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Synthesis, structure, catechol oxidase activity and antibacterial studies of Mn^{III} complex with sterically constrained phenol-based N_2O_2 ligand

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Abstract : Mn^{III} complex with sterically constrained phenol based tetradentate N_2O_2 ligand together with acetylacetone as ancillary ligand has been synthesized and characterized. Sterically constrained tetradentate ligand *N*,*N*′-dimethyl-*N*,*N*′-bis(2-hydroxy-3,5-dimethylbenzyl)-ethylenediamine (H_2L) has been used here to synthesize mononuclear octahedral mixed ligand complex [Mn^{III}L(acac)] 1. Characterization of this compound is carried out by various spectroscopic tools. Compound 1 crystallizes in orthorhombic space group *P*na2_1 with *a* = 8.325 Å, *b* = 23.150 Å, *c* = 13.428 Å. The compound shows both antibacterial activity as well as catecholase activity. Antibacterial activity of complex 1 was performed by well plate technique. In the above experiment, *V. harveyi, V. vulnificus, V. parahaemolyticus, A. hydrophila* and *E. coli* were found sensitive to the mononuclear mixed ligand complex [Mn^{III}L(acac)] 1. At the same time, the mixed ligand Mn^{III} complex catalyses the oxidation of 3,5-di-tert-butylcatechol in methanol in the presence of molecular oxygen with first order reaction kinetics. The kinetic studies confirm that the turnover number is 1.2×10^5 h^{-1}.

Keywords : Syntheses, characterization, X-ray structure, antibacterial activity, catecholase activity.

Introduction

Catechol oxidase is an enzyme with a type-3 di-copper active site that catalyzes the oxidation of a range of *ortho*-diphenol (catechol) substrates to the corresponding *ortho*-quinones. The generated *o*-quinones are auto polymerized producing a brown polyphenolic pigment, i.e. melanin, a process which is considered to protect damage tissues against pathogens or insects[1]. X-Ray crystallographic characterization of catechol oxidase, isolated from sweet potatoes, was reported in 1998, reveals that the active center consists of a hydroxo-bridged dicopper(II) center in which each copper(II) center is coordinated to three histidine nitrogens and adopts a trigonal pyramidal environment with one nitrogen at the apical site[2]. From the reports of various research groups, the ability of di-copper complexes to oxidize phenols and catechols is well established[3]. In recent, catechol oxidase activity of metal complexes with other metal ion such as Co^{III}, Fe^{II}, Ni^{II}, Mn^{III} and Zn^{II} have been investigated[4]. There are only few reports where manganese complexes were found to display such activity[5]. Therefore design and synthesis of functional model of catechol oxidase containing manganese ion is a challenging and interesting for the development of bio-inspired catalysts for oxidation reactions.

At the same time, synthesis of metal based drugs is a research area of increasing interest for inorganic, pharmaceutical and medicinal chemistry and has concentrated much attention as an approach to new drug development. In recent times, many transition metal complexes with phenol-based ligand have been reported in literature possessing antimicrobial, antibacterial, antifungal, anti-inflammatory and antitumor properties[6]. Therefore, designing of coordination compounds with antimicrobial activity is also enormously important in drug delivery and therapeutic applications.

Herein, we report synthesis and characterization of a manganese(III) complex with sterically constrained phenol based tetradentate N_2O_2 ligand together with acetylacetone as ancillary ligand. X- Ray crystallography, electronic spectroscopy and ESI-MS have been carried out to characterize this complex. The octahedral mononuclear mixed ligand compound $[Mn^{III}L(acac)]$ **1** catalyzes the oxidation of 3,5-di-tert-butylcatechol (3,5-DTBC) to 3,5-di-tert-butylbenzoquinone (3,5-DTBQ) with molecular oxygen in methanol at 25 °C. An investigation of the Michaelis-Menten kinetics and calculation of the turnover number are observed. Antibacterial activity of Mn^{III} complex was performed by well plate technique. In the above experiment, *V. harveyi, V. vulnificus, V. parahaemolyticus*, *A. hydrophila* and *E. coli* were sensitive to the mononuclear mixed ligand complex $[Mn^{III}L(acac)]$ **1**.

