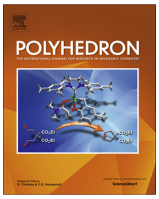
Polyhedron 78 (2014) 85–93

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Synthesis, characterization and catalytic properties of multinuclear copper(II) complexes

Shibashis Halder [a,1], Sudipto Dey [a,1], Corrado Rizzoli [b], Partha Roy [a,*]

[a] *Department of Chemistry, Jadavpur University, Jadavpur, Kolkata 700 032, India*
[b] *Universita' degli Studi di Parma, Dipartimento di Chimica, Parco Area delle Scienze 17/A, I-43124 Parma, Italy*

ARTICLE INFO

Article history:
Received 17 December 2013
Accepted 11 April 2014
Available online 20 April 2014

Keywords:
Copper
Multinuclear
Crystal structure
Homogeneous catalysis
Epoxidation

ABSTRACT

Four tetranuclear $[Cu_4(O)(\mathbf{L^n})_2(CH_3COO)_4]$ (**1**, **2**, **4** and **5**) and one pentanuclear $[Cu_5(OH)_2(\mathbf{L^3})_2(CH_3COO)_6]$ (**3**) with N_2O-donor Schiff-base ligands have been synthesized, where $\mathbf{HL^1}$ = 4-methyl-2,6-bis(2-hydroxyethyliminomethyl)phenol for complex **1**, $\mathbf{HL^2}$ = 4-methyl-2,6-bis(3-hydroxypropyliminomethyl)phenol for complex **2**, $\mathbf{HL^3}$ = 4-methyl-2,6-bis(4-hydroxybutyliminomethyl)phenol for complex **3**, $\mathbf{HL^4}$ = 4-methyl-2,6-bis(5-hydroxypentyliminomethyl)phenol for complex **4** and $\mathbf{HL^5}$ = 4-methyl-2,6-bis(6-hydroxyhexyliminomethyl)phenol for complex **5**. These complexes have been characterized by elemental analysis, FT-IR, UV–Vis spectroscopy. The structures of **1**, **3**, **4** and **5** have been determined by single crystal X-ray diffraction studies. X-ray analysis reveals that complexes **1**, **4** and **5** are μ_4-oxido-bridged tetrameric copper(II) complexes, where four copper atoms arrange themselves around an oxidooxygen atom at the vertices of a distorted tetrahedron. The pentanuclear complex, **3**, has been found to have two μ_3-hydroxido bridging ligands each connecting three copper atoms. These complexes have been employed as catalyst for the epoxidation of olefins in the presence of *tert*-butyl hydroperoxide (TBHP) as the oxidant under mild conditions.

1. Introduction

Multinuclear transition metal complexes of Schiff-base ligands have been drawing attention of researchers over few decades because of their diverse structures and their applications in various fields *e.g.* magnetism, biology, and catalysis [1–7]. Schiff-base ligands can induce substrate chirality, alter the metal center electronic factor or increase the solubility and stability of metal complexes. In 1970, Robson reported for the first a dinucleating N,O donor Schiff-base ligand involving 4-methyl-2,6-diformylphenol as the aldehyde and 2-aminophenol as the amine [8,9]. After that, a huge number of Schiff-base ligands, cyclic or acyclic, involving this aldehyde have been reported [9–13]. Acyclic N,O donor ligands of this aldehyde have been used to prepare oligo or polynuclear metal complexes [12]. Tetranuclear complexes of such donor systems can adopt different coordination geometries [14,15]. In μ_4-oxido bridge complexes, it has been seen that four metal atoms arrange themselves in the vertices of a tetrahedron around the bridging oxygen atom at the center. Deprotonation of phenolic oxygen atom of such Schiff-base ligand makes it suitable to connect two metal ions. These metal ions extend their coordination with linkage to other ancillary ligands such as halides, carboxylates, or both to get extra stability. The magnetic properties of these ligands with copper(II) metal ion have been studied extensively. In general, it has been found that there are antiferromagnetic interactions among copper atoms in their μ_4-oxido bridge complexes [1,2,15].

Multinuclear copper compounds have been used as catalysts in different types of organic transformations, *e.g.* epoxidation, sulfoxidation, olefin aziridination, atom transfer radical addition (ATRA) [4,5,16–20] etc. in homogeneous as well as heterogeneous media. Many mono- and multinuclear copper(II) complexes have been employed as active catalysts for peroxidative oxidation of alkanes. Recent reviews nicely describe the employment of transition metal complexes as the catalyst for alkane oxidation [21,22]. Different transition metal compounds have been used as catalysts for the epoxidation of olefins in the past few decades [23]. Schiff-base complexes of manganese(III), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) have been described in the literature where they were used as active catalysts for the oxidation of alkanes and alkenes. A Ga(III) complex has been used recently as homogeneous catalyst for the epoxidation of alkenes at mild temperatures and under optimum conditions [24]. Apart from metal compounds, gold nanoparticles supported on gold doped titania have been used

---

* Corresponding author. Tel.: +91 3324572267; fax: +91 3324146414.
E-mail address: proy@chemistry.jdvu.ac.in (P. Roy).

[1] Contributed equally.

http://dx.doi.org/10.1016/j.poly.2014.04.028
0277-5387/© 2014 Elsevier Ltd. All rights reserved.

as the active catalysts for epoxidation of stilbene [25]. Even though copper(II) Schiff-base complexes have been well known for a long time, they have barely been used as catalysts in olefin epoxidation reactions in homogeneous medium. Recently many groups are using copper(II) complexes for the epoxidation of various alkenes. Koner et al. have synthesized copper(II) complexes with Schiff-base ligands and employed them as catalyst in the epoxidation of styrene [18], cyclooctene [19], etc. in homogeneous medium. Copper(II) complexes with N,O donor ligands have been used for the epoxidation of different alkenes in homogeneous as well as heterogeneous media in the presence of different oxidant [17,26,27].

In this context, we report here the synthesis, characterization and catalytic properties of multinuclear copper(II) complexes with N_2O donor dinucleating Schiff-base ligands. Four μ_4-oxido bridged tetranuclear and one μ_3-hydroxido bridged pentanuclear copper(II) complexes have been synthesized and characterized by elemental analysis, FTIR, UV–Vis spectroscopy and X-ray diffraction analysis. These complexes have been used as the catalysts for epoxidation of cyclohexene, styrene, α-methyl styrene and *trans*-stilbene in acetonitrile in the presence of *tert*-butyl hydroperoxide as the oxidant.

2. Experimental

2.1. Materials and physical methods

Ethanolamine, 3-amino-1-propanol, 4-amino1-butanol, 5-amino-1-pentanol, 6-amino-1-hexanol, copper(II) acetate monohydrate, styrene, α-methyl styrene, *trans*-stilbene and *tert*-butyl hydroperoxide were purchased from Sigma Aldrich and used without purification. Other reagents were purchased from commercial source and used without further purification. 4-methyl-2,6-diformylphenol was synthesized following a published procedure [28]. Solvents used for spectroscopic studies were purified and dried by standard procedures before use [29]. Elemental analysis was carried out in a 2400 Series-II CHN analyzer, Perkin Elmer, USA. FT-IR spectra were obtained on a Nicolet MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. Absorption spectra were studied on a Shimadzu UV 2100 spectrophotometer. Gas chromatography analysis was performed with an Agilent Technologies 7890A network GC system equipped with a fused silica capillary column (30 m × 0.32 mm) and a FID detector. All experiments were carried out at room temperature in air unless reported otherwise.

Ligand, $\mathbf{HL^1}$, was synthesized following a literature procedure [30].

2.2. Synthesis of $[Cu_4(L^1)_2(O)(CH_3COO)_4]\cdot 3H_2O\cdot CH_3CN$ (**1**)

To an acetonitrile solution (10 mL) of ligand, $\mathbf{HL^1}$, (0.3 mmol, 0.075 g) was added copper(II) acetate monohydrate (0.6 mmol, 0.120 g). The mixture was stirred for 45 min and refluxed for 1 h on appearance of a green color. The mixture was finally cooled and filtered to remove any undissolved or suspended materials. The filtrate was kept at ambient temperature. Green single crystals suitable for X-ray diffraction study were produced within few days.

