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Oxidation of hindered aniline to iminocyclohexa-2,4-dienone by copper(II) complex of an N-substituted bis-benzimidazolyl ligand

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A R T I C L E I N F O

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ABSTRACT

Copper(II) complex of an N-octylated bis-benzimidazolyl ligand is synthesized and characterized. X-ray diffraction study revealed that copper(II) is in a distorted square-planar environment of two benzimidazolyl imine nitrogens and two nitrato ligands. This complex carries out the oxidation of 2,4,6-tritert-butylaniline at room temperature utilizing low amounts of tert-butylhydroperoxide (TBHP) as an alternate source of oxygen. 3,5-Di-tert-butyl-6-iminocyclohexa-2,4-dienone is found to be the major product along with 3,5-di-tert-butylcyclohexa-3,5-diene-1,2-dione. The oxidation products have been isolated and characterized by ¹H NMR, ¹³C NMR and COSY experiments. The catalytic oxidation proceeds via a copper(II)/copper(III) cycle.

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1. Introduction

Oxidation of aniline to generate oxygen containing derivative's by using green oxidizing agents has been the focus of attention in the past [1,2]. The oxidation of anilines is known to result mainly in azo-compounds [3–7], nitroso-compounds [8,9] and benzoquinones [10]. Aniline is normally not susceptible to the Co(II) Schiff basepromoted oxygenation with molecular oxygen [11]. However the effect of different central atoms (Co, Mn) and various chelating ligands (schiff bases, porphyrins, oximes) on the catalytic oxidation of substituted aniline and the product distribution has been investigated [12]. Oxidation of 2,4,6-trisubstituted aniline with tert-butylhydroperoxide (TBHP) using cobalt Schiff base complexes has been reported gives 4-tert-butylperoxy-2,5-cyclohexadien-1imine and nitrobenzene derivative [13,14]. Oxidation reaction of 2,4,6-tri-tert-butylaniline has been reported with various oxidants and the major products are acetoxyimino-tri-t-butylcyclohexadiene and tri-tert-butylnitrosobenzene [15].

Earlier we have reported the oxidation of hindered aniline using manganese(II) complexes having a 1:1 ratio of substrate to oxidant $(H_2O_2, tert-butylhydroperoxide)$ and organoperoxyl products were obtained [16]. The present study utilizes threefold lower amounts of Tert-butylhydroperoxide (TBHP) with respect to substrate in the catalytic oxidation of 2,4,6-tri-tert-butylaniline to 3,5-di-tert-

butyl-6-iminocyclohexa-2,4-dienone using a copper(II) complex of a bis-benzimidazolyl ligand. To the best of our information this is the first report where an iminocyclohexadienone has been isolated as a major product and its kinetics studied.

2. Experimental

2.1. Materials required

Freshly distilled solvents were used for all synthetic purposes. Spectroscopic grade solvents were employed for spectral experiments. All other chemicals were of AR grade. 2,4,6-Tri-tert-butylaniline was procured from Sigma Aldrich.

2.2. Physical measurements

Elemental analysis of ligand and copper(II) complex were obtained on VARIO EL III instrument from USIC, University of Delhi, Delhi, India. Electronic spectra were recorded on a Shimadzu 1601 spectrometer at the Department of Chemistry, University of Delhi, Delhi. ¹H and ¹³C NMR spectra of ligand were recorded in d_6 -DMSO on a 400 MHz JEOL instrument at the Department of Chemistry, University of Delhi, Delhi. IR spectra were recorded in the solid state as KBr pellets on a Perkin-Elmer FTIR-2000 Spectrometer in the region of 400–4000 cm⁻¹. Cyclic Voltammetric measurements were carried out on BAS-CV 50 W electrochemical analysis system. Cyclic voltammograms of the complex were recorded in DMSO: MeCN (3:7) solution with 0.1 M TBAP as a supporting electrolyte.





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Fig. 1. ¹H NMR spectrum of 3,5-di-tert-butyl-6-iminocyclohexa-2,4-dienonein d_6 -DMSO.



Fig. 2. COSY 2D NMR spectra in *d*₆-DMSO of the product 3,5-di-tert-butyl-6-iminocyclohexa-2,4-dienone. (a) COSY 2D- NMR spectra in *d*₆-DMSO of the product 3,5-di-tert-butyl-6-iminocyclohexa-2,4-dienoneinexpanded form.