Experimental

Materials :

N,N′-Dimethylethylenediamine, 2,4-dimethylphenol and 3,5-di-tert-butylcatechol were purchased from Aldrich. Solvents were reagent grade, purified using appropriate drying agents and distilled under nitrogen prior to their use[7]. All other chemicals were commercially available and were of reagent grade and used as received without further purification. Pure culture of the test bacteria were collected from the microbiology lab of Vidyasagar University, Medinipur.

Syntheses :

Ligand :

N,N′-Dimethyl-N,N′-bis(2-hydroxy-3,5-dimethylbenzyl)-ethylenediamine (H_2L) : *N,N′*-Dimethylethylenediamine (0.88 g, 10 mmol) was taken in methanol (50 mL). To the methanolic solution about 0.60 g (20 mmol) of paraformaldehyde was added. The solution was put under reflux for 3 h. To this 2,4-dimethylphenol (2.44 g, 20 mmol) was added slowly with constant stirring. The resulting mixture was refluxed further for 12 h to obtain a white crystalline precipitate which was filtered off, washed with methanol (2×10 mL) and diethyl ether (2×10 mL) and finally dried *in vacuum*. The compound was recrystallized from acetone-pet ether (60–80 °C) mixture. Yield : 3.1 g (87%); m.p. 119 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C), δ/ppm : 2.20 (12H, s, CH_3), 2.25 (6H, s, N-CH_3), 2.64 (4H, s, CH_2-CH_2), 3.62 (4H, s, benzylic), 6.59 (2H, s, aryl), 6.85 (2H, s, aryl); IR (KBr disk, cm^{-1}) : 2916, 2813, 1480, 1311, 1250, 1011, 848, 825; UV-Vis (CH_2Cl_2), [λ_{max}/nm (ε/mol^{-1} cm^2)] : 231 (11000), 287 (6900).

Preparation of complex :

$[Mn^{III}L(acac)]$ **1** : $Mn(acac)_3$ (0.175 g, 0.5 mmol) was added to the methanol solution of H_2L (0.18 g, 0.5 mmol) and the resulting mixture was stirred. After 1 h stirring, solution was turned into dark color. Resulting solution was filtered. The filtrate was kept undisturbed in open air at room temperature for crystallization. A brown crystalline compound along with single crystal was obtained. IR (KBr disk, cm^{-1}) : 2912, 1595, 1515, 1471, 1380, 1251, 821; UV-Vis (CH_2Cl_2), [λ_{max}/nm (ε/mol^{-1} cm^2)] : 562 (1717); ESI-MS in CH_2Cl_2 : *m/z* 251 ($M+H^+$) : 508.

Physical measurements :

UV-Visible spectra in solution were recorded on a Perkin-Elmer 950 UV/VIS/NIR spectrophotometer, while for infrared spectra were employed a Nicolet Magna 750 FT-IR spectrometer, series II with samples prepared as KBr pellets. Mass spectra (ESI-MS in positive ion mode) were recorded on a QTOF Model YA263 Micro Mass Spectrometer.

X-Ray crystallography :

Diffraction quality crystals of **1** were grown at room temperature by slow diffusion of methanol solution of the compound. Intensity data for the compound was measured on a Bruker SMART 1000 CCD diffractometer using a graphite monochromated Mo K_α radiation (λ = 0.71073 Å) at 293 K. Intensity data were collected with θ_{max} of 24.99 deg. No crystal decay was observed during the data collections. Relevant crystal data and refinement details are given in Table 1. No crystal decay was observed during the data collections. The structures were solved by direct methods[8] and refined on F^2 by a full-matrix least-squares procedure[9] using the program SHELXL 97.

Table 1. Summary of the crystallographic data for the complex **1**

Complex	**1**
Empirical formula	$C_{27}H_{37}MnN_2O_4$
Formula weight	508.53
T (K)	293 (K)
λ (Mo K_α) (Å)	0.71073
Crystal size (mm^3)	0.24×0.22×0.20
Space group	$Pna2_1$
Crystal system	orthorhombic
a (Å)	8.325
b (Å)	23.150
c (Å)	13.428
V ($Å^3$)	2588
Z	4
$D_{Calcd.}$ ($g\ cm^{-3}$)	1.305
μ (mm^{-1})	0.545
F (000)	1080
θ ranges (°)	2.60–28.46
Index ranges	$-9 \le h \le 9$
	$-27 \le k \le 27$
	$-15 \le l \le 15$
Reflections collected	19598
R_{int}	0.0552
Goodness of fit	1.081
No. of parameters	315
$R1^a(F_0)$, $wR2^b(F_0)$ (all data)	0.0289, 0.0648
Largest diff. peak, deepest hole ($eÅ^{-3}$)	0.297, –0.599

