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PAPER

Aerobic oxidation of primary alcohols catalyzed by copper complexes of 1,10-phenanthroline-derived ligands

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Five copper complexes $[(L^1)_2Cu(H_2O)](ClO_4)_2$ (1), $[(L^1)Cu(H_2O)_3](ClO_4)_2$ (1a), $[(L^3)_2Cu(H_2O)](ClO_4)_2$ (2), $[(L^5)_2Cu(H_2O)](ClO_4)_2$ (3) and $[(L^6)_2Cu](ClO_4)$ (4) (where $L^1 = 1,10$ -phenanthroline, $L^3 = 1,10$ -phenanthroline-5,6-dione, $L^5 = 1,10$ -phenanthrolinefuroxan and $L^6 = 2,9$ -dimethyl-1,10phenanthrolinefuroxan), and *in situ* prepared copper complexes of 2,9-dimethyl-1,10-phenanthroline (L^2) or 2,9-dimethyl-1,10-phenanthrolinedione (L^4) were used for aerial oxidation of primary alcohols to the corresponding aldehydes under ambient conditions. The copper catalysts have been found to catalyze a series of primary alcohols including one secondary alcohol with moderate turnover numbers and selectivity towards primary alcohols. Copper(II) complexes 1 (or 1a) and 2 were found to be the better catalysts among all other systems explored in this study. A copper(II)-superoxo species is implicated to initiate the oxidation reaction. Structural and electronic factors of 1,10-phenanthroline-based ligands affecting the catalytic results for aerial oxidation of alcohols are discussed.

Introduction

Controlled oxidation of primary alcohol to aldehyde is considered as one of the important reactions in organic chemistry. This challenge has fuelled the interests of chemists in developing catalytic systems that can selectively oxidize alcohols to the corresponding carbonyl compounds using aerial oxygen as the terminal oxidant. Copper has drawn the attention as metal of choice for the catalytic oxidation of alcohols because of its presence in the active site of galactose oxidase (GO), an enzyme that couples the oxidation of primary alcohols to aldehydes with concomitant reduction of dioxygen to hydrogen peroxide.¹⁻⁴ A number of biomimetic copper complexes of polydentate ligands have been developed as functional models of GO.⁵⁻¹⁴ Copper complexes of pyridine-based ligands like 2,2'-bipyridine and 1,10-phenanthroline have been used for oxidation of primary alcohols.^{15–19} Merko et al. reported very active catalytic systems comprising of CuCl, 1,10-phenanthroline and hydrazine derivatives for aerobic oxidation of allylic and benzylic alcohols.²⁰⁻²³ Copper complexes of various nitrogen donor ligands in combination with TEMPO have been developed as catalysts for alcohol oxidation.²⁴⁻³¹ Efficiency of TEMPO based catalytic systems leads to design a ligand system containing TEMPO on its backbone, which exhibits remarkable catalytic activity.³² It has been proposed that TEMPO radical takes part in the H-atom abstraction process,³³ similar to that by a copper(II)-superoxide species proposed in the reaction mechanism of GO. The mechanism of alcohol oxidation is controlled by the Cu²⁺/Cu⁺ potential of the catalyst. This potential can be tuned in copper(II)complexes of ligands derived from 1,10-phenanthroline by electronic and structural tuning on the ligand backbone. Solvents also play an important role in the redox reactions. A varying degree of catalytic reactivity of copper(II) complexes of functionalized 1,10-phenanthrolines is expected that would provide the mechanistic insight about the oxidation reaction. We report in this paper, a series of mononuclear copper complexes of phenanthroline-derived ligands (Chart 1) that serve as catalysts in aerial oxidation of alcohols under ambient conditions. Four copper(II) complexes $[(L^1)_2Cu(H_2O)](ClO_4)_2$ (1), $[(L^1)Cu(H_2O)_3](ClO_4)_2$ $(1a), [(L^3)_2Cu(H_2O)](ClO_4)_2 (2), [(L^5)_2Cu(H_2O)](ClO_4)_2 (3) and$ one Cu(I) complex $[(L^6)_2Cu](ClO_4)$ (4) have been used for alcohol oxidation. The effect of different functional groups on 1,10-phenanthroline backbone controlling the catalytic reactivity is discussed. Complexes 1 and 2 oxidize primary alcohols including aromatic, heterocyclic and unsaturated alcohols to the



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corresponding aldehydes including one secondary alcohol to the corresponding ketone with moderate yield.

