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Synthesis and characterization of mononuclear copper(II) complexes of pyridine 2-carboxamide: Their application as catalyst in peroxidative oxidation and antimicrobial agents

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Abstract. Four water soluble copper(II) complexes, $[Cu(HL)_2(H_2O)_2]Cl_2$ (**1**), $[Cu(HL)_2(ClO_4)_2]$ (**2**), $[Cu(HL)_2(SCN)_2]$ (**3**) and $[CuL_2]\cdot 8H_2O$ (**4**), where HL is pyridine 2–carboxamide, have been synthesized and characterized by various spectroscopic techniques. Structures have been determined by single crystal X-ray crystallography. The pH induced inter-conversion of $Cu(HL)_2(H_2O)_2]Cl_2$ (**1**) and $[CuL_2]\cdot 8H_2O$ (**4**) through co-ordination mode switching was investigated thoroughly with the help of absorption spectroscopy. Complexes **1**–**3** were found to be active catalysts for the oxidation of toluene, ethyl benzene and cyclohexane in the presence of hydrogen peroxide as the oxidant under mild conditions. Toluene was oxidized to benzyl alcohol and benzaldehyde, ethyl benzene was oxidized to 1-phenylethanol and acetophenone and cyclohexane was oxidized to yield cyclohexanol and cyclohexanone Antimicrobial activities have been investigated with these copper(II) complexes against gram +ve bacteria, gram −ve bacterial and fungal species.

Keywords. Homogeneous catalysis; Copper; Amide ligand; Oxidation; Antimicrobial activity.

1. Introduction

Oxidation reactions play a significant role in organic synthesis and presently there is a demand for more selective and efficient oxidation methods.[1] In recent times, much emphasis has been given to the need for sustainable and environmentally friendly processes. So, the use of oxidants such as molecular oxygen and hydrogen peroxide which are environmentally friendly and produce no toxic waste is highly desirable. The use of molecular oxygen and hydrogen peroxide as the primary oxidant has several benefits such as low cost, improved safety, "green" and water as the sole byproduct.[2]

The oxidation of organic compounds catalyzed by copper(II) complexes under mild condition has also drawn significant attention over the last few decades.[3] Relatively high abundance of copper in the Earth's crust and its redox properties make it ideally suited for catalytic oxidation processes. In natural enzymes, several copper containing enzymes are known with mono-, di-, tri- or polynuclear Cu centers that catalyze mild and highly selective oxidative transformations.[4] These reactions include the poorly characterized particulate methane monooxygenase (pMMO) which is composed of tri- or multinuclear clusters of copper that catalyze conversion of alkanes and alkenes.[1f–h] Several copper(II) complexes have been exploited as catalyst in various liquid-phase oxidation reactions,[5] e.g., catechol oxidation,[6] alkane oxidation (especially cycloalkane),[7] oxidation of aromatic hydrocarbons,[7i,8] sulfoxidation,[9] epoxidation,[10] etc.

The antibacterial properties of copper(II) have also been known for thousands of years.[11] Copper(II) complexes with diverse drugs have been the subject of a large number of research studies,[12] apparently due to the biological role of copper(II) and its synergetic activity with the drug.[13] The antifungal and antibacterial properties of a range of copper(II) complexes have been evaluated against several pathogenic fungi and bacteria.[14] In the literature, it has also been reported that organic ligands exhibit enhanced antibacterial activity once coordinated to copper.[14b]

The carboxamide group, [–C(O)NH–], ubiquitous throughout nature in the primary structure of proteins, is versatile and important ligand construction unit for synthetic coordination chemists.[15] It is noteworthy to

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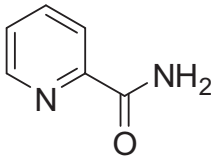
mention that neutral amides predominately coordinate to metal ion *via* the lone pair on the carbonyl oxygen atoms whereas deprotonated amides preferably coordinate to metal ions *via* their amido nitrogen atom.[16] The presence of deprotonated carboxamido-*N* coordination in some metalloenzymes has also motivated the synthetic chemists to design ligand systems with the amide functional group.[17] A wide variety of pyridine 2-carboxamide ligands have been synthesized for investigating their coordination properties with metal.[18–23] Structural investigation of some copper(II) complexes of the simplest pyridine 2–carboxamide ligand (HL) have been reported previously.[24] But systematic studies of their spectroscopic and electrochemical behaviours are lacking. In the present work, we report X-ray structural characterization, pH induced co-ordination mode switching phenomenon, peroxidative oxidation catalysis, antimicrobial activity of water soluble discrete mononuclear complexes of copper(II) using the simplest pyridine 2–carboxamide ligand (HL) and its deprotonated form.



HL

2. Experimental

2.1 *Materials*

All reagents and solvents were purchased from commercial sources and were used as received. The solvents were purified and dried according to standard methods.[25] Ligand pyridine 2–carboxamide (HL) was synthesized according to the method reported earlier.[26]

2.2 *Synthesis of the metal complexes*

2.2a *[Cu(HL)$_2$(H$_2$O)$_2$]Cl$_2$ (**1**)*: 10 mL solution of $CuCl_2 \cdot 6H_2O$ (1 mmol, 0.24 g) in methanol was added dropwise to a methanolic solution (25 mL) of pyridine 2–carboxamide (HL, 2 mmol, 0.23 g) with stirring at room temperature. The stirring was continued for 1 h, during which time a light blue compound was separated out. The product was filtered off and recrystallized from methanol. Yield 0.35 g (85%). Anal. Calcd. for $C_{12}H_{16}CuCl_2N_4O_4$: C, 34.92; H, 3.99; N, 13.36. Found: C, 34.75; H, 3.89; N, 13.51. FT–IR (KBr, ν/cm^{-1}) 3448(s), 3269(s, br), 3078(s, br), 1666(s), 1568(s), 1438(s), 1309(w), 1278(w), 1126(m), 1033(m), 783(m), 761(m), 657(m), 503(m). UV-Vis (in MeOH) [λ_{max}, nm (ε/M^{-1} cm^{-1})]: 756 (86).