$^aR = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^bwR = [\Sigma[w((F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]$

Catalytic oxidation of 3,5-DTBC :

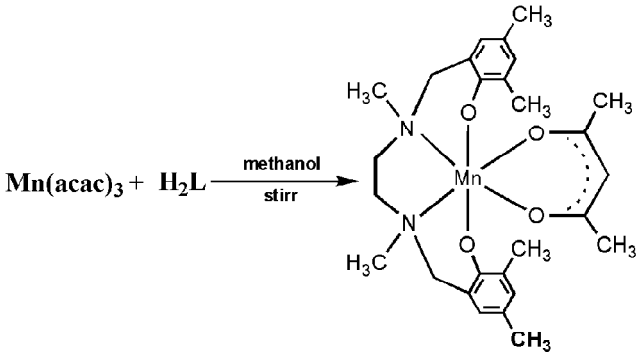
The catechol oxidase activity of complex **1** was monitored using most familiar 3,5-di-tert-butylcatechol (3,5-DTBC) as the substrate in a methanol solution under aerobic conditions at room temperature[10]. In order to examine the catecholase activity of the complex, a 10^{-4} *M* solution of **1** in methanol solvent was treated with 100 equiv. of 3,5-di-tert-butylcatechol (3,5-DTBC) under aerobic conditions at room temperature. The reaction was carried out spectrophotometrically by monitoring the increase in the maximum absorbance of the quinone band at 400 nm as a function of time[11]. Absorbance vs wavelength of the solution was recorded at a regular time intervals of 2 min. It may be noted here that a blank experiment without catalyst does not show formation of the quinone up to 6 h in MeOH.

To determine the dependence of rate on substrate concentration and upon various kinetic parameters, 1.75×10^{-4} *M* solution of complex **1** was treated with increasing amounts of 3,5-DTBC from 1.4×10^{-3} *M* to 5×10^{-3} *M*. In each case, the reaction was observed spectrophotometrically by monitoring the increase in the absorbance at 400 nm up to 30 min. The rate constant versus substrate concentration data were then analyzed on the basis of the Michaelis-Menten approach of enzymatic kinetics to get the Lineweaver-Burk plot as well as the values of the parameters V_{max}, K_M and K_{cat}.

Results and discussion

Synthesis :

The mixed ligand complex has been prepared readily by mixing the $Mn(acac)_3$ with the methanolic solution of sterically hindered phenol based N_2O_2 ligand in stoichiometric amounts (1 : 1 mole ratio). The detailed strategy is summarized in Scheme 1. Mononuclear mixed ligand compound $[Mn^{III}L(acac)]$ **1** was obtained with nearly octahedral geometry and the compound is stable in air at room temperature. The compound was characterized using IR, UV-Vis spectroscopy, mass spectroscopy and single crystal X-ray crystallography.



Scheme 1. Schematic presentation of preparation of complex **1**.

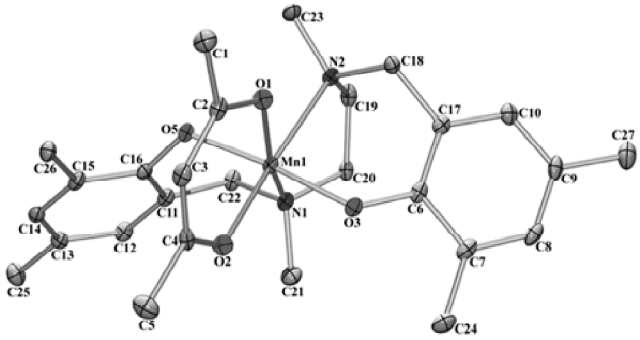


Fig. 1. Molecular structure of the complex **1** showing the atom-numbering scheme.

