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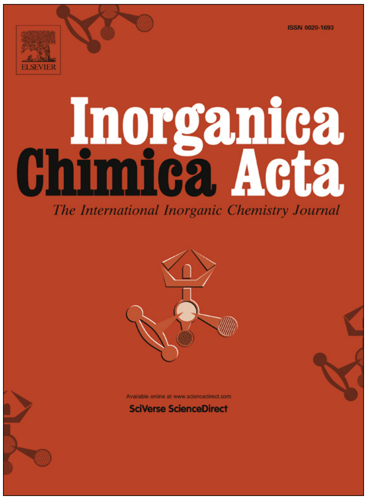

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Single end to end azido bridged adduct of a tridentate schiff base copper (II) complex: synthesis, structure, magnetism and catalytic studies

Sourajit Banerjee[a], **Chandan Adhikary**[a,*], **Corrado Rizzoli**[b], **Rammohan Pal**[c]

[a]*Department of Chemistry, Governement College of Education, Burdwan, 713102, India*

[b]*Departimento di Chimica, Parco Area delle Scienze 17/A, 43124, Parma, Italy*

[c]*Department of Chemistry, Acharya Jagadish Chandra Bose College, Kolkata 700020, India*

Abstract

Copper (II) azido complex $[CuL(\mu_{-1,3}\text{-}N_3)]_n$ (**1**) of a NNO donor tridentate Schiff base (HL = 2-[1-(Methylamino-ethylimino)-methyl]-phenol containing single end-to-end $\mu_{-1,3}$-azido bridged 1D infinite chain has been synthesized and characterized by elemental analysis, FT-IR spectroscopy. X-ray single crystal structure analysis reveals that in **1**, the central copper (II) ion displays a distorted square pyramidal coordination geometry and are linked by single EE azide bridges forming chains running parallel to the crystallographic *b* axis. The magnetic interaction revealed that **1** is antiferromagnetic in nature (J = -19.5 (± 0.2) cm^{-1}). The catalytic activity of the complex is investigated in a series of solvents for the oxidation of olefins using *tert*-butyl-hydroperoxide as oxidant. The results showed highest selectivity for **1** in acetonitrile medium.

Keywords: Copper(II)-azido complex; Schiff-base ligand; X-ray crystal structure; Magnetic study; Olefin oxidation

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[*] Corresponding author. Tel: +91-0342-2656853; e-mail. cadhikary123@gmail.com

1. Introduction

The Schiff bases derived from the mono-condensation of diamines with carbonyl compounds (salicylaldehyde, o-hydroxyacetophenone, acetylacetone or benzoylacetone) are a group of mono-negative NNO donor ligands which readily react with transition metal ions and auxiliary ligand to form mono and polynuclear complexes with varied functionalities and applications. Depending on the number, nature and relative position of the donor atoms of a Schiff base, the ligand allows a good control over the stereochemistry of the metallic centers in homo- and heteropolynuclear complexes [1-3]. All these advantages make Schiff bases privileged ligands in the effort to synthesize metal complexes having relevance to bioinorganic chemistry, catalysis, encapsulation, transport and separation processes [4]. Copper(II) Schiff base complexes find wide applicability in the field of catalysis, antimicrobial activities, synergistic action on insecticides, plant growth regulator, antitumor and cytotoxic activity, harmonic generation activity etc [5]. Furthermore copper(II) azido complexes have also received intense attention in the field of molecular magnetism [6]. Keeping such observations in mind we have directed our investigation in synthesizing Schiff base copper(II) complexes and their azido adducts and simultaneous study of their magnetic property and catalytic efficacy. Schiff base copper complexes can now be extensively used as active catalysts in several oxidation reactions both in homogeneous [7-11] and heterogeneous condition [12-16]. So far our knowledge goes, catalytic oxidations involving Schiff base copper azido complexes have been scarcely reported in the literature [17-18]. Although molecular oxygen and hydrogen peroxide (30%, an environmental friendly oxidant) catalyzed epoxidation reactions are well documented in the literature yet due to the explosive nature of hydrogen peroxide, the industrial processes still mainly have to rely on *tert*-butyl-hydroperoxide (TBHP) [19].In industrial epoxidation involving Halcon-Arco and Sumitomo processes [20-23] alkyl-hydroperoxides are used on a large scale. The recycling of co-products *e.g. tert*-BuOOH has been realized in the Sumitomo process. Notably, TBHP has seldom been used as an oxidant in the investigations of the catalytic efficiency of copper(II) complexes towards epoxidation/oxidation reactions in homogeneous medium. Here we report the synthesis, characterization, X-ray single crystal structure and magnetic study of an azido derivative of a Schiff base Cu(II) complex. The catalytic epoxidation acivity of the complex has been investigated in a variety of alkenes using *tert*-butyl-hydroperoxide as an oxidant.

