

Catalytic chemical and electrochemical wet oxidation of phenol using new copper(II) tetraazamacrocyclic complexes under homogeneous conditions

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Abstract

Two new macrocycle complexes $[\text{Cu}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}]\text{Cl}_2$ and $[\text{Cu}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}](\text{C}_6\text{H}_5\text{O})_2$ (where $\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4 = 5,7,12,14$ -tetramethylbenzo[*b,i*]-1,4,8,11-tetraazacyclotetradecane) were synthesized and characterized using spectral and microanalytical data. The $[\text{Cu}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}]\text{Cl}_2$ was found to catalyze chemical oxidation of phenol by H_2O_2 to dihydroxy benzenes. The reaction products were analyzed using gas chromatograph. Catalysis was highly stereoselective and led to predominant formation of *ortho*-dihydroxy benzene (catechol, CAT) as a major product, 93.0% at 50 °C and the remainder as *para*-dihydroxy benzene (hydroquinone, HQ) with no appreciable detection of other oxidized phenol derivatives. Product selectivity decreased with increasing reaction temperature or increasing relative amount of the oxidant. In the electrochemical investigation the complex $[\text{Cu}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}](\text{C}_6\text{H}_5\text{O})_2$ exhibited a new irreversible oxidation wave, particularly the presence of traces of water in acetonitrile, due to catalysed electro-oxidation of the phenoxide counter ions. Based on the coordination behaviour of the complex, a plausible mechanism for the catalytic process has been proposed. The chemical catalysis reported here is suitable for the stereoselective transformation of monohydroxy aromatic compounds to *ortho*-dihydroxy derivatives, particularly in the manufacture of fine chemicals and pharmaceuticals.

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1. Introduction

Catalyzed wet oxidation of phenol is being extensively investigated with dual objectives of removal of phenolic wastes in industrial effluents and surface water streams and secondly to achieve regioselective oxidation to useful products [1–5]. The latter processes often involve milder reaction conditions. Various copper(II) compounds in solution under homogeneous conditions [6–11] as well as copper(II) oxide immobilized on solid supports like alumina [12,13], zeolites and clays [14,15], polymers [16,17] activated carbon [18,19], etc., have been found to catalyze phenol oxidations. Some copper(II) complexes exhibit

superior catalysis under heterogeneous conditions when immobilization on solid supports or when encapsulation in zeolites as well as under homogeneous conditions, in the catalytic transformation of phenol to useful chemicals or its catalyzed degradation [20–24].

It was found that in the fixed bed reactors utilizing solid CuO catalyst, leached copper(II) ions in the solution contribute significantly to the catalytic wet oxidation of phenol [7]. Since these processes often employ extreme conditions of high temperature (>150 °C) and high pressure (10–15 atm), they lead to formation of CO_2 , and mixture of other short chain carboxylic acids, *viz.* formic acid, maleic acid, acetic acid and oxalic acid as final products [7,9,19]. However, under otherwise milder catalytic conditions wet oxidation of phenol leads to formation of catechol (CAT) and hydroquinone (HQ) as final products with varying degrees of selectivities and no appreciable formation of any degradation product [4,5]. It has been demonstrated that copper(II) catalyzed phenol degradation also

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proceeds through formation of catechol and hydroquinone as intermediates [7].

Copper(II) salicylaldimine, amine and imidazole complexes have been successfully employed as catalysts in the hydroxylation of phenol to catechol and hydroquinone [20–24] and so are the square planar metallo-macrocyclic complexes, particularly with copper(II) and nickel(II). A comparison of the epoxidation reactions reveals that metallo-macrocyclics lacking any pendent arms act as superior catalysts [25] as they exert little steric hindrance around the metal centre and allow an easy axial approach of the oxidant. We have previously reported an efficient two-step synthesis of nickel(II) complexes with a new macrocyclic ligand [26] and its homogeneous catalysis in the selective transformation of phenol to dihydroxy products [4]. As an extension of our previous work we herein report the synthesis and spectral characterization of two new copper(II) macrocyclic complexes, $[\text{Cu}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}]\text{Cl}_2$ and $[\text{Cu}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}](\text{C}_6\text{H}_5\text{O})_2$ (where $\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4 = 5,7,12,14$ -tetramethyldibenzo[*b,i*]-1,4,8,11-tetraazacyclotetradecane) and their catalyst characteristics. The structural parameters of the complex cation $[\text{Cu}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}]^{2+}$ in these complexes, deduced through DFT computations, suggest a relatively rigid framework and a saddle-shaped geometry for the complex in which the copper(II) ion sits off the N_4 plane. The catalytic efficiency of these complexes towards wet chemical oxidation of phenol using hydrogen peroxide and electrochemical oxidation over glassy carbon electrode have been investigated and effect of reaction parameters, viz. temperature, time, pH, relative amounts of phenol and oxidant and catalyst on the conversion efficiency have been investigated.

