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Synthesis, Structure, Magnetic and Catalytic Competency of a Tetradentate (NNOO) Schiff Base Mediated Dimeric Copper(II) Complex

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One dinuclear copper(II) complex {μ-[2,2′-{ethane-1,2-diyl*bis*[(azanylylidene)methanylylidene]}*bis*(phenolato)]}-{μ-[2,2′-{ethane-1,2-diyl*bis*[(azanylylidene)methanylylidene]}*bis*(phenolato)]}dicopper(II), $[Cu_2(salen)_2]$ (**1**) [$salen^{2-}$ = [2,2′-{ethane-1,2-diyl*bis*-[(azanylylidene)methanylylidene]}*bis*(phenolato)] has been isolated and characterized by X-ray diffraction analysis and spectroscopic studies. X-ray single crystal structure examination revealed that each Cu(II) center in the asymmetric unit of **1** adopts a distorted square planar geometry with a CuN_2O_2 chromophore, where two asymmetric units are attached through congregation of Salen involving Cu-O bond to form dinuclear molecular unit $[Cu_2(salen)_2]$. In crystalline state, these dinuclear entities in **1** are extended through C-H···π interactions and π···π interactions displaying a 3D network structure. The variable-temperature magnetic susceptibility measurement asserted a dominant antiferromagnetic interaction between the copper(II) centers through Cu-O-Cu linkage in **1** with $J = -1.46$ cm^{-1}. The catalytic efficacy of complex **1** was studied in a series of solvents for the oxidation of styrene and cyclooctene using *tert*-butyl-hydroperoxide (TBHP) as an active oxidant under mild conditions. The catalytic reaction mixture has been analyzed by gas chromatography and it displayed that the yield of the epoxidation and its selectivity is optimum in acetonitrile medium.

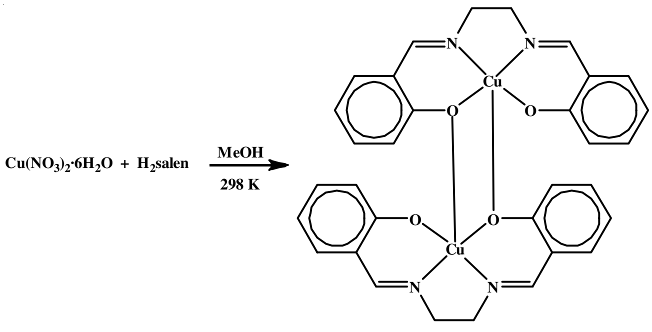
Keywords: Dimeric copper(II) complex, Tetradentate Schiff base, Structure, Magnetism, Catalytic competency.

INTRODUCTION

Metal-organic frameworks (MOFs) [1] constructed through strong metal-ligand covalent bonds [2] and multiple weak non-covalent forces [3] have drawn great attention of many research groups in isolation of different advanced functional materials [4-8]. Single-pot synthesis [9] is an efficient synthetic approach using judiciously chosen metal ions and organic in pre-assigned molar ratios to isolate such target materials. Copper(II), a $3d^9$ ion, affords [10] a variety of geometries that may lead to significant differences in overall molecular and crystalline architectures and thereby different biological and catalytic activities [11,12].

Schiff bases [13] are the important organic ligands because of their straightforward synthesis, structural varieties, varied denticities and are moderate electron donors with easily-tunable electronic and steric effects [14]. Salen refers to a tetradentate C_2-symmetric ligand synthesized from salicyaldehyde and ethylenediamine, which are structurally related to the classical salen ligand, primarily *bis*-Schiff bases. The metal-free salen compound (H_2salen or $salenH_2$) has two phenolic hydroxyl groups. The salen ligand is usually its conjugate base ($salen^{2-}$), resulting from the loss of protons from those hydroxyl groups. Salen ligands are notable for coordinating a wide range of different metals, which they can often stabilize in various oxidation states [15]. Copper(II) Schiff base complexes find wide applicability in the field of catalysis, antimicrobial activities, antifungal and antiviral activities, synergistic action on insecticides, plant growth regulator, antitumor, cytotoxic activity, harmonic generation activity, *etc*. Schiff base copper(II) complexes can now be extensively used as active catalysts [16-28]. In the present endeavour, we have successfully isolated a neutral dinuclear complex, {μ-[2,2′-{ethane-1,2-diyl*bis*[(azanylylidene)methanylylidene]}*bis*(phenolato)]}-{μ-[2,2′-{ethane-

1,2-diyl*bis*[(azanylylidene)methanylylidene]}*bis*(phenolato)]}-dicopper(II), $[Cu_2(salen)_2]$ (**1**) [salen^{2-} = [2,2′-{ethane-1,2-diyl-*bis*[(azanylylidene)methanylylidene]}*bis*(phenolato)]. Structure of complex **1** has been resolved by X-ray diffraction measurements to define the exact coordination sphere. This work has addressed to the synthesis, characterization, magnetic property and catalytic efficacy has been justified by the oxidation of cyclooctene by employing *tert*-butyl-hydroperoxide (TBHP) as an efficient oxidant in different solvent media.