Data for **1**. (Yield = 0.43 g, 72%). *Anal.* Calc. for $C_{34}H_{46}Cu_4N_4O_{15}$: C, 40.64; H, 4.61; N, 5.58. Found: C, 40.58; H, 6.57; N, 5.62%.

2.3. Syntheses of $[Cu_4(L^2)_2(O)(CH_3COO)_4]$ (**2**), $[Cu_5(L^3)_2(OH)_2(CH_3COO)_6]\cdot H_2O$ (**3**), $[Cu_4(L^4)_2(O)(CH_3COO)_4]\cdot CH_3CN$ (**4**) and $[Cu_4(L^5)_2(O)(CH_3COO)_4]$ (**5**)

Complexes **2**, **3**, **4** and **5** were synthesized following a similar procedure. Typically, to an acetonitrile solution (10 mL) of 4-methyl-2,6-diformyl (0.3 mmol, 0.049 g) was added respective amine (0.6 mmol) (0.045 g of 3-amino-1-propanol for complex **2**; 0.053 g of 4-amino1-butanol for complex **3**; 0.062 g of 5-amino-1-pentanol for **4**; 0.070 g of 6-amino-1-hexanol for complex **5**). The mixture was stirred for 1 h and after that it was refluxed for 4 h. It was then cooled to room temperature. This ligand was used to synthesize copper(II) complexes without any purification or identification. Copper(II) acetate monohydrate (0.6 mmol, 0.120 g) was added and the solution stirred again for 45 min. The mixture was then refluxed for about 1 h, after which it was cooled to room temperature and filtered. The filtrate was kept at ambient temperature. Single crystals of complexes **3**, **4** and **5** suitable for X-ray diffraction were grown from the filtrate upon slow evaporation within few days.

Data for **2**. (Yield = 0.45 g, 70%). *Anal.* Calc. for $C_{38}H_{54}Cu_4N_4O_{15}$: C, 43.02; H, 5.13; N, 5.28. Found: C, 42.98; H, 5.10; N, 5.23%.

Data for **3**. (Yield = 0.48 g, 60%). *Anal.* Calc. for $C_{46}H_{74}Cu_5N_4O_{22}$: C, 40.84; H, 5.51; N, 4.14. Found: C, 40.78; H, 5.55; N, 4.17%.

Data for **4**. (Yield = 0.47 g, 65%). *Anal.* Calc. for $C_{48}H_{73}Cu_4N_5O_{15}$: C, 47.48; H, 6.06; N, 5.77. Found: C, 47.44; H, 5.99; N, 5.72%.

Data for **5**. (Yield = 0.55 g, 75%). *Anal.* Calc. for $C_{50}H_{78}Cu_4N_4O_{15}$: C, 48.85; H, 6.40; N, 4.56. Found: C, 48.81; H, 6.44; N, 4.57%.

2.4. X-ray data collections and structure determinations

Details of the data collection and refinement parameters for complexes **1**, **3**, **4** and **5** are summarized in Table 1. The diffraction experiments were carried out on a Bruker APEX-2 CCD diffractometer using graphite monochromated Mo Kα radiation at 296 K for **1** and **3** and 150 K for **4** and **5**. Data were processed using the Bruker SAINT package [31]. Absorption corrections based on multi scans using the SADABS software [31] were applied to all intensity data. The structures were solved by direct methods using SHELXS-97 [32] and refined with full-matrix least-squares on F^2 on all unique reflections using SHELXL-97 [32]. All the non-hydrogen atoms of the complexes were refined anisotropically. In **1** the acetonitrile solvent molecule was found to be disordered over two sets of orientations with refined site occupancy ratio of 0.760(8):0.240(8). In complex **4** an acetonitrile solvent molecule is disordered over two orientations sharing the nitrogen atom close to an inversion center with refined site occupancy ratio of 0.310(2):0.190(2). The disorder of the solvent molecule compels the methyl group of an acetato anion and the pentyl group of a pentanol side chain to be also disordered over two sets of orientations with refined site occupancy ratio of 0.619(5):0.381(5). During the refinement of the disordered molecules and groups soft restraints on bond lengths and angles to regularize their geometry were applied and the anisotropic displacement parameters for paired components of disorder were constrained to be equivalent. The water H atoms in 3 were located in a difference Fourier map and refined as riding on the oxygen atoms, with the O—H bond lengths and H···H separations restrained to be 0.86(1) and 1.36(1) Å, respectively. All other H atoms were placed geometrically and refined using a riding model approximation, with $U_{iso}(H) = 1.2\ U_{eq}(C)$ or $1.5\ U_{eq}(C, O)$ for methyl and hydroxyl H atoms.

2.5. Epoxidation of olefins

Typically, 10.0 mmol of the substrate was taken in a magnetically stirred two necked round-bottomed flask fitted with a condenser in 5 ml acetonitrile, followed by the addition of 0.05 mmol of the complex. The mixture was heated to 50 °C. The reaction was started with the addition of *tert*-butyl hydroperoxide (20 mmol). Aliquots from reaction mixtures were collected at regular intervals. 10 ml of diethylether were added for extracting the reactants and products. The substrate and product(s) from the

Table 1
Crystal data for complexes **1**, **3**, **4** and **5**.

Complex	**1**	**3**	**4**	**5**
Formula	$C_{34}H_{46}Cu_4N_4O_{15}\cdot 3H_2O\cdot C_2H_6N$	$C_{46}H_{70}Cu_5N_4O_{20}\cdot 2H_2O$	$C_{46}H_{70}Cu_4N_4O_{15}\cdot 1.5C_2H_3N$	$C_{50}H_{78}Cu_4N_4O_{15}$
Formula weight	1100.01	1352.79	1234.80	1229.32
T (K)	296(2)	296(2)	150	150
Colour	green	green	green	green
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	9.596(4)	11.4395(13)	12.5810(9)	14.8592(8)
b (Å)	12.147(5)	14.4005(16)	14.8446(11)	24.1904(13)
c (Å)	20.975(9)	18.053(2)	15.1852(11)	16.7730(10)
α (°)	103.830(12)	90.00	87.720(2)	90.00
β (°)	94.967(13)	98.513(3)	85.554(2)	107.252(2)
γ (°)	103.193(13)	90.00	82.089(2)	90.00
V (Å^3)	2285.3(16)	2941.2(6)	2799.3(4)	5757.8(6)
Z	2	2	2	4
Crystal dimensions (mm)	0.45 × 0.25 × 0.15	0.40 × 0.25 × 0.15	0.40 × 0.23 × 0.12	0.45 × 0.25 × 0.15
Minimum and maximum transmission factors	0.311–0.885	0.302–0.935	0.649–0.829	0.211–0.901
$F(000)$	1132	1398	1286	2568
D_c (g cm^{-3})	1.598	1.528	1.465	1.522
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
θ Range (°)	1.8–23.8	1.8–24.1	1.4–23.1	1.5–23.3
Reflection collected/unique/observed	19255, 6961, 5067	31177, 4609, 3628	22633, 7818, 5896	45827, 8303, 5340
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
R_{int}	0.0493	0.0622	0.0552	0.0830
Final R_1 index [$I > 2\sigma(I)$]	0.0455	0.0374	0.0413	0.0432
Final wR_2 index (all reflections)	0.1309	0.0983	0.0998	0.1125
Goodness-of-fit	1.025	1.048	1.040	1.012

reaction mixture were analyzed by gas chromatography and identified by the comparison with known standards.

