Reactivity of Dinuclear Copper(II) Complexes with *N*-Salicylidene Glycine Schiff Bases as Carboxylesterase Models

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ABSTRACT: Two phenoxo-bridged dinuclear copper(II) complexes ($Cu_2L^1{}_2$, $Cu_2L^2{}_2$) with *N*-salicylidene glycine Schiff bases were prepared and evaluated their performance for catalyzing the hydrolysis of *p*-nitrophenyl picolinate (PNPP). The observations reveal that the as-prepared dinuclear copper(II) complexes exhibited better activity by two to three orders of magnitude rate enhancement in comparison with the autohydrolysis rate of PNPP. Chloro-containing $Cu_2L^2{}_2$ aroused approximately three times kinetic advantage over chloro-free $Cu_2L^1{}_2$ at pH 7.0, which is probably contributed to the electron-withdrawing inductive effect of the 5′-chloride group. Moreover, it was found that the pH-responded kinetic behavior displayed an enzyme-like property for the PNPP hydrolysis by the two complexes. © 2015 Wiley Periodicals, Inc. Int J Chem Kinet 47: 191–198, 2015

INTRODUCTION

Schiff bases derived from various amines and aldehydes were widely studied for the coordination chemistry of metal ions [1,2]. In spite of the above-mentioned

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application, amounts of metal complexes with various Schiff bases were proved to play vital roles in the fields of anticancer [3,4] and antimicrobial activity [5,6]. Besides, chemists focused on hydrolytic reactivity of Schiff base metal complexes toward esters [7–9] as well on the interaction between DNA and Schiff base complexes [9–12].

Especially, amino acid Schiff bases and corresponding metal complexes were attracted attention due to the physiologically activity and compatibility of amino acids [13–15]. However, it is noteworthy that main aspects of the relevant researches only concentrated on the synthesis, structural analysis, as well potential medicinal values of metal complexes with various amino acid Schiff bases. To expand the applications of amino acid Schiff bases metal complexes, some research groups began to evaluate their esterolytic reactivity [16–19]. These studies not only facilitate the understanding of the esterolytic mechanism but also prompt the development of novel cleave reagents toward phosphates [16–18] and carboxylic acid esters [19].

Despite many reports that are correlative with the reactivity of metal complexes with amino acid Schiff bases for the cleavage of DNA or small molecular phosphates, to our knowledge, only one paper reported the reactivity of dinuclear copper(II) with L-threonine-type Schiff bases toward the hydrolysis of small molecular carboxylate [19] so far. To probe the catalytic efficiency of metal complexes with different amino acid Schiff bases, here we probably report the second case that involves the hydrolysis performance of *p*-nitrophenyl picolinate (PNPP) by two kinds of phenoxo-bridged dinuclear copper(II) complexes ($Cu_2L^1{}_2$, $Cu_2L^2{}_2$) with *N*-salicylidene glycine Schiff base (Fig. 1).

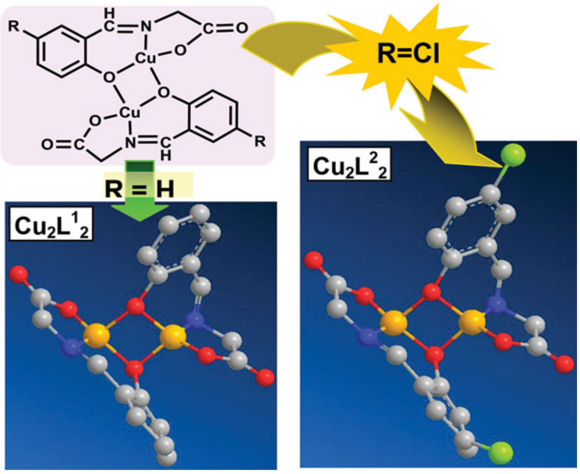


Figure 1 Schemetical illustrations of plane structures and three-dimensional optimum geometries of the two dinuclear copper complexes used in the current work.