$[Cu_2(salen)_2]$ (1)

Scheme-I: Synthetic route for complex **1**

EXPERIMENTAL

High purity salicylaldehyde (E. Merck, India), ethanediamine, cyclooctene and *tert*-BuOOH (70% aq.) (Aldrich, USA), copper(II) nitrate hexahydrate (E. Merck, India) were purchased and used as received. Schiff base, H_2salen was synthesized by the condensation of 1:2 molar ratio of ethylenediamine and salicylaldehyde in dehydrated alcohol [29]. All other chemicals and solvents were of AR grade. The solvents were distilled and dried before use.

Physical measurements: Microanalysis (CHN) was performed in a Perkin-Elmer 240 elemental analyzer. IR spectra were recorded on a Bruker Alpha T200140 FT-IR spectrometer. Absorption spectra were studied on Shimadzu UV2100 UV-vis recording spectrophotometer. Magnetic measurement of **1** was performed with a Cryogenic SQUID S600 magnetometer operating between 2 and 300 K at an applied field of 1T. The magnetic data were corrected for the diamagnetism of the sample holder, measured in the same range of temperature field and the intrinsic diamagnetism of the samples was estimated through Pascal's constants.

Synthesis of $[Cu_2(salen)_2]$ (1): A methanolic solution (5 mL) of H_2salen (0.268 g, 1.00 mmol) was added dropwise to a solution of copper(II) nitrate hexahydrate (0.296 g, 1.00 mmol) in the same solvent (10 mL). The final deep blue solution was filtered and the supernatant liquid was kept undisturbed in open air for slow evaporation. After 3 days, a dark green crystalline product of complex **1** was isolated by filtration, washed with dehydrated alcohol and dried *in vacuo* over silica gel (**Scheme-I**). Yield: 0.462 g (70%). Elemantal anal. calcd. (found) % for $C_{32}H_{28}N_4O_4Cu_2$ (**1**): C, 58.26 (58.50); H, 4.28 (4.36); N, 8.49 (9.12). IR (KBr, cm^{-1}): ν(CH=N), 1620-1655; ν(C-O), 1332-1355. UV-Vis (λ_{max}, nm; DMF): 266, 296, 388, 620; Λ_M (DMF): 7 Ω^{-1} cm^2 mol^{-1}.

X-ray data collection and structure refinement: A single crystal of complex **1** suitable for X-ray analysis was selected from those obtained by slow evaporation of a methanol solution at room temperature. Diffraction data were collected on a Bruker SMART 1000 CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å) and were used to measure cell dimensions and diffraction intensities. Data were collected using the ω-θ scan technique in the range to a maximum 1.54° < θ < 25.24°. For data collection, data reduction and cell refinement the program SAINT-Plus [30] was used. The structure was solved by direct methods using SIR97 [31] and refined with version 2018/3 of SHELXL [32] using least squares minimization. A summary of the crystallographic data and structure determination parameters for complex **1** is shown in Table-1.

TABLE-1
CRYSTALLOGRAPHIC DATA FOR COMPLEX **1**

Empirical formula	$C_{32}H_{28}N_4O_4Cu_2$
Formula weight	659.66
Crystal system, space group	Monoclinic, *C*2/c
Temperature	293(2) K
Wavelength	0.71073 Å
Unit cell dimensions	a = 26.752(6) Å, b = 7.0118(15) Å, c = 14.772(3) Å, α = 90.00°, β = 97.423(3)°, γ = 90.00°
Volume	2747.7(10) Å^3
Z, calculated density	4, 1.595 mg/cm^3
Absorption coefficient	1.595 mm^{-1}
F(000)	1352
Crystal size	0.23 × 0.16 × 0.09 mm^3
Theta range	1.54 to 25.24 °
Limiting indices	-32 <= h <= 32, -8 <= k <= 8, -16 <= l <= 16
Reflections collected/unique	12859/2503 [R(int) = 0.049]
T_{max} and T_{min}	0.872 and 0.710
Data/restraints/parameters	2503/0/190
Goodness-of-fit on F^2	1.064
Final R indices [I>2σ(I)]	R = 0.0329 and wR = 0.0869
R indices (all data)	R = 0.0386 and wR = 0.0917
Largest peak and hole	0.435 and -0.767

Weighting scheme: $R = \Sigma||F_o| - |F_c||/ \Sigma|F_o|$, $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, calcd. $w = 1/[\sigma^2(F_o^2) + (0.0500P)^2 + 2.7518P]$ where $P = (F_o^2 + 2F_c^2)/3$.

