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# Synthesis, characterization and catalytic activities towards epoxidation of olefins of dinuclear copper(II) complexes

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# ABSTRACT

Two copper(II) complexes,  $[Cu_2(L^1)Cl_3].2H_2O(1)$  and  $[Cu_2(L^2)(N_3)Cl_2](2)$  where  $HL^1 = 4$ -methyl-2,6bis((2-morpholinoethylimino)methyl)phenol and  $HL^2 = 4$ -methyl-2,6-bis((3-morpholinopropylimino) methyl)phenol have been synthesized and characterized by elemental analysis, various spectroscopic methods, TGA and single crystal X-ray diffraction analysis. Single crystal X-ray diffraction analysis reveals that in both the complexes, two copper atoms are linked by phenoxo oxygen atom and a bridging ligand, namely chloride and azide, respectively. These complexes have been used as catalyst for the epoxidation of cyclohexene, styrene,  $\alpha$ -methyl styrene, *trans*-stilbene and norbornene using *tert*-butyl hydroperoxide as the oxidant in acetonitrile under mild conditions. All of the substrates undergo conversion to produce respective epoxide as the major product.

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# 1. Introduction

Mono-, di- and polynuclear transition metal complexes with Schiff-base ligands are of great interest to the researchers from all over the globe because of their diversity in structural topology and effective applications in many fields of scientific investigations e.g. magnetism, catalysis, biochemical reactions, sensing etc. [1–10]. Metal complexes with this type of ligands have become research hot spot over few decades because Schiff-base ligands could be easily synthesized by one step condensation reaction and many properties of the complexes with these ligands could be controlled by introducing various substitutions (e.g. electron pushing group, electron withdrawing group, bulky group, etc.) on both the amine and the aldehyde/ketone groups. Usually, Schiff base ligands produce stable complexes with a large number of transition metal ions, providing the platform to study different aspects of such complexes and their applications. These types of ligands stabilize different metal ions at their various oxidation states. Therefore, Schiff-base ligands play a crucial role in controlling the conversions of a number of organic reactions catalyzed by transition metal complexes with Schiff-base ligands.

\* Corresponding author. *E-mail address:* proy@chemistry.jdvu.ic.in (P. Roy). Dinuclear complexes can be synthesized by the reaction of metal ions and suitable ligands with appropriate 'donor pocket'. Ligands are designed in such a way that it can accommodate two metal ions by linking through N,O donor atoms. Acyclic Schiff-base ligands derived from 4-methyl-2,6-diformylphenol (DFP) are suitable to produce dinuclear metal complexes under controlled reaction conditions [11]. Deprotonated phenolic oxygen atom of such ligand binds two metal centers simultaneously and at the same time, other O and/or N donor atoms of the same ligand coordinate to metal ions to form a chelate. Ancillary ligands e.g. hydroxido, azido, carboxylato, halido etc. may be present in the metal complex to provide some extra stability to the metal complex.

Many published research articles described syntheses of transition metal complexes and their applications in different catalytic reactions. These complexes were found to be active catalyst for various catalytic reactions and selectivity of the desired product was excellent. Copper(II) compounds were widely used as catalysts in catechol oxidation, epoxidation, sulfoxidation, olefin aziridination, alkane oxidation, atom transfer radical addition (ATRA) [3,4] etc. in homogeneous as well as heterogeneous media. Epoxidation of olefins is an important reaction in organic chemistry because epoxides are versatile building blocks for the synthesis of many bioactive molecules and organic fine chemicals [12,13]. Cu(II) complexes were employed extensively as efficient catalysts for epoxidation of various substrates where epoxides were detected as





the major product [14–18].

In continuation to our interest in C–H activation [19–22], we report here synthesis, characterization and catalytic properties of two copper(II) complexes,  $[Cu_2(L^1)Cl_3].2H_2O$  (1) and  $[Cu_2(L^2)(N_3)$   $Cl_2]$  (2) where  $HL^1 = 4$ -methyl-2,6-bis((2-morpholinoethylimino) methyl) phenol and  $HL^2 = 4$ -methyl-2,6-bis((3-morpholinopropylimino)methyl)phenol. These complexes have been characterized by elemental analysis, various spectroscopic methods and single crystal X-ray diffraction analysis. They were found to be active catalyst for epoxidation of various olefins in acetonitrile in the presence of *tert*-butyl hydroperoxide as the oxidant under mild conditions.

