

Tetranuclear copper(II)–Schiff-base complexes as active catalysts for oxidation of cyclohexane and toluene†

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Three new Cu(II) complexes, $[\text{Cu}_4(\text{O})(\text{L}^n)_2(\text{CH}_3\text{COO})_4]$ where HL^1 = 4-methyl-2,6-bis(2-fluoroethyliminomethyl) phenol for complex **1**, HL^2 = 4-methyl-2,6-bis(2-chloroethyliminomethyl) phenol for complex **2**, $0.25\text{CH}_3\text{CN}$ and HL^3 = 4-methyl-2,6-bis(2-bromoethyliminomethyl) phenol for complex **3** have been synthesized and characterized by elemental analysis, FTIR, UV-vis spectroscopy, and electrospray ionization mass spectroscopy. The structure of complex **2**· $0.25\text{CH}_3\text{CN}$ has also been confirmed by single crystal X-ray diffraction analysis. These complexes have been found to be active catalysts for the oxidation of cyclohexane and toluene in the presence of hydrogen peroxide as the oxidant under mild conditions. Cyclohexane is oxidized to yield cyclohexanol and cyclohexanone, whereas toluene is oxidized to benzyl alcohol and benzaldehyde.

Introduction

The oxidation of various hydrocarbons catalyzed by metal complexes has drawn considerable attention over the last few decades. Copper(II) complexes have been found to show excellent catalytic activity towards different oxidation reactions. These reactions include a poorly characterized particulate methane monooxygenase (pMMO) which is composed of tri- or multinuclear clusters of copper that can carry out catalytic conversion of alkanes and alkenes.^{1–4} The catalytic activities of multinuclear copper(II) complexes, along with monomeric compounds, towards oxidation of cycloalkanes, alkenes, benzene, catechol, ascorbic acid *etc.* are amply reported.^{3,5–9} Research on the oxidation of cyclohexane assumes special attention because its oxidized products are of immense industrial importance.¹⁰ For example, cyclohexanol is mainly used in the manufacture of adipic acid, which is again a raw material of nylon-6,6', soaps and detergents, rubber chemicals, pesticides *etc.*, whereas cyclohexanone is utilized as an industrial solvent and activator in oxidation reactions. Pombeiro *et al.* have been using different transition metal complexes as catalysts to ensure the optimum, or highest, yield of one product selectively.^{11–19} Among other substrates, substituted aromatic hydrocarbons occupy a prominent position with regard to their role in commercial purpose, as well as their hazardous impact on the environment.²⁰ The controlled oxidation of toluene leads to a variety of products such as benzyl alcohol, benzaldehyde and benzoic acid^{21,22} which are industrially very important. The use of copper complexes as catalysts for such reactions is scant. Recent reports have described the reactivity of copper–peroxo species with toluene to produce benzaldehyde and benzyl alcohol.^{23,24} Recently we have reported the oxidation of cycloalkane and toluene using Cu(II)

complexes as catalysts.^{6,25,26} Barton and co-workers have reported a number of research articles covering oxidation of saturated hydrocarbons with different catalytic systems.^{27–32} Sawyer *et al.* have also significantly contributed to this field.^{33–35}

Complexes with N_2O donor ligands having tetranuclear $\{\text{Cu}_4(\mu_4\text{-O})\}$ cores are described in research articles and have been studied extensively.^{36–41} The four copper atoms arrange themselves in a distorted tetrahedron keeping the $\mu_4\text{-O}$ at the center. These complexes have been widely studied because of their interesting structure in solution or solid state, their magnetic behavior^{41–43} and catalytic properties.^{6,44} Magnetic properties of Cu(II) ions in such complexes are widely explored because copper(II) ions produce various and distorted coordination geometries and have a simple electronic configuration.^{45,46} Temperature dependent magnetic studies reveal that there are antiferromagnetic interactions between the metal atoms. Verani *et al.* have been working with such Cu_4O core of N_2O donor Schiff-base ligands to develop amphiphilic cluster-containing materials capable of film formation.^{47,48}

