RSC Advances

PAPER

Copper(II) induced oxidative modification and complexation of a schiff base ligand: synthesis, crystal structure, catalytic oxidation of aromatic hydrocarbons and DFT calculation†

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A mononuclear square planar complex [Cu^{II}(L^f)] (1) was synthesized and structurally characterized by single crystal X-ray diffraction studies. Though we have started with the Schiff base H$_2$L^a with two −CH$_2$OH groups for complexation with Cu^{2+}, the final product appears to have two formyl groups where two carbinols were oxidized during the course of the reaction with Cu^{2+}. It opens up the possibility of using this complex as a precursor for condensation with suitable amines to give symmetric/asymmetric cyclic/acyclic Schiff base complexes. Systematic studies on catalytic oxidation of aromatic hydrocarbons like toluene and xylenes by an environmentally benign oxidant, H$_2$O$_2$ in the presence of 1 as a catalyst reveals that it is an efficient catalyst leading to the formation of the corresponding alcohol as the major product with TON ∼300 and alcohol selectivity of ∼72%.

Introduction

Mononuclear Schiff-base complexes are important in modelling metallobioenzymes[1–4] as well as from the industrial perspective.[5] As a result, a great deal of research attention has been paid to understanding the reactivity of metalloradicals involved in free radical catalysis, such as galactose oxidase (GOase),[6–8] along with some industrially important catalytic reactions, such as oxidative coupling polymerization of phenol derivatives,[9] oxidation of hydrocarbons,[10–13] etc., which provides an environmentally benign method. Soil and sediment bacteria like Pseudomonas putida are the most extensively characterized catabolic plasmid that encodes enzymes for the mineralization of toluene, m- and p-xylenes, m-ethyl-toluene and 1,3,4-trimethylbenzene[14,15] in which the methyl group at carbon-1 in the aromatic ring is sequentially oxidized in a number of steps to give pyruvate and aldehydes as the final products.[16] The chemical catalytic oxidation of a hydrocarbon to the corresponding alcohol, phenol, carbonyl or carboxylic acid is an extremely fascinating area of research, owing to their extensive applications as precursors in a wide variety of organic syntheses in the laboratory as well as in industry.[17–19]

Recently, it has been observed that many transition metal complexes, in combination with various oxidizing agents, can catalyze the oxidation of a variety of hydrocarbons including lower alkanes.[20] Although copper-Schiff base compounds have been widely used as catalysts in the oxidation of hydrocarbons, the yield and TON (turn over number) obtained are not very remarkable so far[10–13] normally falling within the range of 15–21.

Recent reports have described the reactivity of copper–peroxo species towards hydrocarbons to produce the corresponding alcohols and acids.[10–13] All these lead us to design and synthesize a copper(II)-Schiff base complex which has the potential ability to catalyze hydrocarbon oxidation. For this purpose, we have designed a bulky hexa-coordinating flexidentate ligand (H$_2$L^a) with potential N$_2$O$_4$ donor atoms which could provide an opportunity to synthesize mono-as well as multinuclear complexes. Moreover, benzaldehyde, an important intermediate for the production of perfumery, pharmaceutical, dyestuff, and agrochemicals, is commercially produced via the hydrolysis of benzyl chloride and as a by-product during the oxidation of toluene to benzoic acid.[21] However, they suffered from limitations like traces of chlorine in the product from the former process and poor benzaldehyde selectivity in the latter process. Vapour phase oxidation of benzyl alcohol to benzaldehyde[22–27] were adopted to avoid these limitations, which again sufferers from significant carbon loss. A few studies have been reported earlier on the liquid phase oxidation of benzyl alcohol to benzaldehyde by O$_2$, H$_2$O$_2$, or t-butyl hydroperoxide (TBHP) using palladium[28,29] Ni–Al-

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hydrotalcite,[30] heteropolyacid,[31] MnO_4^--exchanged Mg–Al-hydrotalcite[32] and other transition-metal containing hydro-tal-cite-like solids[33,34] as active/selective catalysts, in the presence and/or absence of the solvent. Here, we have been able to observe an interesting transformation of alcoholic group in (H_2L^a) to corresponding aldehyde by areal oxidation in presence of Cu(II) perchlorate, which in turn form complex with Cu(II) to give [Cu(L^f)]. Moreover, the formation of such aldehydic functionality in complex **1** provides an opportunity to explore the condensation of [Cu(L^f)] with suitable amines to give symmetric/asymmetric cyclic/acyclic Schiff base complexes and will be the subject of separate publication.

Results and discussion

Synthesis of complex

During the synthesis of complex [Cu(L^f)] (**1**) some interesting transformations on the ligand fragment were noticed. Here, ligand H_2L^a, characterized by CHN and HRMS analysis, when treated with Cu(ClO$_4$)$_2$·6H$_2$O under reflux it is transformed into H_2L^f. The two carbinol groups attached to two benzene rings were selectively oxidized to the corresponding aldehyde groups (Scheme 1). The synthesized complex with two formyl groups is important and interesting in the sense that it is very difficult to get this ligand by direct condensation of diformyl-*p*-cresol with ethylenediamine in free state. Furthermore, the complex **1** can be used as precursor to synthesize various symmetric/asymmetric, cyclic/acyclic metal ion complexes. This was confirmed by reacting [Cu(L^f)] with benzyl amine and ethylenediamine under reflux to afford crystalline complexes [Cu(L^g)] and [Cu(L^h)] as evidenced from the HRMS analysis (Fig. 8d). This will pose some interesting chemistry of the ligand and their complexes and are under investigation.

