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Oxidation of benzyl alcohols to benzaldehydes in water catalyzed by a Cu(II) complex with a zwitterionic calix[4]arene ligand

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ABSTRACT

A water-soluble cationic mononuclear copper(II) complex $[\text{Cu}(\text{II})\text{L}(\text{H}_2\text{O})]_2$ (**1**, H_4L = 5,11,17,23-tetrakis(trimethylammonium)-25,26,27,28-tetrahydroxycalix[4]arene) was employed as a catalyst in the oxidation of benzyl alcohols to benzaldehydes in water. In the presence of TEMPO and H_2O_2 , complex **1** exhibited good catalytic activity towards primary benzyl alcohols with a less catalyst loading (0.25 mol%) and a lower temperature (60 °C). The isolated yields of the aldehydes achieved 63–98% within 12 h.

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Introduction

Copper compounds have been well investigated in catalyzing the selective oxidation of alcohols to aldehydes in the past decade [1]. Compared to the other transition metal compounds, copper catalysts are commercially inexpensive, easily to be prepared and handled, and more importantly, less pollutive [2]. Although some Cu(I)/Cu(II) salts [3] and their composites [4] have shown good catalytic activity towards such reactions, the coordination compounds of copper with various ligands are mostly investigated because the solubility, the steric hindrance, the stability and the redox properties of these catalysts could be easily adjusted by the ligands used [5–8]. However, as many organic ligands are hydrophobic, which greatly influenced the solubility of the coordination compounds, most of the reported oxidation reactions are performed in organic solvents or in mixed solvents. As modern green chemistry require safer and more environmental friendly reaction mediates, some approaches using ionic and supercritical liquids [9] or halogen-free solvents [10] have been developed, whereas water

remains the undisputed solvent of choice from the economic and environmental viewpoints. The water-phase oxidation of alcohols to aldehydes has always attracted significant interests in recent years [11–14]. For example, Repo reported the oxidation of benzylic alcohols to benzaldehydes catalyzed by Cu(II) diimine-based or 2-N-arylpyrrolecarbalimine-based complexes in aqueous solution [11]. Pombeiro also described the water-phase oxidation of benzylic alcohol catalyzed by several water-soluble Cu(II) complexes with some N/O hybrid ligands [12].

Recently, some cyclic oligomers such as cyclodextrins are introduced into the water-phase catalytic systems because they have hollow truncated conical structures with hydrophobic cavities and hydrophilic external surfaces and may simultaneously work as both the ligand and the phase transfer agent. Zhang proposed an efficient and recyclable copper catalytic system assisted by water-soluble pytl- β -CD ligand and $\text{Cu}(\text{OAc})_2$ in the aerobic oxidation of alcohols [13]. Metal complexes of calixarenes, known as another kind of cyclic oligomers, have exhibited excellent catalytic performances in various water-phase reactions [15], but are rarely reported in the copper-catalyzed alcohol oxidation reactions.

We have recently been involved in employing a unique zwitterionic calix[4]arene **L** (H_4L = 5,11,17,23-tetrakis(trimethylammonium)-25,26,27,28-tetrahydroxycalix[4]arene) [16]. The NMe_3^+ groups of **L** may not only increase the solubility and stability of the resulting coordination compounds in water, but also act as

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phase transfer groups [17] in aqueous/organic biphasic systems. We once prepared a mononuclear copper(II) complex $[\text{Cu}(\text{II})\text{L}(\text{H}_2\text{O})]_2$ (**1**) (Scheme 1), which showed excellent catalytic activity towards the oxidative polymerization of 2,6-dimethylphenol [18]. Could complex **1** work as a catalyst to initiate the selective oxidation reaction of alcohol to aldehydes in water? In this article, we described that complex **1** was employed to catalyze the oxidation of several benzylic alcohols in aqueous solution and the resulting oxidation products, benzaldehydes, could be isolated in good yields, which represents an interesting example in the Cu(II)-catalyzed alcohol oxidation reactions.