2.2b *[Cu(HL)$_2$(ClO$_4$)$_2$](**2**)*: Ligand HL (2 mmol, 0.23 g) was dissolved in 25 mL of methanol and a 10 mL solution of $Cu(ClO4)_2 \cdot 6H_2O$ (1 mmol, 0.37 g) in methanol was added to it. Solution was stirred for 1 h during which time a deep blue compound appeared. This was filtered and recrystallized from acetonitrile. Yield 0.35 g (80%). Found. C, 28.56; H, 2.51; N, 11.23. Calcd. For $C_{12}H_{12}Cl_2CuN_4O_{10}$: C, 28.45; H, 2.39; N, 11.06. FT-IR (KBr, ν/cm^{-1}) 3215(w, br), 3026(s, br), 1666(s), 1560(s), 1438(m), 1037(w), 1145(s), 1110(s), 1087(s), 786(m), 676(m), 661(m), 630(m). UV-Vis (in MeOH) [λ_{max}, nm (ε/M^{-1} cm^{-1})]: 748 (115).

2.2c *[Cu(HL)$_2$(SCN)$_2$] (**3**)*: 5 mL methanolic solution of $CuCl_2 \cdot 6H_2O$ (0.24 g, 1 mmol) was added to a solution of ligand HL (2 mmol, 0.23 g) in 20 mL methanol. 10 mL aqueous solution of NH_4SCN (2.1 mmol, 0.16 g) was then added to the resulting faint blue mixture and solution turned to deep green. Solution was stirred for another 20 min at room temperature. The deep green product was filtered, dissolved in methanol and allowed to stand at room temperature for slow evaporation. Green crystals were obtained after three days. Yield: 0.32 g, (74%). Found. C, 39.52; H, 2.81; N, 19.90. Calcd. For $C_{14}H_{12}CuN_6O_2S_2$: C, 39.66; H, 2.85; N, 19.82. FT-IR (KBr, ν/cm^{-1}) 3269(w, br), 3056(m, br), 2048(s), 1670(s), 1568(m), 1494(w), 1436(s), 1305(m), 1276(w), 1137(m), 1107(w) 1031(m), 952(w), 817(w), 792(w), 754(m), 732(m), 678(m), 663(m). UV-Vis (in MeOH) [λ_{max}, nm (ε/M^{-1} cm^{-1})]: 672 (60).

2.2d $[CuL_2]\cdot 8H_2O$ (**4**): 1 mL of aqueous solution of sodium hydroxide (2 mmol, 0.08 g) was added slowly to aqueous solution of complex **1** (1 mmol, 0.40 g) and stirred for about 5 min. Violet colored crystalline compound that appeared was filtered off and washed with cold ethanol and diethyl ether. Yield 0.35g (85%). Anal. Calcd. for $C_{12}H_{26}CuN_4O_{10}$: C, 32.12; H, 5.80; N, 12.55. Found: C, 32.04; H, 5.83; N, 12.45. FT–IR (KBr, ν/cm^{-1}) 3431(s, br), 3307 (w), 3240(w), 1631(s), 1597(s), 1566(m), 1440(s), 1271(m), 1047(w), 1022(w), 786(m), 649(w), 607(w), 567(w). UV-Vis (in MeOH) [λ_{max}, nm (ε/M^{-1} cm^{-1})]: 570 (80).

2.3 *Catalytic activity studies*

2–12 mmol of hydrogen peroxide (30% in H_2O) was added to the catalyst (0.02 mmol) in 5 mL of acetonitrile

in a two-neck round bottom flask fitted with a condenser. To this, HNO_3 (0.2 mmol) was added followed by the addition of 1.0 mmol of substrate (toluene, ethyl benzene or cyclohexane). The reaction mixture was stirred for 6–14 h at 60°C under atmospheric pressure. After the reaction was over 90 μL of chlorobenzene was added as an internal standard and the substrate and products from the reaction mixture were extracted with 10 mL diethyl ether and then triphenylphosphine (PPh_3) (1.0 g) was added to reduce the organo-hydroperoxides. The resultant mixture was stirred for 15 min and then the sample taken from the organic phase was analyzed by gas chromatography. The identification was done by the comparison with known standards. Blank experiments for the oxidation of substrates were carried out without any catalyst keeping other experimental conditions unaltered.

2.4 *Antimicrobial activity*

The antimicrobial activities of all the synthesized copper(II) complexes were investigated against bacterial strains Gram-positive *Bacillus subtilis* (MTCC 441), *Staphylococcus aureus* (MTCC 96), Gram-negative *Escherichia coli* (MTCC 2939), *Pseudomonas aeruginosa* (MTCC 2453), *Klebsiella pneumonia* (MTCC 618) and yeast *Saccharomyces cerevisiae* (MTCC 170), *Candida albicans* (MTCC 227) following reported method.[27] The stock solutions (1 mg mL^{-1}) of the complexes were prepared by dissolving 10 mg of the test compound in 10 mL of water. The stock solution was suitably diluted with sterilized distilled water to get dilution in between 400–3 μg mL^{-1}.

The bacteria were sub-cultured in Müller-Hinton agar. The Petri dishes were incubated for 24 h at 37°C. The fungi were sub-cultured in potato dextrose agar medium. The Petri dishes were incubated for 48 h at 37°C. Activity was determined by measuring the diameter of the zone (mm) showing complete inhibition of microbial growth that a clear zone surrounding the test sample (in sterile disc) where bacterial growth does not occur (or is inhibited). The growth of the bacteria and fungi were measured by observing the minimum inhibitory concentration.

2.5 *Physical measurements*

Elemental (C, H and N) analyses were performed on a Perkin-Elmer 2400 II elemental analyzer. IR spectra were recorded using KBr disks on a Shimadzu FTIR 8400S spectrometer. The electronic spectra were recorded at room temperature using an Agilent 8453 diode array spectrophotometer. Gas chromatographic analyses were conducted using an Agilent Technologies 6890 N network GC system equipped with a fused silica capillary HP–5 column (30 m × 0.32 mm) and a FID detector. X-band EPR measurements were carried out using a JEOL JES-FA 200 instrument. ^{1}H NMR spectra were obtained using a Bruker Avance DPX 300 MHz spectrometer. Electrochemical measurements were carried out in N, N-dimethylformamide (DMF) at 25°C under nitrogen atmosphere using a Bioanalytical Systems BAS 100B electrochemical analyzer. The concentration of the supporting electrolyte, tetramethylammonium perchlorate (TEAP), was 0.1 M, while that of the complex was 1 mM. Cyclic voltammetric (CV) and square wave voltammetric (SWV) measurements were carried out using a three-electrode assembly comprising a glassy carbon or platinum working electrode, a platinum auxiliary electrode, and an aqueous Ag/AgCl reference electrode. Under the given experimental conditions, the potential of the external standard ferrocene/ferrocenium (Fc/Fc^+) couple was measured at +0.390 V vs. Ag/AgCl.

