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ARTICLE TYPE

Copper(II) induced oxidative modification and complexation of a Schiff base Ligand: synthesis, crystal structure, catalytic oxidation of aromatic hydrocarbons and DFT calculation†Surajit Biswas^a, Arpan Dutta^a, Malay Dolai^a, Mainak Debnath^a, Atish Dipankar Jana^b and Mahammad Ali^{a*}

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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 H₂L^a with two –CH₂OH groups for complexation with Cu²⁺, the final product appears to have two formyl groups where two carbinols were oxidized during the course of reaction with Cu²⁺. It opens up the possibility of using this complex as precursor for the 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, H₂O₂ in presence of **1** as catalyst reveals that it is to be an efficient catalyst leading to the formation of corresponding alcohol as major product with TON ~300 and alcohol selectivity ~72%.

Introduction

Mononuclear Schiff-base complexes are important in modelling metalloenzymes¹⁻⁴ as well as from the industrial perspectives.⁵ As a result, a great deal of research attention has been paid to understand 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 hydrocarbons¹⁰⁻¹³ etc, which provide an environmentally benign method. Soil and sediment bacteria like *Pseudomonas putida* is 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 Chemical catalytic oxidation of 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 synthesis in the laboratory as well as in the industry.¹⁷⁻¹⁹

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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 Though, copper-Schiff base compounds have been widely used as catalyst in the oxidation of hydrocarbons, but yield and TON (turn over number) obtained are not very remarkable so far¹⁰⁻¹³ normally falling in the range 15-21.

Recent reports have described the reactivity of copper-peroxy 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 (H₂L^a) with potential N₂O₄ 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 benzaldehyde²²⁻²⁷ 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 O₂, H₂O₂,

or *t*-butyl hydroperoxide (TBHP) using palladium^{28,29} Ni-Al-hydrotalcite,³⁰ heteropolyacid,³¹ MnO₄⁻-exchanged Mg-Al-hydrotalcite³² and other transition-metal containing hydro-talcite-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 (H₂L^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.

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

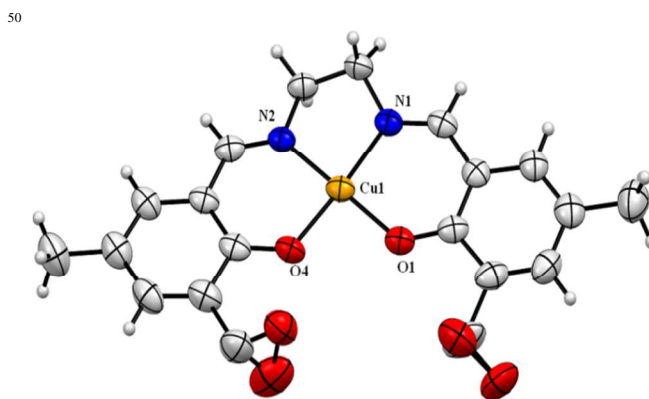
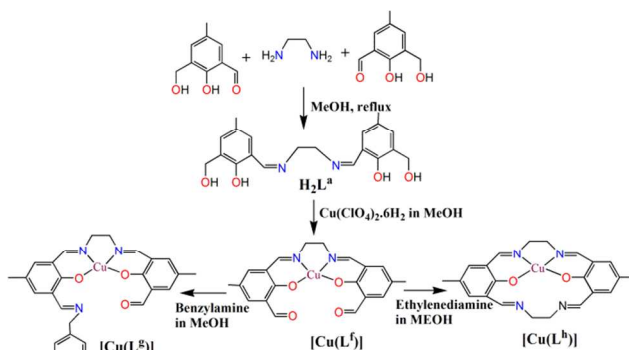


Fig. 1 ORTEP plot of complex 1 with 50% thermal ellipsoid probability.

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]



Scheme 1 Schematic presentation of complex syntheses.