Experimental

General

All chemicals used for the synthetic purposes were purchased from commercial sources. Solvents were distilled and dried prior to use unless otherwise stated. Ligands L¹, L² and L³ are commercially available. Ligand L⁴ was prepared according to a modification of the procedure described in the literature.^{34,35} Syntheses and characterizations of complexes [(L⁵)₂Cu(H₂O)]- $(ClO_4)_2$ (3) and $[(L^6)_2Cu](ClO_4)$ (4), and ligands L^5 and L^6 have been reported from our group.^{36,37} Fourier transform infrared spectra were recorded on a Shimadzu FT-IR 8400S instrument. Elemental analyses were performed on a Perkin Elmer 2400 series II CHN analyzer. Solution electronic spectra were measured at room temperature on an Agilent 8453 diode array spectrophotometer. Electro-spray Ionization Mass spectra were recorded with Waters QTOF Micro YA263. Gas chromatographic data were recorded in an Agilent 6890N Network GC system. X-band EPR measurements were performed on a JEOL JES-FA 200 instrument.

Synthesis

 $[(L^1)_2Cu(H_2O)](ClO_4)_2$ (1). 1,10-Phenanthroline monohydrate (0.198 g, 1 mmol) was reacted with $Cu(ClO_4)_2 \cdot 6H_2O$ (0.185 g, 0.5 mmol) in dichloromethane at room temperature. The resulting green solution was stirred at room temperature for 12 h. The solution was then filtered and kept for slow evaporation of solvent to isolate a light blue solid. Yield: 0.18 g (56%). Anal Calcd for C₂₄H₁₈Cl₂CuN₄O₉ (640.87 g mol⁻¹): C, 44.98; H, 2.83; N, 8.74. Found: C, 45.09; H, 2.92; N, 9.02%. FTIR (KBr): 3439(br), 3068(w), 2924(w), 1627-1587(w), 1521(m), 1431(s), 1342(w), 1147–1093(vs), 848(s), 721(s), 623(s) cm⁻¹. UV-Vis (in MeCN) $[\lambda_{max}, nm (\varepsilon, M^{-1} cm^{-1})]$: 910, 725 (52), 345 (sh), 325 (sh). ESI-MS (positive ion in MeCN): m/z = 422.96 (60%, $[(L^{1})_{2}Cu]^{+}$, 181.02 (75%, $[L^{1} + H]^{+}$).

 $[(L^1)Cu(H_2O)_3](ClO_4)_2$ (1a). 1,10-Phenanthroline monohydrate (0.198 g, 1 mmol) was reacted with Cu(ClO₄)₂·6H₂O (0.37 g, 1 mmol) in acetonitrile at room temperature. After 12 h the blue solution was filtered and the filtrate was kept for slow evaporation of solvent to isolate a blue solid. Yield: 0.29 g (58%). Anal Calcd for $C_{12}H_{14}Cl_2CuN_2O_{11}$ (496.70 g mol⁻¹): C, 29.02; H, 2.84; N, 5.64. Found: C, 28.54; H, 2.75; N, 5.39%. FTIR (KBr): 3437(br), 3051(w), 2924(w), 1628-1583(w), 1516 (m), 1423(s), 1348(w), 1144–1088(vs), 852(s), 719(s), 630(s) cm⁻¹. UV-Vis (in MeOH) $[\lambda_{max}, nm (\varepsilon, M^{-1} cm^{-1})]$: 702 (36), 345 (sh), 330 (sh). ESI-MS (positive ion in MeCN): m/z = $521.87 (22\%, \{[(L^1)_2Cu](ClO_4)\}^+), 482.50 (5\%, [(L^1)_2Cu(H_2O) (CH_3CN)^+$, 341.85 (100%, { $[(L^1)Cu](ClO_4)\}^+$), 242.93 (98%, $[(L^{1})Cu]^{+}).$

