Journal of Molecular Catalysis A: Chemical 333 (2010) 173–179

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Synthesis, single crystal structures and efficient catalysis for tetralin oxidation of two novel complexes of Cu(II) with 2-aminomethyl pyridine

Chunling Wang, Yuecheng Zhang, Baoguo Yuan, Jiquan Zhao*

School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, PR China

ARTICLE INFO

Article history:
Received 13 August 2010
Received in revised form 12 October 2010
Accepted 12 October 2010
Available online 12 November 2010

Keywords:
Tetralin
α-Tetralone
Oxidation
tert-Butyl hydroperoxide
Cu(II) complex

ABSTRACT

Two novel Cu(II) complexes were synthesized through the reaction of 2-aminomethyl pyridine (AMP) with $CuCl_2{\cdot}2H_2O$ by changing the metal/ligand ratio. Their structures were thoroughly characterized by FT-IR, elemental analysis and X-ray diffraction method. The results revealed that complex **1** $[Cu(AMP)Cl_2]$ consists of isolated binuclear molecules unit and displays distorted tetragonal pyramid. Complex **2** $[Cu(AMP)_2(H_2O)_2]Cl_2$ exhibits a octahedral geometry. The complexes were both evaluated as catalysts in the tetralin oxidation with TBHP as oxidant. Complex **1** showed high catalytic activity and selectivity towards α-tetralone under mild conditions. Thus, under the optimized conditions (acetonitrile 10 ml, catalyst 0.045 mmol, tetralin 4.5 mmol, 65% TBHP 22.5 mmol, $T = 50\,^{\circ}C$), the conversion of tetralin reached 89% with a selectivity of 71% towards α-tetralone. Compared with complex **1**, complex **2** displayed low catalytic activity mainly due to the strong steric hindrance from the two coordinated 2-aminomethyl pyridine molecules.

1. Introduction

In recent years, a considerable amount of work has been carried out on the oxidation of organic compounds with transition metals as catalysts and great progress has been made. Copper catalysts are widely used in this field for their economical and multifunctional characteristics, especially for its less harmfulness to human compared with other metals, such as chromium, cadmium, lead. Now, it has been applied to the oxidation of alkanes [1–3], alkenes [4], alcohols [5–8], arenes [9–11], benzylic substrates [12], and other substrates [13] to corresponding aldehydes, ketones, epoxides and quinones with molecular oxygen [12], hydrogen peroxide [14,15], *tert*-butyl hydroperoxide (TBHP) [16–19] and peroxyesters [20–22] as oxidants. Many of these oxidation products are useful and valuable intermediates for further synthesis of a wide variety of compounds with industrial or medicinal value [23,24].

Tetralone, an oxidation product of tetralin, is an important intermediate for the production of dyes, pharmaceuticals and agrochemicals [25–27]. For example, it can be used in the synthesis of carboryl, sertaline, 18-methyl norethisterone and a number of medicinally useful derivatives [28,29]. Therefore, seeking for catalyst with high performance for the oxidation of tetralin to tetralone is meaningful and promising. Actually, a variety of homogeneous and heterogeneous catalysts have been reported in literatures for the oxidation of tetralin with environmentally friendly oxidants [28–34]. To the best of our knowledge, in 1984, Cu^{2+} was first used for the oxidation of tetralin [31], however, only a conversion of 27% was obtained. Then in 1990, Small [32] improved the catalytic efficiency with $Cu(OH)_2$ as catalyst, but strict conditions such as high pressure and temperature were needed. In 1998, Rothenberg et al. [33] employed a copper(II) complex with n-$Bu_4N^+Br^-$ as ligand as catalyst in the oxidation of tetralin with TBHP as oxidant and a conversion of 50% was achieved. Late, several other copper complexes [28,34] were reported in succession and their catalytic activities in the oxidation of tetralin with TBHP as oxidant were discussed. Though many complexes have been described in the literature for the oxidation of tetralin, only few of them achieved results both in high reaction rate and yield in mild conditions. Therefore, it would make great sense to discover new complexes which can act as efficient catalyst in the oxidation of tetralin to α-tetralone with environmentally friendly oxidants.

For the purposes to seek highly efficient catalyst in the preparation of tetralone from tetralin, herein, we report the synthesis of two novel copper complexes **1** $[Cu(AMP)Cl_2]$ and **2** $[Cu(AMP)_2(H_2O)_2]Cl_2$ (AMP = 2-aminomethyl pyridine), and their catalytic performances in the oxidation of tetralin towards α-tetralone with TBHP as oxidant.

2. Experimental

2.1. Reagents

Tetralin, 2-aminomethyl pyridine, urea hydrogen peroxide (UHP) and *tert*-butyl hydroperoxide (TBHP) were purchased from

* Corresponding author. Tel.: +86 22 60202926/60204279; fax: +86 22 60202926.
E-mail address: zhaojq@hebut.edu.cn (J. Zhao).

1381-1169/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2010.10.014

Alfa Aesar. All other reagents and solvents were obtained from commercial sources and used as received without further purification.

2.2. Physical measurements

IR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets as the IR matrix. Elemental analyses were performed on an Elementar Vario E1. Oxidation reactions were monitored by a Shandong Lunan Ruihong gas chromatograph, SP-6800A, equipped with an FID detector. The products were determined on a Thermo DSQ gas chromatograph–mass spectrometer.

2.3. Synthesis of the complexes

The complexes were synthesized based on the procedure described by Detoni et al. [35] with some modifications. The synthesis of complex **1** [Cu(AMP)Cl_2] was carried out by the addition of 1 equivalent of 2-aminomethyl pyridine in 2 ml of methanol to 1 equivalent of $CuCl_2{\cdot}2H_2O$ in 2 ml of methanol. The mixture was then stirred for 30 min at room temperature and a large amount of blue precipitate was formed. The precipitate was isolated by filtration, washed with methanol and dried in vacuum.