2. Experimental

2.1. Materials and methods

The catalyst precursor, $[\text{Ni}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}]\text{Cl}_2$ was synthesized using literature method reported elsewhere [26]. Phenol (Aldrich), AR grade $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Loba Chemie) and solvents (Loba Chemie) were used in this study. Solvents used in the electrochemical and chemical oxidations were suitably purified before use. The acetonitrile used in the electrochemical studies was dried and distilled over P_2O_5 .

2.2. Instrumentation

Electronic spectra of all compounds were recorded on a Shimadzu UV1601 spectrophotometer either in dichloromethane or in methanol solvent, IR spectra on a Thermo Nicolet Nexus spectrometer as KBr pellets, while ^1H NMR on a Bruker DRX 300 NMR spectrometer, in chloroform-*d*. Electrospray ionization (ESI) mass spectra were recorded on a Micromass Quattro-II triple quadrupole mass spectrometer and ESR spectra on a Varian X-band spectrometer. Elemental analyses were carried out on a Elementar Vario ELIII analyzer. Voltammetry studies were carried out on a CHI 600A electrochemical analyser. Three-electrode assembly with $\text{Ag}/\text{AgCl}/\text{KCl}$ (sat.) reference electrode, Pt wire counter electrode and glassy

carbon working electrode were used. All voltammetry investigations were carried out in acetonitrile solution in presence of tetraethylammonium perchlorate (TEAP) as supporting electrolyte. Catalyzed chemical oxidations were carried out in flasks immersed in controlled temperature water baths. Oxidation products were analyzed using PerkinElmer Clarus 500 gas chromatograph fitted with FID detector and a $2\text{ m} \times 2\text{ mm}$ (i.d.) OV-17 column.

2.3. Syntheses

The copper(II) macrocyclic complex, $[\text{Cu}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}]\text{Cl}_2$ was synthesized in a two-step procedure by first obtaining free-base macrocyclic from $[\text{Ni}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}]\text{Cl}_2$ using a literature method [26] followed by complexation of the copper(II) with the free-base macrocyclic. The phenoxide salt $[\text{Cu}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}](\text{C}_6\text{H}_5\text{O})_2$ was obtained by the metathesis reaction.

2.3.1. Synthesis of free-base macrocyclic $\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4$

$[\text{Ni}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}]\text{Cl}_2$ (4.0 g, 8.3 mmol) and sodium cyanide (4.0 g, *ca.* 81.6 mmol) were refluxed together in 200 cm^3 water for 5 h. The resulting brown suspension was cooled to room temperature, mixed with 2.0 g NaOH and was subsequently evaporated to near dryness. The viscous semi-solid mass was extracted in boiling CH_2Cl_2 and was purified by passage through a $10\text{ cm} \times 2.5\text{ cm}$ neutral alumina column eluting with CH_2Cl_2 . Yield 1.4 g (47%). mp 86°C . ESI MS observed m/z 352 (M^+) calcd. for $(\text{C}_{22}\text{H}_{32}\text{N}_4)^+$ 352. Analyses found: C, 74.5; H, 8.7; N 16.2%. $\text{C}_{22}\text{H}_{32}\text{N}_4$ calcd.: C, 75.0; H, 9.1; N, 15.9%. I.r. (KBr pellet, $\bar{\nu}$, cm^{-1}): 3465m, 3160m, 2913w, 1621s, 1541m, 1450vs, 1405vs, 1266s, 737m. UV–vis (in CH_2Cl_2 , λ_{max} , nm/ ϵ_{max} , $\text{mol}^{-1}\text{ cm}^2$): 247 (28,000), 273 (30,000). ^1H NMR (in CDCl_3 , δ , ppm): 1.23 (d, 12H, CH_3), 1.52 (m, 2H, CH_2), 1.80 (m, 2H, CH_2), 2.79 (m, 4H, CH), 3.74 (br, 4H, NH), 6.00–6.50 (d–d, 8H, Ph–H).

2.3.2. Synthesis of $[\text{Cu}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}]\text{Cl}_2$

A solution of free-base macrocyclic $\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4$ (0.70 g, 2.0 mmol) in 50 cm^3 methanol was added to a 50 cm^3 aqueous solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.50 g, 2.9 mmol) under stirring. The resulting mixture was initially heated at reflux for 15 h followed by complete removal of the solvent in a rotary evaporator. The dry residue was extracted in acetone and extract was evaporated to dryness. The residue was re-extracted in acetone and was purified by passage through a $20\text{ cm} \times 2.5\text{ cm}$ alumina column eluting with 2:1 acetone/ CHCl_3 mixture. The slow moving main purple colored band was collected and solvent was removed under reduced pressure. Yield 0.61 g (63%). mp 193°C . ESI MS observed m/z 208 (M^{2+}) calcd. for $(\text{C}_{22}\text{H}_{32}\text{N}_4\text{Cu})^{2+}$, 208. Analyses found: C, 55.2; H, 7.0; N 11.3; Cl, 14.0; Cu, 12.2%. $\text{C}_{22}\text{H}_{32}\text{N}_4\text{Cl}_2\text{Cu}$ calcd.: C, 54.3; H, 6.6; N, 11.5; Cl, 14.6; Cu, 13.1%. I.r. (KBr pellet, $\bar{\nu}$, cm^{-1}): 3477m, 3456m, 2910w, 1635vs, 1506w, 1461w, 1400m, 750m. UV–vis (in methanol, λ_{max} , nm/ ϵ_{max} , $\text{mol}^{-1}\text{ cm}^2$): 243 (28,000), 280 (30,000) 520 (100). E.s.r. (powder, g): 2.06, 2.20.