2.6 *X-ray crystallography*

Crystals suitable for structure determinations of **1**, **2**, **3** and **4** were obtained by slow evaporation of their water-methanol solutions. The crystals were mounted on glass fibers using perfluoropolyether oil. Intensity data were collected on a Bruker–AXS SMART APEX diffractometer at 123(2) K using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The data were processed with SAINT[28] and absorption corrections were made with SADABS software.[28] The structures were solved by direct and Fourier methods and refined by full-matrix least-squares methods based on F^2 using SHELX-97.[29] For the structure solutions and refinements the SHELX-TL software package[30] was used. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were placed at geometrically calculated positions with fixed thermal parameters. Crystal data and details of structure determination for complex **4** are summarized in table 1.

3. Results and Discussion

3.1 *Synthesis and characterization*

The synthesis of ligand pyridine 2-carboximidine was carried out following the method reported earlier.[26] The mononuclear copper(II) complexes, $[Cu(HL)_2(H_2O)_2]Cl_2$ (**1**) and $[Cu(HL)_2(ClO_4)_2]$ (**2**) are obtained by the reacting methanolic solution of ligand with $CuCl_2{\cdot}6H_2O$ or

Table 1. Crystallographic data for $[Cu(L)_2]\cdot 8H_2O$ (**4**)[a].

	4
Empirical formula	$C_{12}H_{18}N_4O_6Cu$
M	377.84
T, K	298(2)
Crystal system	Triclinic
Space group	P-1
a/Å	10.6100(8)
b/Å	11.1360(9)
c/Å	14.7224(11)
α/°	68.237(2)
β/°	73.419(2)
γ/°	83.203(2)
U/Å^3	1548.2(2)
Z	4
D/g cm^{-3}	1.621
μ/mm^{-1}	1.448
F(000)	780.0
Crystal size/mm	0.38×0.22×0.18
No. of measured reflections	21791
No. of observed reflections	6941
Parmeter refined	486
No. of reflections [$I > 2\sigma$ (I)]	4963
Goodness of fit, S[a]	1.005
Final R_1[b], wR_2[c] [$I > 2\sigma$ (I)]	0.0373 , 0.0917
R_1[b], wR_2[c] (all data)	0.0607, 0.1027

[a] $S = [\sum w(Fo^2 - Fc^2)/(N - P)]^{1/2}$ where N is the number of data and P the total number of parameters refined. [b] $R_1(F) = \Sigma\|F_o| - |F_c\|\Sigma|F_o|$. [c] $wR2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

$Cu(ClO_4)_3\cdot 6H_2O$, respectively, while the complex $[Cu(HL)_2(SCN)_2]$ (**3**) is prepared by the direct reaction between the ligand HL, $CuCl_2\cdot 6H_2O$ and NaSCN in a 1:2:1 ratio in methanol medium. Both compounds **1** and **2** upon treatment with 2 equiv of aqueous alkali, undergo deprotonation to produce the compound $[CuL_2]\cdot 8H_2O$ (**4**).

The IR spectra of the complexes exhibit several diagnostic features. A weak band observed between 3080 and 3025 cm^{-1} in **1–3** is due to the hydrogen bonded N-H stretching vibration of the amide $-NH_2$ group. The free ligand has characteristic IR band at 1680 cm^{-1} due to amide I [(C=O)] vibration. The metal-coordinated C=O vibration in the compounds **1–3** are observed in between 1670–1665 cm^{-1}. On the other hand, compound **4** exhibits two strong bands at 1631 and 1597 cm^{-1}, due to C=O and C=N vibrations, respectively. In a deprotonated N-coordinated amide group it is expected that the negative charge would be delocalized along the amide C–N and C–O bonds, leading to two resonance forms which have different C–N and C–O bond lengths. These bonds can also be intermediate between double and single bonds. Due to this partial single bond character, C=O vibration appears at much lower frequency (1631 cm^{-1}) and a strong peak due to C=N is also observed at 1597 cm^{-1}.

The compound **2** shows four characteristic ClO_4^- vibrations for coordinated perchlorate at 1145, 1115, 1088 and 627 cm^{-1}. On the other hand, compound **3** exhibits a strong band at 2048 cm^{-1} with an ill-defined shoulder at lower energy side due to the presence of thiocyanate group.

3.2 *Description of crystal structure*

The X-ray crystal structures of complexes **1–4** have been determined. It should be mentioned that after determination of the structures of the compounds **1**, **2** and **3**, we found that the X-ray structure of these three compounds have been reported earlier.[24] The structure determination of **2** by us has been made at 120 K whereas the reported one was made at 293 K. Accordingly, the unit cell parameters found in the present case are relatively shorter as compared to the earlier reported values.[24] The influence of temperature can be appreciated by comparing the unit cell volume, which is 442.3(2) Å^3 at 120 K as against 457.26(15) Å^3 at 293 K. In terms of Cu–N and Cu–O(amide) distances, the difference observed in the two sets of studies are insignificant, albeit the Cu–O(ClO_4) distance reported here [2.612 (2) Å] is somewhat shorter compared to the reported value [2.649(3) Å]. The thermal ellipsoid plot of the compounds **1–3** are shown in figures S1–S3 and relevant bond distances and bond angles are given in tables S1–S3. Crystal data and details of structure determinations for complex **1–3** are summarized in table S4. Figure S4–S6 show intermolecular hydrogen bonding network in compounds **1–3**.

3.2a *$[CuL_2]\cdot 8H_2O$ (**4**)*: In compound **4**, the asymmetric unit contains three independent $[CuL_2]$ molecules and eight water molecules of crystallization. A thermal ellip soid plot of the structural arrangement of the asymmetric unit is shown in figure 1 and the relevant metrical parameters involving the metal centers are given in table 2. In all the three units, the coordination environment around the four-coordinated metal centre $[CuN_4]$ may be considered perfect square planar. The Cu-N (pyridine) distances are almost equal lying in all the units between 2.0179 (19) to 2.027 (2) Å but somewhat longer relative to the Cu-N (amide) distances which are also nearly identical, lying in all the units between 1.924 (2) to 1.932 (2) Å. The *cisoid* angles vary from 81.26(8)° to 98.89(8)°, while the *transoid* angles are 175.24(7)° and 180.00(2)°. Thus, copper centres have a near perfect square planar geometry.