The same procedure was conducted for the synthesis of complex **2** $[Cu(AMP)_2(H_2O)_2]Cl_2$ using 2 equivalents of the ligand.

(1) [Cu(AMP)Cl_2]: blue solid. Yield about 82%. IR(KBr, disc, cm^{-1}): 3288, 1602, 1481, 1433, 1287, 1162, 1094, 1038, 784. Elemental analysis calculated for $C_6H_8Cl_2CuN_2$ (242.58): C, 11.54; H, 29.69; N, 3.32%. Found: C, 11.53; H, 29.69; N, 3.31%.
(2) $[Cu(AMP)_2(H_2O)_2]Cl_2$: purple solid. Yield about 79%. IR(KBr, disc, cm^{-1}): 3211, 1604, 1485, 1434, 1373, 1291, 1144, 1031, 809. Elemental analysis calculated for $C_{12}H_{20}Cl_2CuN_4O_2$ (386.76): C, 37.27; H, 5.21; N, 14.49%. Found: C, 37.26; H, 5.21; N, 14.47%.

2.4. X-ray structure analysis

Suitable crystal was obtained by slow solvent diffusion techniques from methanol at 2–3 °C. Diffraction data of the complexes **1** and **2** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Structure solutions were found by the Patterson method. Structure refinement was carried out by full-matrix least-squares on F2 using SHELXL-97 with first isotropic and later anisotropic displacement parameters for all non-hydrogen atoms [36]. The H atoms were included in the calculation without refinement. The crystal and instrumental parameters used in the unit cell determination and data collection were summarized in Table 1.

2.5. General procedure for tetralin oxidation and analysis

The oxidation reactions were performed in a 25 ml round bottomed flask equipped with a reflux condenser and immersed in a water bath with temperature control. In a typical experiment, 0.045 mmol of the catalyst, 10 ml of acetonitrile and 4.5 mmol of substrate were mixed in the flask. To the above mixture 22.5 mmol of oxidant was added to start the reaction. The reaction mixture analyses were carried out on a Shandong Lunan Ruihong SP-6800A gas chromatograph equipped with a SE-30 column (30 m × 0.25 mm internal diameter, 0.25 μm film thickness) and an FID detector. The oven temperature programmed was 40 °C (hold 3 min), to 250 °C at 10 °C min^{-1} and hold for 5 min. Nitrogen was used as carrier gas at 0.5 mL min^{-1} flow rate. The products were identified by comparing with standard compounds and validated on a gas chromatograph–mass spectrometer. The conversion and selectivity are calculated from the following formulas:

$$\text{conversion}\,(\%) = \frac{\text{moles of tetralin consumed}}{\text{moles of tetralin loaded}} \times 100\,;$$

$$\text{selectivity}\,(\%) = \frac{\text{moles of}\,\alpha\text{-tetralone}}{\text{moles of tetralin consumed}} \times 100$$

Table 1
Crystallographic data for the complexes.

Complex	**1**	**2**
Empirical formula	$C_6H_8Cl_2CuN_2$	$C_{12}H_{20}Cl_2CuN_4O_2$
Formula weight	242.58	386.76
Temperature (K)	113(2)	143(2)
Wave length (Å)	0.710 73	0.710 73
Crystal system	Monoclinic	Monoclinic
Space group	*P*2/*c*	$P2_1/c$
a (Å)	14.427(3)	8.289 9(17)
b (Å)	6.218 7(12)	7.749 1(15)
c (Å)	19.113(4)	112.229(2)
β (°)	100.41(3)	92.11(3)
V (Å^3)	1 686.5(6)	785.0(3)
Z	8	2
D_c (g cm^{-3})	1.911	1.636
Size (mm)	0.20 × 0.16 × 0.10	0.20 × 0.18 × 0.10
Limiting indices	−17 < h < 15, −7 < k < 7, −22 < l < 22	−10 < h < 10, −10 < k < 7, −15 < l < 16
Absorption coefficient (mm^{-1})	3.154	1.740
F(0 0 0)	968	398
θ range for data collection (°)	2.17–25.02	3.60–27.87
Reflections collected	11 507	6 113
independent reflections (R_{int})	2 959 (0.043 3)	1 844 (0.031 0)
Reflections observed [$I > 2\sigma(I)$]	2 008	1 590
Data/restraints/parameters	2 959/0/199	1 844/3/109
Goodness-of-fit (GOF)	1.082	1.124
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.039 0, wR_2 = 0.093 5	R_1 = 0.030 7, wR_2 = 0.083 0
R indices (all data)	R_1 = 0.050 1, wR_2 = 0.099 7	R_1 = 0.033 5, wR_2 = 0.083 7
Largest diff. peak hole (e Å^{-3})	0.630 and −1.496	0.449 and −1.018

3. Results and discussion

3.1. Synthesis of complexes

By changing the number of the ligands coordinated to the central Cu(II) ion, several Cu(II) complexes containing 2,2′-bipyridyl or 1,10-phenantroline ligands were synthesized by others previously [28]. Inspired by the results, herein, we use 2-aminomethyl pyridine as ligand reacting with $CuCl_2{\cdot}2H_2O$ to synthesize the corresponding Cu(II) complexes. Two mononuclear Cu(II) complexes as shown in Fig. 1 were obtained smoothly by employing 1 or 2 equivalents of ligand to Cu(II). We also tried to prepared the three ligands coordinated complex by dropping 1 equivalent of $CuCl_2{\cdot}2H_2O$ or anhydrous $CuCl_2$ to 3 equivalents or more fold-excess of 2-aminomethyl pyridine in methanol. However, the separated solid was confirmed to be complex **2** after characterization not the target complex in any cases. The failure for the synthesis of the three ligands coordinated complex is due to the large space requirement of the complex and therefore high activation energy is needed to overcome a great structure changes from complex **2**, as observed in a similar case by others [37].