Herein, we report the synthesis, characterization and catalytic properties of three copper(II) complexes, $[\text{Cu}_4(\text{O})(\text{L}^n)_2(\text{CH}_3\text{COO})_4]$ where HL^1 = 4-methyl-2,6-bis(2-fluoroethyliminomethyl)phenol for complex **1**, HL^2 = 4-methyl-2,6-bis(2-chloroethyliminomethyl)phenol for complex **2**, $0.25\text{CH}_3\text{CN}$ and HL^3 = 4-methyl-2,6-bis(2-bromoethyliminomethyl) phenol for complex **3**. The complexes play a catalytic role in the oxidation of cyclohexane and toluene in the presence of H_2O_2 as the oxidant. Cyclohexane and toluene are oxidized to cyclohexanol and cyclohexanone, and benzyl alcohol and benzaldehyde, respectively, with good yields.

Experimental

Materials and physical methods

Copper(II) acetate monohydrate, 2-chloroethylamine hydrochloride, 2-bromoethylamine hydrobromide, cyclohexane, cyclohexanol, cyclohexanone, cycloheptanone and toluene were purchased

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from Sigma Aldrich and used as received. All other reagents were of analytical reagent grade. Solvents used for spectroscopic studies were purified and dried by standard procedures before use.⁴⁹ Elemental analysis was carried out in a 2400 Series-II CHN analyzer, Perkin Elmer, Norwalk, CT. FT-IR spectra were obtained on a Nicolet MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. Absorption spectra were studied on a Shimadzu UV 2100 spectrophotometer. The ESI-MS was recorded on Qtof Micro YA263 mass spectrometer. Gas chromatography analysis was performed with an Agilent Technologies 6890 N network GC system equipped with a fused silica capillary column (30 m × 0.32 mm) and a FID detector.

4-Methyl-2,6-diformylphenol was synthesized following a published procedure.⁵⁰

Synthesis of complexes **1**, **2·0.25CH₃CN** and **3**

Complexes **1**, **2·0.25CH₃CN** and **3** were synthesized in a similar way. Typically, to an acetonitrile (10 mL) solution of 4-methyl-2,6-diformyl (0.5 mmol, 0.082 g) was added the respective amine (1.0 mmol) (0.01 g of 2-fluoroethylamine hydrochloride for **1**, 0.115 g of 2-chloroethylamine hydrochloride for **2·0.25CH₃CN** and 0.205 g of 2-bromoethylamine hydrobromide for **3**). Triethylamine (1.0 mmol, 0.101 g) was added to the mixture. It was stirred for 45 min and then refluxed for 4 h. It was then cooled to room temperature. To it, solid copper(II) acetate monohydrate (1.0 mmol, 0.2 g) was added and again stirred for 1 h. The mixture was again refluxed for about 1 h. The reaction mixture was then cooled to room temperature and filtered. The filtrate was kept at ambient temperature. Single crystals of **2·0.25CH₃CN** suitable for X-ray diffraction were grown from the filtrate upon slow evaporation within a few days. After several attempts, we failed to produce X-ray quality single crystals of **1** and **3**.

Data for **1**. (Yield = 78%.) Found: C, 40.23; H, 4.12; N, 6.87. C₃₄H₄₂F₄Cu₄N₄O₁₁ requires C, 40.32; H, 4.18; N, 6.91%.

Data for **2·0.25CH₃CN**. (Yield = 75%.) Found: C, 37.81; H, 3.84; N, 6.56. C₃₄H₄₂Cl₄Cu₄N₄O₁₁ requires C, 37.86; H, 3.92; N, 6.49%.

Data for **3**. (Yield = 70%.) Found: C, 32.49; H, 3.30; N, 5.67. C₃₄H₄₂Br₄Cu₄N₄O₁₁ requires C, 32.55; H, 3.37; N, 5.58%.

