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# Copper(II) azide complexes with NNO donor ligands: Syntheses, structure, catalysis and biological studies

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ABSTRACT

Three copper(II) tridentate (NNO) Schiff base azido complexes, $[Cu(L^1)(N_3)]$ (**1**), $[Cu_2(L^2)_2(\mu_2\text{-}1,1\text{-}N_3)_2]$ $[Cu(L^2)(N_3)]$ (**2**) and $[Cu(L^3)(N_3)]$ (**3**) have been synthesized and characterized [where $HL^1$ = 1-(N-5-methoxy-ortho-hydroxyacetophenimino)-2,2-dimethyl-aminoethane], $HL^2$ = 1-(N-ortho-hydroxyacetophenimine)-2,2-diethyl-aminoethane and $HL^3$ = 1-(N-salicylideneimino)-2-(N,N-diethyl)-aminoethane]. The structure of complex (**1**) has been determined by single crystal X-ray diffraction analysis. In **1**, out of four coordination sites of copper(II) ion, three are occupied by the NNO donor atoms of a tridentate Schiff base ligand, $HL^1$ and the remaining site is occupied by terminal nitrogen of azido moiety. All the complexes exhibit high catalytic activity in epoxidation reactions of a variety of olefins with *tert*-butyl-hydroperoxide in acetonitrile. The catalytic efficacy of the copper(II) complexes has been studied in different solvent media. The antimicrobial activity of the complexes and their Schiff base ligand has also been studied.



## 1. Introduction

Schiff bases and their transition metal complexes continue to be of interest even after over a hundred years of study [1–4]. Schiff bases have a chelating structure and are in demand because they are straightforward to prepare and are moderate electron donors with easily-tunable electronic and steric effects thus being versatile [5,6]. Schiff base metal complexes are still widely used in catalysis but increasingly with a slightly modified concept [5,7–19]. Complexes have been immobilised on solid supports such as alumina, silica, or polystyrene [20–24] or assembled inside a DNA duplex [25]. However, the number of studies where Schiff base complexes especially copper(II) complexes have been used for olefin oxidation in homogeneous condition has been scarcely reported [26–29] and the interesting matter is that olefinic oxidation involving Schiff base copper(II) complexes have yet not been well documented in literature [30,31].

There are few reports of molecular oxygen catalyzed epoxidation [32], and a 30% hydrogen peroxide is usually considered an environmental friendly oxidant, nevertheless, due to explosive nature of hydrogen peroxide, the industrial processes still mainly rely on *tert*-BuOOH [33]. Alkyl-hydroperoxides are used on a large scale in industrial epoxidation, for example in Halcon-Arco and Sumitomo processes [34–36]. The recycling of co-product e.g. *tert*-BuOH has been realized in the Sumitomo process. Notably, *tert*-BuOOH has seldom been used as an oxidant in the investigations of catalytic efficiency of copper(II) complexes towards epoxidation/oxidation reactions in homogeneous medium.

Here we report the synthesis, characterization, X-ray single crystal structure analyses of azido adduct of NNO donor tridentate Schiff base (Scheme 1) copper(II) complexes and their catalytic efficacy towards epoxidation of a variety of olefins using *tert*-BuOOH as an oxidant in different solvent media. The antimicrobial activity of the complexes and their Schiff base ligands has also been investigated.

## 2. Experimental

### 2.1. Materials

All solvents used are of AR grade and were distilled and dried before use. 5-Methoxy-2-hydroxy-acetophenone, 2-hydroxy-acetophenone, salicylaldehyde, and copper(II) nitrate trihydrate were purchased from Merck (India) and used as received. Styrene, α-methylstyrene, cyclooctene, cyclohexene, *tert*-BuOOH (70% aq.), N,N-diethylethylenediamine were purchased form Aldrich and used as received.

### 2.2. Physical measurements

Microanalysis (CHN) was performed in a Perkin Elmer 240 elemental analyzer. IR spectra were recorded on a Bruker Alpha T

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200140 FT–IR spectrometer. Absorption spectra were studied on Shimadzu UV2100 UV–Vis recording spectrophotometer. GC analysis was carried out with an Agilent Technologies 6890N network GC system equipped with a fused silica capillary column (30 m × 0.32 mm) and a FID detector.

