Hydrolysis of phosphate diester catalysed by transition metal complexes of a salicylaldimine Schiff base bearing dibenzo-18-crown-6

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A new crowned Schiff base ligand and its cobalt(II) and manganese(III) complexes were synthesised and characterised. These complexes were used to catalyse the hydrolysis of bis(4-nitrophenyl) phosphate (BNPP) in order to mimic the action of hydrolytic metalloenzymes. The kinetics and the mechanism of the titled reactions were investigated. The change of the characteristic ultraviolet spectra of the reaction systems was also analysed. A kinetic mathematical model of BNPP cleavage catalysed by the complexes is proposed. The function of the crown ether ring and the effects of the reaction conditions on the catalytic hydrolysis of BNPP are discussed.

Keywords: BNPP hydrolysis, Schiff base, transition metal complex, kinetics

In recent years, transition metal complexes have been used to mimic phosphate ester hydrolase,[1] and various simple or complicated chemical systems have been used as mimics of the natural enzyme. Investigations of the catalytic activity of enzyme mimics by both chemists and biologists, have helped to understand the functions of the metal ions and ligands in natural enzymes.[2,3] Previous studies[4-12] on the catalytic hydrolysis of phosphate esters to mimic hydrolytic metalloenzymes involved a large number of complexes of such metal ions as Co^{3+}, Ir^{3+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+} and La^{3+} etc., and ligands with such electron donating atoms as N and O. The studies of Schneider *et al.* [13] and Roigk *et al.*[14] showed that complexes with transition metal ions laying in a crown ring are catalytically effective for phosphatic diester hydrolysis. Morrow *et al.*[15] found that some Schiff base transition metal complexes had high catalytic activity in the cleavage of DNA.

To our knowledge, there has been no kinetic study on the hydrolysis of phosphate esters using crown Schiff base complexes of cobalt(II) and manganese(III) ions. We have therefore designed and synthesised a salicylaldimine Schiff base bearing dibenzo-18-crown-6, and its cobalt (II) and manganese (III) complexes (Fig. 1), and studied the kinetics of BNPP hydrolysis catalysed by these complexes in buffer solution. A kinetic mathematical model is now proposed and the catalytic mechanism is also discussed.

Experimental

Melting points were determined on a Yanaco MP-500 micro-melting point apparatus and uncorrected. Infrared spectra were recorded on a Nicolet-1705X IR spectrometer. ^{1}H NMR spectra were recorded on a Bruker AC-200MHz spectrometer using tetramethylsilane as internal standard. Mass spectra were obtained on a Finnigan MAT 4510 spectrometer and Finnigan LCQ^{DECA} spectrometer. The metal content was measured by an IRIS-Advantage ICP emission spectrometer method. Other elementary analysis was performed on a Carlo Erba 1106 elemental analyzer. Molar conductance was obtained on a DDS-11A conductometer. Molar magnetic susceptibility was obtained on a magnetic balance T3-200. Kinetic studies were carried out by UV-vis methods with a GBC 916 UV-vis spectrophotometer equipped with a thermostatic cell holder.

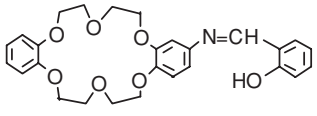
Each kinetic run was initiated by injecting an aqueous solution of BNPP with known concentration into a 1-cm cuvette, in which 3 ml buffer solution containing one of the two crowned Schiff base complexes with desired concentration had been pre-added. The reaction rate was examined by monitoring the increase of the absorbance of *p*-nitrophenol at 400 nm (pH>6), and pseudo-first–order rate constant (k_{ob}) for the hydrolysis of the substrate (BNPP) was obtained by the initial rate method, under the conditions of more than 10-fold excess of substrate concentration over the concentration of the catalyst. Kinetic tests were carried out with uncertainty of less than 3 %.

The H_2O used was obtained by redistilling deionised H_2O. Bis(4-nitrophenyl) phosphate (BNPP) and the buffering agent [tri(hydroxymethyl) aminomethane] were purchased from Sigma Chemical Co. The ionic strength of the buffer solution was maintained at 0.1 M KNO_3, and its pH was measured at 25 °C using a Radiometer PHM 26 pH meter fitted with G202C glass and K4122 calomel electrodes. The BNPP stock solution was prepared in redistilled deionised H_2O. 4'-aminodibenzo-18-crown-6 was synthesised according to reference 16. All reagents, unless otherwise indicated, were of analytical grade and were used without further purification.