EXPERIMENTAL

Instruments and Materials

All reagents were of analytical grade and used as received unless otherwise noted. Glycine, salicylaldehyde, 5-chlorosalicylaldehyde, and triethylamine were obtained from Chengdu Kelong Chemical (Chengdu, P.R. China). Tris (tris(hydroxymethyl) aminomethane) and potassium chloride were purchased from Sigma-Aldrich (Shanghai, P.R. China). PNPP was synthesized according to a previous report [20]. The two copper(II) complexes, i.e., $Cu_2L^1{}_2$ and $Cu_2L^2{}_2$, were prepared by a similar method described [21]. Highly purified water was obtained using a Waters purification systems (Nex Power 1000; Human Corporation, Seoul, South Korea) and used throughout for kinetic runs. The ionic strength (*I*) was maintained a constant value (0.1 M) with KCl. To avoid the spontaneous hydrolysis of PNPP, anhydrous acetonitrile was freshly prepared anhydrous acetonitrile was used for the preparation of the PNPP stock solution.

Kinetic measurements of the PNPP hydrolysis were recorded on a GBC960 UV–vis spectrometer (GBC, Braeside, Australia). Elemental analysis was preformed on a CHNOS elemental analyzer Vario EL Cube (Elementar, Hanau, Germany). Molecule weights of complexes were determined on an Agilent 1100 liquid chromatography–mass spectrometer (Agilent Technologies, Santa Clara, CA). Characterizations of the two complexes were shown as follows. Determined data that are accordance with theoretic values confirm their structures of the two dinuclear complexes depicted in Fig. 1.

Synthesis of Dinuclear Copper(II) Complexes ($Cu_2L^1{}_2$ and $Cu_2L^2{}_2$) with Glycine –Salicylaldehyde Schiff Base. Appropriate salicylaldehyde or 5-chlorosalicylaldehyde (7 mmol) in 200 mL of anhydrous ethanol was added to an ethanol solution containing 7 mmol of glycine; 1 mL triethylamine was added synchronously. The mixture was refluxed at 75°C for 1 h, leading to a yellow-green solution. And then, anhydrous methanol solution of equimolar copper(II) chloride dihydrate (7 mmol) was dropwise added to the above yellow-green solution. The yellow-green system became to dark green one. The reaction mixture was kept refluxing at 75°C for another 3 h. The reaction mixture was then cooled to room temperature and filtered under reduced pressure.

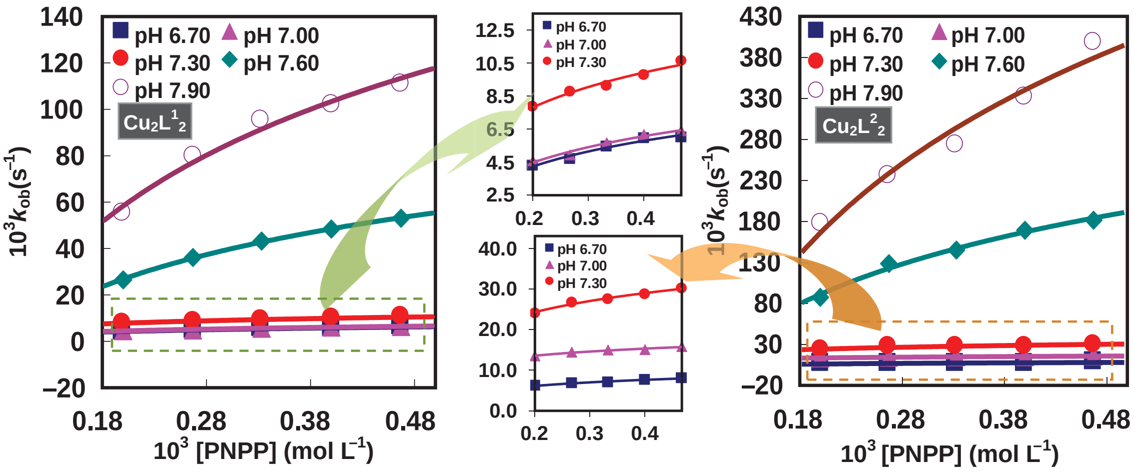


Figure 2 Dependence of rate constant upon the PNPP concentration for the Cu_2L_2-promoted hydrolysis of PNPP. Conditions: 25°C, [complex] = 0.01 mM, $I = 0.1$ M (KCl). To enhance the visibility of k_{ob}–pH plots at different pH values (6.70, 7.00, 7.30), two partial enlarged profiles from the dashed rectangles are sandwiched between the two full k_{ob}–pH profiles.