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 H₂L^a, characterized by CHN and HRMS analysis, when treated with Cu(ClO₄)₂·6H₂O under reflux it is transformed into H₂L^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 benzylamine and ethylenediamine under reflux to afford crystalline complexes [Cu(L^g)] and [Cu(L^h)] as evidenced from the HRMS analysis (Fig. 9). 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 P21/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

UV-VIS Spectra

A UV-Vis spectrum of [Cu(L^f)] (**1**) in MeCN shows an intense band at 359 nm ($\epsilon = 1.1 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) and a weak band at 548 nm ($\epsilon = 1.81 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) (Fig. 2). Both bands arise due to LMCT transitions of a Cu(II) complex in a square planar geometry. On addition of H₂O₂ in presence of triethylamine

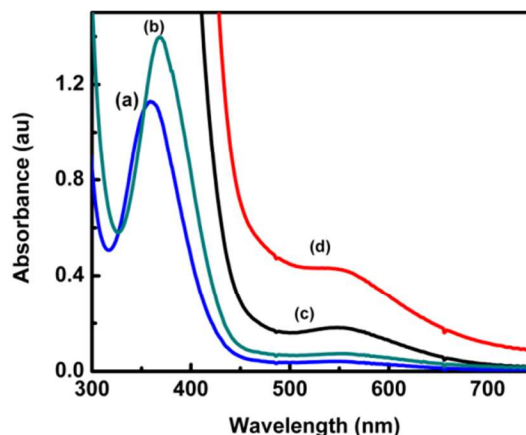


Fig. 2 Spectral change at room temperature for the reaction of (a) **1** (0.1 mM); (b) **1** (0.1 mM) + H₂O₂ (1.0 mM) + NEt₃ (1.0 mM); (c) **1** (0.2 mM); (d) **1** (0.2 mM) + H₂O₂ (50.0 mM) + NEt₃ (50.0 mM).

(TEA) there are shifts of bands at 359 and 548 nm to 368 nm ($\epsilon = 1.3 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) and 538 nm ($\epsilon = 4.32 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), respectively with increase in intensities of the initial bands,

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which clearly indicate the formation of hydroperoxo species of the complex $[\text{Cu}(\text{L}^{\text{f}})(\text{OOH})]^{-}$ (**1a**) which was further characterized by ESI-MS⁻ (m/z) analysis (Fig. 3 and Fig.S5) and supported by DFT calculation.

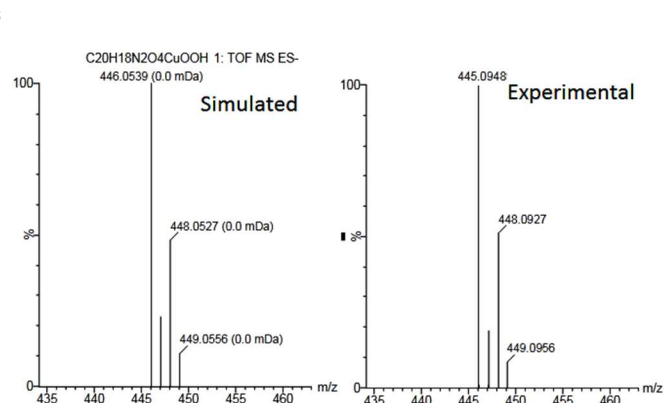


Fig. 3 HRMS spectra of $[\text{Cu}(\text{L}^{\text{f}})(\text{OOH})]^{-}$ generated *in situ* by the reaction between $[\text{Cu}(\text{L}^{\text{f}})]$ and H_2O_2 in presence of **1** and equivalent amount of TEA.

ESR Spectra

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

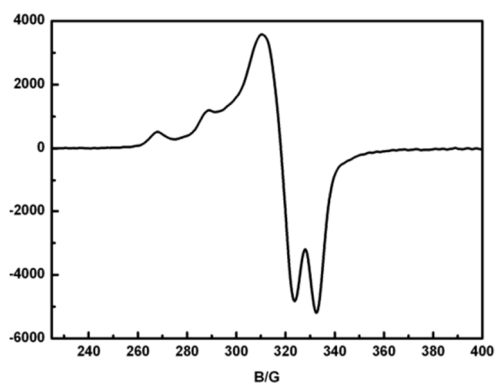


Fig. 4 X-band EPR spectra of **1** (0.5 mM in MeCN) at 70 K.

Copper(II)-hydroperoxo complex and its characterization

The copper(II)-hydroperoxo complex, $[\text{Cu}(\text{L}^{\text{f}})(\text{OOH})]^{-}$ (**1a**) was prepared by adding 10 equivalents of H_2O_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 ($\epsilon = 1.3 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) and a weak band at 538 nm ($\epsilon = 4.32 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) (Fig. 2), which are similar to those of previously reported $\text{Cu}^{\text{II}}\text{-OOR}$ complexes.³⁶⁻³⁸ On addition of H_2O_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_2O_2 and TEA appears at 445.08 that corresponds to $[\text{Cu}^{\text{II}}(\text{L}^{\text{f}})(\text{OOH})]^{-}$ (Fig. 3 and Fig. S5).

