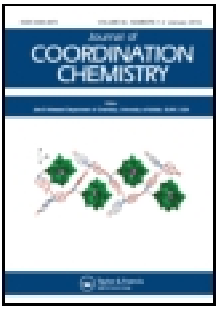

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2,2′-Bipyridyl-acetylphenolato mixed ligand copper(II) complexes: syntheses, characterizations and catalytic activity in styrene epoxidation

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Two copper(II) complexes, [Cu(bipy)(5-Br-2-hap)(ClO_4)]$_2$ (**1**) and [Cu(bipy)(2-hap)(ClO_4)] (**2**) (where bipy = 2,2′-bipyridine, 5-Br-2-hap = 5-bromo-2-hydroxyacetophenone, 2-hap = 2-hydroxyacetophenone), were synthesized and characterized. The crystal structure of **1** was determined by single crystal X-ray diffraction while **2** was reported earlier. Structural characterization reveals that the presence of bromine in 5-Br-2-hap plays a structure-determining role in dimeric **1** in comparison with the mononuclear **2** where 2-hap was used. Studies of the catalytic potential toward styrene epoxidation in homogeneous system using H_2O_2 as oxidant reveal that **1** is more efficient than **2** with respect to epoxide selectivity.

Keywords: Mixed ligand copper(II) complexes; Spectral and structural characterizations; Homogeneous catalysis; Hydrogen peroxide; Styrene epoxidation

1. Introduction

Mixed ligand copper complexes of 2,2′-bipyridine (bipy) or similar ligands (rigid or semi-rigid) give a variety of complexes depending on the oxidation state of copper and the nature of other coordinating ligands [1, 2]. Such complexes have been extensively studied over several decades due to their magnetic, optical and catalytic properties [1, 3]. Mono-/binuclear copper(II) complexes of this type are also important as biological model systems in understanding the role of bimetallic centers in several metalloproteins and metalloenzymes [4–7] as the active sites of such proteins/enzymes usually involve coordination of copper by at least two nitrogen and oxygen donors from other ligands [8]. Thus, synthesis and characterization of mixed ligand complexes with diamine and other oxygen donors are of continuous interest. Some copper(II) complexes with diamines and other ligands exhibit unique biological activities against various bacterial and fungal strains [1] as well as strong antitumor activities [8–10].

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Focus has been made on synthesis and characterization of mono-/binuclear copper(II) complexes with bipy and salicylaldiminato ligands [2, 11]; however, the catalytic potential of such copper(II) complexes is yet to be explored. Olefin epoxidation catalyzed by transition metal complexes has widespread applications in chemical and pharmaceutical industries [12, 13]. Attempts to use Schiff-base copper(II) complexes in homogeneous catalytic epoxidation have been reported [14–17]. Several oxidants such as 30% hydrogen peroxide, tert-butyl hydroperoxide (tert-BuOOH), sodium hypochlorite and even molecular oxygen are used for the production of epoxides from alkenes. Among them, 30% hydrogen peroxide attracts increased attention in industrial use because it is environmentally friendly. As recently outlined by Beller [18], H_2O_2 is characterized by unique features and advantages [19] such as high atom efficiency [20], moderate cost, safe handling and storage and production of water as the only byproduct [21, 22], making it the most interesting oxidant after molecular oxygen and stimulating its use in liquid-phase oxidations, especially for fine chemicals production [23].

In this article, we describe the synthesis of a mixed ligand copper(II) complex, $[Cu(bipy)(5\text{-}Br\text{-}2\text{-}hap)(ClO_4)]_2$ (**1**). The use of 5-Br-2-hap having electron-withdrawing bromine on the acetylphenolato moiety leads to dimeric **1** in comparison with monomeric **2** [2]. Complex **1** was characterized by elemental analyzes, Fourier transform infrared spectra (FTIR), UV–vis, cyclic voltammetry and single crystal X-ray diffraction, and compared with **2**. The catalytic potential in homogeneous medium of the complexes has been investigated and compared, which reveal that **1** is more efficient than **2** with respect to epoxide selectivity.

2. Experimental

2.1. *Materials and physical measurements*

Caution! Perchlorate salts of metals in the presence of organic ligands are potentially explosive. Even though we did not encounter any problems, they should be prepared in small amounts and handled with caution.