# 2. Experimental section

# 2.1. Materials and physical methods

4-(2-Aminoethyl)morpholine and 4-(3-aminopropyl)morpholine were purchased from Sigma Aldrich. All other reagents were obtained from commercial source and used as received. 4-Methyl-2,6-Diformylphenol (DFP) was synthesized following a published procedure [23]. Solvents used for spectroscopic studies were purified and dried by standard procedures before use [24]. FT-IR spectra were obtained on a RX-1 Perkin Elmer spectrophotometer with samples prepared as KBr pellets. Elemental analysis was carried out in a 2400 Series-II CHN analyzer, Perkin Elmer, USA. The ESI-MS was recorded on Otof Micro YA263 mass spectrometer. Absorption spectra were recorded on Lambda 25 Perkin Elmer spectrophotometer. Thermogravimetric analysis was performed on a Mettler Toledo instrument (Model no.: TGA/SDTA-851e). Gas chromatography analysis was performed with a Shimadzu made next generation high speed gas chromatography system (model: GC-2025 AF) equipped with a fused silica capillary column and a FID detector. All experiments were carried out at room temperature in air unless reported otherwise.

# 2.1.1. Synthesis of 4-methyl-2,6-bis((2-morpholinoethylimino) methyl) phenol ( $HL^1$ )

To a 20 mL methanolic solution of DFP (0.065 g, 0.4 mmol), 4-(2-aminoethyl)morpholine (0.104 g, 0.8 mmol) was added. The resulting mixture was stirred for 15 min and then it was refluxed for 2 h. This 'solution of  $\rm HL^{1}$ ' was used for subsequent reactions without isolation and further purification or characterization.

# 2.1.2. Synthesis of 4-methyl-2,6-bis((3-morpholinopropylimino) methyl) phenol ( $HL^2$ )

4-(3-Aminopropyl)morpholine (0.115 g, 0.8 mmol) was added to methanolic solution (20 mL) of DFP (0.065 g, 0.4 mmol) and the resulting solution was stirring for 15 min and then refluxed for 2 h. This 'solution of  $\rm HL^{2}$ , was used for subsequent reactions without isolation and further purification or characterization.

# 2.1.3. Synthesis of $[Cu_2(L^1)Cl_3].2H_2O(1)$

Copper(II) chloride dihydrate (0.136 g, 0.8 mmol) was added into the Schiff base solution ( $HL^1$ , '0.4 mmol') in methanol and stirred for 30 min. Aqueous solution (2.0 mL) of sodium azide (0.026 g, 0.4 mmol) was added drop by drop into the mixture with constant stirring. After its addition, the mixture was refluxed for 1 h. Then it was cooled to room temperature. The mixture was filtered and the filtrate was kept at ambient temperature. From the filtrate, green colored crystals of complex **1** suitable for single crystal X-ray diffraction were obtained on evaporation of solvent within few days. Yield: 0.170 g, 65%. *Anal.* Calc. for  $C_{21}H_{35}Cl_3N_4O_5Cu_2$ : C, 38.39; H, 5.37; N, 8.52. Found C, 38.33; H, 5.30; N, 8.60.

# 2.1.4. Synthesis of $[Cu_2(L^2)(N_3)Cl_2]$ (2)

Copper(II) chloride dihydrate (0.136 g, 0.8 mmol) was added into the Schiff base solution ( $HL^2$ , '0.4 mmol') in methanol and stirred for 30 min. Aqueous solution (2.0 mL) of sodium azide (0.026 g, 0.4 mmol) was added dropwise into the mixture with constant stirring. After that, it was refluxed for 1 h. Then it was cooled to room temperature. The mixture was filtered and the filtrate was kept at ambient temperature. From the filtrate, brown colored crystals of complex **2** suitable for X-ray diffraction were obtained on evaporation of solvent within two weeks. Yield: 0.117 g, 45%. *Anal.* Calc. for C<sub>23</sub>H<sub>35</sub>Cl<sub>2</sub>N<sub>7</sub>O<sub>3</sub>Cu<sub>2</sub>: C, 42.10; H, 5.38; N, 14.95. Found C, 42.03; H, 5.33; N14.99.

