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Mn(III) and Cu(II) complexes of 1-((3-(dimethylamino)propylimino)methyl) naphthalen-2-ol): Synthesis, characterization, catecholase and phenoxazinone synthase activity and DFT-TDDFT study

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Two new complexes, $[MnL_2](ClO_4)$ (1) and $[CuL_2]$ (2) (where LH = (E)-1-((3-

(dimethylamino)propylimino)methyl)naphthalen-2-ol), have been synthesized and characterized by spectroscopic techniques and their molecular structures are established by single-crystal X-ray diffraction study. Complex **1** adopts an octahedral geometry around the central manganese atom which is in +3 oxidation state, whereas in complex **2**, the Cu⁺² ion preferred a square pyramidal environment around it through the ligand donor atoms. Both complexes were tested for catecholase and phenoxazinone synthase activity. Complex **1** catalyzes the oxidation of 3,5ditertiary-butyl catechol with a k_{cat} value of 6.8424×10^2 h⁻¹ in acetonitrile whereas the same for complex **2** is 3.7485×10^2 h⁻¹ in methanol. Phenoxazinone synthase activity was shown only by complex **2** having $k_{cat} = 74.225$ h⁻¹. Structures of both the title complexes have been optimized by means of DFT calculations. Experimental electronic spectra of the complexes have been corroborated by TDDFT analysis. Electrochemical investigations by means of cyclic voltammetry have been carried out to study the electron transfer processes in the complexes.

Keywords: Metal complex; Catecholase; Phenoxazinone synthase; DFT

1. Introduction

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Oxidation is a fundamental reaction in organic transformation. Molecular oxygen has been employed as a popular oxidizing agent for its availability and environmentally benign nature. But activation of molecular oxygen is a major challenge due to its kinetic inertness. This kinetic inertness arises due to the mismatch of the spin state of the reactants in ground state: O₂ has spin triplet with two unpaired electrons whereas typical organic substrates are singlet with no unpaired electrons. However nature has evolved an excellent solution to overcome this obstacle by incorporating metal ions in the protein chain in the form of metalloenzymes which provide suitable alternative pathway and reduces the energy barrier. Metalloenzymes use various types of active sites [1], *e.g.* heme and non-heme iron site, heteronuclear iron-copper site or mono- and binuclear copper site for dioxygen activation. Oxidation of alcohol to carbonyl functionality is an important class of oxidative transformation [2].

Catechol oxidase (CO) is a type-III copper protein which catalyzes the oxidation of o-diphenol to corresponding quinone (scheme 1). Highly reactive quinone then undergoes autopolymerization forming melanin. In this way, CO protects damaged tissues of plants against pathogens or insects.

Klabunde *et al.* [3] determined the X-ray crystal structure of CO from sweet potato (Ipomoea batatas) both in oxidized Cu^{II}-OH-Cu^{II} and reduced Cu^I-OH-Cu^I form. Both contain a binuclear hydroxo-bridged Cu₂ site, each copper being coordinated by three histidine nitrogen atoms. Quite naturally large number of binuclear copper complexes [4] with similar ligand environment have been synthesized and screened for the catecholase activity for the elucidation of the catalytic mechanism. Besides, other metals, *e.g.* Mn- and Co-based models, have also been reported with comparable catecholase activity to Cu-based mimics.

Details of catecholase activity have been described in earlier reviews [5]. Recently, Mukherjee *et al.* published an excellent review article [6] describing different mechanisms for catecholase activity proposed to date where the authors deal the active site with a number of metals, *e.g.* Cu, Co and Mn. For binuclear Cu mimics, a catecholato-bridged intermediate is formed prior to the formation of quinine [7]. For mononuclear Cu^{II} complex, chelated Cu^{II}-DTBC (3,5 DTBCH₂ = 3,5-ditertiary-butyl catechol) is converted to a Cu^I-semiquinone intermediate which reacts with molecular oxygen to form superoxo-complex. The latter then releases DTBQ (3,5-ditertiary-butyl quinone) and H₂O₂ [8]. Among other metals, Mn^{II} mimics have a comparable catecholase activity to that of dicopper system. This may be due to the multielectron transfer capability of manganese which can easily change the oxidation state between Mn^{II} and Mn^{IV} . Recently progress in development of nickel- and zinc-based mimics for CO has been started. Das *et al.* [9] and Ghosh *et al.* [10] reported binuclear nickel complexes with quite high k_{cat} value.

Phenoxazinone synthase (PHS) is another kind of multicopper oxidase [11] which catalyzes the oxidative condensation of two molecules of 3-hydroxy-4-methylanthranilic acid pentapeptide lactone, the last step in the biosynthesis of the antibiotic actinomycin D (scheme 1). This reaction produces the phenoxazinone chromophore. The reaction proceeds *via* three consecutive two-electron oxidation processes which cumulatively lead to six-electron oxidation process. The enzyme PHS was first isolated in 1962 by Katz and Weissbach from *Streptomyces antibiotus* [12]. However, the structure was solved only in 2006 by Allen and Francisco [13]. PHS exists in two oligomeric forms with varied catalytic activity; low-active dimer and hexamer of high activity. The hexamer contains five copper atoms: one type 1, two type 2 and one binuclear type 3 centers. Biomimetic model systems of PHS with copper were reported by different groups: Speier and co-workers [14], Halligudi *et al.* [15] and Chaudhuri *et al.* [16]. Although not observed in nature, manganese- [17] and cobalt-based [18] mimics have been successfully employed as potential candidates to show PHS activity.



Scheme 1. Catecholase and phenoxazinone synthase activity.

Researchers have tried to get the mimics not only to understand the underlying mechanism of the oxidation process but also to enhance the catalytic activity of the synthetic mimics for the industrial application.