Structural description

Single crystal X-ray structural analysis showed that the complex is crystallised in monoclinic system with space group *P*21/*c* (no. 14) and Cu(II) atom in **1** (Fig. 1) is in square planar geometry. The two ethylenediamine N atoms (N1 and N2) and two phenoxido O (O1 and O4) atoms satisfy four coordination sites. Cu1–N and Cu1–O (phenoxido) bond distances comparable
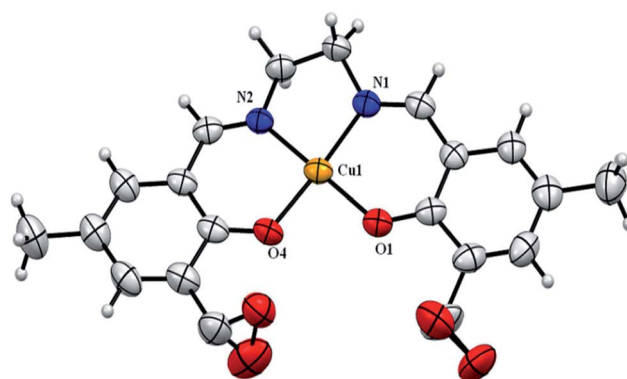

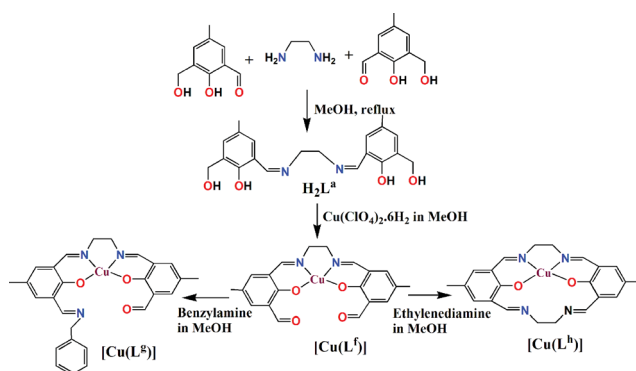**Fig. 1** ORTEP plot of complex **1** with 50% thermal ellipsoid probability.

with theoretical values (Table 1, *vide infra*) and typical for a square planar Cu complex.[35]

UV-vis spectra

A UV-vis spectrum of [Cu(L^f)] (**1**) in MeCN shows an intense band at 359 nm ($\varepsilon = 1.1 \times 10^5$ M^{-1} cm^{-1}) and a weak band at 548 nm ($\varepsilon = 1.81 \times 10^4$ M^{-1} cm^{-1}) (Fig. 2). Both bands arise due to LMCT transitions of a Cu(II) complex in a square planar geometry. On addition of H$_2$O$_2$ in presence of triethylamine (TEA) there are shifts of bands at 359 and 548 nm to 368 nm

Table 1 Selected bond lengths (Å) and bond angles (°) for complex **1**; values in parentheses are for the DFT optimized structure of **1**

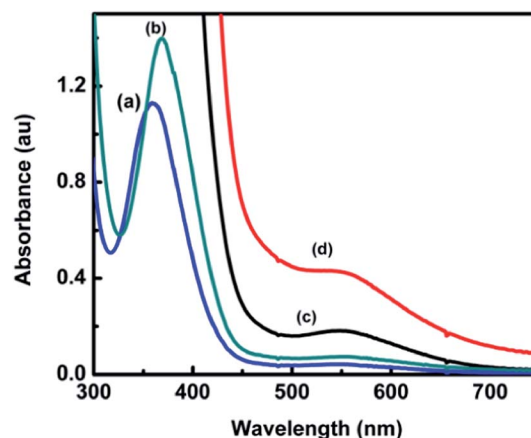| Bond lengths (Å)	Bond angles (°)
Cu1–O1 1.891(4) [1.9009]	O1–Cu1–O4 88.52(18) [92.742]
Cu1–O4 1.899(4) [1.9028]	O1–Cu1–N1 93.81(18) [92.145]
Cu1–N1 1.931(5) [1.9412]	O1–Cu1–N2 174.38(18) [165.693]
Cu1–N2 1.933(4) [1.9419]	O4–Cu1–N1 174.20(18) [162.274]
	O4–Cu1–N2 93.3(2) [91.702]
	N1–Cu1–N2 84.9(2) [85.576]

Fig. 2 Spectral change at room temperature for the reaction of (a) **1** (0.1 mM); (b) **1** (0.1 mM) + H$_2$O$_2$ (1.0 mM) + NEt$_3$ (1.0 mM); (c) **1** (0.2 mM); (d) **1** (0.2 mM) + H$_2$O$_2$ (50.0 mM) + NEt$_3$ (50.0 mM).