*Caution!* Azide salts are potentially explosive and should be handled in small quantities with care. No problems were faced with the complexes reported herein.

#### 2.1.5. X-ray data collection and structure determination

The crystal data of complexes 1 and 2 are summarized in Table 1. The structures of the complexes were determined by single crystal X-ray diffraction analysis. Single crystal data collections were performed with an automated Bruker SMART APEX CCD diffractometer using graphite monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Reflection data were recorded using the  $\omega$  scan technique. Unit cell parameters were determined from least-squares refinement of setting angles with  $\theta$  in the range 1.62  $< \theta < 26.50^{\circ}$ . For complex 1, out of 18,842 collected data 5379 with I >  $2\sigma$  (I) were used for structure solution. For complex 2. out of 40.108 collected data 5697 with  $I > 2\sigma(I)$  were used for structure solution. The structures were solved and refined by full-matrix least-squares techniques on  $F^2$ using the SHELXS-97 program [25]. The absorption corrections were done by the multi-scan technique. All data were corrected for Lorentz and polarization effects, and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated using SHELXL-97 [25] and their positions calculated based on the riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of the final R-indices.

#### 2.1.6. Catalytic activity

10.0 mmol of the substrate in 5.0 mL of acetonitrile was taken in a magnetically stirred two necked round-bottomed flask fitted with a condenser, followed by the addition of 0.03 mmol of the metal complex. The mixture was heated to 323 K. 20.0 mmol of *tert*-butyl hydroperoxide was added to the mixture to initiate the catalytic reaction. Aliquots from the mixture were collected at regular time interval. 10.0 mL of diethylether were added for extracting the reactants and product(s). The substrate and product(s) were analyzed by gas chromatography and identified by the comparison with known standards.

A blank experiment, namely epoxidation of cyclohexene, was carried out as the representative case without addition of any catalyst under the same experimental conditions. Another blank reaction for the epoxidation of cyclohexene was performed in the presence of copper(II) chloride in place of copper(II) complex with all other parameters unchanged.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

Complexes **1** and **2** were synthesized following a reaction pathway as shown in Scheme 1. The ligand, **HL**<sup>1</sup>, was prepared by refluxing one equivalent of DFP and two equivalents of 4-(2-aminoethyl)morpholine in methanol for 2 h. Complex **1** was synthesized by *in situ* reaction between the ligand, copper(II) chloride

	Complex 1	Complex <b>2</b>
Formula	C <sub>21</sub> H <sub>31</sub> Cl <sub>3</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>5</sub>	C <sub>23</sub> H <sub>35</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>7</sub> O <sub>3</sub>
Formula weight	652.95	655.58
Temperature (K)	294(2)	293(2)
Color	green	green
Crystal system	triclinic	monoclinic
Space group	P-1	P21/C
a (Å)	7.522(5)	14.255(5)
b (Å)	10.600(5)	10.519(5)
c (Å)	17.040(5)	20.629(5)
α (°)	100.377(5)	90.000(5)
B (°)	98.547(5)	100.104(5)
γ(°)	91.971(5)	90.000(5)
V(Å <sup>3</sup> )	1319.0(11)	3045.6(3)
Z	2	4
Crystal dimensions (mm)	$0.14 \times 0.09 \times 0.06$	$0.15\times0.09\times0.07$
F(000)	668	1256
$D_c (g cm^{-3})$	1.644	1.430
λ(Mo Kα) (Å)	0.71073	0.71073
θ range (°)	27.98-1.96	25.40-1.45
Reflection collected/unique	19,810, 6343	40,981, 5613
Absorption correction	multi-scan	multi-scan
R <sub>int</sub>	0.0592	0.0697
Final R indices $[I > 2\sigma(I)]$	$R_1=0.0836$ , $wR_2=0.2575$	$R_1 = 0.0516$ , $wR_2 = 0.1541$
Goodness-of-fit	1.107	0.915