The complex was initially characterized by IR spectroscopy. IR spectra of this complex display all the characteristic bands of the coordinated $(L)^{2-}$ ligand. One such prominent band appears at 1301 cm^{-1} due to υ(C-O/phenolate) stretching vibrations[12]. Corresponding signature vibrations for the β-diketone moiety in complex **1** appear in the form of a twin band at *ca*. 1535 and 1606 cm^{-1} due to υ(C=C) and (C=O) stretching respectively[13].

Description of crystal structure :

The molecular structure of complex **1** is shown in Fig. 1. Its important inter atomic parameters are listed in Table 2. The complex crystallizes in orthorhombic space group $Pna2_1$. The Mn^{III} center in this mononuclear complex is six-coordinated using a doubly deprotonated tetradentate ligand $(L)^{2-}$, providing O(3), N(1), N(2) and O(5) donor sites and a bidentate acetylacetonate via O(1) and O(2) donor sites. The basal plane is formed by the coordination of O(1), O(2), N(1), N(2) with Mn i.e. they are in equatorial position and O(5) and O(3) occupy axial position. The bond distances of Mn-N (2.212(2)–2.261(3) Å) and Mn-O (1.862(2)–2.076(2) Å) are all in the expected ranges[14]. Mn-O(3) (1.883 Å) and Mn-O(5) (1.862 Å) bond distances are different from the rest four as expected for Jahn-Teller distortion of Mn^{III} complexes[12b,15]. There is no hydrogen bonding interaction present within the molecule, as well as no ion dipole interaction is present.

Mass spectroscopy :

The ESI mass spectrum (in positive ion mode) of complex **1** in CH_2Cl_2 medium shows the molecular ion peak at m/z = 508 $(M+H^+)$ with 100% relative abundance and expected isotope pattern. The isotope distribution pattern for the base peak of **1** is displayed in Fig. 2 as a representative example together with its simulation pattern. The result confirms the purity of this compound.

Electronic spectra :

The electronic spectrum of the compound was recorded in DCM solution, and the data are summa-

Table 2. Selected bond distances (Å) and angles (deg) for **1**

Bond distances (Å)		Bond angles (deg)			
Mn-N(2)	2.261(3)	O(1)-Mn-N(2)	84.84	O(1)-Mn-O(5)	88.10
Mn-N(1)	2.212(2)	O(1)-Mn-O(2)	88.45	O(1)-Mn-O(3)	93.75
Mn-O(3)	1.883(2)	N(1)-Mn-N(2)	79.48	N(1)-Mn-O(3)	91.14
Mn-O(2)	2.047(2)	N(1)-Mn-O(2)	107.73	N(1)-Mn-O(5)	88.44
Mn-O(5)	1.862(2)	N(1)-Mn-O(1)	163.42	N(2)-Mn-O(3)	88.29
Mn-O(1)	2.076(2)	N(2)-Mn-O(5)	96.77	O(5)-Mn-O(2)	89.40
		O(2)-Mn-O(3)	85.74	O(5)-Mn-O(3)	174.75
		O(2)-Mn-N(2)	170.71		

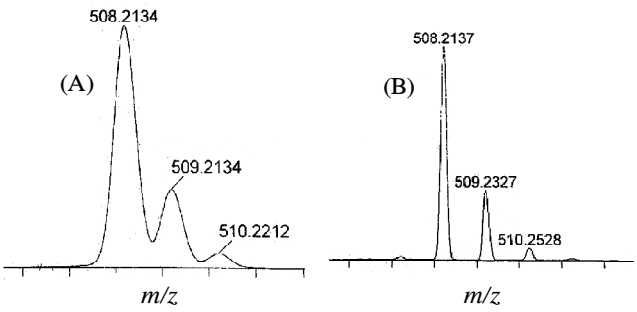


Fig. 2. (A) Dominant $[M+H^+]$ peak cluster in the electrospray ionization mass spectrum of **1**. (B) Comparison of the simulated isotope pattern for $[M+H^+]$ of **1**.

rized in the Experimental section. The spectrum shows a broad band at around 562 nm in the visible region with high molar extinction coefficient (ε, 1717 mol^{-1} cm^2) which can be assigned to L→M charge transfer transition which is characteristic of the transition metal complexes with phenol-based ligand[16]. The remaining band maxima appearing below 400 nm are due to ligand internal transitions.

