

A nitrate bridged one-dimensional copper(II) coordination polymer with a tridentate (NNO) Schiff base: synthesis, X-ray structure and catalytic efficacy

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Received: 25 May 2020 / Accepted: 18 July 2020 © Springer Nature Switzerland AG 2020

Abstract

A one-dimensional Cu(II) coordination polymer of $[Cu(L)(\mu-ONO_2)]_n$ (1) (HL=4-methoxy-2-[1-(methylaminoethylimino) methyl]-phenol) with bidentate bridging nitrate has been isolated and characterized by X-ray diffraction analysis and spectroscopic studies. Single crystal X-ray analysis revealed that each copper(II) center in the asymmetric unit of complex 1 adopts a distorted square pyramidal geometry with a CuN₂O₃ chromophore ligated through a tridentate Schiff base (L) with (NNO) donor sets and two O atoms of bridging nitrate ion. The adjacent copper atoms are connected by bridging nitrate (μ -ONO₂) in bidentate fashion affording a 1D coordination polymeric chain structure along the crystallographic *b*-axis. In the polymeric framework, the Cu...Cu separation is 4.3749(4) Å. The catalytic efficacy of complex 1 was studied in a series of solvents for the epoxidation of cyclooctene using *tert*-butyl-hydroperoxide (TBHP) as an efficient oxidant under mild conditions. The catalytic reaction mixture was analyzed by gas chromatography and the data indicated that the yield of the epoxidation reaction and its selectivity is maximum in acetonitrile medium.

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s11243-020-00415-7) contains supplementary material, which is available to authorized users.

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Introduction

Coordination polymers (CPs) [1] and metal-organic frameworks (MOFs) [2] through strong metal-ligand covalent bonds [3] and multiple weak non-covalent forces [4] have attracted great attention of many research groups in the isolation of different advanced functional materials [5–9]. Single-pot synthesis [10] is an efficient synthetic approach using judiciously chosen metal ions, organic ligands and bridging units in pre-assigned molar ratios to isolate such target materials. Cu(II), a $3d^9$ ion, affords [11] a variety of geometries that may lead to significant differences in overall molecular and crystalline architectures and thereby produce different biological and catalytic activities [12]. The copper ion also finds significant use in bioinorganic chemistry [13]. A group of mono-negative NNO donor tridentate Schiff base ligands derived from the mono-condensation of diamines with carbonyl compounds (salicylaldehyde, o-hydroxyacetophenone, acetylacetone or benzoylacetone), readily react with transition metal ions and auxiliary ligands to form mono- and polynuclear complexes with varied functionalities and versatile applications. Depending on the relative position, number and nature of the donor atoms of a Schiff base, the ligand approves a favourable control over the stereochemistry of the metallic centers in homo- and heteropolynuclear compounds

Fig. 1 Different coordination motifs of the nitrate ion



Fig. 2 Framework of tridentate (NNO) Schiff base ligand (HL)

Η

[14]. All these opportunities make Schiff bases privileged ligands in the attempt to synthesize metal complexes having relevance to bioinorganic chemistry, catalysis, encapsulation, transport and separation processes [14]. Schiff base copper complexes can now be extensively used as active catalysts in several oxidation reactions, both in homogeneous [15–18] and heterogeneous condition [19, 20]. Nitrate ion (NO_3^{-}) [21] acts as monodentate, bidentate bridging and bidentate chelating ligand (Fig. 1) for the construction of supramolecular architectures. In the framework of our research efforts constituting a part of our continuing study on metal complexes of tridentate Schiff base ligands based on substituted ethylenediamines, we have chosen a tridentate Schiff base (HL) (Fig. 2) to isolate a neutral coordination polymer, $[Cu(L)(\mu - ONO_2]_n (1) (HL = 4-methoxy-2-[1-$ (methylaminoethylimino)methyl]-phenol). The structure of complex 1 has been determined by X-ray diffraction measurements and the catalytic efficacy of 1 for the epoxidation of cyclooctene, employing tert-butyl-hydroperoxide (TBHP) as an efficient oxidant in different solvent media, is also reported.