Copper(II) perchlorate hexahydrate, 2,2′-bipyridine, 2-hydroxyacetophenone, 5-bromo-2-hydroxyacetophenone, styrene, 3-Me styrene and 4-Me styrene were purchased from Aldrich Chemical Co. and used as received. Hydrogen peroxide (30 wt.% aqueous) and solvents were purchased from E. Merck (India). The solvents were distilled and dried before use. Complex **2** was synthesized according to the literature procedure [2]. Elemental analyzes (carbon, nitrogen and hydrogen) were carried out using a Perkin-Elmer 2400 II elemental analyzer. The copper content in **1** has been estimated by standard iodometric method. Infrared spectra were recorded on a Perkin-Elmer Spectrum RX FTIR instrument from 4000–400 cm^{-1} as KBr pellets. UV–vis spectra in solution were recorded at room temperature on a Perkin-Elmer *Lambda* 40 UV–vis spectrophotometer using acetonitrile in 1 cm quartz cuvettes. Electrochemical measurements were performed using a PAR VersaStat-potentiostat/Galvanostat II electrochemical analysis system under dry argon using conventional three-electrode configurations in acetonitrile with tetrabutylammonium perchlorate as the supporting electrolyte. Platinized platinum millielectrode and saturated calomel electrode (SCE) were used as working and reference electrodes, respectively, along with a platinum counter electrode in cyclic voltammetry performed at a scan rate of $v = 50\,mV\,sec^{-1}$. The products of the catalytic reactions were identified and quantified by an Agilent HP 6890 series gas chromatograph using a HP-5 GC column.

2.2. *Synthesis of 1*

To a methanolic solution (20 mL) of copper(II) perchlorate hexahydrate (2 mM, 0.741 g), 5-Br-2-hap (2 mM, 0.430 g) was added very slowly with constant stirring. The mixture was stirred for 30 min, followed by the addition of a methanolic solution (20 mL) of bipy (2 mM, 0.312 g). The reaction mixture was filtered and the filtrate kept for slow evaporation at room temperature. Deep green crystals of **1** separated after 5 days. Anal. Calcd. for [$C_{36}H_{28}Br_2Cl_2Cu_2N_4O_{12}$]: C, 35.26; H, 2.30; N, 4.57; Cu, 10.36%. Found: C, 35.20; H, 2.25; N, 4.55; Cu, 10.32%.

2.3. *Structure determination*

Diffraction-quality block-shaped dark green crystal of **1** (dimension; 0.36×0.27 0.15 mm) was mounted on a Nonius KappaCCD APEXII diffractometer equipped with rotating anode generator Nonius FR591, the radiation was monochromated with a Montel mirror (Mo $K_\alpha = 0.71073$ Å). Intensity data were collected at 223 K using φ and ω scans. No significant loss in intensities was observed during data collection. Multi-scan absorption corrections were applied to the intensity data ($T_{\max} = 0.6339$ and $T_{\min} = 0.3790$) empirically using Denzo [24]. Data collection, reduction and refinement were performed using Collect [25] and Denzo-SMN [26] softwares. Crystal structures were solved by direct methods using SHELXS-97 [27] and refined with full-matrix least-squares based on F^2 using SHELXL-97 [27]. All non-hydrogen atoms were refined anisotropically. Hydrogens were first located in the Fourier difference map, then positioned geometrically and allowed to ride on their respective parent. The molecular graphics and crystallographic illustrations for **1** were prepared using SCHAKAL [28] and ORTEP [29]. Crystallographic parameters, details of data collection and refinement procedures for **1** are summarized in table 1.

2.4. *Catalytic reactions*

Catalytic reactions were carried out in a glass batch reactor according to the following procedure. Substrate (5 mM), solvent (5 mL) and catalyst (2 mg) were first mixed. The mixture was then equilibrated to the desired temperature in an oil bath. After the addition of hydrogen peroxide (7.5 mM, 1.5 equiv.), the reaction mixture was stirred continuously. Reactions were performed in open air. The products of the epoxidation were collected at different time intervals, identified and quantified by gas chromatography.

