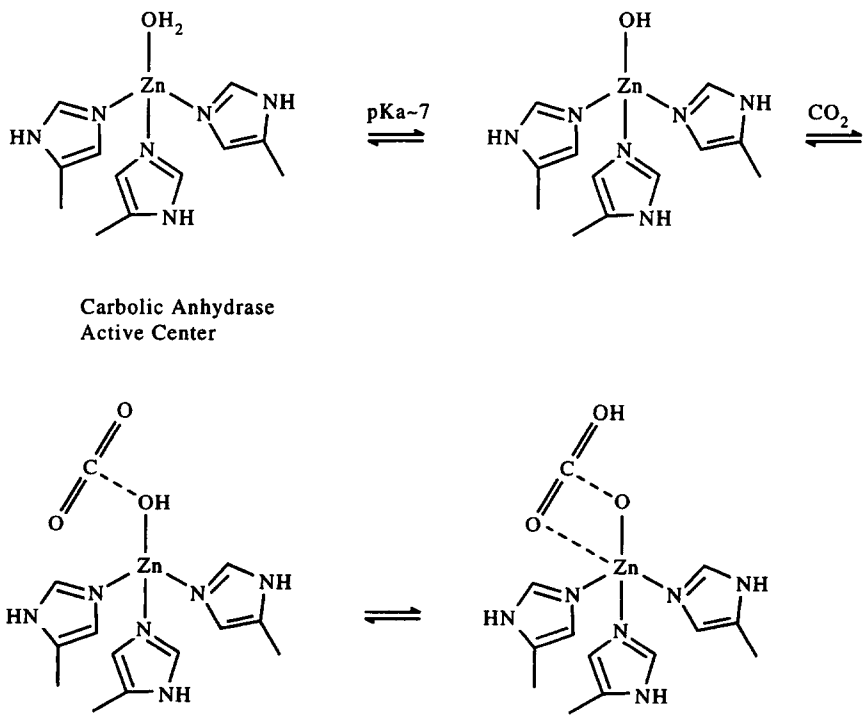
Recently, several groups studied some zinc enzyme model compounds to catalyze the hydrolysis of carboxylic esters and phosphate esters [24–27]. All the model compounds use external H_2O or internal alcoholic residues as nucleophiles to react with electrophilic substrates. Although Krebs reported the structure of a phenoxy-bridged homodinuclear Zn complex for the active site of phospholipase [28], no kinetic study to demonstrate its catalytic ability has been reported. To our knowledge, it is still unclear whether coordinated phenolate can catalyze the hydrolysis of esters.

The key role of metal ion in promoting hydrolysis appears to be the intramolecular delivery of the nucleophile. By virtue of its Lewis acidity, the metal ion reduces the pKa value of the nucleophile. In our studies, we showed that phenolic hydroxyl group of the ligand is activated upon interact with zinc(II). The phenol deprotonates with pKa values of about 8.6 upon coordination to zinc(II) ion. Whether this activated phenol can mimic carbonic anhydrase or alkaline phosphatase enzymes to hydrolyze carboxyester(4-nitrophenyl acetate) is of great interest, which would enable us to further elucidate the function of the intriguing pictures about the essential role of zinc(II) in enzymes although there is no natural importance for this particular carboxyester. A great advantage of the present tetraamine over previous triamine and other model compounds was that the Zn^{II} ion is more firmly held, which allows us to study the behavior of the model compounds in a wide range of pH without worry about degradation of the complexes.

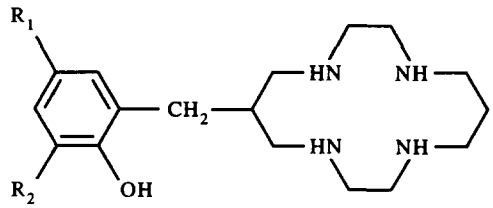
EXPERIMENTAL

General methods

Commercial reagents of analytical grade were used without further purification. Phenolic-pendant macrocyclic polyamine, 6-(2′-hydroxy)-benzyl-1,4,8,11-tetraazacyclotetradecane (L_A), 6-(2′-hydroxy-5′-bromo)-benzyl-1,4,8,11-tetraazacyclotetradecane (L_B) and 6-(2′-hydroxy-3′,5′-dibromo)-benzyl,1,4,8,11-tetraazacyclotetradecane (L_C), were synthesized as described previously [29]. Acetonitrile(CH_3CN) was distilled over calcium hydride and stored in a dark bottle. 4-Nitrophenyl acetate was recrystallized from dry diethyl ether. The pH titration technique was the same as in the literature [30]. (See Scheme 2).