In this work, we demonstrate the synthesis and characterization of a Mn(III) and a Cu(II)

complex of a Schiff base ligand derived from the condensation of 2-hydroxyl-naphthaldehyde and N,N-dimethylpropanediamine (scheme 2). Details of spectroscopic and single-crystal X-ray crystallographic characterization, electrochemical and magnetic measurements along with catalytic study for the catecholase and phenoxazinone synthase-like activity using these complexes have also been reported. Although the copper [19] and nickel [20] complexes with the ligand have been reported earlier by different groups, nobody has studied the biological oxidation catalysis with the reported molecules.



Scheme 2. Synthesis of the ligand and complexes.

2. Experimental

2.1. Materials

N,N-Dimethyltrimethylenediamine, 2-hydroxy-1-naphthaldehyde and 3,5-di-tert-butyl catechol were purchased from Acros Organics and used as received. For spectrochemical and electrochemical analysis HPLC grade solvents from Rankem were used. Manganese and copper perchlorate salts were synthesized from respective metal carbonates in laboratory according to the procedure reported in literature [21]. Tetraethylammonium perchlorate (TEAP) used for the

electrochemical studies was prepared according to the literature procedure [22].

Caution: Perchlorate salts of the metals are potentially explosive and must be handled with care. In present work no problem was faced.

2.2. Physical measurements

Infrared (IR) spectra of the ligand and the complexes were recorded on model IR prestige 21, SHIMADZU Corporation (Japan) between 400 cm⁻¹ to 4000 cm⁻¹ in KBr pellet. UV-vis spectra were recorded in a PERKIN-ELMER (LAMBDA-750) UV/VIS/NIR spectrophotometer in the range 250-1800 nm. ¹H-NMR spectra of the ligand were recorded in a JEOL JNM-ECZ400S/L1 spectrometer. Cyclic voltammograms and differential pulse voltammograms were recorded in CHI6003E Potentiostat in a typical three-electrode system: Pt or glassy carbon working electrode, Ag/AgNO₃ reference electrode and Pt counter electrode. TEAP was used as supporting electrolyte. Ferrocene/ferrocenium couple was observed at E⁰ (Δ E_p) = 0.4 V (100 mV) under these experimental conditions.

2.3. Procedure for the oxidation of 3,5-di-tertiary-butyl catechol (3,5-DTBC) and determination of the rate of formation of 3,5-di-tertiary-butyl quinone (3,5-DTBQ)

In the kinetic investigation air saturated 10 mL methanolic solution of 1×10^{-5} M of complex was prepared and then the solution was treated with 1×10^{-3} M of substrate 3,5-DTBC. 2 mL solution of catalyst was taken in a quartz cell and externally 100 eq of substrate was added to the cell solution. The investigation was then followed by UV-vis spectral scan at the interval of every 10 min up to 3 h. Catalytic study of complexes **1** and **2** was studied in methanol and acetonitrile solvent. In both acetonitrile and methanol, the absorbance was monitored at 400 nm (ε = 1900 M⁻¹cm⁻¹) as reported by Krebs *et al.* [23]. The kinetic measurements were performed at 25 °C. Time-dependent spectral profiles for the catalytic study by complex **1** are shown in figure 1 (in acetonitrile) and figure S11 (in methanol), while for complex **2** the same profiles are shown in figure S13 (in methanol) and figure S15 (in acetonitrile), respectively. Same experiments performed without catalyst under identical conditions did not show any significant growth of the band at respective positions.

For the detection of hydrogen peroxide during catalysis, a fresh set of reaction mixture was prepared by mixing 10 mL (50×10^{-5} M) of catechol and 10 mL (2.5×10^{-5} M) of the

complexes. The reaction mixture was stirred at 25 °C. After 1 h, pH of the solution was adjusted to 2 by adding H_2SO_4 and an equal volume of water was added to stop further oxidation. The quinone formed was extracted with dichloromethane followed by the addition of 1 mL of 10% potassium iodide solution and 4 drops of 3% ammonium molybdate solution to the aqueous layer. Formation of I_3 ⁻ was monitored spectrophotometrically by measuring the intensity of the characteristic band at 353 nm ($\epsilon = 26,000 \text{ M}^{-1}\text{cm}^{-1}$).

2.4. Procedure for the oxidation of 2-amino phenol and determination of the rate of formation of phenoxazinone chromophore

In this kinetic investigation, same procedure is applied. Here 10 mL methanol solution of 1×10^{-5} M of complex **2** was prepared and then the solution was treated with 1×10^{-2} M of substrate: *o*-amino phenol (OAPH). The UV-vis spectral total scan time was 3 h with intervals of 10 min. In MeOH, the absorbance was monitored at 430 nm ($\varepsilon = 9095$ M⁻¹cm⁻¹) following earlier report [24]. The kinetic measurements were performed at 25 °C. Time-dependent spectral profiles for the catalytic study by complex are shown in figure 2. Similar experiment performed without catalyst under identical conditions did not show any significant growth of the absorption band at respective positions.

2.5. Synthesis of the ligand (E)-1-((2-(dimethylamino)ethylimino)methyl)naphthalene-2-ol (LH)

In a round bottomed flask, 0.688 g (4 mmol) of 2-hydroxy-napthaldehyde was dissolved in 25 mL of methanol. Another solution of 0.408 g (4 mmol) of N,N-dimethylpropanediamine in 25 mL methanol was added dropwise to the former. The solution mixture turned from pink to light yellow. Then the reaction mixture was refluxed for 5 h with constant stirring. The resulting solution was subjected to evaporation under vacuum to give a deep brown viscous liquid. Yield-crude: 73.5%. The liquid mass was purified in silica using 1:1 hexane-CH₂Cl₂ mixture as eluent. Yield-pure: 50.5%. NMR (¹H, 400 MHz, CDCl₃), δ (ppm): 8.1-7.0 (6H, ArH), 6.1 (1H, ArCH), 5.0 (s, 1H, O-H), 2.0-2.1 (6H, CH₂), 1.7 (m, 6H, CH₃). NMR (¹3C, 100 MHz, CDCl₃) δ (ppm): 135.0 (C_a), 132.7 (C_k), 132.2 (C_j), 131.6 (C_g), 130.4 (C_i), 130.0 (C_d), 129.58 (C_f), 129.4 (C_e), 129.1 (C_c), 124.7 (C_b), 56.8 (C₁), 37.1 (C_n), 32.7 (C_o), 30.9 (C_p), 29.7 (C_m). Notation for NMR is given in figure S1. FTIR (KBr) (v_{max} cm⁻¹): 3414(s, br OH), 2943 (s board, C-H of -N(CH₃),