The filtrate was kept for 1 week at room temperature. Blue-green rod-like crystals of $Cu_2L^1_2$ or turquoise rod-like crystals of $Cu_2L^2_2$ were collected after filtering and drying processes under vacuum. $Cu_2L^1_2$ (blue-green rod-like crystals): yield 69.8%. mp >260°C (dec.). *m/z*: Anal. calcd. for $C_{18}H_{14}Cu_2N_2O_6$: 481.41; found: 482.43 (M + H), 504.42 (M + Na). Anal. calcd. For $C_{18}H_{14}Cu_2N_2O_6$ C 44.91, H 2.93, N 5.82 found C 44.90, H 2.95, N 5.87. $Cu_2L^2_2$ (turquoise rod-like crystals): yield 71.4%. mp >260°C (dec.). *m/z*: Anal. calcd. for $C_{18}H_{12}Cl_2Cu_2N_2O_6$: 550.30; found: 551.31(M + H), 573.34 (M + Na). Anal. calcd. For $C_{18}H_{12}Cl_2Cu_2N_2O_6$ C 39.29, H 2.20, N 5.09 found C 39.32, H 2.23, N 5.16.

Kinetic Measurements

Kinetics of PNPP hydrolysis was preformed at 25°C in a pH range 6.70–7.90 ± 0.01. The final substrate concentration varied from 0.200 to 0.467 mM, i.e., 0.200, 0.267, 0.333, 0.400, 0.467 mM. In all kinetic runs, a fixed concentration of the copper(II) complex (0.01 mM) was adopted here. Mole ratios of substrate (PNPP) to the complex were in a range of 20–46.7. Apparent first-order rate constants (k_{ob}) were determined using the initial rate method. Kinetic measurements were carried out spectrophotometrically by following the absorbance with time at λ_{max} (400 nm) corresponding to the absorption maximum of *p*-nitrophenolate anion. The experimental data are averages of two or three runs with uncertainty of less than 5%.

RESULTS AND DISCUSSION

Apparent First-Order Rate Constants (k_{ob}) of the PNPP Hydrolysis by Cu_2L_2

Figure 2 presents the variations of apparent first-order rate constants (k_{ob}) of the PNPP hydrolysis by the two dinuclear copper(II) complexes used. The rate constants–[PNPP] profiles are able to give at least two pieces of information. First, hydrolytic rates of PNPP positively correlate with systematic pH ranging from 6.70 to 7.90. At the same time, the marked increase in rate achieved for both catalysts when pH was above 7.30, which suggests the formation of certain active species. Second, the saturation curves for the two catalysts indicate the relationship between the rate constant and the concentration of substrate, representing the PNPP hydrolysis by both of the as-prepared complexes is accordance with Michaelis–Menten kinetics [22,23].

In addition, $Cu_2L^2_2$ with a 5-chloro-substitued Schiff base is ca. 1.3–3.6 folds reactive than $Cu_2L^1_2$ without the chloride group in the operated range of the substrate concentration. As compared with the background value ($k_0 = 7.8 \times 10^{-6}$ s^{-1}) of the PNPP spontaneous hydrolysis [20], the hydrolysis reactions were, respectively, accelerated by a factor of ca. 5.90×10^2 for $Cu_2L^1_2$ and 1.77×10^3 for $Cu_2L^2_2$ at pH 7.0. Our previous study [19] reported the reactivity of two copper(II) complexes with L-threonine Schiff bases. It is found that the current results are more predominant in comparison with those previous observations. For example, at pH 7.0 $Cu_2L^1{}_2$ as a catalyst in the present study is about 1.2 times reactive than the previous dinuclear copper(II) complex. Relevant causes about the distinguishable reactivity of these complexes are specially elucidated in the later section.