Scheme 1.



L_A: $R_1 = R_2 = H$; L_B: $R_1 = Br$, $R_2 = H$;
L_C: $R_1 = R_2 = Br$

Scheme 2. Structure of the ligands

Kinetics of 4-nitrophenyl acetate hydrolysis

Kinetic study was carried out by visible spectral method using a Shimadzu UV-160A spectrophotometer equipped with a thermostatic cell (298 ± 0.1 K). The hydrolysis rate of 4-nitrophenyl acetate (NA) in aqueous solution was measured by an initial slope method following the increase in 400 nm absorption of the released 4-nitrophenolate. The reaction solution was maintained at 298 ± 0.1 K and the ionic strength was adjusted to 0.10 with $NaClO_4$. Tris (pKa = 8.21) buffer (20 mM) was used to maintain pH. In this condition, tris does not coordinate to metal ions [31]. To increase the solubility of NA, 10% CH_3CN–H_2O solution was used. For the initial rate determination, the following typical procedure was employed: After 4-nitrophenyl acetate and complexes in 10% CH_3CN solution at appropriate pH (the reference experiment did not contain the catalyst) were mixed, the UV absorption increase was recorded immediately. The increase in concentration of nitrophenylate was measured every 5–60 s. The initial slope (< 5% conversion) of a plot of the measured absorbance *vs* time was determined (correlation coefficient > 0.99). All the experiments were run in triplicate and the tabulated data represented the average of these experiments.

RESULTS AND DISCUSSION

Protonation and complexation

The acid–base behavior of the ligands and their zinc(II) complexes in aqueous 0.1 mol.l^{-1} $NaNO_3$ at 298 K has been investigated through pH titration. From the titration curve of the L_A–Zn binary system we can see that the zinc(II) complex was formed at pH 4. At pH 6, all the zinc(II) underwent complexation. The complex is stable up to pH 11 without precipitation. The complex dissociates a proton in alkaline solution with pKa 8.8. The pKa values of L_B– and L_C–Zn complexes are 8.7 and 8.5 respectively. This shows that bromo-substituents decrease the pKa value, which indicates that, unlike cyclam zinc(II) complex, the pKa value decrease of the present zinc(II) complexes should be attributed to the coordinated phenol hydroxyl group. Similar zinc(II) complex (cyclam complex) also deprotonate with pKa 9.8 under the same conditions [32], which is the deprotonation of coordinated water molecule (Scheme 3). The present pKa values decrease an order of magnitude compared with the cyclam complex. Such decrease in pKa value cannot be attributed to coordinated water. We therefore attribute this deprotonation to the coordinated phenolic group. The free phenolic group has a pKa value about 10, that is, the deprotonation constant is increased at least 10-fold upon coordination to the zinc(II) ion. The phenolic-containing cyclam zinc(II) complex has a pKa value of 5.8 (Scheme 2) [33]. The present phenolic pKa decrease is less than that in similar phenolic-containing cyclam derivatives (Scheme 2). The strong acidity in the latter complex is attributed to the formation of six-membered ring when phenol is coordinated to zinc(II). In the L_A–Zn^{II} complex, an eight-membered ring was formed when the phenol was coordinated to zinc(II). The eight-membered ring is obviously less stable than the six-membered ring, therefore, the pKa value of phenolic OH group in the six-membered ring is three orders larger than that in the eight-membered ring. We have tried to further prove phenolic coordination by obtaining single crystal of the complex, but failed.

As the phenolic OH group can be coordinated to zinc(II) ion, therefore, we try to investigate whether axially coordinated phenolate can catalyze hydrolysis of esters. Upon hydrolysis, the 4-nitrophenyl acetate (NA) decomposed into 4-nitrophenolate and acetate. Because of protonation/deprotonation, the absorption coefficient of 4-nitrophenolate varies considerably with pH values of the solution. To determine the rate constant, one should know the absorption coefficient, therefore, we determined the absorption coefficient (ε_{obs}) of 4-nitrophenolate in corresponding buffer solution. Table 1 lists the ε_{obs} values of 4-nitrophenolate at 400 nm.