X-Ray data collections and structure determination

Crystal data of complex **2·0.25CH₃CN** are summarized in Table 1. The diffraction experiment was carried out on a Bruker SMART CCD area-detector diffractometer at 150 K. No crystal decay was observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT,⁵¹ and an empirical absorption correction was applied (SADABS)⁵² to the collected reflections. The calculations were performed using the Personal Structure Determination Package⁵³ and the physical constants are tabulated therein.⁵⁴ The structures were solved by direct methods (SHELXS)⁵⁵ and refined by full-matrix least-squares using all reflections and minimising the function $\sum w(F_o^2 - kF_c^2)^2$ (refinement on F^2). The CH₃CN solvent molecule is disordered, with an occupancy of 50% instead of 100%. The C11 atom lies on a crystallographic two-fold axis, and the occupation factors of the atoms of this molecule are 0.25 each. Bond parameters of this solvent molecule are slightly different from the ideal ones

Table 1 Crystallographic information for complex **2·0.25CH₃CN**†

Empirical formula	C ₃₆ H ₄₅ Cl ₄ Cu ₄ N ₅ O ₁₁
Formula weight	1119.76
Colour	Green
Crystal system	Tetragonal
Space group	<i>I</i> 4 ₁ / <i>a</i>
<i>a</i> /Å	12.3084(6)
<i>b</i> /Å	12.3084
<i>c</i> /Å	33.3164(17)
<i>V</i> /Å ³	5047.3(5)
<i>Z</i>	4
<i>D</i> _{calc} /g cm ⁻³	1.473
Crystal dimensions/mm	0.50 × 0.20 × 0.20
μ (Mo K α)/mm ⁻¹	1.934
Minimum and max. transmission factors	0.824–1.00
<i>F</i> (000)	2272
<i>T</i> /K	150
λ (Mo K α)	0.71073
Scan mode	ω
Frame width/°	0.30
Time per frame/s	10
No. of frames	5460
Detector-sample distance/cm	6.00
Maximum and minimum θ /°	28.0–3.0
Total data, unique data	71176, 3460
<i>R</i> _{int}	0.0217
Reciprocal space explored	Full sphere
Final <i>R</i> ₂ and <i>R</i> _{2w} indices ^a (<i>F</i> ² , all reflections)	0.072, 0.117
Conventional <i>R</i> ₁ index (<i>I</i> > 2 σ (<i>I</i>))	0.034
Reflections with <i>I</i> > 2 σ (<i>I</i>)	2229
No. of variables	168
Goodness of fit ^b	1.064

^a $R_2 = \frac{\sum (|F_o^2 - kF_c^2|)}{\sum F_o^2}$, $R_{2w} = \frac{[\sum w(F_o^2 - kF_c^2)^2 / \sum w(F_o^2)^2]^{1/2}}{[\sum w(F_o^2 - kF_c^2)^2 / (N_o - N_v)]^{1/2}}$, where $w = 4F_o^2 / \sigma(F_o^2)^2$, $\sigma(F_o^2) = [\sigma^2(F_o^2) + (0.04F_o^2)^2]^{1/2}$, *N_o* is the number of observations and *N_v* the number of variables.

because of disorder. The C,C,N atoms of the disordered solvent molecule were refined with isotropic thermal parameters. All the other non-hydrogen atoms were refined with anisotropic thermal factors. The three hydrogen atoms of the solvent molecule, and the three hydrogen atoms bonded to C5, were not detected in the final Fourier maps, and were neglected. On the contrary, the three hydrogen atoms bonded to C10 were detected in the final Fourier maps, and included in structure factor calculations, but not refined. All the other hydrogen atoms were placed in their ideal positions (C–H = 0.97 Å), with the thermal parameter *U* being 1.10 times that of the atom to which they are attached, and not refined. In the final Fourier map the maximum residual was 0.94(46) e Å⁻³ at 0.34 Å from C5.