2. Experimental

2.1. Materials

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

2.2. Physical Measurements

Microanalysis (CHN) was performed in a Perkin Elmer 240 elemental analyzer. IR spectra were recorded on a Bruker Alpha T 200140 FT-IR spectrometer. Absorption spectra were studied on Shimadzu UV2100 UV-Vis recording spectrophotometer. Magnetic measurements of **1** were performed with a Cryogenic SQUID S600 magnetometer operating between 2 and 300 K at an applied field of 1T. Magnetic data were corrected for the diamagnetism of the sample holder, measured in the same range of temperature and field, and for the intrinsic diamagnetism of the samples estimated through Pascal’s constants. GC analysis was carried out with an Agilent Technologies 6890N network GC system equipped with a fused silica capillary column (30 m x 0.32 mm) and a FID detector.

2.3. Synthesis

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

*2.3.1. Synthesis of [CuL($\mu_{1,3}$-N$_3$)] (**1**)*

A methanolic solution (20 ml) of N-methylethylenediamine (1mmol, 0.074g) was added to a methanolic solution (20 ml) of salicylaldehyde (1mmol, 0.122g). The reaction mixture was refluxed for 1h and evaporated on a water bath until the volume reduced to ca. 5 ml to obtained a viscous yellow orange liquid. Copper (II) nitrate trihydrate (1mmol, 0.241g) dissolved in methanol was added and the mixture was refluxed for another 30 min Finally 5 ml aqueous solution of NaN_3 (2mmol, 0.130g) was added dropwise to the mixture with continuous stirring and the resulting solution was then filtered. The green filtrate was kept in the open atmosphere. From the green solution block pale yellow crystals were formed within few days. (Yield ca. 80%). Anal. Calcd. for $C_{10}H_{13}CuN_5O$ (282.79): calcd: C, 42.4; H, 4.6; N, 24.8. Found: C, 42.2; H, 4.8; N, 24.9. FTIR (cm^{-1}): ν_{as} (N$_3$), 2030; ν_s(N$_3$), 1332 and 1345; δ(N$_3$), 620; ν(C=N), 1640 cm^{-1}. λ_{max}/nm (methanol), 299; 266; 360; 621.

2.4. X-ray Crystallography

*2.4.1. X-ray Crystal data of [CuL($\mu_{1,3}$-N$_3$)]$_n$ (**1**)*

$C_{10}H_{13}CuN_5O$, M = 282.79, Orthorhombic, space group $P2_12_12_1$, a = 7.1631(9), b = 8.3919 (10), c = 19.652 (2) Å, $\alpha = \beta = \gamma = 90°$, V = 1181.3 (2) Å^3, Z = 4, R_{int} = 0.050, $D_{\text{calc.}}$ = 1.590 Mg m^{-3}, F_{000} = 580, μ = 1.84 mm^{-1}, dimensions = 0.16 × 0.10 × 0.07 mm, T = 295 K.

2.4.2. X-ray single crystal structure determination of [CuL($\mu_{1,3}$-N_3)]$_n$ (***1***)

Single crystal X-ray diffraction data for **1** were mounted on a Bruker SMART 1000 CCD diffractometer at room temperature using graphite monochromated Mo-K_α radiation (λ = 0.71073Å) and were used to measure cell dimensions and diffraction intensities. The crystals were found to belong to the orthorhombic system and the systematic absences identified the correct space group as $P2_12_12_1$. For data collection, data reduction and cell refinement the programs APEX2 and SAINT [24] were used. The structure was solved by direct methods using SIR97 [25] and refined by SHELX97-L [26]. The N-bound H atom was located in a difference Fourier map and refined isotropically. All other H atoms were positioned geometrically and refined using a riding model, with C–H = 0.93-0.97 Å and with Uiso = 1.2 Ueq(C) or 1.5 Ueq(C) for methyl H atoms. A rotating model was used for the methyl group.

2.5. Catalytic reactions

The homogeneous oxidation reactions were carried out under stirring in a two-neck round-bottom flask fitted with a water condenser and placed in an oil bath at 333-353 K. The proportions used were: substrate (10mmol), solvent (10 ml) and catalyst (0.005 mmol). *tert*-BuOOH (20 mmol) was added immediately before the start of the reaction and the mixture was stirred continuously for 24 h. At different time intervals, the products were collected from the reaction mixture and analyzed by gas chromatography. The products were identified by known standards.

3. Results and Discussion

3.1. Description of structure of [CuL($\mu_{1,3}$-N_3)]$_n$ (***1***)

The structure determination reveals that the neutral [CuL($\mu_{-1,3}$-N_3)]$_n$ units in complex **1** are connected by the single $\mu_{-1,3}$-azido ligands to form an infinite 1D polymeric chains. A perspective view of the chain structure running parallel to the crystallographic *b*-axis is depicted in Fig. 1 and an Ortep diagram of the monomer with atom labelling scheme is shown in Fig. 2.