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

3. Results and discussion

3.1. Synthesis and characterization

The general reaction route adopted for the synthesis of all complexes is schematically shown in Scheme 1. Complex **1** was synthesized by the reaction between the appropriate ligand and copper(II) acetate in acetonitrile. For all the complexes other than **1**, the ligand was prepared by simple Schiff-base condensation between 4-methyl-2,6-diformyl phenol and respective amine in 1:2 M ratio in acetonitrile. These *in situ* Schiff-base ligands in acetonitrile reacted with copper(II) acetate to produce the complexes. The acetate ion from copper(II) acetate probably deprotonated the phenolic proton of the ligand and attached to copper to give extra stability to the complex.

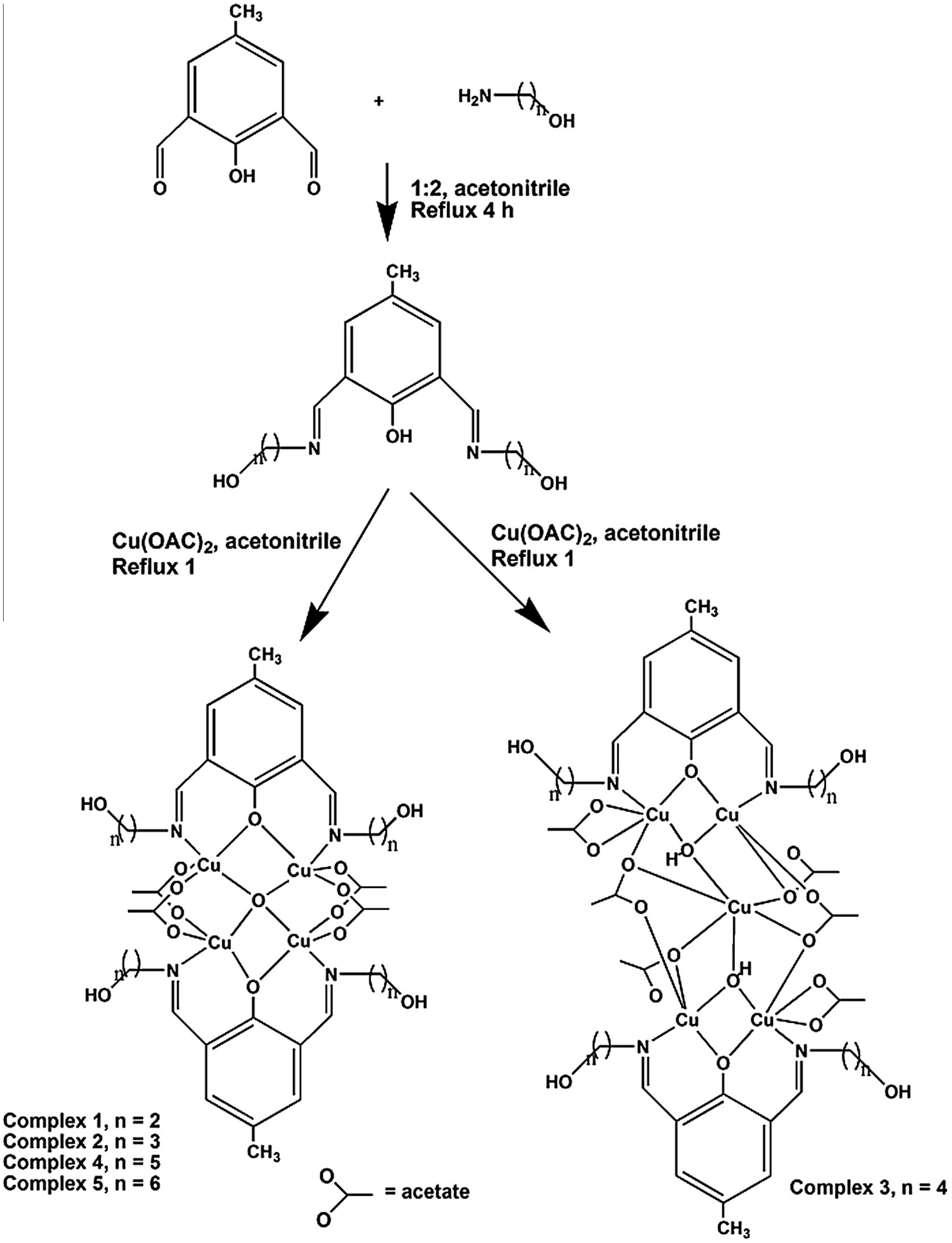
FTIR spectra of the complexes were recorded with samples prepared as KBr pellets. All the complexes show strong ν_{C-H} bands at 2800–3000 cm^{-1} [11,33]. Complexes **1**, **2**, **3**, **4** and **5** show IR bands at 1627, 1625, 1633, 1638 and 1632 cm^{-1} respectively confirming the presence of C═N bonds. All complexes except **3** show a sharp band of medium intensity at 560–570 cm^{-1} indicating that the ligand is coordinated to the metal atoms [34,35].

UV–Vis spectra of all the complexes were recorded in acetonitrile at room temperature. All of them behave similarly in solution. They exhibited peaks in the range 252–257 nm which can be attributed to $\pi \rightarrow \pi^*$ transitions within the ligands part. Their peaks in the range of 382–386 may be assigned to charge transfer transitions (LMCT). All of them show typical d-d transitions in range of 570–650 nm.

Magnetic properties of the complexes have been analyzed with powdered samples at 298 K. Complexes **1**, **2**, **4** and **5** have been expected to show a behavior similar to that of complexes with comparable metal-donor connectivities. The reported complexes with similar N,O-donor ligands exhibited strong antiferromagnetic coupling among the four copper atoms. The calculated magnetic moment of four isolated copper(II) ions is 4.9 BM, but the measured magnetic moment has been found to be smaller than the calculated value indicating antiferromagnetic coupling among four copper atoms at 298 K. The pentanuclear complex **3** should differ from the other complexes. The observed magnetic moment of **3** at 298 K has been found to be 1.79 BM. This value is smaller than that of 5.9 BM expected for five isolated Cu(II) ions (d^9, $S = ½$), indicating strong antiferromagnetic interactions amongst copper atoms at 298 K, and is very close to that of 1.73 BM expected for one paramagnetic copper(II) ion. The observed magnetic moments of complexes **1**, **2** and **5** are found to be 2.16, 1.77 and 1.75 BM respectively at 298 K. These values are remarkably small as compared to the value of 4.9 BM expected for four isolated Cu(II) ions indicating strong antiferromagnetic interactions amongst copper atoms at 298 K.

3.2. Description of crystal structures of complexes

Selected bond lengths and bond angles are listed in Tables 2–4 for **1**, **4** and **5**, respectively, and in Table 6 for **3**. Perspective views of the complexes of with partial atom labeling are shown in Figs. 1–4, respectively. Due to the similarity of their crystal structures, complexes **1**, **4** and **5** are described hereafter jointly. The asymmetric unit of complexes **1**, **4** and **5** consists of four crystallographically independent Cu^{2+}cations, two μ_2-bridging tridentate ligands $\mathbf{L}^{n-}$, one μ_4-oxido anion and four μ_2-bridging acetato anions. In **1** and **4** water and/or acetonitrile solvent molecules are also present in a complex/water/acetonitrile molar ratio of 1:3:1 for **1** and in a complex/acetonitrile molar ratio of 1:1.5 for **4**. The main feature of these structures is the presence of a $Cu_4O_{11}N_4$ inner core, where each copper metal displays a distorted square pyramidal coordination geometry, with the basal planes provided by one nitrogen and one oxygen atom of



Scheme 1. Schematic presentation of synthesis of the complexes.

a ligand, the μ_4-oxido oxygen atom and one oxygen atom of an acetato anion (r.m.s. deviations in the range 0.100–0.195, 0.137–0.377 and 0.057–0.112 for **1**, **4** and **5**, respectively; metal displacement in the range 0.0453(8)–0.1378(8), 0.0282(5)–0.0915(5) and 0.1311(6)–0.2286(6) Å for **1**, **4** and **5**, respectively), and the apical positions occupied by the oxygen atom of a different acetato anion. The magnitude of the distortion from the ideal geometry may be esteemed from the value of the trigonal index, τ. This may be defined as the difference between the two largest donor-metal-donor angles divided by 60, which results in a value of 1 for the ideal trigonal bipyramid coordination and 0 for the square pyramid coordination [36]. Table 5 shows the trigonal index value of the copper atoms in complexes **1**, **4** and **5**. The Cu–O and Cu–N bond distances are in good agreement with those reported for related (μ_4-oxo)-(μ_2-2,6-bis(alkyl)-4-methylphenolato)-tetrakis(μ_2-acetato)-tetracopper complexes [16,17,30,35,47,48]. The Cu···Cu separations in complex **1** are remarkably different, ranging from 2.9732(15) to 3.3631(13) Å, whereas in **4** and **5** these distances fall in a narrow range of values (3.0107(7)–3.2145(7) Å and 3.0168(9)–3.2046(10) Å, respectively). It may be noted that the shortest metal···metal separation increases with the increase in the number of carbon atom of the alkyl side chain.