Experimental

Materials and method

High purity 5-Methoxysalicyladehyde (E. Merck, India), N-methyl ethanediamine (Aldrich, USA) and Cu(II) nitrate hexahydrate (E. Merck, India) were purchased from their respective concerns and used as received. Cyclooctene and

Scheme 1 Synthetic route for Schiff base HL



use. The synthetic reactions and work-up were done in the open air. Microanalysis (CHN) was performed using a Perkin Elmer 240 elemental analyzer. IR spectra were recorded with a Bruker Alpha T 200140 FT-IR spectrometer. Absorption spectra were studied with a Shimadzu UV2100 UV-Vis recording spectrophotometer. GC analysis was carried out with an Agilent Technologies 6890 N network GC system equipped with a fused silica capillary column $(30 \text{ m} \times 0.32 \text{ mm})$ and a FID detector.

Synthesis of Schiff base (HL)

5-Methoxysalicyladedehyde (0.15 g, 1 mmol) was refluxed (10 h) with N-methylethylenediamine (0.07 g, 1 mmol) in dehydrated alcohol (20 ml) with a little modification [22]. After 10 h the reaction solution was evaporated under reduced pressure to yield a gummy mass, which was dried and stored in vacuo over CaCl₂ for subsequent use (Scheme 1). Yield 0.28 g (80% based on amine). Elemental Anal. Calcd for C₁₁H₁₆N₂O₂ (HL): C, 63.4; H, 7.7; N, 13.5%. Found: C, 63.8; H, 8.2; N, 13.5%. FTIR (cm⁻¹): ν(C=N), 1632; ν(N-H), 3120.

Synthesis of $[Cu(L)(\mu - ONO_2)]_n$ (1)

A solution of HL (0.21 g, 1 mmol) in MeOH (5 ml) was added dropwise to a solution of Cu(II) nitrate hexahydrate (0.29 g, 1 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 5 days, a blue crystalline product of 1 was isolated by filtration, washed with dehydrated alcohol and dried in vacuo over silica gel. Yield 0.44 g (70% based on ligand). Anal. Calcd for C₁₁H₁₅N₃O₅Cu (1): C 39.7; H 4.5; N 12.6%. Found: C 40.2; H 4.1; N 13.0%. FTIR (KBr/cm⁻¹): ν_s (NO₃) 1735, 1794. UV–Vis in DMF $[\lambda_{\text{max}}, \text{nm} (\varepsilon_{\text{max}}/\text{dm}^3\text{mol}^{-1} \text{ cm}^{-1})]: 266, 296 (1.20 \times 10^4), 387$ (1.15×10^4) , 607 (2.30×10^2) ; Λ_M (DMF/ohm⁻¹ cm² mol⁻¹):

6. $\mu_{\text{eff.}}$ (B.M.)=1.78. ESR (solid state): g_{\parallel} =2.042; g_{\perp} =2.013, g_{av} =2.022; G=4.753.

X-ray crystallographic analysis

A single crystal of 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 Mo-Ka radiation ($\lambda = 0.71073$ Å) and were used to measure cell dimensions and diffraction intensities. Data were collected using the $\omega - \theta$ scan technique in the range to a maximum $2.7^{\circ} < \theta < 25.5^{\circ}$. For data collection, data reduction and cell refinement. the program SAINT-Plus [23] was used. The structure was solved by direct methods using SIR97 [24] and refined with version 2018/3 of SHELXL [25] using Least Squares minimisation. The model was refined. The amine H atoms were located on a difference Fourier map and refined freely. C-bound H atoms were positioned geometrically and refined using a riding model, with C-H=0.96-0.97 Å and with U iso = 1.2 U eq(C) or 1.5 U eq(C) for methyl H atoms. The final positional and thermal parameters are available as supplementary material. A summary of the crystallographic data and structure determination parameters for complex 1 is set in Table 1. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 2000429 for 1). A copy of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax:+44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: https://www. ccdc.cam.ac.uk).