 $[(L^3)_2Cu(H_2O)](ClO_4)_2$ (2). To a solution of 1,10-phenanthroline-5,6-dione (0.21 g, 1 mmol) in dichloromethane, Cu-(ClO₄)₂·6H₂O (0.185 g, 0.5 mmol) was added with stirring at room temperature. A green solid was precipitated from the solution after stirring for 12 h. The solid was isolated by filtration and dried. The filtrate was kept for slow evaporation of solvent to isolate another portion of green solid. Yield: 0.25 g (71%). Anal Calcd for C₂₄H₁₄Cl₂CuN₄O₁₃ (700.83 g mol⁻¹): C, 41.13; H, 2.01; N, 7.99. Found: C, 41.20; H, 2.03; N, 8.10%. FTIR (KBr): 3421(br), 3068(w), 1699(s), 1575(s), 1483(m), 1454(m), 1427(s), 1371(m), 1301(w), 1259(w), 1109-1041(vs), 816(m), 725(m), 625(m) cm⁻¹. UV-Vis (in MeCN) $[\lambda_{max}, nm (\varepsilon, M^{-1})]$ cm^{-1}]: 682 (48), 485 (53), 360 (sh), 313 (13706), 302 (14 795). ESI-MS (positive ion in MeCN): m/z = 500.85 (20%, $[(L^3)_2Cu(H_2O)]^+)$, 482.84 (100%, $[(L^3)_2Cu]^+)$, 232.96 (30%, $[L^3 + Na]^+$), 210.97 (15%, $[L^3 + H]^+$).

Catalytic oxidation of alcohols. Copper catalyst (0.01 mmol) was dissolved in 5 mL acetonitrile. To that, 1 mmol alcohol and 0.5 mmol tetrabutylammonium methoxide solution (20% solution in methanol) were added. The reaction mixture was allowed to stir under oxygen at room temperature. After the reaction, the solution was passed through a silica gel column of 60-120 mesh and washed with 15 mL acetonitrile. To the eluent 0.5 mL standard solution of naphthalene was added and the products were quantified by GC.

Results and discussion

All the ligands and their copper complexes were purified and characterized prior to use. In the oxidation of alcohols using O₂ as the oxidant, either copper(II) complexes of phenathrolinebased ligands or combinations of copper(II) salt and ligands were used (Fig. 1). All six ligands, in the presence of copper(II) perchlorate and a base in acetonitrile, were found to oxidize primary alcohols to the corresponding aldehydes under ambient conditions. The oxidized products were isolated by filtration through silica gel column and were analysed by gas chromatography using an internal standard. It is to note that in the absence of any ligand, only copper(II) in acetonitrile is able to oxidize benzyl alcohol to benzaldehyde in a stoichiometric amount, whereas benzyl alcohol remains unreacted in the absence of copper(II) salt in the system (Table 1). The binding of alcoholate to the copper(II) centre does not take place in the absence of a base which is confirmed from the stoichiometric conversion in the





Fig. 1 Different copper complexes used for the oxidation of alcohols.

reaction. Therefore, a combination of ligand, copper(II) salt and a base is needed to carry out the catalytic aerobic oxidation of alcohols.

To standardize the reaction conditions, a set of catalytic experiments were carried out using $Cu(ClO_4)_2 \cdot 6H_2O$ and L^3 in a 1 : 1 ratio (catalyst), 100 equivalents of benzyl alcohol and 50 equivalents of tetrabutylammonium methoxide (TBAM). The resulting solution was allowed to stir under air (O₂) and the formation of benzaldehyde was monitored with time (Fig. 2a). The conversion of alcohol to aldehyde increases with time up to 7 h; thereafter no further oxidation was observed. To see the effect of base, catalytic reactions were carried out with different concentration of TBAM. The highest conversion (turnover number, TON) of alcohol was observed in the presence of 50 mol% of base (Fig. 2b).