Experimental section

General procedures

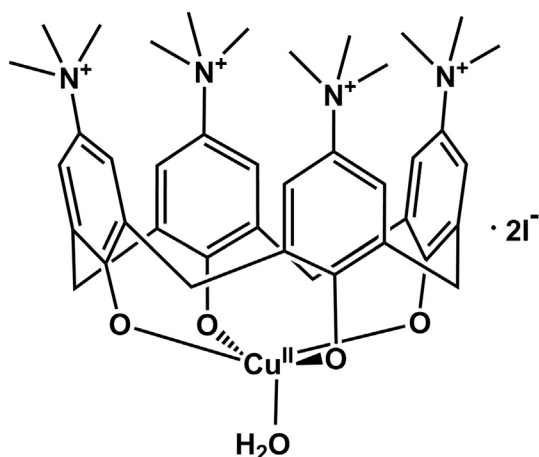
All chemicals were purchased from commercial sources and used without purification. Complex **1** was obtained according to the published procedure [18]. The oxidation products were quantitatively analyzed by GC analysis using internal standards on an Agilent 7820A Gas Chromatograph with an Agilent HP-5 chromatographic column and N_2 as the mobile phase. The ^1H and ^{13}C NMR spectra in CDCl_3 or $\text{DMSO}-d_6$ were recorded at ambient temperature on a Varian UNITYplus- 400 (400 MHz) spectrometer and the chemical shifts were referenced to the TMS signal.

Typical procedure for the formation of aldehydes (3a–q)

A test tube equipped with a magnetic stirring bar was charged with **1** (5 mg, 0.005 mmol, 0.25 mol%), TEMPO (16 mg, 0.10 mmol, 5 mol%), and K_2CO_3 (69 mg, 0.50 mmol, 25 mol%). Alcohols (**2a–q**, 2.0 mmol), H_2O (5 mL) and H_2O_2 (30%, 1 mL) were added. The mixed light green solution was stirred at 60°C for 12 h, cooled to room temperature, and then extracted by Et_2O (3×5 mL). The organic layers were combined, washed with brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. On elution with petroleum ether and ethyl acetate, the crude product was further purified by column chromatography on silica. All aldehyde products synthesized in this work are known and confirmed by ^1H NMR spectra.

Benzaldehyde (3a)

Colorless oil; yield: 208 mg, 98%; ^1H NMR (400 MHz, CDCl_3 , ppm): δ 9.99 (s, 1H), 7.86 (d, $J = 7.2$ Hz, 2H), 7.60 (t, $J = 7.6$ Hz, 1H),



Scheme 1. Schematic representation of complex **1**.

7.50 (t, $J = 7.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 192.18, 136.23, 134.28, 129.52, 128.83.

2-Methoxybenzaldehyde (3b)

Colorless solid; yield: 258 mg, 95%; ^1H NMR (400 MHz, CDCl_3 , ppm): δ 10.45 (s, 1H), 7.80 (d, $J = 7.0$ Hz, 1H), 7.53 (t, $J = 8.4$ Hz, 1H), 6.95–7.01 (m, 2H), 3.89 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 189.53, 161.10, 135.87, 128.19, 124.64, 120.46, 111.58, 55.46.

3-Methoxybenzaldehyde (3c)

Light yellow oil; yield: 259 mg, 95%; ^1H NMR (400 MHz, CDCl_3 , ppm): δ 9.94 (s, 1H), 7.36–7.43 (m, 3H), 7.13–7.16 (m, 1H), 3.82 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 192.10, 160.15, 137.82, 130.04, 123.47, 121.45, 112.12, 55.45.

4-Methoxybenzaldehyde (3d)

Light yellow oil; yield: 264 mg, 97%; ^1H NMR (400 MHz, CDCl_3 , ppm): δ 9.73 (s, 1H), 7.69 (d, $J = 8.8$ Hz, 2H), 6.86 (d, $J = 8.8$ Hz, 2H), 3.727 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 190.51, 164.41, 131.72, 129.75, 114.13, 55.35.

2-Methylbenzaldehyde (3e)

Colorless oil; yield: 211 mg, 88%; ^1H NMR (400 MHz, CDCl_3 , ppm): δ 10.26 (s, 1H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.35 (t, $J = 7.6$ Hz, 1H), 7.25 (d, $J = 7.6$ Hz, 1H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 192.97, 140.77, 134.31, 133.80, 132.20, 131.92, 126.48, 19.74.

3-Methylbenzaldehyde (3f)

Colorless oil; yield: 219 mg, 91%; ^1H NMR (400 MHz, CDCl_3 , ppm): δ 9.96 (s, 1H), 7.66 (s, 2H), 7.39 (t, $J = 7.6$ Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 192.71, 139.05, 136.62, 135.41, 130.14, 129.00, 127.35, 21.31.

4-Methylbenzaldehyde (3g)

Colorless oil; yield: 224 mg, 93%; ^1H NMR (400 MHz, CDCl_3 , ppm): δ 9.96 (s, 1H), 7.77 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 137.41, 135.45, 129.20, 128.04, 71.8, 21.32.

