



Coordination Complex of Cu(II) with Ligand Containing Carboxylic Acid Group: Synthesis, Characterization and Catecholase Activity

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Present work reports the synthesis, characterization and catecholase like activity of a diaqua Cu(II) complex of type $[(L^{2-})Cu(H_2O)_2]$ (**1**) with a tridentate ligand (*E*)-2-(3-hydroxy-3-phenyltriaz-1-en-1-yl)benzoic acid (LH₂). Complex **1** is characterized by FT-IR, mass, EPR and UV-Vis spectroscopy. The isotropic hyperfine four line EPR spectrum of complex **1** in solution confirms the Cu(II) state in complex **1**. The complex exhibits catalytic activity towards the oxidation of 3,5-di-*tert*. butyl catechol (3,5-DTBC) to 3,5-di-*tert*. butyl benzoquinone (3,5-DTBQ) with turnover number (K_{cat}) = 132.8 h⁻¹ via formation of radical intermediate. The oxidation of 3,5-DTBC in presence of complex **1** is confirmed by the UV-Vis spectroscopy, mass spectra and EPR spectra. Complex **1** is EPR active in solution but the solution containing complex **1** and 3,5-di-*tert*. butyl catechol is EPR silent authenticating the formation of an organic radical in the catalytic oxidation process. In cyclic voltammetry of complex **1**, an irreversible cathodic peak appear at -0.19 V may be due to the Cu²⁺/Cu⁺ couple and an irreversible anodic wave appear at +1.35 V may be due to the oxidation of N₃⁻ to N₃[•]. Cyclic voltammetry of complex **1** with 3,5-DTBC gives a new anodic peak at +0.11 V, which is assigned as cat/sq^{•-} redox couple [cat= 3,5-DTBC, sq^{•-} = benzosemiquinonate anion radical].

Keywords: Copper(II), Carboxylic acid ligand, Catecholase activity.

INTRODUCTION

Transition metal complexes of organic ligand containing carboxylic acid are very promising in coordination chemistry. Transition metal complexes containing carboxylic acid imparts several biological activities including antibacterial, antibiotic, anti-coagulants, antifungal, anti-inflammatory and anticancer agents [1-10]. Among the transition metals, copper have important contributions to the functional sites of several metalloenzymes such as catechol oxidase, phenoxazinone synthase, superoxide dismutase, lysine oxidase, N₂O reductase, etc. [11-14]. In biological systems, copper(II) complexes play an important role in active sites of a large number of metalloproteins and helps for numerous catalytic processes in living organisms where electron transfer reactions or activation involves [15]. The above said process widespread to bioinorganic [16] and in medicinal field [17]. In fact, copper(II) chelate complexes have been found to interact with active site of biological systems and exhibit antibacterial, antifungal [18,19], antineoplastic [20-22] and anticancer activity [23]. Some copper(II) complexes having N,S,O or N,N donor ligands have good affinity towards the

binding to the base pairs of DNA and hence acts as anticancer agents [24]. Moreover, dinuclear copper(II) complexes impart significant role towards mimicking of functional activities to the type-3 copper proteins with high efficiency [25-28]. Therefore, assembles of copper ion with organic ligand containing carboxylic acid has become progressively more important in several areas of chemistry. For these reasons, researchers are focussing their aim to synthesize, characterize and explore their catalytic activities toward the mimicking of different metal ion dependent enzymes.

The present work focuses the synthesis and characterization of a new Cu(II) diaqua complex $[(L^{2-})Cu(H_2O)_2]$ (**1**) and explore its catecholase activity. Complex **1** is an effective catalyst for catecholase activity with a good turn over number (K_{cat}) = 132.8 h⁻¹ is very similar with the several complexes reported in literature [29-39].