2.3.3. Synthesis of $[\text{Cu}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}](\text{C}_6\text{H}_5\text{O})_2$

A solution of $[\text{Cu}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}]\text{Cl}_2$ (0.24 g, 0.5 mmol) dissolved in 0.5 cm^3 of water was added to *ca.* 1.0 cm^3 of concentrated solution of $\text{C}_6\text{H}_5\text{ONa}$ and the resulting suspension was shaken for 2 h. Purplish brown solid that separated out was collected by filtration. It was subsequently washed twice with 2 cm^3 cold water and was dried over CaCl_2 . Yield 0.25 g (83%). mp 139°C . Analyses found: C, 67.1; H, 7.5; N 10.0; Cu, 12.1%. $\text{C}_{34}\text{H}_{42}\text{N}_4\text{O}_2\text{Cu}$ calcd.: C, 67.8; H, 7.0; N, 9.3; Cu, 10.6%. I.r. (KBr pellet, $\bar{\nu}$, cm^{-1}): 3473m, 3456m, 2910w, 1635vs, 1522w, 1461w, 1400m, 1391s, 1239w, 1161w, 1110w, 1035w, 757m. UV–vis (in CH_2Cl_2 , λ_{max} , nm/ ϵ_{max} , $\text{mol}^{-1}\text{cm}^2$); 245 (25,000), 278 (30,000) 516 (90). E.s.r. (powder, g): 2.06, 2.20.

2.4. Catalyzed electrochemical oxidation of phenol

Catalysed electro-oxidation was investigated using cyclic voltammetry technique. The current voltage characteristics were recorded (a) in blank runs for phenol (0.001 M) and (b) for the phenoxide complex, $[\text{Cu}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}](\text{C}_6\text{H}_5\text{O})_2$ (0.001 M) at different scan rates, initially in dry acetonitrile followed by introduction of increasing amount of water.

2.5. Catalyzed chemical oxidation of phenol

The catalytic oxidation of phenol was carried out using H_2O_2 as an oxidant in a two-necked round bottom reaction flask fitted with a water condenser and immersed in a thermostated water bath, which was maintained at different preset temperatures. Samples were periodically withdrawn through the second neck for analysis.

In a typical oxidation reaction, phenol (0.5 g, 5.3 mmol), 30% H_2O_2 (0.6 g, 5.3 mmol) and Na_2CO_3 (1.0 g, 9.7 mmol) were mixed together and volume was made up to 100 cm^3 by adding distilled water. It was transferred to the round-bottomed flask containing 10 mg of the catalyst compound. Solution was stirred and warmed at a constant temperature. A 10 cm^3 sample was

withdrawn periodically at 10, 20, 30, 40, 50, 60, 120, 180 min intervals. These samples were acidified with 1 cm^3 of 0.1 M HCl each, extracted in 10 cm^3 of CH_2Cl_2 and analyzed by gas chromatograph. The reaction has been studied as a function of time, temperature, relative amount of substrate and oxidant, amount of catalyst and pH.

3. Results and discussion

3.1. Syntheses, spectral and structural studies

The catalyst copper complex was synthesized by the demetallation reaction of the previously reported nickel(II) complex, $[\text{Ni}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}]\text{Cl}_2$ [26] followed by coordination of the copper(II) ion with the free base macrocycle ligand. The $[\text{Cu}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}]\text{Cl}_2$ complex, thus obtained was converted to phenoxide derivative, $[\text{Cu}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}](\text{C}_6\text{H}_5\text{O})_2$, by metathesis reaction and both of the products were characterized using spectral and elemental analyses data. Electronic spectra of the chloro and phenoxo complexes showed a very weak absorption band at λ_{max} 520 and 515 nm, respectively, besides the ligand centered strong absorption bands in the UV region. It is known that copper(II) N_4 -macrocycle complexes exhibit weak d-d absorption bands in the visible region [27,28]. The Cl^- appears to be present as counter ion only and do not have any significant coordination interaction with the metal ion, as evident from the fact that change of the counter ions from Cl^- to $\text{C}_6\text{H}_5\text{O}^-$ had almost negligible effect over the electronic spectra of the complexes. The g_{\parallel} and g_{\perp} values observed in these complexes are in conformity with the literature values for the corresponding $[\text{Cu}(\text{cyclam})]^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) complex and support the square planar coordination arrangement around the copper(II) [27,29,30]. Hyperfine coupling with the donor nitrogen nuclear spins was not observed. This is not uncommon as the $\text{Cu}^{\text{II}}(d^9)$ unpaired electron resides in a d_{xy} orbital and hence is less likely to couple with nitrogen nuclear spins [27,31]. The geometry of $[\text{Cu}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}]^{2+}$ was optimized using