In fact, 4-nitrophenolate (HNP) deprotonates in the following scheme:

$$HNP = H^+ + NP^-$$

$$Ka = [NP^-][H^+]/[HNP] \quad (1)$$

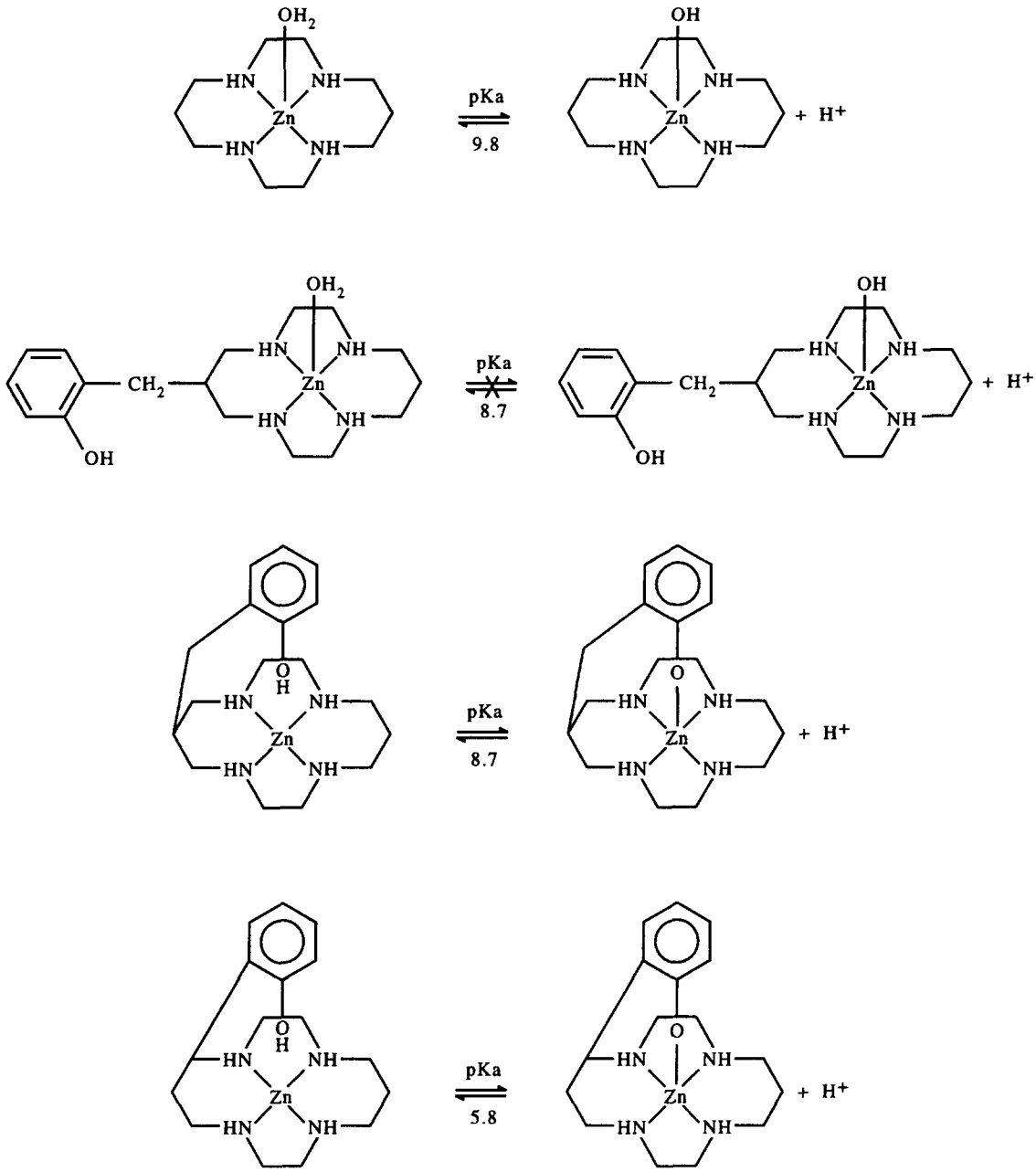
$$[H^+] = Ka C\varepsilon b/A - Ka \quad (2)$$

Where C is the total concentration of 4-nitrophenolate, ε is the extinction coefficient of NP^- anion, b is the cell length and A is the absorption of the samples. Plots of $[H^+]$ *vs* $1/A$, from the slope and intercept, we have:

$$Ka = 7.382 \times 10^{-8}, \quad \varepsilon = 1.890 \times 10^4, \quad r = 0.9994$$

This Ka value is in good agreement with the literature value [34] and indicates the reliability of the experiments.