3.2. X-ray crystal structures of complexes 1 and 2

The crystal structures of complexes **1** and **2** are shown in Figs. 2 and 3, respectively, while selected bond lengths and angles

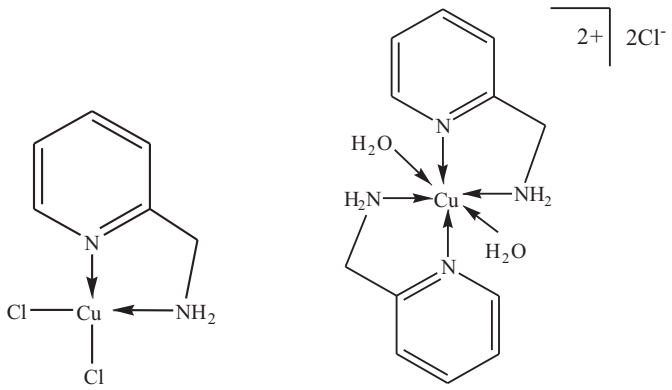


Fig. 1. Schematic representation of the Cu(II) complexes.

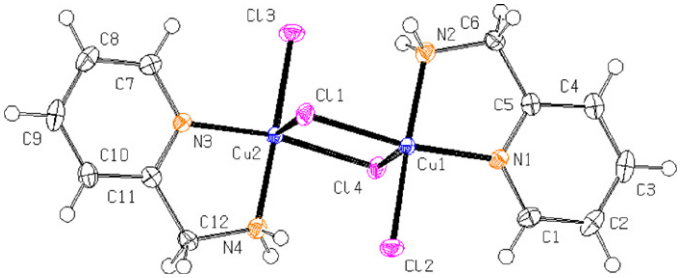


Fig. 2. Molecular structure of complex **1**.

are listed in Tables 2 and 3. Crystals of **1** and **2** are both monoclinic with space group $P2/c$ and $P2_1/c$ separately.

The crystal structure of **1**, basically similar to that of dimeric $[\{CuCl(PyTn)\}_2(\mu\text{-}Cl)_2]$ [38], consists of isolated binuclear molecules unit with two bridging chloro ligands. But different from that of $[\{CuCl(PyTn)\}_2(\mu\text{-}Cl)_2]$ with a symmetric crystal structure unit, the crystal structure unit of **1** is unsymmetrical account for a little difference in the corresponding bond lengths and angles of each five-coordinated copper subunit (see Table 2). In the structure unit of **1**, two chloro ligands bridge the copper atoms forming a four-membered ring, a terminal chloro ligand and a bidentate chelating molecule of 2-aminomethyl pyridine complete five-coordination at each metal. The bridging $[Cu_2Cl_2]$ unit is planar by the presence of the crystallographic inversion centre in the middle of the dimer. The geometry around Cu(1) can be described

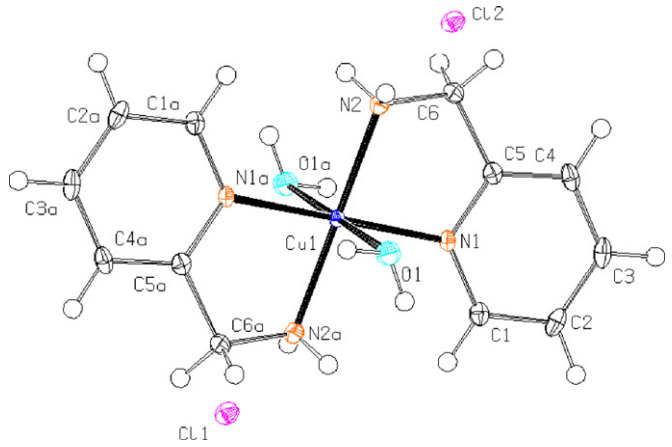


Fig. 3. Molecular structure of complex **2**.

Table 2
Selected bond lengths (Å) and angles (°) of complex **1**.

$[Cu(AMP)Cl_2]$			
Cu(1)–N(1)	1.995(3)	Cu(2)–N(3)	1.997(2)
Cu(1)–N(2)	2.004(2)	Cu(2)–N(4)	2.002(2)
Cu(1)–Cl(2)	2.251 0(11)	Cu(2)–Cl(3)	2.250 7(11)
Cu(1)–Cl(1)	2.272 0(10)	Cu(2)–Cl(4)	2.273 5(10)
N(1)–Cu(1)–N(2)	82.58(10)	N(3)–-Cu(2)–N(4)	82.71(10)
N(1)–Cu(1)–Cl(2)	97.08(7)	N(3)–Cu(2)–Cl(3)	97.23(7)
N(2)–Cu(1)–Cl(2)	173.04(6)	N(4)–Cu(2)–Cl(3)	174.87(6)
N(1)–Cu(1)–Cl(1)	170.99(7)	N(3)–Cu(2)–Cl(4)	170.53(7)
N(2)–Cu(1)–Cl(1)	88.41(8)	N(4)–Cu(2)–Cl(4)	87.99(8)
Cl(2)–Cu(1)–Cl(1)	91.90(3)	Cl(3)–Cu(2)–Cl(4)	91.89(3)

as a slightly distorted tetragonal pyramid. The basal plane is built up by two nitrogen atoms N(1), N(2) provided by the chelating ligand and two chlorine atoms Cl(1), Cl(2), one being terminal and the other acting as bridging atom. While the apical site is occupied by the other bridging chloro ligand Cl(4).