A perspective view with partial atom labeling of complex **3** is shown in Fig. 4. The pentanuclear discrete complex molecule has

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

Cu1–O1	1.929(4)	Cu3–O1	1.933(3)
Cu1–O2	1.961(3)	Cu3–O3	1.963(4)
Cu1–O8	1.945(4)	Cu3–O14	1.944(4)
Cu1–N1	1.975(4)	Cu3–N3	1.962(5)
Cu1–O10	2.283(4)	Cu3–O9	2.464(4)
Cu2–O1	1.908(3)	Cu4–O1	1.929(3)
Cu2–O2	1.975(4)	Cu4–O3	1.992(4)
Cu2–O12	1.939(4)	Cu4–O11	1.948(5)
Cu2–N2	1.984(4)	Cu4–N4	2.003(4)
Cu2–O15	2.508(5)	Cu4–O13	2.295(4)
O1–Cu1–O2	79.31(15)	O1–Cu3–N3	162.82(16)
O1–Cu1–O8	92.32(15)	O3–Cu3–N3	91.13(16)
O2–Cu1–O8	170.84(16)	O14–Cu3–N3	96.05(17)
O1–Cu1–N1	163.30(17)	O1–Cu3–O9	96.32(14)
O2–Cu1–N1	91.80(17)	O3–Cu3–O9	83.46(15)
O8–Cu1–N1	97.22(17)	O14–Cu3–O9	88.00(17)
O1–Cu1–O10	95.54(15)	N3–Cu3–O9	97.05(17)
O2–Cu1–O10	87.88(16)	O1–Cu4–O3	79.11(15)
O8–Cu1–O10	89.23(16)	O1–Cu4–O11	97.55(16)
N1–Cu1–O10	98.25(16)	O3–Cu4–O11	176.20(17)
O1–Cu2–O2	79.47(15)	O1–Cu4–N4	162.99(16)
O1–Cu2–O12	99.64(16)	O3–Cu4–N4	90.48(16)
O2–Cu2–O12	165.59(16)	O1–Cu4–N4	92.32(17)
O1–Cu2–N2	169.05(16)	O1–Cu4–O13	94.56(15)
O2–Cu2–N2	90.69(18)	O3–Cu4–O13	88.55(15)
O12–Cu2–N2	91.09(19)	O11–Cu4–O13	93.56(18)
O1–Cu2–O15	90.05(14)	N4–Cu4–O13	98.63(17)
O2–Cu2–O15	91.01(16)	Cu3–O1–Cu4	102.01(15)
O12–Cu2–O15	103.48(16)	Cu3–O1–Cu1	105.56(16)
N2–Cu2–O15	85.31(17)	Cu4–O1–Cu1	108.55(16)
O1–Cu3–O3	79.73(14)	Cu3–O1–Cu2	115.52(16)
O1–Cu3–O14	95.15(15)	Cu4–O1–Cu2	122.50(17)
O3–Cu3–O14	169.46(17)	Cu1–O1–Cu2	101.60(15)

Table 3
Selected bond lengths (Å) and angles (°) of complex **4**.

Cu1–O1	1.921(3)	Cu3–O1	1.914(3)
Cu1–O2	1.971(3)	Cu3–O3	1.977(3)
Cu1–O10	1.958(3)	Cu3–O14	1.933(3)
Cu1–N1	1.963(3)	Cu3–N4	1.968(3)
Cu1–O8	2.383(3)	Cu3–O11	2.332(3)
Cu2–O1	1.917(3)	Cu4–O1	1.913(3)
Cu2–O3	1.975(3)	Cu4–O2	1.981(3)
Cu2–O9	1.934(3)	Cu4–O13	1.955(3)
Cu2–N3	1.955(3)	Cu4–N2	1.961(3)
Cu2–O12	2.308(3)	Cu4–O15	2.293(3)
O1–Cu1–O2	78.27(11)	O1–Cu3–O3	158.85(12)
O1–Cu1–O10	93.67(11)	O3–Cu3–O3	89.86(15)
O2–Cu1–O10	169.68(11)	O14–Cu3–O3	96.19(15)
O1–Cu1–N1	162.13(13)	O1–Cu3–O11	94.01(10)
O2–Cu1–N1	91.45(13)	O3–Cu3–O11	85.71(10)
O10–Cu1–N1	97.95(13)	O14–Cu3–O11	86.79(11)
O1–Cu1–O8	94.58(10)	N4–Cu3–O11	102.76(13)
O2–Cu1–O8	82.29(10)	O1–Cu4–O2	78.21(11)
O10–Cu1–O8	92.05(11)	O1–Cu4–O13	95.69(11)
N1–Cu1–O8	98.50(11)	O2–Cu4–O13	173.16(12)
O1–Cu2–O3	78.51(11)	O1–Cu4–N2	162.09(13)
O1–Cu2–O9	96.59(12)	O2–Cu4–N2	90.70(13)
O3–Cu2–O9	170.74(11)	O13–Cu4–N2	95–96(13)
O3–Cu2–N3	160.97(13)	O1–Cu4–O15	96.42(11)
O9–Cu2–N3	90.67(12)	O2–Cu4–O15	86.28(11)
O1–Cu2–N3	96.10(12)	O13–Cu4–O15	91.39(11)
O1–Cu2–O12	94.90(11)	N2–Cu4–O15	96.85(12)
O3–Cu2–O12	85.77(11)	Cu1–O1–Cu2	109.28(14)
O9–Cu2–O12	86.84(11)	Cu1–O1–Cu3	113.47(13)
N3–Cu2–O12	99.91(13)	Cu1–O1–Cu4	103.87(12)
O1–Cu3–O3	78.52(11)	Cu2–O1–Cu3	103.59(13)
O1–Cu3–O14	97.54(12)	Cu2–O1–Cu4	114.11(14)
O3–Cu3–O14	171.25(12)	Cu3–O1–Cu4	112.77(13)

Table 4
Selected bond lengths (Å) and angles (°) of complex **5**.