4'-salicylaldiminodibenzo-18-crown-6 (H_2L): A solution of 4'-aminodibenzo-18-crown-6 (3.75 g, 10 mmol) and salicyclaldehyde (1.22 g, 10mmol) in EtOH (10 ml) was stirred for 4h under N_2 at 80°, then the mixture was cooled. The yellow precipitate was filtered and washed with ethanol. After recrystallisation from ethanol, yellow crystals (3.08 g) were obtained in 85 % yield, m.p. 142–144 °C. ^{1}H NMR($CDCl_3$) δ: 13.85 (s, 1H, OH, D_2O exchange), 8.55 (s, 1H, CH=N), 7.50–7.30 (4H, m, ArH), 7.00–6.90 (7H, m, ArH), 4.25–4.12(m, 8H, $ArOCH_2$), 3.89–3.70(m, 8H, CH_2OCH_2) ppm; I.R (KBr) ν_{max}: 3320, 1618, 1257, 1130cm^{-1}; MS *m/z*: 480 (M^++1). Anal. Calcd. for $C_{27}H_{29}NO_7$: C 67.6, H 6.1, N 2.9. Found: C 67.8, H 5.9, N, 2.7.

General methods for preparation of complexes

A solution of ligand (2.0mmol) and $MnCl_2.4H_2O$ or $Co(AcO)_2{\cdot}4H_2O$ (1.1mmol) in EtOH (15ml) was stirred for 2h under N_2 at 80°, then



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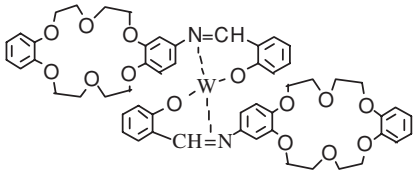

WL_2 W= Co(II), Mn(III)

Fig. 1 The structure of ligand and complexes.

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the mixture was cooled and filtered, washed with ethanol to give the complexes, and the pure product was obtained after recrystallisation from ethanol.

CoL_2: brown solid 0.73g, 71.9 % yield, m.p. 168–171 °C; IR (KBr, film) ν_{max}: 1604, 1252, 1132 cm^{-1}. ESI-MS *m/z*: 1016(M^++1). Anal. Calcd. for $CoC_{54}H_{56}N_2O_{14}$C: 63.8, H 5.5, N 2.8,Co 5.8. Found: C 64.0, H 5.4, N, 2.6, Co 6.0 ^m(s cm^2 mol^{-1}) 6.5 Molar magnetic susceptibility χ_M = 6.101 × 10^{-9} m^3 mol^{-1}, magnetic moment μ_m = 3.458 × 10^{-23} JT^{-1}. (indicating 3 non-paired electrons)

MnL_2Cl: purple solid 0.72g, 68.8% yield, m.p. 158–160 °C.IR (KBr, film) ν_{max}: 1607, 1256, 1128 cm^{-1}. ESI-MS *m/z*: 1047(M^+). Anal. Calcd. for $C_{54}H_{56}N_2O_{14}$ClMn: C 61.9, H 5.4, N 2.7, Mn 5.3,Cl 3.4: Found C 62.1, H 5.2, N, 2.8, Mn 5.1,Cl 3.6.:). $^{\wedge}_m$(s cm^2 mol^{-1}) 131.3. Molar magnetic susceptibility χ_M = 1.012 × 10^{-8} m^3 mol^{-1}, magnetic moment μ_m = 4.454 × 10^{-23} J T^{-1} (indicating 4 non-paired electrons).

The elemental analysis of the complexes indicates that the ratio of ligand to metal ion is 2:1 in the complexes. The observed molar conductance of the complexes in DMF solution (1.0 × 10^{-5} mol dm^{-3}) at 25°C also shows that the cobalt complex is a non-electrolyte and the manganese complex is an electrolyte.[17] These data indicate that cobalt is divalent and manganese is trivalent in the complexes, respectively. The IR spectra of the complexes are almost the same as the ligand except for the slight shift (11–14 cm^{-1}) to lower frequency of the C=N stretch and the disappearance of the OH stretch (3320 cm^{-1}), which accords with the suggested structure of the complexes, as shown in Fig. 1.