Scheme 1 Schematic presentation of complex syntheses.

($\varepsilon = 1.3 \times 10^5$ M^{-1} cm^{-1}) and 538 nm ($\varepsilon = 4.32 \times 10^4$ M^{-1} cm^{-1}), respectively with increase in intensities of the initial bands, which clearly indicate the formation of hydroperoxo species of the complex [Cu(L^f)(OOH)]$^-$ (**1a**) which was further characterized by ESI-MS (m/z) analysis (Fig. 3 and S5†) and supported by DFT calculation.

ESR spectra

The ESR spectrum of **1** is shown in Fig. 4, which clearly indicates a square planar geometry of the copper(II) center ($g_\| = 2.566$, $g_\perp = 2.38$, $A_\| = 170$ G) with rhombic pattern.

Copper(II)–hydroperoxo complex and its characterization

The copper(II)–hydroperoxo complex, [Cu(L^f)(OOH)]$^-$ (**1a**) was prepared by adding 10 equivalents of H$_2$O$_2$ to a reaction solution containing **1** in the presence of 2 equivalents of triethylamine (TEA) in MeCN at 25 °C; the colour of the solution changes from brown to brownish-green. UV-vis spectra of **1a** shows an intense band at 368 nm ($\varepsilon = 1.3 \times 10^5$ M^{-1} cm^{-1}) and a weak band at 538 nm ($\varepsilon = 4.32 \times 10^4$ M^{-1} cm^{-1}) (Fig. 2), which are similar to those of previously reported Cu^{II}–OOR complexes.[36–38] On addition of H$_2$O$_2$ in presence of a base there are red shifts by ~9 nm and blue shifts ~10 nm for the absorption peaks at 359 and 538 nm, respectively of the parent complex **1** along with the increase in intensities. The ESI-MS$^-$ (m/z) of **1** in MeCN in presence of H$_2$O$_2$ and TEA appears at 445.08 that corresponds to [Cu^{II}(L^f)(OOH)]$^-$ (Fig. 3 and S5†).

Geometrical optimization and electronic structure

The optimized geometry of [Cu(L^f)(OOH)]$^-$ (**1a**) is shown in Fig. 5. Both complexes [Cu(L^f)] (**1**) and [Cu(L^f)(OOH)]$^-$ (**1a**) have $C1$ point group. Main optimized geometrical parameters of the complex **1** are compared with those obtained from the X-ray diffraction studies and **1a** are listed in Tables 1 and 2 respectively.

In **1a**, the –OOH group is coordinated to the copper centre axially, which is expected to be the reactive intermediate of the catalytic cycle in the oxidation of aromatic hydrocarbons. The geometry of the penta-coordinated metal center can be ascertained by the Addison parameter τ ($\tau = (\alpha - \beta)/60$; where α and β are the two largest Ligand–Metal–Ligand angles of the coordination sphere; $\tau = 0$ for a perfect square pyramid and $\tau = 1$ for a perfect trigonalbipyramid), which is 0.32 for **1a**, in this case, suggesting a slightly distorted square pyramidal geometry. The Cu–O5 (hydroperoxo) bond length is 1.957 Å and close to the value of 1.888 Å reported by Masuda and co-workers.[39] The Cu–O5–O6 angle of 109° is also in good agreement with the value reported by Masuda (114.5°).
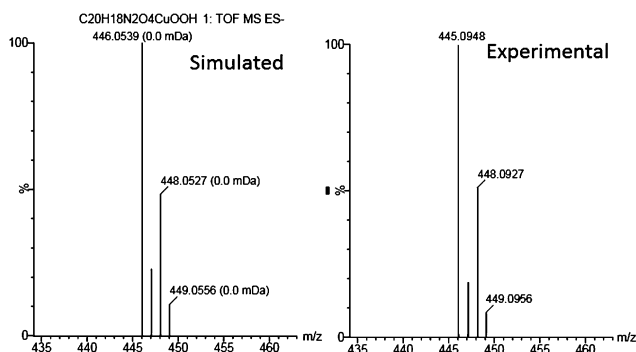

Fig. 3 HRMS spectra of [Cu(L^f)(OOH)]$^-$ generated *in situ* by the reaction between [Cu(L^f)] and H$_2$O$_2$ in presence of 1 equivalent of TEA.