Geometrical optimization and electronic structure

The optimized geometry of $[\text{Cu}(\text{L}^{\text{f}})(\text{OOH})]^{-}$ (**1a**) is shown in Fig. 5. Both complexes $[\text{Cu}(\text{L}^{\text{f}})]$ (**1**) and $[\text{Cu}(\text{L}^{\text{f}})(\text{OOH})]^{-}$ (**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 Table 1 and Table 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°).

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).

Table 2 Selected optimized geometrical parameters for **1a** in the ground state calculated at B₃LYP 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

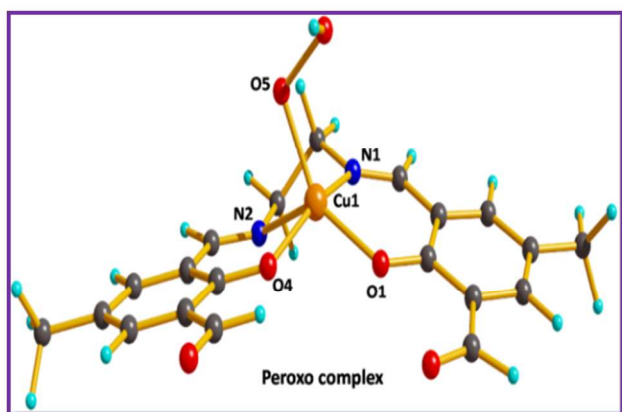


Fig. 5 Optimized geometry of [Cu(L)(OOH)]⁻ (**1a**).

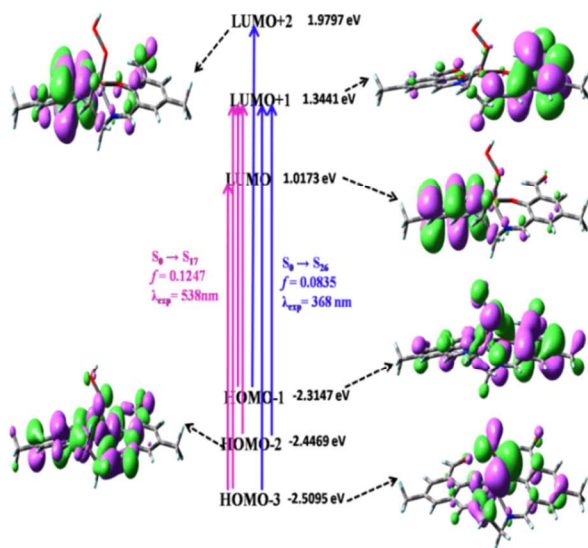


Fig. 6 Frontier molecular orbitals involved in the UV-Vis absorption of **1a**.

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 S₀ → S₁₇, and S₀ → S₂₅ transitions, respectively.

20 Probable mechanism of catalytic hydrocarbons oxidation

Complex **1** has been tested for the peroxidative oxidation of toluene and xylenes by H₂O₂ 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 H₂O₂ and TEA showed the presence of copper-hydroperoxy 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**, **Fig. S7** and **Fig. 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(H₂O₂)/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 equation (1) to extract the first-order rate constants for the oxidation of aromatic hydrocarbons which are listed in **Table 4**, **S1** and **S2**.

$$y = A*(1-\exp(-kt)) \quad (1)$$

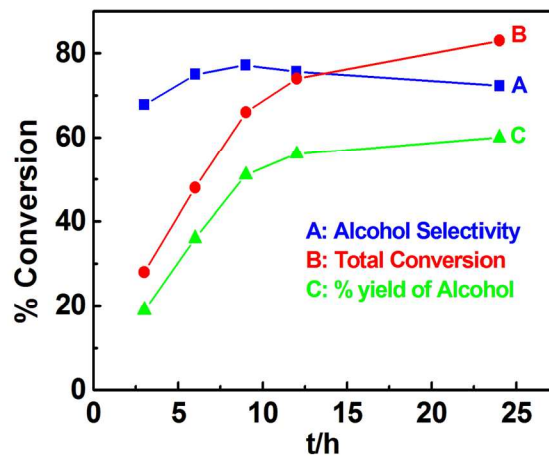


Fig. 7 Liquid phase partial oxidation of toluene by H₂O₂ using complex **1** as catalysts.