Catalytic activity studies

The oxidation of cyclohexane and toluene were performed following the same procedure. Typically, 2.5–10 mmol of hydrogen peroxide (30% in H₂O) was added to the metal complex (0.03 mmol) in 5 mL of acetonitrile in a two-neck round bottom flask fitted with a condenser. To this, HNO₃ (15 mmol) was added followed by the addition of 1.5 mmol of substrate. The reaction mixture was stirred for 48 h at room temperature under atmospheric pressure. Aliquots were collected after regular time intervals and 90 μ L of cycloheptanone was added as an internal standard. The substrate and products from the reaction mixture were extracted with 10 mL diethyl ether and then triphenylphosphine (PPh₃)

(0.6 g) was added to reduce the alkyl hydroperoxides.^{56,57} The resultant mixture was stirred for 20 min and then a sample taken from the organic phase was analyzed by gas chromatography. The identification was attained by the comparison with known standards. Blank experiments for the oxidation of cyclohexane and toluene were carried out without any catalyst keeping other experimental conditions unaltered.

Results and discussion

Synthesis and characterization

The complexes **1**, **2·0.25CH₃CN** and **3** were synthesized according to Scheme 1. The Schiff-base condensation occurs between one equivalent of 4-methyl-2,6-diformyl phenol and two equivalents of amine. Two equivalents of triethylamine were added to neutralize the acid part of the amine. Then, Cu(II) acetate reacts with this ligand, to form tetranuclear species. The acetate ion from copper(II) acetate may deprotonate the phenolic proton of the ligand. Complex **2·0.25CH₃CN** bears solvent molecule in its crystal structure in solution, but it loses solvent when it is dry and consequently loses crystalline nature. Elemental analysis of complex **2·0.25CH₃CN** is in accordance with this fact. FTIR spectra of all the complexes were of similar type. The complexes show a number of strong ν_{C-H} bands at 2800–3000 cm^{-1} .^{58,59} **1**, **2·0.25CH₃CN** and **3** show IR bands at 1632, 1625, 1622 cm^{-1} , respectively, confirming the presence of a C=N bond in the complex. The complexes show a sharp band of medium intensity at around 560 to 570 cm^{-1} for the characteristic T_2 mode of the Cu₄O core.^{43,60} The electrospray ionization mass spectra of complexes **1**, **2·0.25CH₃CN** and **3** were recorded in acetonitrile. These show peaks at m/z = 953.85, 1019.66 and 1195.47, respectively. These peaks can be assigned to $[\text{Cu}_4(\text{O})(\text{L}^1)_2(\text{CH}_3\text{COO})_3]^+$, $[\text{Cu}_4(\text{O})(\text{L}^2)_2(\text{CH}_3\text{COO})_3]^+$ and $[\text{Cu}_4(\text{O})(\text{L}^3)_2(\text{CH}_3\text{COO})_3]^+$, respectively, since the theoretical isotopic distribution patterns are in excellent agreement with the experimental ones. So it is clear from this spectral study that all

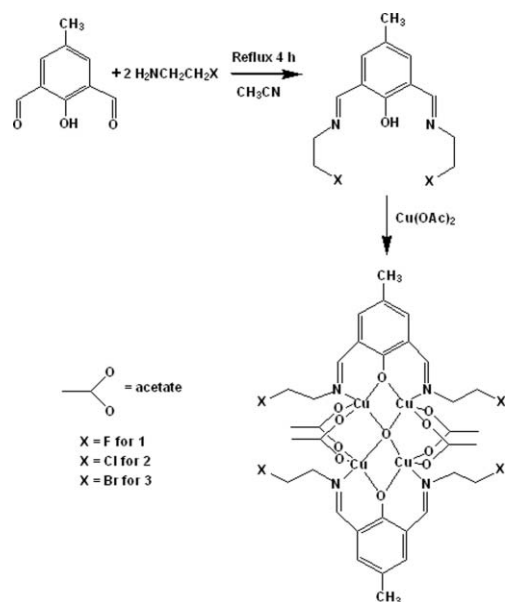


Table 2 Selected bond lengths (Å) and angles (°) for complex **2** with estimated standard deviations (e.s.d.s) in parentheses