Results and discussion

Pseudo-first-order rate constants of the BNPP catalytic hydrolysis at 25 °C: Pseudo-first-order rate constants (k_{ob}) of the catalytic hydrolysis of BNPP in Table 1 were obtained by varying pH of the buffer solution under each concentration of BNPP with given concentration of the crowned Schiff base complex. It was speculated that the pseudo-first-order rate constant (k_0) of BNPP hydrolysis in absence of catalyst[18] was about 1.12 × $10^{-11}s^{-1}$. Comparison of k_0 with k_{ob} in Table 1 shows that the rate for the catalytic hydrolysis of BNPP increases by a factor of *ca* 1.22 × 10^6 for the complex CoL_2, and by a factor of *ca* 1.64 × 10^6 for the complex MnL_2Cl at pH = 7.00, [BNPP] =1.0 × 10^{-3} mol dm^{-3}, respectively. These results indicate that the two crowned Schiff base cobalt (II) and manganese (III) complexes are efficient catalysts for BNPP hydrolysis.

Analysis of the products and intermediate in reaction

To determine the state change of the substrate in the process of BNPP hydrolysis, UV-vis absorption spectra were measured in the range of 190–700 nm under the scaning speed of 500 nm/min, wavelength step 1 nm and smoothing step 2 nm. Water was used as reference solution in examining the UV absorption of BNPP in aqueous solution, and the complex aqueous solution was used as reference in examining the variation of UV absorption of BNPP in the presence of the complex. The characteristic spectra of BNPP observed were as follows: the maximum absorbance wavelengths were 282 nm in aqueous solution, 296 nm in CoL_2 aqueous solution, and 298 nm in MnL_2Cl aqueous solution, respectively. The red shift of the maximum absorbance wavelength of BNPP in the presence of the complex shows that the energy of light wave absorbed is lower for BNPP in the solution containing the complex than that in H_2O, which means an intermediate was made up from the complex and BNPP.[19,20] In order to confirm the interaction of BNPP with the complex, we measured the absorption spectra of the solutions containing the complexes and BNPP in various molar ratios under the wavelength range 190-700 nm. These molar ratios of BNPP to the complex were 0.2, 0.5, 0.8, 1.0, 1.2, 1.5, 2.0, 5.0, 8.0, 10.0 and 20.0, respectively. The results show that the maximum absorbance wavelengths of mixed solution containing the complex and BNPP in various molar ratios were all at 296 nm in CoL_2 aqueous solution, and 298 nm in MnL_2Cl aqueous solution, respectively. However, the intensity of the absorbance increased with increase in the molar ratios of BNPP to complexes from 0.2 to 1.2, and kept almost constant with further increase of the molar ratios over 1.2. These facts suggest that the BNPP does coordinate to the complex with a molar ratio of 1:1.[20]

In order to determine the interaction of water with the complex, we measured the UV/vis spectra of the complexes in acetonitrile and in water. The maximum absorbances of the complexes were observed at 200 nm for CoL_2, 211 nm for MnL_2Cl in acetonitrile; and 249 nm for CoL_2, 252 nm for MnL_2Cl in water, respectively. When water was added to the acetonitrile solution containing the complex, absorbances at 249 nm for CoL_2 and 252 nm for MnL_2Cl also appeared, respectively. These facts suggest that water coordinates to the complex.[20,21]

To identify the products of BNPP hydrolysis, authentic specimens of *p*-nitrophenol and BNPP solution containing the complex were scanned, respectively, by UV-vis spectrophotometry under the same conditions. The following phenomena were observed: the maximum absorbance of the characteristic spectra of *p*-nitrophenol was at 400 nm, and the characteristic spectra of BNPP solution containing the complex at 400 nm appeared, and the intensity at 400 nm increased along with increasing time. This shows that the products of the catalytic hydrolysis of BNPP included *p*-nitrophenol. To probe more information about the reaction mechanism and the final products, the catalytic hydrolysis rate of the *p*-nitrophenyl phosphate ester (NPP) by the crowned Schiff base complex was examined. The result shows that the rate of the catalytic hydrolysis of NPP is over 100 times faster than that of the catalytic hydrolysis of BNPP by the same complex. According to the structure of NPP, phosphoric acid should be generated when it is hydrolysed. These results indicate that phosphoric acid (the product of the second step of BNPP hydrolysis) is generated quickly, so long as NPP (the product of the first step of BNPP hydrolysis) was generated. The above facts confirm that the ultimate products of BNPP hydrolysis are *p*-nitrophenol and phosphoric acid.