1635 (m, C=N), 1546 (w, C_{ar}-O), 1041 (s, C-N). MS: m/z 256 {LH}. $\lambda_{max}/nm (\epsilon/M^{-1} \text{ cm}^{-1})$: 305(5680), 399(4312), 418(4443).

2.6. Synthesis of the complexes

Complex 1, $[MnL_2](ClO_4)$: In a round bottomed flask, 0.502 g ligand LH (2 mmol) was dissolved in 25 mL of methanol with the subsequent addition of 0.202 g (2 mmol) of Et₃N. Then a methanolic solution of 0.363 g (1 mmol) Mn(ClO₄)₂ was added dropwise into the ligand solution. The mixture was refluxed for another 6 h with constant stirring. A deep-brown solid appeared which was filtered and washed with methanol (5 mL) and diethyl ether (5 mL). Yield: 348 mg (52.4%). X-ray quality single crystals were obtained by evaporation of acetronitrile solution of complex 1. ESI-MS(+ve) (m/z): 565.4 ([MnL₂]⁺); FTIR (KBr, v/cm^{-1'}): 2993(w, br), 1597(s) ($v_{C=N}$), 1539(m) ($v_{Ar-C=C}$), 1454(m), 1336(m), 1255(w), 1067(s), 983(w), 833(w), 759(m); Anal. Calc. for C₃₂H₃₈N₄O₆ClMn: C, 57.83; H, 5.72; N, 8.43. Found: C, 57.56; H, 5.44; N, 8.76. λ_{max}/nm ($\varepsilon/M^{-1}cm^{-1}$): 314 (9263), 336 (9166), 454 (1913), 531 (392), 575 (329).

Complex **2**, [CuL₂]: The complex was prepared in similar method described as that of complex **1** using Cu(ClO₄)₂·6H₂O as the metal precursor. In this case, deep-green crystalline solid was obtained. Yield: 317 mg (55.23%). Single-crystals were obtained from the evaporation of a methanol solution of the complex. ESI-MS(+ve) (m/z): 672.70 ([Cu(LH)₂ClO₄]⁺); FTIR (KBr, ν /cm⁻¹): 2926(w, br), 1614(s) (ν _{C=N}), 1532(w), 1462(m), 1369(m), 1255(w), 1184(w), 1060(w), 968(w), 827(w), 750(m), 489(w); Anal. Calc. for C₃₂H₃₈N₄O₂Cu: C, 66.89; H, 6.62; N, 9.75. Found: C, 67.12; H, 6.47; N, 9.44. λ _{max}/nm (ε /M⁻¹cm⁻¹): 323 (11423), 384 (4912), 402 (4287), 611 (155).

2.7. X ray crystallography

Single-crystals of complexes 1 and 2 were obtained from the evaporation of acetonitrile and methanol solutions, respectively. In each case, a crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed at 200 (for 1) and 293 (for 2) K. The measurements were made either on an Enraf Nonius Kappa CCD diffractometer with Mo-K α (0.71073 Å for 1) or an Agilent Supernova X-calibur Eos CCD detector with graphite-monochromatic Cu-K α (1.54184 Å, for 2) radiation. Crystal data and structure refinement parameters are summarized in table 1. The structures were solved by direct

methods (SIR2004) [25] and refined on F² using the full-matrix least-squares method, using SHELXL-97 [26]. Non-hydrogen atoms were anisotropically refined. Hydrogens were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w(Fo^2-Fc^2)^2]$ (w = 1 / $[\sigma^2(Fo^2) + (aP)^2 + bP]$), where P = $(Max(Fo^2,0) + 2Fc^2) / 3$ with $\sigma^2(Fo^2)$ from counting statistics. The function *R1* and *wR2* were $(\Sigma ||Fo|-|Fc||) / \Sigma |Fo|$ and $[\Sigma w(Fo^2-Fc^2)^2 / \Sigma (wFo^4)]1/2$, respectively. Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1561130 (1) and 1561131 (2). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + (44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

2.8. Computational details

The calculations were performed by density functional theory (DFT) implemented in GAUSSIAN09 [27]. The ligand and the complexes were optimized using B3LYP hybrid functional and 6-31g(d) basis set for hydrogen, carbon, oxygen and nitrogen and LANL2DZ basis set for metals. The electronic spectra were simulated by Time-Dependent Density Functional Theory (TD-DFT). Computational studies were carried out in DMSO solvent using Polarizable Continuum Model (PCM) implemented in Gaussian 09.

3. Results and discussion

3.1. Synthesis

The ligand was synthesized by simple Schiff base condensation reaction. The ligand was liquid oil at room temperature and the crude product contained starting materials, particularly the amine. The pure compound was obtained from a 1:1 hexane:dichloromethane mixture in silica column. Both complexes 1 and 2 were obtained in good yield from the reaction between respective metal perchlorates and the protic ligand in the presence of triethyl amine under refluxing condition in methanol.

3.2. Description of the X-ray crystal structures

Representative molecular structures along with the atom numbering scheme for complexes 1 and 2 are depicted in figure 3.