A three electrode configuration composed of Pt-disk working electrode, a Pt wire counter electrode, and an Ag/AgNO₃ reference electrode was used for measurements. The reversible one electron Fc⁺/Fc (ferrocenium/ferrocene) couple has an $E_{1/2}$ of +106 mV versus Ag/AgNO₃. The EPR measurement were made on a X-Band Bruker system ER035M gaussmeter and a HP microwave counter from Indian Institute of Kanpur, india.

3. Synthesis and analysis

The compound 1,2-bis(2-benzimidazolyl oxa methyl)benzene (BBB) was prepared by following the procedure as reported earlier [17], and its N-octylation [18] results in the formation of the new N-substituted ligand 1-octyl-2-((2-((1-octyl-1H-benzo[d]imidazol-2-yl)methoxy)phenoxy)methyl)-1H-benzo[d]imidazole [L].



Fig. 3. ¹H NMR spectrum of product 3,5-di-tert-butylcyclohexa-3,5-diene-1,2-dione in d_6 -DMSO.

A solution of BBB (1 g, 2.7 mmol) in DMF was stirred for 3 h with K_2CO_3 (1.24 g, 9 mmol) at 70 °C. When turbidity appeared, 1-bromooctane was added and the solution was stirred for another 24 h at 70 °C. The reaction mixture was filtered and treated with distilled water to obtain a light brown colored crude product. The product was recrystallised from hot methanol and water (2:1). A light brownish crystalline powder was obtained that analyzed for the composition $C_{38}H_{50}N_4O_2$ ·H₂O, Yield (%) = 80%. Anal. Calc. C, 73.9; N, 9.6; H, 9.0. Found: C,

74.4; N, 9.1; H, 8.5%. Single crystals of ligand suitable for X-ray diffraction studies were grown by dissolving the complex in hot methanol and allowing the solution to stand for a few days.

 Λ_{max} (nm), [log ε]: 274[4.36], 279[4.38], 288[4.23].

¹H NMR (ppm in DMSO- d_6): 0.76 (t, 6H, J = 7.32 Hz), 1–1.1 (m, 20H), 1.6(q, 4H), 4.3 (t,3H, J = 7.66 Hz), 5.3 (s, 4H), 6.9 (m, 2H), 7.17–7.29 (m, 6H), 7.5 (d, 2H, J = 8.04 Hz), 7.6 (d,2H, J = 7.32 Hz) (Fig. S1 Supplementary Material).



Fig. 4. ORTEP diagram of the ligand $(C_{38}H_{50}N_4O_2 \cdot H_2O)$ drawn in 20% thermal probability ellipsoids showing atomic numbering scheme.

Table 1

Crystallographic Data and Structure Refinement of Ligand (L) and its complex.

	Ligand (L)	Copper complex
Empirical formula	$C_{38}H_{52}N_4O_3(L)$	C38H50CuN6O8
Formula weight	612.84	782.39
T (K)	298	293
λ (Å)	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	ΡĪ
a (Å)	11.0315(9)	9.2336(7)
b Å	30.474(2)	13.9630(11)
c (Å)	11.8639(11)	16.0076(12)
α (°)	90	75.151(7)
β(°)	115.024	81.094(6)
γ (°)	90	76.274(3)
V (Å ³)	3614.0(5)	1928.2(3)
Ζ	4	2
D_{calc} (Mg m ⁻³)	1.126	1.348
μ (mm ⁻¹)	0.071	0.625
F(000)	1328	826
R _{int}	0.0380	0.0829
Crystal size (mm)	$0.18 \times 0.14 \times 0.12$	$0.22\times0.16\times0.12$
Reflections collected	32 587	25247
Independent reflections	6240	6783
Goodness-of-fit (GOG) on F ²	1.145	1.036
R indices (all data)	$R_1 = 0.1106$,	$R_1 = 0.0848$,
	$wR_2 = 0.2531$	$wR_2 = 0.2440$
Largest difference in peak and hole (e $Å^{-3}$)	0.365 and -0.294	0.775 and –0.614

¹³C NMR (ppm in DMSO-*d*₆): 149.1, 147.6, 142.1, 135.2, 123.0, 122.7, 119.4, 114.5, 110.5, 63.7, 43.1, 31.1, 29.3, 28.5, 28.4, 26.2, 22.0, 13.9 (Fig. S2 Supplementary Material).