### 2.3. Synthesis

*Caution!* Although our samples never exploded during handling, azide metal complexes are potentially explosive: only a small amount of material should be prepared and it should be handled with care.

#### 2.3.1. Synthesis of the Schiff base ligands $HL^1$

The ligand $HL^1$ (Scheme 1) was prepared by refluxing a methanolic solution (10 $cm^3$) of 5-methoxy-2-hydroxy-acetophenone (0.166 g, 1 mmol) and 2-(diethylamino)-ethylamine (0.106 g, 1 mmol) for 30 min. Methanol was removed completely from the resultant orange solution under vacuum to obtain a highly viscous orange liquid. Upon keeping in a refrigerator (~0 °C), yellow crystals separated out from the orange liquid. The crystals were isolated, washed with a minimum volume of methanol, dried over $CaCl_2$ in a refrigerator and characterized. The crystals melt down into the previously mentioned viscous orange liquid at room temperature. Yield 0.210 g (80%). *Anal.* Calc. for $C_{15}H_{24}N_2O_2$ (264): C, 68.2; H, 9.1; N, 10.6. Found: C, 67.9; H, 9.0; N, 10.3%. IR (Nujol, $cm^{-1}$): $\nu$(azomethine) 1616. $^1H$ NMR (300 MHz, $CDCl_3$): ($\delta$ 2.25 (m, 9H, $CH_3$); 2.6 (t, 2H, $CH_2$); 3.6 (t, 2H, $CH_2$); 7.2 (m, 4H, aromatic).

The ligands $HL^2$ and $HL^3$ (Scheme 1) were synthesized by applying exactly same procedure as stated above, refluxing methanolic solution (20 $cm^3$) of 2-hydroxy-acetophenone (0.136 g,1 mmol) and salicylaldehyde (0.122 g, 1 mmol) with 2-(diethylamino)-ethylamine (0.106 g, 1 mmol), respectively.

#### 2.3.2. Synthesis of the complex $[Cu(L^1)(N_3)]$ (**1**), $[Cu_2(L^2)_2(_2\text{-}1,1\text{-}N_3)_2]$ $[Cu(L^2)(N_3)]$ (**2**) and $[Cu(L^3)(N_3)]$ (**3**)

To prepare **1**, methanolic solution of $HL^1$ (1 mmol, 0.264 g) was added to a methanolic solution of copper nitrate trihydrate (1 mmol, 0.241 g) and stirred for 45 min. The resulting solution upon slow evaporation afforded deep green crystals (Yield 60%). *Anal.* Calc. for $C_{15}H_{23}N_5O_2Cu$: C, 48.8; H, 6.2; N, 19.0. Found: C, 49.4; H, 6.0; N, 19.3%. FTIR ($cm^{-1}$): $\nu_{as}$ ($N_3$), 2030; $\nu_s$($N_3$), 1332 and 1345; $\delta$($N_3$), 620; $\nu$(C=N), 1620 $cm^{-1}$. $\lambda_{max}$/nm (methanol), 620, 370, 297. $\mu_{eff.}$ = 1.83 B.M.

**2** and **3** were synthesized by following the reported procedures [37,38]. *Analysis* of complex (**2**), *Anal.* Calc. for $C_{14}H_{21}N_5OCu$: C, 49.6; H, 6.2; N, 20.7. Found: C, 49.9; H, 7.0; N, 21.3%. IR (KBr): $\nu_{as}$(-$N_3$), 2055, 2031; $\delta$($N_3$), 640; $\nu$(C=N), 1598 $cm^{-1}$. $\lambda_{max}$/nm (methanol), 268, 296, 385. *Analysis* of complex (**3**), *Anal.* Calc. for $C_{13}H_{19}N_5OCu$: C, 48.02; H, 5.84; N, 21.54. Found: C, 48.2; H, 5.9; N, 22.0%. IR (KBr): $\nu_{as}$($N_3$), 2020 $cm^{-1}$; $\nu_s$($N_3$),1320 and 1340 $cm^{-1}$; $\delta$($N_3$), 610 $cm^{-1}$; $\nu$(C=N), 1630 $cm^{-1}$ .