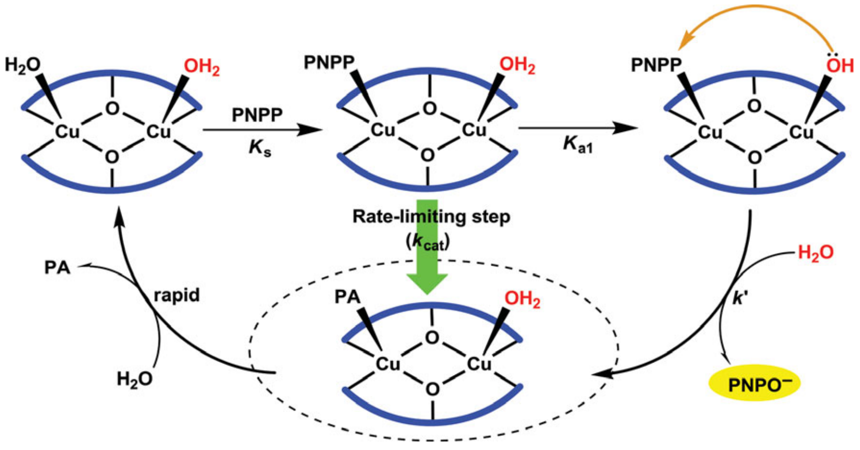
Proposed Hydrolysis Mechanism of PNPP by Cu_2L_2

Nowadays, a few proposed esterolysis mechanisms probably involve in an acid- or general base–catalyzed process [24]. In the metal-induced esterolysis, it is popularly accepted that a nucleophilic attack of the metal-coordinated hydroxide anion on the carbonyl or phosphoryl groups of carboxylic acid esters or phosphates [25]. As we know, dinuclear complexes generally possessed much better hydrolytic reactivity than mononuclear one, which probably originated from an alternative bimetallic cooperative route [26–28] concerning the efficient linkage of substrate and intramolecular nucleophilic attack.

Scheme 1 presents the possible mechanism of PNPP hydrolysis by the as-synthesized complexes. Owing to the formation of the catalyst–substrate binary complex (K_s), $Cu_2L_2(H_2O)(PNPP)$, a transformation of the original intermolecular reaction to an intramolecular one leads to a greater acceleration of the PNPP hydrolysis. And then, the deprotonated form of H_2O bound to another central copper(II) nucleophilically attacks the copper-linked PNPP, releasing the UV-responded *p*-nitrophenolate anion ($PNPO^-$) at 400 nm. This process was widely considered as a rate-determining step [29] with a catalytic constant (k_{cat}). At the end, another free water rapidly displaces the Cu(II)-bound *alpha*-picoline acid (PA), arousing the next catalytic cycle.

In this pathway, the two copper centers play important roles in the positive effects of Cu_2L_2 on the PNPP hydrolysis. Three vital roles of the copper centers include activating substrate molecules, stabilizing the negative tetrahedral transition state, and lowering the pK_a of the Cu(II)-bound H_2O. To explore the hydrolysis mechanism, we carried out the spectral scans under selected conditions (pH 7.0, 25°C, $[Cu_2L_2] = 0.01$ mM). UV spectra shown in Fig. 3 provide direct evidence for the formation of binary catalyst–PNPP intermediates and the generation of $PNPO^-$. The inserts of Fig. 3 reveal the distinguishable spectra of Cu^2L^2 in absolute ethanol and buffered aqueous solution, respectively. As shown in the inserts, the introducing of water, respectively, led to a blueshift of $\sim$3.3 and $\sim$4.2 nm for the UV–vis absorption spectrum of Cu_2L_2 ($L = L^1, L^2$), suggesting the formation of dihydrate species ($Cu_2L_2(H_2O)_2$). Therefore, the proposed mechanism is believable and reasonable due to the two facts mentioned above.

In the present work, saturation curves of k_{ob}–[PNPP] shown in Fig. 2 are in agreement with the Michaelis–Menten equation. Classic double reciprocal plots (Fig. 4), which are based on the Lineweaver–Burk formula ($1/k_{ob} = 1/k_{cat} + 1/(k_{cat}K_s[S])$), are depicted to determine kinetic parameters (Table I) using the slopes and intercepts of linear $k_{ob}{}^{-1}$–$[PNPP]^{-1}$ plots. Kinetic parameters in Table I testify that the chloro-containing $Cu_2L^2{}_2$ indeed exhibited dominated catalytic activity against $Cu_2L^1{}_2$, which is a result of their distinguishable structures.