Fig. 5 Optimized geometry of [Cu(L^f)(OOH)]$^-$ (**1a**).
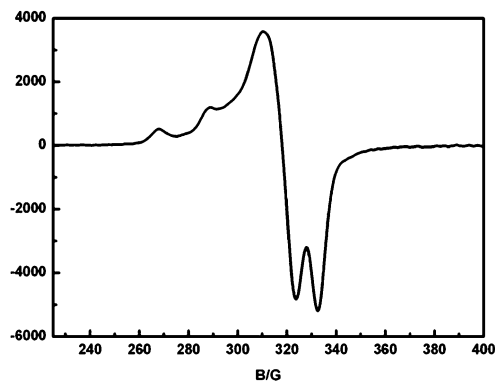
Fig. 4 X-band EPR spectra of **1** (0.5 mM in MeCN) at 70 K.
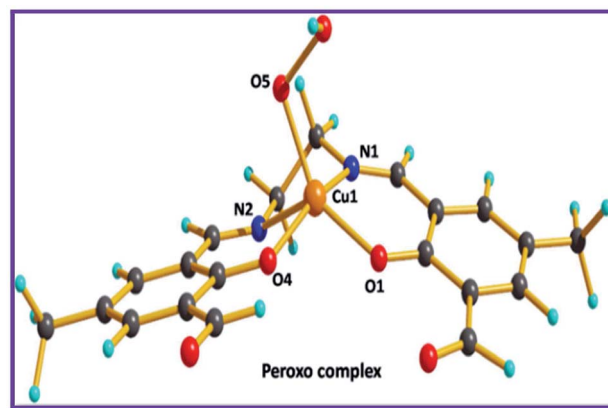
Table 2 Selected optimized geometrical parameters for **1a** in the ground state calculated at B$_3$LYP levels

Bond lengths (Å)			
Cu1–O1	1.9985	Cu1–N2	2.2373
Cu1–O4	1.9615	Cu1–O5	1.9569
Cu1–N1	1.9860		

Bond angles (°)			
O1–Cu1–O4	93.971	O5–Cu1–N1	92.913
O1–Cu1–N1	87.875	O5–Cu1–N2	86.681
O1–Cu1–N2	131.643	O5–Cu1–O1	140.786
O4–Cu1–N1	160.250	O5–Cu1–O4	97.931
O4–Cu1–N2	85.146	N1–Cu1–N2	79.033

In case of **1a**, all the LUMO, LUMO+1 and LUMO+2, molecular orbitals are mainly originating from ligand π and π* orbital while the HOMO−3, HOMO−2 and HOMO−1 molecular orbitals arise from metal d-orbitals along with ligand π orbitals. These compositions are useful in understanding the nature of transition as well as the absorption spectra of both the ligand and complex (Fig. 6).

The complex shows two absorption bands at 538 and 368 nm in MeCN solution at room temperature. The calculated absorption bands are located at 528 and 352 nm for **1a** (Fig. 6), which are in good agreement with experimental results (Table 3). This assignment was also supported by TDDFT calculations. These two absorption bands can be assigned to the $S_0 \rightarrow S_{17}$, and $S_0 \rightarrow S_{26}$ transitions, respectively.

Probable mechanism of catalytic hydrocarbons oxidation

Complex **1** has been tested for the peroxidative oxidation of toluene and xylenes by H_2O_2 as the oxidant. The main oxidation products are the corresponding alcohols and aldehydes. The yield has been optimized by varying the relative proportion of

hydrogen peroxide with respect to the catalyst, and also varying the reaction time. TOF-MS⁻ (m/z) mass spectra of complex in presence of H_2O_2 and TEA showed the presence of copper-hydroperoxo species in the medium. The results of the oxidation of toluene, p-xylene and o-xylene are shown in Table 4, S1 and S2† respectively. Fig. 7, S7 and S8† display the % of total conversion, % of the yield of alcohol and alcohol selectivity as a function of time in h. It is observed that total conversion increases with time, reaches a maximum at ~12 h and then remains almost constant. This is also true for % yield of alcohol. It is interesting to notice that the alcohol selectivity initially increases very slightly upto 12 h and then decreases slightly and this may be a consequence of further oxidation of alcohol to aldehydes and acids and this is reflected in the % yield of aldehydes. It can be clearly seen from Table 4 that complex **1** is an efficient catalyst for the oxidation of toluene with 83% conversion (TON = 298) when, $n(H_2O_2)/n$(catalyst) ratio is 500, with a reaction time of 24 h. It has been observed for all the catalytic conversions that the yield increases with time. The 'time–% of total conversion' data were fitted to eqn (1) to extract the first-order rate constants for the oxidation of aromatic hydrocarbons which are listed in Table 4, S1 and S2.†
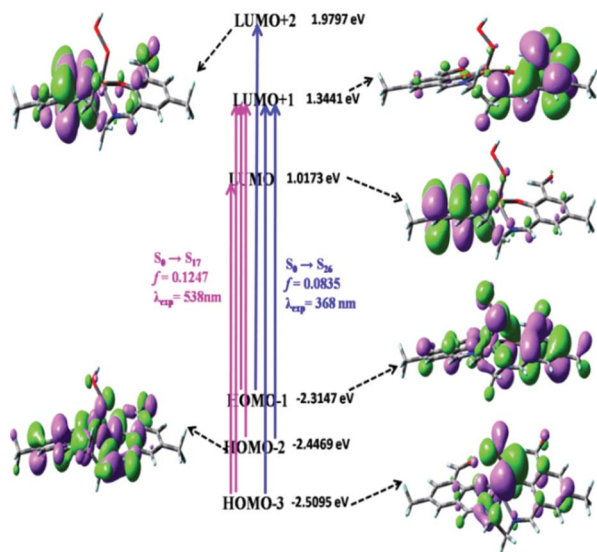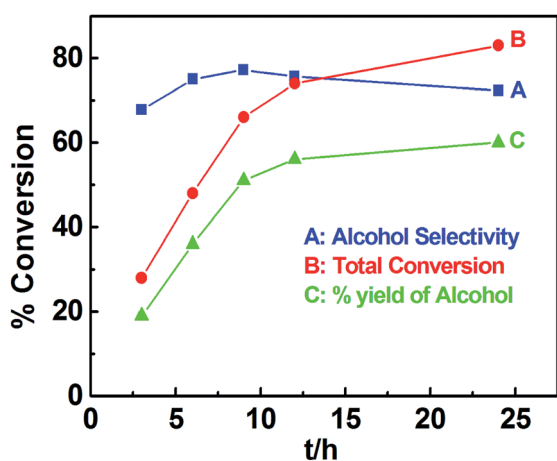
$$y = A(1 - \exp(-kt)) \qquad (1)$$