Scheme 1. Synthesis of complex 1 and 2.

dihydrate and one equivalent of sodium azide in methanol/water mixture. No external base was used. However, complex **1** does not contain any azide ion. So another reaction was performed without sodium azide to get **1**. Even after several attempts, complex **1** could not be obtained when sodium azide was not used. Here, sodium azide may act as weak base to deprotonate phenolic proton of **HL**<sup>1</sup>. The ligand, **HL**<sup>2</sup>, was prepared by the reaction between one equivalent of DFP and two equivalents of 4-(3-aminopropyl)morpholine in methanol. Complex **2** was also synthesized by *in situ* reaction between the ligand, two equivalents of copper(II) chloride dihydrate and one equivalent of sodium azide in methanol/water mixture. It contains one azide ion to bridge two copper centers. Here also no external base was used.

FT-IR spectra of complexes **1** and **2** were recorded with sample prepared as KBr pellet. In the spectrum of complex **1**, the band around 1660 cm<sup>-1</sup> is due to the presence of C=N moiety. The band at 3402 cm<sup>-1</sup> may be assigned to the  $v_{Cu-O}$  of ligand. The band at 589 cm<sup>-1</sup> may be attributed to  $v_{Cu-N}$  [26]. FT-IR spectrum of complex **1** shows strong  $v_{C-H}$  bands at 2800–3000 cm<sup>-1</sup> [27]. The sharp band at 2095 cm<sup>-1</sup> indicates the presence of azido moiety in complex **2**. The presence of C=N bond in Schiff-base complex has been confirmed from the band that appeared at 1638 cm<sup>-1</sup>. The band at 3402 cm<sup>-1</sup> may be assigned to the  $v_{Cu-O}$  of ligand. The band at 509 cm<sup>-1</sup> may be assigned to the  $v_{Cu-O}$  of ligand. The band at 509 cm<sup>-1</sup> may be assigned to the  $v_{Cu-O}$  of ligand. The band at 509 cm<sup>-1</sup> may be attributed to  $v_{Cu-N}$  [26]. FT-IR spectrum of complex **2**, like complex **1**, also exhibits strong  $v_{C-H}$  bands in the region of 2800–3000 cm<sup>-1</sup>.

Magnetic susceptibilities of the complexes **1** and **2** were measured with powdered sample at 298 K using Guoy balance method. Both the complexes have been expected to show a similar behavior. The dinuclear complexes of copper(II) with Schiff-base ligands have reported to show antiferromagnatic interactions between the metal centers [28,29]. The magnetic moment of two isolated copper(II) ions has been calculated to be 2.83 BM. If the measured magnetic moment is found to be smaller than the calculated value, then it indicates antiferromagnetic coupling among the copper atoms at 298 K. The magnetic moments of complexes **1** and **2** have been determined to be 0.97 and 0.29 BM respectively. These values are too small compared to 2.83 BM expected for isolated copper atoms indicating strong antiferromagnetic interactions amongst copper atoms at 298 K.