The distance of Cu(1)–Cl(1) is 2.2720(10) Å slightly longer than that of Cu(1)–Cl(2) [2.2510(11) Å]. Obviously the bridging role of Cl(1) atoms lead to the slight lengthening of the Cu(1)–Cl(1) bond distance compared with that of Cu(1)–Cl(2). The value of Cu(1)–Cl(4) distance is about 2.904 Å indicating a very weak coordination of Cl(4) to Cu(1). There are no distinct differences among the Cu(1)–N and Cu(2)–N bond lengths, and the average Cu(1)–N and Cu(2)–N value is about 2.000 Å which falls in a normal range of Cu–N bond distance. The same Cu–N bond lengths also indicates that N(2) or N(4) from the aminomethyl moiety has same coordination capacity compared with that on the pyridine ring.

The Cl(1)–metal–basal ligand angles differ slightly from the ideal value of a square pyramid (90°) as the angle values of N(2)–Cu(1)–Cl(1) and Cl(2)–Cu(1)–Cl(1) are 88.41° and 91.90°, respectively.

The crystal structure of **2** consists of two di-nitrogen chelating ligands, two water molecules and two dissociated chlorine atoms. In this structure, Cu(II) cation resides on a symmetry center and the $[Cu(AMP)_2]$ part of the complex shows strictly planarity. A view of the crystal structure along the crystallographic *b*-axis reveals a layered arrangement of metal complexes. The plane on which the metal cation locates forms octahedral geometry with the water molecules at a semicoordination distance.

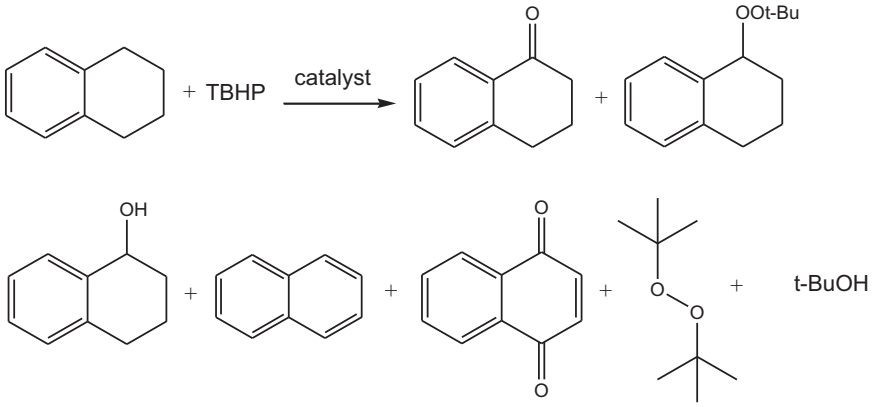
The bond lengths of Cu–N in the basal plane are 2.0001(16) and 2.0238(16) Å, respectively, which have no great changes compared with those of complex **1**. The axial Cu–O distances are about 2.539 Å showing a very weak coordination. The chloride ions are excluded from the complexation form with a dissociated state.

3.3. General aspect of the oxidation of tetralin

The complex **1** as a catalyst was first applied to the partial oxidation of tetralin with 65% TBHP as oxidant. The reaction proceeded readily in high yield at 50 °C in acetonitrile and the reaction mixture was analyzed by GC–MS. The results showed the main product is α-tetralone, together with a major byproduct determined as 1-*tert*-butylperoxytetralin and some other minor ones including α-tetralol, naphthalene and 1,4-naphtoquinone (Scheme 1).

Table 3
Selected bond lengths (Å) and angles (°) of complex **2**.

$[Cu(AMP)_2(H_2O)_2]Cl_2$			
Cu(1)–N(1)	2.0238(16)	Cu(1)–N(1a)	2.0238(16)
Cu(1)–N(2)	2.0001(16)	Cu(1)–N(2a)	2.0001(16)
N(2)–Cu(1)–N(2a)	180.000(1)	N(1)–Cu(1)–N(1a)	180.000
N(2)–Cu(1)–N(1)	83.16(7)	N(2a)–Cu(1)–N(1a)	83.16(7)
N(2)–Cu(1)–N(1a)	96.84(7)	N(2a)–Cu(1)–N(1)	96.84(7)



Scheme 1. Tetralin oxidation into different products.

The complex showed rather low selectivity to tetralol compared with 1,10-phenantroline and bipy-Cu^{2+} complexes reported by Atunes and colleagues [28]. The reason may be that 2-aminomethyl pyridine has strong electron donation capacity compared with 1,10-phenantroline and bipyridine. The effect of electron donation capacity of ligand on the electivity to α-tetralol was also observed from the result that 1,10-phenantroline with lower electron donation capacity than bipyridine gave higher selectivity to tetralol in the Cu^{2+} complex catalyzed oxidation of tetralin [28]. The combined results support the idea that one can tailor the catalytic property of the Cu(II) catalyst to either produce the hydroxylated product or the ketone one. In addition, the radical of α-tetralol ($TO^{\bullet}$) derived from the decomposition of 1-(*tert*-butylperoxy)-tetralin was more prone to eliminating a hydrogen atom to generate α-tetralone than capturing a hydrogen atom to form α-tetralol in the oxidation of tetralin with TBHP as oxidant.

Here, the products are derived from the pathways as shown in Scheme 2.