Simple copper salts, like $Cu(NO_3)_2$, under the same reaction conditions exhibit less than 4% conversion using the above mentioned substrates at $[n(H_2O_2)/n$(catalyst) = 500]. So it is evident that the presence of N and O donor ligand is quite relevant.[12] The mechanism of the catalytic conversion is schematically given in Scheme 2. The L^fCu^{II} complex reacts with H_2O_2 in presence of TEA to form L^fCu^{II}–OOH intermediate. The L^fCu^{II}–OOH now releases one HO˙ radical with the formation to L^fCu^{III}=O which on further steps reacts with another molecule of HOOH leading to the formation of L^fCu^{II}–OH with the concerted release of HOO˙ radical. L^fCu^{II}–OH on abstracting proton from TEAH⁺ releases one water molecule to regenerate the catalysts. Thus in one catalytic cycle two H_2O_2 molecules release one ˙OH and one ˙OOH radicals. These radicals could be formed from the metal-assisted decomposition of hydrogen peroxide i.e., through Fenton-like reactions. These free radicals

Fig. 6 Frontier molecular orbitals involved in the UV-vis absorption of **1a**.

Table 3 Main calculated optical transition for the complex **1a** with composition in terms of molecular orbital contribution of the transition, vertical excitation energies, and oscillator strength in MeCN

Electronic transition	Composition	Excitation energy	Oscillator strength (f)	CI	λ_{exp} (nm)
$S_0 \rightarrow S_{17}$	HOMO − 4 → LUMO	2.3481 eV (528 nm)	0.1247	0.12995	538
	HOMO − 3 → LUMO			0.23446	
	HOMO − 3 → LUMO + 1			0.13286	
	HOMO − 1 → LUMO + 1			0.74158	
	HOMO − 2 → LUMO + 1			0.15800	
$S_0 \rightarrow S_{26}$	HOMO − 1 → LUMO + 2	3.2658 eV (352 nm)	0.0835	0.20176	368
	HOMO − 3 → LUMO + 1			0.39312	
	HOMO − 2 → LUMO + 1			0.46418	

Table 4 Oxidation of toluene complex **1**, catalyst = 0.055 mmol

Substrate	$n(H_2O_2)/n$(catalyst)	Reaction time (h)	Conversion	Yield		Major product	TON	Rate constant (h^{-1})
				Major	Minor			
		3	20	17	03			
		6	39	31	08			
	150	9	55	44	11		255	
		12	71	55	16			
		24	77	58	19			
CH₃	300	3	24	16	08	CH₂OH	273	
		6	44	34	10			
		9	59	47	12			
		12	73	57	16			
		24	79	59	20			
	500	3	28	19	09		298	0.142 ± 0.01
		6	48	36	12			
		9	66	51	15			
		12	74	56	18			
		24	83	60	23			

Fig. 7 Liquid phase partial oxidation of toluene by H₂O₂ using complex **1** as catalysts.

now react with hydrocarbons to produce alcohols and aldehydes as delineated in Scheme 2.

Table 5 listed some recent results on the catalytic oxidation of toluene by TBHP–H₂O₂ in MeCN catalyzed by different mono- and polynuclear copper(II) Schiff base complexes. In most cases, the % conversions as well as the TON are not remarkable and TON lies between 15 and 21. Here, [Cu^{II}(L^f)] was found to be highly efficient catalyst with almost 83% conversion within 24 h with TON ~300 and only comparable to our previously reported results.[12d] So we have been able to design and synthesize a mononuclear Cu(II) Schiff base complex which showed remarkable catalytic oxidation of aromatic hydrocarbons to the corresponding alcohol with high selectivity (~72%) and so far highest TON.
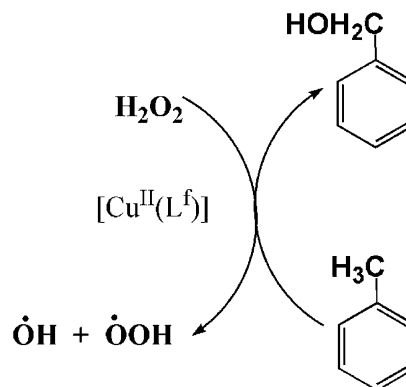
Experimental section