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

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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 (<i>f</i>)	CI	λ_{exp} (nm)
$S_0 \rightarrow S_{17}$	HOMO – 4 \rightarrow LUMO	2.3481eV (528 nm)	0.1247	0.12995	538
	HOMO – 3 \rightarrow LUMO			0.23446	
	HOMO – 3 \rightarrow LUMO+1			0.13286	
	HOMO – 1 \rightarrow LUMO+1			0.74158	
	HOMO – 2 \rightarrow LUMO+1			0.15800	
$S_0 \rightarrow S_{26}$	HOMO – 1 \rightarrow LUMO + 2	3.2658 eV (352 nm)	0.0835	0.20176	368
	HOMO – 3 \rightarrow LUMO + 1			0.39312	
	HOMO – 2 \rightarrow LUMO + 1			0.46418	

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

Substrate	$n(\text{H}_2\text{O}_2)/n$ (Catalyst)	Reaction time (h)	Conversion	Yield		Major product	TON	Rate constant (h^{-1})
				Major	Minor			
	150	3	20	17	03		255	0.142 ± 0.01
		6	39	31	08			
		9	55	44	11			
		12	71	55	16			
		24	77	58	19			
	300	3	24	16	08	273		
		6	44	34	10			
		9	59	47	12			
		12	73	57	16			
		24	79	59	20			
500	3	28	19	09	298			
	6	48	36	12				
	9	66	51	15				
	12	74	56	18				
	24	83	60	23				

Simple copper salts, like $\text{Cu}(\text{NO}_3)_2$, under the same reaction conditions exhibit less than 4% conversion using the above mentioned substrates at $[n(\text{H}_2\text{O}_2)/n(\text{catalyst}) = 500]$. 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 $\text{L}^{\text{f}}\text{Cu}^{\text{II}}$ complex reacts with H_2O_2 in presence of TEA to form $\text{L}^{\text{f}}\text{Cu}^{\text{II}}\text{-OOH}$ intermediate. The $\text{L}^{\text{f}}\text{Cu}^{\text{II}}\text{-OOH}$ now releases one $\text{HO}\cdot$ radical with the formation to $\text{L}^{\text{f}}\text{Cu}^{\text{III}}=\text{O}$ which on further steps reacts with another molecule of HOOH leading to the formation of $\text{L}^{\text{f}}\text{Cu}^{\text{II}}\text{-OH}$ with the concerted release of $\text{HOO}\cdot$ radical. $\text{L}^{\text{f}}\text{Cu}^{\text{II}}\text{-OH}$ 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 $\cdot\text{OH}$ and one $\cdot\text{OOH}$ radicals. These radicals could be formed from the metal-assisted decomposition of hydrogen peroxide i.e., through Fenton-like reactions. These free radicals now react with hydrocarbons to produce alcohols and aldehydes as delineated in **Scheme 3**.

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Table 5 Comparison of the catalytic efficiency of **1** with other reported copper(II) catalysts for the oxidation of toluene with TBHP/H₂O₂ 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 (μ _{1,1} -N ₃)(N ₃)]	60.2	57.5	15.2	12c
[Cu ₂ (L ²)(μ _{1,1} -N ₃)(μ _{1,3} -N ₃) ₂] [∞]	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

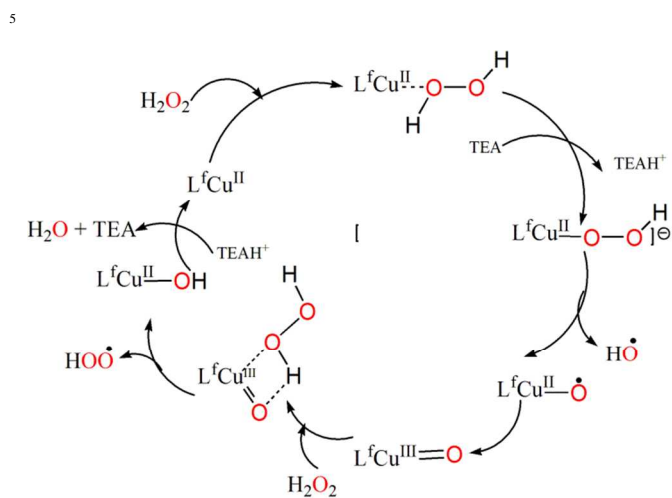
**Scheme 2** Mechanistic pathway of catalytic hydrocarbon oxidation.