In **1**, each Cu(II) ion is placed in a distorted square pyramidal environment, in which the basal plane is made up by two nitrogens, N(1) and N(2), one deprotonated phenoxo oxygen O(1), of the tridentate Schiff base ligand HL and one azido nitrogen, N(3). A second azido nitrogen, N(5)^{i} from a symmetry related unit (symmetry operation, i = $-x+1$, $y+1/2$, $-z+1/2$) at the apical position occupies the remaining fifth position of the coordinated polyhedron. Thus the azido nitrogen N(5) bridges two copper(II) centers. Selected bond lengths and angles are listed in Table 1.

The basal Cu-N(3)(azido) distance [1.973(4)Å] is an intermediate between the other two basal Cu-N(1) and Cu-N(2) distances [1.940(4), 2.054(4)Å, respectively], while the apical Cu-N(5)^{i} (symmetry operation i = $-x+1$, $y+1/2$, $-z+1/2$) distance [2.506(4)Å] is remarkably longer, indicating a rather weak axial coordinative interaction. The axial Cu-N distance is significantly longer than those observed in other similar single end-to-end azido bridged 1D copper(II) complexes [6].

The diagonal basal angles, N(1)-Cu(1)-N(3) = 165.54(16)° and N(2)-Cu(1)-O(1) = 176.51(15)° and the basal-apical angles, O(1)-Cu(1)-N(5)^{i} = 87.66(12)° and N(1)-Cu(1)-N(5)^{i} = 94.61(5)° (symmetry operation i = $-x+1$, $y+1/2$, $-z+1/2$) significantly deviate from the ideal values. The trigonality index τ (0.18) [= $\Phi_1 - \Phi_2)/60$, where Φ_1, Φ_2 are the two largest L-M-L angles of the coordination sphere] as calculated for the pentagonal copper site [27] confirms the square pyramidal environment. The Cu(1)-N(3)...N(5)-Cu(1)^{ii} torsion angle (symmetry operation ii = 1-x, -1/2+y, 1/2-z) is -90.3(2)° and the angle formed by the lines through the Cu(1)-N(3) and N(5)-Cu(1)^{ii} (symmetry operation ii = 1-x, -1/2+y, 1/2-z) bonds is 99.73(13)°. The Cu···Cu distance is 5.0748(8) Å.

In **1**, the hydrogen atom H(2N) bonded to the sp^3 hybridized amino nitrogen N(2) is involved in a weak hydrogen bond contact with an adjacent phenoxo oxygen atom, O(1)^{i} (symmetry operation i = −x+1, y+1/2, −z+1/2). The hydrogen atom H(9B) bonded to the sp^3 hybridized C(9) methylene carbon atom is also involved in hydrogen bonding with the terminal azide nitrogen N(5)^{iii} (symmetry operation iii = x, y+1, z).

*3.2. Magnetic study of complex [CuL($\mu_{1,3}$-N$_3$)]$_n$ (**1**)*

The temperature dependence of the molar magnetic susceptibility, χ_M, for **1** in the 2-300 K temperature range was measured with a Cryogenic SQUID S600 magnetometer operating between 2 and 300 K at an applied field of 1T and is shown in Fig. 3. The χ_M value of 5.5×10^{-3} cm^{3}mol^{-1} at 300 K is slightly higher than the value expected for an isolated magnetically uncoupled copper(II) ion ($\chi_M = 1.25\times10^{-3}$ cm^{3}mol^{-1} for g = 2.0). Upon cooling the χ_M value increases gradually with temperature until ca. 125 K, and then rapidly, reaching a maximum of 3.7×10^{-2} cm^{3}mol^{-1} at *ca.* 22 K. The χ_M versus *T* curve explains a bulk antiferromagnetic interaction prevailed. An isotropic infinite chain model of equally spaced copper (II) ions bridged through μ-1,3-azido ligands with S = ½ local spins has been considered to explain the magnetic properties of **1**. The spin Hamiltonian of such a system considering isotropic interaction between nearest neighbouring ions is

$$H = -J\sum_{i=1}^{n-1} S_{A_i}\cdot S_{A_{i+1}} \qquad \ldots(1)$$

where summation runs over the n site of the chain. For the condition $n \to \propto$ no analytical method is available so as to determine the energies of low-lying states and magnetic susceptibility. The ring structure permits the limiting condition as follows [28-29]:

$$S_{A_{i+n}} = S_{A_i} \qquad \text{for any } n \qquad \ldots(2)$$

Finally, to fit magnetic susceptibility data a numerical expression can be used as follows [30]:

$$\chi_M = \frac{Ng^2\beta^2}{kT} \frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3} \qquad \ldots(3)$$

where

$$x = |J| / kT \qquad \ldots(4)$$

Fitting of the magnetic susceptibility data considering the equation (3) yielded the parameter values J = -19.5(±0.2) cm^{-1}, g = 2.2(±0.01). A comparative account of structural and magnetic parameters of the similar End to End azido bridged 1D chain copper(II) complexes [31-38] are collated in the Table 2. Even a cursory look at the Table 2 it is evident that most of the complexes listed there are ferromagnetic in nature. However, the coupling parameters are small. For copper(II) systems, the magnitude of the super exchange parameter J is strongly dependent on main two factors, *viz.* the atomic orbitals of the copper atoms involved and the ∠Cu–N–N and Cu–N_3–Cu torsion angle in the bridging region. The coupling may be strongly AF when the end-to-end azido ligands are bonded to the equatorial coordination sites of the two copper atoms, in which case two $d_{x^2-y^2}$ orbitals is involved in the super exchange mechanism. In contrast, very weak coupling should be expected when the interaction is axial-equatorial in nature involving $d_{x^2-y^2}$ and d_{z^2} atomic orbitals.

The different magnetic behavior is related to the low unpaired electronic density found in the $d_z{}^2$ atomic orbital in the square pyramidal or octahedrally coordinated copper atoms. Classical attempts to relate the magnitude of the super exchange coupling and the structural data for the axial-equatorial case conclude a greater AF coupling for the trigonal bipyramidal arrangement which is in agreement with the greater mixing of the $d_{x^2-y^2}$ and $d_z{}^2$ atomic orbitals in such cases [6]. In a recent study the electronic structures of two asymmetrical EE azido-bridged copper(II) complexes $[Cu(L^2)(N_3)]_n(ClO_4)_n$ and $[Cu(L^3)(N_3)]_n(ClO_4)_n$ [32] were studied. The result shows that the spin population in these two complexes is largely distributed on the equatorial plane of the square pyramid surrounding the copper(II) ions. Ferromagnetic coupling through the asymmetrical azido ligand in these two complexes has been mainly attributed to the spin delocalization and weak spin polarization effect.

3.3. Catalytic activities

The catalytic activity of **1** in the epoxidation of various olefins in homogeneous medium is summarized in table 3.The graphical representation of different alkene conversion for **1** is shown in Fig. 4. For **1** the conversion trend of alkenes follows the order α–methyl styrene ~ styrene > cyclooctene > cyclohexene while the observed epoxide selectivity is cyclooctene (73%) > α–methyl styrene(62%) > styrene(54%) ~ cyclohexene (54%). From this observation it is evident that epoxide selectivity is higher in cyclooctene due to its active double bond and the relative stability of 1,2- epoxy cyclooctene. For cyclohexene, epoxide selectivity was least since its active allylic site could also be activated in the process of oxidation. When styrene is considered, 100% styrene conversion occurred with 54% epoxide selectivity. The remaining 46% products were benzaldehyde and benzoic acid. The yield of epoxide increases from 54% to 62% when an electron donating methyl group was introduced at the ortho position of styrene. Along with the epoxide 4-methyl benzaldehyde and 4-methyl benzoic acid were also formed. The difference in the conversion between styrene and α–methyl styrene may be attributed to the electronic effect of the substituent [39]. It is known that copper (II) can bind peroxo- groups on treatment with peroxides [40] and the pre-catalyst species containing L_xCu-OOR (where L = ligand) type moieties seemed to be capable of transferring oxo functionality to the organic substrates to give the corresponding oxidized products [41-42]. We speculate that, in our case, a similar kind of mechanism is operative.

The effect of various reaction media on epoxidation of cyclooctene catalyzed by **1** has been compared. The graphical representation of catalytic efficacy in different solvent media for **1** is shown in Fig. 5. The best performance of the catalyst was observed in the acetonitrile medium. The efficiency of the catalyst followed the order acetonitrile > dichloromethane >methanol >chloroform which is consistent with the earlier report of cyclooctene catalyzed epoxidation of single end on azido bridged Schiff base copper (II) complexes [17]. A comparison of the catalytic efficiency of **1** with copper salt (copper(II) nitrate trihydrate) in homogeneous medium involving acetonitrile (Table 4) solvent clearly indicates that complex **1** performs as a more efficient catalyst than simple copper salt.

4. Conclusion

In summary, we have synthesized and characterized a 1D chain copper(II) azide complex with NNO donor ligands. The magnetic interaction revealed that **1** is antiferromagnetic (J = -19.5 (± 0.2) cm^{-1}) in nature. The complex also showed moderate catalytic activity in acetonitrile compared to the other solvents in homogeneous alkene oxidation.