Material and reagents

2-(Hydroxylmethyl)-6-carbaldehyde-4-methylphenol was prepared by reported methods.[40] All reagents and solvents are commercially
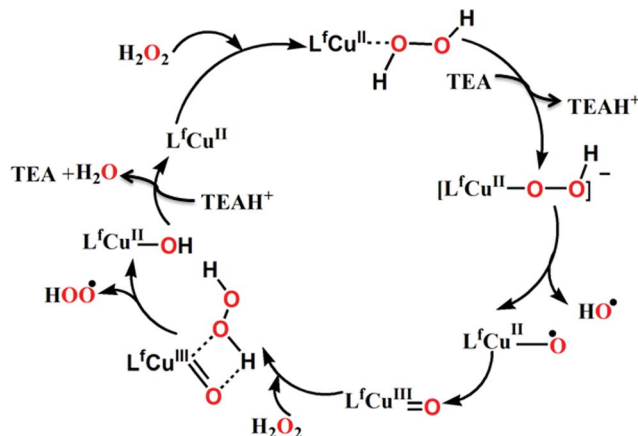
Scheme 2 Mechanistic pathway of catalytic hydrocarbon oxidation.

Scheme 3 Representative oxidation of toluene to benzyl alcohol.

Table 5 Comparison of the catalytic efficiency of **1** with other reported copper(II) catalysts for the oxidation of toluene with TBHP–H_2O_2 in MeCN

Catalyst	Conversion (%)	Selectivity (%) towards alcohol	TON	Ref.
Cu(NMP)$_2$	59.2	17.5		12a
Cu(CNMP)$_2$	77.5	18.9		12a
Cu(BNMP)$_2$	65.4	19.6		12a
[Cu$_4$(O)(**L^1**)$_2$(CH$_3$COO)$_4$]	39.6	60.6	19.8	12b
[Cu$_4$(O)(**L^2**)$_2$(CH$_3$COO)$_4$]·0.25CH$_3$CN	41.3	63.9	20.7	12b
[Cu$_4$(O)(**L^3**)$_2$(CH$_3$COO)$_4$]	42.4	62.3	21.2	12b
[Cu$_2$(**L^1**)(μ_2-pz)(CH$_3$COO)$_2$]	47.3	62.2	11.9	12c
[Cu$_4$(**L^1**)$_2$(μ_4-O)(μ_2-CH$_3$COO)$_2$($\mu_{1,1}$-N$_3$)(N$_3$)]	60.2	57.5	15.2	12c
[Cu$_2$(**L^2**)($\mu_{1,1}$-N$_3$)($\mu_{1,3}$-N$_3$)$_2$]$_\infty$	40.0	74.6	10.1	12c
[Cu^{II}(**L**)]	82	80.4	298	12d
[Cu^{II}(**L^f**)]	83	72.3	298	This paper

available. THF was dried using sodium metal and benzophenone and other solvents were used without further purification.

Physical measurements

Elemental analyses were carried out using a Perkin-Elmer 240 elemental analyzer. ^{1}H NMR were recorded in CDCl$_3$ on a Bruker 300 MHz NMR Spectrophotometer using tetramethylsilane ($\delta = 0$) as an internal standard. Electronic spectra were recorded on Agilent-8453 diode array UV-vis spectrophotometer. TOF-MS$^+$ spectra were generated on a waters HRMS instrument (model: XEVO G2QTOF) and ESR spectra were recorded on JOEL JES-FA 200 ESR spectrometer.

Computational details

Ground state electronic structure calculations in MeCN solution of both the complexes [Cu(L^f)] (**1**) and [Cu(L^f)(OOH)]$^-$ (**1a**) have been carried out using DFT[41] method associated with the conductor-like polarizable continuum model (CPCM).[42] Becke's hybrid function[43] with the Lee–Yang–Parr (LYP) correlation function[44] was used through the study. The geometry of the complex **1** and **1a** were fully optimized without any symmetry constraints. On the basis of the optimized ground state geometry, the absorption spectral properties in MeCN medium were calculated by time-dependent density functional theory (TDDFT)[45] approach associated with the conductor-like polarizable continuum model (CPCM).[42] We computed the lowest 40 singlet–singlet transitions and results of the TD calculations were qualitatively very similar.[46] The effective core potential (ECP) approximation of Hay and Wadt was used for describing the (1s^{2}2s^{2}2p^6) core electron for copper whereas the associated "double-ξ" quality basis sets were used for the valence shell.[47] For H atoms we used 6-31(g) basis set; for C, N and O atoms we employed 6-31(g) and for Cu atom we adopt 6-31 + g(d,p) as basis set for the optimization of the ground state. The calculated electronic density plots for frontier molecular orbitals were prepared by using Gauss View 5.1 software. All the calculations were performed with the Gaussian 09W software package.[48] GaussSum 2.1 program[49] was used to calculate the molecular orbital contributions from groups or atoms.

