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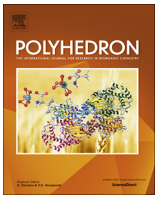

Homogeneous oxidation of alcohols in water catalyzed with Cu(II)-triphenyl acetate/bipyridyl complex

Hakan Ünver, Ibrahim Kani *

Department of Chemistry, Faculty of Science, Anadolu University, Eskisehir 26210, Turkey

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ABSTRACT

A water-soluble mononuclear copper(II) complex, $[Cu(OOCC(C_6H_5)_3)(C_{10}H_8N_2)(H_2O)](ClO_4)(CH_3OH)$ (triphenylacetic acid = $HOOCC(C_6H_5)_3$, 2-2′-bipyridyl (bipy) = $C_{10}H_8N_2$) was synthesized and used as a catalyst precursor in the oxidation of primary (cinnamyl alcohol, benzyl alcohol, cyclohexanol, and 1-heptanol) and secondary alcohols (1-phenylethanol, 3-pentanol, and 2-octanol) to corresponding aldehydes, ketones, and acids. The complex exhibited high catalytic activity toward benzyl alcohol to benzaldehyde as one product (97% conversion in 6 h) and cinnamyl alcohol to benzaldehyde (91.5%) and cinnamaldehyde (6.6%), in 6 h reaction time with less catalyst loading (1 mol%) at a moderate temperature (70 °C). Water was used as a solvent and H_2O_2 as an oxidant for alcohol oxidation. Thus, the Cu(II)/H_2O/H_2O_2 catalytic system could serve as an environmentally benign "green chemistry" alternative to oxidation methods in traditional organic solvents.

1. Introduction

The catalytic oxidation of alcohols is a basic transformation reaction in synthetic organic chemistry [1]. A variety of reagents and catalytic systems have been developed to improve this oxidation process in terms of economic and environmental reasons. Unfortunately, these reagents are very active and involve stoichiometric amounts of traditional toxic metal–containing oxidizing agents (i.e., CrO_3 and $KMnO_4$ [2]). That is why growing attention has been paid to the replacement of these reagents with less toxic oxidants such as H_2O_2 or O_2. Another problem with these systems is the use of hazardous organic solvents that cause unwanted wastes, side products, and environmental problems. The catalytic reactions in water could be favorable with lower cost, greater safety, easier isolation of products and catalyst recovery, more importantly, in terms of green chemistry, compared with those performed in organic solvents; however, the effective catalytic systems for alcohol oxidation in water were scarcely explored [3].

Transition metal salts and metal–organic frameworks such as Cu, Co, V, Pd, Ru, Rh, and Mo [4–10] have been used as catalyst precursors for the catalytic oxidation of alcohols with O_2 or H_2O_2. Reports on catalytic oxidation reactions using the Cu catalyst with organic nitrogen-based ligands are mostly presented by other groups [11–15]. The first water-soluble palladium(II) complex for the catalytic oxidation of alcohols in water was reported by the Sheldon Group. In addition to the use of expensive metal complexes, higher temperature (100 °C), oxygen pressure (30 bar), some external acid or base and organic solvents were required for these catalytic systems [16]. Among the above mentioned metal salts or metal–organic complexes, Cu is the most interesting one because of the biomimetic functional model of the galactose oxidase enzyme, which is a mononuclear copper compound [17]. It is known that the structure of the molecule organic framework of metal complexes with different organic ligands should be highly related to their catalytic activity. Although Cu(I)- and Cu(II)-containing complexes with nitrogen donor–containing ligands were studied as catalyst precursors for alcohol oxidations [18], carboxylate and neutral nitrogen–based ligand (i.e., bipyridyl and phenanthroline) together with Cu(II) is not reported yet to the best of our knowledge [19]. This study is the first report of this type on the water-soluble Cu(II) complex, $[Cu(OOCC(C_6H_5)_3)(C_{10}H_8N_2)(H_2O)](ClO_4)(CH_3OH)$, explored to the oxidation of alcohols without the use of any promoter in aqueous medium. Therefore, in this work, our purpose is to extend the carboxylate group/nitrogen ligand sets with Cu(II) and report on the solid-state structure of the copper(II) complex based on these ligands.