3. Results and discussion

3.1. *FTIR*

IR spectra from 4000–400 cm^{-1} provide some information regarding the mode of coordination of ligands in copper(II) complexes and were analyzed in comparison with each other. Coordination of the η^1-bonded carbonyl stretching vibrations for **1** and **2** is at 1602 and 1604 cm^{-1}, respectively [30]. The phenolic–OH generally at 3550–3200 cm^{-1} (s, br) is absent in spectra of the complexes, indicating deprotonation of phenolic–OH during complexation. Coordination of this phenolic oxygen is substantiated by lowering of C–O

Table 1. Crystal data and structure refinement parameters for **1**.

	1
Empirical formula	$C_{36}H_{28}Br_2Cl_2Cu_2N_4O_{12}$
Formula weight	1066.42
Crystal dimension (mm)	0.36 × 0.27 × 0.15
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	11.8248(3)
b (Å)	10.2297(3)
c (Å)	17.0683(5)
β (°)	109.097(1)
V (Å^3)	1951.03(10)
Z	2
T (K)	223(2)
$\lambda_{\text{Mo-K}\alpha}$ (Å)	0.71073
D_c (g cm^{-3})	1.815
μ (mm^{-1})	3.343
F (000)	1060
θ Range (°)	4.1–28.6
hkl ranges	$-15 \le h \le 15$, $-12 \le k \le 13$, $-23 \le l \le 21$
Total data	10,217
Unique data	4777
Observed data [$I > 2\sigma(I)$]	4111
$N_{ref;}$ N_{par}	4777; 263
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0549$, $wR_2 = 0.1173$
R indices (all data)	$R1 = 0.0675$, $wR_2 = 0.1288$
R_{int}	0.035
Goodness-of-fit on F^2	1.07
$\Delta\rho_{max}$ (e.Å^{-3})	1.27
$\Delta\rho_{min}$ (e.Å^{-3})	−1.06

stretching frequencies in the complexes (1213 cm^{-1} for **1** and 1230 cm^{-1} for **2**) when compared to that of the free ligand (~1279 cm^{-1}) [31]. Characteristic absorptions for coordinated bipy were observed at 3032 (s, br), 1587, 778 cm^{-1} for **1** and 3088 (s, br), 1590, 780 for **2**. Monodentate coordination of ClO_4^- to copper(II) center is evident from the splitting of v_3 into two bands at 1143 and 1066 cm^{-1} for **1** and 1146 and 1078 cm^{-1} for **2**, respectively [32, 33]. Coordination of pyridine nitrogen is shown by weak bands at 434 and 417 cm^{-1} for **1** and 434 and 416 cm^{-1} for **2** [30, 31].

3.2. *UV–vis spectra*

Electronic spectra of **1** and **2** in acetonitrile show strong bands at 240, 300 nm and 247, 305 nm, respectively, assigned to π→π* and intraligand charge-transfer transitions [34]. The ligand-to-metal charge-transfer transitions for **1** and **2** at 390 and 394 nm, respectively, indicate the coordination of ligands to metal [34, 35]. The very weak bands at 613 and 632 nm may be assigned to d→d transitions, in support of the distorted octahedral and distorted square pyramidal geometries for copper(II) in **1** and **2**, respectively [34–36].

3.3. *Electrochemistry*

Electrochemical behaviors of the complexes were studied at room temperature in acetonitrile using tetrabutylammonium perchlorate as supporting electrolyte at a scan rate of 50 mVs^{-1} from + 1.5 to −1.5 V. On anodic scan, cyclic voltammograms of **1** and **2** (Supplementary Material) show single oxidative response at 0.91 and 0.95 V, respectively, believed to be due to Cu(II)→Cu(III) oxidation. However, the oxidized complex is too reactive to survive for the cathodic scan. **1** and **2** show an irreversible reductive response at −0.64 and −0.69 V (versus SCE), assignable to Cu(II)→Cu(I) reduction. Since both the acetylphenolato ligands have the same coordination sites, the observed less negative reduction potential for **1** than **2** may be correlated with electronic effects of the substituent present in the ligand. The presence of electron-withdrawing bromine in 5-Br-2-hap used in **1** decreases the electron density on copper(II), thereby lowering the redox orbital energies compared to those of **2** [37, 38].