Experimental set up for catalytic oxidation

In a clean and dry two necked round bottom flask of 50 mL capacity fitted with a condenser and a rubber septum the catalyst, complex **1** (21 mg, 0.05 mmol) and the substrate, hydrocarbons (20 mmol) and a magnetic needle were placed. 10 mL dry MeCN was added to dissolve the reactants. To the above solution was then added 2 mL of 30% H_2O_2 and the resulting solution immediately turned brownish green. The solution was then heated on an oil bath to reflux for 24 h and 0.5 mL of H_2O_2 was added intermittently at a time interval of 60 min. An aliquot (0.1 mL) of the reaction solution was withdrawn with the help of long needle syringe and was subjected to multiple ether extraction and 1 μL of concentrated ether extract was injected to the GC port with the help of 10 μL syringe. The retention times of the peaks were compared with those of commercial standards and the unknown peaks were characterized by TOF-MS$^+$ and TOF-MS$^-$ analysis.

2-(Hydroxyl methyl)-6-carbaldehyde-4-methylphenol

It was prepared by the literature method[40] and characterized by ^{1}H NMR analysis. ^{1}H NMR (in CDCl$_3$, 300 MHz, ppm): δ 2.34 (3H, s, –CH$_3$), 4.73 (2H, s, –CH$_2$), 7.29 (1H, s, –ArH), 7.40 (1H, s, –ArH), 9.86 (1H, s, –CHO), 11.18 (1H, s, –ArOH).

Synthesis of H$_2$L^a

0.232 g (2 mmol) of 2-(hydroxymethyl)-6-carbaldehyde-4-methylphenol was refluxed with 0.06 g (1 mmol) ethylene-diamine in methanol (30 mL) for 1 h. Yellow solid deposited were collected by filtration and washed with ethanol. Yield ~80%. Elemental analysis: ana. cal. value for molecular formula, C$_{20}$H$_{24}$N$_2$O$_4$ (MW = 356.42): C, 67.39; H, 6.79; N, 7.86; found C, 67.34; H, 7.85; N, 7.88. TOF-MS$^+$ (**H$_2$L^a** + Na$^+$) m/z 379.2020 (Fig. 8a & S1†).

Syntheses of complexes [Cu(L^f)] (**1**)

The ligand **H$_2$L^a** 0.356 g (1 mmol) and (CuClO$_4$)$_2$·6H$_2$O (0.370 g, 1 mmol) in 30 mL methanol were refluxed together for 90 minutes whereupon the yellow solution turned brown which
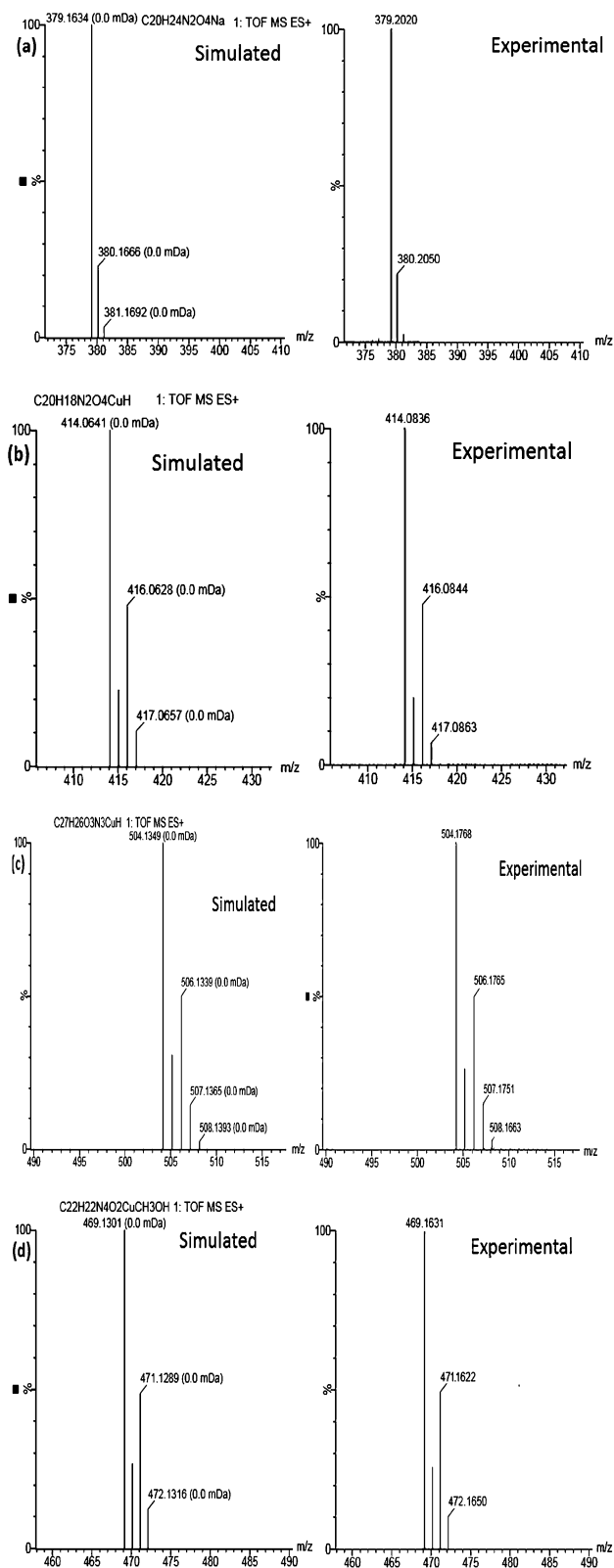
Fig. 8 HRMS spectra of (a) H_2L^a, (b) [Cu(L^f)], (c) [Cu(L^g)] and (d) [Cu(L^h)].

was filtered and kept in a rack. Slow evaporation of methanol gives rod shaped brown crystals suitable for X-ray studies.