The pathways clearly elucidates the formation of all the products provided that 1-*tert*-butylperoxytetralin is the key intermediate which is formed in the initial process as the mechanism proposed by Sasson and colleagues [33] as shown in Scheme 3.

3.4. Effect of the solvent

Oxidation of tetralin can be carried out in different solvent in literature [28,33,34]. The initial conditions studied for this reaction were based on previous tetralin oxidation studies [28]. For selecting a suitable solvent for the oxidation of tetralin using complex **1** as catalyst and TBHP as oxidant, the reactions were carried out in methanol, acetonitrile, acetone and dichloromethane at 30 °C, respectively, considering their low boiling point and volatility. The results are given in Table 4.

Generally speaking aprotic polar solvents such as acetonitrile and acetone are superior to low polar solvent methylene chloride and protic solvent methanol. Moreover, acetonitrile is the best among the selected solvents both in conversion of tetralin and selectivity of α-tetralone. One explanation may be the stabilization of Cu(I) species during the catalytic cycle caused by the coordination of acetonitrile molecules as in other oxidations reported by others [39]. Acetone led to a lower activity than acetonitrile, which may be due to the low-coordination of acetone molecules to the metal centre of active Cu(I) species. Methylene dichloride has no tendency to coordinate to metal therefore gave the lowest activity. On the contrary the protic solvent methanol can coordinate to the copper ion strongly originating poorly active species, which led to low reaction rate in the case. Otherwise, it is possible that the oxidation of the methanol molecules took place, competing with that of tetralin as in the case of copper catalyzed oxidation of other substrates [40].

3.5. Effect of molar ratio of substrate to catalyst

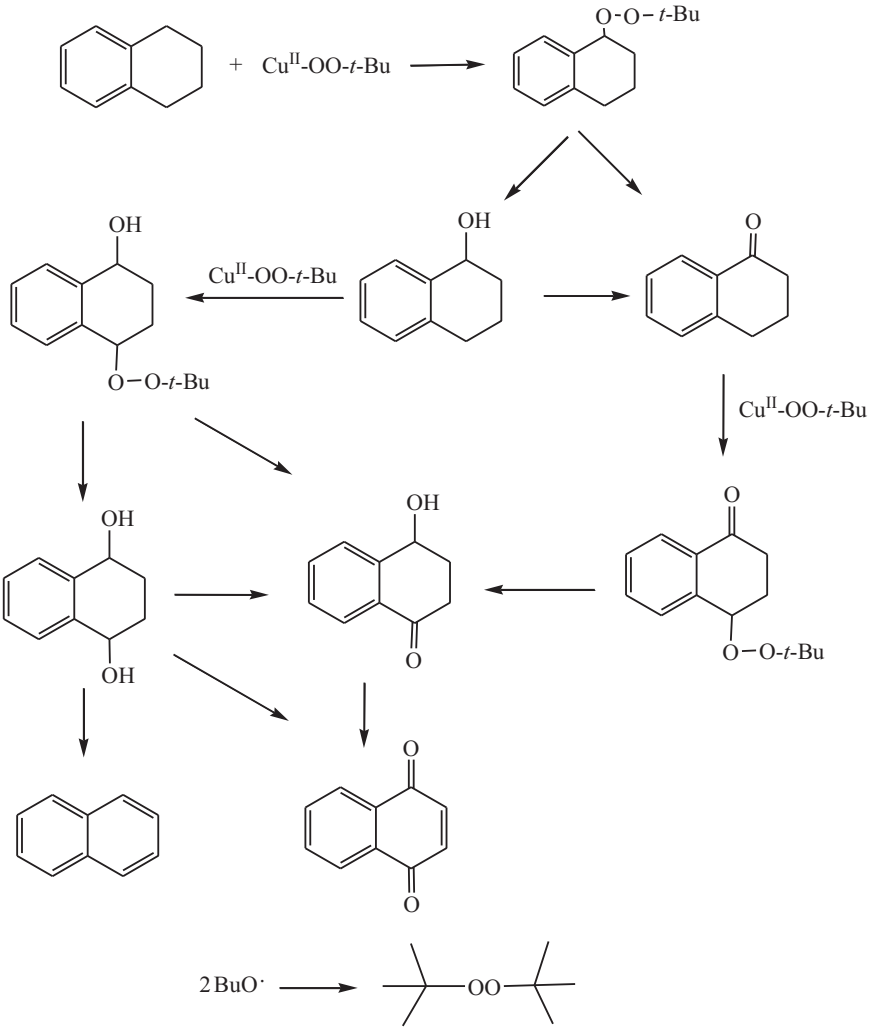
Four different catalyst loadings (0.009, 0.0225, 0.045 and 0.45 mmol) corresponding to the molar ratio of catalyst/substrate/oxidant = 1/500/2500 (1), 2.5/500/2500 (2), 5/500/2500 (3) and 10/500/2500 (4) were chosen to study the effect of molar ratio of substrate to catalyst on the reaction. The results were shown in Fig. 4.

As can be seen from Fig. 4, that the higher the molar ratio of catalyst/substrate/oxidation was, the more product was obtained at the same reaction stage most of the time. In other words, the reaction depended on the concentration of catalyst. It was also observed that the reaction under the catalyst/substrate ratios of 5/500 and 10/500 reached the same value being the highest yield of α-tetralone received when the reaction proceed for 11 h. Actually, the curves representing the yield variation with time in the above two cases already overlapped after the reaction proceeded for about 8 h, which indicated the presence of decomposition of overloaded catalyst in the catalytic run especially in the later period. After reached its maximum the yield decreased gradually with reaction time, which was probably resulted from the α-tetralone's further oxidation to 1,4-naphthalenedione as shown in Scheme 2.