EXPERIMENTAL

Cupric chloride dihydrate and other AR grade solvents were purchased from reputed commercial suppliers and used without purification. Ligand (*E*)-2-(3-hydroxy-3-phenyltriaz-

1-en-1-yl)benzoic acid was synthesized by the reported procedure [40]. For spectroscopic and electrochemical measurements, spectroscopic grade solvents were used. The C, H and N contents of the complex was obtained from a Perkin-Elmer 2400 Series II elemental analyzer. The elemental analyses were performed after evaporating the solvents under high vacuum. Infrared spectra of the sample was measured from 4000 to 400 cm^{-1} by making KBr pellet at 295 K on a Perkin-Elmer Spectrum RX 1 Fourier transform infrared (FTIR) spectrophotometer. Electronic absorption spectra of the complex and catalytic oxidation were studied with a Perkin-Elmer Lambda 750 spectrophotometer in the range of 3300-175 nm. Mass spectra were obtained from LCMS 2020 mass spectrometer using electrospray ionization (ESI) process. Cyclic voltammetric experiments were done with BASi Epsilon-EC in acetonitrile solution using 0.2 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. The BASi platinum working electrode, platinum auxiliary electrode, Ag/AgCl reference electrode were used for the measurements. Magnetech GmbH MiniScope MS400 spectrometer (equipped with temperature controller TC H03, Magnetech, Berlin, Germany) was used to measure the X-band EPR spectra, where the microwave frequency was measured with an FC400 frequency counter.

Synthesis of $[(L^2)Cu(H_2O)_2]$ (1): Ligand (LH_2) (65 mg, 0.25 mmol) was refluxed with 20 mL methanol at 313 K. The $CuCl_2 \cdot 2H_2O$ (25 mg, 0.25 mmol) was dissolved in 20 mL (1:3) aqueous methanol solution. Then, two solutions were mixed and refluxed with another 10 min. The solution was cooled to room temperature and allowed to evaporate slowly. After 3-4 days, green crystalline metal complex separated out, which were collected upon filtration and dried in air. Yield: 66 mg (~75% with respect to copper). Mass spectral data [electrospray ionization (ESI) positive ion, CH_3OH]: m/z 353 for $[1]^+$. Elemental analysis calcd. (found) % for $C_{13}H_{13}N_3O_5Cu$: C, 44.01 (43.62); H, 3.69 (3.35); N, 11.84 (11.27). IR (KBr, ν_{max} , cm^{-1}): 3435 (br), 2924 (s), 1744 (m), 1600 (s), 1582 (s), 1511 (m), 1465 (m), 1451 (m), 1406 (s), 1351 (m), 1321 (s), 1226 (s), 1211 (m), 1054 (m), 760 (s).

Catecholase mimicking activity: Catalytic activity of complex **1** towards oxidation of 3,5-di *tert*-butyl catechol was studied by measurement of UV-visible spectroscopy of complex **1**, 3,5-DTBC and mixture of the solution containing complex **1** and 3,5-di-*tert*-butyl catechol (3,5-DTBC). Activity of complex **1** was monitored in the wavelength region of 250 nm to 800 nm by mixing 1×10^{-5} M solution of complex to the $(5-25) \times 10^{-4}$ M 3,5-DTBC in methanol under atmospheric condition at room temperature. The progress of reaction was monitor with respect to time at the wavelength 405 nm in methanol medium for 2 h.

RESULTS AND DISCUSSION

Synthesis and characterization: Reaction of $CuCl_2$ with LH_2 in aqueous methanol affords the complex in good yields. The IR stretching vibrations at 3425 and 2924 cm^{-1} is due to $-OH$ bond of H_2O molecule and C-H bond, respectively. The peaks at 1744 and 1211 cm^{-1} is assigned as for C=O and C-O bonds of the carboxylic acid group. Stretching vibration of

N=N and N-N bonds of azo moiety of ligand appear at 1582 and 1054 cm^{-1} , respectively. The peak at 1226 cm^{-1} is assigned as C-N bond stretching of the ligand. A significant peak at 760 cm^{-1} is representing the N-O bond of the N-oxide group of ligand fragment.