#### 3.2. Description of crystal structure of complex 1

Complex 1 crystallizes in the P-1 space group from methanol. A perspective view of the molecule is shown in Fig. 1. Selected bond angles and bond lengths are listed in Table 2. Complex 1 consists of one deprotonated molecule of ligand, 4-methyl-2,6-bis((3morpholinopropylimino)methyl)phenol, two copper atoms and three chlorine atoms. Two water molecules are present in the unit cell as solvent of crystallization. Both the copper atoms are in a pentacoordinated environment. Cu1 is coordinated to one phenolic oxygen atom (O1), two nitrogen atoms (N1 and N2) from the ligand, HL<sup>1</sup>, and two chlorine atoms Cl1 and Cl3. Phenolic oxygen atom O1 and chlorine atom Cl3 act as bridging center. On the other hand, Cu2 is bonded to one phenolic oxygen atom (O1), two nitrogen atoms (N3 and N4) from the ligand, and two chlorine atoms Cl2 and Cl3. Both the copper atoms are in distorted square pyramidal geometry as revealed by trigonal index.  $\tau$  value. The value of trigonal index is defined as the difference between the two largest donor-metal-donor angles divided by 60, a value which is 0 for the ideal square pyramid and 1 for trigonal bipyramid geometry [30].  $\tau$  values for Cu1 and Cu2 have been found to be 0.155 and 0.017 respectively. O1, N1, N2 and Cl3 form the basal plane of square pyramid while Cl1 occupies the apical position. Cu1-chlorine distances are longer compare to other Cu1-donor distances. Cu1--Cl1<sub>apical</sub> distance is quite longer than the others. Cu1 is out of the mean plane formed by O1, N1, N2 and Cl3 and towards Cl1 by 0.182 Å. O1, N3, N4 and Cl3 form the basal plane of square pyramid while Cl2 occupies the apical position. Cu2-chlorine distances are longer compare to other Cu2-donor atom distances. Cu1-Cl1<sub>apical</sub> distance is quite longer than the others. Cu2 is out of the mean plane formed by O1, N3, N4 and Cl3 and towards Cl2 by 0.328 Å.

#### Table 2

Selected coordination bond lengths (Å) and angles (°) for complex **1**.

Cu01-N1	1.949(4)	Cu2-N3	1.936(4)
Cu01-01	1.979(3)	Cu02-01	2.006(4)
Cu01-N3	2.072(5)	Cu02-N4	2.082(4)
Cu01–Cl3	2.3148(18)	Cu02-Cl3	2.3005(17)
Cu01–Cl1	2.5230(2)	Cu02-Cl2	2.528(2)
N1-Cu01-01	91.67(17)	N2-Cu02-01	91.35(16)
N1-Cu01-N3	84.70(19)	N2-Cu02-N4	84.45(18)
01-Cu01-N3	165.80(17)	01-Cu02 N4	163.01(17)
N1-Cu01-Cl3	156.50(15)	N2-Cu02-Cl3	160.28(13)
01-Cu01-Cl3	82.87(11)	01-Cu02-Cl3	82.66(10)
N3-Cu01-Cl3	95.02(14)	N4-Cu02-Cl3	95.81(13)
N1-Cu01-Cl1	95.50(15)	N2-Cu02-Cl2	94.35(13)
01-Cu01-Cl1	99.37(12)	01-Cu02-Cl2	102.04(12)
N3-Cu01-Cl1	94.64(14)	N4-Cu02-Cl2	94.70(14)
Cl3-Cu01-Cl1	107.93(8)	Cl3-Cu02-Cl2	105.26(8)

#### 3.3. Description of crystal structure of complex 2

Complex 2 crystallizes in the P21/C space group from methanol. A perspective view of the molecule is shown in Fig. 2. Selected bond angles and bond lengths are given in Table 3. Complex 2 is composed of one deprotonated molecule of ligand, 4-methyl-2,6bis((3-morpholinopropylimino)methyl)phenol, two copper atoms. two chlorine atoms and one azide mojety. Both the copper atoms are in pentacoordinated environment. Cu1 is coordinated to one phenolic oxygen atom (O1), two nitrogen atoms (N1 and N2) from the ligand, HL<sup>2</sup>, and one chlorine atom Cl1 and one azide. Phenolic oxygen atom O1 and one azide  $(\mu_{1,1})$  act as bridging center. On the other hand, Cu2 is bonded to one phenolic oxygen atom (O1), two nitrogen atoms (N3 and N4) from the ligand, one chlorine atom Cl1 and one azide. Both the copper atoms are in distorted square pyramidal geometry as revealed by trigonal index,  $\tau$  value,  $\tau$  values for Cu1 and Cu2 have been calculated to be 0.212 and 0.294 respectively. Cl1, N5, O1 and N1 form the basal plane of square pyramid for Cu1 while N2 occupies the apical position. Cu1–N2<sub>apical</sub> distance is quite longer than the others. Cu1 is out of the mean plane formed



Fig. 1. A perspective view of complex 1. Hydrogen atoms and water molecules were omitted for clarity.