Appendix A. Supplementary data

CCDC 937470 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Legends to the figures

Fig. 1. The polymeric chain in complex $[CuL(\mu_{-1,3}-N_3)]_n$ (**1**) running parallel to the *b* axis. Symmetry codes: (i) 1-x, -1/2+y, 1/2-z; (ii) 1-x, 1/2+y, 1/2-z; (iii) x, -1+y, z; (iv) x, 1+y, z; (v) 1-x, 3/2+y, 1/2-z.

Fig. 2. ORTEP diagram of the asymmetric unit of complex $[CuL(\mu_{-1,3}-N_3)]_n$ (**1**), with displacement ellipsoids drawn at the 50% probability level.

Fig. 3. χ_M *versus T* (Δ) plot for complex $[CuL(\mu_{-1,3}-N_3)]_n$ (**1**). Solid lines represent the best fit of the data with the model described in the text.

Fig. 4. Reaction profile for the oxidation of olefins with *tert*-BuOOH in presence of complex $[CuL(\mu_{-1,3}-N_3)]_n$ (**1**).

Fig. 5. Effect of solvent on the conversion in olefin oxidation reactions catalyzed by complex $[CuL(\mu_{-1,3}\text{-}N_3)]_n$ (**1**) .

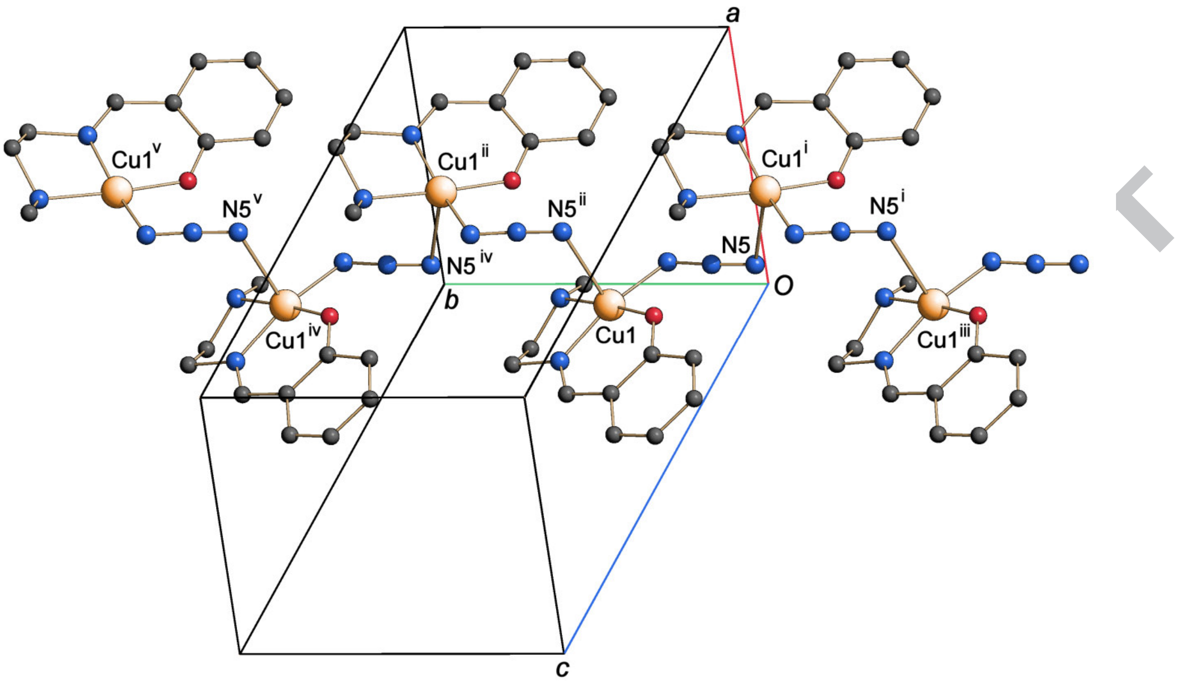


Fig.1.