Catalytic reactions

The catalytic reactions were carried out in a glass batch reactor, according to the following procedure. Substrate (10 mmol), solvent (8 ml) and catalyst (0.005 mmol) were first mixed in a round-bottom flask. The mixture was then equilibrated to 65 °C in an oil bath. After addition of *tert*-BuOOH (20 mmol), the mixture was stirred continuously for 24 h. The products of the oxidation reactions were collected at different time intervals and were identified and quantified by a VARIAN CP-3800 gas chromatograph equipped with an FID detector. A CP-Sil 8 CB capillary column was used for analysis of the products.

Results and discussion

Synthesis and physical measurements

A nitrate bridged 1D chain Cu(II) coordination polymer, $[Cu(L)(\mu-ONO_2)]_n$ (1)

Table 1 Crystallographic data and structure refinement parameters for ${\bf 1}$

Crystal parameters	1
Empirical formula	C ₁₁ H ₁₅ N ₃ O ₅ Cu
Formula weight	332.80
Crystal system	Monoclinic
Space group	P 21/n
A (Å)	12.8738 (10)
$b(\text{\AA})$	7.8553 (6)
c (Å)	13.0713 (10)
α^0	90
β°	93.6188 (12)
γ^0	90
$V(\text{\AA}^3)$	1319.23 18)
λ (Å)	0.71073
$\rho_{\rm calcd} ({\rm g}{\rm cm}^{-3})$	1.672
Z	4
<i>T</i> (K)	294(2)
$\mu (\mathrm{mm}^{-1})$	1.676
<i>F</i> (000)	684
Crystal size (mm ³)	$0.17 \times 0.09 \times 0.08$
θ ranges (°)	2.15 to 25.25
Index ranges	$-14 \le h \le 15$
	$-9 \le k \le 9$
	$-15 \le l \le 15$
Reflections collected	8498
Independent reflections	2401
$T_{\rm max}$ and $T_{\rm min}$	0.878 and 0.812
Data/restraints/parameters	2401/1/187
R (int)	0.025
Goodness-of-fit on F^2	1.066
Final <i>R</i> indices $[I > 2\sigma(I)]$	R = 0.0275 and wR = 0.0734
<i>R</i> indices (all data)	R = 0.0307 and wR = 0.0756
Largest peak and hole $(e\dot{A}^{-3})$	0.333 and -0.186

Weighting scheme: $R = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$, $wR = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2]^{1/2}$, calcd $w = 1 / [\sigma^2 (F_0^2) + (0.0422P)^2 + 0.5323P]$ where $P = (F_0^2 + 2F_c^2) / 3$

HL = 4-methoxy-2-[1-(methylaminoethylimino)methyl]phenol) has been isolated using a one-pot reaction of a 1:1 molar ratio of Cu(NO₃)₂·6H₂O and a Schiff base (HL) in methanol at room temperature. The typical synthesis is summarized in Eq. (1):

$$\operatorname{Cu}(\operatorname{NO}_{3})_{2} \cdot 6\operatorname{H}_{2}\operatorname{O} + \operatorname{HL} \underset{[298 \text{ K}]}{\overset{\text{MeOH}}{\longrightarrow}} \left[\operatorname{Cu}(\operatorname{L})(\mu - \operatorname{ONO}_{2})\right]_{n}$$
(1)

Complex 1 was characterized by microanalytical (C, H and N), spectroscopic and other physico-chemical results. The microanalytical data are in good agreement with the formulation of the complex. The air stable moisture insensitive compound is stable over a long period of time in powder and crystalline states and is soluble in MeOH, EtOH, MeCN,



Fig.3 An ORTEP diagram of the asymmetric unit of $[Cu(L) (\mu-ONO_2)]_n$ (1) with displacement ellipsoids drawn at the 50% probability level



Fig. 4 Perspective view of molecular unit of 1

DMF and DMSO, but is insoluble in water. In DMF solution, the complex **1** is a non-electrolyte as reflected from the low conductivity value (6 Ω^{-1} cm²mol⁻¹).