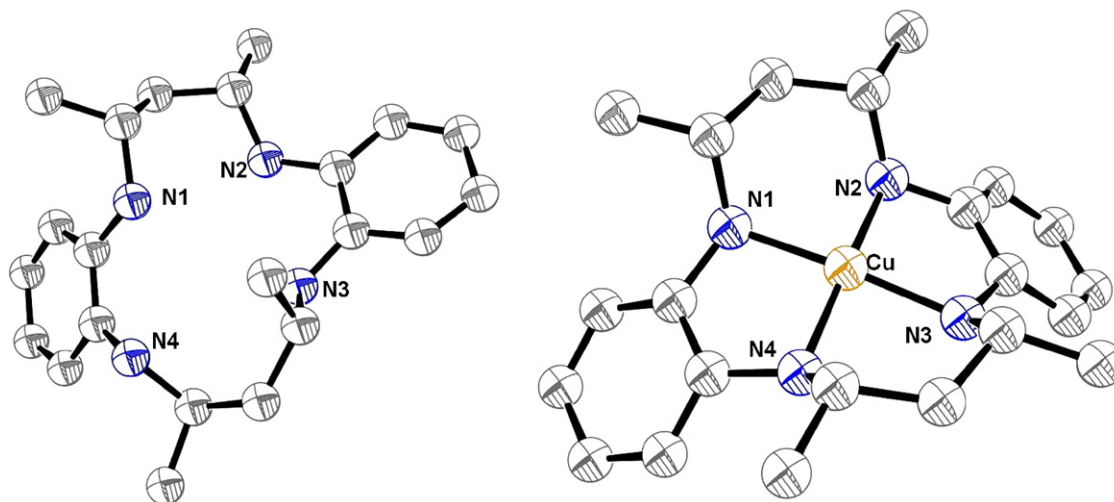


Fig. 1. ORTEP diagram of the DFT optimized geometry of free-base macrocycle and $[\text{Cu}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}]^{2+}$.

Table 1
Theoretical interatomic distances in the metal free macrocycle and the complexed cation

Atomic distance	Me ₄ Bzo ₂ [14]aneN ₄ (Å)	[Cu{Me ₄ Bzo ₂ [14]aneN ₄ }] ²⁺ (Å)
N1–N2	3.441	2.737
N1–N4	2.842	2.851
N2–N3	2.938	2.812
N3–N4	3.027	2.734
N1–N3	3.500	3.923
N2–N4	4.935	3.925
N–Cu	–	1.965
Cu–N ₄ (plane)	–	0.109

Kohn–Sham equations [32] to determine the molecular energy in a self-consistent field (SCF) molecular orbital approximation. A valence polarized double zeta quality basis set and Dirac; Vosco, Wilk, Nussair [33,34] functional and the Perdew, Wang (PW91) correlation functional [35] were used. The optimized geometry is shown in Fig. 1 and key structural parameters are listed in Table 1. Calculations reveal a saddle-shaped geometry for the complex cation in which the two benzo- units are tilted in a direction opposite to that of the two C₅H₁₀ units. The N–H hydrogens are projected within the benzo-groove while the Cu²⁺ ion resides in the C₅H₁₀ groove 0.109 Å above the N₄ plane.

3.2. Electrochemistry and electrocatalysis

The complex [Cu{Me₄Bzo₂[14]aneN₄}]Cl₂ in acetonitrile exhibited two quasi-reversible oxidation waves at $E_{p,a}$ 0.31 and 1.15 V versus Ag/AgCl in acetonitrile over glassy carbon electrode (Fig. 2a). The Cu(II)/Cu(III) oxidation in saturated N₄-macrocycle complexes is reported between $E_{p,a}$ 1.3 and 1.6 V versus Ag/AgCl under identical conditions [27,28,36,37], that lies closer to the second oxidation wave in this complex. Therefore, it is quite likely that the first quasi-reversible oxidation wave in [Cu{Me₄Bzo₂[14]aneN₄}]Cl₂ arise from partial oxidation of the coordinated macrocycle. Presence of the two benzorings are likely to exert a stabilizing influence and thereby facilitate oxidation of the coordinated macrocycle leading to formation of oxidized metallocyclic π -systems. The presence of the low-lying oxidation is helpful in the catalytic activity of the complex. The electrochemical characteristics of the phenoxide complex, [Cu{Me₄Bzo₂[14]aneN₄}(C₆H₅O)₂] was also investigated in dry acetonitrile. This complex exhibited only the [Cu{Me₄Bzo₂[14]aneN₄}]²⁺ centered oxidation waves, but upon addition of ca. 1% water (v/v) a new oxidation wave emerged at $E_{p,a}$ 0.50 V versus Ag/AgCl (Fig. 2b). With further addition of water (ca. 5%, v/v) wave moderately shifted to more positive potential with significantly enhanced peak current. Behaviour of the phenoxide complex is unlike that of NaOC₆H₅ that exhibited an irreversible oxidation wave at $E_{p,a}$ 0.60 V versus Ag/AgCl under identical conditions. Hence it was concluded that presence of the [Cu{Me₄Bzo₂[14]aneN₄}]²⁺ was essential to facilitate oxidation of the phenoxide counter ions at a less positive potential.