Scheme 1 Schemetic pathway of the hydrolysis of PNPP catalyzed by Cu_2L_2. "$PNPO^-$" means the leaving group, *p*-nitrophenolate anion. "PA" is α-picoline acid, which can be replaced by one free H_2O.

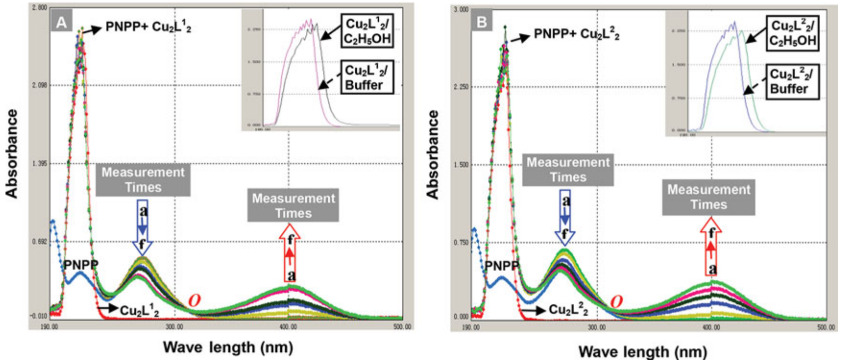


Figure 3 UV spectral scanning for the hydrolysis of PNPP catalyzed by $Cu_2L^1{}_2$ (A) or $Cu_2L^2{}_2$ (B). Inserts of Fig. 3 show the changing spectra of the two complexes in various solvents, i.e., anhydrated ethanol and buffered aqueous solution.

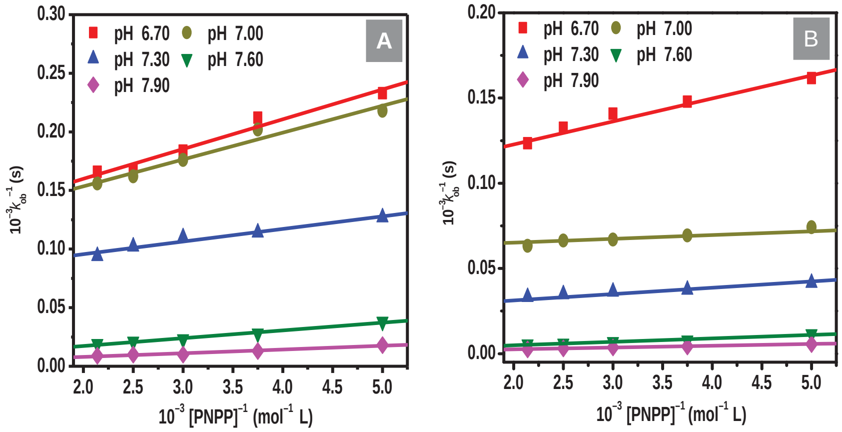


Figure 4 Plots of $k_{ob}{}^{-1}$–$[PNPP]^{-1}$ for the hydrolysis of PNPP catalyzed by $Cu_2L^1{}_2$ (A) or $Cu_2L^2{}_2$ (B). Conditions: 25°C, [complex] = 0.01 mM, $I = 0.1$ M (KCl).

pH Dependence of Catalytic Activity of Cu_2L_2

Generally, natural enzymes display their optimum activity only under mild conditions. Besides other factors (e.g., temperature, catalyst concentration, substrate concentration), pH is also an important influencing factor in the stability of enzymes. Extremely low or high pH values probably result in complete or partial deactivation for most enzymes [30]. In our study, k_{ob}–pH profiles in Fig. 5 indicate that the rate constants respond nonlinearly to the changing pH for

Table I Kinetic Parameters for the PNPP Hydrolysis by the Current Dinuclear Copper Complexes at 25°C