Mechanism of catalytic hydrolysis of BNPP in the complex solution

Phosphate diester hydrolysis catalysed by phosphate diester enzyme is generally regarded as an intramolecular nucleophilic substitution reaction. The investigations of Sargeson *et al*. and

Table 1 k_{ob} (s^{-1}) of BNPP hydrolysis catalysed by the complexes in *buffer solution*.

10^4 [BNPP] (mol•dm^{-3})	10^5k_{ob} (s^{-1}) (CoL_2)					10^5k_{ob} (s^{-1}) (MnL_2Cl)				
	pH7.00	7.50	8.00	8.50	9.00	pH7.00	7.50	8.00	8.50	9.00
2.50	0.61	0.63	0.66	0.68	0.84	0.63	0.65	0.74	0.91	1.00
5.00	0.99	1.05	1.11	1.23	1.60	1.13	1.22	1.33	1.71	1.96
10.00	1.37	1.63	1.79	1.99	2.53	1.84	1.96	2.22	2.83	3.58
20.00	1.71	2.39	2.75	3.12	3.53	2.65	2.93	3.30	3.98	5.62
30.00	1.84	2.65	3.12	3.72	4.05	2.85	3.24	3.65	4.78	6.45

Condition: 25°C, I =0.1, [complex] =2.5×10^{-5} mol•dm^{-3}

Chin[22,23] indicated that phosphate diester hydrolysis catalysed by transition metal enzymes generally contains four steps: (1) the deprotonation of the complex with coordinated water; (2) the coordination of phosphate diester to central metal ions; (3) the attack of hydroxyl from deprotonation of H_2O on the P atom of the phosphate diester; (4) the cleavage of the P–O bond of the phosphate diester.

It is well known that the inner oxygen atom and outer ethylene groups in crown ether rings are hydrophilic and hydrophobic,[24] respectively. The rigid dibenzo-18-crown-6 crown ether ring can provide a micro-environment of hydrophilicity and hydrophobicity simultaneously, and may therefore allow the water molecule and lipophilic BNNP to approach to the active site of the complexes. Due to the structure of the complexes and the coordination capacity of the central ion, H_2O could coordinate to the metal ion of the complexes resulting in the formation of hydrated complex in aqueous solution. This hydrated complex may be the real active species[25] for the catalytic hydrolysis of BNPP. This is evidenced by the spectrum analysis. These results suggest that the mechanism of BNPP hydrolysis catalysed by the crowned Schiff base complexes should be similar to that catalysed by hydrolytic metalloenzyme. In addition, the data in Table 1 show that the first-order-rate constant k increases with the increase of pH value, indicating that the k of the catalytic hydrolysis of BNPP is correlated to the acidity of the reaction system, and this implies the reaction process may involve proton transfer in the rate-determining step.[20] Hence, a mechanism involving proton transfer shown in Scheme 1 is tentatively proposed for the catalytic hydrolysis of BNPP.

Where ML_2 is the hydrated complex, ML_2S represents the intermediate formed from ML_2 and S, S is the substrate BNPP, K is the association constants between the substrate and the active species, ROH represents *p*-nitrophenol, k is the first-order-rate constant for the product formation, and is pH-dependent. ML_2S^- is the anion of the intermediate, K_a is acidic dissociation constants of H_2O coordinated to the metal ion, k_1 is the first-order-rate constant that is pH-independent.

Scheme 1 predicts that: at the first step, the pre-equilibrium between ML_2 and ML_2S is established quickly with equilibrium-constant K and the intermediate is generated quickly; at the second step, a water molecule to a metal ion coordinated is activated by that ion and the metal hydroxide thus produced acts as a nucleophile to attack the positively charged P atom of the BNPP molecule. This promotes the departure of the *p*-nitrophenyl group with a first-order-rate constant (k), which is the rate-determining step of the total reaction; the second step contains both acid ionisation (step II–1) and p-nitrophenol release (step II–2). The second *p*-nitrophenol is then released and the catalyst is recovered quickly.