IR (KBr pellets, cm^{-1}): 3370_{V(OH)}, 1458_{V(C=N-C=C-benzim)}, 739_{V(C=C benz)}.

3.1. Synthesis of complex

A solution of $Cu(NO_3)_2 \cdot 3H_2O$ (39.5 mg, 0.16 mmol) in methanol (1 ml) was added to a solution of the ligand (100 mg, 0.16 mmol) in methanol (5 ml). The solution turns blue in color and after 10 min's of stirring a bluish product is obtained. This was centrifuged and washed with small amount of cold methanol and dried over P_2O_5 . The complex crystallized from methanol upon standing at

room temperature for a few days. Crystals were found to be suitable for X-ray diffraction analysis.

Anal. Calc. for $C_{38}H_{50}CuN_8O_8$ (fw 782.39 g/mol) Anal. Calc. C, 51.41; H, 4.28; N, 14.11. Found: C, 51.64; H,4.46; N, 13.96% λ_{max} (nm) (DMF), $[\log \varepsilon] = 273[4.27]$, 279[4.36], 288[4.31], 330[3.17], 658[1.81] λ_{max} (nm) (MeOH), $[\log \varepsilon] = 653[1.83]$

 $\begin{array}{ll} IR(KBr \ \ pellets, \ \ cm^{-1}): \ \ 1597_{\nu(C=NPyr)}, \ \ 1384_{\nu(O-N-O)}, \\ 1481_{\nu(C=N-C=C-benzim)}, \ 750_{\nu(C=C \ \ benz)}. \end{array}$

3.2. Cyclic voltammetry

Cyclic voltammogram of the complex was recorded in DMSO: MeCN (3:7) solution with 0.1 M TBAP as a supporting electrolyte. The complex $[CuL(NO_3)_2]$ display a quasi-reversible redox wave due to the Cu(II)/Cu(I) reduction process (Fig. S3). The half wave potential of the Cu(II)/Cu(I) couple with respect to the internal standard ferrocene is -96 mV.

3.3. EPR

X-band EPR spectra of $[Cu(L)(NO_3)_2]$ complex was recorded in methanol at 120 K. The spectra typically indicate a $d_{x^2-y^2}$ ground state ($g_{II} > g > 2.00232$) with low hyperfine coupling constant. The EPR spectra of the complex shows nitrogen super hyperfine structure in the perpendicular region, arising from the interaction of the copper(II) odd electron with two imine nitrogen atoms and is depicted in Fig. S4. A five line pattern is found in the perpendicular region for the complex with coupling constant $a_N = 13$ gauss, indicating that the imine nitrogen from the two benzimidazole are coordinated to Cu(II) atom in the basal plane. The EPR parameters are found to be: $g_{\perp} = 2.06$, $g_{II} = 2.30$, $A_{II} = 169$, and (g_{II}/A_{II})*10⁴ = 136.

3.4. Oxidation of tri-tert-butylaniline and isolation of reaction products

2 ml of 2,4,6-tri-tert-butylaniline solution (110 mM) in methanol was mixed with 1 ml of copper complex solution (3.4 mM) followed by addition of TBHP (37.0 mM) as an alternate source of oxygen. The solution was stirred at room temperature for 30 h. The formation of oxidation product was monitored by TLC by using 100% chloroform solvent system. A TLC of the reaction mixture on silica gel gives two spots with 2,4-dinitrophenylhydrazine. Two products were found at $R_f = 0.60$ (**A**) and 0.41 (**B**). These were isolated using preparative TLC. The yield of the products was 35% (**A**) and 12% (**B**).

¹H NMR spectrum of product **A** in *d*₆-DMSO (Fig. 1) displays signals at δ (ppm): 1.25 (s, 9H), 1.35 (s, 9H), 6.2 (m, 1H, *J* = 1.24 Hz), 6.3 (m, 1H, *J* = 2.14 Hz), 11.75 (bs, 1H).

While two-dimensional COSY experiment (Fig. 2) found cross peaks between the triplet CH(5), CH(3) and broad singlet C=NH(1) of **A**.