	$Cu_2L^1{}_2$			$Cu_2L^2{}_2$				
pH	$10^{-3}K_S$ (M)	10^3k_{cat} (s^{-1})	$k_{cat}K_S$ ($M{\cdot}s^{-1}$)	$10^{-3}K_S$ (M)	10^3k_{cat} (s^{-1})	$k_{cat}K_S$ ($M{\cdot}s^{-1}$)	$k_{cat}K_S$ Ratios of $Cu_2L^2{}_2/Cu_2L^1{}_2$	k Ratios of $Cu_2L^2{}_2/Cu_2L^1{}_2$
6.70	4.33	9.13	39.53	7.85	10.03	78.74	1.99	1.10
7.00	4.65	9.30	43.29	16.14	17.70	285.7	6.60	1.90
7.30	6.94	13.46	93.46	9.86	36.23	357.1	3.82	2.69
7.60	0.60	252.1	151.5	0.39	1264.2	488.3	3.22	5.02
7.90	0.51	622.3	315.9	0.29	3325.8	934.6	2.96	5.19

Conditions are the same as in Fig. 2.

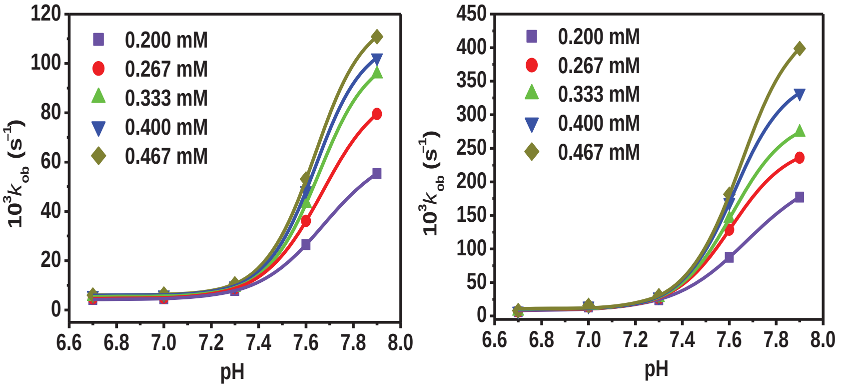


Figure 5 Variations of the apparent first-order rate constant with pH for the PNPP hydrolysis catalyzed by $Cu_2L^1{}_2$ (left) and $Cu_2L^2{}_2$ (right).

the PNPP hydrolysis. When pH is below 7.5, the hydrolysis of PNPP by the both complexes is almost pH independent, indicating a nucleophilic reaction by the metal-bound H_2O. Meanwhile, sharp hydrolysis acceleration was observed when pH was above 7.50, suggesting certain pH-dependent changes in catalytic species that is described below.

Binding constants (K_s) in Table I display an interested bell-shaped trend for each catalyst used in this work; the strongest binding strength of PNPP to catalyst was, respectively, achieved at pH 7.30 (for $Cu_2L^1{}_2$) and 7.00 (for $Cu_2L^2{}_2$). In addition, the catalytic constant (k_{cat}) also exhibits a similar nonlinear increase in the k_{ob}–pH profiles. It is noteworthy to point out that this kind of similarity likely results from the favorable conversion of the dehydrated complex to the real catalytic species in the reaction medium.

The sigmoid logk_{cat}–pH curves (see Fig. 6) imply the first-order deprotonated form of the copper-bound H_2O is the real nucleophiles. Systematic pK_{a1} values of the two catalysts are determined as ~7.49 for $Cu_2L^1{}_2$ and ~7.45 for $Cu_2L^2{}_2$ from the respective inflection points of logk_{cat}–pH curves. According to the ionization equilibrium of the Cu(II)-bound H_2O, the Cu-OH species as real nucleophiles gradually form with the pH values of reaction media above the pK_{a1} of the Cu(II)-coordinate H_2O. For this reason, an obvious jump in the hydrolysis rate was observed as the pH was adjusted to above 7.50, which provides evidence for the sharp increase in the rate shown in Fig. 5. Herein, it is emphasized that the smaller pK_{a1} for $Cu_2L^2{}_2$ may be a result of the electron-withdrawing induced effect of the 5′-chloride substituent. That is, at the same pH the efficient concentration of the active intermediate $Cu_2L^2{}_2(PNPP)(OH^-)$ is relatively higher than that for another system containing the chloride-free $Cu_2L^1{}_2$. Similar substitute effects on the esterolysis were reported by other groups [31,32] and our laboratory [19,33]. As a whole, $Cu_2L^2{}_2$ still exhibited 1.3–3.6 times kinetic advantage over $Cu_2L^1{}_2$ even though two pK_{a1} values were very close to each other, displaying only a small difference of 0.04 pK_a unit.