Crystal structure of $[Cu(L)(\mu-ONO_2)]_n$ (1)

Single crystal X-ray diffraction study of $[Cu(L)(\mu-ONO_2)]_n$ (1) was made to define the coordination sphere. An ORTEP diagram of asymmetric units, molecular unit and packing view of 1D polymeric chain structure of 1 are depicted in Figs. 3, 4 and 5, respectively. Selected bond distances and angles relevant to the coordination spheres are presented in Table 2. X-ray structural analysis reveals that each Cu(II) center in the asymmetric unit of 1 adopts a distorted square pyramidal geometry ($\tau = 0.07$) with a CuN₂O₃chromophore [26] coordinated by two N atoms (N1, N2) and one O atom (O1) of the tridentate Schiff base ligand (L) and two O atoms (O3, O4) of the bridging nitrate (Fig. 3). A considerable deviation from ideal square pyramidal geometry is seen, which is presumably due to the smaller bite angles produced by ligand [N1-Cu1-N2 84.54(7)°] and nitrate $[O3-Cu1-O4 \ a \ 79.37(6)^{\circ}]$. The coordination sites of the



Fig. 5 Partial and complete crystal packing views of 1 showing a polymeric chain extending along b axis

Table 2 Selected bond distances (Å) and bond angles (°) for 1

Bond distances			
Cu1–N1	1.9384 (17)	Cu1–O4_a	2.4319 (16)
Cu1–N2	2.0386 (19)	Cu1_b-O4	2.4319 (16)
Cu1–O1	1.9026 (15)	O3–N3	1.276 (2)
Cu1–O3	2.0531 (15)	O4-N3	1.242 (2)
Cu1–O4	2.5817 (16)	O5–N3	1.215 (2)
Bond angles			
N1-Cu1-N2	84.54 (7)	N2-Cu1-O4_a	86.94 (7)
N1–Cu1–O1	94.14 (7)	O1–Cu1–O3	89.76 (6)
N1–Cu1–O3	172.11 (7)	O1–Cu1–O4	91.72 (6)
N1–Cu1–O4	119.12 (6)	O1–Cu1–O4_a	90.05 (7)
N1–Cu1–O4_a	107.44 (7)	O3-Cu1-O4	53.81 (6)
N2–Cu1–O1	176.19 (7)	O3–Cu1–O4_a	79.37 (6)
N2-Cu1-O3	91.99 (7)	O4–Cu1–O4_a	133.12 (6)
N2-Cu1-O4	92.04 (7)	Cu1–O4–Cu1_b	121.50 (7)

Symmetry code: (a) 1/2-x, -1/2+y, 1/2-z; (b) 1/2-x, 1/2+y, 1/2-z

basal plane are occupied by two N atoms (N1, N2) and one O atom of the Schiff base (L) and two O atoms (O3, O4) of bridging nitrate acting as a bidentate ligand. The bond distance of Cu1-N1^(amine) [1.9384(17)Å] is smaller than Cu1–N2^(imine) [2.0386(19) Å]. The three Cu–O bond lengths are different, where Cu1-O1(ligand) [1.9026(15) Å] is smallest than the other two Cu1-O3(nitrate) [2.0531(15) Å] and Cu1–O4(nitrate) [2.5817(16) Å] (Table 2). The Cu(II) center deviates 0.0314(2) Å from the N1/N2/O1/O3 mean plane. The apical position is occupied by O atom [Cu1–O4_a: 2.4319(16) Å; symmetry code: $a = \frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$ of the other bridging nitrate (Fig. 6). Complex 1 is an example of a coordination polymer containing a bidentate bridging nitrate. The adjacent copper atoms are connected by a bidentate bridging nitrate with μ -ONO₂ bridging mode affording a 1D polymeric chain structure (Fig. 5). The Cu1–O4–Cu1 b

(symmetry code: $b = \frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$) bridging angle is 121.49(6)°. In the polymeric framework, the Cu...Cu separation is 4.3749(4) Å.