2. Experiment

2.1. Materials–instrumentation–physical measurements

All chemicals were purchased from commercial sources and used as received. IR spectra were measured with Jasco FT/IR-300

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* Corresponding author.
E-mail address: ibrahimkani@anadolu.edu.tr (I. Kani).

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E Spectrophotometer using the KBr pellet in the range of 4000–400 cm^{-1}. UV–Vis spectra of **1** were recorded on a Shimadzu UV-2450 spectrophotometer. Crystallographic data were collected at room temperature with a Bruker APEX II CCD using Mo-Ka radiation and corrected for absorption with SADABS. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2. The magnetic susceptibility measurements were performed using a Sherwood Scientific MXI model Gouy magnetic balance at room temperature.

2.2. Synthesis of $[Cu(OOCC(C_6H_5)_3)(C_{10}H_8N_2)(H_2O)](ClO_4)(CH_3OH)$

A neutralized solution of triphenylacetic acid (150 mg, 0.52 mmol, 5 mL methanol) with NaOH (1.04 mL, 0.5 M) was added to a solution of copper(II) perchlorate, $Cu(ClO_4)_2 \cdot 6(H_2O)$ (192.6 mg, 0.52 mmol) in MeOH (15 mL). After 1 h of stirring, the solution of bipy (81.2 mg, 0.52 mmol) in MeOH (2 mL) was added to the mixture. The final solution was refluxed in 5 h. The solution was filtered off over Celite. Blue crystals were obtained through evaporation of the solvent for 3 days. (205 mg; Yield: 55.4% m.p.: 283 °C; soluble in polar organic solvents, *Anal.* Cald. for $C_{31}H_{28}ClCuN_2O_8$ (656.55 g/mol) C, 57.70; H, 4.04; N, 4.49. Found: C, 59.27; H, 4.83; N, 3.97%) (Significant IR bands (KBr, v cm^{-1}) (s, strong; m, medium; w, weak): 3479w vN—H, 1602m vC=N; 1694m $v\mathrm{COO}_{asym}$; 1444m $v\mathrm{COO}_{sym}$; 1492m $v\mathrm{C{=}N{-}C{=}C}_{sym}$; 1102m vO—H; 1085s vC—O; 768m vC—N; 731m $v\mathrm{Cu{-}O{-}Cu}_{sym}$; 625m $v\mathrm{Cu{-}O{-}Cu}_{asym}$) (UV–Vis λ_{max} nm (CH_3CN): 198, 245, 299. Magnetic moment (μ) = 1.4 B.M. at room temperature.

2.3. X-ray crystallography

Diffraction data for the complex collected with Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 296 (2) K, respectively using graphite monochromated Mo Kα radiation at λ = 0.71073 Å. The data reduction was performed with the Bruker SMART program package [20]. The structures were solved by direct methods and the non-hydrogen atoms were located through subsequent difference Fourier syntheses [21]. Structure solution was found with the SHELXS-97 package using the direct methods and were refined SHELXL-97 [22] against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure model at calculated positions. The molecular drawing was obtained using MERCURY [23]. Geometric calculations were performed with PLATON [24].

2.4. General procedure of the catalytic oxidation experiments

The oxidation reactions were performed in a 50 mL reaction flask with a reflux condenser under vigorous stirring at 70 °C in a temperature-controlled oil bath. In a typical experiment, the reaction mixture was prepared as follows: 7.6×10^{-3} mmol of catalyst into a 10 mL water solvent (0.76 mmol) of substrate alcohol (substrate/cat. = 100) and an excess amount of H_2O_2 (30% in water, 1.95 mmol) in this order. The reactions were monitored by withdrawing small aliquots at certain time intervals and analyzed on a GC with an HP-5 quartz capillary column (30 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID). Each sample was repeated twice. Identification of peaks was made by comparing with chromatograms of authentic samples.