Under our experimental conditions, the hydrolysis



Scheme 3. Deprotonation process of the polyamine-zinc(II) complexes

Table 1. Observed absorption coefficient ε_{obs} values of 4-nitrophenolate at 400 nm (298 K, I = 0.1 mol.l^{-1} KNO_3, 0.020 mol.l^{-1} tris buffers)

pH	2.0	7.067	7.481	7.904	8.220	8.577	8.753	9.007	9.536	9.742
ε_{obs}	0	8780	12800	16080	17380	18400	18610	18780	18860	18830

rate increases linearly with the increase of [NA]. That is, the hydrolysis is first-order in [NA], which indicates that the hydrolysis rate can be written in the following form:

$$v = dA/\varepsilon dt = k_{obs}[NA] \quad (3)$$

where v is the hydrolysis rate, k_{obs} is the rate constant. k_{obs} should include all the catalytic species, such as zinc(II) complex, base and some other species, therefore, k_{obs} can be written in the following form:

$$k_{obs} = k_{cat}[\text{complex}]^m + k_{OH}[OH]^{n+\cdots} \quad (4)$$

Table 2. NA hydrolysis rate $dA/\varepsilon dt \times 10^{-7}$ (s^{-1}) for zinc(II) complex of L_3 at different pH and complex concentration (298 K, I = 0.1 mol.l^{-1} KNO_3, [NA] = 2.0 mM)

pH	7.001	7.456	8.014	8.226	8.490	8.769	8.993	9.232
[Zn](mM)								
0.0	0.1458	0.1775	0.3862	0.5197	0.7899	1.239	1.834	2.818
0.50	0.2198	0.3289	0.6636	0.8806	1.365	2.068	2.961	4.156
1.00	0.3101	0.4242	0.9007	1.188	2.017	2.915	4.076	5.248
1.50	0.3762	0.5099	1.166	1.548	2.068	3.715	5.184	6.323
2.00	0.4473	0.6643	1.393	1.886	3.251	4.385	6.194	7.362
2.50	0.5200	0.7211	1.692	2.229	3.710	5.038	7.254	8.390

Where m and n are constants, k_{cat} and k_{OH} are the catalytic rate constants of zinc(II) complex and OH^-, respectively. When the observed hydrolysis rate v was plotted against complex concentration at a given pH, we can obtain k_{cat} and m values. Table 2 gives the hydrolysis rate at different pH and complex concentration. As shown in Table 2, hydrolysis rate linearly increases with the increase of complex concentration and shows a first-order dependence on zinc(II) complex ($m = 1$).

From Table 2 we can see that in the absence of complexes, hydrolysis does take place, this means that OH^- and/or solvent can catalyze NA hydrolysis. Plots of reaction rate v in the absence of zinc(II) complex *vs* $[OH^-]$, first-order dependence on $[OH^-]$ was observed.

In the absence of zinc(II) complex,

$$k_{obs} = k_0 + k_{OH}[OH^-],$$

least squares gives:

$$k_0 = 1.12 \times 10^{-5}\ s^{-1}, \quad k_{OH} = 7.84\ M^{-1}\ s^{-1},$$
$$r = 0.996.$$

The second-order rate constant k_{OH} is nearly the same as the literature value [35]. Besides k_{OH}, there is a slow reaction with $k_0 = 1.12 \times 10^{-5}\ s^{-1}$. The small value k_0 is probably due to the solvolysis of NA (i.e. water attack on the ester). These results show that NA can be hydrolyzed by solvolysis, but the reaction rate is rather small. The reaction rate is of first-order with respect to complex and NA concentration. Regression analysis of the observed rate v *vs* concentration of complex and $[OH^-]$, k_{cat} and k_{OH} (first-order dependence on OH^-) can be obtained. In Table 3 are summarized the k_{cat} values. From the above results, we have the following kinetic equation:

$$v = -d[NA]/dt = dA/\varepsilon dt$$
$$= (k_{cat}[ZnL] + k_{OH}[OH^-] + k_0)[NA] \quad (5)$$