4-Chlorobenzaldehyde (3h)

Light yellow solid; yield: 213 mg, 76%; ^1H NMR (400 MHz, CDCl_3 , ppm): δ 9.99 (s, 1H), 7.83 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 190.99, 141.09, 134.85, 131.04, 129.60.

4-Nitrobenzaldehyde (3i)

Light yellow solid; yield: 269 mg, 89%; ^1H NMR (400 MHz, CDCl_3 , ppm): δ 10.17 (s, 1H), 8.41 (d, $J = 8.8$ Hz, 2H), 8.09 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 190.43, 151.20, 140.15, 130.58, 124.38.

2-Thiophenecarboxaldehyde (3j)

Light red oil; yield: 141 mg, 63%; ^1H NMR (400 MHz, CDCl_3 , ppm): δ 9.96 (d, $J = 1.2$ Hz, 1H), 7.77–7.80 (m, 2H), 7.21–7.24 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 182.95, 143.85, 136.42, 135.07, 128.31.

3-Pyridinecarboxaldehyde (3k)

Colorless oil; yield: 156 mg, 73%; ^1H NMR (400 MHz, CDCl_3 , ppm): δ 10.19 (s, 1H), 9.13 (d, $J = 9.2$ Hz, 1H), 8.89 (d, $J = 6.4$ Hz, 1H), 8.23 (d, $J = 2.0$ Hz, 1H), 7.54–7.56 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 190.59, 154.31, 151.57, 135.58, 131.11, 123.82.

1-Naphthaldehyde (3l)

Light yellow solid; yield: 266 mg, 85%; ^1H NMR (400 MHz, CDCl_3 , ppm): δ 10.37 (s, 1H), 9.24 (d, $J = 8.8$ Hz, 1H), 8.06 (d, $J = 8.0$ Hz, 1H), 7.95 (d, $J = 6.8$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.67 (t, $J = 7.6$ Hz, 1H), 7.58 (q, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 193.61, 136.75, 135.35, 133.77, 131.44, 130.57, 129.13, 128.54, 127.02, 124.93.

Piperonyl aldehyde (3m)

White solid; yield: 238 mg, 79%; ^1H NMR (400 MHz, CDCl_3 , ppm): δ 9.81 (s, 1H), 7.41 (d, $J = 7.6$ Hz, 1H), 7.33 (s, 1H), 6.93 (d, $J = 8.0$ Hz, 1H), 6.08 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 190.40, 153.21, 148.82, 131.98, 128.78, 108.46, 107.00, 102.22.

1,4-Phthalaldehyde (3n)

White solid; yield: 244 mg, 91%; ^1H NMR (400 MHz, $\text{DMSO}-d_6$, ppm): δ 10.14 (s, 2H), 8.12 (s, 4H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, ppm): δ 193.13, 139.77, 130.04.

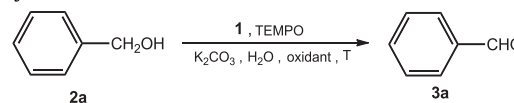
Results and discussion**The oxidation of benzyl alcohol catalyzed by 1**

Complex **1** is insoluble in common organic solvents, but readily dissolves in water. As reported previously, the Cu(II) center in **1** is weakly coordinated by a H_2O molecule, and could be the active catalytic site when this weak Cu(II)– OH_2 bond is cleaved by some donor ligands. In various Cu catalytic systems, TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) was used to make more efficient and controllable oxidation of alcohols [19]. Based on these considerations, a model oxidation reaction using benzyl alcohol (**2a**) as a substrate in the presence of **1**, TEMPO (5 mol%) and K_2CO_3 (25 mol%) was performed to produce benzaldehyde (**3a**) in aqueous solution. When the reaction was carried out under the oxidation of O_2 and 1% catalyst loading, the yields of **3a** amounted to be 61% and 73% at 60 °C and 100 °C, respectively (Table 1, entries 1 and 2) after 24 h. Since these results were not good, we chose H_2O_2 as the terminal oxidant that has higher oxidation potential than O_2 [11c]. The yield of **3a** could be slightly increased to 78% at 100 °C (Table 1, entry 2), but significantly raised up to 99% at 60 °C (entry 4). The better catalytic activity at 60 °C was probably due to the H_2O_2 decomposition under the higher temperature in alkaline conditions [11c]. Continuous reducing the temperature to 40 °C made the yield somewhat lower (83%, entry 5). At 60 °C, the amount of catalyst loading was also investigated. As shown in entries 6–9, the yields of **3a** were almost the same (99%) when 0.5 mol% (entry 6) and 0.25 mol% (entry 7) of **1** were used, but decreased to 90% when the catalyst loading was lowered to 0.20 mol% (entry 9). However, this reaction did not work without **1** (entry 9). When the reaction time was reduced to 12 h and 10 h, the yield of **3** slightly decreased to 98% and 94% (entries 10 and 11), respectively.