3. Results and discussion

3.1. Synthesis of the complex

The stoichiometric reaction of triphenyl acetic acid and bipy with copper(II) perchloride in a methanol formed a blue solution, from which suitable blue crystals of complex, $[Cu(OOCC(C_6H_5)_3)(C_{10}H_8N_2)(H_2O)](ClO_4)(CH_3OH)$, were obtained through evaporation of the solution in 3 days. Complex crystallized in a monoclinic space group, $P-1$, with 2 formula units in the unit cell as a mononuclear complex cation, which is consistent with the molecular structure found through elemental analysis. An ORTEP structure is presented in Fig. 1. Crystallographic data, bond distances and angles relevant to the metal coordination sphere of the complex are listed in Tables 1 and 2.

Crystallographic analysis reveals that the Cu(II) ion is coordinated with donor atoms O and N in a monomeric distorted square-planar geometry. Cu(II) is surrounded by two nitrogen atoms of chelating bipy ligand and by one oxygen atom of water and one oxygen atom of the carboxylate group of the triphenylacetate ligand, giving an overall CuN_2O_2 binding set. Outside the complex cation, one methanol molecule and one perchlorate ion cyclize as counter ion. The Cu—N distances are 1.986(2) Å and 1.993(2) Å. The carboxylate group coordinates in a monodentate manner with a Cu1—O2 distance of 1.932(2) Å, which is shorter than the water coordination Cu1—O7 distance of 1.968(2) Å. The distance (3.240 Å) between the dangling oxygen atom of the carboxylate group and the copper ion is too large for the coordination of the oxygen and the copper ion. The geometry around Cu(II) is a distorted square-planar geometry with coordination angles within the range of 81.8(1)–93.8(1) deviating from 90° and 173.0(1)° and 175.5(2)° deviating from 180°. The smaller angle (81.8 Å) corresponds to that formed by the copper ion and the two N of the bipy molecule, as it is common in copper–bipy complexes. The bipy ligand is closer to planarity, as indicated by the N1—C5—C6—N2 torsion angle at −0.44°.

In the unit cell structure, two mononuclear units are linked by two O—H…O hydrogen bonds between O—H of the coordinated water molecule and two oxygen atoms of the lattice perchlorate ion, with an O3…O7 distance of 2.848 (4) Å (O3–H3A…O7) and an O3…O6 distance of 3.258 (4) Å (O3–H3B…O6) (Fig. 2, Table 3).

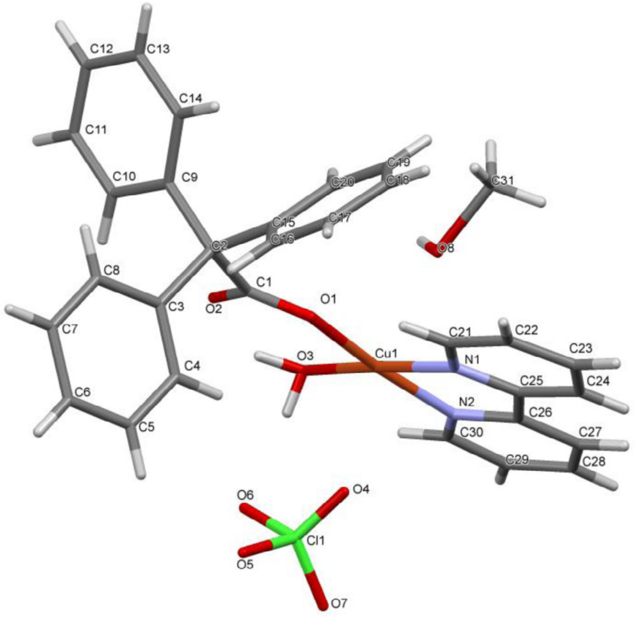


Fig. 1. Molecular structure of complex.

Table 1
Crystal data and structure refinement for complex.