¹³C NMR of product **A** in d_6 -DMSO displays signals at δ (ppm) 187.60 (C-2), 165.11 C-1), 161.99 (C-4), 156.11 (C-6), 127.38 (C-3), 126.44 (C-5), 36.35 (C-7), 34.73 (C-9), 30.38 (C-8, C-10) (Fig. S5).

¹H NMR spectrum of product **B** in d_6 -DMSO (Fig. 3) displays signals at δ (ppm): 1.14(s, 9H), 1.17(s, 9H), 6.09(d, 1H, J = 2.44 Hz), 6.9(d,1H, J = 2.44 Hz).

Product **A** shows UV band at 309 nm (log ε = 2.76), 262 nm (log ε = 3.11), and a band(sh) at 400 nm (log ε = 2.04). Product **B** shows UV band at 258 nm (log ε = 2.85), 400 nm (log ε = 2.49), and 546 nm (log ε = 1.55).



Fig. 5. ORTEP diagram of copper(II) complex (C₃₈H₅₀CuN₆O₈) drawn in 20% thermal probability ellipsoids showing atomic numbering scheme. Hydrogen is omitted for the sake of clarity.

3.5. Procedure for kinetic studies

2 ml of 2,4,6-tri-tert-butylaniline and 1 ml of copper(II) complex were mixed followed by addition of TBHP as oxidant. The molarities are 2.1 mM (catalyst), 63.9 mM (aniline) and 25.0 mM (oxidant), giving the ratio of 1:30:12 respectively. A 0.5 ml of this reaction mixture was diluted to 2.5 ml by MeOH (final Molarities: 0.43 mM (catalyst), 12.7 mM (substrate) and 5 mM (TBHP)) and was placed in a 1 cm path length optical cell in a spectrophotometer. Spectra were recorded with time interval of 5 min's in the range of 300–900 nm at room temperature for a period of 60 min. The formation of oxidation products was followed by observing the increase in intensity of absorption bands in the region 300–500 nm.

4. Results and discussion

4.1. Crystal structure description

4.1.1. Structure of ligand (L)

The ligand crystallizes in the monoclinic $P2_1/n$ space group with one molecule of water per asymmetric unit. The crystal structure of ligand is shown in Fig. 4 (Table 1).

4.1.2. Structure of [Cu(L)(NO₃)₂]

The crystal structure of the complex is shown in Fig. 5 (Table 1). The complex crystallizes in a triclinic crystal system with $P\bar{1}$ space group. The Cu(II) atom is coordinated by two imine nitrogens of two benzimidazole rings and nitrato ligands, affording a square-planar coordination geometry. Table S3 gives the bond lengths and bond angles.

4.2. Discussion of NMR

¹ H NMR spectrum of the product **A** shows signals for aliphatic and aromatic protons with splitting. Two singlet's are

observed at 1.2, 1.3 ppm for nine protons each, suggesting that two tert-butyl groups are present in different chemical environment. This suggests an ortho product rather than a para product [19]. The aromatic protons are observed at 6.2, 6.3 ppm and are mixed doublets, suggesting an interaction with other protons. A broad singlet is observed at low field at 11.7 ppm for one proton. This signal is assigned to the proton on the N-atom attached to the ring. Addition of D₂O to the sample in d_6 -DMSO solution diminishes this peak at 11.7 ppm, suggesting that proton is replaceable, and the signals at 6.2 and 6.3 ppm show two clean doublets; this implies that the proton associated with the Natom is interacting with aromatic proton *c* and *d* at position 3 and 5.

Above interaction is confirmed by performing a 2D NMR, COSY experiment and it is found that protons at 6.2 and 6.3 ppm interact with the proton found at 11.7 ppm. Thus confirming the NH proton interacts with aromatic proton c and d (expanded spectra in Fig. 2a).

Proton *d* is coupled to proton *c* and vice versa giving rise to a doublet. Further because of interaction with NH proton this doublet splits to give a double doublet. However due to merging of two inner peaks of the double doublet a distortion results causing a three line peak. Similar interaction causes the double doublet associated with proton *c* to give a distorted doublet.

In the ¹³C NMR spectrum the C1 carbon absorbs at 165 ppm, and is assigned to the carbon C1 carrying the NH group (C=NH) [16]. This is quite different from the carbon carrying the carbonyl group (C2) which is observed at 187.6 ppm [19]. The signals of C3 and C5 are found at127.3 and 126.4. The signals at 161.9, 156.1 ppm were assigned to C4 and C6. Signals for C7, C9 ppm are found at 36.3 and 34.7 ppm. The signal for C8 and C10 observed at 30.3 ppm. All the above assignment are in keeping that reported earlier [16,19].