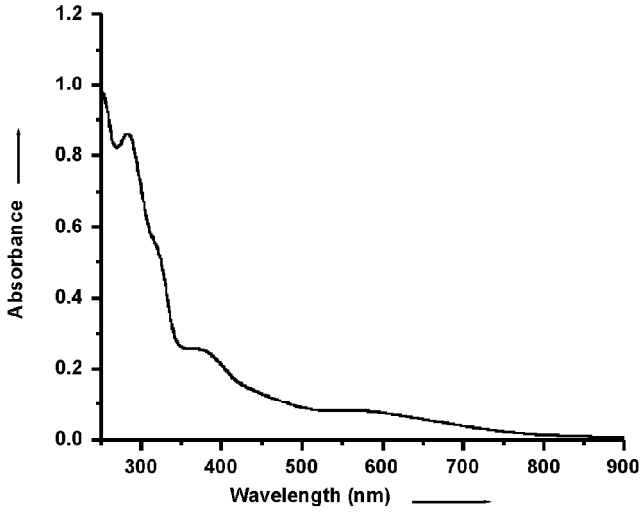


Fig. 3. Electronic absorption spectrum of complex **1** in CH_2Cl_2.

Antibacterial activity :

Antibacterial activity of $[Mn^{III}L(acac)]$ **1** complex, dimethyl sulphoxide as solvent and the ligand (H_2L) were performed by agar well diffusion method. Here nutrient agar media was prepared and autoclaved under 121 °C (15 lb) for 15 min for sterilization. Sterilized nutrient agar plates containing 30 ml of the media were inoculated with 500 µL each of *Vibrio harveyi, Vibrio vulnificus, Vibrio parahaemolyticus, Aeromonas hydrophila* and *Escherichia coli* separately inside laminar flow chamber. In each plate two wells of 6 mm diameter were made using a sterile cork borer where one of them filled up with complex and other with DMSO as control. In the same way another set was prepared for ligand only. After 24 h of incubation at 37±1 °C the zone of inhibition in agar plates were observed, measured and photographed. During the incubation period, the test solutions were diffused through nutrient agar and the growth of the inoculated microorganisms were affected. The zone of growth inhibition of each sample is given in Table 3.

Catecholase activity :

The catecholase activity of mixed ligand mononuclear complex $Mn^{III}L(acac)]$ **1** was studied using 3,5-di-tert-butylcatechol (3,5-DTBC) as a model substrate in methanol under aerobic condition at room temperature. When the complex was treated with 3,5-di-tert-butylcatechol in methanol under areobic condition, there was a gradual increase in absorbance at 400 nm as shown in Fig. 6 characteristic to the formation of 3,5-di-tert-butylbenzoquinone. Most widely used 3,5-di-tert-butylcatechol (3,5-DTBC) has been utilized as the substrate as it can easily be oxidised to 3,5-di-tert-butylbenzoquinone (3,5-DTBQ). Two bulky

Table 3. Antibacterial activity of the complex **1**, ligand (H_2L) and DMSO (inhibition zone in mm)

	Zone of inhibition (mm) against pathogenic bacteria				
Test pathogen	*V. harveyi*	*V. vulnificus*	*V. parahaemolyticus*	*A. hydrophila*	*E. coli*
Complex **1**	11.5	10.5	13	13	10
Ligand (H_2L)	10.5	11.5	11.5	10.5	10
DMSO	–	5	5	–	–

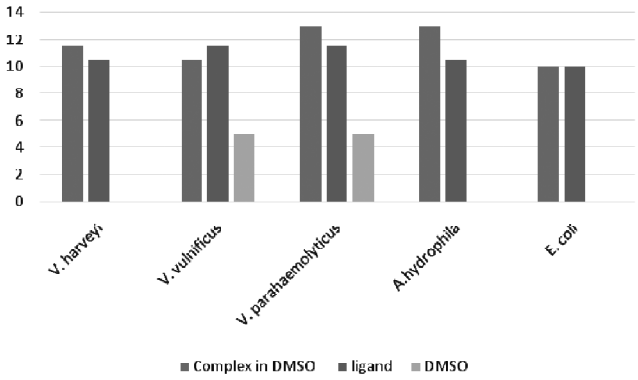


Fig. 4. Antibacterial activity of the complex **1**, ligand (H_2L) and DMSO solvent by using five pathogenic bacteria (*V. harveyi, V. vulnificus, V. parahaemolyticus, A. hydrophila* and *E. coli*).