RESULTS AND DISCUSSION

A new dinuclear copper(II) Schiff base complex {μ-[2,2′-{ethane-1,2-diyl*bis*[(azanylylidene)methanylylidene]}*bis*-(phenolato)]}-{μ-[2,2′-{ethane-1,2-diyl*bis*[(azanylylidene)-methanylylidene]}*bis*(phenolato)]}dicopper(II), $[Cu_2(salen)_2]$ (**1**) [salen^{2-} = [2,2'-{ethane-1,2-diyl*bis*[(azanylylidene)methanylylidene]}*bis*(phenolato)] has been isolated using a one-pot reaction of a 1:1 molar ratio of $Cu(NO_3)_2·6H_2O$ and a tetradentate Schiff base (H_2salen) in methanol at room temperature.

Complex **1** was characterized by microanalytical, spectroscopic and other physico-chemical results. The microanalytical data are in good conformity with the formulation of the complex. The air stable moisture insensitive compound is stable over a long period of time in powdery and crystalline state and soluble in MeOH, EtOH, MeCN, DMF and DMSO, but are insoluble in water. In DMF solution, complex **1** behaves as non-electrolytes as reflected from their low conductivity value (7 ohm^{-1} cm^2 mol^{-1}).

Spectral studies: In IR spectrum, complex **1** shows a band in the range 1655-1620 cm^{-1} attributable due to azomethine group [33]. A sharp band in the range 1355-1332 cm^{-1} is assigned to ν(C-O). A broad band around 3460 cm^{-1} due to ν(O-H) for free ligands was absent for complex, suggesting the coordination of Schiff base as a dianionic ligand. In the UV-vis spectrum, a low-intensity absorption band at 620 nm allocated to *d-d* transition, congruent with the square pyramidal (*sp*) geometry of the copper(II) centers [34]. The absorption band observed at 388 nm may be attributed to the ligand to copper(II) charge transfer transition (LMCT). Additionally, two strong absorption bands in the region 266 and 296 nm may be assigned to a ligand based charge transfer transitions.

Crystal structure of [Cu$_2$(salen)$_2$] (1): Single-crystal X-ray diffraction measurement of [Cu$_2$(salen)$_2$] (**1**) reveals that the crystal belongs to the monoclinic system corresponding from the space group C2/*c*. Single crystal X-ray diffraction study of [Cu$_2$(salen)$_2$] (**1**) was made to define the coordination sphere. An ORTEP diagram of asymmetric units, molecular unit and packing views of 2D sheet and 3D network structures of complex **1** are depicted in Figs. 1-4. Selected bond distances and angles relevant to the coordination spheres are presented in Table-2. Parameters of C-H···π and π···π interactions are given in Tables 3 and 4, respectively. X-ray structural analysis revealed that each Cu(II) center in asymmetric unit of complex **1** adopts a distorted square planar geometry with a CuN$_2$O$_2$ chromophore coordinated by two N atoms (N1, N2) and two O atoms (O1, O2) of the tetradentate Schiff base ligand (salen) (Fig. 1). The coordination sites of the basal plane in square are occupied by (N1 and O2) and (N2 and O1) in *trans* position. Angles of *cisoid* and *transoid* are in [83.60(9)-94.79(8)°] and [170.37(8)-171.10(8)°] ranges, respectively (Table-2). These two asymmetric units are connected through congregation of salen ligand involving Cu-O bond to form dinuclear molecular unit [Cu$_2$(salen)$_2$] (Fig. 2), where each Cu(II) center completes its penta-coordination in a distorted square pyramidal environment. The Cu···Cu separation in each dinuclear entity is 3.207 Å and bond angle of Cu1-O1-Cu1^i core is 93.78(7)° [symmetry code: (i) 1/2-x,1/2-y,-z]. The primary bond distances of Cu-N and Cu-O are ranges from 1.9168(17)-1.964(2) Å, while Cu1-O1^i/Cu1^i-O1 are comparatively larger [2.4212(18) Å] indicating weaker in nature. In crystalline state, these dinuclear entities

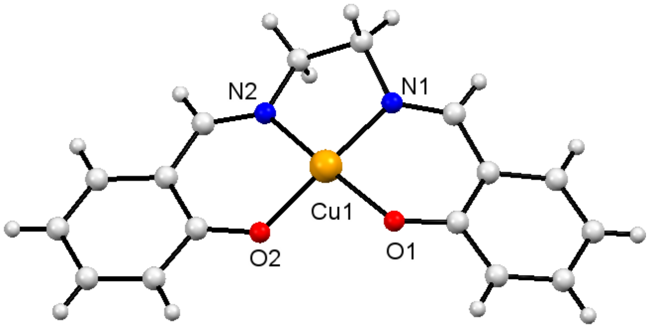


Fig. 1. Perspective view of the asymmetric unit of [Cu$_2$(salen)$_2$] (**1**) with displacement ellipsoid drawn at the 50% probability level