 $[MnL_2](ClO_4)$: Complex 1 crystallizes in $P2_1/n$ space group. Although the crystal structure gives a formula of $[(L_2)Mn]_2(ClO_4)(MeCN)$, which implies a mixed-valent Mn(II/III) formulation analysis of the Mn-O and Mn-N bond lengths suggests the metal to be present in +3 oxidation state. This is further supported by the fact that the structures of all four cations are essentially identical. Despite several attempts, we could not grow good-quality single-crystals which led us to report the present crystal structure for this molecule. The ligand coordinates to the metal in a tridentate facial manner through phenolic-O, imine-N and amine-N atoms. Thus, two ligands fulfill the coordination sphere leading to an octahedral geometry around the metal center. In the unit cell, there are four different Mn-residues, besides there are disordered perchlorate ions and MeCN molecule. For any given Mn-residue, half of the molecule is symmetric with the other half. In the unit cell, the MnL₂ moiety has occupancy 0.5, whereas perchlorate anions have full occupancy. As the ligand is mono-deprotonated, the charge of manganese can be assigned to +3. The Mn^{III}-O and Mn^{III}-N bond lengths are comparable to a previous report [28]. The equatorial plane is formed by the imine nitrogen atoms (N1A and NiAa) and phenolic oxygen atoms (O1A and O1Aa), whereas the axial sites are occupied by the amine nitrogen atoms (N2A and N2Aa). Equatorial Mn-O and Mn-N distances are 1.858 Å and 2.02 Å, respectively. Axial Mn-N distances (2.45 Å) are much longer than the equatorial distances, indicating the presence of strong Jahn-Teller elongation along the Mn-N_{imine} bonds. Except two cis angles (80.91°) N1A-Mn1A-N2A and N1A a-Mn1A-N2A a, all the cis and trans angles are very close to the ideal values. High electron density of 1.79 e A⁻³ in complex 1 is due to perchlorate ion which is loosely bound to the crystal structure. The percholate ion in complex 1 is only loosely bound in the crystal structure. Thus, the oxygen atoms of this ion show strong displacement with high residual electron density in their close environment.

[CuL₂]: Green-colored complex **2** crystallizes in monoclinic $P2_1/c$ (No. 14) space group having four molecules in the unit cell. Complex **2** possesses an interesting geometrical feature. Considering the usual Cu-N and Cu-O covalent bond distances, the molecule adopts distorted square planar geometry. All *cis* angles are very close to 90° (89.02° - 91.16°). One *trans* angle O1-Cu1-O2 (162.74°) deviates from the standard value whereas the other (N1-Cu1-N3 = 178.90°) is in close proximity to 180°. Value of four-coordinate geometry index τ_4 ($\tau_4 = [360^\circ - (\alpha+\beta)]/141$, α and β are two largest angles) for complex **2** is 0.13. This suggests the structure is close to perfect square planar (For perfect geometry: $\tau_4 = 0$ for square planar and 1 for

9

tetrahedral). However this description is not absolutely correct if we consider the terminal -NMe₂ groups of the ligands. C-C bonds connecting the imine and amine functionality of the ligands rotate in such a way that one -NMe₂ group comes very close to the Cu center while the other moves apart a large distance from Cu. Therefore, the former -NMe₂ group can interact with metal. The Cu1-N4 bond distance (2.511 Å) is longer than the covalent Cu-N distance but shorter than the sum of their van der Waals radii. The N atom is also placed in such a position that it can provide a square pyramidal ligand environment around Cu. In this second type of geometry, all the bonds (*viz.*, Cu-N and Cu-O) are similar to the literature except Cu-N4, the axial bond which is longer to some extent. All the *cis* angles containing the axial Cu1-N4 bond deviate from regular value of 90°. The values are in the range 82.73° to 105.22°.

3.3. Electronic spectra

Electronic spectra of both complexes were measured in acetonitrile medium. Complex 1 displays two high-energy ligand-based transition bands at 314 nm ($\varepsilon = 9263 \text{ M}^{-1}\text{cm}^{-1}$) and 336 nm ($\varepsilon =$ 9166 M⁻¹cm⁻¹) (figure 4a). One band of moderate intensity is observed at 454 nm ($\varepsilon =$ 1913 M⁻¹cm⁻¹). This latter band is attributable to LMCT transition presumably occurring as phenolic-O \rightarrow Mn^{III} ion. In the low-energy region, low-intensity bands are observed at 531 nm ($\varepsilon = 392 \text{ M}^{-1}\text{cm}^{-1}$) and 575 nm ($\varepsilon = 329 \text{ M}^{-1}\text{cm}^{-1}$). Absorptivity at these band positions and comparison with the existing report [29] clearly suggests ligand-field transitions. Comparatively high value of extinction coefficient may be due to intensity borrowing from the nearby allowed LMCT transitions. Presence of two such d-d bands clearly indicates the existence of fairly strong tetragonal distortion in the octahedral ligand field.

In case of complex **2**, the ligand-centered transition band is observed at 323 nm ($\varepsilon = 11423 \text{ M}^{-1}\text{cm}^{-1}$). Absorptions of medium intensity are observed at 384 nm ($\varepsilon = 4912 \text{ M}^{-1}\text{cm}^{-1}$) and 402 nm ($\varepsilon = 4287 \text{ M}^{-1}\text{cm}^{-1}$) (figure 4b). These two bands are assigned to be phenolic-O to Cu^{II} transitions. The low energy d-d transition band is observed at 611 nm ($\varepsilon = 155 \text{ M}^{-1} \text{ cm}^{-1}$). All these transitions observed are in accordance to the earlier reports [30].

3.4. FTIR spectra

FTIR spectra of the ligand and the complexes are given in SI (figures S7-S9). FTIR spectrum of the ligand shows a strong broad band at 3414 cm⁻¹ attributed to the stretching of the O-H bond.