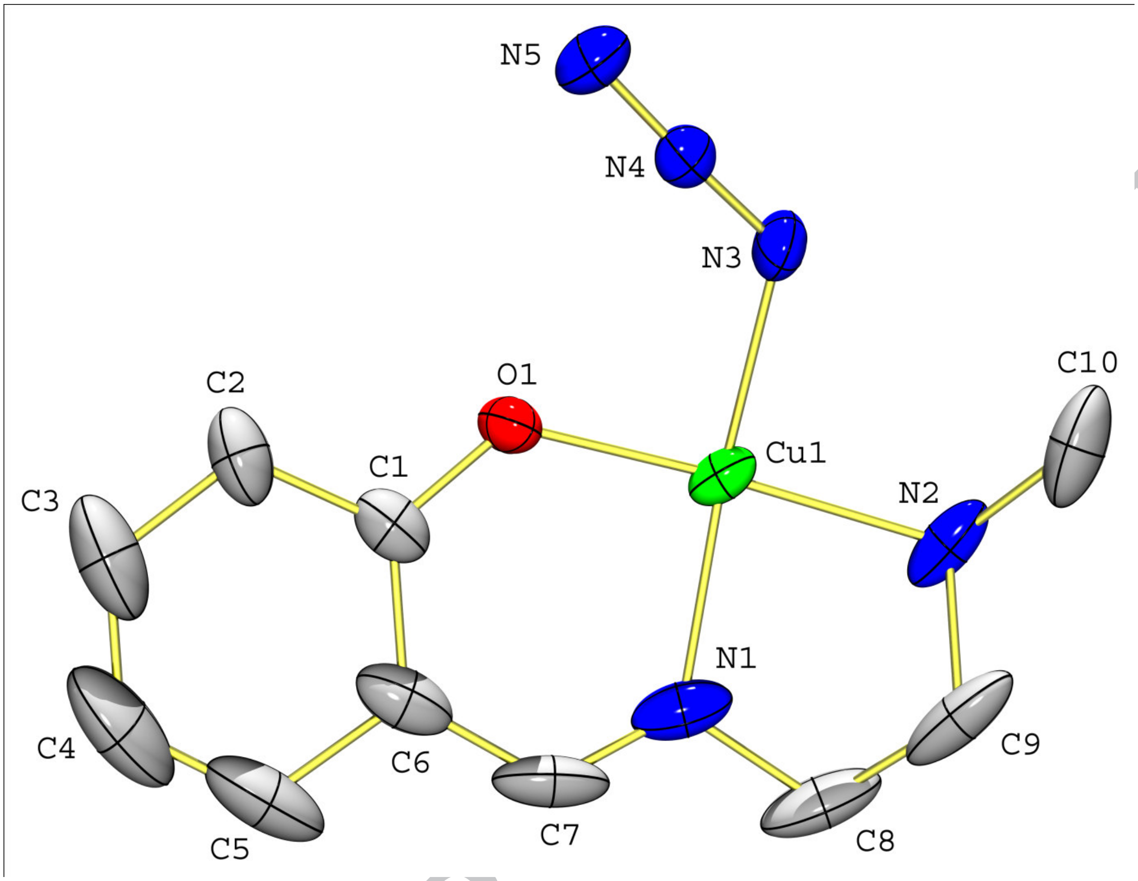


Fig. 2.

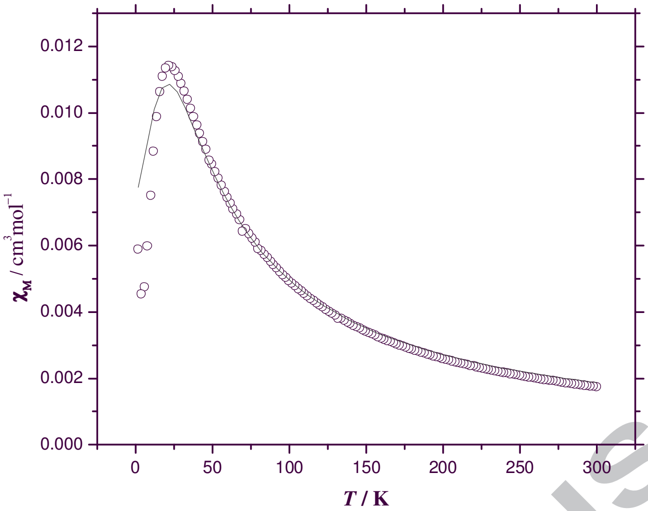

0.000
0.002
0.004
0.006
0.008
0.010
0.012
χ_M / cm^{3}mol^{-1}
0
50
100
150
200
250
300
T / K

Fig. 3.