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.

25 Experimental section

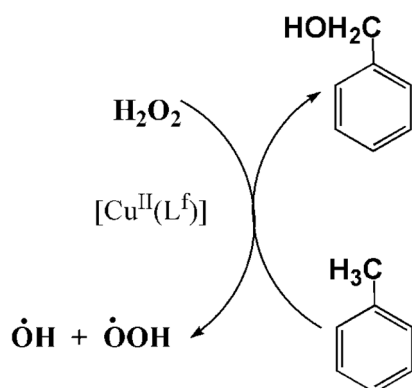
Material and reagents

2-(hydroxylmethyl)-6-carbaldehyde-4-methylphenol was prepared by reported methods.⁴⁰ All reagents and solvents are commercially available. THF was dried using sodium metal and benzophenone and other solvents were used without further purification.

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Scheme 3 Representative oxidation of toluene to benzyl alcohol.

Physical measurements

Elemental analyses were carried out using a Perkin–Elmer 240 elemental analyzer. ¹H NMR were recorded in CDCl₃ on a Bruker 300 MHz NMR Spectrophotometer using tetramethylsilane (δ = 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 DFT⁴¹ method associated with the conductor-like polarizable continuum model (CPCM).⁴² Becke's hybrid function⁴³ with the Lee-Yang-Parr (LYP) correlation function⁴⁴ 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 (1s²2s²2p⁶) core electron for copper whereas the associated “double-ζ” 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 program⁴⁹ 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% H₂O₂ 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 H₂O₂ 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 method⁴⁰ and characterized by ¹H NMR analysis. ¹H NMR (in CDCl₃, 300 MHz, ppm): δ 2.34 (3 H, s, –CH₃), 4.73 (2H, s, –CH₂), 7.29 (1H, s, –ArH), 7.40 (1H, s, –ArH), 9.86 (1H, s, –CHO), 11.18 (1H, s, –ArOH).

Synthesis of H₂L^a

0.232 gm (2 mmol) of 2-(hydroxyl methyl)-6-carbaldehyde-4-methylphenol was refluxed with 0.06 gm (1 mmol) ethylenediamine 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, C₂₀H₂₄N₂O₄ (M. W. = 356.42): C, 67.39; H, 6.79; N, 7.86; *Found* C, 67.34; H, 7.85; N, 7.88. TOF–MS⁺(H₂L^a + Na⁺) m/z 379.2020 (**Fig. 8a & Fig. S1**).

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

The ligand H₂L^a 0.356 g (1 mmol) and CuClO₄·2.6H₂O (0.370 gm, 1 mmol) in 30 mL methanol were refluxed together for 90 minutes whereupon the yellow solution turned brown which 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, $C_{20}H_{18}N_2O_4Cu$ (M. W. = 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 Fig. S2).

[Cu(L^g)]: The complex **1** (0.413 gm, mmol) and benzyl amine (0.107 gm, 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, $C_{27}H_{25}N_3O_3Cu$ (M. W. = 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 Fig. S3).

[Cu(L^h)]: The complex **1** (0.413 gm, mmol) and ethylenediamine (0.06 gm, 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, $C_{22}H_{22}N_4O_2Cu$ (M. W. = 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 Fig. S4).