Fig. 2. A perspective view of complex 2. Hydrogen atoms were omitted for clarity.

 Table 3

 Selected coordination bond lengths (Å) and angles (°) for complex 2.

	9 · · ( ) ·	0 ( ) I I	
Cu1-N1	1.941(4)	Cu2–N2	1.939(4)
Cu1-N5	1.960(4)	Cu2-N5	1.963(4)
Cu1-01	2.026(3)	Cu2-01	2.024(3)
Cu1–Cl1	2.2797(15)	Cu2–Cl2	2.2705(17)
Cu1-N3	2.430(5)	Cu2–N4	2.374(4)
N1-Cu1-N5	165.78(17)	N2-Cu2-N5	165.65(17)
N1-Cu1-01	91.39(14)	N2-Cu2-01	91.16(14)
N5-Cu1-01	75.17(14)	N5-Cu2-01	75.13(15)
N1-Cu1-Cl1	99.08(12)	N2-Cu2-Cl2	98.51(13)
N5-Cu1-Cl1	91.28(13)	N5-Cu2-Cl2	91.25(13)
01-Cu1-Cl1	153.05(11)	01-Cu2-Cl2	148.02(11)
N1-Cu1-N3	83.69(17)	N2-Cu2-N4	83.96(17)
N5-Cu1-N3	104.61(18)	N5-Cu2-N4	104.92(17)
01-Cu1-N3	107.94(16)	01-Cu2-N4	112.10(15)
Cl1-Cu1-N3	97.91(13)	Cl2-Cu2-N4	99.25(11)

by Cl1, N5, O1 and N1 towards N2 by 0.286 Å. Cl2, N5, O1 and N3 form the basal plane of square pyramid for Cu1 while N4 occupies the apical position. Cu1–N4<sub>apical</sub> distance is quite longer than the others. Cu1 is out of the mean plane formed by Cl2, N5, O1 and N3, and towards N4 by 0.650 Å. It is to be noted that for complex **1**, Cl atoms occupy the apical position of square pyramid around Cu1 and Cu2 whereas for complex **2**, morpholinium-N atoms of the ligand reside in the apical possible for complex **2** because of longer C–C chain length.

# 3.4. UV-vis spectra

The electronic spectrum of complex **1** was recorded in acetonirtile. It exhibits a broad band at 615 nm (molar extinction coefficient: 3010  $M^{-1}s^{-1}$ ), which may be assigned to d-d transition. Higher intensity charge-transfer transitions are obtained at 370 and 253 nm, with molar extinction coefficients of 6390  $M^{-1}s^{-1}$  and 31,200  $M^{-1}s^{-1}$ , respectively, attributed to PhO<sup>-</sup>  $\rightarrow$  Cu(II), N(amino)  $\rightarrow$  Cu(II) LMCT and intraligand charge transfer transitions [31].

The electronic spectrum of complex **2** in acetonitrile shows several absorption bands in the visible region that are assigned to d-d and charge-transfer transitions. It exhibits a broad band at 712 nm (molar extinction coefficient: 337 M<sup>-1</sup>s<sup>-1</sup>) due to d-d transition. The band at 372 nm (molar extinction coefficient: 733 M<sup>-1</sup>s<sup>-1</sup>) may be attributed to PhO<sup>-</sup>  $\rightarrow$  Cu(II) and N(amino)  $\rightarrow$  Cu(II) LMCT. Higher intensity charge-transfer transitions at 254 nm, with molar extinction coefficient 3480 M<sup>-1</sup>s<sup>-1</sup> may be assigned to intraligand charge transfer transitions [31].