From the above experiments it is confirmed that the isolated product **A** is o-quinoneimine.

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Table 2Rate of oxidation of 2,4,6-tri-tert-butylaniline with varying substrate concentration.

-					
_	S. No	Conc. of substrate (mM)	Conc. of catalyst (mM)	Ratio	Rate of reaction $(mM min^{-1}) * 10^{-6}$
	1	2.12	0.42	1:5	0.88
	2	6.38	0.42	1:15	3.28
	3	8.52	0.42	1:20	6.02
	4	12.78	0.42	1:30	7.72
	5	17.04	0.42	1:40	5.35



Fig. 6. Plot of rate of formation reaction of imino-quinone for the oxidation of 2,4,6-tritertbutylaniline vs the concentration of catalyst at fixed substrate concentration. Inset: rate of reaction vs concentration of substrate at fixed catalyst concentration.



Fig. 7. Plot of rate of formation reaction for o-quinone for the oxidation of 2,4,6-tritertbutylaniline vs the concentration of catalyst at fixed substrate concentration. Inset: Rate of reaction for the o-quinone vs concentration of substrate at fixed catalyst concentration.



¹H NMR spectrum of product **B** in d_6 -DMSO displays two signals in the aromatic region and two signals in the aliphatic region. The two aromatic protons at 6.09 and 6.9 are meta-coupled and show doublet in this region. The presence of two different types of tert-

Table 3
Rate of oxidation of 2.4.6-tri-tert-butylaniline with varying catalyst concentration

S. No.	Conc. of substrate (mM)	Conc. of catalyst (mM)	Ratio	Rate of reaction $(mM min^{-1}) * 10^{-6}$
1	9.58	0.063	0.2:30	1.10
2	9.58	0.128	0.4:30	2.34
3	9.58	0.216	0.68:30	2.45
4	9.58	0.318	1.0:30	5.69
5	9.58	0.478	1.5:30	5.47





5. Kinetic studies

The kinetics of the oxidation reaction between 2,4,6-tritert-butylaniline (TBA) and TBHP in presence of catalytic amount of $[Cu(L)(NO_3)_2]$ was performed at room temperature under the following conditions:

5.1. Substrate variation

The amount of substrate (2.1, 6.3, 8.5, 12.7, 17.0 mM) was varied while keeping the amount of catalyst fixed at 0.43 mM. Plot of concentration of 3,5-di-tert-butyl-6-iminocyclohexa-2,4-dienone against time is given in Fig. S6(a) while plot for 3,5-di-tert-butylcyclohexa-3,5-diene-1,2-dione against time is shown in Fig. S6(b). The rates are given in Table 2 and Table S1. The rate of oxidation reaction with varying substrate concentration is given in Fig. 6 (inset) and Fig. 7 (inset). This shows that the rate of reaction increases as the concentration of the substrate increases at a fixed catalyst concentration, up to an optimum ratio of substrate:complex (30:1). The logarithm of average rate of reaction was plotted against the ln[substrate] while keeping the concentration of



Fig. 8. X-band EPR spectra of (a) copper(II) complex, 2.13 mM + 2,4,6-tritertbutylaniline, 63.8 mM, (b) copper(II) complex, 2.13 mM + 2,4,6-tritert-butylaniline 63.8 mM + TBHP, 25.6 mM after 30 min.



Fig. 9. Cyclic voltammograms of (a) substrate (2,4,6-tri-tert-butylaniline,10.64 mM) [inset: blowup region, 600 to -400] (b) substrate + tert-butylhydroperoxide, 25.6 mM) [Inset: blowup region 400 to -400] (c) Cu(II) complex (2.13 mM) + substrate (10.64 mM) + TBHP (25.6 mM).

catalyst constant. These plots are shown in Fig. S8(a and b) from where the slope is found to be 0.9 for **A** and 1.2 for **B** suggesting a first order dependence on the substrate concentration in a limited range.