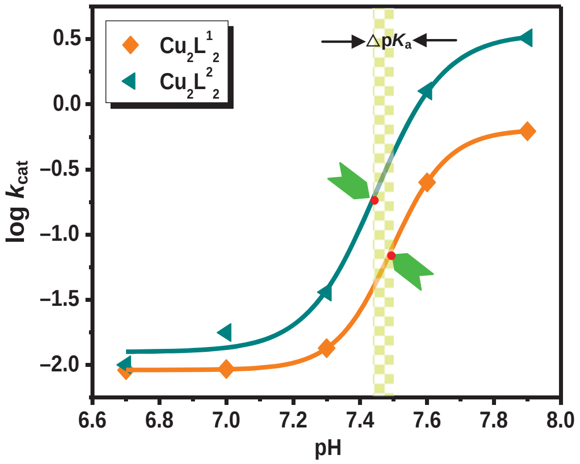


Figure 6 pH dependence on logk_{cat} for the hydrolysis of PNPP induced by the as-prepared catalysts, $Cu_2L^1{}_2$ and $Cu_2L^2{}_2$. Conditions are the same as in Fig. 1. Swallow-tail shaped arrows indicate the inflection points (red dots) of the two sigmodal-shaped curves. Light green zone highlights the pK_{a1} difference between the Cu-bound H_2O of both of copper complexes used.

Effects of the Structures of Dinuclear Copper(II) Complexes

Designing small molecule mimic hydrolases is a major challenge, as they must incorporate structural elements of the enzyme active site as well as accommodating metal binding. Metal ions, forming the enzyme's catalytic core, are known to catalyze the hydrolysis of various esters [34,35] and amides [36]. Typically, these hydrolysis reactions involve the catalytically active $M^{x+}(OH^-)$ with the metal ion, serving three possible purposes (activating substrate and coordinated water, activating leaving group, and stabilizing the transition state) [37].

In this case, both binuclear copper(II) complexes have higher activity toward the PNPP hydrolysis. The one complex ($Cu_2L^2{}_2$) with the 5′-chloride group was more active than its chloride-free analogue, $Cu_2L^1{}_2$. Figure 7 presents the variations of the relative data of enzyme efficiency ($k_{cat}K_s$) and k_{cat} values as a function of pH. The enzyme efficiency of $Cu_2L^2{}_2$ is about 2.0–6.6 folds higher than that of $Cu_2L^1{}_2$. Meanwhile, the catalytic constant k_{cat} has a 1.1–5.2 times difference between the two complexes. Besides, relative values of $k_{cat}K_s$ display bell-shaped change giving a maximum difference at pH 7.00, and whereas k_{cat} ratios is sigmoid-shaped pH respondent.

We have once studied the catalytic activity of two dinuclear copper(II) complexes with L-threonine-type Schiff bases for the hydrolysis of PNPP [19]. In this report, both of complexes exhibited better reactivity by 2–3 order of magnitude over the spontaneous hydrolysis of PNPP. Under compared conditions, moreover, glycine-type Schiff base copper(II) complexes in the current work were approximately 1.13–4.79 folds active than those dinuclear copper(II) complexes with *N*-salicylidene L-threonine Schiff base. For dinuclear $Cu_2L^1{}_2$ with *N*-salicylidene glycine Schiff base, its smaller pK_a value (7.49) leads to much higher efficient concentration of active Cu(II)-OH species compared to its dinuclear analogue with *N*-salicylidene L-threonine Schiff base ($pK_a = 7.65$). Sigmoid-shape curves in Fig. 8 show that at various concentration levels of PNPP, the rapidly increased difference in a reaction rate was achieved within the pH range 7.4–7.6, which is probably due to the easier deprotonation of H_2O bound to the two dinuclear copper(II) complexes with *N*-salicylidene glycine Schiff bases.