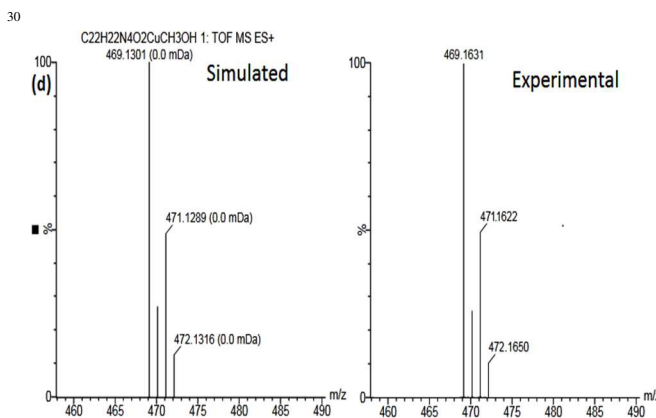
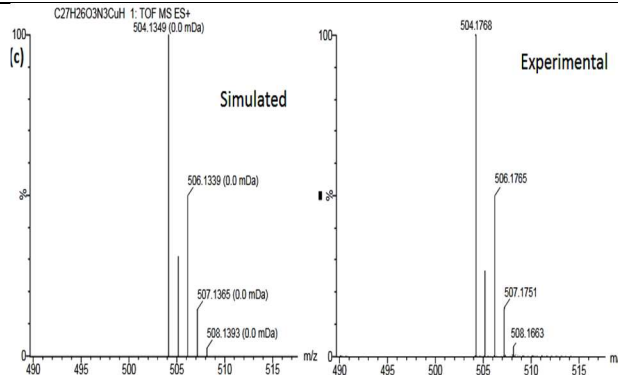
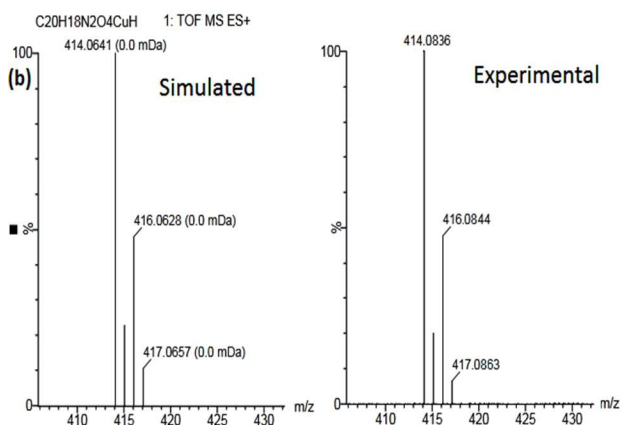
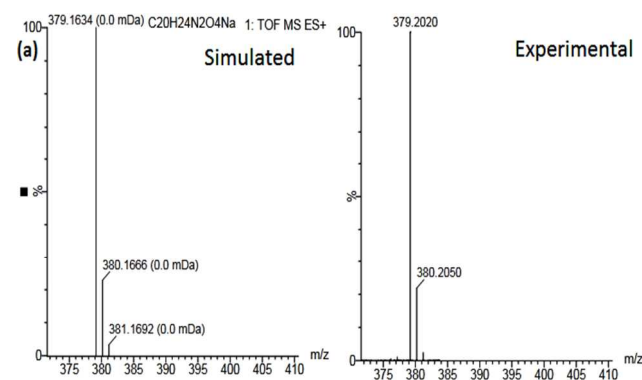


Fig. 8 HRMS spectra of (a) H_2L^a , (b) $[Cu(L^f)]$, (c) $[Cu(L^g)]$ and (d) $[Cu(L^h)]$.

Single Crystal X-ray Diffraction.

Intensity data for complex **1** was collected at 273K on a Bruker SMART APEX-II CCD diffractometer using graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) and the ω -2 θ scan mode in the range $2.0 < 2\theta < 25.8^\circ$. 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 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-97⁵⁰ refined anisotropically on F^2 using the full-matrix least-squares procedure of SHELXL-97.⁵⁰ The positional disorder of aldehydic O-atoms in **2**, 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.

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Table 6 Crystal data and refinement parameters of complex 1

Formula	C ₂₀ H ₁₆ Cu N ₂ O ₄
Formula Weight	411.90
Crystal System	Monoclinic
Space group	P21/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 _α) [/mm]	1.109
F(000)	844
Temperature (K)	273
Radiation [Å] MoK _α	0.71073
θ Min-Max [°]	1.6, 27.2
Dataset	-16: 16 ; -29: 29 ; -9: 9
Tot., Uniq. Data, R(int)	32430, 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

Conclusions

In summary, we have synthesized one mononuclear complex [Cu(L¹)] (**1**) from a compartmental ligands H₂L^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 H₂L^a bearing hydroxymethyl group in the benzene ring, during the course of reaction with Cu²⁺ 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.