Electrochemical studies: The redox activities of complex **1** and mixture of complex **1** with 3,5-DTBC were elucidated by cyclic voltametry experiment in CH_3CN at 295 K. The cyclic voltammograms (Fig. 1) displays an irreversible cathodic wave at -0.19 V due to Cu^{2+}/Cu^+ redox couple and an anodic wave at +1.35 V, which is irreversible in nature due to oxidation of N_3^-/N_3^+ at the ligand fragment [41]. Therefore, cyclic voltammogram suggests the +2 oxidation state of the copper in complex **1**. In presence of 3,5-DTBC, the cathodic peak of Cu^{2+}/Cu^+ redox couple shifted to -0.80 V and a new anodic peak was observed at +0.11 V. The new anodic peak suggests the oxidation of 3,5-DTBC to benzosemiquinone in presence of complex **1** under aerobic condition. Thus, the peak at +0.11 V is assigned as cat/sq^+ redox couple. The cyclic voltametry experiment strongly supports the coordination of 3,5-DTBC to $Cu(II)$ ion. Therefore, the catalytic process is said to be a metal mediated oxidation.

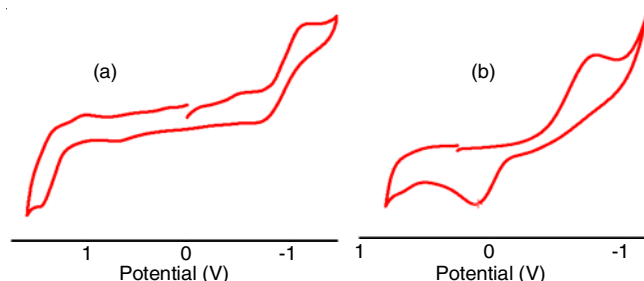
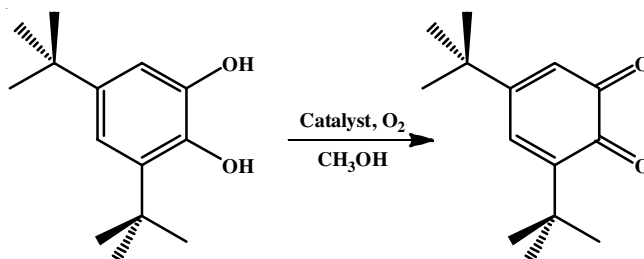


Fig. 1. Cyclic voltammograms of (a) complex **1** and (b) mixture of complex **1** and 3,5-DTBC in CH_3CN (0.20 M $[N(n-Bu)_4]PF_6$) at 295 K

Study of oxidation of 3,5 di-*tert*-butylcatechol (3,5-DTBC): To investigate the catalytic activity of complex **1**, 3,5-DTBC used as substrate. For the catecholase activity study, 3,5-DTBC is used as a standard substrate because on long time exposure to air, catechol gets oxidized to *o*-benzoquinone but 3,5-DTBC resist the oxidation either in air or in solution. The catecholase activity study of complex **1** is depicted in Scheme-I.



Scheme-I: Catalytic oxidation of 3,5-DTBC to 3,5-DTBQ in air saturated methanol

In general, 3,5-DTBQ is highly stable in solution and exhibits an absorption maximum at 401 nm in methanol [42]. Catalytic activity was measured in a solution of 1×10^{-5} M metal complex and $(5-25) \times 10^{-4}$ M 3,5-DTBC in CH_3OH . The

progress of catalytic process was measured by recording UV-visible spectra on a Perkin-Elmer Lambda 750 spectrophotometer in the range of 800-250 nm. The UV-vis spectra of the solution in methanol containing complex **1** and 3,5-DTBC gives a new band at 405 nm which is neither absorb by complex **1** nor by 3,5-DTBC (Fig. 2). The band intensity at 405 nm is increases gradually with time during the catalytic oxidation process as illustrated in Fig. 3. The appearance of new band at 405 nm and its increasing intensity with time strongly support the oxidation of 3,5-DTBC to 3,5-DTBQ in presence of complex **1**. At first 3,5-DTBC coordinate to the Cu centre by removal of water molecules and then undergoes $1e^-$ oxidation in presence of oxygen to the benzosemiquinonate anion radical. Benzosemiquinonate anion radical then further oxidized by $1e^-$ to *o*-benzoquinone. The binding of 3,5-DTBC to the Cu(II) centre and formation of 3,5-DTBQ was substantiated by mass spectra of the solution containing complex **1** and 3,5-DTBC in methanol. The two significant mass appear at m/z 539 and m/z 221 confirms the substrate catalyst binding and formation of 3,5-DTBQ as oxidation product in catalytic process. During the