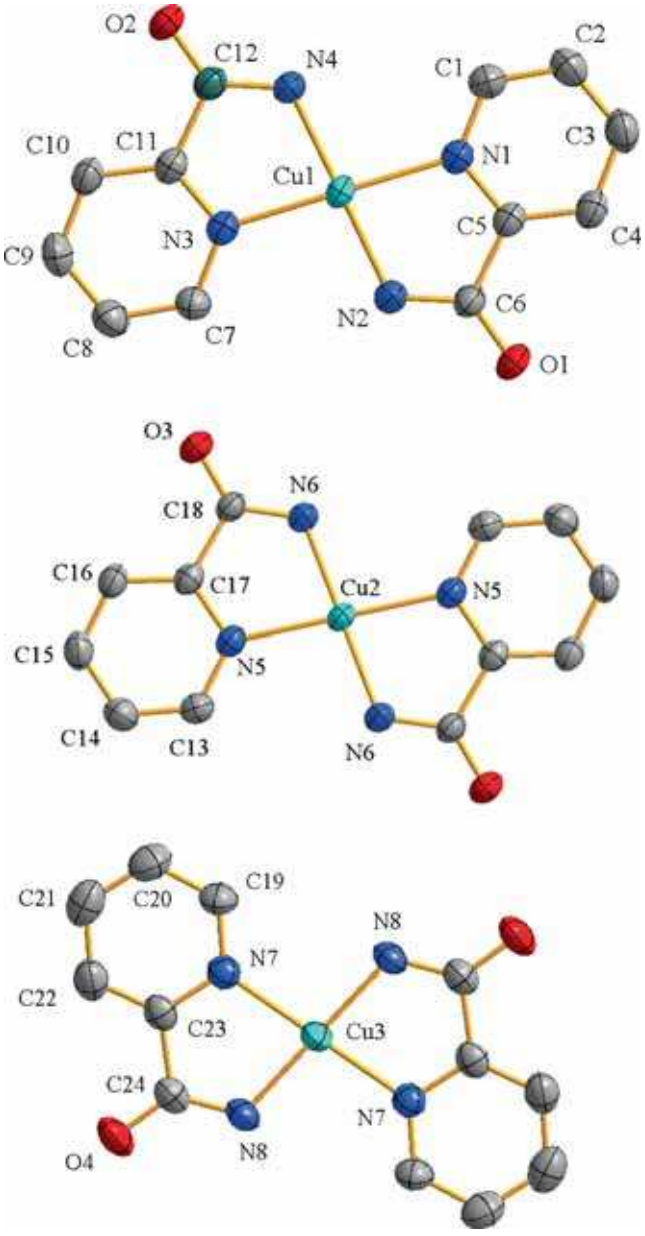


Figure 1. An ORTEP representation of the molecule $[Cu(L)_2]\cdot 8H_2O$ (**4**) showing 50% probability displacement ellipsoids. Hydrogen atoms and waters of crystallization are removed for clarity.

Interestingly, this framework hosts chains of hydrogen-bonded clusters of molecules of crystallization water (figure S7). Each tetradecameric, $(H_2O)_{14}$, cluster is formed by a cyclic water decamer and four pendent water molecules (figure 2a). Among the eight water molecules, five water molecules are generated by an inversion centre to form a cyclic water decamer. The cyclic decamer assumes a boat-chair-boat conformation (figure 2b). In the $(H_2O)_{14}$ cluster, the average $O_{water}\cdots O_{water}$ separation of ca. 2.789 Å (table S5) within the decameric core is almost same as that of ca. 2.829 Å [O(7)–H(7B)$\cdots$O(5) and O(12)–H(12A)$\cdots$O(11), table S5] connecting dangling water molecules. Both values are comparable to the average $O_{water}\cdots O_{water}$ contact of ca. 2.85 Å found in liquid water and in other H_2O clusters hosted by metal-organic frameworks.[31] The O$\cdots$O$\cdots$O angles range from 84.24° to 131.02° (table S5), considerably deviating from the preferred ideal tetrahedral geometry of water. The tetradecameric water clusters are further linked by hydrogen bonds to form infinite parallel two dimensional sheet intercalated in voids of the host metal-organic matrix of **4** (figure S7). The four dangling H_2O molecules of every water cluster also have a structure-stabilizing effect, each of them being hydrogen bonded to oxygen atoms of amide group of a pyridine 2-carboxamide ligand. Thus, $(H_2O)_{14}$ cluster forms two-dimensional sheets, and copper complexes act as connectors to those sheets to form three-dimensional packing arrays (figure S7).

The packing diagram of compound **4** also reveals the presence of two intermolecular π–π interaction between the pyridine ring C1, C2, C3, C4, C5, and N1 with the pyridine ring C13, C14, C15, C16, C17, and N5 [the distance between the two centroids is 3.701 Å] and second one is between the pyridine ring C13, C14, C15, C16, C17, and N5 with the pyridine ring C7, C8, C9, C10, C11, and N3 [the distance between the two centroids is 3.693 Å].

The N, N-coordination mode of pyridine-2-carboxamide is quite rare.[24d,e] The structure of $[Cu(pia)_2]\cdot 4H_2O$[24d] and $[Cu(pia)_2]\cdot 2H_2O$[24e] have been reported previously. The main difference between the previous two complexes with our complex, apart from the number of co-crystallized water molecules, is the presence of three independent $[CuL_2]$ molecules in an asymmetric unit.

3.3 *Electronic spectra*

The absorption spectroscopic behaviour of compounds **1–4** have been studied in methanol. The Vis–NIR spectral data for these compounds in methanol are given in Experimental Section. The six-coordinated octahedral copper(II) complexes, **1–3** exhibit a broad band in the visible and Near IR range due to *d–d* transition (675–760 nm) though three transition bands are expected for tetragonally elongated octahedral geometry. The broadness of these bands with a low energy tail are indicative of the presence of more than one transitions at lower energies, as expected for copper(II) in a tetragonally elongated octahedral environment. In general, the electronic spectra of octahedrally coordinated copper(II) complexes are dominated by Jahn-Teller-induced tetragonal distortions, which give rise to a characteristic broad band formed due to overlap of the three bands. Indeed,

Table 2. Selected bond lengths [Å] and angles [°] for $[Cu(L)_2]\cdot 8H_2O$ (**4**)[a].