### 2.4. X-ray crystallography

#### 2.4.1. X-ray crystal data of $[CuL(N_3)]$ (**1**)

$C_{15}H_{23}N_5O_2Cu$, $M$ = 368.93, monoclinic, space group $P2_1/c$, $a$ = 18.319 (5), $b$ = 9.252 (2), $c$ = 10.113 (3) Å, $\beta$ = 92.53(2)°, $V$ = 1712.4(8) $Å^3$, $Z$ = 4, $R_1(I > 2\sigma(I))$ = 0.0709, $D_{calc}$ = 1.431 g $cm^{-3}$, $F_{000}$ = 772, $\mu$ = 1.29 $mm^{-1}$, $T$ = 293 K.

#### 2.4.2. X-ray single crystal structure determination of $[CuL(N_3)]$ (**1**)

Crystals of **1** were mounted on a Enraf Nonius CAD4 diffractometer which was equipped with graphite monochromated Mo-Kα radiation ($\lambda$ = 0.71073 Å). Unit cell dimensions and intensity data were measured at 293 K. All calculations for data reduction, structure solution and refinement were done by standard procedures (SHELXS-97) [39], (SHELXL-97) [39]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques on $F^2$. All the hydrogen atoms of **1** were included at calculated positions and refined isotropically. Neutral atom scattering factors were taken from Cromer and Weber [40] and anomalous dispersion effects were included in $F_{calc}$ [41]. Information concerning crystallographic data collection and refinement of the structure are summarized in Section 2.4.1.

### 2.5. Catalytic reactions

The homogeneous oxidation reactions were carried out under stirring in a two-neck round-bottom flask fitted with a water condenser and placed in an oil bath at 333 K. The proportions used are: Substrate (10 mmol), solvent (10 ml) and catalyst (0.005 mmol). The *tert*-BuOOH (20 mmol) was added immediately before the start of the reaction and the mixture was stirred continuously for 24 h. At different time intervals, the products were collected from the reaction mixture and analyzed by gas chromatography. The products were identified against known standards.

### 2.6. Biological activity

The biological activities of synthesized Schiff bases ($HL^1$, $HL^2$ and $HL^3$) and their copper azido complexes **1**, **2** and **3** have been studied by the standard disc diffusion method [42]. The Schiff bases and their complexes were screened for their antifungal activity against fungi *viz. Aspergillus niger* and *Fusarium oxysporum*. These fungal species were isolated from potato dextrose agar. The cultures of the fungi were purified by single spore isolation technique. A concentration of 1.0 mg/ml of each compound in DMSO solution was prepared for testing against spore germination of each fungus. Filter paper discs of 5 mm in size, prepared by using Whatman filter paper No. 1, sterilized in an autoclave were saturated with 10 µl of the compounds dissolved in DMSO solution. The fungal culture plates were inoculated and incubated at 25 °C for 48 h. The plates were then observed and the diameters of the inhibition zones (in mm) were measured and tabulated.

The antibacterial activity of the complexes was studied against gram-positive bacteria *Staphylococcus aureus* (MTCC 96) and gram-negative bacteria *Escherichia coli* (MTCC 443). Each of the compounds dissolved in DMSO at a concentration of 1.0 mg/ml was prepared. Paper disc of Whatman filter paper No. 1 were cut and sterilized in an autoclave. The paper discs were saturated with 10 µl of the compounds dissolved in DMSO solution and was placed in the petridishes containing Nutrient agar media inoculated with the above mentioned two bacteria separately. The petridishes were incubated at 37 °C and the inhibition zones were recorded after 24 h of incubation.