Quantitative treatment of the reaction of BNPP catalytic hydrolysis

In Scheme 1, the association constant K and acid ionisation constant can be expressed in terms of concentrations:

$$K = [ML_2]/[ML_2][S] \quad (1)$$

$$K_a = [H^+]\,[ML_2S^-]/[ML_2S]_t \quad (2)$$

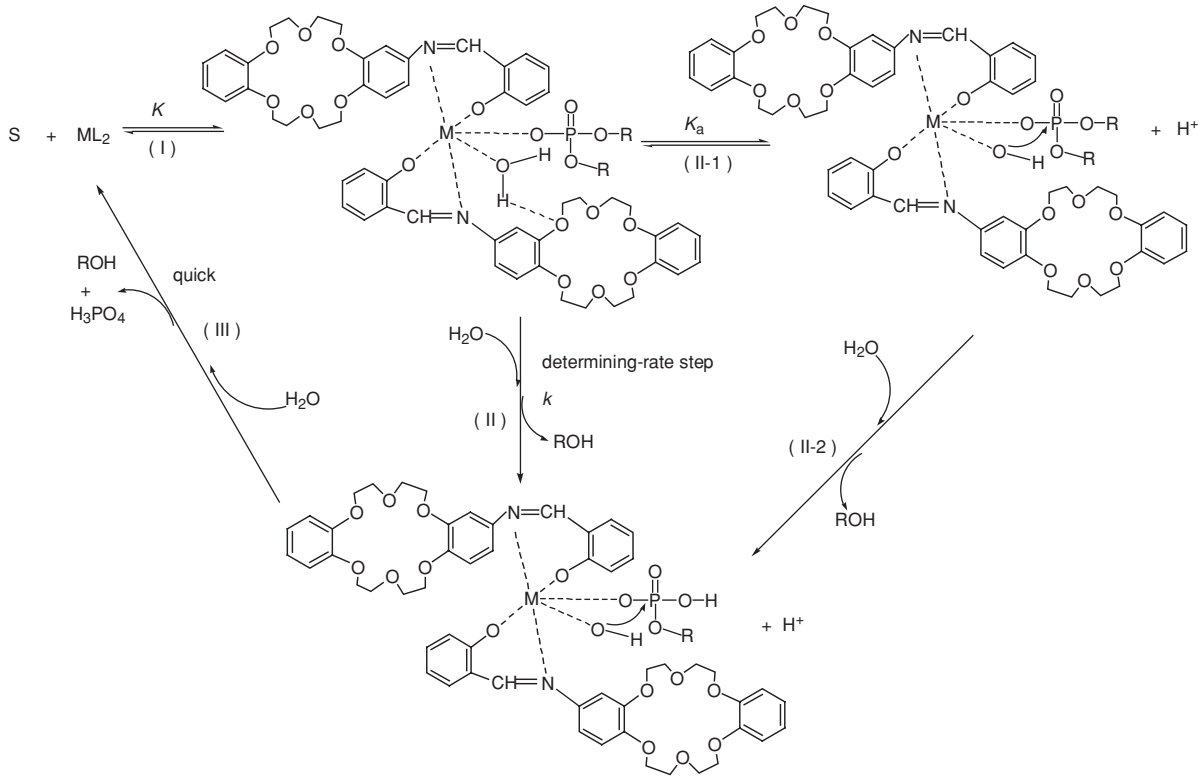
According to the mass balance, we have:

$$[ML_2]_T = [ML_2] + [ML_2S] \quad (3)$$

$$[ML_2S] = [ML_2S]_t + [ML_2S^-] \quad (4)$$

Combination of Eqns (1) and (3) leads to:

$$\left[ML_2S\right] = \frac{K[S][ML_2]_T}{1 + K[S]} \quad (5$$



M= Co(II), Mn(III)Cl

Scheme 1

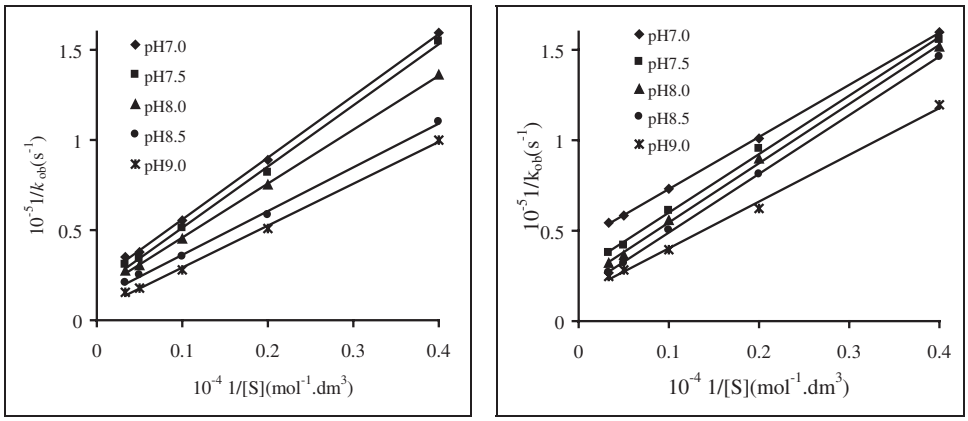


Fig. 2 The plots of $1/k_{ob}$ *vs* 1/[S]for BNPP hydrolysis catalysed by the complexes in buffer solution.

Combination of Eqns (2) and (4) leads to:

$$\left[ML_2S^-\right] = \frac{K_a[ML_2S]}{[H^+]+K_a} \quad (6)$$

Since the rate of spontaneous hydrolysis of BNPP is much lower than that of catalytic hydrolysis, the products of spontaneous hydrolysis of BNPP can be neglected in kinetics equations. Furthermore, the rate-determining step of the total reaction could be assumed to be step (II), as shown Scheme 1. Hence, the rate equation of the catalytic reaction can be simplified as follows:

$$dc/dt = k_{ob}\,[M_2L]_T = k[ML_2S] \quad (7)$$

$$k[ML_2S] = k_1\,[ML_2S^-] \quad (8)$$

Combination of Eqns (5) and (7) leads to:

$$k_{ob} = \frac{Kk[S]}{1+K[S]} \quad (9)$$

Rearranging Eqns (6) give:

$$\frac{1}{k_{ob}} = \frac{1}{k} + \frac{1}{Kk[S]} \quad (10)$$

Combining Eqns (6) and (8), we have:

$$k = \frac{K_a k_1}{[H^+]+K_a} \quad (11)$$

Rearranging Eqn (12) gives:

$$\frac{1}{k} + \frac{1}{k_1} + \frac{1}{k_1 K_a}[H^+] \quad (12)$$

In the above equations, $[ML_2]$ and $[ML_2]_T$ are the free and the total concentration of the active species, respectively; [S] is the free substrate BNNP concentration and can be substituted by the initial concentration of the substrate based on the initial rate method; dc/dt is the rate of catalytic reaction, $[ML_2S]$ is the concentration of the intermediate formed by the substrate and the active species in the buffer solution. $[ML_2S^-]$ is the dissociated concentration of the intermediate ML_2S, $[ML_2S]_t$ is the undissociated concentration of the intermediate M L_2S.

Based on Eqn (10), straight lines for $1/k_{ob}$ *vs* 1/[S] were obtained using the data in Table 1 for the evalution of *k* for the BNPP catalytic hydrolysis. The results are shown in Fig. 2.

From Fig. 2, it can be seen that the plots show a good linear relationship, indicating that the mechanism proposed above for the BNPP catalytic hydrolysis is reasonable. On the basis of Fig. 2, the results of the linear fit by the least-squares method are made and shown in Table 2.

Table 2 *k* (s^{-1})of BNPP hydrolysis catalysed by the complexes in *buffer solution.*

pH	7.0	7.5	8.0	8.5	9.0
10^5k (CoL_2)	2.12	3.79	4.95	6.05	6.99
10^5k (MnL_2Cl)	3.24	5.86	7.95	9.85	12.11

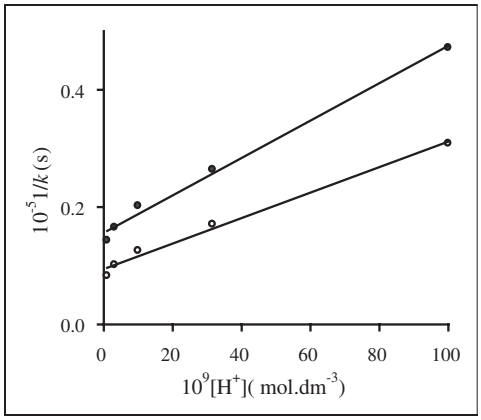


Fig. 3 The plot of $1/k$ *vs* $[H^+]$ for BNPP hydrolysis catalysed by the complexes in the buffer solution.