			4		
Cu1–N1	2.0179(19)	Cu2–N5	2.027(2)	Cu3–N7	2.013(2)
Cu1–N2	1.928(2)	Cu2–N6	1.929(2)	Cu3–N8	1.931(2)
Cu1–N3	2.0233(19)	Cu2–N5A	2.027(2)	Cu3–N7B	2.013(2)
Cu1–N4	1.924(2)	Cu2–N6A	1.930(2)	Cu3–N8B	1.932(2)
N1–Cu1–N2	81.39(8)	N5–Cu2–N6	81.49(8)	N7–Cu3–N8	81.99(9)
N1–Cu1–N3	175.24(7)	N5–Cu2–N6A	98.51(8)	N7–Cu3–N8B	98.01(9)
N1–Cu1–N4	98.89(8)	N6–Cu2–N6A	180.00(12)	N7 –Cu3–N7B	180.00(19)
N2–Cu1–N3	98.34(8)	N5A–Cu2–N6A	81.49(8)	N7B–Cu3–N8	98.01(9)
N2–Cu1–N4	178.45(9)	N5–Cu2–N5A	180.00(9)	N8–Cu3–N8B	180.00(2)
N3–Cu1–N4	81.26(8)	N5A–Cu2–N6	98.51(8)	N7B–Cu3–N8B	81.99(9)

[a] 'A' indicates atoms at (-x, -y, 1-z) and 'B' indicates atoms at (2-x, -y, -z).

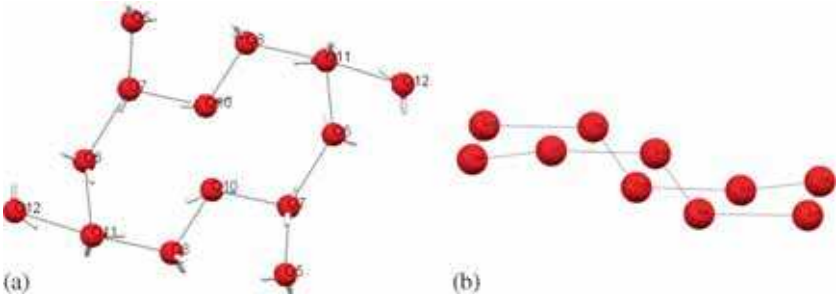


Figure 2. (a) Perspective representations of the tetradecameric, $(H_2O)_{14}$, cluster formed by a cyclic water decamer and four pendent water molecules. (b) The boat-chair-boat conformation of cyclic water decamer.

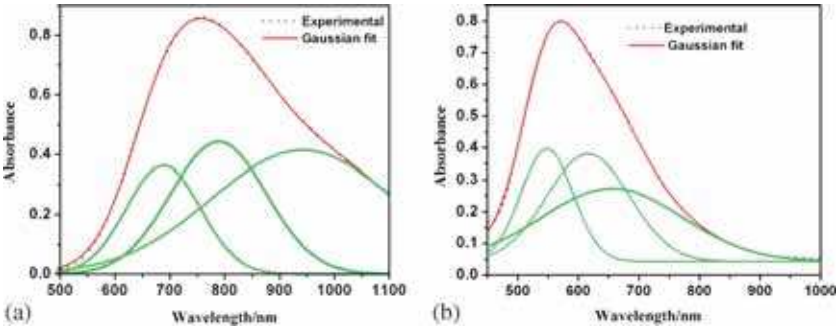


Figure 3. Visible and near infrared absorption spectra of the compounds (a) $[Cu(HL)_2(H_2O)_2]Cl_2$ (**1**) and (b) $[Cu(L)_2]\cdot 8H_2O$ (**4**) in methanol (1×10^{-2} M). The three bands below the spectrum are obtained by Gaussian line-shape analysis and added together give the experimental line.

deconvolution of the absorption spectra of **1–3** in methanol by Gaussian line-shape analysis gives rise to three peaks. The spectral data and the deconvoluted peak positions of **1–4** in methanol are listed in table S6. Square planar copper(II) complex, **4**, also shows one broad band at relatively higher energy (570 nm) due to *d–d* transition. Deconvolution of the absorption spectrum of **4** in methanol by Gaussian line-shape analysis gives rise to three peaks as expected for square planar Cu(II) complexes. Figure 3 shows deconvoluted peaks in compounds **1** and **4**.

3.4 *EPR spectra*

X-band EPR spectrum of the complexes **1–4**, have been carried out in 4:1 ethanol-methanol solution at 77 K (figure 4). EPR spectra of complexes **1–3**, show axially symmetric copper(II) centres[32] with $g_\perp = 2.073$, $g_\parallel = 2.31$; $g_\perp = 2.045$, $g_\parallel = 2.19$; $g_\perp = 2.046$, $g_\parallel = 2.34$ for complexes **1**, **2** and **3**, respectively. These values also indicate that the ground state of Cu(II) is predominantly $d_{x-y}^{2\ 2}$. Complex **4** exhibits a slight rhombic signal with $g_\parallel$ (2.24) > $g_\perp$(2.063) and $g_{av} = 2.063$. This type of signal

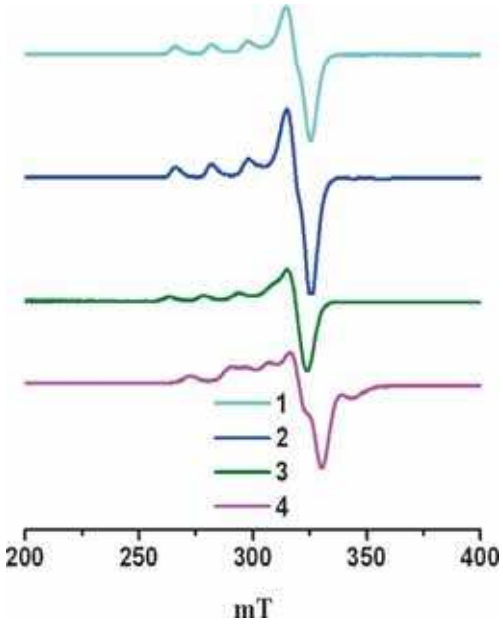


Figure 4. X-band EPR spectra of the complexes **1**–**4** under nitrogen in a frozen EtOH–MeOH (4:1) solvent mixture at 77 K.

is common for square planar copper(II) complexes with ($d_{x-y}^{2}{}^{2}$) magnetic orbital.[32]

3.5 *Electrochemistry*

The electrochemical characteristics of complexes **1**–**4** in dimethyl formamide have been investigated by cyclic and square wave voltammetric methods. The $E_{1/2}$ values obtained by the two methods agree within ±5 mV. The conventional accuracy of the $E_{1/2}$ values by these techniques, of course, is taken as ±10 mV. In case of complexes **1**–**3**, the metal-centered reductions take place quasi-reversibly. The relevant electrochemical data for the complexes **1**–**4** are given in table S7. In dimethyl formamide, the $E_{1/2}$ value of $[CuL_2(H_2O)_2]Cl_2$ (**1**) is 435 mV with $\Delta E_p = 130$ mV (figure S8a), that of $[Cu(HL)_2(ClO_4)_2]$ (**2**) is 60 mV with $\Delta E_p = 115$ mV (figure S8b) and finally for the $[Cu(HL)_2(SCN)_2]$ (**3**) the $E_{1/2}$ and ΔE_p values are 390 mV and 135 mV (figure S8c). Square planar complex $[CuL_2]\cdot 8H_2O$ (**4**) exhibits one irreversible reduction peak (figure S8d) at about 570 mV ($E_{p,c}$).