5.2. Catalyst variation

The amount of copper(II) catalyst (0.06, 0.12, 0.21, 0.31, 0.47 mM) was varied while keeping the amount of 2,4,6-tritert-



Fig. 10. Curve 1: d–d band spectrum of the pure Cu(II) complex. Curve 2: d–d band spectrum of the Cu(II) complex + TBHP + 2,4,6-tri-tert-butylaniline. Curve 3: d–d band spectrum of the reaction mixture after 8 min. Curve 4: d–d band spectrum of the reaction mixture after 16 min. Curve 6: d–d band spectrum of the reaction mixture recorded after 32 min. Curve 9: d–d band spectrum of the reaction mixture recorded after 56 min [Cu(II) complex = 2.1 mM, TBHP = 25.6 mM, 2,4,6-tri-tert-butylaniline = 63.8 mM].

butylaniline (substrate) fixed at 9.5 mM. Plot of concentration of 3,5-di-tert-butyl-6-iminocyclohexa-2,4-dienone against time is given in Fig. S7(a) while plot for 3,5-di-tert-butylcyclohexa-3, 5-diene-1,2-dione against time is shown in Fig. S7(b). The rates are given in Table 3 and Table S2. The rate of oxidation reaction with varying catalyst concentration is given in Figs. 6 and 7. This depicts a linear increase in the rate of reaction, up to an optimum ratio of substrate:complex (30:1). The logarithm of average rate of reaction was plotted against the ln[catalyst] while keeping the concentration of substrate constant. This plot is shown in Fig. S9(a and b) from where the slope is found to be 1.0 for **A** and 0.73 for **B** suggesting a first order dependence on the catalyst concentration in a limited range.



Fig. 11. Curve 1: d–d band spectrum of the pure Cu(II) complex. Curve 2: d–d band spectrum of the Cu(II) complex + TBHP + 2,4,6-tri-tert-butylaniline. Curve 3: d–d band spectrum of the reaction mixture after 8 min. Curve 4: d–d band spectrum of the reaction mixture after 16 min. Curve 6: d–d band spectrum of the reaction mixture recorded after 32 min. Curve 9: d–d band spectrum of the reaction mixture recorded after 56 min [Cu(II) complex = 2.1 mM, TBHP = 25.6 mM, 2,4,6-tri-tert-butylaniline = 85.2 mM].



$L + Cu(NO_3)_2.3H_2O$	СН ₃ ОН	[Cu(L)(NO ₃) ₂]
	5-10 min stirring	

Scheme 1. Synthesis of ligand and Copper(II) complex.



Scheme A. Tentative catalytic cycle for the oxidation of hindered aniline using TBHP as an alternate source of oxygen.



Scheme B. Tentative inhibition of the catalytic cycle.

5.3. EPR and d-d band changes

In an attempt to identify the changes occurring during the catalytic turnover, the following experiments were conducted:

- (1) EPR spectra were recorded at 120 K in methanolic medium for (a) A mixture of the copper(II) catalyst and the substrate, tri-tert-butylaniline (Fig. 8 Curve 1) and (b) after the addition of tert-butylhydroperoxide to (a) and keeping for 30 min (Fig. 8 Curve 2). The Area of the two curves are found to be 268 (Curve 1) and 85 (Curve 2). The drop in the intensity of EPR spectrum upon reaction is analyzed in terms of the formation of a EPR silent species. Under oxidizing conditions (hydroperoxide), formation of Cu(I) may be ruled out, therefore the other likely product is either a Cu(III) species or antiferromagnetically coupled dimeric copper(II) species which are known to be EPR silent [20,21]. The EPR experiment also shows the presence of residual copper(II) complex, having slightly altered EPR parameters when compared to the parent Copper(II) complex: $A_{II} = 163$, $g_{II} = 2.26$, $g \perp = 2.03$, $(g_{II}/A_{II})^*100 = 138$.
- (2) Cyclic voltammogram of the following were obtained in DMSO: MeCN (3:7), as described in physical measurement section.
 - (i) Fig. 9(a) shows the voltammogram of tri-tert-butylaniline (10.64 mM); this shows a weak quasi-reversible wave with E_a (anodic) at +290 mV and E_c (cathodic) at +154 mV, giving a $E_{1/2}$ of +222 mV.
 - (ii) Fig. 9(b) shows the change in voltamogram when tertbutylhydroperoxide (25.6 mM) is added to (i) above. It is observed that there is a slight shift of the E_a (anodic) to +314 mV, while the E_c (cathodic) is hardly discernible.
 - (iii) Fig. 9(c) shows the voltamogram when the parent Copper(II) complex (2.13 mM) is added to (ii). The cyclic voltamogram shows two clean quasi reversible waves. One with E_a (anodic) 122 mV and E_c (cathodic) -74 mV with $E_{1/2}$ = 24 mV, corresponding to the Cu(II)/Cu(I) couple. The second wave is positively shifted, with E_a (anodic) = +676 mV and E_c (cathodic) at +466 mV giving a $E_{1/2}$ of +571 mV.