On the basis of Eqn (12), k_1 and K_a values can be obtained from the slope and the intercept of the plot $1/k$ *vs* $[H^+]$ (see Fig.3). The results show k_1 and K_a values are 6.39×10^{-5} s^{-1} and $3.39 \times 10^{-8}$for CoL_2, 10.58×10^{-5} s^{-1} and 4.68×10^{-8} for MnL_2Cl, respectively.

Effects of the metal ions in the complexes

The results in Table 1 show that the rate of BNPP hydrolysis catalysed by the complex MnL_2Cl system is faster than that by complex CoL_2 system, reflecting the differences between the metal ions inside these complexes and their charge._One of the major functions for the metal ions inside the complexes is both binding the molecule of PNPP and activating H_2O in the intermediate simultaneously. The higher activity of MnL_2Cl may be attributed to the relatively higher positive charge, which leads to the stronger coordination of the BNPP to the complex. As a result, the reaction rate can be accelerated.

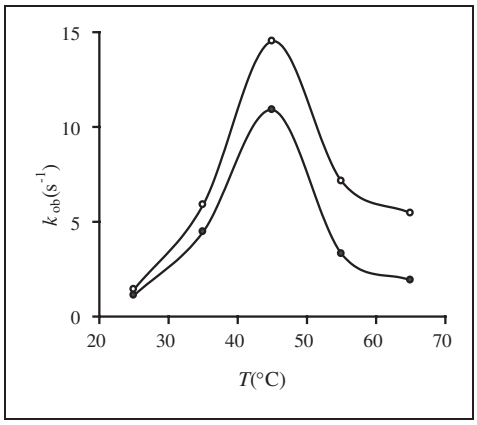


Fig. 4. The plot of k_{ob} *vs* T for BNPP hydrolysis catalysed by the complexes in the buffer solution at pH 8.00.

Effect of temperature on the rate of BNPP catalytic hydrolysis
It is well known that the catalytic activity of a natural enzyme is dependant on temperature; enzymes with different structures have different optimal temperatures. Liu *et al*.[26] have studied the catalytic activity of horseradish peroxidase (HRP) in buffer solution, and found the optimal temperature of HRP to be 40 °C. The catalytic activity of HRP decreases above 40 °C and disappears at 60 °C. Xiang *et al*.[27] also investigated macrocyclic polyamine complexes as catalysts of the hydrolysis of BNPP and found the optimal temperature to be 40 °C. Therefore, in order to find out the optimal temperature for the present system, pseudo-first order rate constants of BNPP hydrolysis have been studied from 25 to 65 °C at pH 8.00 The results (Fig. 4) show that from 25 to 65 °C the rate constants of BNPP hydrolysis firstly increase with increase in reaction temperature and then, above 45 °C, decrease with further temperature increase, following the general rules of biocatalytic activity.[28] Presumably at low temperature the intermediate and its anion could not form easily, so the catalytic reaction rate is low. From the results obtained, the optimal temperature of the present catalytic system is about 45 °. Likewise, Chin *et al*.[29] investigated the hydrolytic efficiency and the mechanism of BNPP hydrolysis catalysed by several mononuclear complexes and found that small change in the complex structure can exert significant effects on the reactivity. Consequently, it could be that structural change of the complexes and intermediates may occur over 45 ° for the present systems. With such a structural change, which is disadvantageous to the coordination of BNPP in the complex, the intramolecular nucleophilic attack of intermediate (ML_2S) is therefore inhibited.

Conclusions

The hydrolysis of BNPP catalysed by crowned Schiff base complexes has been investigated in the present paper. The following conclusions could be drawn: (1) the new cobalt (II) and manganese (III) complexes exhibit high catalytic activity for the catalytic hydrolysis of BNPP; (2) the results of the spectra and kinetics analysis show that the catalytic hydrolysis of BNPP is an intramolecular nucleophilic substitution reaction; (3) the ultimate products of BNPP hydrolysis, p-nitrophenol and phosphoric acid are identified by examining the hydrolytic rate of the *p*-nitrophenyl phosphate ester (NPP) in the complex solution; (4) a mechanism of the catalytic hydrolysis of BNPP is proposed, and supported by the results of the quantitative treatment of the kinetic data.

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