Empirical formula	C31 H29 Cl Cu N2 O8
Formula weight	656.55
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	a = 8.5570(8) Å alpha = 91.701(4)° b = 9.6193(9) Å beta = 93.799(4)° c = 19.1802(18) Å gamma = 103.103 (4)°
Volume	1532.7(2) A^3
Z, Calculated density	2, 1.423 Mg/m^3
Absorption coefficient	0.852 mm^{-1}
$F(000)$	678
Crystal size	0.31 × 0.28 × 0.07 mm
Theta range for data collection	2.13–28.42 (°)
Limiting indices	$-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-25 \leq l \leq 25$
Reflections collected/unique	38996/7618 [R(int) = 0.0277]
Completeness to theta =	28.42 98.7%
Absorption correction	None
Max. and min. transmission	0.9427 and 0.7780
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7618/0/395
Goodness-of-fit (GOF) on F^2	1.056
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0640, wR_2 = 0.2001
R indices (all data)	R_1 = 0.0714, wR_2 = 0.2096
Largest difference peak and hole (e A^{-3})	1.972 and −0.714

Table 2
Selected bond lengths (Å) and angles (°).

Cu(1)-O(1)	1.932(2)
Cu(1)-O(3)	1.968(2)
Cu(1)-N(1)	1.986(3)
Cu(1)-N(2)	1.992(3)
N(1)-C(21)	1.331(4)
N(1)-C(25)	1.344(4)
N(2)-C(30)	1.338(4)
N(2)-C(26)	1.346(4)
O(1)-Cu(1)-O(3)	92.87(10)
O(1)-Cu(1)-N(1)	91.57(11)
O(3)-Cu(1)-N(1)	175.52(10)
O(1)-Cu(1)-N(2)	173.01(10)
O(3)-Cu(1)-N(2)	93.82(11)
N(1)-Cu(1)-N(2)	81.76(11)

The dangling oxygen atom (O2) of the carboxylate group forms an intramolecular hydrogen bond with the hydrogen atom of the coordinated water molecule (O2…O3 distance of 2.533 (4) Å). The shortest π···π distance between two parallel rings of bipy ligands (N1C21-C25 and N2C26-C30) is 10.057 Å. Moreover, some intermolecular contacts are observed between the carbon atoms of bipy rings and the oxygen atoms of the perchlorate ion (Table 3). The Cu···Cu distance is 7.687 Å in the unit cell.

3.2. Spectroscopic study

The infrared spectra of the complex are consistent with the determined X-ray structure (Fig. SP1). A broad band observed at 3479 cm^{-1} is due to O—H stretching of the coordinated aqua ligand. The band observed between 3034 and 3086 cm^{-1} is attributed to aromatic v(C—H) vibrations of both neutral and anionic ligands. The symmetric v_{sym}(OCO) and asymmetric v_{asym}(OCO) vibrational peaks of the carboxylate group were observed as strong peaks at 1694 and 1444 cm^{-1}. The magnitude of separation between the antisymmetric and the symmetric carboxylate stretching of complex is 250 cm^{-1}, which indicates a monodentate coordination in deference to Nakamoto's method [25]. Free bipy ligand azomethine v(C=N) bond frequency shifted from 1589 to 1602 cm^{-1}, indicating that the coordination occurs via nitrogen atom with a metal center. Strong bands at 768 and 731 cm^{-1} correspond to chelating bipy frequencies.

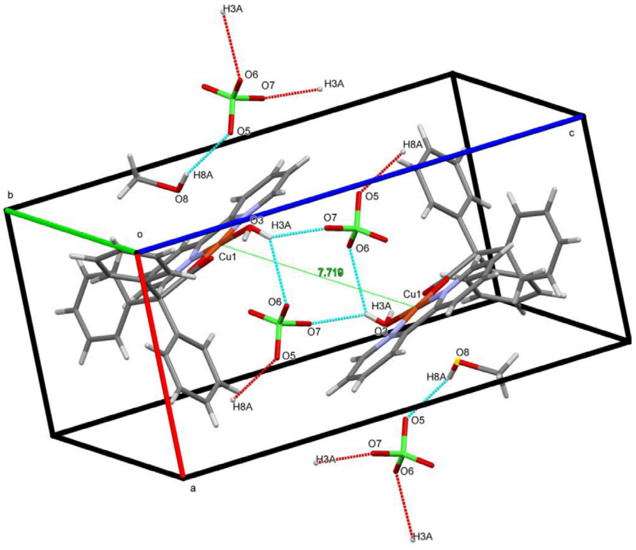


Fig. 2. Unit cell of complex.