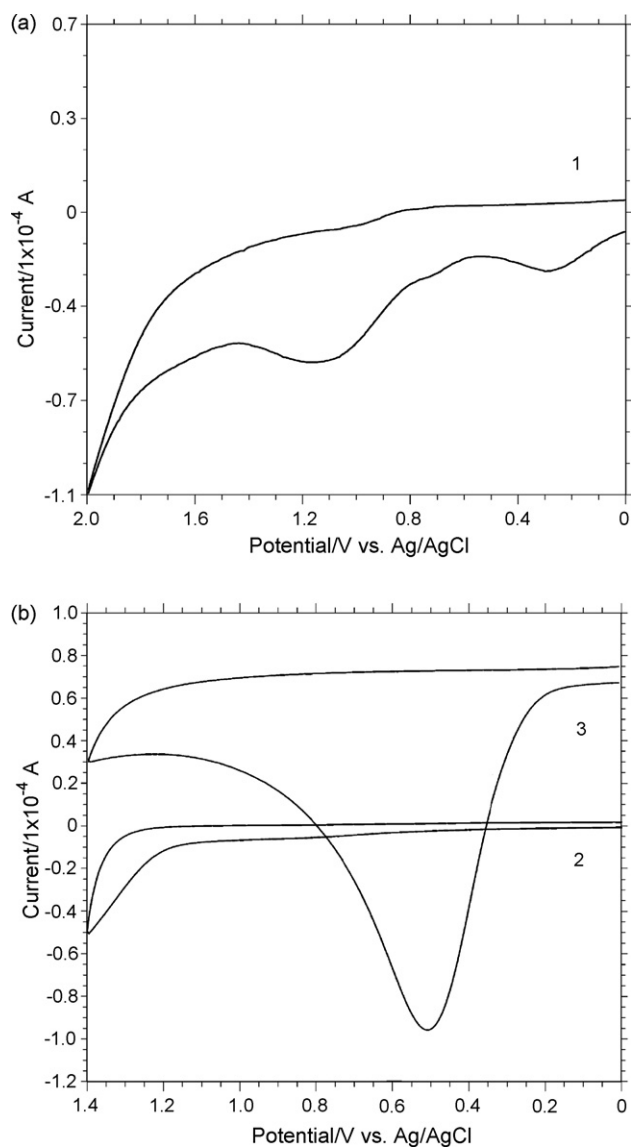


Fig. 2. Cyclic voltammograms of [Cu{Me₄Bzo₂[14]aneN₄}]Cl₂, **1**, phenol, **2** in dry acetonitrile and [Cu{Me₄Bzo₂[14]aneN₄}(OC₆H₅)₂] in presence of ~1% water, **3**.

Pure phenol did not exhibit any significant electrode activity up to E_{λ} 2.0 V versus Ag/AgCl over the glassy carbon electrode in dry acetonitrile, nor even in presence of the complex [Cu{Me₄Bzo₂[14]aneN₄}]Cl₂. However, the presence of trace amount of water (<5%) and moderately alkaline conditions (pH ~ 8.0) that led to partial formation of phenoxide ions, the voltammogram of the solution changed significantly, showing a very prominent irreversible oxidation wave similar to that observed in phenoxide complex.

3.3. Oxidation of phenol using synthesized [Cu{Me₄Bzo₂[14]aneN₄}]Cl₂ catalyst

The wet hydrogen peroxide oxidation of phenol was studied using synthesized complex, [Cu{Me₄Bzo₂[14]aneN₄}]Cl₂, as a catalyst as a function of time under mild temperature and pressure conditions. The main products of the catalyzed phenol

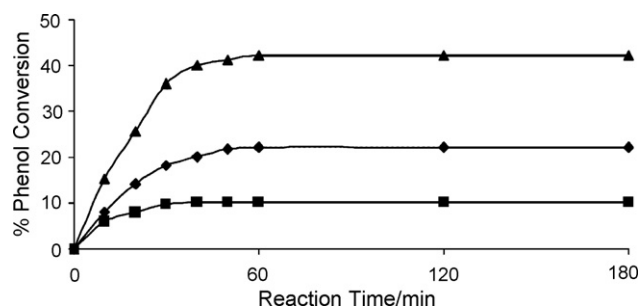


Fig. 3. Effect of reaction temperature on the % phenol conversion as a function of time (■) 50 °C, (◆) 65 °C, (▲) 80 °C (reaction conditions: phenol 0.5 g; 30% H₂O₂ 0.6 g; [Cu{Me₄Bzo₂[14]aneN₄}]Cl₂ 0.010 g).

oxidation under these conditions were identified by GC as CAT and HQ and no other oxidation product was detected. The oxidation of phenol with H₂O₂ in absence of catalyst was found to be very slow (<2% over all conversion). Parameters like effect of reaction temperature, amount of catalyst, H₂O₂ concentration, phenol concentration, reaction time and pH were studied in details in presence of [Cu{Me₄Bzo₂[14]aneN₄}]Cl₂ catalyst, in order to determine optimum reaction conditions for the maximum transformation of phenol as well as for improved product selectivity.