## 3. Results and discussion

### 3.1. Description of the structure of **1**

The principal structural features of **1** are given in Fig. 1. The structure consists of a discrete molecule of $[Cu(L^1)(N_3)]$. The copper ion occupies the central position of a regular square planar arrangement. Out of its four coordination sites three are occupied by the tridentate Schiff base through two nitrogen (amino and imino) atoms and de-protonated phenoxo group. The remaining fourth coordination site is satisfied by an azido group which is linked to copper(II) ion through terminal nitrogen atom. The Cu–N bond lengths are found to be Cu(1)–N(1) = 1.914(5); Cu(1)–

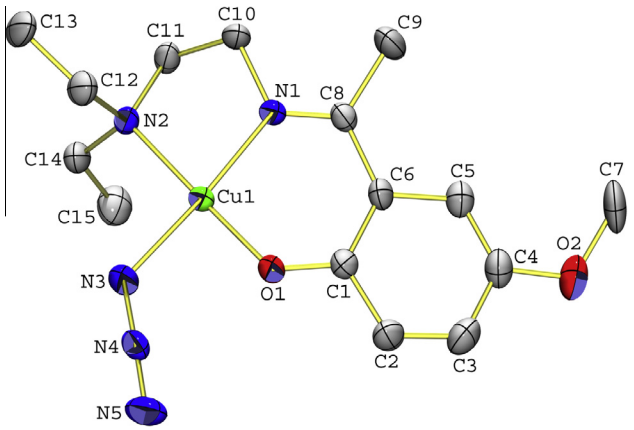
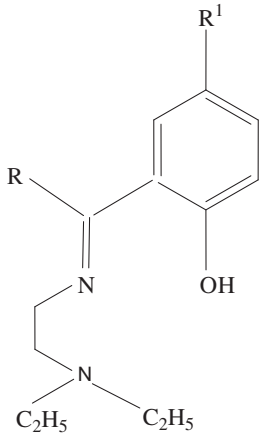



**Fig. 1.** Molecular structure of complex **1**. All hydrogen atoms have been omitted for clarity.




$R=CH_3$, $R^1=OCH_3$:$HL^1$
$R=CH_3$,$R^1$=H:$HL^2$
R=H,$R^1$=H:$HL^3$

**Scheme 1.** Schematic representation of the ligands.

N(2) = 2.020(5); Cu(1)–N(3) = 1.905(7) Å while the Cu(1)–O(1) bond length is 1.844(4) Å. The azide group, which acts as a monodentate ligand is slightly asymmetric [N(3)–N(4) = 1.193(8) and N(4)–N(5) = 1.171(8) Å] and linear within the experimental error [N(5)–N(4)–N(3) = 178.6(8)]. The other bond lengths and angles are summarized in Table 1. The bond lengths and bond angles determined from X-ray measurements are in agreement with the other similar reported systems [37,38]. The structure of **1**, however, differs from the other X-ray crystallographically investigated copper(II) azide complexes containing terminal azido ligand

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

| | | | |
|---|---|---|---|
| *Bond distances (Å)* | | | |
| Cu1–N1 | 1.914(5) | Cu1–N3 | 1.905(7) |
| Cu1–N2 | 2.020(5) | Cu1–O1 | 1.844(4) |
| *Bond angles (°)* | | | |
| N1–Cu1–N2 | 84.0(2) | O1–Cu1–N1 | 95.2(2) |
| N2–Cu1–N3 | 92.2(3) | N1–Cu1–N3 | 175.7(3) |
| N3–Cu1–O1 | 88.3(2) | N2–Cu1–O1 | 175.8(2) |
| N4–N3–Cu1 | 122.1(5) | N5–N4–N3 | 178.6(8) |

[43,44]. In most of the cases the coordination geometry around copper ions are either pseudo octahedral or distorted trigonal bipyramidal while square planar is not so common. The present complex acquires a square planar environment around the copper ion probably due to the presence of two ethyl groups attached to the N atom in 1,1 position of ethylenediamine backbone of the Schiff base ligand.