Cu1–O1	1.919(3)	Cu3–O1	1.901(3)
Cu1–O2	1.978(3)	Cu3–O2	1.994(3)
Cu1–O8	1.947(3)	Cu3–O13	1.949(3)
Cu1–N1	1.975(3)	Cu3–N2	1.976(3)
Cu1–O10	2.269(4)	Cu3–O15	2.282(4)
Cu2–O1	1.925(3)	Cu4–O1	1.903(3)
Cu2–O3	1.967(3)	Cu4–O3	1.988(3)
Cu2–O14	1.961(3)	Cu4–O11	1.955(4)
Cu2–N3	1.976(4)	Cu4–N4	1.961(4)
Cu2–O12	2.264(3)	Cu4–O9	2.294(3)
O1–Cu1–O2	78.39(13)	O1–Cu3–N2	163.93(16)
O1–Cu1–O8	94.75(13)	O2–Cu3–N2	89.78(14)
O2–Cu1–O8	170.57(13)	O13–Cu3–N2	94.93(14)
O1–Cu1–N1	160.40(14)	O1–Cu3–O15	99.39(13)
O2–Cu1–N1	91.17(15)	O2–Cu3–O15	88.06(13)
O8–Cu1–N1	93.45(16)	O13–Cu3–O15	96.84(13)
O1–Cu1–O10	95.65(13)	N2–Cu3–O15	91.00(13)
O2–Cu1–O10	87.24(12)	O1–Cu4–O3	78.53(13)
O8–Cu1–O10	99.98(13)	O1–Cu4–O11	95.54(13)
N1–Cu1–O10	100.41(14)	O3–Cu4–O11	172.97(13)
O1–Cu2–O3	78.52(13)	O1–Cu4–N4	163.48(16)
O1–Cu2–O14	94.42(13)	O3–Cu4–N4	90.44(14)
O3–Cu2–O14	170.77(13)	O11–Cu4–N4	94.52(14)
O1–Cu2–N3	157.66(14)	O1–Cu4–O9	98.69(13)
O1–Cu2–N3	91.13(15)	O3–Cu4–O9	87.71(13)
O14–Cu2–N3	93.41(16)	O11–Cu4–O9	96.98(13)
O1–Cu2–O12	96.31(13)	N4–Cu4–O9	93.05(14)
O3–Cu2–O12	86.02(13)	Cu1–O1–Cu2	110.94(16)
O14–Cu2–O12	100.79(13)	Cu1–O1–Cu3	104.33(15)
N3–Cu2–O12	102.72(14)	Cu1–O1–Cu4	111.81(15)
O1–Cu3–O2	78.43(13)	Cu2–O1–Cu3	111.43(15)
O1–Cu3–O13	95.95(13)	Cu2–O1–Cu4	103.74(15)
O2–Cu3–O13	173.12(13)	Cu3–O1–Cu4	114.79(16)

Table 5
τ values for the coordination polyhedra about the copper atoms in complexes **1**, **4** and **5**.

Complex **1**	Cu1	0.13	Cu2	0.06
	Cu3	0.11	Cu4	0.22
Complex **4**	Cu1	0.13	Cu2	0.16
	Cu3	0.21	Cu4	0.18
Complex **5**	Cu1	0.17	Cu2	0.22
	Cu3	0.15	Cu4	0.16

crystallographically imposed inversion symmetry and consists of five Cu^{2+} cations, two binucleating ligands 2,6-bis(4-hydroxybutyl)iminomethylphenolate, $\mathbf{L}^{3-}$, two μ_3-hydroxido and six acetato anions, two of which adopt a μ_2-bridging mode. Water molecules of crystallization are also present in a complex/solvent molar ratio of 1:2. Contrarily to what observed in complexes **1**, **4** and **5**, where all copper atoms display a similar coordination geometry, the three independent metals of the $Cu_5O_{12}N_4$ inner core of **3** assume different coordination modes. In fact, the central Cu2 atom, which lies on a centre of symmetry, exhibits a distorted octahedral coordination provided by the two μ_3-hydroxido anions and by the oxygen atoms of four different acetato anions, whereas atom Cu3 displays a distorted square pyramidal geometry, with the basal plane defined by one nitrogen and one oxygen atom of the ligand, the μ_3-hydroxido-oxygen atom and one oxygen atom of an acetato anion (r.m.s. deviation 0.046; Cu3 is displaced by 0.0922(5) Å from the least-square basal plane), and the apical position occupied by the oxygen atom of a different acetato anion. The trigonal index τ is only 0.02, suggesting an almost perfect square pyramidal geometry about Cu3, but the coordination polyhedron is in fact rather distorted as indicated by the dihedral angle of 13.71(8)° between the Cu3–O9^i line ($i = -x, 1 - y, 1 - z$) and the normal to the mean basal plane. Coordination about atom Cu1 should be best described as distorted square planar (r.m.s. deviation 0.176, with the metal atom displaced by 0.0505(5) Å from the least-square mean plane through the donor atoms) provided by one nitrogen and one oxygen atom of the ligand, the μ_3-hydroxidooxygen atom and one oxygen atom of an acetato anion. As observed for complexes **1**, **4** and **5**, the

Table 6
Selected bond lengths (Å) and angles (°) of complex **3**.

Cu1–N1	1.932(3)	Cu2–O9	2.231(3)
Cu1–O1	1.934(3	Cu2–O9^{i}	2.231(3)
Cu1–O2	1.975(2)	Cu3–O1	1.936(2)
Cu1–O5	1.934(3)	Cu3–O2	1.975(2)
Cu2–O1	1.976(2)	Cu3–N2	1.948(2)
Cu2–O1^{i}	1.976(2)	Cu3–O7	1.926(3)
Cu2–O8	2.227(3)	Cu3–O9	2.364(3)
Cu2–O8^{i}	2.227(3)		
O1–Cu1–O2	77.16(10)	O1–Cu2–O8^{i}	88.47(10)
O1–Cu1–O5	95.78(11)	O9–Cu2–O8^{i}	91.48(10)
O1–Cu1–N1	166.47(12)	O9^{i}–Cu2–O8^{i}	88.52(10)
O2–Cu1–O5	165.12(12)	O8–Cu2–O8^{i}	180(-)
O2–Cu1–N1	92.24(12)	O1–Cu3–O2	77.13(10)
O5–Cu1–N1	96.40(12)	O1–Cu3–O7	94.29(10)
O1–Cu2–O1^{i}	180(-)	O2–Cu3–O7	168.50(11)
O1–Cu2–O9^{i}	86.73(10)	O1–Cu3–N2	169.54(12)
O1–Cu2–O9	93.27(10)	O2–Cu3–N2	92.68(11)
O1^{i}–Cu2–O9^{i}	93.27(10)	O7–Cu3–N2	95.55(12)
O1–Cu2–O9^{i}	86.73(10)	O1–Cu3–O9	78.88(9)
O9–Cu2–O9	180(–)	O2–Cu3–O9	86.11(9)
O1–Cu2–O8^{i}	88.47(10)	O7–Cu3–O9	99.88(10)
O1–Cu2–O8	91.53(10)	N2–Cu3–O9	102.57(11)
O8–Cu2–O9	88.52(10)	Cu1–O1–Cu2	109.62(11)
O8^{i}–Cu2–O9	91.48(10)	Cu1–O1–Cu3	104.32(11)
O1^{i}–Cu2–O8^{i}	91.53(10)	Cu2–O1–Cu3	99.31(11)

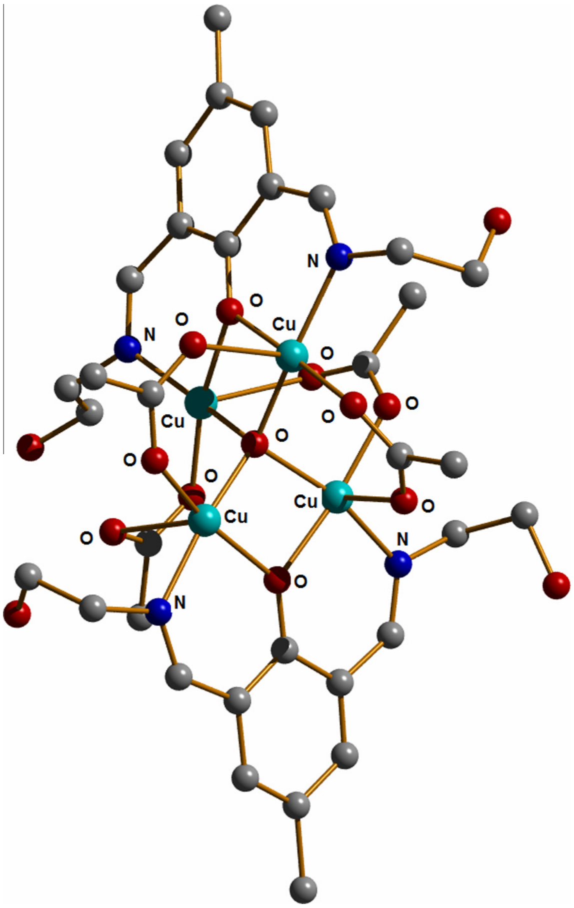


Fig. 1. A perspective view of complex **1**. Hydrogen atoms and solvent molecules were omitted for clarity.