3.4. Effect of reaction temperature and time

The performance of the catalyst was investigated at three different temperatures, *viz.* 50, 65 and 80 °C, while keeping other parameters constant over a period of 3 h. The results are shown in Fig. 3. It was observed that at higher temperatures the reaction reached maximum conversion at a faster rate, but with decreased product selectivity. At reaction temperature of 80 °C the maximum percentage conversion of phenol (42.2%) was observed, whereas the percentage of phenol conversion at 65 and 50 °C were significantly lower, *i.e.* 18.0 and 10.1%, respectively. Although the CAT and HQ are the two likely oxidation products, the [Cu{Me₄Bzo₂[14]aneN₄}]Cl₂ catalyzed oxidation of phenol showed a high degree of selectivity for the formation of CAT, particularly at lower temperature of 50 °C (molar ratio ~13:1). With increasing reaction temperature product selectivity dropped to 3.2:1.0 (at 80 °C), although CAT was still the predominant product (Table 2). The turn over frequency (TOF = moles of product formed per mole of catalyst per hour) during the first hour of the reaction was found to be highest (~109) at 80 °C. In all cases the reaction reached maximum conversion within the first hour and thereafter only a negligible change was observed.

Table 2
Effect of reaction temperature on phenol oxidation^a, product selectivity and TOF values

Reaction temperature (°C)	Phenol conversion (%)	Product selectivity (%)		CAT/HQ ratio	TOF (h ⁻¹)
		CAT	HQ		
50	10.3	93.0	7.0	13.3	27.7
65	22.0	85.7	14.3	6.0	56.9
80	42.2	76.0	24.0	3.2	108.8

^a Reaction conditions: phenol 0.5 g; 30% H₂O₂ 0.6 g; [Cu{Me₄Bzo₂[14]aneN₄}]Cl₂ 0.010 g; reaction time = 3 h.

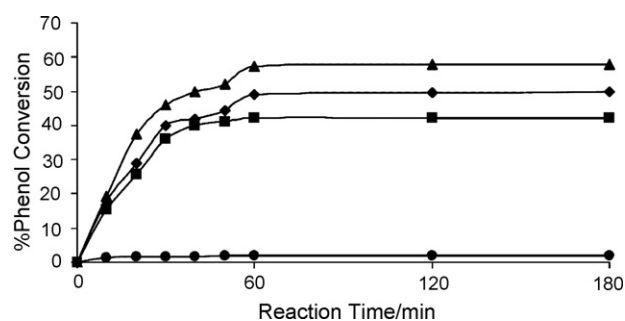


Fig. 4. Effect of amount of catalyst on phenol oxidation catalyzed by [Cu{Me₄Bzo₂[14]aneN₄}]Cl₂ complex, (■) 10 mg, (◆) 20 mg, (▲) 30 mg, (●) no catalyst (reaction conditions: phenol 0.5 g; 30% H₂O₂ 0.6 g; T = 80 °C).

Table 3
Effect of amount of catalyst on phenol oxidation

Catalyst weight (g)	Phenol/catalyst molar ratio	Phenol oxidation after 6 h (%)	TOF (h ⁻¹)
0.000	–	1.9	–
0.010	259	42.2	108.8
0.020	129	49.8	64.1
0.020	86	54.5	47.0

Reaction conditions: phenol 0.5 g; 30% H₂O₂ 0.6 g; T = 80 °C; reaction time = 3 h.

3.5. Effect of amount of catalyst

The amount of catalyst present in the system tremendously affects the over all oxidation efficiency and the selectivity pattern. Three different weights, 10, 20 and 30 mg of [Cu{Me₄Bzo₂[14]aneN₄}]Cl₂ were used to study the influence of the amount of catalyst on percent phenol conversion in different sets at 80 °C. A blank set was also placed with similar amounts of phenol and H₂O₂ but without any catalyst. Results are shown in Fig. 4 and Table 3. It was found that increasing the amount of catalyst from 10 mg to 20 mg resulted into 7.6% increase in the overall % phenol oxidation. Further increases in catalyst amount had further diminutive incremental effect on product yield, *i.e.* with 30 mg of catalyst only 4.2% higher overall conversion (*i.e.* 54.5% overall oxidation) was achieved.

3.6. Effect of reagent concentration

In order to determine the efficiency of H₂O₂ for phenol oxidation, three different H₂O₂:phenol molar ratios, *viz.* 0.5:1, 1:1 and 2:1 were investigated at 80 °C and the results are presented in

Table 4
Influence of H₂O₂:C₆H₅OH molar ratio on the phenol conversion^a, product selectivity and percent H₂O₂ efficiency

H ₂ O ₂ :C ₆ H ₅ OH molar ratio (%)	Phenol conversion	H ₂ O ₂ efficiency ^b (%)	Product selectivity (%)	
			CAT	HQ
0.5:1	8.0	16.0	91.3	8.7
1:1	42.2	42.2	76.0	24.0
2:1	58.0	29.0	67.5	32.5

^a Reaction conditions: [Cu{Me₄Bzo₂[14]aneN₄}]Cl₂ 0.010 g; T = 80 °C; reaction time = 3 h.