When the zinc(II) complex catalyzed hydrolytic rate constant k_{cat} is plotted versus pH, the resulting sigmoidal curve is the same in shape as the distribution curve of phenolate coordinated zinc(II) complex, indicating characteristics of a kinetic process controlled

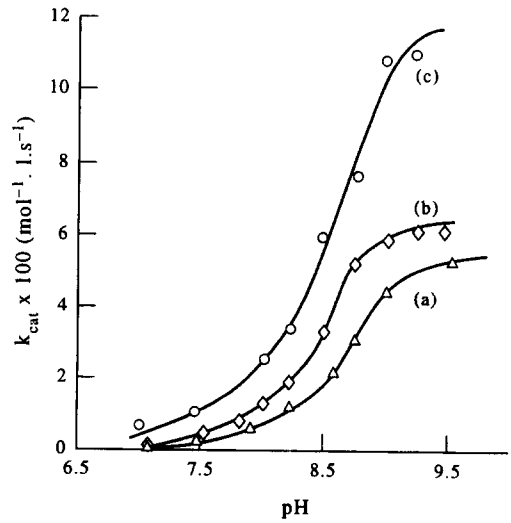


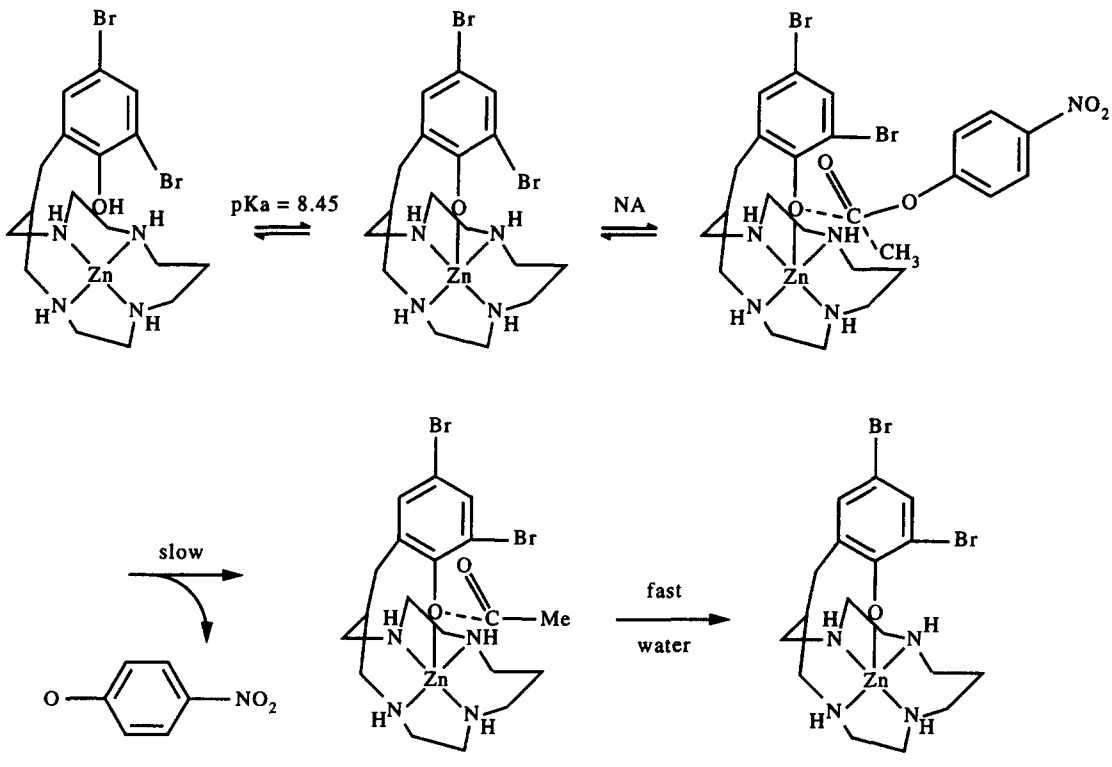
Fig. 1. pH–rate profile for the second-order rate constants of NA hydrolysis with Zn^{II} macrocyclic polyamine complexes at 298 K, I = 0.1 M KNO_3 in 10% CH_3CN aqueous solution. a: L_A–Zn^{II} complex b: L_B–Zn^{II} complex c: L_C–Zn^{II} complex.