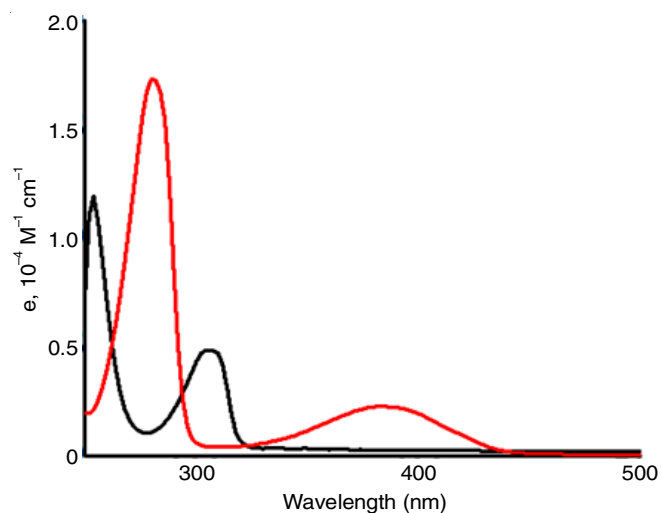


Fig. 2. UV-vis spectra of 3,5-DTBC (black) and mixture of 3,5-DTBC and complex (red) in MeOH solution at room temperature

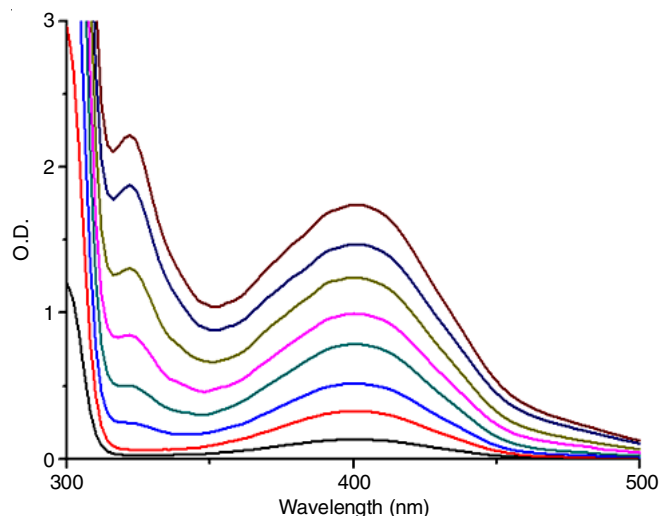


Fig. 3. Change of UV-vis spectra during catalytic process of 3,5-DTBC to 3,5-DTBQ in methanol

catalytic oxidation process hydrogen peroxide was generated as byproduct and identified by the iodometric method reported earlier [43]. During catalytic process benzosemiquinonate anion radical was generated as an intermediate and authenticated by the EPR spectra.

EPR spectroscopy: X-band EPR spectroscopy was study to insight the mechanistic path of the catecholase oxidation process. For this purpose, EPR spectra were performed with complex **1** and mixture of solution containing complex **1** and 3,5-DTBC in dichloromethane solution at 298 K. Complex **1** gives four lines hyperfine spectra at $g_{iso} = 2.12$ as depicted in Fig. 4a due to presence of Cu^{2+} ion (^{63}Cu nuclei with $I = 3/2$). Whereas, the EPR spectrum of solution containing complex **1** and 3,5-DTBC was almost quenched (Fig. 4b) due to antiferromagnetic coupling between Cu^{2+} ($S = 1/2$) and benzosemiquinone anion radical ($S=1/2$). Therefore, EPR study strongly supports that the generation of *o*-benzosemiquinonate anion radical, which is formed during the catalytic oxidation of 3,5-DTBC in presence of Cu^{2+} .