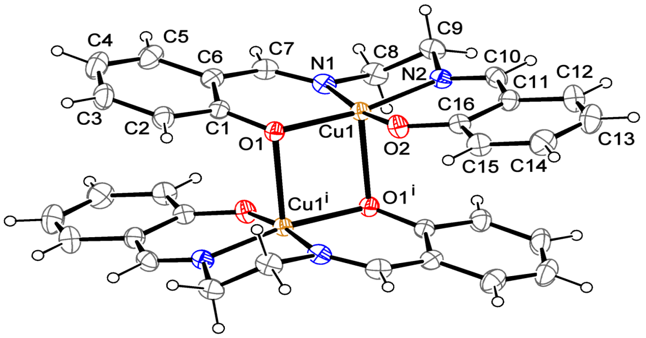


Fig. 2. An ORTEP diagram of dinuclear molecular unit of [Cu$_2$(salen)$_2$] (**1**) with displacement ellipsoid drawn at the 40% probability level; symmetry code: (i) 1/2-x, 1/2-y, -z

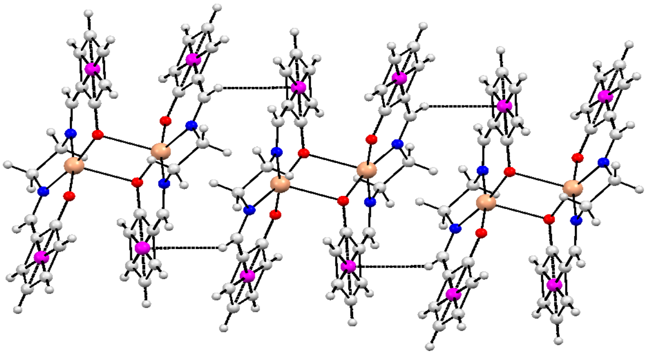


Fig. 3. Crystal packing view of 2D sheet structure in complex **1** through C-H···π interactions viewed along crystallographic *b* axis

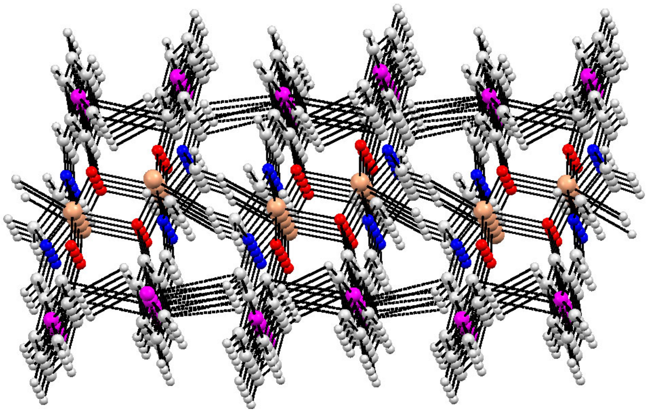


Fig. 4. 3D network structure of complex **1** involving both C-H···π and π···π interactions

TABLE-2
SELECTED BOND DISTANCES (Å)
AND BOND ANGLES (°) FOR COMPLEX **1**

Bond distances (Å)			
Cu1-N1	1.958(2)	Cu1-O2	1.9168(17)
Cu1-N2	1.964(2)	Cu1-O1^i	2.4212(18)
Cu1-O1	1.9488(16)	Cu1^i-O1	2.4212(18)
Bond angles (°)			
N1-Cu1-N2	83.60(9)	N2-Cu1-O1^i	102.27(7)
N1-Cu1-O1	91.26(8)	O1-Cu1-O2	91.34(7)
N1-Cu1-O2	171.10(8)	O1-Cu1-O1^i	86.22(7)
N1-Cu1-O1^i	94.79(8)	O2-Cu1-O1^i	93.87(7)
N2-Cu1-O1	170.37(8)	Cu1-O1-Cu1^i	93.78(7)
N2-Cu1-O2	92.58(8)		

Symmetry code: (i) 1/2-x, 1/2-y, -z.

in complex **1** are engaged through C-H···π interactions [C10-H10···Cg(5): 2.94 Å, 135.00°; Cg(5) = C(1)→C(2)→C(3)→C(4)→C(5)→C(6)] (Table-3) to give 2D sheet structure (Fig. 3) viewed along crystallographic *b*-axis. These 2D sheet structure are further stabilized through π···π interaction [Cg(6)···Cg(6): 5.477(2)°; Cg(6) = C(11)→C(12)→C(13)→C(14)→C(15)→C(16)] (Table-4) to result a supramolecular 3D network structure (Fig. 4).