Cu–O and Cu–N bond lengths are in good agreement with the literature values. The shortest and longest Cu···Cu separations within the $Cu_5O_{12}N_4$ inner core are 2.982(–) and 6.3919(8 Å, respectively.

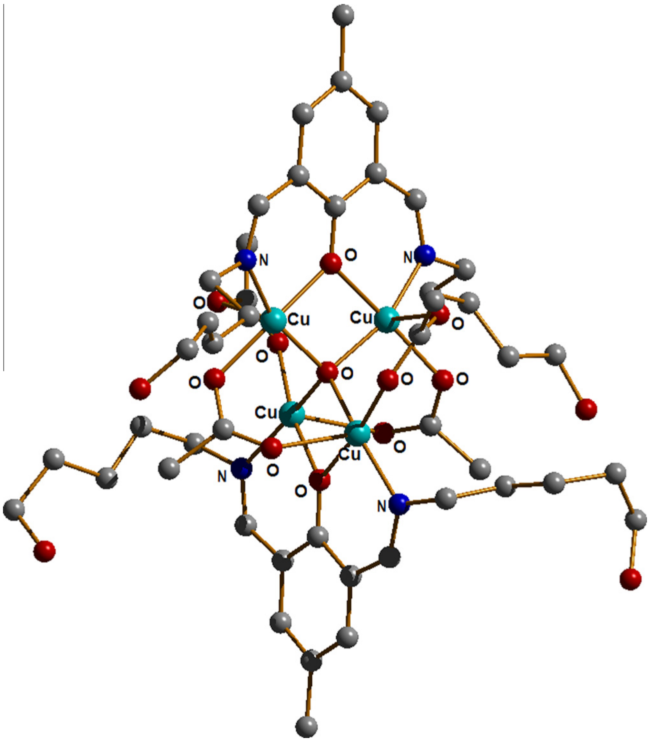


Fig. 2. A perspective view of complex **4**. Hydrogen atoms and solvent molecule were omitted for clarity.

3.3. Catalysis

Complexes **1**, **2**, **3**, **4** and **5** have been used as catalyst for the epoxidation of cyclohexene, styrene, α-methylstyrene and *trans*-stilbene using *tert*-butyl hydroperoxide as the oxidant at 50 °C. The results of the oxidation reactions are shown in Table 7. It can be evidently seen from the table that all substrates are converted in good yield with the formation of the corresponding epoxides as the major product for the each reaction. Among all the substrates, the conversion of cyclohexene has been found to be the highest with 84% yield in the presence of complex **4** as the catalyst. Selectivity of the corresponding epoxide in this case is 86%. However, conversions of cyclohexene by catalysts **1**, **2**, **3** and **5** are 80%, 83%, 80% and 82% respectively with formation of the corresponding epoxide with high selectivity. 2-Cyclohexen-1-ol and 2-cyclohexen-1-one are detected as the minor products. Epoxidation of styrene draws a special attention of researchers from the view point of academics and industry. Complexes **1**, **2**, **3**, **4** and **5** can act as catalyst to convert styrene with 76%, 74%, 72%, 73% and 75% yields respectively into its products. Apart from the formation of epoxide as the major product, a small amount of benzaldehyde has been detected as the by-product. α-Methyl styrene has been transformed with 76%, 74%, 72%, 73% and 75% yields into its products by **1**, **2**, **3**, **4** and **5** respectively. It can be clearly noticed from Table 7 that these complexes are better catalyst for the epoxidation of cyclohexene and *trans*-stilbene in comparison to styrene and its derivative. *Trans*-stilbene is converted in 82%, 78%, 75%, 82% and 77% yields in the presence of **1**, **2**, **3**, **4** and **5** respectively. It is worth noting that for each reaction the corresponding epoxide has been obtained as the major product.

It has been observed that during the catalytic reaction, the yield of the reaction increases with time and after a certain time the conversion seems to reach its saturation. Samples were collected from the reaction mixtures at regular time interval and analyzed by GC to calculate the yield of reaction at different time intervals. A plot

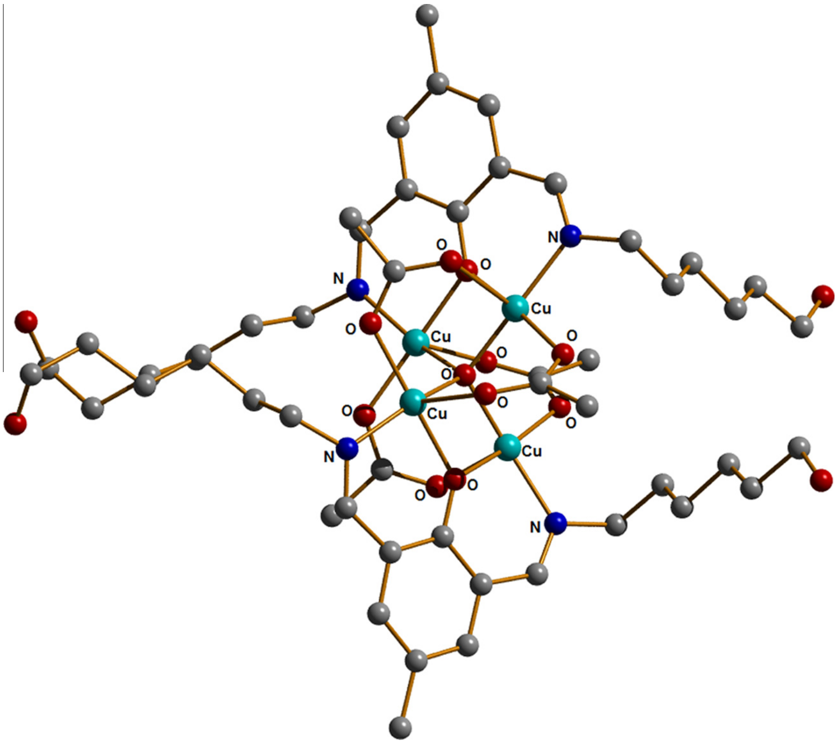


Fig. 3. A perspective view of complex **5**. Hydrogen atoms were omitted for clarity.

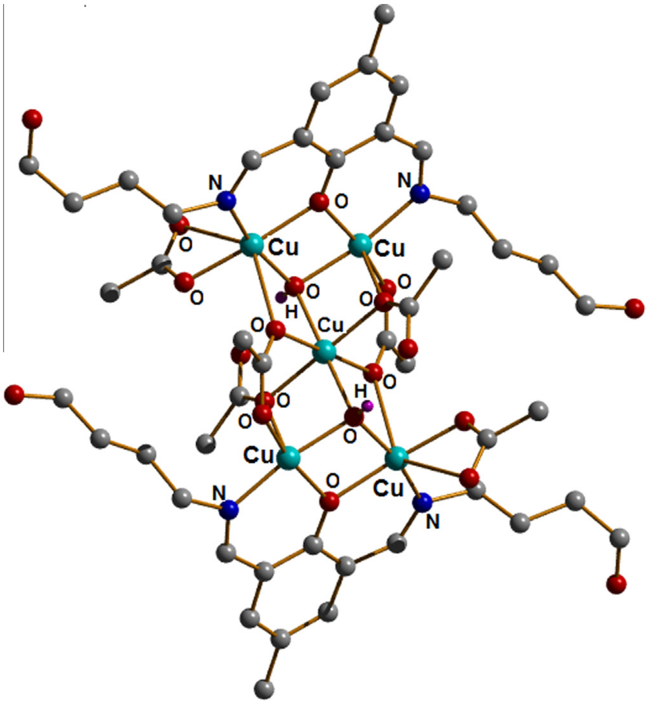


Fig. 4. A perspective view of complex **3**. All hydrogen atoms except hydrogen atoms of hydroxide ions and solvent molecule were omitted for clarity.