3.6 *pH induced co-ordination mode switching*

The possible inter-conversion between $[Cu(HL)_2(H_2O)_2]Cl_2$ (**1**) and $[CuL_2]\cdot 8H_2O$ (**4**) through co-ordination mode switching was then investigated. In aqueous medium, $[Cu(HL)_2(H_2O)_2]Cl_2$ (**1**) and $[CuL_2]\cdot 8H_2O$ (**4**) show one broad band at 685 and 575 nm, respectively, due to *d*–*d* transition. Upon addition of sodium hydroxide solution to an aqueous solution of compound **1**, the light blue solution ($\lambda_{max} = 685$ nm) turned gradually violet ($\lambda_{max} = 575$ nm) in accordance with the formation of the $[CuL_2]\cdot 8H_2O$ (**4**) complex (figure 5). No further change in spectrum was observed after addition of two equivalent of alkali. Conversely, upon the addition of hydrochloric acid to a violet solution of $[CuL_2]\cdot 8H_2O$ (**4**), the initial absorption at $\lambda_{max} = 575$ nm was replaced by a band at 685 nm characteristic of the compound **1** in aqueous solution.

We have also carried out potentiometric titration to obtain the pK_a values for the amide hydrogens. The potentiometric titration was carried out over a pH range of 3.5–10.5. The titration of $[Cu(HL)_2(H_2O)_2]Cl_2$ (**1**) (10 mM) in water at 25°C and $I = 0.1$ M (sodium perchlorate) gave one well-defined inflection. The pKa value was determined from the titration curve to be 7.15 and the deprotonating number was determined to be two at the inflection point as shown in figure S9.

3.7 *Oxidation of Toluene, Ethyl Benzene and Cyclohexane*

We investigated the catalytic potential of compounds **1**, **2** and **3** for the oxidation of various organic substrates such as toluene, ethyl benzene and cyclohexane by aqueous hydrogen peroxide under mild conditions. The reaction occurs in acetonitrile solution, and nitric acid in low concentration is a necessary component of the reaction mixture. It has been reported earlier[33] that the nitric acid increases the unsaturation at the metal center by protonation of the ligand of the catalyst and hence increases oxidative properties of the catalyst. In

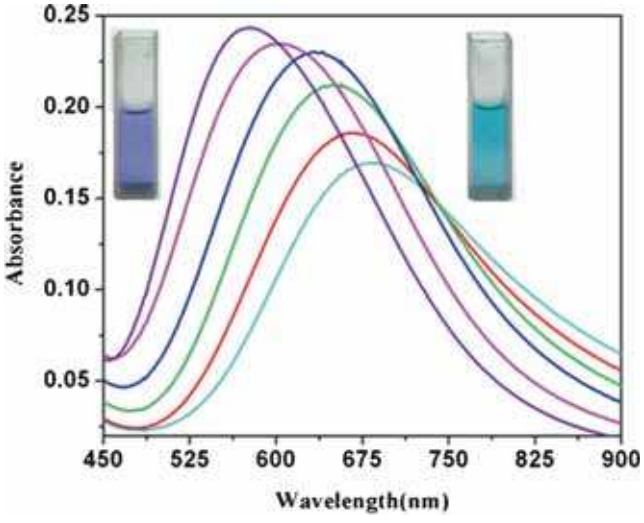


Figure 5. Change in absorption spectra of **1** in aqueous solution upon the addition of OH^- ion.

Table 3. Oxidation[a] of toluene by complexes **1**, **2** and **3**.

Entry	Catalysts	n (H_2O_2)/ n(catalyst)	Time/h	Yield (%)[b] Benzyl Alcohol	Benzaldehyde	Total	Benzyl Alcohol Selectivity (%)	TON[c]
1	1	100	10	46.4	24.1	70.5	65.8	35.25
2		200	10	51.2	30.8	78.4	65.3	39.20
3		400	10	49.1	31.9	81.0	60.6	40.50
4		500	10	49.9	36.4	86.3	57.8	43.15
5		600	10	51.0	41.4	92.4	55.2	46.20
6		600	8	51.4	40.6	92.0	55.9	46.00
7		600	6	51.1	40.9	92.0	55.6	46.00
8	2	100	12	48.1	19.9	68.0	70.7	34.00
9		200	12	49.5	23.0	72.5	68.3	36.25
10		400	12	49.8	26.1	75.9	65.6	37.95
11		500	12	50.3	29.8	80.1	62.8	40.05
12		600	12	53.1	36.6	89.7	59.2	44.85
13		600	10	54.5	36.4	90.9	59.9	45.45
14		600	8	52.9	37.3	90.2	58.6	45.10
15	3	100	14	28.2	20.0	48.2	58.4	24.10
16		200	14	35.4	25.9	61.3	57.7	30.65
17		400	14	36.8	29.9	66.7	55.2	33.35
18		500	14	37.7	33.3	71.0	53.1	35.50
19		600	14	40.6	36.2	76.8	52.9	38.40
22		600	12	40.0	35.2	75.2	53.2	37.60
21		600	11	39.9	33.8	73.7	54.1	36.85
22	$Cu(ClO_4)_2{\cdot}6H_2O$	600	12	5.9	3.1	9.0	–	4.50
23	$CuCl_2{\cdot}6H_2O$	600	12	6.1	3.3	9.4	–	4.70
24	None	600	12	2.7	2.1	4.8	–	2.40

[a] solvent = CH_3CN, 333 K, oxidant = hydrogen peroxide. [b] Calculated after treatment with PPh_3. [c] TON: turn over number = moles of product/mole of catalyst.

presence of nitric acid, decomposition of peroxide, which is present in the reaction medium, is slowed down and thus, the stability of peroxo intermediate is enhanced. The yield has been optimized by varying the relative proportions of nitric acid and hydrogen peroxide with respect to the catalysts, and also by varying the reaction time. The reaction gives alkyl or aryl hydroperoxides which are gradually transformed into the corresponding ketones (aldehydes) and alcohols. The final concentrations of the ketones (aldehydes) and alcohols were measured after the addition of PPh_3 in accord with the method developed earlier by Shulpin.[34] As catalytic reaction was done in presence of acidic medium, compound **4** has not been considered as catalyst.