Magnetic studies: The temperature dependence of the molar magnetic susceptibility (χ_M) for complex **1** in the 5-300 K temperature range was measured with a superconducting quantum interference device (SQUID) magnetometer, under magnetic fields of 10 kG (Fig. 5). The $\chi_M T$ value of 0.019 cm^3 mol^{-1} at 300 K for complex **1** is higher than the value expected for an isolated magnetically uncoupled copper(II) ion ($\chi_M T$ = 0.013 cm^3 mol^{-1} for g = 2.0). Upon cooling the χ_M value of complex **1** remains almost the same until about 65 K and then increases rapidly to reach a minimum of 0.13 cm^3 mol^{-1} K at about 5 K. This clearly indicates that magnetic interaction between copper(II) ions through Cu-O-Cu linkage is antiferromagnetic in nature. To estimate the magnitude of the antiferromagnetic coupling the magnetic susceptibility data were fitted to the modified Bleaney-Bowers equation for two interacting copper (II) ions (S = ½) with the Hamiltonian in the form $H = -J\,\hat{S}_1\cdot\hat{S}_2$. The susceptibility equation for such a dimeric system can be written as follows in eqn. 1 [35-37]:

$$\chi = \frac{2Ng^2\beta^2}{kT}\,[3+\exp(-J/kT)]^{-1}(1-\rho)+\frac{Ng^2\beta^2}{2kT}\rho \qquad (1)$$

where N, g, β and ρ parameters in the equation bear their usual meaning. The best fit parameters were J = - 1.46 cm^{-1}, g = 2.11 and r = 0.0005.

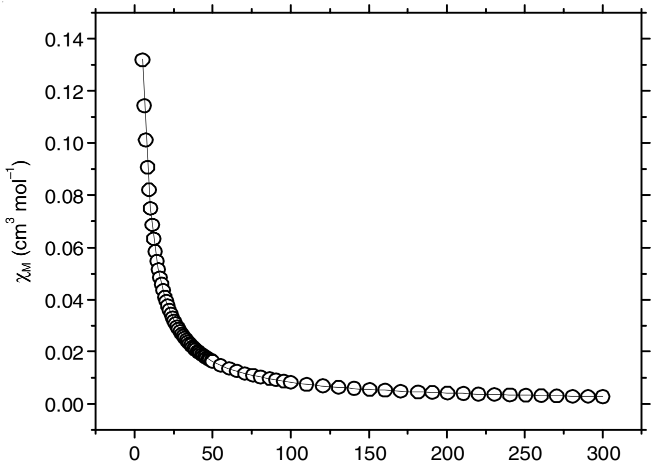


Fig. 5. Thermal dependence of χ_M for complex **1**

Catalytic activities of $[Cu_2(salen)_2]$ (1): The catalytic activity of complex **1** in the oxidation of styrene and cyclooctene in homogeneous medium is summarized in Table-5. The graphical representation of alkene conversion in the presence of complex **1** is shown in Fig. 6. Styrene was efficiently converted to 97% with epoxide selectivity of 54%. Along with this a considerable amount of benzaldehyde and benzoic acid are also formed. Copper(II) Schiff base complexes have been used as homogeneous catalysts in olefin oxidation reactions with different oxidizing agents in the recent past. Koner *et al.* [16] studied this reaction over a series of copper(II) Schiff base complexes, which gives styrene epoxide in 54-39% yield (selectivity 72-39%) under homogeneous conditions with *tert*-BuOOH. Recently, a diazido-bridged dinuclear copper(II) compound containing a tridentate Schiff base ligand shows 82% coversion of styrene with 60% epoxide selectivity [17].

TABLE-3
C-H···π INTERACTION PARAMETERS (Å, °) FOR COMPLEX **1**

C-H···π interactions (Å, °)					
D-H···A	D-H	H···A	D···A	D-H···A	Symmetry code
C10-H10···Cg(5)	0.9300	2.94	3.676(3)	135	1/2-x, -1/2+y, 1/2-z

Cg(5) = C(1)→C(2)→C(3)→C(4)→C(5)→C(6)

TABLE-4
π···π INTERACTION PARAMETERS (Å, °) FOR COMPLEX **1**

π···π interaction (Å, °)					
Ring-ring	Cg-Cg distance	Dihedral angle (i, j)	Perpendicular distances between baricenters (i, j)	Slippage	Symmetry code
Cg(6)-Cg(6)	5.477(2)	56.01	0.2485	4.541	-x,1-y,-z

Cg(6) = C(11)→C(12)→C(13)→C(14)→C(15)→C(16)

TABLE-5
HOMOGENEOUS CATALYTIC OXIDATION OF OLEFINS CATALYZED BY COMPLEX **1** IN ACETONITRILE MEDIA

Substrate	Reaction time (h)	Conversion (wt.%)	Yield of products (%)	
			Epoxide	Others
Styrene	24	97	52	45[a]
Cyclooctene	24	82	68	14[b]

Reaction conditions: Cyclooctene (10 mmol); catalysts (0.005 mmol); *tert*-BuOOH (20 mmol); acetonitrile (8 mL); temperature (70 °C)
[a]Benzaldehyde and benzoic acid; [b]cyclooct-2-en-1-ol and cyclooct-2-en-1-one