The other components of this catalyst system could also greatly affect the catalytic performance of this reaction. The yield of **3a** was gradually reduced to be 91% when the TEMPO loading was reduced from 5 mol% to 4 mol% (Table 1, entry 12), indicating that the addition of TEMPO was indispensable. Because the catalytic reaction in our work resembled that reported in the literature [20], we followed that mechanism and proposed a similar mechanism for the oxidation of benzyl alcohols to benzaldehydes (Fig. S1). In such a mechanism, the TEMPO radical was assumed to attack the possible Cu(II)–substrate complex in a bimolecular process and produce a benzyl radical Cu(II) compound by the extraction of $\text{H}\cdot$ in the α -position. Such a step was believed to be slow and rate-determining because the embracing tetradentate nature of **1** could avoid direct coordination of TEMPO at the Cu(II) centre.

Table 1

Optimizing the reaction conditions for the oxidation conversion of benzyl alcohol to benzaldehyde.



Entry ^a	Catalyst (mol %)	Oxidant	Temperature (°C)	Time (h)	Yield ^b (%)
1	1.00	O_2	60	24	61
2	1.00	O_2	100	24	73
3	1.00	H_2O_2	100	24	78
4	1.00	H_2O_2	60	24	99
5	1.00	H_2O_2	40	24	83
6	0.50	H_2O_2	60	24	99
7	0.25	H_2O_2	60	24	99
8	0.20	H_2O_2	60	24	90
9	–	H_2O_2	60	24	Trace
10	0.25	H_2O_2	60	12	98
11	0.25	H_2O_2	60	10	94
12 ^c	0.25	H_2O_2	60	12	91
13 ^d	0.25	H_2O_2	60	12	55
14 ^e	0.25	H_2O_2	60	12	80
15 ^f	0.25	H_2O_2	60	12	77
16 ^g	0.25	H_2O_2	60	12	28
17 ^h	0.25	H_2O_2	60	12	43

^a 2.0 mmol benzyl alcohol, 25 mol% K_2CO_3 , 5 mol% TEMPO, 1 mL 30% H_2O_2 in 5 mL H_2O .

^b GC yield.

^c 4 mol% TEMPO.

^d $\text{Cu}(\text{OAc})_2$.

^e $\text{Cu}(\text{OAc})_2/p$ -butylcalixarene.

^f $\text{Cu}(\text{OAc})_2/\text{calixarene}$.

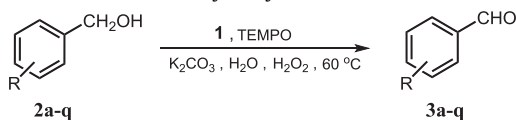
^g $\text{Cu}(\text{OAc})_2/2,2'$ -bipyridine.

^h $\text{Cu}(\text{OAc})_2/1,10$ -phenanthroline.

In addition, comparative runs demonstrated lower catalytic activity towards this reaction using other Cu(II) systems such as $\text{Cu}(\text{OAc})_2$ (yield 63%, entry 13), $\text{Cu}(\text{OAc})_2/p$ -butylcalixarene (yield 80%, entry 14), $\text{Cu}(\text{OAc})_2/\text{calixarene}$ (yield 77%, entry 15), $\text{Cu}(\text{OAc})_2/2,2'$ -bipyridine (yield 28%, entry 16) and $\text{Cu}(\text{OAc})_2/1,10$ -phenanthroline (yield 43%, entry 17). Thus the optimized reaction conditions were identified as follows: catalyst loading $[\text{Cu}] = 0.25$ mol%, 5 mol% TEMPO, 25 mol% K_2CO_3 , 1 mL H_2O_2 (30%) as an oxidant, H_2O (5 mL) as a solvent, $T = 60$ °C, and 12 h for the reaction time.