The influence of various parameters such as the relative amounts of nitric acid, hydrogen peroxide, and catalyst on the catalytic activity has been investigated aiming at the optimization of the oxidation process. No oxidation products (or only traces) were obtained in the absence of catalyst or hydrogen peroxide. We have also verified that the presence of nitric acid is important in such oxidation reactions. When the oxidation of the substrate is carried out without nitric acid, it results in much lower yields for all complexes. The amount of oxidized products increased drastically with addition of acid up to 10 equiv, beyond which the yield drops. The relatively low amount of acid required to reach a maximum of activity of **1–3** is in agreement[35] with the low-coordination number of copper and the presence of labile H_2O, ClO_4^- or SCN^- ligands. On the basis of these observations, further catalytic activity tests were run at the $n(HNO_3)/n$(catalyst) molar ratio of 10. Simple copper salts, like $Cu(NO_3)_2{\cdot}6H_2O$ or $CuCl_2{\cdot}6H_2O$, under the same reaction conditions exhibit a much lower activity towards oxidation of all substrates (entries 22, 23 and 24 of table 6), under the same experimental conditions. So it is evident that the presence of N and O donor ligands is quite relevant. The oxidation reactions were also carried out at 333 K. On increasing temperature from room temperature to 333 K, yield increases significantly. When the temperature of the oxidation reactions was increased further, no significant improvement in yield was observed. So we have performed all the catalytic reactions at 333 K.

The results of the oxidation of toluene, ethyl benzene and cyclohexane are shown in tables 3, 4 and 5, respectively. It can be clearly seen from table 3 that among all the catalysts, complex **1** is the most efficient catalyst for the oxidation of toluene with 92.0% (entry 7, table 3) conversion of toluene when the $n(H_2O_2)/n$(catalyst) ratio is 600, with a reaction time of 6 h. The maximum conversions of toluene achieved are 90.2% (entry 14, table 3) and 73.7% (entry 21, table 3) with complexes **2** and **3**, respectively, in the presence of different amounts of hydrogen peroxide and with somewhat longer reaction time. It has been observed for all the catalytic conversions that the yield increases with time. Catalytic conversions are also dependent on the amount of oxidant used. The results of the oxidation of toluene show good conversion rate as well as TON and TOF (table 3, entries 7, 14 and 21).

Among three catalysts, complexes **1** and **2** are almost equally efficient catalyst for the oxidation of ethyl benzene with 74.0% (entry 7, table 4) and 72.2% (entry 14, table 4) conversion of ethyl benzene when the $n(H_2O_2)/n$(catalyst) ratio is 600, with a reaction time of 8 h. The maximum conversion of ethyl benzene achieved is 57.6% (entry 21, table 4) with complex **3**, in the presence of different amounts of hydrogen peroxide.

The results of cyclohexane oxidation are shown in table 5. It is clearly seen that the conversion of cyclohex ane is influenced by the relative amounts of hydrogen peroxide and the reaction period. The corresponding products are cyclohexanol and cyclohexanone in the case of cyclohexane oxidation. Among three catalysts, again complexes **1** and **2** are almost equally efficient catalyst for the oxidation of cyclohexane with 862% (entry 6, table 5) and 841% (entry 12, table 5) conversion of cyclohexane when the $n(H_2O_2)/n$(catalyst) ratio is 500, with a reaction time of 6 h. The maximum conversion of cyclohexane achieved is 73.0% (entry 18, table 5) with complex **3**, in the presence of different amounts of hydrogen peroxide.

The proposed mechanism of the catalytic conversion is schematically given in scheme S1. Metal-assisted decomposition of H_2O_2 could lead to the formation of hydroxyl radical ($HO^{\cdot}$) which, upon H-abstraction from RH, would form the alkyl radical ($R^{\cdot}$). The formation of the $HO^{\cdot}$ radical involves proton-transfer steps among H_2O_2, hydroperoxo and peroxo metal-species, as suggested earlier,[35b,f] which can be promoted by the N,O-donor pyridine 2–carboxamide ligand. The alkyl radical, on reaction with a metal-peroxo intermediate species LCu–OOH, could form ROOH which, upon

Table 4. Oxidation[a] of ethyl benzene by complexes **1**, **2** and **3**.

Entry	Catalysts	$n(H_2O_2)$/ n(catalyst)	Time/h	Yield (%)[b] 1-phenylethanol	Acetophenone	Total	1-phenylethanol Selectivity (%)	TON[c]
1	1	100	10	36.7	17.4	54.1	67.8	27.05
2		200	10	39.1	19.9	59.0	66.3	29.50
3		400	10	40.1	24.0	64.1	62.6	32.05
4		500	10	41.4	29.0	70.4	58.8	35.20
5		600	10	41.9	34.0	75.9	55.2	37.95
6		600	9	41.2	33.8	75.0	54.9	37.50
7		600	8	41.2	32.8	74.0	55.7	37.00
8	2	100	10	33.7	12.7	46.4	72.7	23.20
9		200	10	36.2	15.4	51.6	70.1	25.80
10		400	10	39.9	17.5	57.4	69.5	28.70
11		500	10	44.6	21.2	65.8	67.8	32.90
12		600	10	47.2	27.5	74.7	63.2	37.35
13		600	9	48.0	25.7	73.7	65.1	36.85
14		600	8	47.9	24.3	72.2	66.3	36.10
15	3	100	12	23.2	11.0	34.2	67.7	17.10
16		200	12	26.6	14.9	41.5	64.2	20.75
17		400	12	27.9	17.7	45.6	61.1	22.80
18		500	12	31.4	22.9	54.3	57.9	27.15
19		600	12	32.7	26.6	59.3	55.2	29.65
20		600	11	31.5	26.7	58.2	54.1	29.10
21		600	10	32.1	25.5	57.6	54.1	28.80

[a] solvent = CH_3CN, 333 K, oxidant = hydrogen peroxide. [b] Calculated after treatment with PPh_3. [c] TON: turn over number = moles of product/mole of catalyst.