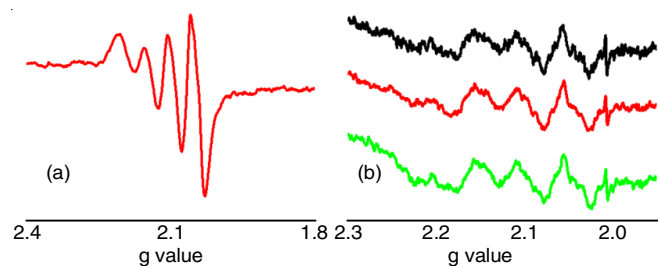


Fig. 4. X-band EPR spectra of (a) complex **1** and (b) mixture of complex **1** and 3,5-DTBC in CH_2Cl_2 at different time interval in solution at 298 K

Electronic spectra: The UV-vis/NIR absorption spectrum of the complex was recorded in CH_3OH at 295 K. The spectrum is illustrated in Fig. 5 and the λ_{max} values are given in Table-1. The complex absorbs 384 nm due to ligand to metal (LMCT) charge transfer transition. The absorption bands at 290 nm and 260 nm is due to the $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ electronic transition, respectively [44].

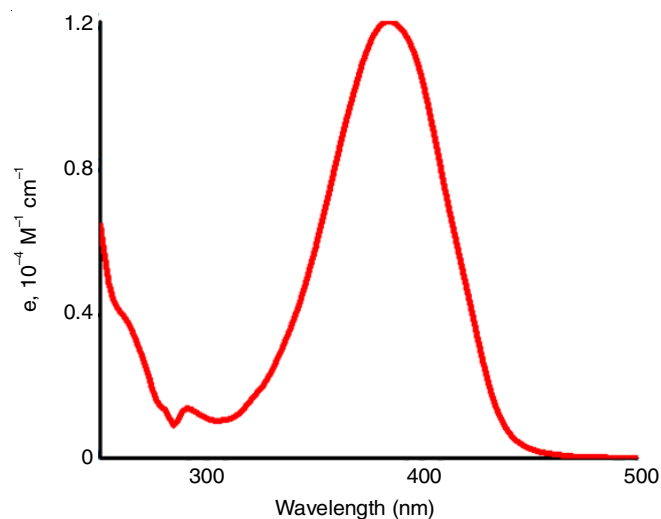


Fig. 5. UV-vis absorption spectra of metal complex in CH_3OH at 298 K

λ_{\max} (nm) (ϵ , $10^4 \text{ M}^{-1} \text{ cm}^{-1}$)	Possible transitions
384 (1.19)	Ligand to metal charge transfer
290 (0.13)	$\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$
260 (0.39)	$\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$

Kinetic studies: The kinetics of oxidation process was performed to evaluate the catalytic efficiency of complex 1. The reaction rates were measured by using complex concentration $1 \times 10^{-5} \text{ M}$ and varying concentration of substrate from 5×10^{-4} to $25 \times 10^{-4} \text{ M}$ and then rate vs. concentration was plotted. The rate constant vs. substrate concentration profile is given in Fig. 6, which disclosed the nature of kinetics.

The nature of kinetics is first order with respect to substrate concentration obeying the Michaelis-Menten model as per the equation given below:

$$V = \frac{V_{\max} [S]}{K_M + [S]}$$

where, V is rate of the reaction, K_M is denoted as Michaelis-Menten constant, V_{\max} is the maximum velocity of the reaction and $[S]$ is concentration of the substrate.

The kinetic parameters were determined from Michaelis-Menten equation as $V_{\max} (\text{MS}^{-1}) = 2.214 \times 10^{-5} \text{ mol L}^{-1} \text{ min}^{-1}$; $K_M = 16.10 \times 10^{-4}$ [Std. Error for $V_{\max} (\text{MS}^{-1}) = 0.074 \times 10^{-5}$