3.4. *Crystal structure of 1*

Crystal structure of **1** reveals that it crystallizes in the monoclinic crystal system, in space group $P2_1/n$. An ORTEP view of **1** is shown in figure 1, and its bonding parameters are summarized in table 2. The crystal structure shows that **1** is a centrosymmetric dimer. Coordination environments of the metal centers are satisfied by bipy, acetylphenolato anion (5-Br-2-hap) and perchlorate. Coordination polyhedra around the metal center may be described as distorted octahedral with bipy coordinated to copper(II) in a bis-chelating fashion through N11 and N22 while bis-chelating acetylphenolato anion (5-Br-2-hap) coordinates to copper(II) through phenolato (O1) and ketonic (O8) oxygens satisfying the basal coordination sites. The perchlorate is mono-coordinated through O34 occupying one apex, while the other is occupied by an additional donor oxygen ($O1^i$) at a longer distance (table 2) from the phenolato moiety of the symmetry-related counterpart. Thus, O1 and $O1^i$ connect two symmetry-related units through equatorial–axial coordination leading to dimeric **1**. Cu-N(eq) and Cu-O(eq) are shorter than Cu-O(axial) [Cu-O34 and Cu-$O1^i$]

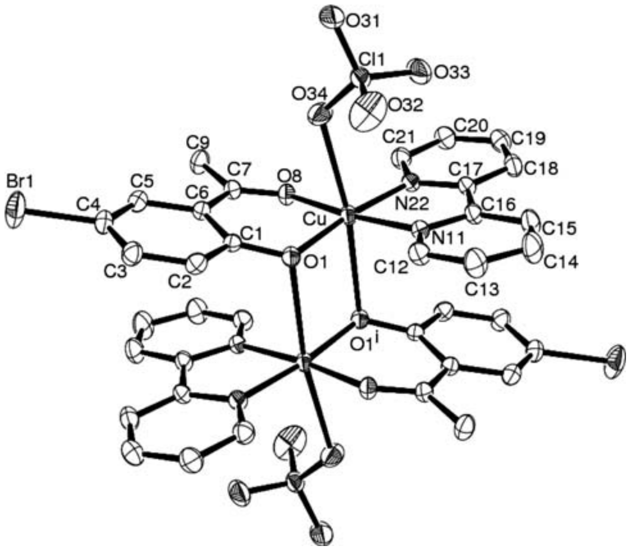


Figure 1. An ORTEP view of **1** (symmetry code: $^i1-x, -y, -z$). Displacement ellipsoids are drawn at the 50% probability level.

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

Cu-O1	1.898(3)	Cu-N11	1.988(4)
Cu-O8	1.949(3)	Cu-O34	2.477(3)
Cu-N22	1.981(3)	Cu-O1^i	2.632(3)
O1-Cu-O8	91.09(12)	O1^i-Cu-O8	90.96(10)
O1-Cu-O34	91.59(14)	O34-Cu-N11	95.79(13)
O1-Cu-N11	94.74(13)	O34-Cu-N22	94.20(15)
O1-Cu-N22	173.40(13)	O1^i-Cu-O34	171.22(11)
O1-Cu-O1^i	83.43(10)	N11-Cu-N22	81.53(14)
O8-Cu-O34	81.88(12)	O1^i-Cu-N11	91.84(12)
O8-Cu-N11	173.80(13)	O1^i-Cu-N22	91.22(11)
O8-Cu-N22	92.87(13)	–	–

Symmetry code: (^{i}) $1-x, -y, -z$.

bond distances, suggesting Jahn Teller distortion [39–41]. Distortion is also evident from the relative displacement of the metal centers by 0.025 Å from the mean equatorial plane and the deviation of *cis* and *trans* angles from their ideal values of 90 and 180°, respectively (table 2). However, the Cu–N and Cu–O bond distances found for **1** are in close agreement with similar six-coordinate copper(II) complexes [2, 42–44]. Four donors (N11, N22, O1, and O8) remain almost coplanar within ±0.06 Å with respect to the mean equatorial plane. Two planar moieties (bipy and 5-Br-2-hap) in the basal plane are also slightly inclined from each other (6.05°). Crystal packing of **1** reveals that the complex units form a 3-D supramolecular structure through various C–H … O interactions (table 3).