Ana. cal. value for Molecular formula, $C_{20}H_{18}N_2O_4Cu$ (MW = 413.91): C, 58.04; H, 4.38; N, 6.77; found C, 58.01; H, 4.48; N, 6.79. TOF-MS$^+$ [Cu(L^f) + H$^+$] m/z 414.0836 (Fig. 8b and S2†).

[Cu(L^g)]. The complex **1** (0.414 g, 1.0 mmol) and benzyl amine (0.107 g, 1 mmol) in 30 mL MeOH were refluxed together for 120 minutes in a round bottom flask fitted with a condenser in open air whereupon the brown solution turned greenish-brown which was filtered and kept in a rack. Slow evaporation of MeOH gives greenish-brown micro crystals. Ana. cal. value for molecular formula, $C_{27}H_{25}N_3O_3Cu$ (MW = 503.05): C, 64.46; H, 5.01; N, 8.35; found C, 64.40; H, 5.11; N, 8.39. TOF-MS$^+$ [Cu(L^g) + H$^+$] m/z 504.1768 (Fig. 8c and S3†).

[Cu(L^h)]. The complex **1** (0.414 g, 1.0 mmol) and ethyl-enediamine (0.06 g, 1 mmol) in 30 mL MeOH were refluxed together for 120 minutes in a round bottom flask fitted with a condenser in open air whereupon the brown solution turned greenish-brown which was filtered and kept in a rack. Slow evaporation of MeOH gives greenish-brown micro crystals. Ana. cal. value for molecular formula, $C_{22}H_{22}N_4O_2Cu$ (MW = 437.98): C, 60.33; H, 5.06; N, 12.79; found C, 60.27; H, 5.10; N, 12.81. TOF-MS$^+$ [Cu(L^h) + MeOH] m/z 469.1631 (Fig. 8d and S4†).

Single crystal X-ray diffraction

Intensity data for complex **1** was collected at 273K on a Bruker SMART APEX-II CCD diffractometer using graphite mono-chromated MoKα radiation λ = 0.71073 Å and the ω−2θ scan mode in the range 2.0 < 2θ < 25.8°. No decomposition of the crystal occurred during the data collection. The intensities were corrected for Lorentz and polarization effects and for absorption using the ψ-scan method. The cell parameters were refined

Table 6 Crystal data and refinement parameters of complex **1**

Formula	$C_{20}H_{16}CuN_2O_4$
Formula weight	411.90
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a [Å]	12.6160(4)
b	23.0976(8)
c	7.0880(3)
α [°]	90.00
β	102.372(2)
γ	90.00
V [Å^3]	2017.47(13)
Z	4
D (calc) [g cm^{-3}]	1.376
μ (MoK$_\alpha$) [mm^{-1}]	1.109
F (000)	844
Temperature (K)	273
Radiation [Å] MoK$_\alpha$	0.71073
θ min–max [°]	1.6, 27.2
Dataset	−16 : 16; −29 : 29; −9 : 9
Tot., uniq. data, R (int)	32 430, 4496, 0.049
Observed data [I > 2.0 sigma(I)]	3037
N_{ref}, N_{par}	4496, 265
R, wR_2, S	0.0772, 0.2677, 1.08

from all strong reflections. The data reductions were carried out using the CrysAlis RED (Oxford Diffraction, UK) program, and analytical absorption corrections were applied. The structures was determined by direct methods using SHELXS-97 (ref. 50) refined anisotropically on F^2 using the full-matrix least-squares procedure of SHELXL-97.[50] The positional disorder of aldehydic O-atoms in **1**, at two positions (O2, O2A and O3, O3A) occur with 50% occupancy. So H-atoms on aldehydic carbon atom cannot be fixed precisely. The crystallographic data for **1** are given in Table 6.

Conclusions

In summary, we have synthesized one mononuclear complex [Cu(L^f)] (**1**) from a compartmental ligands **H$_2$L^a**. The complex has been characterized by single crystal X-ray diffraction method and the central metal ion was found to assume square planar geometry. In complex **1** though we have started with ligand **H$_2$L^a** bearing hydroxymethyl group in the benzene ring, during the course of reaction with Cu^{2+} it was oxidized to the corresponding aldehyde, which is otherwise impossible to synthesize in the free state. It is also interesting that the complex **1** can be used as precursor for the condensation with suitable amines to give symmetric/asymmetric cyclic/acyclic Schiff base complexes. This complex showed catalytic hydrocarbon oxidation of toluene and xylenes to the corresponding alcohol with high selectivity and TON under homogeneous conditions.

Acknowledgements

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