Table 5. Oxidation[a] of cyclohexane by complexes **1**, **2** and **3**.

Entry	Catalysts	$n(H_2O_2)$/ n(catalyst)	Time/h	Yield (%)[b] Cyclohexanol	Cyclohexanone	Total	Cyclohexanol Selectivity (%)	TON[c]
1	1	100	10	39.5	26.6	66.1	59.7	33.05
2		200	10	42.8	29.7	72.5	59.1	36.25
3		400	10	43.8	33.1	76.9	56.9	38.45
4		500	10	45.8	35.7	81.5	56.2	40.75
5		500	9	46.8	40.1	86.9	53.8	43.45
6		500	8	48.0	38.2	86.2	55.7	43.10
7	2	100	10	43.5	16.0	59.5	73.1	29.75
8		200	10	45.7	17.9	63.6	71.9	31.80
9		400	10	45.7	20.8	66.5	68.7	33.25
10		500	10	51.3	24.3	75.6	67.9	37.80
11		500	9	58.1	26.7	84.8	68.5	42.40
12		500	8	58.1	26.0	84.1	69.1	42.05
13	3	100	11	23.5	13.0	36.5	64.3	18.25
14		200	11	31.0	17.4	48.4	64.1	24.20
15		400	11	37.1	22.4	59.5	62.3	29.75
16		500	11	38.4	25.2	63.6	60.3	31.80
17		500	11	44.2	29.7	73.9	59.8	36.95
18		500	10	41.8	31.2	73.0	57.2	36.50

[a] solvent = CH_3CN, 333 K, oxidant = hydrogen peroxide. [b] Calculated after treatment with PPh_3. [c] TON: turn over number = moles of product/mole of catalyst.

Table 6. Minimum inhibitory concentrations (MIC) for the complexes **1–4** (μg ml^{-1}).

Compound	Antibacterial activity *S. aureus*	*B. subtilis*	*E. coli*	*P. aeruginosa*	*K. pneumonia*	Antifungal activity *C. albicans*	*S. cerevisiae*
1	>50	>50	25	50	>50	>50	>50
2	25	12.5	50	6.25	50	>50	>50
3	>50	6.25	>50	12.5	>50	50	6.25
4	>50	>50	>50	>50	>50	25	12.5

metal-promoted homolytic decomposition, would lead to O-centred organoradicals. These are the oxyl ($RO^{\cdot}$) and the peroxyl ($ROO^{\cdot}$) radicals formed upon O-O and O-H bond cleavage, respectively, from which the final oxidation products could be obtained. Alcohols (ROH) could then be formed by H-abstraction from RH by $RO^{\cdot}$ or upon decomposition of $ROO^{\cdot}$ to both alcohol and aldehyde/ketone.[34a,36b,d,37] The presence of ROOH at the end of the reaction is shown by the increase of the amount of alcohol with a corresponding decrease in that of the aldehyde/ketone, upon treatment of the final reaction solution with an excess of PPh_3 prior to the GC analysis, according to the method reported by Shuĺpin. Reduction of ROOH by PPh_3 gives alcohol, thus eliminating the decomposition of ROOH to both alcohol and aldehyde/ketone in the gas chromatograph.

3.8 *Antimicrobial activity*

The amide ligand and its copper(II) complexes (**1–4**) were evaluated for *in vitro* antibacterial activity against Gram-positive *Bacillus subtilis*, *Staphylococcus aureus*, Gram-negative *Escherichia coli*, *Pseudomonas aeruginosa*, *Klebsiella pneumonia* and *in vitro* antifungal activity against *Saccharomyces cerevisiae*, *Candida albicans*. Muller Hinton, Potato dextrose broth and agar were employed for bacterial and fungal growth, respectively. Minimum Inhibitory Concentrations (MIC) were determined by disc diffusion method[27] and are presented in table 6. Neither the free ligand nor the copper(II) salts inhibited growth of the tested organisms at concentrations below 500 μg mL^{-1}.

Table 6 indicates that metal complex **2** and **3** showed good antibacterial activity against *Bacillus subtilis* and

Pseudomonas aeruginosa. Complex **2** showed no activity against fungi whereas complex **4** exhibited no antibacterial activity. It can be noted that complex **3** inhibited growth of both bacterial and fungal strains. On the other hand, complex **1** behaves neither as good antimicrobial agent nor as antifungal agent. Complexes **3** and **4** showed good antifungal activity against *Saccharomyces cerevisiae*. All the metal complexes exhibited better activity than ligand and copper(II) salts such as $Cu(ClO_4)_2{\cdot}6H_2O$ and $CuCl_2{\cdot}6H_2O$.

4. Conclusions

Four water soluble copper(II) complexes with pyridine 2–carboxamide (HL), namely $[Cu(HL)_2(H_2O)_2]Cl_2$ (**1**), $[Cu(HL)_2\ (ClO_4)_2]$ (**2**), $[Cu(HL)_2(SCN)_2]$ (**3**) and $[CuL_2]{\cdot}8H_2O$ (**4**) were synthesized and fully characterized by spectroscopic methods. Structures of the complexes were determined by single-crystal X-ray analysis. Complexes **1**–**3** have been effectively used as catalysts for the oxidation of toluene, ethyl benzene and cyclohexane in the presence of hydrogen peroxide as the oxidant under mild conditions to give the corresponding alcohols, aldehydes or ketones. Among the three complexes, **1** emerged as the most effective catalyst. Antimicrobial properties of all four synthesized copper(II) complexes were investigated thoroughly. Complexes **2** and **3** showed good antibacterial activity against *Bacillus subtilis* (MTCC 441) and *Pseudomonas aeruginosa* (MTCC 2453). Complexes **3** and **4** revealed promising results as antifungal agents, especially against *Saccharomyces cerevisiae* (MTCC 170).

Supplementary Information

ORTEP representations and H-bonding (figures S1–S3), crystal packing views of **1**–**3** (figure S4–S7), cyclic voltammograms of complexes **1**–**4** (figure S8), potentiometric titration curve for the complex **1** (figure S9), tables S1–S7, scheme S1, synthesis and characterization of the ligand HL, and crystal structure descriptions for complexes **1** and **3** are available at www.ias.ac.in/chemsci. CCDC-1011671(**1**), 1011672(**2**), 1011673(**3**) and 1011674(**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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