### 3.2. Catalytic activities

The catalytic activity of **1**, **2** and **3** in the epoxidation of various olefins in homogeneous medium is summarized in Table 2. The graphical representation of various alkene conversions has been shown in Fig. 2 for **1** (for **2** and **3**, see Figs. S1 and S2 respectively in supporting information). It is evident that all the complexes follow the alkene conversion order as α-methyl styrene > styrene > cyclooctene > cyclohexene while epoxide selectivity follows the sequence cyclooctene > α-methylstyrene > styrene > cyclohexene. The results show that for all complexes epoxide selectivity is highest in cylcooctene due to its active double bond and the relative stability of 1,2-epoxycyclooctane. For cyclohexene, epoxide selectivity is least for all complexes since its active allylic site could also be activated in the process of oxidation. For **1** styrene has been converted 98% to its oxidized products, giving 60% yield of epoxide, while the remaining 38% products were benzaldehyde and benzoic acid. When **2** and **3** are considered 96% and 90% styrene conversion occurred with 54% and 49% epoxide selectivity, respectively. Thus in styrene the catalytic efficacy follows the trend 1 > 2 > 3. Similar trend is also observed for other alkenes. The yield of epoxide increased to 65% for**1** and 62% for **2** and 60% for **3** when an electron-donating methyl group was introduced at the ortho-position of styrene; along with the epoxide, 4-methylbenzaldehyde and 4-methylbenzoic acid were also formed. The difference in the conversion between styrene and α-methylstyrene may be attributed to the electronic effect of the substituents [45]. From the above results it is further noticed that **1** is more efficient catalyst than **2** and **3**, respectively. This might be due to the slight variation in structural morphologies of the complexes. Thus absence of electron donating group decreases the efficiency of the catalyst (Scheme 1). It is known that copper(II) can bind peroxo group on treatment with peroxides [46] and thepre-catalyst species containing $L_xCu$-OOR (where L = ligand) type moieties are seemed to be capable of transferring oxo functionality to the organic substrates to give the corresponding oxidized products [47,48]. We speculate that, in our case, a similar kind of mechanism is operative. The probable mechanism for the catalytic cycle is depicted in Fig. 3.

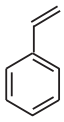
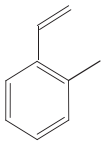
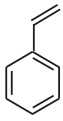
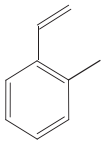
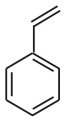
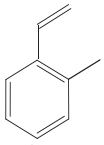
The effect of various reaction media on epoxidation of cyclooctene catalyzed by **1**, **2** and **3** has also been studied. The results of this study have been collected in Table 3 and the graphical representation of catalytic efficiency in different solvent media for **1** has been shown in Fig. 4 (for **2** and **3**, see Figures S3 and S4 respectively in supporting information). The best performance of the catalyst was observed in acetonitrile medium for all complexes (Table 3). The catalytic efficiency of all complexes follows the order: acetonitrile > dichloromethane > methanol > chloroform. An exactly similar trend was reported by Bera et al. [30] in the study of cyclooctene catalyzed epoxidation of single end on azido bridged Schiff base copper(II) complex.

### 3.3. In-vitro antimicrobial assay

#### 3.3.1. Antibacterial activity

A comparative account of the growth inhibition zone values of Schiff bases ($HL^1$, $HL^2$ and $HL^3$) and their complexes **1**, **2** and **3** revealed that azido complexes exhibited higher antibacterial activity

**Table 2**
Homogeneous alkene oxidation catalyzed by complex $[Cu(L^1)(N_3)]$ (**1**), $[Cu_2(L^2)_2(\mu_2\text{-}1,1\text{-}N_3)_2]$ $[Cu(L^2)(N_3)]$ (**2**) and $[Cu(L^3)(N_3)]$ (**3**)[a] in acetonitrile medium.

| Catalyst | Substrate | Reaction time (h) | Conversion (wt%) | % Yield of products | | TON[b] | TOF[c] ($h^{-1}$) |
|---|---|---|---|---|---|---|---|
| | | | | Epoxide | Others | | |
| $[Cu(L^1)(N_3)]$ (**1**) |  | 24 | 98 | 60 | 38[d] | 14208 | 592 |
| |  | 24 | 100 | 65 | 35[e] | 15480 | 645 |
| |  | 24 | 82 | 39 | 43[f] | 14040 | 585 |
| |  | 24 | 95 | 70 | 25[g] | 14160 | 590 |
| $[Cu_2(L^2)_2(\mu_2\text{-}1,1\text{-}N_3)_2]$ $[Cu(L^2)(N_3)]$ (**2**) |  | 24 | 96 | 54 | 42[e] | 14280 | 595 |
| |  | 24 | 100 | 62 | 38[e] | 15336 | 639 |
| |  | 24 | 84 | 45 | 39[f] | 14040 | 585 |
| |  | 24 | 90 | 65 | 25[g] | 15360 | 604 |
| $[Cu(L^3)(N_3)]$ (**3**) |  | 24 | 90 | 49 | 41[e] | 13752 | 573 |
| |  | 24 | 100 | 60 | 40[e] | 15240 | 635 |
| |  | 24 | 70 | 45 | 25[f] | 13680 | 570 |
| |  | 24 | 85 | 65 | 20[g] | 12912 | 538 |