It is thus concluded that in the presence of substrate and tert-butylhydroperoxide, a new quasi-reversible wave with $E_{1/2}$ = +571 mV is observed. This wave could be assigned to the couple Cu(III)/Cu(II). Thus cyclic voltammetry provides evidence of the formation of a Cu(III) species in the reaction medium.

(3) The pure copper (II) complex in MeOH has a d-d band at 653 nm (Curve 1, Fig. 10), upon mixing with tert-butylhydroperoxide and2,4,6-tri-tert-butylaniline (1:30:12), initially the d-d band intensity and the position of band remains nearly unchanged (Curve 2, Fig. 10). Subsequent time dependant scan of the oxidation reaction are shown in curves 3-9 (Fig. 10); it is found that during catalytic turnover, there is a slight shift of the d-d band towards 662 nm and a continuous increase in its intensity along with the formation of a new prominent shoulder at ~735 nm curves 4-9 (Fig. 10) This suggests that besides the parent copper(II) complex a new copper species is being formed which has a higher extinction coefficient for its d-d bands than the parent copper(II) complex explaining the increase in intensity. The presence of two prominent d-d bands in the new copper-species also suggests an enhanced equatorial ligand field, causing the splitting of overlapping transition $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ and $d_{xy}, d_{yz} \rightarrow d_{x^2-y^2}$ in a square planar

complex [22,23]. In this context it is known that Cu(III) and dimeric Cu(II) complexes possess d–d bands in the region of 600–700 nm [20,21,24–27].

(4) In order to resolve the fact that there is a nearly 30% drop in the rate of reaction (given in Table 2) when the stoichiometry of the substrate is increased to 40-fold; A d-d band study was carried out as in (2) keeping other conditions same except an increase in the substrate amount (complex: substrate: oxidant::1:40:12), and changes in the d-d band were again monitored. Fig. 11 shows the changes as the reaction proceeds. It is found that there is a similar shift of position of the parent d-d band along with the formation of a prominent shoulder at \sim 735 nm with continued increasing intensity up to 56 min. However there is a faster growth of the new copper-species in comparison to the reaction where the substrate has a lower concentration (30-fold) Fig. S10. This suggests that there is some role of the enhanced substrate in the formation of a new- copper species. This new copper species appears to have a lowered reactivity towards the oxidation reaction being carried out in comparison to the parent copper(II) complex, causing a overall drop in the rate of reaction (see Scheme 1).

In view of the above EPR and d–d spectral changes a tentative catalytic Scheme A and its inhibition, Scheme B is proposed; this considers the decomposition of tert-butylhydroperoxide by the copper(II) catalyst, to generate the tertbutylperoxyl and tertbutyloxy free radicals [28]. The tert-butyloxy radical is possibly involved in abstraction of a hydrogen atom from the hindered aniline, and subsequent attack of the peroxyl radical on the aniline, generates the imino-quinone.

6. Conclusion

Distorted square planar copper(II) complex of a N-octylated bis-benzimidazolyl ligand has been synthesized and structurally characterized. This complex carries out the oxidation of 2,4,6-tritertbutyl aniline utilizing low amounts of tert-butylhydroperoxide (TBHP) as an alternate source of oxygen, to 3,5-di-tert-butyl-6-iminocyclohexa-2,4-dienone as a major product. Kinetic study shows that the reaction follows first order with respect to catalyst and substrate. The catalytic oxidation proceeds via a copper(III)/ copper(II) cycle.

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Appendix A. Supplementary material

CCDC 1010813 and 1010814 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. ¹H NMR, ¹³C NMR of ligand and ¹³C NMR of product **A**, kinetics data, X-ray crystallographic tables are given in supplementary material. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2014.11.025. A. Yadav, P. Mathur/Inorganica Chimica Acta 427 (2015) 62-71

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