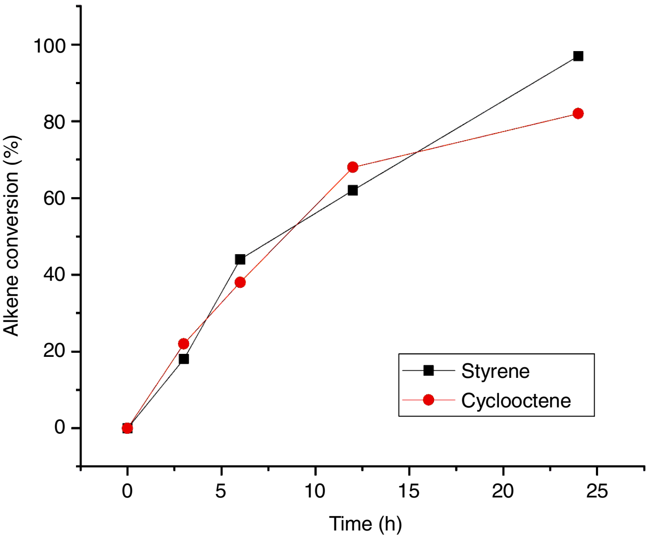


Fig. 6. Reaction profile for the oxidation of olefins with *tert*-BuOOH in presence of complex **1**

The catalytic efficacy of different azido-bridged Schiff base copper(II) complexes which gives styrene epoxide in 100-90% yield (selectivity 72-54%) was also studied under homogeneous condition using same oxidant [18,19]. Das *et al.* [20] have obtained a moderate yield of olefin epoxide using a copper(II) Schiff base complex as a catalyst in the presence of 2-methylpropanal using molecular oxygen as oxidant under homogeneous conditions [20]. A maximum yield of 15% of styrene epoxide has been achieved using iodosyl benzene as oxidant over Schiff base copper(II) complexes [21]. Rayati *et al.* [22] studied epoxidation of styrene over two copper(II) Schiff base complexes under homogeneous conditions using *tert*-BuOOH, which shows over 95% conversion with epoxide selectivity 25%. Saha *et al.* [23] reported styrene epoxidation reaction over a copper(II) Schiff base complex, [Cu(HL^1)(NO$_3$)] (H$_2$L^1 = 1-(*N*-orthohydroxyacetophenimine)ethane-2-ol), which shows 86% conversion with 100% epoxide selectivity [23].

The results of reported epoxidation reactions of styrene using *tert*-BuOOH as oxidant over copper(II) Schiff base complexes under homogeneous conditions are collated in Table-6. Cyclooctene was converted in good yield (conversion 82%) to their oxides, with high epoxide selectivity (83%) when reacted with *tert*-BuOOH. In addition, a small amount of cyclooctane-1,2-diol was also formed. We have earlier studied the oxidation reactions of a variety of olefins over copper(II) Schiff base complexes, which exhibit excellent catalytic activity with *tert*-BuOOH in different solvent media, where cyclooctene has been converted to its epoxide (conversion 76-75%, selectivity 63-56%) in acetonitrile media [16]. Likewise, the epoxidation of cyclooctene using a single end-on azido bridged 1D chain Schiff base copper(II) complex as catalyst is also reported [24], where the highest conversion occured also in acetonitrile conversion 86%, selectivity 81%) with *tert*-BuOOH as oxidant. We have successfully converted cyclooctene to cyclooctene oxide by some azido-bridged Schiff base copper(II) complexes (conversion 96-85%, selectivity 76-72%) in recent past [18,19]. In our very recent attempt, we converted cyclooctene with 86% epoxide yield using a neutral nitrate bridged coordination polymer of copper(II) containing a tridentate Schiff base as catalyst [25]. Rayati *et al.* [22] studied the oxidation of cyclooctene with *tert*-BuOOH in the presence of electron-rich salen type Schiff base copper(II) complexes, where the highest conv-

TABLE-6
COMPARISON OF CATALYTIC EFFICACY OF THE COMPLEX **1** WITH OTHER REPORTED COPPER(II) CATALYSTS FOR THE OXIDATION OF STYRENE AND CYCLOOCTENE WITH *tert*-BUOOH IN CH$_3$CN MEDIUM

Complexes	Conversion (%)		Ref.
	Styrene	Cyclooctene	
[Cu(L^1)(H$_2$O)](ClO$_4$)	86	75	[16]
[Cu(L^2)]	75	75	[16]
[Cu(L^3)]	99	76	[16]
[Cu$_2$(L^4)$_2$(μ$_2$-1,1-N$_3$)$_2$]	82	78	[17]
[CuL^5(μ$_3$-1,3-N$_3$)]$_n$	100	96	[18]
[Cu(L^6)(N$_3$)]	98	95	[19]
[Cu$_2$(L^7)$_2$(μ$_2$-1,1-N$_3$)$_2$] [Cu(L^8)(N$_3$)]	96	90	[19]
[Cu(L^8)(N$_3$)]	90	85	[19]
[Cu{salnptn(3-OMe)$_2$}]	97^a	70^b	[22]
[Cu(hnaphnptn)]	96^a	70^b	[22]
[Cu(HL^9)(NO$_3$)]	98	–	[23]
CuL^{10}(μ -1,1-N$_3$)]$_n$	–	86	[24]
[Cu(L^{11})(μ-ONO$_2$)]$_n$	–	88	[25]
(CuL$_n$, n = 1–4)	–	69	[26]
[Cu$_2$(salen)$_2$] (**1**)	97	82	This work