Cu–O1	1.908(1)	Cu–O3	1.940(2)
Cu–O2	1.971(2)	Cu–N1	1.978(3)
O1–Cu–O2	77.9(1)	O2–Cu–O3	171.2(1)
O1–Cu–O3	95.8(1)	O2–Cu–N1	90.5(1)
O1–Cu–N1	159.7(1)	O3–Cu–N1	97.2(1)

the complexes behave similarly in solution. These lose one acetate moiety and are tetranuclear species in solution.

Description of the crystal structure of **2·0.25CH₃CN**

The complex crystallizes in the tetragonal system, space group $I4_1/a$. A perspective view of complex **2·0.25CH₃CN**, with partial atom numbering scheme, is shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 2. It is a discrete tetranuclear complex, with one copper atom in the asymmetric unit. The molecule has crystallographic site symmetry 4 $^-$. The Cu atom is bonded to a μ_4 -oxido oxygen atom O1, one μ_2 -phenoxido oxygen atom O2 and one nitrogen atom N1 of the binucleating ligand, 4-methyl-2,6-bis(2-chloroethyliminomethyl)-phenolate (L^{2-}), and to two acetato oxygen atoms, O3 and O4 from two different acetate moieties. The metal atom is in a slightly distorted trigonal bipyramidal geometry as revealed by the trigonal index value, τ which is calculated to be 0.19. The trigonal index value may be defined as the difference between the two largest donor–metal–donor angles divided by 60, a value which is 1 for the ideal trigonal bipyramid and 0 for the square pyramid.⁶¹ O1, O2, N1 and O3 form the basal plane of the square pyramid whereas O4 atom occupies the apical position. O1, O2, N1 and O3 atoms are coplanar within 0.197 Å with Cu atom displaced out of the plane by 0.092 Å towards O4. Cu–O_{apical} (2.324 Å) distance is quite longer compared to the other metal–donor distance. The metal–donor bond lengths are well in agreement with reported values.^{3,5,6}

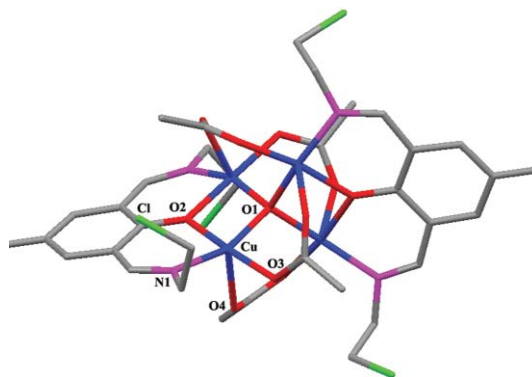


Fig. 1 A view of complex **2·0.25CH₃CN**. Hydrogen atoms and the CH₃CN molecule were omitted for clarity.

Oxidation of cyclohexane and toluene

Complexes **1**, **2·0.25CH₃CN** and **3** have been tested for the liquid biphasic (acetonitrile–water) peroxidative oxidation of cyclohexane and toluene by H₂O₂ as the oxidant, in a slightly acidic medium under ambient conditions. The products of the oxidation of cyclohexane are cyclohexanol and cyclohexanone,

Table 3 Oxidation ^a of cyclohexane by complexes **1**, **2-0.25CH₃CN** and **3**