Table 3
Hydrogen bonding in complex.

D–H…A	D–H (Å)	H…A (Å)	D…A (Å)	D–H…A (°)
O3–H3B…O2	0.91	1.72	2.533(4)	146(6)
O3–H3A…O6	0.82	2.65	3.258(8)	132(3)
C4–H4…O1	0.93	2.59	3.222(4)	125
C10–H10…O2	0.93	2.35	2.781(4)	108
C21–H21…O1	0.93	2.43	2.946(4)	115
C30–H30…O3^{ii}	0.93	2.54	3.056(5)	115
O3–H3A…O7^{i}	0.82	2.16	2.848(4)	142
O8–H8A…O5^{ii}	0.82	2.29	3.004(9)	146
C23–H23…O6^{iii}	0.93	2.55	3.213(8)	129
C27–H27…O4^{iv}	0.93	2.57	3.298(10)	136
C27–H27…O7^{iv}	0.93	2.57	3.468(6)	163

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $-1+x, y, z$; (iii) $x, 1+y, z$; (iv) $1-x, 2-y, 1-z$.

The UV–Vis spectrum of complex was measured in an acetonitrile solution and revealed three absorption bands at 198, 245, and 299 nm (Fig. SP2). The band at 198 nm is assigned to $\pi \rightarrow \pi^*$ transitions of a carboxylate ligand. The other observed bands are attributed to bipy ligand (C=N) $n \rightarrow \pi^*$ transitions. Any $d \rightarrow d$ transitions were not observed in the spectrum of the complex.

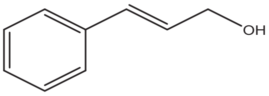
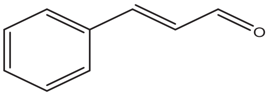
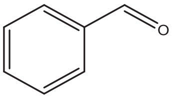
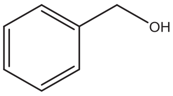
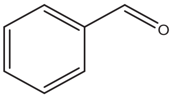
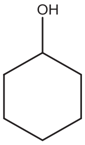
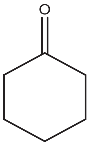
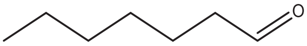
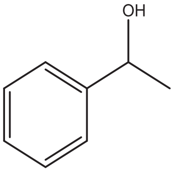
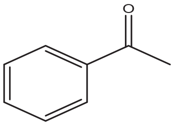
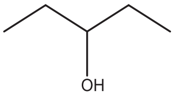
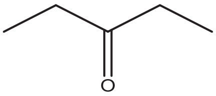
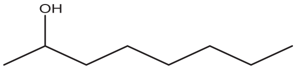
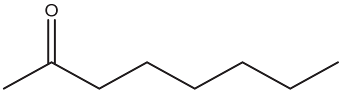
The magnetic property of complex in the solid state at room temperature was examined by using a Gouy magnetic balance. The complex exhibits the magnetic moment value of 1.40 which correspond to one unpaired electron. This result is lower than the spin only value (1.73 BM) indicate magnetic exchange interaction between adjacent complex unit [26].

3.3. Catalytic studies

We have tested the copper(II) compound as homogeneous catalyst precursor for the oxidation of primary and secondary alcohols to the corresponding alcohols and ketones. The catalytic reactions were performed under mild conditions (70 °C) in green solvent water and using H_2O_2 (30% in water) as an oxidant.