Another strong band at 2943 cm⁻¹ may be due to stretching of the C-H bond of $-N(CH_3)_2$. Stretching of the C=N bond is indicated by a moderately strong band at 1635 cm⁻¹. In both complexes, the broad band at 3414 cm⁻¹ in the ligand is completely vanished, indicating deprotonation of the -OH functionality during coordination to the metals. Moreover, the $v_{C=N}$ band in the ligand at 1635 cm⁻¹ shifts to lower energy in both complexes at 1597 cm⁻¹ and 1614 cm⁻¹ for **1** and **2**, respectively. This also supports the coordination through the imine-N atom in the ligand.

3.5. Magnetic properties

Experimentally observed magnetic moment of complex 1 is 4.878 BM. It suggests the presence of four unpaired electrons usually obtained in the case of high spin d^4 electronic configuration of Mn(III) ion in complex 1. Magnetic moment for complex 2 was 1.8386 BM. This also confirms a Cu(II) ion with d^9 electronic configuration in complex 2.

3.6. DFT Study

Quantum chemical calculation using DFT with the B3LYP hybrid functional was performed to get the optimized geometry of the ligand and complexes **1** and **2** in acetonitrile. Table 2 summarizes the energy and composition of the frontier molecular orbitals of the complexes while the metrical parameters of the optimized geometry and crystal geometry for both **1** and **2** have been compared in tables 3 and 4, respectively. Similarity among the parameters for crystal and optimized structure suggests that the optimization process was suitable for this type of molecules. Composition of frontier molecular orbitals for complex **1** shows that HOMO-3, LUMO and LUMO+3 possess major contribution from Mn, HOMO-2 is equally contributed by Mn and the ligand while HOMO-1, HOMO, LUMO+1 and LUMO+2 are majorly occupied by ligand electrons. In complex **2**, only LUMO has significant contribution of metal copper, while the rest of the MOs in the range HOMO-3 to LUMO+3 are exclusively contributed by the ligands. Optimized structures of the complexes are displayed in figure S18. According to single-crystal X-ray study, complex **2** can possess either the square planar or the square pyramidal geometry. Therefore both structures were optimized which shows that the square pyramid is slightly more stable than the other geometry.

3.7. TDDFT Analysis

UV-visible spectra of the complexes are well reproduced with TDDFT analysis. Vertical transitions are shown in figure 5 (complex 1) and figure 6 (complex 2), while the band assignments are displayed in table 5.

In complex 1, high-energy intraligand transition band at 313 nm in the experimental spectrum is observed at 304 nm in the calculated spectrum. The transition band at 338 nm corresponds to the transition at 348 nm in the theoretical spectrum. Analyzing the composition of the participating orbitals, this transition may be interpreted as mixed intra-ligand and MLCT nature. Experimental band at 454 nm is observed at 460 nm in the simulated spectrum and corresponds to HOMO-4 \rightarrow LUMO transition. This transition band is mostly of LMCT nature. There are two transition bands in the experimental spectrum at 531 nm and 575 nm, absorptivity of which shows to be d-d transitions. A careful inspection in the calculated spectrum enabled us to find those d-d transitions at 524 nm (HOMO-3 \rightarrow LUMO) and 623 nm (HOMO-3 \rightarrow LUMO+3). Although there is some ligand-character, these last two transitions are mostly of d-d nature.

In complex 2 the intraligand transition band at 310 nm is observed at 288 nm in the calculated spectrum and corresponds to the HOMO(B) \rightarrow LUMO+3(B) excitation. Two LMCT transition bands at 384 nm and 400 nm appear at 377 nm (HOMO-6(B) \rightarrow LUMO(B)) and 394 nm (HOMO-3(B) \rightarrow LUMO(B)) in the theoretical spectrum. The d-d transition band at 610 nm in the experimental spectrum is also supported by the simulated spectrum at 538 nm (HOMO-14(B) \rightarrow LUMO(B)), where significant d-d nature is observed along with the LMCT character.

3.8. Catecholase activity by complexes 1 and 2

For the kinetic study, initial rate method was followed. To determine the dependence of rate on the substrate concentration, solution of fixed concentration $(1 \times 10^{-5} \text{ M})$ of catalyst (complex 1 or complex 2) was treated with increasing concentration of substrate 3,5-DTBCH₂ (20 to 200 eq) in a pseudo-first order environment under aerobic condition at 25 °C. Time-dependent spectral profiles are displayed in figure 1 (1 in MeCN), figure S11 (1 in MeOH), figure S13 (2 in MeOH) and figure S15 (2 in MeCN). The rate constant of catalyst-substrate mixture was determined from the difference in absorbance with increasing time. A linear relationship was obtained

between the differences in absorbance *versus* time plot. The slope of initial rate of reaction *versus* concentration of substrate plot shows a rate-saturation kinetic (figure 7a for 1 in MeCN, figure S12a for 1 in MeOH and figure S14a for 2 in MeOH). The dependence of the saturation rate on the concentration of substrate can be treated with the Michaelis-Menten approach. The treatment on the basis of the Michaelis-Menten approach was applied by means of Lineweaver-Burk plot (figure 7b for 1 in MeCN, figure S12b for 1 in MeOH and figure S14b for 2 in MeOH) to calculate all the kinetic parameters such as K_M , V_{max} and K_{cat} . Kinetic data are given in table 6. The turn-over number (TON) of the complex was calculated by dividing the value of V_{max} by the complex concentration. From the experimental data, Michaelis binding constant (K_m) were 2.13×10^{-5} M and 2.53×10^{-5} M for 1 in acetonitrile and methanol, respectively, and 9.87×10^{-2} M for 2 in methanol. However, 1 shows better catalytic activity than 2. Complex 1 has k_{cat} value of 684.24 h⁻¹ in acetonitrile and 547.45 h⁻¹ in MeOH, whereas 2 has slightly lower k_{cat} value (374.85 h⁻¹) in MeOH.