Entry	Catalysts	<i>n</i> (H ₂ O ₂)/ <i>n</i> (catalyst)	Time/h	Yield (%) ^b			Selectivity of cyclohexanol in (%)	TON ^c
				Cyclohexanol	Cyclohexanone	Total		
1	1	125	6	13.2	9.1	22.3	59.2	11.2
2			48	15.0	13.4	28.4	52.8	14.2
3		250	6	15.6	11.8	27.4	56.9	13.7
4			48	19.4	14.7	34.1	56.9	17.1
5		500	6	15.5	9.7	25.2	61.5	12.6
6			48	21.1	14.3	35.4	59.6	17.7
7	2-0.25CH₃CN	125	6	15.0	12.2	27.2	55.1	13.6
8			48	19.3	15.4	34.7	55.6	17.4
9		250	6	17.3	11.0	28.3	61.1	14.2
10			48	22.0	15.0	37.0	59.5	18.5
11		500	6	14.9	10.3	25.2	59.1	12.6
12			48	17.9	13.6	31.5	56.8	15.8
13	3	125	6	14.4	10.3	24.8	58.0	12.4
14			48	17.3	12.8	30.1	57.5	15.1
15		250	6	18.9	11.5	30.4	62.2	15.2
16			48	19.4	15.0	34.4	56.4	17.2
17		500	6	21.3	14.4	35.7	59.7	17.9
18			48	24.0	14.2	38.2	62.8	19.1
19	Cu(NO ₃) ₂	125	48	1.2	1.7	2.9	—	—
20	Cu(NO ₃) ₂	250	48	1.0	2.0	3.0	—	—
21	Cu(NO ₃) ₂	500	48	1.7	3.6	5.3	—	—

^a Reaction time = 48 h, solvent = CH₃CN, room temperature, oxidant = hydrogen peroxide. ^b Calculated after treatment with PPh₃. ^c TON: turn over number = moles of product/mole of catalyst.

Table 4 Toluene oxidation^a by complexes **1**, **2-0.25CH₃CN** and **3**

Entry	Catalysts	<i>n</i> (H ₂ O ₂)/ <i>n</i> (catalyst)	Time/h	Yield (%) ^b			Selectivity of benzyl alcohol in (%)	TON ^c
				Benzaldehyde	Benzyl alcohol	Total		
1	1	125	6	9.2	17.3	26.5	65.3	13.3
2			48	11.0	23.5	34.5	68.1	17.3
3		250	6	12.4	23.6	36.0	65.6	18.0
4			48	15.6	24.0	39.6	60.6	19.8
5		500	6	14.0	19.2	33.2	57.8	16.6
6			48	17.5	20.4	37.9	53.8	19.0
7	2-0.25CH₃CN	125	6	8.2	17.1	25.3	67.6	12.7
8			48	10.6	23.5	34.1	68.9	17.1
9		250	6	12.4	25.4	35.8	70.9	17.9
10			48	16.6	26.4	41.3	63.9	20.7
11		500	6	14.2	18.0	32.2	55.9	16.1
12			48	16.5	21.2	37.7	56.2	18.9
13	3	125	6	10.2	18.5	28.7	64.5	14.4
14			48	11.8	24.3	36.1	67.3	18.1
15		250	6	12.8	25.1	35.9	69.9	18.0
16			48	16.0	26.4	42.4	62.3	21.2
17		500	6	15.1	19.1	34.2	55.9	17.1
18			48	14.0	23.7	37.7	62.9	18.9
19	Cu(NO ₃) ₂	125	48	1.0	2.1	3.1	—	—
20	Cu(NO ₃) ₂	250	48	1.3	2.0	3.3	—	—
21	Cu(NO ₃) ₂	500	48	1.2	2.4	3.6	—	—

^a Reaction time = 48 h, solvent = CH₃CN, room temperature, oxidant = hydrogen peroxide. ^b Calculated after treatment with PPh₃. ^c TON: turn over number = moles of product/mole of catalyst.

whereas toluene is oxidized to benzyl alcohol and benzaldehyde. The yield has been optimized by varying the relative proportions of nitric acid and hydrogen peroxide with respect to the catalysts, and also varying the reaction time.