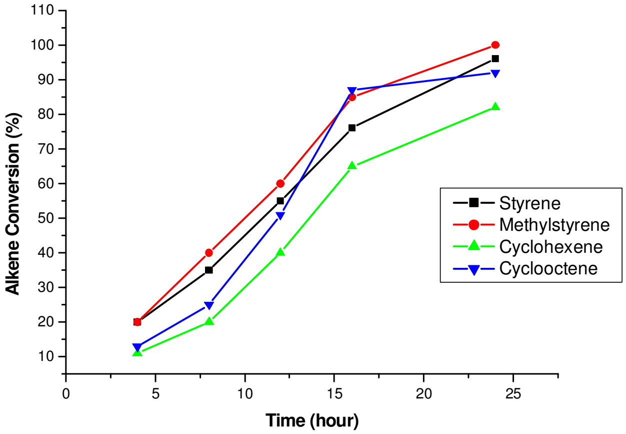
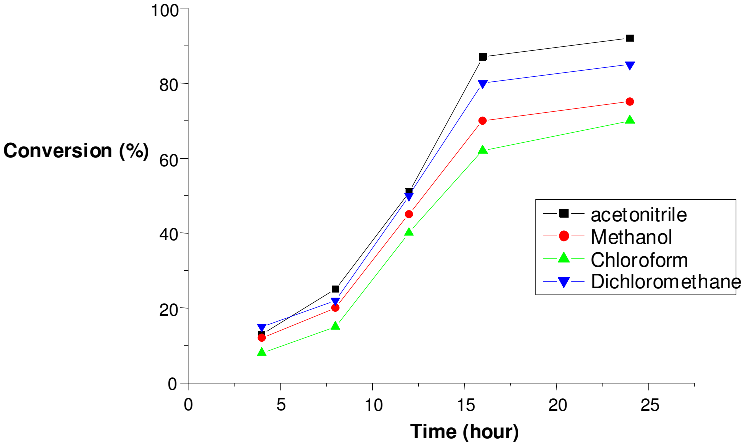

Alkene Conversion (%)
110
100
90
80
70
60
50
40
30
20
10
0
5
10
15
20
25
Time (hour)
Styrene
Methylstyrene
Cyclohexene
Cyclooctene

Fig. 4.


100
80
60
40
20
0
Conversion (%)
0
5
10
15
20
25
Time (hour)
acetonitrile
Methanol
Chloroform
Dichloromethane

304

305 Fig. 5.

Table 1. Selected bond lengths (Å) and bond angles (°) of $[\mathrm{CuL}(\mu_{-1,3}\text{-}\mathrm{N}_3)]_n$ (**1**)

Bond distances (Å)			
Cu(1) –O(1)	1.894(3)	Cu(1)–N(1)	1.940(4)
Cu(1) –N(2)	2.054(4)	Cu(1)–N(3)	1.973(4)
N(3) –N(4)	1.178 (5)	Cu(1)–N(5) ^{i}	2.506(4)
Cu(1)–Cu(1)^{i}	5.0748(8)	N(4)–N(5)	1.158 (5)
Bond angles (^{o})			
O(1)–Cu(1)–N(1)	92.46 (17)	O(1)–Cu(1)–N(2)	176.51 (15)
O(1)–Cu(1)–N(3)	89.78 (13)	N(1)–Cu(1)–N(2)	84.6 (2)
O(1)–Cu(1)–N(2)	176.51 (15)	N(1)–Cu(1)–N(3)	165.54 (16)
N(2)–Cu(1)–N(3)	92.57 (17)	Cu(1)–N(3)–N(4)	119.1 (3)
N(1)–Cu(1)–N(5)^{i}	94.61 (15)	O(1)–Cu(1)–N(5)^{i}	87.86 (12)
N(2)–Cu(1)–N(5)^{i}	94.27 (13)	N(3)–Cu(1)–N(5)^{i}	99.74 (13)
N(3)–N(4)–N(5)	177.1 (4)		

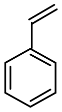
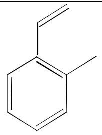
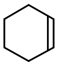
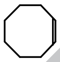
Symmetry code: $^{(i)}$ $-x+1$, $y+1/2$, $-z+1/2$

Table 2. Structural and magnetic parameters for one-dimensional systems with $\mu_{1,3}$-azido unit: Cu–N bond distances (Å) , Cu–N–N bond distances (Å), Cu–N_3–Cu bond angles (°) and *J* values (cm^{-1}).

Complexes	Cu–N(Å)	Cu–N–N (Å)	Cu–N_3–Cu (Δ)	*J* (cm^{-1})	Ref
$[Cu(L^1)(N_3)]_n(ClO_4)$	1.936, 2.486	125.6	91.6	1.36	[31]
$[Cu(L^2)(N_3)]_n(ClO_4)_n$	1.991, 2.266	134.4,136.7	31.3	2.69	[32]
$[Cu(L^3)(N_3)]_n(ClO_4)_n$	1.946, 2.398	122.5,135.1	102.7	2.02	[32]
$[Cu(L^4)(N_3)]_n(ClO_4)_n$	1.947, 2.355	126.5,131.2	97.8	2.15	[33]
$[Cu(L^5)(N_3)]_n(ClO_4)_n$	1.965, 2.311	131.2,139.1	50.4	3.61	[33]
$[Cu(L^6)(N_3)]_n(ClO_4)_n$	1.951, 2.270	139.0,132.2	40.4	2.06	[33]
$[Cu(L^7)(N_3)]_n(ClO_4)_n$	1.955, 2.880	133.5,100.3	92	1.60	[34]
$[Cu(R\text{-}L^8)_2(N_3)]_n(ClO_4)_n$ or	1.975, 2.683	127.7,128.0	–	0.70	[35]
$[Cu\ (S\text{-}L^8)_2((N_3)]_n(ClO_4)_n$	1.971, –				
$[Cu(L^9)_2(N_3)_2]_n$	2.029, 2.611	115.7, 123.0	–71	1.6	[37]
$[Cu(L^{10})(N_3)]_n(H_2O)_{2n}$	1.948, 2.563	129.0	17.0	– 4.30	[37]
$[Cu(L^{11})(N_3)]_n$	1.980, 2.473	–	–	–22.5	[38]
$[CuL(\mu_{-1,3}\text{-}N_3)]_n$ (**1**)	1.973, 2.51	143.6, 109.7	-151	–19.5	[This Work]