FT-IR and electronic spectra of 1

In the FT-IR spectrum, complex **1** exhibits a band at 1794 cm^{-1} with a shoulder at 1735 cm^{-1} due to the bidentate bridging nitrate [21]. Also, the bands of weak intensity at 3062, 2945 and 2840 cm⁻¹ are assigned to the C–H stretching vibrations of aromatic rings, methylene and methoxy groups, respectively [27]. In the UV–Vis spectrum, a weak low-intensity absorption band at 600 nm is assignable to *d*–*d* transition, consistent with the square pyramidal (sp) geometry of the Cu(II) centers [28]. The absorption band observed at 380 nm may be attributed to the ligand -to -Cu(II) charge transfer transition (LMCT) [29]. Additionally, two strong absorption bands in the region 265 and 295 nm may be assigned to ligand-based transitions.

Magnetic study and EPR spectroscopy of 1

Room-temperature solid-phase magnetic susceptibility measurement shows that compound (1) has a magnetic moment of 1.78 BM, which is close to the expected spinonly value. The powder EPR spectrum of complex 1 in the solid state is depicted in Fig. 6. The principal *g* values have been determined by conventional methods of EPR spectroscopy [30]. The g_{\parallel} and g_{\perp} values of the complex were calculated to be 2.18 and 2.08 with $g_{av} = 2.022$; G = 4.753. This is a typical axial spectrum in which the copper(II) ion possesses either a square planar or five-coordinate geometry. The X-ray crystal structure shows that the complex indeed displays a square-pyramidal coordination geometry.

Catalytic activities

The catalytic activity of $[Cu(L)(\mu-ONO_2)]_n$ (1) was studied in the epoxidation of cyclooctene with *tert*-BuOOH as an oxidant. Cyclooctene was converted to cyclooctene epoxide in

Fig. 6 Powder EPR spectrum of the complex 1

good yield with high selectivity in different solvents when catalyzed by complex 1. The results of the catalytic epoxidation of cyclooctene are given in Table 3. As evident from Table 3, complex 1 exhibits the highest conversion of 88% with 86% epoxide selectivity. A graphical representation of the relative efficacy of complex 1 as catalyst for the epoxidation of cyclooctene in different solvents has been given in Fig. S1. In general, the catalytic efficiency in different solvents followed the order: acetonitrile > chloroform > dichloromethane > methanol. The optimum polarity of acetonitrile that is suitable to dissolve both tert-BuOOH and cyclooctene might be facilitating the highest catalytic activity. We studied the reactions by varying the temperature from room temperature to 75 °C in acetonitrile to determine the optimum temperature. It was found that the maximum conversion occurred at 65 °C (Fig. S2). The results of control experiments in the epoxidation of cyclooctene with tert-BuOOH at 65 °C are presented in Table 4. Control experiments without using catalyst failed to produce the desired product. The conversion of cyclooctene was only 4% in the absence of the catalyst. The $Cu(NO_3)_2$ salt, however, achieved a conversion of 66%, but selectivity was lower (53%). The results of reported epoxidation reactions of cyclooctene using tert-BuOOH as oxidant over Cu(II) Schiff base complexes under homogeneous conditions are collated in Table 5 [15-18]. We have earlier studied the oxidation reactions of a variety of olefins over Cu(II) Schiff base complexes, $[Cu(L^1)(H_2O)](ClO_4)$

Table 3 Homogeneous oxidation of cyclooctene catalyzed by the complex $[Cu(L)(\mu$ -ONO₂)]_n (1) at 65 °C in different solvents

Solvents	Reaction time	tion time Conversion (wt%)	Yield of products	
	(Hr)		Epoxide	Others
CH ₃ CN	24	88	86	2 ^a
CH ₂ Cl ₂	24	64	59	5 ^a
CHCl ₃	24	58	53	5 ^a
CH ₃ OH	24	55	44	11 ^a