### 3.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis of complex **1** has been carried out with the powdered samples under nitrogen atmosphere in the range 30–700 °C. Thermal analysis of complex **2** could not be performed due to the presence of azide ion which could be a potential explosive under heating conditions. Mass *vs* temperature plot of complex **1** is given in Supplementary information. Complex **1** shows four step weight loss upto 700 °C. It is clear from the figure that it is stable about 70 °C. After that it starts to lose water molecules from it. Within 150 °C, complex **1** lost two water molecules (2.74% weight loss vs. 2.75% calculated weight loss). After that complex **1** loses some unidentified organic moiety and mass lost becomes quite stable near temperature region of 700 °C. Thus, the presence of water molecule is also indicated by the TGA study.

## 3.6. Epoxidation of olefins

Complexes 1 and 2 have been used as catalysts for the oxidation of cyclohexene, styrene,  $\alpha$ -methyl styrene, *trans*-stilbene and norbornene with tert-butyl hydroperoxide as the oxidant at 323 K. Respective epoxides have been detected as the major products in each reaction. The results of catalytic conversions have been given in Table 4. It is clear from the initial inspection of the table that complexes 1 and 2 are effective catalysts for such organic transformations. Complex 2 has been found to be the most active catalyst and it catalyzes cyclohexene epoxidation with 86% conversion and 91% selectivity whereas complex 1 transforms cyclohexene with 84% conversion and 88% selectivity. 2-Cyclohexen-1-ol and 2cyclohexen-1-one have been detected as the minor products. Epoxidation of styrene draws special attention from industry and academics. Complexes 1 and 2 can act as catalyst for the epoxidation of styrene with 72% and 75% conversions, respectively. Styrene oxide has been detected as the major product with the formation of small amount of benzaldehyde. *a*-Methyl styrene has been converted to its epoxide in the presence of both the metal complexes with good yield and selectivity. Epoxidation of trans-stilbene reveals that conversions of it in the presence of complexes 1 and 2 are 78% and 81%, respectively. Corresponding epoxide formation selectivity for 1 and 2 is also quite high (87% and 85% respectively). These metal complexes can also effectively convert bulkier alkene. In this respect, we have tried with norbornene. Excepoxvnorbornane has been identified as the major product in the case of norbornene epoxidation. Norbornene is converted to 80% and 82% in the presence of **1** and **2**, respectively, with high selectivity towards the corresponding epoxide. All these results for the epoxidation of olefins are comparable to those reactions catalyzed by different transition metal complexes [17-19,32-35]. Although there is scope for the improvement of the yield, selectivity and reaction time, these experiments show that these copper(II) complexes can be used as catalysts for such reactions.

Hydrogen peroxide could have been a better oxidant in comparison to *tert*-butyl hydroperoxide considering the end product(s) from an environmental view point. Water is obtained at the end when  $H_2O_2$  is used while butanol is formed when *tert*-butyl hydroperoxide is employed as the oxidant. However, we have carried out epoxidation of cyclohexene in the presence of complex **2** with different oxidants at 323 K to determine the most effective oxidant. Conversion of cyclohexene has been found to be 86%, 58% and 42% in the presence of *tert*-butyl hydroperoxide, hydrogen peroxide and NaOCl, respectively.

Acetonitrile has been selected as solvent in the epoxidation of

**Table 4**Epoxidation<sup>a</sup> of olefins by complexes 1 and 2.

Catalysts	Substrate	Conversion <sup>b</sup>	Selectivity	TOF
1	Cyclohexene	84	88	11.7
	Styrene	72	85	10.0
	$\alpha$ -Methyl styrene	74	86	10.3
	trans-Stilbene	78	87	10.8
	Norbornene	80	82	11.1
2	Cyclohexene	86	91	11.9
	Styrene	75	86	10.4
	$\alpha$ -Methyl styrene	74	83	10.3
	trans-Stilbene	81	85	11.2
	Norbornene	82	84	11.4

<sup>a</sup> Solvent: CH<sub>3</sub>CN; temperature: 323 K; oxidant: *tert*-butyl hydroperoxide; catalyst: 0.03 mmol; substrate: 10.0 mmol.

<sup>b</sup> Conversions were measured after 24 h of the reaction (average of two measurements carried out under identical reaction conditions).

 $^{\rm c}$  TOF: turnover frequency = moles of substrate converted per mole of metal complex per hour.

the substrates because the catalyst, substrate and product(s) are soluble in this solvent. It is difficult for acetonitrile to undergo oxidation under the present reaction conditions.