There are two different mechanisms for the catecholase activity where H_2O and H_2O_2 are formed as by-products. To get an idea about the possible pathway, the catalytic reaction was performed in the presence of potassium iodide. The procedure has been explained in the Experimental section. Production of hydrogen peroxide was confirmed by the oxidation of I⁻ to I_3 ; the latter was detected by the appearance of peak at 353 nm in the UV-vis spectrum. Formation of hydrogen peroxide was detected for both complexes 1 (figure 8) and 2 (figure S16).

Therefore, the results obtained may be summarized as: complex **1** has less activity than complex **2** in acetonitrile and methanol. Further, complex **2** is almost inactive in acetonitrile. A possible reason for the lower catalytic activity of complex **2** may be due to its structure. As a mimic of natural catecholase enzyme, binuclear copper complexes usually exhibit high turnover number following the mechanism (3,7) which includes the formation of catecholase-bridged binuclear copper core. Complex **2** is mononuclear in nature with an almost square planar geometry that cannot stabilize the catecholase-bridged intermadiates. Still complex **2** has higher activity than the other mononuclear copper complexes reported earlier [31, 32]. Inactivity of complex **2** in acetonitrile may be due to the stabilization of the reduced Cu^I species by acetonitrile which restricts the vacant axial sides to make available to the substrate. This type of stabilization of Cu^I species has also been reported by other groups [33]. Although manganese is not the part of the native catecholase enzyme, manganese complexes in different oxidation states

of the metal show excellent catalytic catecholase activity due to its large redox window. In the present case, the higher activity of Mn^{III} species (complex 1) may also be due to its electrochemical properties. Mn^{III/II} couple (complex 1) is observed at higher potential than the Cu^{II/I} (complex 2) couple, *i.e.* formation of the reduced species is more feasible in complex 1.

3.9. *Phenoxazinone synthase like activity by complex 2*

For this kinetic study, initial rate method was also followed using *o*-amino phenol (OAPH) as substrate. Both complexes **1** and **2** were employed as catalysts. Only complex **2** exhibited significant catalytic activity whereas complex **1** was inactive. Time dependent spectral profile (figure 2), rate saturation kinetics (figure 9a) and Lineweaver-Burk plot (figure 9b) for the oxidation of *o*-aminophenol are shown below. The TON of the complex was calculated by dividing the value of V_{max} ($V_{max} = 8.84 \times 10^{-4}$ M h⁻¹) by the complex concentration. From the experimental data, Michaelis binding constant (K_m) was 8.02×10^{-4} M and k_{cat} value was 74.23 h⁻¹.

In order to get an idea about the substrate-catalyst interaction we study the possible complex-substrate intermediates by monitoring the ESI-MS spectra of both complexes mixed with the respective substrates, *i.e.* 3,5-DTBCH₂ and 2-aminophenol in 1:100 ratio. The spectrum was recorded within 15 min of mixing in methanol. After addition of 3,5-DTBCH₂ to the solutions of complex 1 (figure 10), some new peaks were generated. The new peaks can be assigned as m/z 530.25 [Mn^{fll}Mn^{ll}L(CH₃O)(ClO₄)(Cl)]⁺, m/z 583.13 [Mn^{III}L₂H₂O]⁺, m/z 682.29 [Mn^{fll}Mn^{II}L₂(CH₃O)₂]⁺, m/z 716.30 [Mn^{III}Mn^{III}L₂(CH₃O)₂(Cl)], m/z 773.02 [Mn^{III}Mn^{III}L(3,5-DTBC-H)(ClO₄)(Cl)₂(H₂O)]⁺, m/z 919.75 [Mn^{III}Mn^{III}L(3,5-DTBC)₂(HO)(OOH)+2Na⁺]⁺, m/z 958.80 [Mn^{III}Mn^{III}L₂(3,5-DTBC-H)(ClO₄)(ClO₄)(H₂O)]⁺ and m/z 1083.09 [Mn^{III}Mn^{III}L(3,5-DTBC-H)₂+Na⁺],

For complex **2** and 3,5-DTBCH₂ mixture, the peaks in the mass spectrum (figure S17) can be correlated as m/z 538.08 $[Cu^{II}Cu^{I}L(ClO_4)(Cl)+Na^+]^+$, m/z 751.83 $[Cu_2^{II}L(3,5-DTBC-H)(CH_3OH)(H_2O)(ClO_4)]^+$, m/z 781.00 $[Cu_2^{I}L(3,5-DTBCH_2)(ClO_4)(OOH)+2Na^+]^+$, m/z 816.97 $[Cu_2^{II}L(3,5-DTBC-H)(ClO_4)(Cl)_2+2Na^+]^+$, m/z 849.11 $[Cu_2^{II}L(3,5-DTBC-H)(ClO_4)(ClO_4)+2Na^+]^+$, m/z 849.11 $[Cu_2^{II}L_2(3,5-DTBC-H)]^+$, m/z 1035.96 $[Cu^{II}Cu^{I}L_2(3,5-DTBC-H)(Cl)(ClO_4)+2Na^+]^+$, m/z 1101.01 $[Cu^{II}Cu^{I}L_2(3,5-DTBC-H)_2+Na^+]^+$ and m/z 1134.01 $[Cu^{II}Cu^{I}L_2(3,5-DTBC-H)(3,5-DTBC-H_2)(CH_3OH)+Na^+]^+$.