Reaction conditions: Cyclooctene (10 mmol); catalysts (0.005 mmol); tert-BuOOH (20 mmol); acetonitrile (8 mL). ^a2-Cyclooctene-1-ol



Table 4 Control experiments in epoxidation of cyclooctene with *tert*-BuOOH at 65 $^{\circ}$ C

Run	Catalyst	Conversion (wt%)	% Yield of epox- ide
1	No catalyst	4	4
2	$Cu(NO_3)_2$	66	35
3	$[Cu(L)(\mu-ONO_2)]_n$	88	86

Reaction condition: Cyclooctene (10 mmol), Catalyst (0.005 mmol), *tert*-BuOOH (20 mmol), CH₃CN (8 ml)

Table 5 Comparison of catalytic efficacy of the complex $[Cu(L) (\mu-ONO_2)]_n$ (1) with other reported copper(II) catalysts for the epoxidation of cyclooctene with *tert*-BuOOH in CH₃CN media

Complexes	Conversion (%)	Reference
$[Cu(L^1)(H_2O)](ClO_4)$	75	[15]
$[Cu(L^2)]$	75	[15]
$[Cu(L^3)]$	76	[15]
$[CuL(\mu - 1, 1 - N_3)]_n$	86	[<mark>16</mark>]
][Cu{salnptn(3-OMe) ₂ }]	70^{a}	[17]
[Cu(hnaphnptn)]	70^{a}	[<mark>17</mark>]
$(CuL^n, n = 1-4)$	69	[18]
Cu-MCM-41	92	[20]
Cu ^{II} (Schiff base)Cl ₂ @GO-CP ^b	88	[32]
Cu-L'-Y	84	[33]
$[Cu(L)(\mu-ONO_2)]_n$	88	This study

 $HL^{1} = 1 - (N - ortho - hydroxy - acetophenimine) - 2 - methyl-pyridine,$ $H_2L^2 = N, N' - (2$ hydroxy-propane-1,3-diyl)-bis-salicylideneimine, $H_2L^3 = N,N'-(2,2-dimethyl-propane-1,3-diyl)-bis-salicylideneimine,$ H_2 {salnptn(3-OMe)₂} = Schiff-base derived by the condensation of 2,2' -dimethylpropandiamineand2-hydroxy-3-methoxybenzaldehyde, H_{2} {hnaphnptn} = Schiff-basederivedbythecondensation of 2,2'dimethylpropandiamine and 2-hydroxy-1-naphthaldehyde, Schiff-base derived from the condensation of meso-1,2-diphenyl-1,2-ethylenediamine with various salicylaldehyde derivatives (x-salicylaldehyde for H₂Ln, x=H (n=1), 5-Br (n=2), 5-Br-3-NO2 (n=3) and 2'-hydroxyacetophenone (n=4).Cu(II) (Schiff base)Cl₂@ GO-CP=Cu(II) Schiff base complex immobilized on Graphene oxide. L'=3,4,11,12-dibenzo-1,14-diaza-5,10-dioxa cyclohexadecane-1,13-diene.^aFor 8 h, ^bFor5hr