^b Mole percent H₂O₂ used in phenol oxidation to the moles of H₂O₂ added.

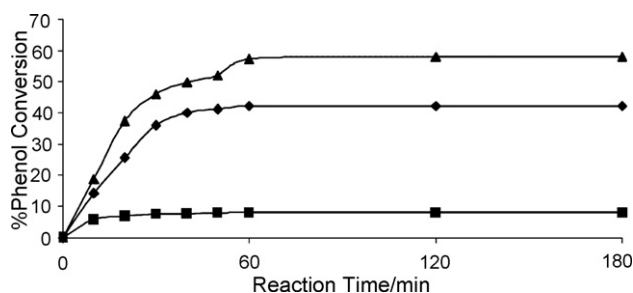


Fig. 5. Effect of H₂O₂:phenol molar ratio (■) 0.5:1, (◆) 1:1, (▲) 2:1 on % phenol conversion (reaction conditions: [Cu{Me₄Bzo₂[14]aneN₄}]Cl₂ 0.010 g; T = 80 °C).

Table 4 and Fig. 5. With higher H₂O₂:phenol (oxidant/substrate) molar ratios higher percent conversion of phenol was observed, but there had also been concomitant decrease in the product selectivity as well as oxidant efficiency. Overall percent phenol oxidation of 58% for H₂O₂:phenol molar ratios of 2:1

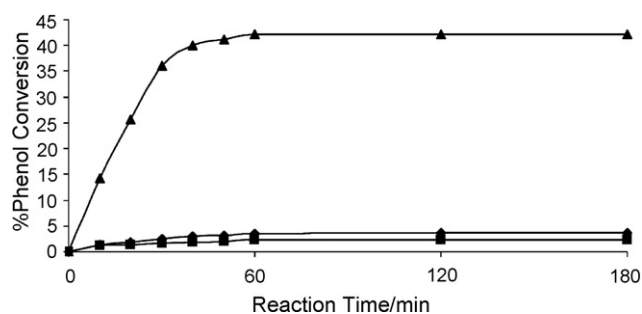


Fig. 6. Effect of reaction medium on the oxidation of phenol as a function of time (■) 0.1 M NH₃, (◆) 0.1 M CH₃COOH and (▲) 0.1 M Na₂CO₃ ([Cu{Me₄Bzo₂[14]aneN₄}]Cl₂ 0.010 g, T = 80 °C).

and 8.0% for H₂O₂:phenol molar ratios of 1:2 were obtained (Table 4). In terms of H₂O₂ efficiency values were lower at higher H₂O₂:phenol molar ratio, which indicates wastage of the oxidant possibly due to its competing catalyzed decomposition. Therefore, in order to obtain high percent conversion and high H₂O₂ efficiency, the molar ratio of 1:1 was considered to be the best.

3.7. Effect of the reaction pH

The oxidation of phenol was also investigated in acidic and alkaline media in presence of 0.1 M glacial acetic acid, 0.1 M ammonia and 0.1 M Na₂CO₃ at 80 °C and the results are shown in Fig. 6. It was found that the catalysis stopped almost completely in the alkaline medium, while it progressed with much slower rate in the acidic medium. On the contrary, catalysis progressed unhindered in presence of 0.1 M Na₂CO₃. The slowing