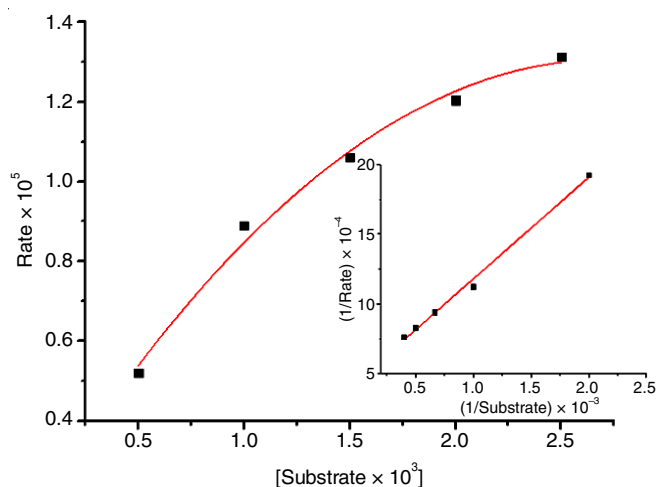
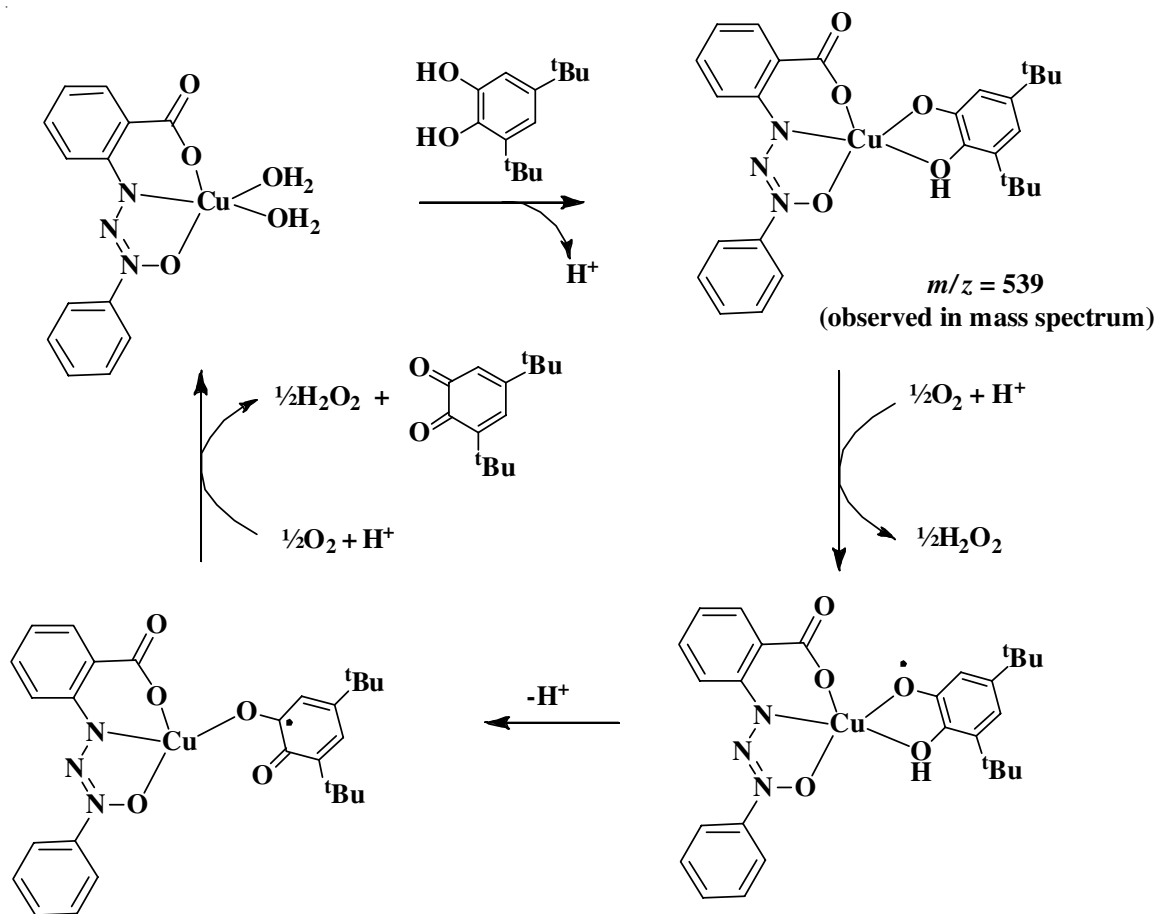


Fig. 6. Plot of rate vs. [3,5-DTBC] for oxidation of 3,5-DTBC by metal complex

$\text{mol L}^{-1} \text{ min}^{-1}$; Std. Error for $K_M (\text{M}) = 1.17 \times 10^{-4}$ mol L^{-1} . The turnover number (k_{cat}) was determined as $132.8 \pm 4.4 \text{ h}^{-1}$.