Table 4
Oxidation reaction of tetralin in different kinds of solvents using complex **1** as catalyst.

Catalyst	Solvent	Time (h)	Conversion (%)	Selectivity (%)[a]
[Cu(AMP)Cl_2]	CH_3OH	10	22	70
	CH_3CN	1	22	75
	CH_3COCH_3	1.5	22	75
	CH_2Cl_2	5	11[b]	71[b]

Reaction conditions: solvent = 10 ml, [Cu(AMP)Cl_2] = 0.045 mol, tetralin = 4.5 mmol, 65% TBHP = 22.5 mmol, T = 30 °C.
[a] Selectivity of α-tetralone.
[b] After 5 h, the reaction reached its end-point.



Scheme 2. The pathways for the generation of the products.

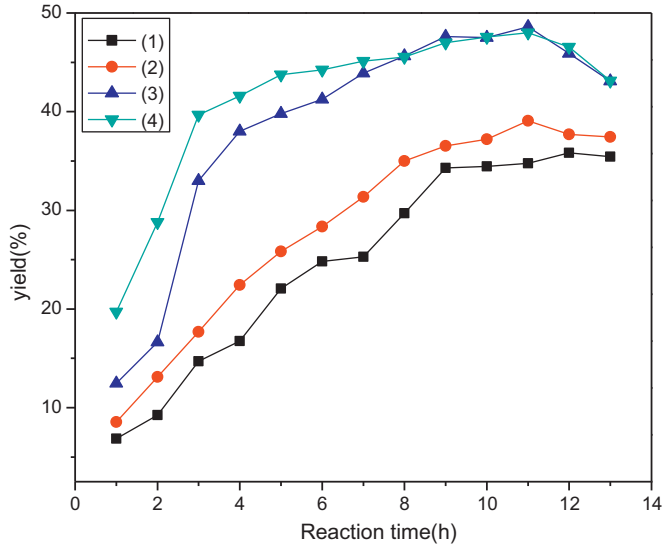


Fig. 4. Effect of the molar ratio of substrate to catalyst on the reaction using complex **1** as catalyst.

3.6. *Effect of temperature*

Four different temperatures (15, 30, 50 and 80 °C) were chosen to study their effect on the oxidation of tetralin with complex **1** as catalyst, and both the selectivity of α-tetralone as well as the time needed to reaching the maximum conversion of tetralin were monitored. The results are listed in Table 5. The results show that higher reaction temperatures are in favor of the tetralin oxidation both in conversion rate and selectivity of α-tetralone in the range of 15–50 °C. At 15 °C, 32 h were needed to reach the conversion of 88% with a selectivity of only 43% to α-tetralone, while at a reaction temperature of 50 °C, the same conversion was achieved in less than 1 h but with a selectivity of 71%. However, the conversion of tetralin at a reaction temperature of 80 °C decreased in some degree compared with that at 50 °C.

$$Cu^{II} + TBHP \longrightarrow Cu^{I} + t\text{-}BuOO^{\cdot} + H^{+} \quad (1)$$

$$Cu^{I} + TBHP \longrightarrow Cu^{II}OH + t\text{-}BuO^{\cdot} \quad (2)$$

$$Cu^{II}OH + TBHP \longrightarrow Cu^{II}\text{-}OO\text{-}t\text{-}Bu + H_2O \quad (3)$$

$$t\text{-}BuO^{\cdot} + RH \longrightarrow t\text{-}BuOH + R^{\cdot} \quad (4)$$

$$Cu^{II}\text{-}OO\text{-}t\text{-}Bu + R^{\cdot} \longrightarrow R\text{-}OO\text{-}t\text{-}Bu + Cu^{I} \quad (5)$$

Scheme 3. The mechanism for the formation of 1-tert-butylperoxytetralin.

Table 5
Effect of the temperature on the oxidation of tetralin using complex **1** as catalyst.

Catalyst	Temperature (°C)	Time (h)	Conversion (%)	Selective (%)
[Cu(AMP)]Cl_2	15	32	88	43
	30	10	88	54
	50	1	89	71
	80	1	87	71

Reaction conditions: acetonitrile = 10 ml, [Cu(AMP)Cl_2] = 0.045 mmol, tetralin = 4.5 mmol, 65% TBHP = 22.5 mmol.

For elucidating the reasons leading to these results, the reaction mixtures at different temperatures were analyzed by GC–MS and it was found that higher content of tetralin peroxide was detected at low temperature than that at high temperature. Therefore, the results listed in Table 5 can be explained as that the radical can be generated at mild temperature and then reacts with tetralin to give 1-*tert*-butylperoxytetralin. Obviously, elevating reaction temperature can accelerate the decomposition of 1-*tert*-butylperoxytetralin to α-tetralone between 15 °C and 50 °C, therefore, increase the reaction rate as well as the selectivity of α-tetralone. With the temperature elevating higher and higher, for example 80 °C, the radical and TBHP might decomposed to other inactive species, which led to the decrease of conversion of tetralin slightly. Besides, high temperature might also lead to the decomposition of catalyst as the cases using Co as catalyst [41].

3.7. Comparison of different oxidants

Besides 65% TBHP, 30% H_2O_2 and UHP were also used as oxidants in the oxidation of tetralin with complex **1** as catalyst. The reactions were carried out in the optimized conditions discussed above and the results are shown in Fig. 5.

Compared to TBHP, 30% H_2O_2 and UHP both performed poorly in the reaction from the point of view of conversion of tetralin. In the case of TBHP as oxidant the reaction completed within 4 h, however, only conversions of 23% and 36% were obtained when using UHP and 30% H_2O_2 as oxidants in the same conditions, respectively. In addition, extending reaction time did not receive prominent increase of the conversion. However, the selectivity towards α-tetralone was higher with 30% H_2O_2 and UHP as oxidants due to their low oxidability preventing the further oxidation of α-tetralone.