The effectiveness of the catalytic system was checked with increasing concentration of the substrate under similar reaction conditions. From the plot of concentration of benzyl alcohol *vs.* TON, (Fig. 3) a sharp increment in TON was observed with increasing alcohol concentration until it reaches a value of 236 in the presence of 1250 equivalents of benzyl alcohol. Upon further increment of alcohol concentration, the catalytic TON does not increase. The involvement of aerial oxygen in the catalytic oxidation was established by carrying out the reaction

 Table 1
 Effect of different components on catalytic oxidation of benzyl alcohol

L ³ (mmol)	$Cu(ClO_4)_2 \cdot 6H_2O$ (mmol)	Benzyl alcohol (mmol)	TBAM (mmol)	% Yield of benzaldehyde ^a
0.01		1	1	_
	0.01	1	0.5	4.5
0.01	0.01	1		1.9
0.01	0.01	1	0.5	55

^{*a*} Yield of benzaldehyde was calculated from GC by comparing the peak area with respect to that for internal standard naphthalene.



With this standardized condition the catalytic oxidations of alcohols were carried out with other phenanthroline-derived ligands. Table 2 shows the catalytic conversion of benzyl alcohol in the reaction with different 1,10-phenanthroline ligands. A good correlation of catalytic yield with the structural and electronic properties of the ligands can be made. In general, ligands derived from 2,9-dimethyl-1,10-phenanthroline (L^2 , L^4 and L^6) show relatively poor yield of aldehyde compared to other three systems. Additionally, no appreciable change in TON was observed by changing the ratio of Cu²⁺ salt and ligand.

The catalytic alcohol oxidations were performed with isolated copper(π) complexes (1, 1a and 2) of L¹ and L³. Attempts were made to isolate the copper(π) complexes with the metal/ligand ratio of 1:1 and 1:2 in acetonitrile. Except for L¹, all other



Fig. 3 Dependence of catalytic TON on the amount of benzyl alcohol. Reaction conditions: 0.01 mmol catalyst in the presence of 0.5 mmol TBAM in acetonitrile for 7 h at 25 $^{\circ}$ C.



Fig. 2 (a) Rate of catalytic oxidation of benzyl alcohol. Reaction conditions: 0.01 mmol catalyst, 1 mmol benzyl alcohol and 0.5 mmol TBAM in acetonitrile for 7 h at 25 °C. (b) Dependence of catalytic TON on the amount of base. Reaction conditions: 0.01 mmol catalyst, 1 mmol benzyl alcohol in acetonitrile for 7 h at 25 °C.

 Table 2
 Catalytic
 oxidative
 conversion
 of
 benzyl
 alcohol
 to

 benzaldehyde
 using different phenanthroline-based copper catalysts
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Table 3	Catalytic	oxidation	of different	alcohols	by 1	and 2
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Catalyst	TON
$Cu^{2+}:L^1(1:1)$	67
$Cu^{2+}: L^{1}(1:2)$	65
$Cu^{2+}: L^2(1:2)$	48
$Cu^{2+}: L^{3}(1:1)$	55
$Cu^{2+}: L^{3}(1:2)$	54
$Cu^{2+}: L^4(1:2)$	24
$[(L^{1})_{2}Cu^{II}(H_{2}O)](ClO_{4})_{2}$ (1)	62
$[(L^{1})Cu^{II}(H_{2}O)_{3}](ClO_{4})_{2}$ (1a)	62
$[(L^3)_2Cu^{II}(H_2O)](ClO_4)_2$ (2)	67
$[(L^5)_2 Cu^{II}(H_2O)](ClO_4)_2$ (3)	47
$[(L^6)_2 Cu^I](ClO_4) (4)$	11