of conversion vs time for complex **2** is shown in Fig. 5. Similar plots (Figs. s1–s4) for other copper(II) complexes are given in the Supplementary information. It can be seen from the figure that the conversion yield followed a sigmoid curve. A blank reaction was carried out without any catalyst using cyclohexene as the model substrate under the same experimental conditions. Cyclohexene has been chosen since maximum conversion has been achieved with it. The result for that reaction shows a significant decrease in the conversion (6%) of the substrate as well as the epoxide selectivity (25%) with no metal complex. Another blank reaction was carried out in the presence of copper(II) chloride under the same experimental conditions. The results show a slight improvement of the conversion (12%) and epoxide selectivity (20%) in comparison to the conversion of cyclohexene with no metal salt, but a much lower conversion yield in comparison to all the complexes

Table 7
Epoxidation[a] of olefins by different catalysts.

Catalysts	Olefins	Conversion[b]	Selectivity	TOF[c]
1	cyclohexene	80	86	66.7
	Styrene	76	82	63.3
	α-Methyl styrene	71	78	59.2
	trans-stilbene	82	80	68.3
2	Cyclohexene	83	88	69.2
	Styrene	74	80	61.7
	α-Methyl styrene	70	79	58.3
	trans-stilbene	78	78	65.0
3	cyclohexene	80	84	66.7
	Styrene	72	75	60.0
	α-Methyl styrene	70	76	58.3
	trans-stilbene	75	83	62.5
4	cyclohexene	84	85	70.0
	styrene	73	82	60.8
	α-methyl styrene	76	78	63.3
	trans-stilbene	82	88	68.3
5	cyclohexene	82	85	68.3
	styrene	75	78	62.5
	α-methyl styrene	69	78	57.5
	trans-stilbene	77	84	64.2

[a] Solvent: Acetonitrile; temperature: 50 °C; oxidant: *tert*-butyl hydroperoxide;

[b] conversions were measured after 24 h of the reaction, average of two measurements done under identical conditions);

[c] TOF: turnover number = moles of substrate converted per mole of metal complex per hour.

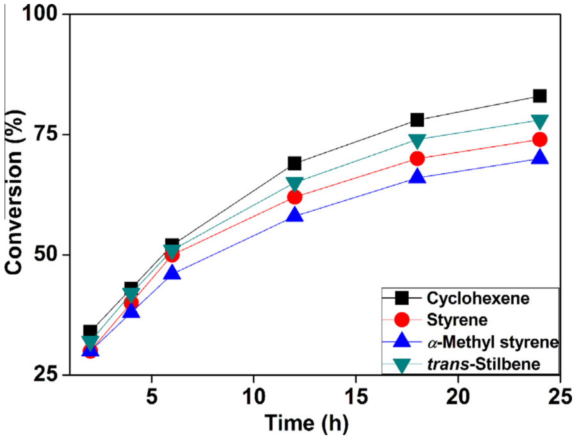


Fig. 5. A plot of conversion vs time for complex **2**.

leading to the relevance of the presence of N,O donor ligands with the metal centers.

The catalytic activities of the complexes in homogeneous medium are lower or comparable in conversion of the substrate and epoxide selectivity in comparison with W(VI) complexes or Mo catalysts [37,38], Mn catalysts [39], and Fe–porphyrin complexes [40], but these are more active catalysts in comparison to previously reported Cu complexes [17–20,26,27,41].

Epoxidation reactions are carried out using different oxidants like hydrogen peroxide [38], *tert*-butyl hydroperoxide [42], molecular oxygen [43], sodium hypochlorite [44], iodosylbenzene [45] etc. The ability to oxidize cyclohexene in the presence of different oxidants such as hydrogen peroxide, TBHP and sodium hypochlorite has been examined in the presence of **1** as the catalyst under identical reaction conditions. The results show 63%, 80% and 48% conversion yields of cyclohexene using hydrogen peroxide, TBHP and sodium hypochlorite as the oxidants respectively. The yield of the reactions has been analyzed after 24 h. It is clear from the results that TBHP serves as the best oxidant among all the oxidants whereas other oxidants show distinctly low activity. Although hydrogen peroxide would have been the most desired oxidant from an environmental view point, TBHP has been selected as the oxidant due to its better activity.

Acetonitrile has been used as the solvent since all the complexes are soluble in acetonitrile. Apart from this, it is difficult to oxidize acetonitrile in the present reaction conditions. In all the reactions, all substrates were converted into their products in good yield.

The catalytic reaction was also performed at different temperatures to study the effect on the catalytic efficacy of the complexes. All the complexes behave similarly for their ability to oxidize olefins at different temperature, showing the best activity in the temperature region near 50 °C.

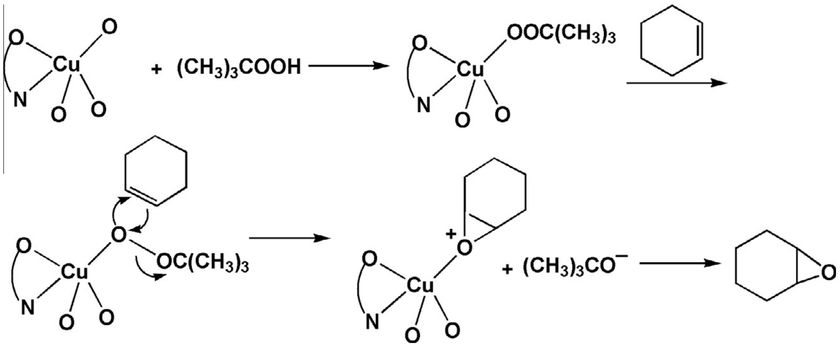
One of the main drawbacks of homogeneous catalysis is the recovery of the catalyst. In this regard, we have tried to recover catalysts after completion of the catalytic reactions. After recovery we have tried to confirm whether the recovered materials were the same as they were before catalytic reaction by elemental analysis, FT-IR and mass spectroscopy. The data of analysis of the recovered materials were not similar to that of materials before catalysis. In conclusion, the complexes acted as catalyst for epoxidation but they were destroyed after the reaction.

3.4. Mechanism

Copper(II) complexes have been found to be active catalysts for epoxidation of olefins while copper-hydroperoxo species has been detected in the reaction mixture [26]. Metal complexes formed metal-hydroperoxo species in the presence of TBHP as evidenced from the UV–Vis spectra. The UV–Vis spectrum of complex **2** in the presence of TBHP was recorded as a representative case. It showed an intense peak at around 400 nm, with a shoulder in the range of 415–440 nm. This fact could be attributed to the formation of Cu-peroxo or Cu-hydroperoxo species [26,46]. This metal peroxo intermediate may be the active species in the conversion of alkenes. It is difficult to identify the exact active species which is responsible for the catalytic transformations. In order to detect the active species or number of copper atom(s) of the complexes in solution we have recorded ESI mass spectra of the complexes in acetonitrile. The spectrum of complex **4** showed peaks at *m*/*z* 395.15 and 457.08 along with a peak at 363.27 corresponding to the existence of one and two copper atoms coordinated to the ligand along with the presence of only ligand respectively. Because of fragmentation of the complex, different species were detected during recording of mass spectrum of **4**. Fragmentation of other complexes during mass spectra analysis has also been noticed. Thus, it became difficult to detect the actual active center by mass spectroscopy. As copper-peroxo or copper-hydroperoxo has been detected in this study like previously reported research, so a similar pathway of epoxide formation is expected here and accordingly a probable mechanism has been proposed (Scheme 2). This reaction may proceed with the formation of copper-peroxo species and *tert*-butyl alcohol since we can detect tert-butyl alcohol during the course of reaction for all the catalysts.