Analysis of the above mentioned peaks suggests, although the catalyst is a mononuclear copper/manganese complex, in presence of substrate, the former undergoes the dissociation of one ligand to form the species ML⁺ which further combines with other ligands/substrates/solvents *etc.* in a number of ways, mostly forming a binuclear species. Here we have been successful in interpreting almost all the peaks produced during the catalytic reaction. In this ESI-MS study, the most significant peak at m/z 781.00 suggests the formation of an intermediate having a hydroperoxo species that indicates the production of hydrogen peroxide during the reaction. Production of hydrogen peroxide has also been observed experimentally. However the low rate in comparison to the binuclear species is also expected as the distance between the copper centers is not fixed like binuclear complexes.

The same procedure is applied for the study of phenoxazinone synthase-like activity by complex **2**. ESIMS(+ve) spectrum of the methanol solution of the mixture of 2-amino phenol and complex **2** (figure S17) was recorded after 15 min of mixing. Three major peaks obtained in this case indicate formation of the intermediates as mentioned here: m/z 744.12 [Cu₂L₂(OAP)]⁺, m/z 875.11 [Cu^{II}₂L₂(OAP)₂+Na⁺] and m/z 1024.03 [Cu^{II}Cu^{II}L₂(OAP)₃(H₂O)+2Na⁺]⁺. Just like catecholase activity, here we also found peaks consisting of binuclear species.

3.10. Electrochemistry

Cyclic voltammograms (figure 11) were measured in acetonitrile medium for ligand and complexes at ambient temperature using TEAP as supporting electrolyte. The measured potentials were referenced *versus* ferrocinium/ferrocene (Fc⁺/Fc) couple. Both complexes as well as the ligand show one quasi-reversible peak on cathodic scan in the range of -1.00 to-1.22 V. Complex 1 shows one more irreversible peak at -0.44 V, which may be due to reduction of Mn(III) to Mn(II). One irreversible cathodic wave at -0.68 V displayed by complex 2 may be due to Cu(II)/Cu(I) reduction. Scanning on the anodic side shows a peak at 0.72 V for ligand and at 0.72 V and 0.66 V for complex 1 and complex 2, respectively, which may be due to the oxidation of phenolic -OH to the phenoxyl radical. In the anodic scan, the reversible anodic wave at 1.525 V depicts Mn^{III/IV} couple. Complex 2 on the anodic side shows another peak at 1.02 V, which may be the phenolic -OH to the phenoxyl radical oxidation of the second ligand.

4. Conclusion

Two mononuclear Schiff base complexes of manganese and copper have been synthesized and well characterized by spectroscopy and single-crystal X-ray diffraction techniques. Both complexes are active in oxidizing catechol with a moderate value of k_{cat} . Possible intermediates in the catalytic reaction have been interpreted on the basis of the ESI-MS techniques. Formation of the hydroperoxo species has been manifested from the analysis of the mass spectroscopy data. Production of hydrogen peroxide has also been monitored during the catalysis by iodometric titration. Copper complex is active for phenoxazinone synthase activity. In this case, we were also able to explain the observed peaks in the mass spectrum. All the processes show the involvement of several binuclear species in the catalytic cycle.

Supplementary data accompanies the on-line manuscript.

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	Complex 1	Complex 2
Empirical formula	2(C ₃₂ H ₃₈ MnN ₄ O ₂) ClO ₄ , CH ₃ CN	$C_{32}H_{38}CuN_4O_2$
Formula weight	1271.71	574.20
Temperature/K	200	293
Crystal system	Monoclinic	Monoclinic
Space group	P 2 ₁ /n	$P2_1/c$ (No. 14)
a/Å	18.1890(9)	17.731(2)
b/Å	20.3144(7)	15.664(2)
c/Å	19.2340(7)	10.5388(7)
α/°	90	90
β/°	100.008(2)	92.609(8)
$\gamma/^{\circ}$	90	90
Volume/Å ³	6998.8(5)	2924.0(5)
Ζ	4	4
$\rho_{calc}g/cm^3$	1.2069(1)	1.304
µ/mm ⁻¹	0.455	1.323
F(000)	2676.0	1212
Crystal size/mm ³	0.04×0.06×0.08	0.21×0.26×0.27
Radiation	MoKα ($\lambda = 0.71073$)	$CuK\alpha$ ($\lambda = 1.54184$)
20 range for data collection/°	1.7 to 31.6	3.8 to 70.8
Dataset	-26: 26; -29: 29; -28: 27	-16: 21; -18: 14; -12: 8
Tot., Uniq. Data, R(int)	162430, 23318, 0.154	11014, 5382, 0.062
Reflections collected	162430	11014
Independent reflections	23318	5382
Nref, Npar	23318, 854	5382,357
Goodness-of-fit on F ²	2.26=s	1.03
Observed Data [I > 2.0 sigma(I)]	7300	2889
R, wR2, S	0.1486, 0.2961, 2.26	0.0726, 0.2332, 1.03
$w = 1/[\sigma^2(Fo^2) + (0.0999P)^2]$	where $P=(Fo^2+2Fc^2)/3$	where $P=(Fo^2+2Fc^2)/3$
Largest diff. peak/hole /e Å-3	1.79/-0.57	0.43/-0.67
Max. and Av. Shift/Err	0.00, 0.00	0.02, 0.00

Table 1. Crystal data and structure refinement parameters for complexes 1 and 2.

Complex 1								
Energy (eV)	-6.57	-6.26	-6.1	-5.89	-3.29	-2.06	-1.97	-1.34
Atom/ligand %	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3
Mn	62	50	23	0	73	0	7	71
Ligand	38	50	77	100	27	100	93	29
Complex 2								$\langle \rangle$
Energy (eV)	-6.15	-5.81	-5.35	-5.27	2.48	-1.5	-1.46	-0.36
Atom/ligand %	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3
Cu	5	0	2	2	60	1		2
Ligand	95	100	98	98	40	99	99	98

Table 2. Compositions and energies of the frontier molecular orbitals of complexes 1 and 2.

Table 3. Bond length and bond distances of the crystal geometry and optimized geometry for complex 1.