It has been evident from previous studies by us and other groups that the presence of nitric acid has an affirmative role in such catalytic reactions.^{5,6,11-19,25,26} Nitric acid has been used, mainly, for two reasons: (1) it increases the unsaturation at the metal center by protonation of the ligand of the catalyst and hence increases oxidative properties of the catalyst; and (2) in the 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.

We have 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, the reaction does not ensue at all. The amount of oxidized products almost does not alter in the 5–15 range of $n(\text{HNO}_3)/n(\text{catalyst})$ ratio, whereas if the ratio is further increased, the yield decreases. The highest conversion of the substrate is obtained when $n(\text{HNO}_3)/n(\text{catalyst})$ is 10 for all the catalysts.

It is difficult to elucidate the exact structure of the complex in solution. The coordination geometry around the Cu center in all the catalysts is pentacoordinated, having labile sites like Cu– μ_4 -O and Cu–acetato. These would require nitric acid to increase the unsaturation at the metal center as a result of the protonation of the ligand. ESI mass spectra of complexes in the presence of nitric acid showed that one acetato moiety was lost from each complex. However, we have maintained the ratio of $n(\text{HNO}_3)/n(\text{catalyst}) = 10$ in the rest of the studies.

The results of the oxidation of cyclohexane and toluene are shown in Table 3 and 4, respectively. It can be clearly seen from Table 3 that among all catalysts, complex **3** is the most efficient catalyst for the oxidation of cyclohexane with 38.2% conversion of cyclohexane when the $n(\text{H}_2\text{O}_2)/n(\text{catalyst})$ ratio is 500, with a reaction time of 48 h. The maximum conversions of cyclohexane achieved are 35.4 and 37.0% with complexes **1** and **2**·0.25CH₃CN, respectively, in the presence of different amounts of hydrogen peroxide. It has been observed for all the catalytic conversions that the yield increases with time. Catalytic conversions are also dependant on the amount of oxidant used. The results of the oxidation of cyclohexane are better than or comparable to the previously reported results in terms of yield and/or reaction time.^{5,11-19,25,26}

Among all the catalysts, **3** has been found to be the most active catalyst with 42.4% yield for the conversion of toluene when $n(\text{H}_2\text{O}_2)/n(\text{catalyst})$ ratio is 250 after 48 h of the reaction (entry 16, Table 4). The highest conversions of toluene to its oxidized products are obtained with 39.6 and 41.3% yields in the presence of complexes **1** and **2**·0.25CH₃CN respectively. These results are comparable with the previously reported studies.^{6,23,24}

Fig. 2 shows the plot of the yields of reaction with reaction time. It can be clearly seen that there is modest improvements in yields observed after 48 h in comparison with these observed after 6 h for both the reactions.

Simple copper salts, like Cu(NO₃)₂, under the same reaction conditions exhibit a much lower activity towards oxidation of both substrates (entries 19, 20 and 21 of both Table 3 and 4), under the

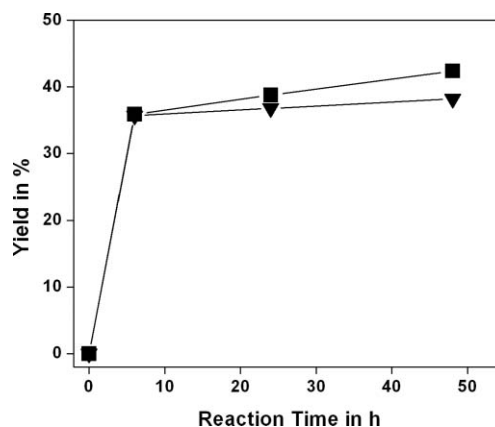
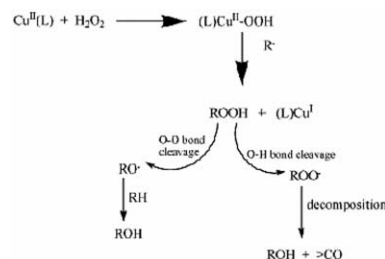


Fig. 2 Percentage of yields of reactions vs. reaction time (h). Triangle and square boxes represent cyclohexane and toluene oxidations respectively.

same experimental conditions. So it is evident that the presence of N and O donor ligands is quite relevant.