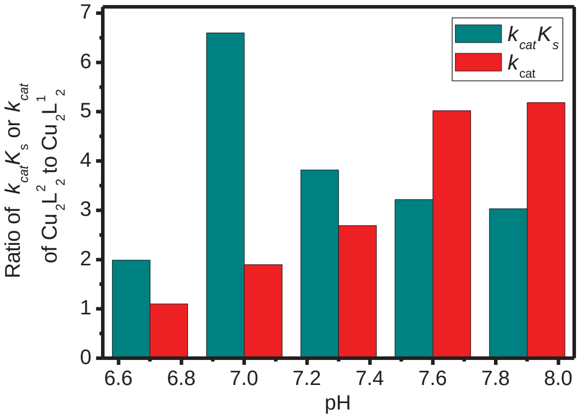


Figure 7 pH dependence on the ratios of $k_{cat}K_s$ or k_{cat} for the hydrolysis of the PNPP by the two dinuclear copper(II) complexes used.

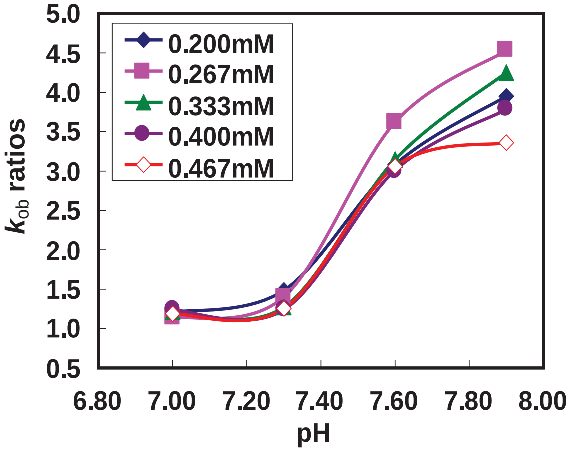


Figure 8 pH-Dependent variations of reactivity ratios of dinuclear $Cu_2L^1{}_2$ (this work) to the dinuclear analogue with *N*-salicylidene L-threonine Schiff base in our previous study [19].

In general, metal ions of metalloenzymes play a vital role in enzyme reactions [38]. On the one hand, substrates can be nucleophilically activated by the metal center as Lewis acid, thereby increasing its electrophilicity. Another reason is that the metal-bound H_2O undergoes a further polarization by the metal ion and readily converts into its conjugated metal-OH base as the real nucleophiles under near-neutral condition. On the other hand, metal centers can stabilize negative tetrahedral transition state (TS) during a hydrolytic procedure of esters [39]. The positive charge density of Cu(II) ions of $Cu_2L^2{}_2$, which comes from the electron-withdrawing effect of 5′-chloro group, is relatively higher than chloro-free $Cu_2L^1{}_2$. In comparison with $Cu_2L^1{}_2$, the strengthened Lewis acidity of the electropositive Cu(II) ions of $Cu_2L^2{}_2$ directly led to the more efficient stabilization of TS, the activation of PNPP, and the bigger lowering of pK_{a1} of the bound H_2O. Consequently, $Cu_2L^2{}_2$ possesses a better activity over its chloride-free analogue ($Cu_2L^1{}_2$), which is consistent with its higher Lewis acidity and lower pK_a value (~7.45). As a result, various constituents perhaps play a vital role in modulating the hydrolytic reactivity of artificial hydrolases toward the esterolysis.

CONCLUSIONS

In summary, two dinuclear copper(II) complexes with *N*-salicylidene glycine Schiff base efficiently accelerated the PNPP hydrolysis. $Cu_2L^2{}_2$ containing the $5'$-chloride group possesses much higher activity than its analogue without $5'$-chloride, denoting a 1.3–3.6 folds kinetic advantage over the whole concentration range of PNPP. Also, the pH-dependent catalytic constant (k_{cat}) gave two pK_{a1} value closed to 7.5, which implies the divalent copper ions have a strong ability to reduce the pK_{a1} of the Cu(II)-bound H_2O. Hence, we are permitted to predict that much better activity of dinuclear metal complexes containing highly stronger electron-withdrawing substituents (e.g., nitro, trifluomethyl group) will be achieved for the hydrolysis of various esters. Moreover, metal complexes with amino acid Schiff bases likely become a class of potential artificial enzymes that will help not only the theoretical researches but also in the development of physiologically active antimicrobial, antifungal, and anticancer agents.

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