3.8. Catalytic evaluation of complexes **1** and **2**

Complex **2** was also used as catalyst in oxidation reaction under conditions optimized for complex **1** with TBHP as oxidant and the results are shown in Fig. 6. It can be seen that complex **2** showed low activity in the reaction compared to complex **1**. It is noteworthy that the conversion with complex **2** as catalyst gradually increased with the reaction time, no conversion jump was observed in the whole course. Therefore, it can be concluded that complex **2** as a whole acted as catalyst to catalyze the reaction advancing, no ligand disassociation taking place. Recalling the structure difference between complex **1** and complex **2**, it is not too hard to understand why the later is less active than the former one. In complex **2** two AMP are coordinated to Cu(II) tightly, which induces a strong steric hindrance preventing the approaching of TBHP to Cu(II) and then slows down the formation of active species to the oxidation reaction. In the other hand, from the structure it also can be seen that the electron density of the central Cu(II) of complex **2** is higher than that of complex **1**, which is disadvantageous to the access of TBHP as a nucleophilic reagent to the metal center and, consequently, brings down the oxidation efficiency.

Though the differences in the catalytic activity are present between complexes **1** and **2**, same selectivity ranging from 60% to 75% towards α-tetralone was observed under the same conversion (different reaction time needed) in the two cases. This can be explained by the fact that the generation of the ligand-involved intermediates to give byproducts needs higher active energy than that of the 1-*tert*-butylperoxytetralin leading to α-tetralone. This phenomenon was also observed in the other copper complexes with a same ligand catalyzed oxidation of tetralin [28,34]. Navarro et al. [34] attributed it to the complexes with the same ligand.

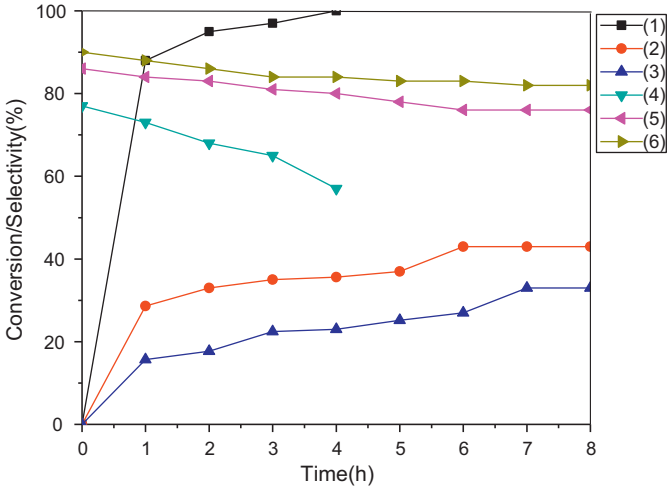


Fig. 5. Comparison results of different oxidants on reactions using complex **1** as catalyst.

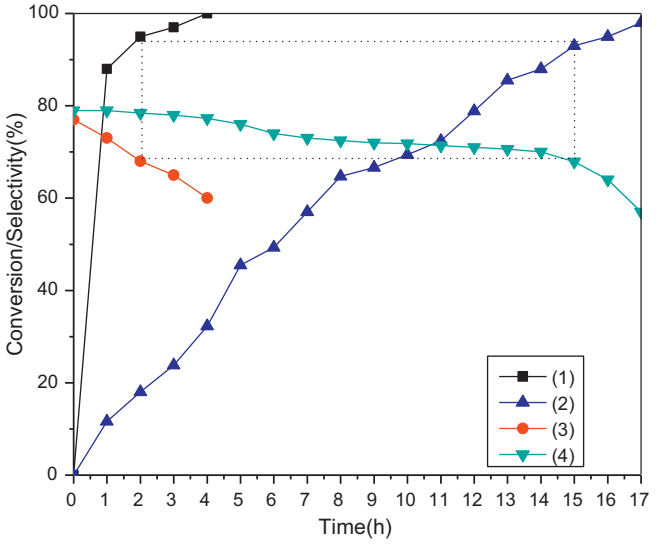


Fig. 6. Conversion and selectivity catalyzed by complexes **1** and **2**.

4. Conclusions

Two mononuclear Cu(II) complexes [Cu(AMP)Cl_2] and [Cu(AMP)$_2$(H_2O)$_2$]Cl_2 were synthesized by the reaction of 2-aminomethyl pyridine with $CuCl_2 \cdot 2H_2O$ through changing the metal/ligand ratios. X-ray structure analysis revealed that the structure of complex **1** consists of isolated binuclear molecules unit, in which copper ions are bridged by two chloro ligands. The geometry about each copper ion exihibits approximately to a distorted square pyramid with each copper atom coordinated to two nitrogen atoms from 2-aminomethyl pyridine, one terminal chloro ligand and two bridging chloro ligands. Complex **2** exhibits an octahedral geometry with the metallic atom coordinated to four nitrogen atoms from two 2-aminomethyl pyridine, and two water molecules.

Both the complexes as catalysts were used in the oxidation of tetralin with TBHP as oxidant. Complex **1** showed high catalytic activity and selectivity towards α-tetralone. Compared with complex **1**, complex **2** displayed low catalytic activity mainly due to the strong steric hindrance from the two coordinated 2-aminomethyl pyridine molecules in the structure.

Acknowledgment

This work was supported by NSFC of China (Grant No. 20776035).