The structure of **1** may be compared with the structure of **2** reported earlier [2]. Both complexes were synthesized from similar reactants bearing identical donor sets. In fact, **2** crystallizes in the space group $P2_1/c$ with similar cell parameters. The arrangement of the molecules in the lattice is also nearly identical. In **2**, two complex units are arranged by the symmetry center but the Cu … O1^i distance is larger 3.019 Å compared to the 2.632 (3) Å in the dimeric structure **1**. The acetylphenolato in **1** contains bromine as substituent, responsible for this difference. The electron-withdrawing inductive effect of bromine in **1** made the metal center electronically unsaturated, leading to the formation of relatively strongly coordinated phenolato oxygen from symmetry related moiety in comparison with **2** where such effect is absent. The Cu-O(ketonic) bond distance in **1** is slightly longer than that of **2**, which also supports the role of bromine in its structure variations.

3.5. *Catalytic epoxidation reactions*

Olefin epoxidation catalyzed by transition-metal-based catalysts under homogeneous conditions is well documented [45]. Styrene oxide is an important organic intermediate for production of a number of fine/specialty chemicals and pharmaceuticals. Epoxidation of

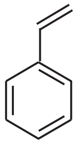
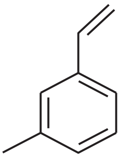
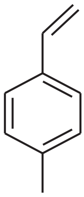
Table 3. Hydrogen bonding parameters (Å, °) for **1**.

D–H … A	d(D–H)	d(H … A)	d(D … A)	(D–H … A)
C12–H12 … O1	0.94	2.55	3.049(6)	113
C14–H14 … O32^a	0.94	2.52	3.135(8)	123
C18–H18 … O31^b	0.94	2.58	3.198(7)	124.00
C18–H18 … O33^b	0.94	2.47	3.401(7)	172.00
C21–H21 … O8	0.94	2.46	2.985(6)	115.00

Symmetry codes: (^{a}) $-x, -y, -z$ (^{b}) $1/2-x, -1/2+y, 1/2-z$.