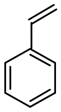
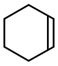
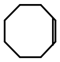
L^1 = Tridentate Schiff base derived from condensation of pyridine-2-aldehyde with 1-(2-aminoethyl)-piperidine; L^2 = Tridentate Schiff base derived from condensation of pyridine-2-aldehyde with N,N,2,2-tetramethylpropane-1,3-diamine; L^3 = Tridentate Schiff base derived from condensation of pyridine-2-aldehyde with 1-dimethylamino-2-propylamine; L^4 = Schiff bases obtained by the condensation of pyridine-2-carbaldehyde with N,N-dimethylethane-1,2-diamine; L^5 = Schiff bases obtained by the condensation of pyridine-2-carbaldehyde with N,N-diethylethane-1,2-diamine; L^6 = Schiff bases obtained by the condensation of pyridine-2-carbaldehyde with 4-(2-aminoethyl)morpholine; L^7= N-(2-pyridylmethyl)-N,N-diethylethylenediamine; R-L8 or S-L9 = R or S-pyridine-2-carbaldehyde-imine; L^9 = 4-(dimethylamino)pyridine, L^{10} = The dinucleating macrocyclic ligand bis-p-xylyl-BISDIEN; L^{11} = Schiff base derived from condensation of salicylaldehyde and N,N-dimethyl-ethylenediamine.

Table 3. Homogeneous alkene oxidation catalysed by complex $[CuL(\mu_{-1,3}\text{-}N_3)]_n$ (**1**)[a] in acetonitrile medium

Catalyst	Substrate	Reaction Time (h)	Conversion (wt %)	%Yield of products		TON[b]	TOF[c] (h^{-1})
				Epoxide	Others		
$[CuL(\mu_{-1,3}\text{-}N_3)]_n$ (**1**)		24	100	54	46[d]	15,624	651
		24	100	62	38[e]	15,744	656
		24	84	45	39[f]	14,208	592
		24	96	70	16[g]	14,496	604

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

Table 4. Homogeneous alkene oxidation catalysed by $Cu(NO_3)_2.3H_2O^{\#}$ in acetonitrile medium

Catalyst	Substrate	Reaction Time (h)	Conversion (wt %)	%Yield of products		TON	TOF (h^{-1})
				Epoxide	Others		
$Cu(NO_3)_2.3H_2O$		24	42	20	22[##]	6,552	273
		24	25	25	-	3,888	162
		24	33	33	-	4,296	179

[#]Reaction conditions were the same as given in the footnote of Table 3. [##] Benzaldehyde and benzoic acid.

Highlights

- Azido bridged copper(II) complex was synthesized and characterized.
- The complex shows antiferromagnetism.
- The complex exhibits good catalytic activity in the oxidation of olefins.
- Catalytic activity depends upon solvent media.
- Catalytic efficacy is due to copper complex rather than copper salt itself.

Single end to end azido bridged adduct of a tridentate schiff base copper (II) complex: synthesis, structure, magnetism and catalytic studies

Sourajit Banerjee, Chandan Adhikary*, Corrado Rizzoli[b], Rammohan Pal[c]

[a]*Department of Chemistry, Governement College of Education, Burdwan, 713102, India*

[b]*Departimento di Chimica, Parco Area delle Scienze 17/A, 43124, Parma, Italy*

[c]*Department of Chemistry, Acharya Jagadish Chandra Bose College, Kolkata 700020, India*

Graphical Abstract

Single end to end azido bridged 1D chain copper(II) complex with tridentate (NNO donor) Schiff-base ligand has been synthesized and characterized by X-ray Crystallography. The magnetic study revealed that the complex is antiferromagnetic in nature. Olefin epoxidation reactions catalyzed by the complex, in different solvent media, have been studied by using *tert*-BuOOH as oxidant.