Catalytic reactions have been carried out at different temperatures to check the effect of temperature on the rate of the reaction. It has been seen that rate of the reaction increases initially but decreases after certain enhancement in temperature. Both the complexes show similar effect of temperature on the rate. The optimized condition for the best result is obtained when reaction has been performed at 323 K.

Reaction mixtures were collected at regular time interval and analyzed by gas chromatography. It has been seen that the conversion increases with increase in time and reaches its maxima after 24 h. Plots of conversion vs. time for complexes **1** and **2** have been given in Fig. 3 and Fig. s7, respectively. It suggests the conversion follows a sigmoid curve.

Main problems associated with homogeneous catalysis are the recovery and reusability of catalyst. We have attempted to recover the complexes after completion of catalytic cycle to use these materials as catalyst again. However, the material recovered after catalytic reaction is not same as the starting complexes. The analyses and comparison of FT-IR and UV–vis spectra of complexes **1** and **2** with the recovered materials does not support that complexes have been recovered successfully. These materials are found to be something else other than complexes **1** and **2**. However, the materials recovered could not be identified fully.

Definite identification of active species in homogeneous catalysis is very complex. It has been reported that copper(II) catalyzed epoxidation of olefin involves generation of copper-hydroperoxido or copper-peroxido species in solution. This species has been identified by recording UV–vis spectrum of solution containing copper(II) complex in the presence of *tert*-butyl hydroperoxide. The UV–vis spectrum shows peak at 400 nm with a shoulder in the range of 415–440 nm. This metal-peroxido intermediate can be the active species for conversion of olefins. Mass spectra of complexes **1** and **2** were recorded in order to get an idea about the number of copper atom(s) present in the complex in solution state. Spectra of complexes **1** and **2** are given in Supplementary information (Fig. S3 and S4). Spectrum of complex **1** shows *m*/*z* peaks at 584.6467,



**Fig. 3.** A plot of conversion vs. time for complex **1.** Representation of substrate – black square box: cyclohexene; red circle: styrene, magenta triangle: $\alpha$ -methyl styrene, blue triangle:trans-stilbene and Cyan diamond:norbornene.(For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

566.6757 and 530.7379. These peaks may be obtained due to the presence of **1**–2Cl, **1**–(2Cl + H<sub>2</sub>O) and **1**–(3Cl + H<sub>2</sub>O) respectively. Mass spectrum indicates that two copper atoms in **1** are also present in solution. However, mass spectrum of complex **2** is not very much conclusive. It shows an *m*/*z* peak at 417.1884. This peak may be due to the presence of **HL**<sup>2</sup> ([HL<sup>2</sup>+H]<sup>+</sup>). In previous study [17,18], it was reported that copper-hydroperoxido or copper-peroxido was identified as active center for epoxidation of olefin when reaction passes through formation of *tert*-butyl alcohol. During analysis of reaction mixture, *tert*-butyl alcohol has been identified as the side-product in our case, thus we expected that catalytic reaction in this study follows similar reaction pathway involving copper-peroxido species. The UV–vis spectrum of complex in the presence of *tert*-butyl hydroperoxide also supports this fact.

#### 4. Conclusions

We have been able to synthesize and characterize two dinuclear copper(II) complexes with N<sub>4</sub>O-donor Schiff-base ligands. These complexes have been characterized by elemental analysis, different spectroscopic methods and single crystal X-ray diffraction analyses. The structural analyses show that complex **1** is Cl-bridged dinuclear compound whereas in complex **2**, two copper atoms are connected by azide ion. Complex **1** and **2** exhibit catalytic activity for epoxidation of olefins. Epoxides were detected as the major products.

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#### Appendix A. Supplementary information

CCDC 1058831 and 1058832 contain the supplementary crystallographic data of complexes **1** and **2** respectively for this paper. These information can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_ request/cif. Supplementary information associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. molstruc.2015.08.017.

#### Appendix B. Supplementary information

Supplementary information related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2015.08.017.

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