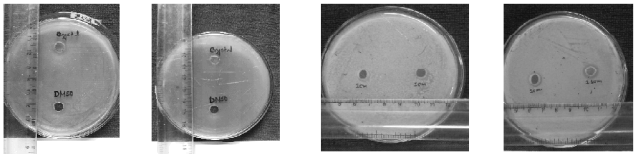


Fig. 5. Inhibition zone photographs of (1) *E. coli* with complex **1**, (2) *V. vulnificus* with complex **1**, (3) *E. coli* with ligand (H_2L) and (4) *V. vulnificus* with ligand (H_2L) based on agar well diffusion assay.

substituents on the catechol ring makes it easily oxidizable to the corresponding *o*-quinone 3,5-DTBQ and shows a maximum absorption at 400 nm in methanol. Kinetic experiments were observed spectrophotometrically with complex **1** and the substrate 3,5-DTBC in methanol at 25 °C. The conversion of 3,5–DTBC to 3,5-DTBQ (quinone band maxima) was monitored with time at a wave length of 400 nm for $Mn^{III}L(acac)$] **1** in methanol. The rate constant for a particular complex – substrate concentration ratio was obtained by change in absorbance versus time plot by employing initial rate method.

The substrate concentration dependence of the oxidation rate was observed under aerobic conditions using 1.75×10^{-4} *M* solution of complex **1** and increasing amounts of 3,5-DTBC from 1.4×10^{-3} *M* to 5×10^{-3} *M*. The rate constant versus substrate concentration data were then analyzed on the basis of the Michaelis-Menten approach of enzymatic kinetics to get the Lineweaver-Burk plot as well as the values of the parameters V_{max}, K_M and K_{cat}. The observed rate vs [substrate] plot in methanol solution, as well as Lineweaver-Burk plot, is given in Fig. 7. The V_{max} value is 5.798×10^{-5} M s^{-1} (Std. error 1.195×10^{-4}) whereas K_M value is 11.83×10^{-3} *M* (Std. error 7.546×10^{-3}). The observed K_{cat} value is 1.2×10^{5} h^{-1} and the result indicates that complex **1** is very efficient catalysts for catechol oxidation as compared with similar reported earlier[5]. To the best of our knowledge, only few Mn^{III} complexes exhibiting catecholase activity with high K_{cat} have been documented[4h].

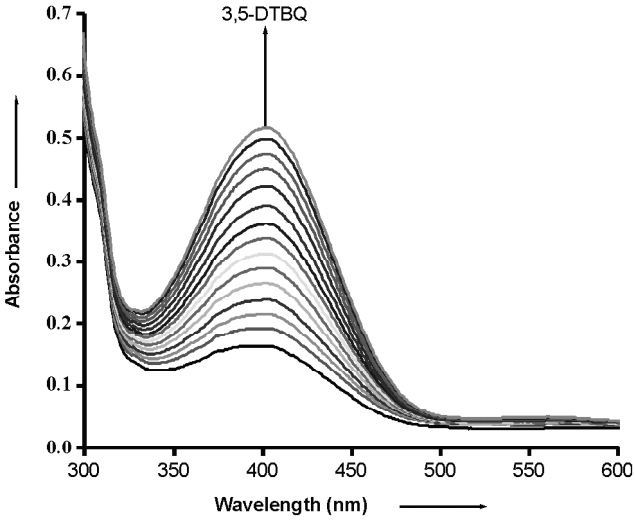


Fig. 6. Increase of quinone band at 400 nm after addition of 100 equivalents of 3,5-DTBC to a solution containing complex **1** (10^{-4} *M*) in methanol at 25 °C. The spectra were recorded after every 2 min.