When the oxidation reactions were carried out at relatively higher temperature (e.g. 323 K), the yield increased slightly. The conversion of cyclohexane with complex **3** is 39.5% at 323 K when the $n(\text{H}_2\text{O}_2)/n(\text{catalyst})$ ratio is 500 as compared to 38.2% at room temperature. So we have performed all the catalytic reactions at room temperature.

When cyclohexanol or benzyl alcohol is used as the substrate instead of cyclohexane or toluene, the conversion of alcohol to >C=O is significantly low (ca. 5%). This indicates that the formation of the >C=O does not appear to progress considerably by oxidation of the alcohol which is produced during oxidation of the substrate. Formation of >C=O may be due to metal-assisted decomposition of alkyl hydroperoxide (ROOH) (cyclohexyl peroxide or benzyl peroxide).¹⁴ The formation of alkyl hydroperoxide has been confirmed by following the method introduced by G. B. Shul'pin.⁵⁷ The reaction mixture was analyzed by GC before and after treating with excess PPh₃. Treatment of the reaction mixture (alkyl hydroperoxide) by PPh₃ leads to the formation of alcohol with subsequent formation of phosphane oxide (OPPh₃). After the reduction, the alcohol peak in the GC rises markedly while the intensity of the >C=O (cyclohexanone or benzaldehyde) peak reduces. The mechanism of the catalytic conversion is schematically given in Scheme 2. The hydroxyl radical HO· could be formed from the metal-assisted decomposition of hydrogen peroxide. The hydroxyl radical abstracts H from the substrate (RH) to form R·.¹⁹ The formation of ROOH may occur by the reaction between a metal-peroxo intermediate, e.g. bearing a Cu(II)–OOH type moiety and the organoradical, R· to form ROOH.⁶²⁻⁶⁵ The formation of Cu–peroxo species has been determined by UV-vis



Scheme 2 Probable mechanistic pathway of catalytic reactions.

spectroscopy (see next paragraph). The metal-assisted homolytic cleavage of alkyl hydroperoxide generates alkoxy (RO[•], upon O–O bond rupture) and alkylperoxy (ROO[•], upon O–H bond breakage) radicals^{57,62,66–69} which can form an alcohol (ROH) upon H-abstraction from the alkane (RH) by RO[•] or both ROH and the >C=O upon decomposition of ROO[•].

UV-vis spectra for all the complexes were recorded in acetonitrile at room temperature. All the complexes behave in a similar way. They showed peaks in the range 255–260 nm. These peaks may be attributed to the $\pi \rightarrow \pi^*$ transition. Their absorption peaks, in the range of 379–385 nm, may be due to the charge transfer transition. They showed a relatively broad band at around 665 nm, which may be assigned to the d–d transition.

To observe the effect of hydrogen peroxide, we recorded the UV-vis spectra of the complexes in the presence of H₂O₂ and nitric acid in acetonitrile. It has been observed that an intense peak at around 400 nm, with a shoulder in the range of 415–440 nm, appears. This may be attributed to the existence of Cu–hydroperoxo or Cu–peroxo species.^{3,6,41,70} ESI mass spectrum of the complexes in the presence of nitric acid showed same *m/z* peaks as in absence of nitric acid. That means that all the complexes retain their tetranuclear entities even after addition of nitric acid. This tetranuclear moiety may be present as the active species in solution.

Conclusions

We have synthesized and characterized three new Cu(II)–Schiff-base complexes by different techniques. These complexes have been effectively used as catalysts for the oxidation of cyclohexane and toluene in the presence of hydrogen peroxide as the oxidant under mild conditions. The oxidized products of cyclohexane are cyclohexanol and cyclohexanone whereas toluene yields benzyl alcohol and benzaldehyde.

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