HL^1 = 1-(*N*-*ortho*-hydroxy-acetophenimine)-2-methyl-pyridine, H$_2$L^2 = *N,N'*-(2- hydroxy-propane-1,3-diyl)-*bis*-salicylideneimine, H$_2$L^3 = *N,N'*-(2,2-dimethyl-propane-1,3-diyl)-*bis*-salicylideneimine, L^4 = 2-[1-(aminoethylimino)ethyl]-phenoxo ion, HL^5 = 2-[1-(methylamino-ethylimino)-methyl]-phenol, HL^6 = 1-(*N*-5-methoxy-*ortho*-hydroxyacetophenimino)-2,2-dimethyl-aminoethane], HL^7 = 1-(*N*-*ortho*-hydroxyacetophenimine)-2,2'-diethyl-aminoethane, HL^8 = 1-(*N*-salicylideneimino)-2-(*N,N*-diethyl)-aminoethane], H$_2${salnptn(3-OMe)$_2$} = Schiff-base derived by the condensation of 2,2'-dimethylpropandiamine and 2-hydroxy-3-methoxybenzaldehyde, H$_2${hnaphnptn} = Schiff-base derived by the condensation of 2,2'-dimethylpropandiamine and 2-hydroxy-1-naphthaldehyde, H$_2$L^9 = 1-(*N*-*ortho*-hydroxyacetophenimine)-ethane-2-ol, HL^{10} = 1-(*N*-*ortho*-hydroxyacetophenimine)-2-(*N*-ethyl)aminoethane, HL^{10} = 4-methoxy-2-[1-(methylaminoethylimino)methyl]-phenol, Schiff-base derived from the condensation of meso-1,2-diphenyl-1,2-ethylenediamine with various salicylaldehyde derivatives (x-salicylaldehyde for H$_2$L$_n$, x = H (n = 1), 5-Br (n = 2), 5-Br-3-NO$_2$ (n = 3) and 2-hydroxyacetophenone (n = 4); ^{a}For 6 h, ^{b}For 8 h ersion was 70% after 8 h in acetonitrile media and epoxide selectivity was 100% [22]. Abbasi *et al.* [26] demonstrated the epoxidation of cyclooctene over a series of mononuclear and dinuclear salen type copper(II) Schiff base complexes using *tert*-BuOOH, where the highest conversion goes to 85% with maximum 67% epoxide selectivity. Along with the epoxide, the allylic oxidation product cyclooct-2-en-1-ol and cyclooct-2-en-1-one were also obtained.

However, in present study, the conversion of cyclooctene by complex **1** displayed favourable epoxide selectivity. We studied some control experiments by varying the solvents, temperature and the ratio of the oxidant to optimize the catalytic reaction. Solvent polarity plays an important role for oxidation reaction. The best performance of the catalyst was observed in acetonitrile media. Due to the optimum polarity of acetonitrile, it can dissolve both olefin and *tert*-BuOOH, which might be facilitating the highest catalytic activity. A graphical representation of the relative efficacy of the catalyst **1** for the oxidation of alkenes in different solvents is shown in Fig. 7. The efficiency of catalyst followed the order: acetonitrile > acetone > chloroform > dichloromethane (Table-7). We acquainted the reactions by varying the temperature from room temperature to 75 ºC for cyclooctene in acetonitrile to determine the optimum reaction temperature (Fig. 8). The reaction profile clearly evidenced that an optimum temperature of 65-70 ºC is needed to activate the catalyst. Control experiments without using catalyst failed to produce the desired product (Table-8). The conversion of cyclooctene was only 4% in the absence of the catalyst. Simple copper nitrate was compared with catalyst **1** to glimpse the structural effect. Although the conversion was good (67%), it showed poor epoxide selectivity (54%). The copper(II) binds the peroxo-group on treatment with peroxides [27] to form the pre-catalyst containing L_xCu-OOH (where L= ligand), which are capable of transferring the oxo-functionality to the organic substrates to produce the oxidized products [28]. It is our assumption that a similar kind of mechanism may be workable in this present case too. The coordination environment around copper(II) is easily cognizable for an external ligand. As a result, *tert*-BuOOH occupies enough space to bind copper in the intermediate stages of the catalytic cycle.