[a] Reaction conditions: alkenes (10 mmol); catalysts (0.005 mmol); *tert*-BuOOH (20 mmol); acetonitrile (10 mL); temperature 70 °C.
[b] TON = turn over number = mol converted/mol of copper (active site) taken for reaction.
[c] TOF = Turn over frequency = mol converted/(mol of copper (active site) taken for reaction × reaction time).
[d] Benzaldehyde and benzoic acid.
[e] 4-Methylbenzaldehyde and 4-methylbenzoic acid.
[f] Cyclohex-2-en-1-ol and cyclohex-2-en-1-one.
[g] Cyclooctane-1,2-diol.

than the free ligand as represented in Table 4. This is probably due to the greater lipophilic nature of the complexes. Such increased activity of the metal chelates can be explained on the basis of Overtone's concept and Tweedy's chelation theory [49]. According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favors the passage of only lipid soluble materials due to which liposolubility is considered to be an important factor that controls the anti microbial activity. On chelation, thepolarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups [50,51]. Further, it increases the delocalization of the π electrons over the whole chelate ring and enhances the lipophilicity of the complex. This increased lipophilicity enhances the penetration of the complexes into lipid membrane and thus blocks the metal binding sites on enzymes of microorganisms [52]. These metal complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organism [53]. The variation in the activity of different complexes against different organisms depend either on the impermeability of the cells of the microbes or difference in ribosomesof microbial cells. The inhibition zones of antibacterial activity have been presented in the Table 4.

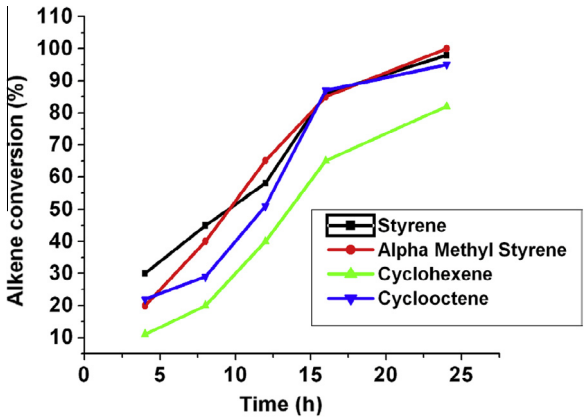



**Fig. 2.** Reaction profile for the epoxidation of olefins with *tert*-BuOOH in presence of **1**.

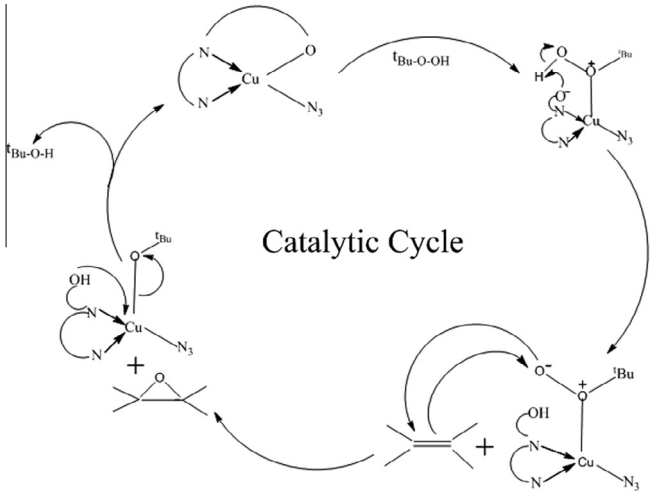



**Fig. 3.** Catalytic cycle for the epoxidation reaction.

**Table 3**
Comparison of catalytic efficacy of complex $[Cu(L^1)(N_3)]$ (**1**), $[Cu_2(L^2)_2(\mu_2\text{-}1,1\text{-}N_3)_2]$ $[Cu(L^2)(N_3)]$ (**2**) and $[Cu(L^3)(N_3)]$ (**3**) in oxidation of cyclooctene with *tert*-BuOOH in different solvent media.