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Notes and references

- 1 D. N. Bolon, C. A. Voigt and S. L. Mayo, *Curr. Opin. Chem. Biol.*, 2002, **6**, 125.
- 2 Y. Lu, S. M. Berry and T. D. Pfister, *Chem. Rev.*, 2001, **101**, 3047-3080.
- 3 M. Faiella, C. Andreozzi, R. T. M. de Rosales, V. Pavone, O. Maglio, F. Nistri, W. F. DeGrado and A. Lombardi, *Nat. Chem. Biol.*, 2009, **5**, 882.
- 4 R. L. Koder, J. L. R. Anderson, L. A. Solomon, K. S. Reddy, C. C. Moser and P. L. Dutton, *Nature*, 2009, **458**, 305.
- 5 A. E. Shilov and G. B. Shul'pin, *Activation and Catalytic Reaction of Saturated Hydrocarbons in the Presence of Metal Complexes*, Kluwer Academic Publishers, Dordrecht, The Netherlands (2000).
- 6 M. M. Whittaker, V. L. DeVito, S. A. Asher and J. W. Whittaker, *J. Biol. Chem.*, 1989, **264**, 7104.
- 7 (a) P. A. Frey, *Chem. Rev.*, 1990, **90**, 1343; (b) T. T. Harkins and C. B. Grissom, *Science*, 1994, **263**, 958; (c) D. Picot, P. J. Loll and R. M. Garavito, *Nature*, 1994, **367**, 243.
- 8 A. B. Jazdzewski and W. B. Tolman, *Coordination Chemistry Reviews*, 2000, **200-202**, 633.
- 9 E. Tsuchida, H. Nishide and T. Nishiyama, *Macromol. Chem. Phys.*, 1975, **176(5)**, 1349.
- 10 M. Ayala and E. Torres, *Appl. Catal.*, 2004, **A272**, 1.
- 11 R. L. Lieberman and A. C. Rosenzweig, *Nature*, 2005, **434**, 177.
- 12 (a) S. S. Lapari and S. Parham, *International Journal of Engineering Science Invention*, 2013, **2**, 62; (b) P. Roy and M. Manassero, *Dalton Trans.*, 2010, **39**, 1539; (c) P. Roy, K. Dhara, M. Manassero and P. Banerjee, *Eur. J. Inorg. Chem.*, 2008, 4404; (d) S. Biswas, A. Dutta, M. Debnath, M. Dolai, K. K. Das and M. Ali, *Dalton Trans.*, 2013, **42**, 13210.
- 13 P. Gamez, P. G. Aibel, W. L. Driessen and J. Reedijk, *Chem. Soc. Rev.*, 2001, **30**, 376.
- 14 D. A. Kunz and P. J. Chapman, *J. Bacteriol.*, 1981, **146**, 179.
- 15 M. J. Worsley, F. C. H. Franklin and P. A. Williams, *J. Bacteriol.*, 1978, **134**, 757.
- 16 M. A. Abril, C. Michan, K. N. Timmis and J. L. Ramos, *J. Bacteriol.*, 1989, **171**, 6782.
- 17 S. Thakurta, P. Roy, R. J. Butcher, M. S. El Fallah, J. Tercero, E. Garribba, and S. Mitra, *Eur. J. Inorg. Chem.*, 2009, 4385-4395.
- 18 E. Battistel, R. Tassinari, M. Fornaroli and L. Bonoldi, *J. Mol. Catal. A: Chem.*, 2003, **202**, 107.