ligands form 1:2 complexes irrespective of the metal/ligand ratio and reaction conditions. The copper(II) complex of L^{1} (1a) with the metal/ligand ratio of 1:1 could be isolated from acetonitrile. Copper(II)-1,10-phenanthroline complexes with metal/ ligand ratio of 1:1 and coordinated solvents are known in the literature.^{38,39} Catalytic reactions with 1 (metal : $L^1 = 1 : 2$) and 1a (metal : $L^1 = 1 : 2$) exhibit almost similar turnover numbers. The experimental results indicate a 1:1 copper(II) complex as the active complex that reacts with alcohol to affect catalytic oxidation. One of the ligands in complex 1 most likely gets dissociated in solution and acetonitrile or water (in solvent) coordinates to the copper(II) center. However, reaction with 2 shows a higher value of TON than that obtained in the reaction when L^3 and copper(II) perchlorate are used separately. Here again a combination of 1:1 metal: ligand ratio and 1:2 afford a similar TON. Therefore 1 and 2 were used for the catalytic oxidation of a few other primary alcohols including the secondary alcohol (Table 3). The catalytic TONs obtained in the oxidation of different alcohols were found to be moderate. The reaction of **2** with a mixture (1:1) of benzyl alcohol and 2-phenyl ethanol shows the formation of 62% benzaldehyde and 10% acetophenone. The catalyst is therefore selective towards the oxidation of primary alcohols. Of note, 6-methyl-2-pyridine methanol (entry 3 in Table 3) is observed to afford poor yield of the oxidized product. A blue shift of the d-d band in the optical spectrum of $[(L^1)Cu^{II}(H_2O)_3](ClO_4)_2$ (1a) from 702 nm to 595 nm is observed upon addition of a basic solution of 6-methyl-2-pyridine methanol. This supports the binding of 6-methyl-2-pyridine methanol to the copper(II) center. The binding of the substrate leads to a thermodynamically stable copper(II) complex which remains inert towards oxygen activation.

The electronic effects of different substituent on the catalytic yields were tested with substituted benzyl alcohols (Table 3, entries 5 to 8). It is found that 3-methoxy benzyl alcohol exhibits excellent yield of the corresponding aldehyde in the presence of both 1 and 2. The yield of aldehyde is decreased with substrate having electron withdrawing substituents (Table 3, entries 6 and 7). This result further supports the electronic effect on the efficiency of the catalyst. In case of 4-hydroxy benzyl alcohol, very poor yield of the corresponding aldehyde may be explained on the basis of the coordination of phenolate oxygen to the copper(π) center. It is worth mentioning here that aliphatic primary and secondary alcohols are not oxidized by the copper(π) complexes under similar experimental conditions.

	Substrate	Product	TON (Time)		
Entry			1	2	
1	HO	СНО	62 (7 h)	67 (7 h)	
2	HO	\mathbf{r}	38 (72 h)	30 (48 h)	
3	Слон	Сно	33 (7 h)	39 (7 h)	
4	Ссн2он	Ссто	58 (27 h)	47 (27 h)	
5	HO OMe	СНО	72 (7 h)	60 (7 h)	
6	HOCI	СНО	40 (7 h)	42 (7 h)	
7			16 (24 h)	42 (24 h)	
8	но	СНО	8 (24 h)	9 (24 h)	



Fig. 4 Optical spectra of (a) 2 (0.5 mM solution in MeCN–THF (1 : 1) solvent mixture), (b) after addition of a basic solution of benzyl alcohol into 2 under nitrogen and (c) solution after 7 h under inert atmosphere at 25 °C.

Mechanistic studies

To get an insight into the mechanism of catalytic oxidation of alcohols, the reaction of 2 (0.5 mM in acetonitrile–tetrahydrofuran (1:1) solvent mixture) with 10 equivalents of benzyl alcohol and TBAM was monitored spectrophotometrically under nitrogen atmosphere at room temperature (Fig. 4). Strong metalto-ligand charge transfer bands at 430 nm and 550 nm are generated in the visible region. The charge-transfer bands are



Fig. 5 X-band EPR spectra of (a) complex **2**, (b) after addition of a basic solution of benzyl alcohol into **2**, (c) solution after 7 h under nitrogen in a frozen MeCN–THF (1 : 1) solvent mixture at 123 K.

characteristic of a copper(I) complex supported by phenanthroline-based ligand.¹⁹ The solution is stable under nitrogen but changes to green upon exposure to air. This result clearly suggests the reduction of copper(II) to copper(I) in the presence of alcohol under an inert atmosphere.