| Complex | % Of conversion (% of epoxide yield) in different solvent | | | |
|---|---|---|---|---|
| | $CH_3CN$ | $CH_3OH$ | $CHCl_3$ | $CH_2Cl_2$ |
| $[Cu(L^1)(N_3)]$ (**1**) | 95 (70) | 80 (62) | 70 (54) | 85 (49) |
| $[Cu_2(L^2)_2(\mu_2\text{-}1,1\text{-}N_3)_2]$ $[Cu(L^2)(N_3)]$ (**2**) | 90 (65) | 75 (53) | 70 (48) | 85 (42) |
| $[Cu(L^3)(N_3)]$ (**3**) | 85 (65) | 70 (54) | 65 (45) | 78 (39) |

### 3.3.2. Antifungal activity

The antifungal activities [54] of the ligands and their metal complexes were tested against seven-day old cultures of *A. niger* and *F. oxysporum* using disc diffusion method. The results show that the metal complexes are more active than the free ligands and can be explained by Overtone's concept and Tweedy's chelation theory. The mode of action of the compounds may involve formation of a hydrogen bond through the azomethine group with the active centres of cell constituents, resulting in an interference with normal cell process [55]. The antifungal activity data (Table 4) indicate that the complexes show an appreciable activity against *A. niger* and *F. oxysporum* at a concentration of 1.0 mg/ml. Ligand has shown a lesser activity as compared to the metal complexes. The experimental results of the compounds are expressed as inhibition zone diameter (in mm).

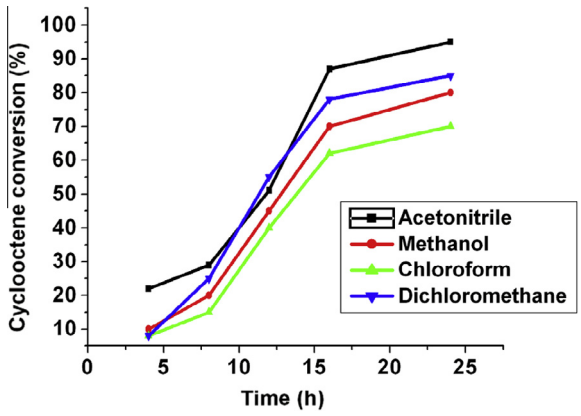



**Fig. 4.** Effect of solvents on the conversion of cyclooctene to its epoxide catalyzed by **1**.

**Table 4**
Growth inhibition zone of microbes in mm.

| Microbes | Ligand | Complex | Ligand | Complex | Ligand | Complex |
|---|---|---|---|---|---|---|
| | $HL^1$ | $[Cu(L^1)(N_3)]$ (**1**) | $HL^2$ | $[Cu_2(L^2)_2(\mu_2\text{-}1,1\text{-}N_3)_2]$ $[Cu(L^2)(N_3)]$ (**2**) | $HL^3$ | $[Cu(L^3)(N_3)]$ (**3**) |
| *E. coli* | 7 | 12 | 6 | 9 | 7 | 10 |
| *S. aureus* | 5 | 12 | 5 | 13 | 6 | 10 |
| *A. niger* | 15 | 22 | 12 | 18 | 12 | 18 |
| *F. oxysporum* | 11 | 15 | 11 | 16 | 12 | 14 |

## 4. Conclusion

In summary, we have synthesized and characterized tridentate Schiff base copper(II) complexes of their azido derivatives. All the complexes exhibited excellent catalytic activity in homogeneous alkene oxidation. A better selectivity was found for all the complexes when acetonitrile was used as a solvent. Biological studies indicate that better activity was found for the complexes when compared to that against their corresponding Schiff base ligands.

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## Appendix A. Supplementary data

CCDC 937471 contains the supplementary crystallographic data for **1**. 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.2013.08.019.

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