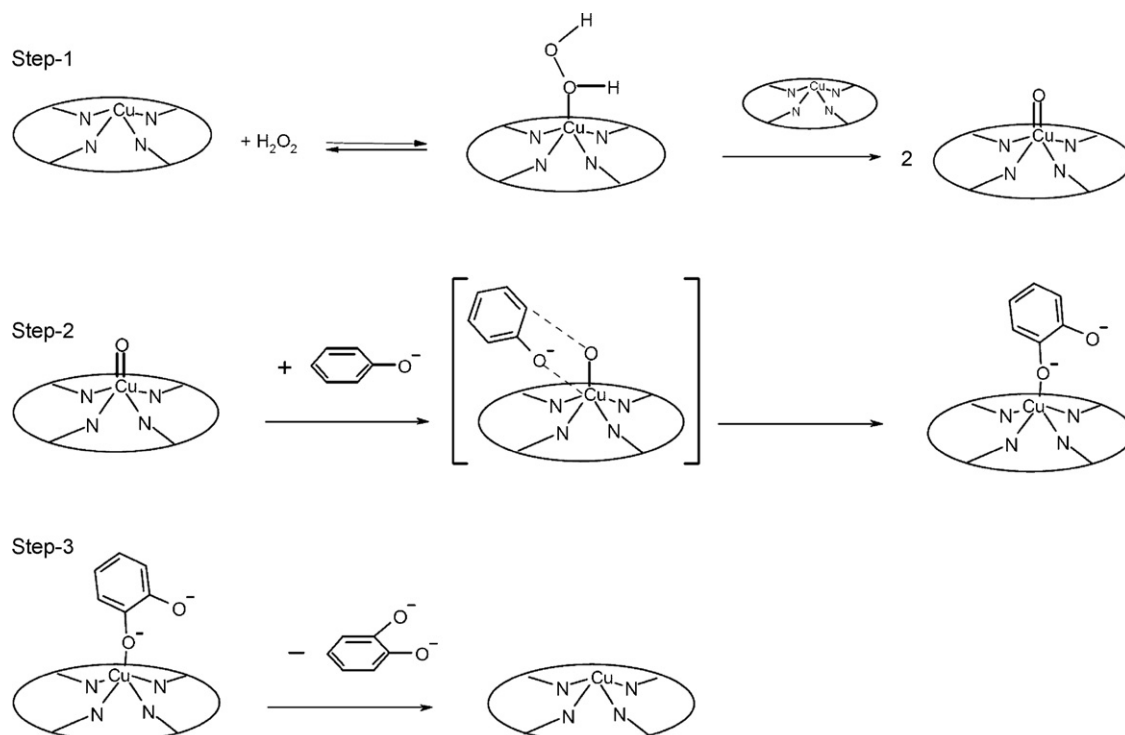


Fig. 7. Mechanism of [Cu{Me₄Bzo₂[14]aneN₄}]Cl₂ catalyzed oxidation of phenol.

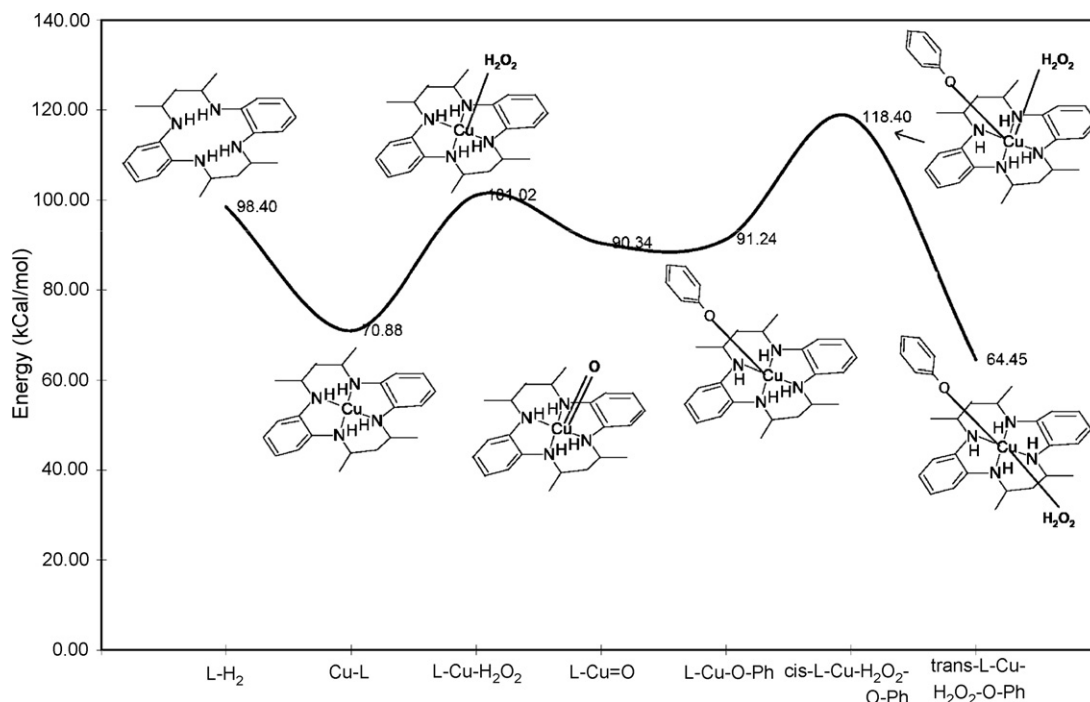


Fig. 8. Energetics of different coordinated forms of $[\text{Cu}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}]^{2+}$.

down of the reaction in the acidic medium is likely to arise from protonation of the phenoxide ion and consequent weaker coordination interaction with the catalyst, while in the alkaline medium the catalyst might have been poisoned due to blocking of the weakly coordinating diaxial sites by the NH_3 binding.

4. Conclusion

Addition of a small amount of $[\text{Cu}\{\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4\}]\text{Cl}_2$ complex to the aqueous phenol– H_2O_2 system leads to significant increase in its wet oxidation to CAT and HQ. Reaction was found to be highly selective with CAT constituting the major product. Product selectivity dropped with increasing reaction temperature or increasing amount of the oxidant. Catalytic process might be useful for the transformation of monohydroxy aromatic compounds to *ortho*-dihydroxy derivatives in the manufacture of fine chemicals and pharmaceuticals [38,39]. Based on the geometry and coordination behaviour of the complex following tentative mechanism has been proposed for the catalytic process (Fig. 7). It is likely that cationic copper(II) oxo complex attracts phenoxide anion with its negative end oriented towards the complex. The aromatic ring π – π interaction could further align the approaching phenol so as electrophilic attack by the oxo-O is facilitated. The DFT computed energetics of various possible intermediates are summarized in Fig. 8.

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