To characterize the species generated under the reaction conditions discussed above, X-band EPR spectra were recorded in frozen solution at 123 K (Fig. 5). EPR spectrum of the mononuclear copper(II) complex (2), exhibiting four-line copper hyperfine pattern with $g_{\perp} = 2.06$, $g_{\parallel} = 2.28$, and $A_{\parallel} = 142 \times$ 10^{-4} cm⁻¹, changes upon addition of a basic solution of benzyl alcohol. The new EPR spectrum shows axially symmetric copper(II) center with $g_{\perp} = 2.03$, $g_{\parallel} = 2.20$, $A_{\perp} = 47 \times 10^{-4} \text{ cm}^{-1}$ and $A_{\parallel} = 160 \times 10^{-4} \text{ cm}^{-1}$, suggesting the formation of a new copper(II) complex with $d_{x^2-y^2}$ ground state. The $g_{\parallel}/A_{\parallel}$ value of 137 predicts a distorted square planar geometry at the copper(II) center.⁴⁰ The intensity of the EPR signal attains a maximum value after 4 h. The EPR parameters of the new copper(II) signal imply an interaction/binding of alcoholate with the metal centre. Interestingly, the EPR signal of the copper(II) disappears after 7 h. The EPR spectral changes confirm the formation of a copper(I) complex upon treatment of the copper(II) complex (2) with a basic solution of benzyl alcohol and the results are in line with the optical spectral observation. The copper(I)-alcoholate species activate molecular oxygen to initiate the oxidation of alcohol.

The activation of dioxygen by copper(1) complex is further supported by the lower yield of aldehyde with sterically demanding 2,9-dimethyl-1,10-phenanthroline-based catalytic systems (Table 2). These ligands prefer to stabilize copper in +1 state with a tetrahedral geometry and thereby increase the Cu⁺/Cu²⁺ potential. Additionally, 1,10-phenanthrolines, being good π -acceptor, decrease the electron density at the metal center and thereby make the complexes less susceptible for dioxygen activation. This effect is more prominent in the oxidation of alcohol with two-electron oxidized furoxan ligands (L⁵ and L⁶) that show low yield of aldehyde.

On the basis of the above results, a mechanism for the catalytic oxidation is proposed in Scheme 1. The copper(I)-alcoholate species (A) activates O₂ to form a putative copper(I)-superoxo



Scheme 1 Proposed mechanism for catalytic aerobic oxidation of alcohols by copper complexes of phenanthroline-based ligands.

species (B), which abstracts the α -H atom of coordinated alcoholate.⁵ It is important to mention here that the presence of TEMPO radical does not affect the yield of benzaldehyde in the catalytic oxidation, suggesting the involvement of an intramolecular H-atom abstraction step. Theoretical study of H-atom abstraction by TEMPO in alcohol oxidation suggest a pathway where the overlap of HOMO of alcoholate to π^* LUMO of TEMPO is proposed.³³ Similarly, a copper(II)-superoxide orbital is proposed to interact with an accessible HOMO of alcoholate in the abstraction of α -H atom. Moreover, the presence of 10 equivalents of TEMPOH, an external superoxide intercepting reagent, lowers the yield of benzaldehyde from 67% to 51%. This confirms the abstraction of H-atom from alcoholate by a copper(II)-superoxide species to form a copper(II)-hydroperoxo species. An electronic rearrangement of copper(II)-hydroperoxide (C) species results in the formation of aldehyde and hydrogen peroxide. The hydrogen peroxide thus produced gets decomposed in solution in the presence of copper complex. The resulting copper(I) complex then undergoes further oxygen activation for catalytic cycle.

Conclusions

We have reported the catalytic oxidation of primary alcohols to the corresponding aldehydes by copper complexes of phenanthroline-derived ligands using dioxygen as the terminal oxidant. A series of primary alcohols including one secondary alcohol were oxidized where the copper complexes show selectivity towards primary alcohols in the catalytic oxidation. A copper(II)superoxo species has been proposed in the reaction mechanism to initiate the catalytic reaction. The electronic property of the supporting ligand has been shown to affect the catalytic efficiency of the copper catalysts. Copper(II) complexes of electron rich 1,10-phenathroline derivative would probably be better catalysts for aerial oxidation of alcohols. Further structural and electronic tuning by functionalization of 1,10-phenanthroline with electron-donating groups towards the development of a more efficient transition metal catalyst for aerial oxidation of alcohols is in progress.

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