References

[1] L.I. Simandi, Catalytic Activation of Dioxygen by Metal Complexes, Kluwer Academic Publishers, Dordrecht, 1992.
[2] D.H.R. Barton, A.E. Martell, D.T. Sawyer, The Activation of Dioxygen and Homogeneous Catalytic Oxidation, Plenum, New York, 1993.
[3] R.A. Sheldon, R.A. van Santen, Catalytic Oxidation: Principles and Applications, World Scientific, Singapore, 1995.
[4] P. Karandikar, M. Agashe, K. Vijayamohanan, A.J. Chandwadkar, Appl. Catal. A: Gen. 257 (2004) 133.
[5] T. Mallat, A. Baiker, Chem. Rev. 104 (2004) 3037.
[6] P. Chaudhuri, M. Hess, T. Weyhermüller, K. Wieghardt, Angew. Chem. Int. Ed. 38 (1999) 1095.
[7] T.K. Paine, T. Weyhermüller, K. Wieghardt, P. Chaudri, Dalton Trans. (2004) 2092.
[8] E.S. Aman, S. Menage, J.L. Pierre, E. Defrancq, G. Gellon, New J. Chem. (1998) 393.
[9] A. Kunai, T. Wani, Y. Ueharan, Y. Iwasaki, S. Kuroda, K. Ito, K. Sasaki, Bull. Chem. Soc. Jpn. 67 (1989) 2613.
[10] S. Ito, T. Yamasaki, H. Okada, S. Okino, K. Sasaki, J. Chem. Soc., Perkin Trans. 2 (1988) 285.
[11] A.H. Heines, Methods for the Oxidation of Organic Compounds, Academic Press, London, 1985.
[12] T. Punniyamurthy, S. Velusamy, J. Iqbal, Chem. Rev. 105 (2005) 2329.
[13] S. Velusamy, A.V. Kumar, R. Saini, T. Punniyamurthy, Tetrahedron Lett. 46 (2005) 3819.
[14] E.D. Park, Y.S. Hwang, C.W. Lee, J.S. Lee, Appl. Catal. A: Gen. 247 (2003) 269.
[15] W.A. Carvalho, M. Wallau, U.J. Schuchardt, J. Mol. Catal. A: Chem. 144 (1999) 91.
[16] R. Raja, P. Ratnasamy, Appl. Catal. A: Gen. 158 (1997), L-7.
[17] G.B. Shulpin, J. Gradinaru, Y.N. Kozlov, Org. Biomol. Chem. 1 (2003) 3611.
[18] U. Schuchardt, R. Pereira, M. Rufo, J. Mol. Catal. A: Chem. 135 (1998) 257.
[19] Z. Bondar, T. Mallat, A. Baiker, J. Mol. Catal. A: Chem. 110 (1996) 55.
[20] D.J. Rawlinson, G. Sosnovsky, Synthesis (1972) 1.
[21] M.B. Andrus, J.C. Lashley, Tetrahedron 58 (2002) 845.
[22] J. Eames, M. Watkinson, Angew. Chem. Int. Ed. 40 (2001) 3567.
[23] S. Tanase, C. Foltz, R. de Gelder, R. Hage, E. Bouwman, J. Reedijk, J. Mol. Catal. 225 (2005) 161–167.
[24] G. Tian, D. Xia, F. Zhan, Energy Fuels 18 (2004) 49–53.
[25] A. Covarrubias-Zuniga, F. Cantu, L.A. Maldonado, J. Org. Chem. 63 (2008) 2918.
[26] H.G. Frank, J.W. Stadelhofer, Industrial Aromatic Chemistry, Springer-Verlag, Heidelberg, Berlin, 1988.
[27] F. Mizukami, J. Imamura, US Patent 4,175,098 (1979).
[28] B. Louis, C. Detoni, N.M.F. Carvalho, C.D. Duarte, O.A.C. Atunes, Appl. Catal. A: Gen. 360 (2009) 218–225.
[29] C. Mahendiran, P. Sangeetha, P. Vijayan, S.J. Sardhar Basha, K. Shanthi, J. Mol. Catal. A: Chem. 275 (2007) 84–90.
[30] S. Sithambarama, E.K. Nyutu, S.L. Suib, Appl. Catal. A: Gen. 348 (2008) 214–220.
[31] R.W. Coon, US Patent 4,473,711 (1984).
[32] R.J. Small, US Patent 4,960,944 (1990).
[33] G. Rothenberg, L. Feldberg, H. Wiener, Y. Sasson, J. Chem. Soc., Perkin Trans. 2 (1998) 2429.
[34] M. Navarro, A. Escobar, V.R. Landaeta, G. Visbal, Appl. Catal. A: Gen. 363 (2009) 27–31.
[35] C. Detoni, N.M.F. Carvalho, D.A.G. Aranda, B. Louis, O.A.C. Antunes, Appl. Catal. A: Gen. 365 (2009) 281–286.
[36] G.M. Sheldrick, SHELXS-97, University of Göttingen, Germany, 1997.
[37] L.X. Lei, X.Q. Xin, J. Solid State Chem. 119 (1995) 299–303.
[38] A. Bernalte-García, A.M. Lozano-Vila, F. Luna-Giles, R. Pedrero-Marín, Polyhedron 25 (2006) 1399–1407.
[39] P. Gamez, C. Simons, R. Steensma, W.L. Driessen, G. Challa, J. Reedijk, Eur. Polym. J. 37 (2001) 1293–1296.
[40] B. Monteiro, S. Gago, S.S. Balula, A.A. Valente, I.S. Gonçalves, M. Pillinger, J. Mol. Catal. A: Chem. 312 (2009) 23–30.
[41] N. Žilková, G.B. Shulopin, P. Lederer, C. Czech, Chem. Commun. 49 (1984) 237.