styrene to styrene oxide is quite difficult, and in many cases, benzaldehyde or phenylacetaldehyde are produced in large excess. Seelan *et al.* studied epoxidation of styrene over copper phthalocyanine-immobilized NaY catalyst under heterogeneous condition, which shows over 95% conversion with epoxide selectivity ~24% [46]. Selectivity of the epoxide improves (~53%) when copper-perchloro-phthalocyanine has been anchored onto MCM-41; however, conversion remains within 47% [47]. In epoxidation of styrene with tert-BuOOH over copper/copper complex immobilized zeolite or molecular sieves catalysts, epoxide selectivity rarely goes above 40% [48]. The yield of styrene epoxidation improved significantly (up to 86%) when copper(II) Schiff-base anchored MCM-41 catalyst was used [49]. Examples of epoxidation reactions, homogeneously catalyzed by copper complexes are limited, and in many of the cases, tert-BuOOH was used as oxidant [14–17]. Rayati *et al.* studied epoxidation of styrene over [Cu(hnaphnptn)] (H_2\{hnaphnptn\} = Schiff-base derived from condensation of 2,2′-dimethylpropandiamine and 2-hydroxy-1-naphthaldehyde) and [Cu\{salnptn(3-OMe)$_2$\}] (H_2\{salnptn(3-OMe)$_2$\} = Schiff-base derived from condensation of 2,2′-dimethylpropandiamine and o-vanillin) under homogeneous conditions using tert-BuOOH, which shows over 95% conversion with epoxide selectivity ~25% [14]. Koner *et al.* studied this reaction over Cu(II) Schiff-base complexes, $[Cu(L^2)(H_2O)](ClO_4)$ (HL^2 = 1-(*N-ortho*-hydroxy-acetophenimine)-2-methylpyridine), $[Cu(L^3)]$ (HL^3 = *N,N′*-(2-hydroxy-propane-1,3-diyl)-bis-salicylideneimine), $[Cu(L^4)]$ (HL^4 = *N,N′*-(2,2-dimethyl-propane-1,3-diyl)-bis-salicylideneimine), which gives styrene epoxide in 54–39% yield (selectivity 72–39%) under homogeneous conditions with tert-BuOOH [15]. Saha *et al.* reported styrene reaction over $[Cu(HL^1)(NO_3)]$ (H_2L^1 = 1-(*N-ortho*-hydroxyacetophenimine)-ethane-2-ol), which shows 86% conversion with ~100% epoxide selectivity [17]. In this study, styrene and substituted styrene react with H_2O_2 to produce epoxides with remarkable selectivity in good yield using **1** and **2** in homogeneous conditions. The results of the catalytic epoxidation of different substrates are given in table 4. The epoxidation of styrene with H_2O_2 gives styrene oxide in 100% conversion (selectivity ~80% for **1** and ~58% for **2**); along with this, a small amount of benzaldehyde is also detected. Homogeneous oxidation of 3-Me styrene proceeded smoothly, showing 100% conversion to form 3-Me styrene oxide as the major product with ~85 and ~64% selectivity for **1** and **2**, respectively; along with this, 3-Me benzaldehyde was also generated. 4-Me styrene has also been effectively converted to 4-Me epoxy-styrene (conversion 100% for **1** and **2**, selectivity 88% for **1** and 66% for **2**); along with this, 4-Me benzaldehyde was also produced. A high turnover frequency has been attained (~166 h^{-1} for **1** and ~189 h^{-1} for **2**) for epoxide production. A graphical representation of relative efficacy of **1** and **2** for epoxidation of styrene/substituted styrene with time is given in figure 2, respectively. Copper(II) can bind the peroxo group on treatment with peroxides [50], and the pre-catalyst species containing L_xCu–OOH seem to be capable of transferring the oxo functionality to the organic substrates to give the corresponding oxidized products [51, 52]. In our case, we propose that a similar kind of mechanism is operative. X-ray crystal structure analysis of **2** shows that the coordination environment around the copper(II) ion is easily accessible for an external ligand, as a result hydroperoxide gets enough space to bind copper in the intermediate stages of the catalytic cycle. In **1**, although the copper(II) ion is six coordinate, the peroxo intermediate may be formed due to replacement of any coordination site. Bezaatpour *et al.* [53] synthesized five nickel(II) Schiff-base complexes and immobilized them on sodium montmorillonite clay matrix and studied the catalytic activity of both nickel(II) Schiff-base complexes and their immobilized systems in cyclooctene epoxidation in the presence of tert-BuOOH as oxidant. In comparison with our

Table 4. Epoxidation of olefins catalyzed by **1**[a] and **2**[a].

Substrate	Reaction time (h)	Conversion (wt.%)	Epoxide yield (wt.%)	Turnover frequency (TOF)[b] (h^{-1})
	a) 8 b) 6	a) 100 b) 100	a) 80 b) 58	a) 166 b) 189
	a) 8 b) 6	a) 100 b) 100	a) 85 b) 64	a) 166 b) 189
	a) 8 b) 6	a) 100 b) 100	a) 88 b) 66	a) 166 b) 189

[a] Reaction conditions: alkenes (5 mM); catalyst (2 mg); 1.5 ml of 30% H_2O_2 (7.5 mM, 1.5 equiv.); acetonitrile (5 mL). Temperature of the reaction medium was kept at 60 °C for **1** and 45 °C for **2**. The products of the epoxidation reactions were collected at different time intervals and were identified and quantified by HP 6890 series gas chromatograph equipped with an FID detector and an HP-5 GC column (Agilent Technologies). Entries (a) and (b) correspond to the catalytic performance of **1** and **2**, respectively.
[b] TOF = moles converted per moles of active site per unit time.

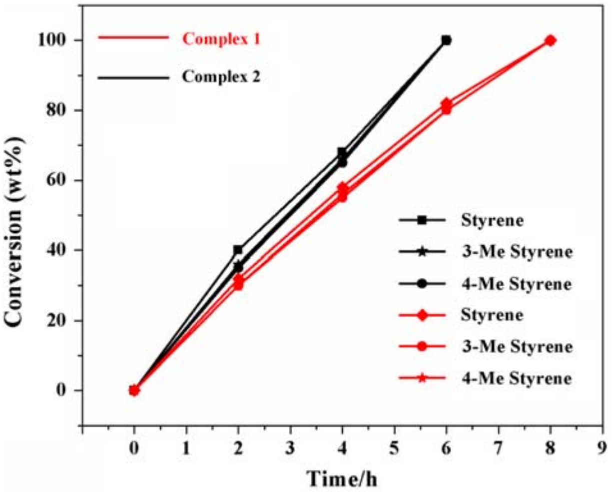


Figure 2. Plot of catalytic efficacy of **1** (red solid line) and **2** (black solid line) for epoxidation of styrene/substituted styrene.