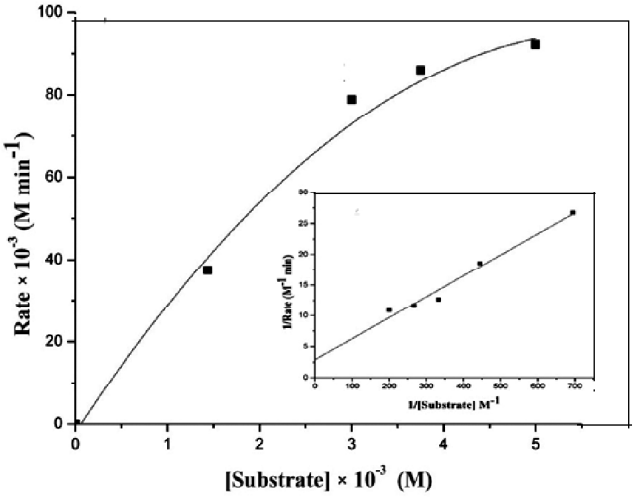
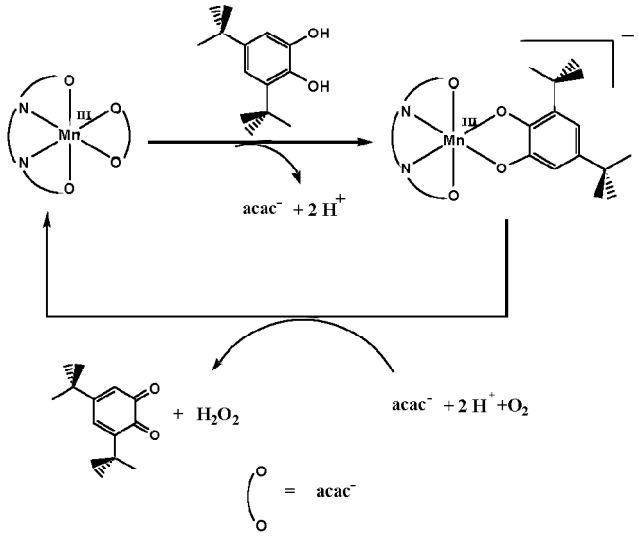


Fig. 7. Plot of rate vs [substrate] in the presence of **1** in MeOH; Inset : Lineweaver-Burk plot.

We have proposed a plausible mechanistic pathway for the aerobic oxidation of 3,5-DTBC to 3,5-DTBQ catalysed by mononuclear mixed ligand manganese complex is depicted in the Scheme 2. Here we believe that the initial step of the catalytic cycle involves binding of the substrate molecule to the catalyst. Krebs *et al*. reported some mononuclear Mn^{III} complexes act as a catalyst in the oxidation of catechol to quinone and the redox participation of the metal center is suggested to be responsible for this activity[17]. Several research group investigated mono



Scheme 2. A plausible mechanistic pathways for the aerobic catechol oxidation catalyzed by complex **1**.

nuclear Mn^{III} complex as efficient catalyst to produce quinone from catechol with molecular oxygen as oxidant under mild condition[5d,5g]. The oxidation process of 3,5-DTBC to 3,5-DTBQ requires two electrons. We assumes that in the catalytic cycle Mn^{III} undergoes reduction to Mn^{II} with concomitant oxidation of 3,5-DTBC to 3,5-DTBQ in the presence of molecular oxygen. The catalytic cycle is completed by the reaction of Mn^{II} species with di-oxygen leading to the oxidation of Mn^{II} to the Mn^{III} and the oxygen that takes part in this process is converted to H_2O_2.

Conclusion

A phenol based tetradentate (N_2O_2) ligand H_2L has been used here to synthesize Mn^{III} complex with acetyl acetone as a ancillary ligand. Ligand and resulting complex are well characterized by IR spectroscopy, UV-Vis spectroscopy, mass spectroscopy, ^1H NMR spectroscopy and X-ray crystallography. The catecholase activity of complex **1** has been investigated following the oxidation of 3,5-di-tert-butylcatechol (3,5-DTBC) to 3,5-di-tert-butylbenzoquinone (3,5-DTBQ) with molecular oxygen in methanol at 25 °C. The observed turnover number for this catalytic process is very large as compared to the reported earlier. This indicates that the complex **1** is a good and effective catalyst towards the aerial oxidation of 3,5-DTBC to 3,5-DTBQ. The complex also shows antibacterial activity. *V. harveyi, V. vulnificus, V. parahaemolyticus A. hydrophila* and *E. coli* were sensitive to the mononuclear mixed ligand complex [Mn^{III} L(acac)] **1**.

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