The substrate scope of the oxidation of substituted benzyl alcohols

Under optimized conditions, the substrate scope of the oxidation of substituted benzyl alcohols catalyzed by **1** was examined. As presented in Table 2, complex **1** exhibited a wide applicability towards a broad range of benzylic alcohols, producing the corresponding benzaldehydes in good yields. It appears that the electronic nature of substituent groups on benzyl alcohols exert some impact on the catalytic dehydrogenation oxidation. The electron-rich methoxyl- (entries 2–4) and electron-neutral methyl- (entries 5–7) substituted benzyl alcohols produced the corresponding benzaldehydes in 88–97% yield. While in the cases of electron-withdrawing chloride- and nitro-substituted benzyl alcohols, the yields could only achieve 76–89% (entries 8 and 9) even after a longer reaction time (18 h). The steric hindrance of the substituent groups seems also have effect on the catalytic activity when the yields of the *o*- (entries 2 and 5), *m*- (entries 3 and 6) and *p*- (entries 4 and 7) substituted benzaldehydes are increased regularly. This may be ascribed to the fact that the *ortho* substituted groups have the greater hindrance than the *meta* and the *para* substituted ones in the benzylic alcohols. It is notable that the

Table 2
Scope of oxidation of alcohols catalyzed by **1** in water.

Entry ^a	Substrate	Product	Yield ^b (%)
1			98
2			95
3			95
4			97
5			88
6			91
7			93
8 ^c			76
9 ^c			89
10			63
11			73

Table 2 (continued)

Entry ^a	Substrate	Product	Yield ^b (%)
12			79
13			85
14 ^d			91
15			Trace
16			Trace
17			Trace

^a Optimized reaction conditions: alcohol (2.0 mmol), 0.25 mol% **1**, 5 mol% TEMPO, 25 mol% K₂CO₃, 1 mL 30% H₂O₂ in 5 mL H₂O, 12 h, 60 °C.

^b Isolated yield.

^c 18 h for 60 °C.

^d 0.50 mol% **1**.

heteroatom-containing aromatic alcohols (entries 10–12), 1-naphthalenemethanol (entry 13) and 1,4-benzenedimethanol (entry 14) could also proceed smoothly to afford the corresponding aldehydes in moderate yields (63–91%), whereas the aliphatic alcohols or secondary alcohols almost remained unreactive under the optimized conditions (entries 15–17).

Reusability of the catalyst

The reusability of the catalyst is of great importance from the viewpoint of the practical and industrial utilization. As each resulting aldehyde is soluble in Et₂O, it could be readily separated by extraction from the aqueous reaction mixture. Therefore the remaining aqueous solution containing **1** may be reused for the oxidation of fresh alcohols. As presented in **Table 3**, the oxidation of benzyl alcohol under the optimized conditions led to the formation of benzaldehyde in 99% yield (GC yield) in the first cycle. The resulting benzaldehyde was then isolated by extraction, and the remaining aqueous solution was subsequently reused for the next

Table 3
Reusability of **1** that catalyzed the oxidation of benzyl alcohol in benzaldehyde.

Cycle ^a	1	2	3
Yield ^b (%)	99	78	47

^a 2.0 mmol benzyl alcohol, 0.25 mol% **1**, 5 mol% TEMPO, 25 mol% K₂CO₃, 1 mL 30% H₂O₂ in 5 mL H₂O, 12 h, 60 °C.

^b GC yield.

run by recharging with benzyl alcohol, K_2CO_3 , TEMPO, and H_2O_2 . The corresponding conversion yields of the 2nd and 3rd runs remained 78% and 47% (GC yield, entries 2 and 3). After each catalytic process, some green precipitate was formed, which may be due to an oxidative degradation of the catalyst into the unknown species. The loss of the catalyst in the former run could account for the low efficiency of the catalyst in the latter runs.

Conclusions

In this paper, we demonstrated the employment of a water soluble complex **1** for the catalytic oxidation of benzylic alcohols to benzaldehydes. Under the optimized conditions, the catalytic system **1**/TEMPO/ H_2O_2 / K_2CO_3 was quite suitable to the oxidation of a variety of substrates including the substituted benzyl alcohols, the heteroatom-containing aromatic alcohols, 1-naphthalenemethanol and 1,4-benzenedimethanol in good yields (63–98%) within 12 h. Compared to other water-phase Cu/TEMPO systems reported previously, our catalytic system requires a less catalyst loading (0.25 mol%) and a lower temperature (60 °C). As the water solubility of **1** is originated from the zwitterionic calix[4]arene ligand **L**, this work opens up a new route to the oxidation of alcohols to aldehydes in water using water soluble Cu(II) catalysts. One problem is that complex **1** did not work for the aliphatic alcohols or secondary alcohols. However, we could modify the calix[4]arene ligands through replacing NMe_3^+ groups by SO_3^- groups or react **L** with other metal ions such as Fe^{3+} , Co^{3+} . The resulting Cu(II) and other metal complexes could be used to tackle this problem, which would be the future research topic in our laboratory.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jorganchem.2015.02.008>.

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