Table 5. Epoxidation of styrene with various oxidants over **1**[a] and **2**[a].

Catalyst	Reaction time (h)	Oxidant	Conversion (wt.%)	Epoxide yield (wt.%)
1	8	None	Not traceable	–
1	8	H_2O_2	100	80
1	8	tert-BuOOH	62	68
1	8	NaOCl	34	42
2	6	None	Not traceable	–
2	6	H_2O_2	100	58
2	6	tert-BuOOH	52	55
2	6	NaOCl	28	28

[a]Reaction conditions were the same as given in footnote of table 4.

Table 6. Solvent effect in epoxidation of styrene catalyzed by **1**[a] and **2**[a].

		% of conversion (% of epoxide yield) in different solvents			
Compound	Reaction time (h)	CH_3CN	CH_3COCH_3	C_2H_5OH	CH_3OH
1	8	100 (80)	68 (72)	42 (78)	36 (75)
2	6	100 (58)	75 (55)	60 (52)	56 (50)

[a]Reaction conditions were the same as given in footnote of table 4.

Table 7. Temperature effect in epoxidation of styrene catalyzed by **1**[a] and **2**[a].

Compound	Reaction time (h)	% of conversion (% of epoxide yield) at different temperature			
1	8	40 °C 50 (80)	50 °C 80 (80)	60 °C 100 (80)	65 °C 100 (80)
2	6	30 °C 60 (58)	40 °C 86 (58)	45 °C 100 (58)	50 °C 100 (50)

[a]Reaction conditions were the same as given in footnote of table 4.

copper(II) complexes, those nickel(II) Schiff-base complexes showed poor catalytic activity (conversion 32–47%, selectivity 48–63%) under homogeneous conditions. Although conversion increased in case of immobilized heterogeneous systems, the conversion 36–67% and selectivity 55–70% were not as impressive as for **1**. Nooraeipour *et al*. [54] studied epoxidation of styrene over multi-wall carbon nanotube supported tungsten hexacarbonyl in the presence of H_2O_2 as oxidant, but the conversion (76%) and selectivity (73%) did not exceed the results obtained for **1**. Thus **1** performed better in epoxidation reaction than these reported transition-metal-based catalysts [53, 54].

The efficacy of different oxidants like tert-BuOOH, H_2O_2 and NaOCl in **1** and **2** catalyzed epoxidation reaction of styrene under homogeneous condition have been studied. The results of this study are given in table 5. H_2O_2 is most efficient. The catalytic reaction was performed in a variety of solvents to study the catalytic efficacy of **1** and **2** in different solvent media. The best performance was observed in acetonitrile (table 6). The optimum polarity of acetonitrile that dissolves both olefin and H_2O_2 might be facilitating the epoxidation reactions in this solvent. The efficiency of catalysts followed the order: acetonitrile > acetone > ethanol > methanol. The catalytic reaction was also performed at different temperatures with best performance for **1** at 60–65 °C and for **2** at 40–45 °C (table 7).

4. Conclusion

To investigate the influence of the electron-withdrawing bromine on structure variation, we synthesized a new copper(II) complex using 5-Br-2-hap (with bromine) and bipy and compared it with an earlier reported compound synthesized from 2-hap along with the same co-ligand. The electron-withdrawing bromine made the metal center electronically unsaturated, leading to a dimeric structure. This structural variation was assessed in homogeneous styrene epoxidation using different oxidants, while best results obtained with hydrogen peroxide. Although the complex reported earlier possesses easy accessible coordination environments for attack of hydrogen peroxide, the complex reported herein shows higher epoxide selectivity.

Supplementary data

CCDC 857874 contains the supplementary crystallographic data for **1** reported in this article. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/ci0066.

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