Experimental results illustrated that complex is an effective catalyst for the oxidation of alcohols. Among the studied alcohols (Table 4, Fig. 3), complex is more active in primary alcohols than

Table 4
Complex catalyzed oxidation of primary and secondary alcohols to carbonyl compounds.[a,b]

Entry	Substrate	Products, Conv. (%)		Total Conv.[c] (%)	TON/TOF (h^{-1})
1		 19.5 (1 min) 16.2 (2 h) 6.6 (6 h)	 11.6 (1 min) 39.2 (2 h) 84.9 (6 h)	31.1 (1 min) 55.4 (2 h) 91.5 (6 h)	31/1866 55/28 92/15
2		 48.6 (2 h) 97.4 (6 h)		97.4 (6 h)	97/16
3		 28.0 (6 h) 52.2 (24 h)		52.2 (24 h)	52/2
4				12.2 (6 h)	11/2
5		 73.0 (6 h) 100 (24 h)		100 (24 h)	100/4
6				29.4 (6 h)	29/5
7				10.7 (24 h)	11/1

[a] Conditions: alcohol (0.76 mmol), catalyst (7.6 × 10^{-3} mmol), H_2O_2 (19.5 mmol), water (10 mL), $T = 70$ °C.
[b] Blank experiment was conducted for each substrate and negligible conversion was obtained (<2%).
[c] Determined with GC.

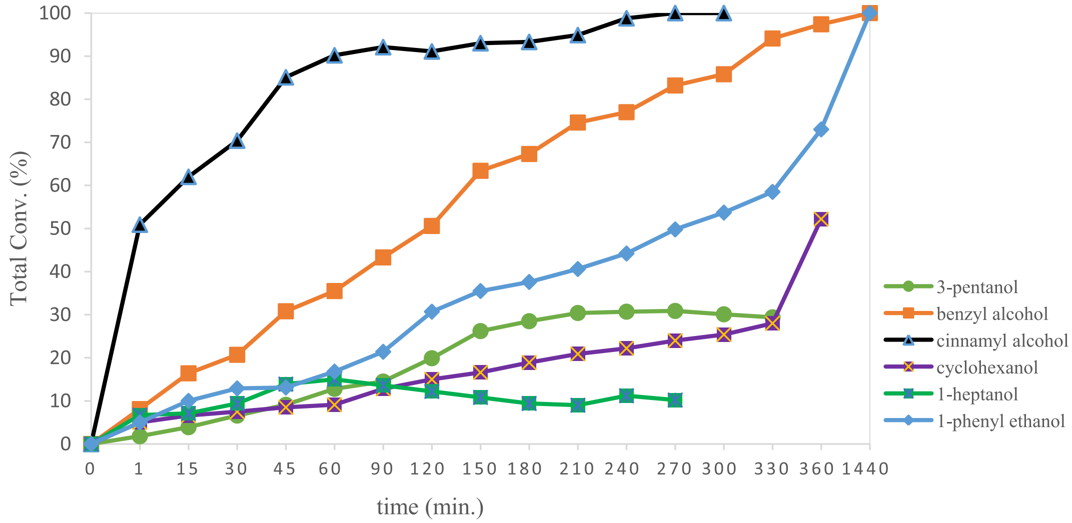


Fig. 3. Comparison of alcohol oxidation with complex in water solvent.

in secondary ones. Entries 1, 2 and 3 illustrate that primary alcohols are more reactive than secondary alcohols and gave a higher TON, up to 100. Notably, primary alcohols (entries 1–4) were not converted into over-oxidation product carboxylic acids, whereas secondary alcohols were oxidized to only the corresponding ketones without C—C chain cleavage (entries 5–7).