Table 3. Second-order reaction rate constant k_{cat} (mol.l^{-1}.s^{-1}) $\times 10^2$ at different pH (298 ± 0.1 K, I = 0.1 mol.l^{-1} KNO_3)

L_1	pH	7.061	7.481	7.904	8.220	8.577	8.753	9.007	9.536	
	k_{cat}	0.122	0.278	0.605	1.21	2.18	3.09	4.43	5.28	
L_2	pH	7.070	7.523	7.820	8.013	8.220	8.499	8.753	9.018	9.257	9.473
	k_{cat}	0.174	0.486	0.836	1.30	1.92	3.32	5.22	5.90	6.11	6.12
L_3	pH	7.001	7.456	8.014	8.226	8.490	8.769	8.993	9.232		
	k_{cat}	0.748	1.09	2.57	3.41	5.96	7.64	10.8	11.0		

by an acid–base equilibrium (due to ionization of the phenolic proton) which exhibits an inflection point at pH 8.77 for L_1–Zn complex (Fig. 1), which is nearly the same as the pKa value for the coordinated phenolate of zinc(II) complex independently measured by potentiometric pH titration in water (8.8). Therefore, the reactive species is likely to be the monodeprotonated (axially coordinated) ZnL species.

Based on the results mentioned above, referring to the catalytic mechanism of carbonic anhydrase, the catalytic mechanism is proposed as follows:



In the mechanism, NA interacted with coordinated phenolic oxygen(nucleophile), *p*-nitrophenolate was dissociated and the phenolic nucleophile formed an ester. The latter can easily decompose into acetate and phenolic coordinated zinc(II) complex in aqueous solution. A catalytic cycle was then completed. According to the mechanism, phenolate deprotonated species is the effective catalyst.

$$ZnHl^{2+} = ZnL^{+} + H^{+}$$

$$Ka = [ZnL^{+}][H^{+}]/[ZnHL^{2+}]$$

$$[ZnL^{+}] = Ka[com]/(Ka + [H^{+}]$$

$$k_{cat}[com] = k[ZnL^{+}]$$

therefore, $k_{cat} = kKa/(Ka + [H^{+}])$

where k is the second-order rate constant catalyzed by phenolate coordinated ZnL^{+} species. From this equation, plots of $1/k_{cat}$ *vs* $[H^{+}]$, a straight line should be obtained. Regression of $1/k_{cat}$ *vs* $[H^{+}]$ for the three complexes, from the slope and the intercept, we have:

$k = 0.056\,M^{-1}.s^{-1}$, pKa = 8.77

for L_A–Zn complex

$k = 0.084\,M^{-1}.s^{-1}$, pKa = 8.74

for L_B–Nz complex

$k = 0.127\,M^{-1}.s^{-1}$, pKa = 8.56

for L_C–Zn complex

The pKa values thus obtained are the same or nearly the same as those obtained by pH titration, this indicates that the supposed mechanism is reasonable. The present results proved that the coordinated phenolate can serve as a good nucleophile that effectively catalyzes NA hydrolysis. The second-order (first-order) each in [com] and [NA]) rate constants of 0.056, 0.084 and 0.127 $M^{-1}.s^{-1}$ for L_A, L_B and L_C are obviously larger than the corresponding value of 0.047 $M^{-1}.s^{-1}$ for $12aneN_3$–Zn^{II}–OH^{-} complex catalyst [32]. These are, to our knowledge, the first-phenolate coordinated zinc(II) complexes (novel nucleophiles) that effectively catalyze the hydrolysis of 4-nitrophenyl acetate (NA).

From k and k_{cat} values, we can see that, structure of the ligands, i.e. substituents on the phenyl group can influence the catalytic activity of their zinc(II) complex. Electron-withdrawing substituents tend to decrease pKa values of coordinated phenolate. Hydrolytic activity of the C-phenolic functionalized macrocyclic polyamine zinc(II) complex increased with the decrease of the pKa values. However, one should keep in mind that much lower pKa values mean stronger deprotonation (i.e. coordination), and thus decrease the nucleophilicity of the coordinated nucleophiles. This clue is very important in the design of hydrolytic enzyme model compounds. The subtle relationship between ligand structure (especially pKa values) and the hydrolytic metalloenzyme activity is worthy of further study.

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