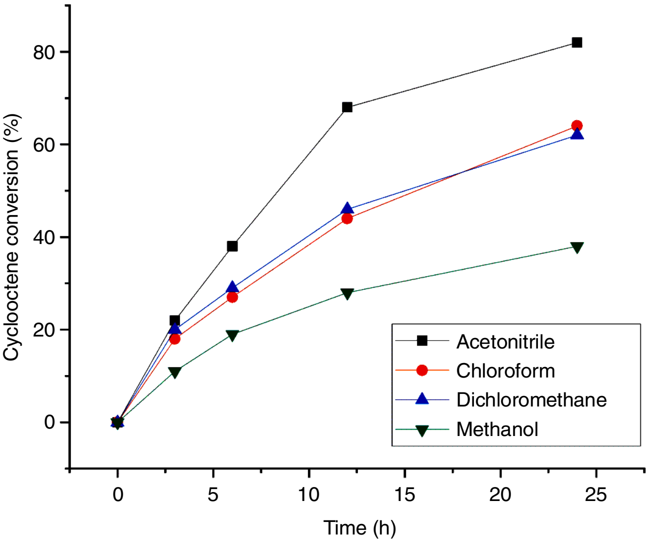


Fig. 7. Reaction profile for the oxidation of cyclooctene with *tert*-BuOOH in different solvents over complex **1**

TABLE-7
HOMOGENEOUS OXIDATION OF CYCLOOCTENE CATALYZED BY THE COMPLEX **1** AT 70 °C IN DIFFERENT SOLVENTS

Solvent	Reaction time (h)	Conversion (wt.%)	Yield of products (%)	
			Epoxide	Others[a]
CH_3CN	24	82	68	14
$CHCl_3$	24	64	47	17
CH_2Cl_2	24	62	46	16
CH_3OH	24	38	24	14

Reaction conditions: Cyclooctene (10 mmol); catalysts (0.005 mmol); *tert*-BuOOH (20 mmol); acetonitrile (8 mL); [a]Cyclooct-2-en-1-ol and cyclooct-2-en-1-one.

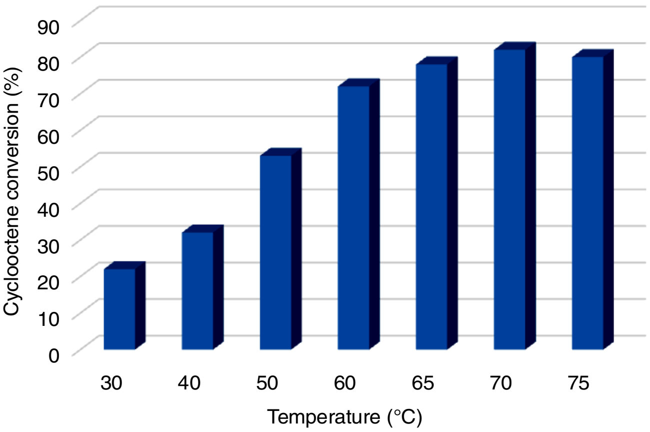


Fig. 8. Comparison of catalytic efficacy of complex **1** at different temperatures

TABLE-8
CONTROL EXPERIMENTS IN OXIDATION OF CYCLOOCTENE WITH *tert*-BUOOH AT 70 °C

Run	Catalyst	Conversion (wt%)	Yield of epoxide (%)
1	No catalyst	5	5
2	$Cu(NO_3)_2$	67	36
3	$[Cu_2(salen)_2]$ (**1**)	82	68

Reaction conditions: Cyclooctene (10 mmol); catalyst (0.005 mmol); *tert*-BuOOH (20 mmol); CH_3CN (8 mL).

Conclusion

In summary, a one neutral dimeric copper(II) complex {μ-[2,2′-{ethane-1,2-diyl*bis*[(azanylylidene) methanylylidene]}-*bis*(phenolato)]}-{μ-[2,2′-{ethane-1,2-diyl*bis*[(azanylylidene)-methanylylidene]}*bis*(phenolato)]}dicopper(II) (**1**) with a tetradentate Schiff base (NNOO) has been synthesized and characterized by X-ray diffraction analysis and spectroscopic studies. X-ray single crystal structure examination indicated that the dimeic structure is embodied through congregation of a tetradentate Schiff base (salen) with (NNOO) donor sets with Cu···Cu separation 3.207 Å. A 3D network structure architects involving dimeric units through C-H···π and π···π interactions in the crystalline state. The variable-temperature magnetic susceptibility measurement revealed an antiferromagnetic interaction between the copper(II) centers. The catalytic competency of complex **1** was studied in a series of solvents for the oxidation of styrene and cyclooctene using *tert*-butyl-hydroperoxide (TBHP) as an efficient oxidant under mild conditions. The catalytic reaction mixture has been analyzed by gas chromatography and it displayed that the yield of the oxidation and its selectivity is maximum in acetonitrile medium.

Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre No. 1551353 for complex **1**. Copy of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0) 1223-336033; or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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