Table 5
Selective oxidation of alcohols with complex in water.[a]

Entry	Alcohols	Products[b]	Conv. (%) / time (h)
1	Benzyl alcohol + 1-phenyl ethanol	Benzaldehyde + acetophenone	20.9 (6 h) 29.6 (24 h) + 9.9 (6 h) 50.2 (24 h)
2	2-octanol + 1-heptanol	2-octanone + 1-heptaldehyde	1.0 (24 h) + 4.2 (24 h)
3	Cyclohexanol + 1-heptanol	Cyclohexanone + 1-heptaldehyde	13.7 (6 h) 16.5 (24 h)+-

[a] Conditions: alcohol (1 mmol), catalyst (7.6×10^{-6} mmol), H_2O_2 (19.5 mmol), water (10 mL), $T = 70$ °C.
[b] Determined with GC.

The catalyst showed high activity in the oxidation of cinnamyl alcohol (31.1% in 1 min) in water with a high conversion value (55.4% in 2 h). In this reaction, cinnamyl alcohol conversion is 91.5% after 6 h and aldehyde selectivity is 93% (Table 4, entry 1). It should be emphasized that in this oxidation, after the oxidation of cinnamyl alcohol to cinnamaldehyde, carboxylation of aldehyde occurred and formed benzaldehyde rapidly in the first minute of the reaction. After 2 h reaction, benzaldehyde formation increased to 39.2%, while cinnamaldehyde was at 15.0%. Finally, after 6 h reaction, the benzaldehyde selectivity reached 93%.

Moreover, primary and secondary aliphatic alcohols are less reactive than benzylic substrates. The primary aliphatic alcohol 1-heptanol (Table 4, entry 4) was converted into the corresponding aldehyde with low conversion (12.2%, 6 h). The secondary aliphatic alcohols 3-pentanol (29.4%) and 2-octanol (5%) were converted into the corresponding ketones in a very low yield in 1-day reaction (Table 4, entries 6 and 7). These results are in agreement with reports that show that aliphatic alcohols are less reactive than benzylic substrates.

The Cu(II)/H_2O_2/H_2O catalytic system has also been tested for intramolecular selective oxidation (Table 5). A mixture of benzyl alcohol (primary alcohol) and 1-phenyl ethanol (secondary alcohol) was reacted with H_2O_2 in the presence of the copper(II) catalyst precursor. A total of 29.6% of the benzyl alcohol was converted, whereas 9.9% of the 1-phenyl ethanol was converted into acetophenone in 6 h. After 1-day reaction, 29.6% benzaldehyde and 50.2% acetophenone were determined. The result shows that both phenylic alcohols coordinate the Cu(II) ion, but the catalytic system proceed toward the secondary alcohol with a long-term reaction time (Table 5, entry 1). The competitive coordination of alcohols may lead to a lower formation of benzaldehyde as fewer binding sites are available for benzyl alcohol when only benzyl alcohol oxidizes benzaldehyde at 97.4% in 6 h.

When a mixture of linear primary alcohol, 1-heptanol and linear secondary alcohol, 2-octanol, was oxidized in a very low yield for both complexes (Table 5, entry 2), the competing reaction between cyclic alcohol, cyclohexanol and linear alcohol, 1-heptanol, showed 16.5% (in 24 h) conversion of cyclohexane, whereas 1-heptanol remained unreacted. These results show that the competition of alcohols lowers the activity of cyclohexanol from 52.2% to 16.5% (Tables 4 and 5, entry 3).

4. Conclusions

In conclusion, a novel water-soluble Cu(II) complex with triphenyl acetate and bipy has been synthesized, and a solid-state structure was characterized through X-ray crystallography. The Cu(II) compound behaves as a homogeneous catalyst precursor for the oxidation of various alcohols with a low to good yield under mild reaction conditions (70 °C) in a green catalytic system (water as a solvent and H_2O_2 as an oxygen source). All studied primary alcohols were selectively oxidized to corresponding aldehydes and overoxidized products carboxylic acids were not determined. Linear secondary alcohols were converted into corresponding ketones in a very low yield, whereas complex showed a higher level of activity in the oxidation of benzylic alcohol (1-phenyl ethanol) to acetophenone in a very good yield (73% in 6 h).

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Appendix A. Supplementary data

CCDC 1545566 contains the supplementary crystallographic data for complex. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2017.06.030.

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