- 19 G. B. Shul'pin and G. Süß-Fink, L. S. Shul'pina, *Chem. Commun.*,2000, 1131.
- 20 R. A. Periana, D. Miranov, D. Taube, G. Bhalla and C.J. Jones, *Science*,2003, **301**, 814.
- 21 J. I. Kroschwitz, *Encyclopedia of Chemical Technology*, Vol. 4, 4th Ed.; Wiley-Interscience Publications: New York 1992, 64.
- 22 S. Tsuruya, H. Miyamoto, T. Sakae and M. Masai, *J. Catal.*,1980, **64**, 260.
- 23 H. Hayashibara, S. Nishiyama, S. Tsuruya and M. Masai, *J. Catal.*,1995, **153**, 254.
- 24 S. J. Kulkarni, R. R. Rao, M. Subramanyam, A. V. Ramarao, A. Sarkany and L. Guzzi, *Appl. Catal. A*,1996, **139**, 59.
- 25 S. Sueto, S. Nishiyama, S. Tsuruya and M. Masai, *J. Chem. Soc. Faraday Trans.*,1997, **93**, 659.
- 26 R. Smith, K. Johnson, B. Vishwanthan and T. K. Varadarajan, *Appl. Catal. A*,1998, **172**, 15.
- 27 N. Idaki, S. Nishiyama and S. Tsuruya, *Phys. Chem. Chem. Phys.*,2001 **3**,1918.
- 28 L. F. Liotta, A. M. Venezia, G. Deganello, A. Longo, A. Martorana, Z. Schay and L. Guzzi, *Catal. Today*,2001, **66**,271.
- 29 M. J. Schultz, C. C. Park and M. S. Sigman, *Chem. Commun.*,2002,3034.
- 30 B. M. Choudary, M. L. Kantam, A. Rahman, C. V. Reddy and K. K. Rao, *Angew. Chem., Int. Ed.*,2001, **40**, 763.
- 31 G. D. Yadav and C. K. Mistry, *J. Mol. Catal. A: Chem.*,2001, **172**, 135.
- 32 V. R. Choudhary, D. K. Dumbre, V. S. Narkhede and S. K. Jana, *Catal. Lett.*,2003, **86**, 229.
- 33 V. R. Choudhary, P. K. Choudhary and V. S. Narkhede, *Catal. Commun.*,2003, **4**,171.
- 34 V. R. Choudhary, D. K. Dumbre, B. S. Uphade and V. S. Narkhede, *J. Mol. Catal. A: Chem.*,2004, **215**,129.
- 35 Y. P. Cai, C. Y. Su, A.W. Xu, B. S. Kang, Y. X. Tong, H. Q. Liu and S. Jie, *Polyhedron*,2001, **20**,657.
- 36 T. Fuji, S. Yamaguchi, Y. Funahashi, T. Ozawa, T. Tosha, T. Kitagawa and H. Masuda, *Chem. Commun.*,2006, 4428.
- 37 T. Tano, M. Z. Ertem, S. Yamaguchi, A. Kunishita, H. Sugimoto, N. Fujieda, T. Ogura, C. J. Cramer and S. Itoh, *Dalton Trans.*,2011, **40**, 10326.
- 38 M. Mizuno, K. Honda, J. Cho, H. Furutachi, T. Tosha, T. Matsumoto, S. Fujinami, T. Kitagawa and M. Suzuki, *Angew. Chem. Int. Ed.*,2006, **45**, 6911.
- 39 A. Wada, M. Harata, K. Hasegawa, K. Jitsukawa, H. Masuda, M. Mukai, T. Kitagawa and H. Einaga, *Angew. Chem., Int. Ed.*, 1998, **37**, 798.
- 40 E. Lambert, B. Chabut, S. Chardon-Noblat, A. Deronzier, G. Chottard, A. Bousseksou, J. Tuchagues, J. Laugier, M. Bardet and J. M. Latour, *J. Am. Chem. Soc.*,1997, **119**, 9424.
- 41 R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, 1989.
- 42 (a) V. Barone and M. Cossi, *J. Phys. Chem. A.*, 1998, **102**, 1995; (b) M. Cossi and V. Barone, *J. Chem. Phys.*, 2001, **115**, 4708; (c) M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comp. Chem.*, 2003, **24**, 669.
- 43 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
- 44 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1998, **37**, 785.
- 45 (a) M. E. Casida, C. Jamoroski, K. C. Casida and D. R. Salahub, *J. Chem. Phys.*, 1998, **108**, 4439; (b) R. E. Stratmann, G. E. Scuseria and M. J. Frisch, *J. Chem. Phys.*, 1998, **109**, 8218; (c) R. Bauernschmitt and R. Ahlrichs, *Chem. Phys. Lett.*, 1996, **256**, 454.
- 46 (a) T. Liu, H.-X. Zhang and B. H. Xia, *J. Phys. Chem., A*, 2007, **111**, 8724; (b) X. Zhou, H.-X. Zhang, Q.-J. Pan, B.-H. Xia and A.-C. Tang, *J. Phys. Chem. A*, 2005, **109**, 8809; (c) X. Zhou, A.-M. Ren and J.-K. Feng, *J. Organomet. Chem.*, 2005, **690**, 338. (d) A. Albertino, C. Garino, S. Ghiani, R. Gobetto, C. Nervi, L. Salassa, E. Rosenverg, A. Sharmin, G. Viscardi, R. Buscaino, G. Cross and M. Milanese, *J. Organomet. Chem.*, 2007, **692**, 1377.
- 47 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.
- 48 M. J. Frisch, et. al. Gaussian 09, (Revision A.1), Gaussian, Inc., Wallingford, CT 2009.
- 49 N. M. O'Boyle, A. L. Tenderholt and K. M. Langner, *J. Comp. Chem.*, 2008, **29**, 839.
- 50 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*,2007, **64**, 112.