(HL¹=1-(N-ortho-hydroxy-acetophenimine)-2-methylpyridine), [Cu(L²)] (HL²=N,N'-(2-hydroxy-propane-1,3-diyl)bis-salicylideneimine),[Cu(L³)](HL³=N,N'-(2,2-dimethylpropane-1,3-diyl)-bis-salicylideneimine), which exhibit high 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 [15]. We have also demonstrated the epoxidation of cyclooctene using a single end-on azido bridged 1D chain Schiffbase copper(II) complex [CuL($\mu_{1,1}$ -N₃]_{*n*}(HL = 1-(N-*ortho*hydroxyacetophenimine)-2-(N-ethyl)aminoethane) as catalyst, where the highest conversion occurs also in acetonitrile (conversion 86%, selectivity 81%) with tert-BuOOH as oxidant [16]. Ravati et al. reported the oxidation of cyclooctene with tert-BuOOH in the presence of electron-rich salen-type Schiff base copper(II) complexes, where the highest conversion was 70% after 8 hr in acetonitrile media and epoxide selectivity was 100% [17] (Table 5). Abbasi et al. studied the epoxidation of cyclooctene using a series of mononuclear and dinuclear salen-type copper(II) Schiff base complexes, where the highest conversion goes to 85%, but epoxide selectivity maximum was 67%. Along with the epoxide, the allylic oxidation product cyclooct-2-enol, and cyclooct-2-enone were also obtained [18]. However, in our present study, the conversion of cyclooctene by complex 1 displayed marked improvement with good selectivity. Cu(II) Schiff base catalysts under heterogeneous conditions have been used for epoxidation of olefins with tert-BuOOH in the recent past. Sakthivel et al. have reported the oxidation of cyclooctene with tert-BuOOH over a tetrahydro-salen Cu(II) complex grafted on iodosilane modified surfaces of MCM-41 and MCM-48, but the conversion was only 53-54% with 78-85% selectivity. However, in homogeneous condition, there was a reported 73.7% conversion and 73% selectivity [31]. Jana et al. have obtained 92% conversion of cyclooctene with 92% epoxide selectivity using a Cu(II) Schiff-base anchored MCM-41 catalyst [20]. Zarnegaryan et al. have reported that the effective conversion of cyclooctene (conversion 88%, selectivity 100%) by Cu(II) Schiff base complex immobilized on graphene nanosheets using tert-BuOOH in acetonitrile media, although the highest conversion (99%) occurred in dichloromethane media [32]. Banaei et al. studied the epoxidation of cyclooctene by zeolite-Y encapsulated Cu(II) complexes with 16- and 17-membered diazadioxa macrocyclic Schiff bases nanocomposite materials, where conversion goes to a highest value of 84% (selectivity up to 82%) with the formation of three by-products [33]. However, in the case of complex 1, allylic C-H oxidation was 2-11% in different solvents. The reaction profile of the epoxidation of cyclooctene with different solvents is shown in Fig. S3. The complex contains five-coordinated coordinatively unsaturated Cu-center; thus, the complex has been used for the Lewis acidic catalysis reaction under homogeneous conditions. The Cu(II) binds the peroxo-group on treatment with peroxides [34] to form the pre-catalyst containing LxCu–OOH (where L=ligand), which are capable of transferring the oxo-functionality to the organic substrates to produce the oxidized products [35]. We assume that a similar kind of mechanism is operative in our case. The probable mechanism for catalytic cycle is depicted in Scheme 2. X-ray crystal structure analysis shows the presence of five-coordinated Cu(II) in $[Cu(L)(\mu-ONO_2)]_n$ (1). So, the coordination environment around Cu(II) is easily accessible for an external ligand. As a result, tert-BuOOH has enough space to bind copper in the intermediate stages of the catalytic cycle.

Scheme 2 Probable mechanism of catalytic cycle for olefinic epoxidation catalyzed by complex 1



Conclusion

In summary, a neutral nitrate bridged coordination polymer **1** of Cu(II) containing a tridentate Schiff base has been isolated and characterized by single crystal X-ray diffraction. Structural analysis revealed that each Cu(II) center features a distorted square pyramidal geometry bearing a CuN₂O₃ chromophore in **1**. The adjacent copper atoms are connected by a bidentate μ -NO₃ bridge to form a one-dimensional coordination polymeric structure. Complex **1** displayed moderate catalytic efficacy in homogeneous cyclooctene epoxidation. The catalytic reaction also revealed the highest selectivity in acetonitrile medium.

Acknowledgements The work was financially supported by the Department of Science and Technology, Government of India, by a grant (SR/S1/IC-13/2010) (to CA).

Compliance with ethical standards

Conflict of interest No potential conflict of interest was reported by the authors.

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