After considering the experimental evidences, a plausible mechanism is also proposed (**Scheme-II**). A literature survey was done with the transition metal complex those are active catalyst for catecholase like activity. By comparing the turnover number (k_{cat}) of those reported complexes, it is worth mentioning that the synthesized metal complex is a effective catalyst for the oxidation of 3,5-DTBC (Table-2).



Scheme-II: Plausible mechanism for oxidation of 3,5-DTBC to 3,5-DTBO

TABLE-2
REPORTED TURN OVER NUMBER (K_{cat}) OF DIFFERENT TRANSITION METAL
COMPLEXES WHICH IMPARTS CATECHOLASE ACTIVITY

Complex	Metal ion present	K_{cat} (h^{-1}) (Solvent)	Ref.
[Mn(L1)(SCN) ₂ (H ₂ O)]	Mn(II)	607.08, DMSO	[29]
[NiL ₁ (H ₂ O) ₃]I ₂ ·H ₂ O	Ni(II)	9.27, CH ₃ OH	[29]
[Cu(L1 ¹)(H ₂ O)(NO ₃) ₂]	Cu(II)	10800, CH ₃ OH	[29]
[Fe ^{III} (μ-O) ₂ (μ-OAc) ₆ (phen) ₂ (H ₂ O) ₂](NO ₃) ₂ ·(H ₂ O) ₃	Fe(III)	9.28 × 10 ² , CH ₃ OH	[31]
[(Co ^{III}) ₂ (H ₃ L) ₂ (OAc) ₂]CH ₃ OH	Co(III)	79, DMF	[34]
[L ²⁻] ⁿ Ni ^{II} (H ₂ O) ₂ ·nH ₂ O	Ni(II)	4.46 × 10 ² , CH ₃ OH	[35]
[(L ²⁻)Cu(H ₂ O) ₂]	Cu(II)	132.8, CH ₃ OH	Present work

Detection of hydrogen peroxide in catalytic oxidation

process: Hydrogen peroxide was generated in the catalytic oxidation process of 3,5-DTBC and identified by modified iodometric method [43]. 3,5-DTBC solution was added to the copper complex solution in methanol medium according to the kinetic experiments. After some time, equal amount of water was added to the reaction mixture. After that the generated quinone was separated from the reaction mixture by extracting with dichloromethane. Few drops of H₂SO₄ were added to the extracted solution to reach the pH ~2. In the resulting reaction mixture few drops of 3% ammonium molybdate solution and 1 mL of 10% KI solution was added. The spectrum gives three absorption bands at 438, 353 and 290 nm indicating the presence of both I₂ and I₃⁻ in solution. The spectrum is well corroborates with the UV-Vis spectrum of I₂ in methanol solution reported earlier [45]. This experiment authenticates the generation I₂ by the oxidation of hydrogen peroxide during catalytic process. The generated I₂ was further reacts with excess of I⁻ to form I₃⁻. The above observations strongly support the formation of hydrogen peroxide as a byproduct in the catalytic oxidation process.

Conclusion

In this work, a concise study of synthesis, characterization and catalytic activity of new Cu(II) complex [(L²⁻)Cu(H₂O)₂] (**1**) containing carboxylic acid group is reported. Complex **1** was characterized by several spectroscopic techniques like IR, UV-Vis, mass and EPR spectroscopy. Electronic state of the complex was elucidated by cyclic voltammetry and EPR spectroscopy. The complex exhibits catecholase activity, which is confirmed by UV-vis, cyclic voltammetry, mass and EPR spectroscopy. The spectroscopic experiments revealed that copper ion exists in +2 oxidation state in complex **1**, which shows catecholase activity with a good turn over number (k_{cat}). The catalytic oxidation of 3,5-di-*tert*-butyl catechol (3,5-DTBC) by the complex passes through the radical formation. In this oxidation process, the metal substrate binding and formation of oxidation product were authenticated by mass spectroscopy. The generation of organic radical as an intermediate was confirmed by EPR spectroscopy.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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