4. Conclusions

Five multinuclear copper(II) complexes with N,O-donor Schiff-base ligands have been synthesized and characterized using various techniques. These complexes have been used as catalysts for the epoxidation of olefins using *tert*-butyl hydroperoxide as



Scheme 2. Probable mechanism for the epoxidation of cyclohexene (representative case).

oxidant. The result shows that olefins are converted into the corresponding epoxide as the major product with good conversion percentage.

Acknowledgements

PR gratefully acknowledges financial support from DST, New Delhi (SERB sanction order no. SB/EMEQ-065/2013 dated 09/07/2013). SH and SD wishes to thank CSIR, New Delhi and UGC, New Delhi respectively for providing them fellowships.

Appendix A. Supplementary data

CCDC 832675, 832677, 832678 and 832679 contains the supplementary crystallographic data for **1**, **3**, **4** and **5**. 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.2014.04.028.

References

[1] M. Sarkar, R. Clérac, C. Mathonière, N.G.R. Hearns, V. Bertolasi, D. Ray, Inorg. Chem. 49 (2010) 6575.

[2] M. Sarkar, R. Clérac, C. Mathonière, N.G.R. Hearns, V. Bertolasi, D. Ray, Inorg. Chem. 50 (2011) 3922.

[3] S. Saha, A. Sasmal, C. Roy Choudhury, C.J. Gómez-Garcia, E. Garribba, S. Mitra, Polyhedron 69 (2014) 262.

[4] K.C. Gupta, A.K. Sutar, Coord. Chem. Rev. 252 (2008) 1420.

[5] K.C. Gupta, A.K. Sutar, C.-C. Lin, Coord. Chem. Rev. 253 (2009) 1926.

[6] K.S. Banu, T. Chattopadhyay, A. Banerjee, S. Bhattacharya, E. Suresh, M. Nethaji, E. Zangrando, D. Das, Inorg. Chem. 47 (2008) 7083.

[7] T. Mukherjee, B. Sen, A. Patra, S. Banerjee, G. Hundal, P. Chattopadhyay, Polyhedron 69 (2014) 127.

[8] R. Robson, Aust. J. Chem. 23 (1970) 2217.

[9] R. Robson, Inorg. Nucl. Chem. Lett. 6 (1970) 125.

[10] P. Roy, M. Manassero, K. Dhara, P. Banerjee, Polyhedron 28 (2009) 1133.

[11] P. Roy, J. Coord. Chem. 62 (2009) 2003.

[12] P.A. Vigato, V. Peruzzo, S. Tamburini, Coord. Chem. Rev. 256 (2012) 953.

[13] A.K. Ghosh, M. Pait, M. Shatruk, V. Bertolasi, D. Ray, Dalton Trans. 43 (2014) 1970.

[14] P. Roy, K. Dhara, M. Manassero, P. Banerjee, Eur. J. Inorg. Chem. (2008) 4404.

[15] A.R. Paital, P.K. Nanda, S. Das, G. Aromi, D. Ray, Inorg. Chem. 45 (2006) 505.

[16] P. Roy, M. Manassero, Dalton Trans. 39 (2010) 1539.

[17] P. Roy, M. Nandi, M. Manassero, M. Ricćo, M. Mazzani, A. Bhaumik, P. Banerjee, Dalton Trans. (2009) 9543.

[18] D. Saha, T. Maity, T. Dey, S. Koner, Polyhedron 35 (2012) 55.

[19] R. Bera, C. Adhikary, S. Ianelli, S. Chaudhuri, S. Koner, Polyhedron 29 (2010) 2166.

[20] A. Rezaeifard, M. Jafarpour, A. Naeimi, R. Haddad, Green Chem. 14 (2012) 3386.

[21] A.M. Kirillov, M.V. Kirillova, A.J.L. Pombeiro, Coord. Chem. Rev. 256 (2012) 2741.

[22] G.B. Shul'Pin, Dalton Trans. 42 (2013) 12794.

[23] L. Canali, D.C. Sherrington, Chem. Soc. Rev. 28 (1999) 85.

[24] W. Jiang, J.D. Gorden, C.R. Goldsmith, Inorg. Chem. 51 (2012) 2725.

[25] V. Mendez, K. Guillois, S. Daniele, A. Tuel, V. Caps, Dalton Trans. 39 (2010) 8457.

[26] P. Roy, K. Dhara, M. Manassero, P. Banerjee, Inorg. Chem. Commun. 11 (2008) 265.

[27] M. Nandi, P. Roy, H. Uyama, A. Bhaumik, Dalton Trans. 40 (2011) 12510.

[28] R.R. Gagne, C.L. Spiro, T.J. Smith, C.A. Hamann, W.R. Thies, A.K. Schiemke, J. Am. Chem. Soc. 103 (1981) 4073.

[29] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, Oxford, UK, 1980.

[30] W.-X. Zhang, C.-Q. Ma, X.-N. Wang, Z.-G. Yu, Q.-J. Lin, D.-H. Jiang, Chin. J. Chem. 13 (1995) 497.

[31] APEX-II, SAINT and SADABS. Bruker AXS Inc., Madison, WI, 2008.

[32] (a) G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112;
(b) G.M. Sheldrick, SHELX97, University of Göttingen, Göttingen, Germany, 1997.

[33] R. Karmakar, C. RoyChoudhury, D.L. Hughes, S. Mitra, Inorg. Chim. Acta 360 (2007) 2631.

[34] J.T. Guy Jr., J.C. Cooper, R.D. Gilardi, J.L. Flippen-Anderson, Inorg. Chem. 27 (1988) 635.

[35] M.S. Jana, S. Dey, J.L. Priego, R. Jiménez-Aparicio, T.K. Mondal, P. Roy, Polyhedron 59 (2013) 101.

[36] A.W. Addison, T.N. Rao, J. Reedijk, J. Vanrijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.

[37] S.K. Maiti, S. Dinda, N. Gharah, R. Bhattacharyya, New J. Chem. 30 (2006) 479.

[38] K. Sato, M. Aoki, M. Ogowa, T. Hasimoto, R. Noyori, J. Org. Chem. 61 (1996) 8310.

[39] R. I. Kureshy, N.-ul. H. Khan, S.H.R. Abdi, I. Ahmad, S. Singh, R.V. Jasra, J. Catal. 221 (2004) 234.

[40] W. Nam, S.W. Jin, M.H. Lim, J.Y. Ryu, C. Kim, Inorg. Chem. 41 (2002) 3647.

[41] G. Das, R. Shukla, S. Mandal, R. Singh, P.K. Bharadwaj, J.v. Hall, K.H. Whitmire, Inorg. Chem. 36 (1997) 323.

[42] H. Kakei, R. Tsuji, T. Ohshima, M. Shibasaki, J. Am. Chem. Soc. 127 (2005) 8962.

[43] X. Meng, Z. Sun, R. Wang, S. Lin, J. Sun, M. Yang, K. Lin, D. Jiang, F.-S. Xiao, Catal. Lett. 76 (2001) 105.

[44] L. Kürti, M.M. Blewett, E.J. Corey, Org. Lett. 11 (2009) 4592.

[45] S. Hailin, W. Beaven, S. Mandimutsira, R. Todd, B. Ramdhanie, J.P. Fox, D.P. Goldberg, J. Am. Chem. Soc. 126 (2004) 18.

[46] J. Reim, R. Werner, W. Haase, B. Krebs, Chem. Eur. J. 4 (1998) 289.

[47] D. Das, A. Guha, S. Das, P. Chakraborty, T.K. Mondal, S. Goswami, E. Zangrando, Inorg. Chem. Commun. 23 (2012) 113.

[48] A.K. Ghosh, D. Ray, Polyhedron 52 (2013) 370.