	Crystal geometry	Optimized geometry		
	Bond/	Distance (Å)	Bond/	Distance (Å)
	Mn1A-O1A	1.858(4)	(1-2)	1.86981
	Mn1A-N1A	2.022(4)	(1-21)	1.9905
	Mn1A-N2A	2.449(5)	(1-31)	2.2767
	Mn1A-O1A_a	1.858(4)	(1-40)	1.8698
	Mn1A-N1A_a	2.022(4)	(1-59)	1.9905
	Mn1A-N2A_a	2.449(5)	(1-69)	2.27666
	Angle	Angle (°)	Angle	Angle (°)
	O1A-Mn1A-N1A	88.62(18)	(2-1-21)	88.711
	O1A-Mn1A-N2A	90.82(17)	(2-1-31)	89.014
	O1A-Mn1A-O1A_a	180.00	(2-1-40)	179.98
	O1A-Mn1A-N1A_a	91.38(18)	(2-1-59)	91.29
	O1A-Mn1A-N2A_a	89.19(17)	(2-1-69)	90.98
	N1A-Mn1A-N2A	80.91(17)	(21-1-31)	84.745
(N1A-Mn1A-O1A_a	91.38(18)	(21-1-40)	91.289
	N1A-Mn1A-N1A_a	180.00	(21-1-59)	179.998
(C <	N1A-Mn1A-N2A_a	99.09(17)	(21-1-69)	95.243
\sim	N2A-Mn1A-O1A_a	89.19(17)	(31-1-40)	90.965
	N2A-Mn1A-N1A_a	99.09(17)	(31-1-59)	95.257
	N2A-Mn1A-N2A_a	180.00	(31-1-69)	179.988
\vee	O1A_a-Mn1A-N1A_a	88.62(18)	(40-1-59)	88.71
	O1A_a-Mn1A-N2A_a	90.82(17)	(40-1-69)	89.037
	N1A_a-Mn1A-N2A_a	80.91(17)	(59-1-69)	84.755

Crystal geometry		Optimized geo	ometry
Bond/	Distance (Å) Bond/	Distance (Å)
Cu(1)-O(1)	1.908(3)	(1-3)	1.99782
Cu(1)-O(2)	1.931(4)	(1-2)	1.97384
Cu(1)-N(1)	1.991(4)	(1-5)	2.04129
Cu(1)-N(3)	1.979(4)	(1-4)	2.02812
Cu(1)-N(4)	2.511(5)	(1-6)	2.49889
Angle	Angle (°)	Angle	Angle (°)
O(1)-Cu(1)-O(2)	162.74(19)	(3-1-2)	164.332
O(1)-Cu(1)-N(1)	89.02(17)	(3-1-5)	91.444
O(1)-Cu(1)-N(3)	89.92(15)	(3-1-4)	87.637
O(1)-Cu(1)-N(4)	105.22(17)	(3-1-6)	101.264
O(2)-Cu(1)-N(1)	89.77(17)	(2-1-5)	88.669
O(2)-Cu(1)-N(3)	91.16(16)	(2-1-4)	89.803
O(2)-Cu(1)-N(4)	92.00(16)	(2-1-6)	93.941
N(1)-Cu(1)-N(3)	178.90(16)	(5-1-4)	170.977
N(1)-Cu(1)-N(4)	97.83(17)	(5-1-6)	103.376
N(3)-Cu(1)-N(4)	82.73(17)	(4-1-6)	85.600

Table 4. Bond length and bond distances of the crystal geometry and optimized geometry for complex **2**.

Table 5. Vertical excitations with band position, oscillator strength and character assignment for complexes 1 and 2.

 $\langle \rangle$

Complex	Experimental wavelength (nm)	Wavelength obtained from TD-DFT (nm)	Oscillator strength (f)	Contributing orbital (s)	Percentage (%)	Transition assignment
1	260	257.37(0.1025)	0.102	HOMO->LUMO +6	(37%)	Intra ligand
	313	303.99(0.1547)	0.155	HOMO-4->LUMO+2	(66%)	Intra ligand
	338	348.39(0.57)	0.57	HOMO-2->LUMO+1	(60%)	Intra ligand +MLCT
	454	459.81(0.0209)	0.021	HOMO-4-> LUMO	(97%)	LMCT
	531	524.68(0.000)	0.00	HOMO-3->LUMO		d-d
	575	623.78(0.000)	0.00	HOMO-3->LUMO+3		d-d
2	310	288.44(0.2338)	0.233	HOMO(B)-> LUMO+3(B)	(19%)	Intra ligand
	384	377.39(0.0795)	0.079	HOMO-6(B)->LUMO(B)	19%)	LMCT
\sim	400	394.86(0.0628)	0.063	HOMO-3(B)->LUMO(B)	(43%)	LMCT
1	610	538.098(0.0105)	0.010	HOMO-14(B)->LUMO(B)	(16%)	d-d + LMCT
	v / ~					

Complex	Solvent	$V_{max}(M h^{-1})$	$K_m(M)$	$k_{cat}(h^{-1})$	$k_{cat}/K_m(M^{-1}h^{-1})$
1	MeOH	6.78×10 ⁻³	2.53×10-5	547.45	2.16×10 ⁷
	MeCN	8.47×10-3	2.13×10-5	6.8424×10 ²	3.21×10 ⁷
2	MeOH	4.46×10-3	9.87×10-2	3.75×10^{2}	3.79×10 ³

Table 6. Kinetic parameters for the oxidation of 3,5-DTBC catalyzed by complexes 1 and 2.

Figure captions

Figure 1. Changes in spectral pattern for complex 1 after addition of 3,5-DTBCH₂ up to 3 h in acetonitrile.

Figure 2. Changes in spectral pattern in complex 2 after addition of OAPH up to 3 h in MeOH.

Figure 3. ORTEP diagram (at 30% probability level) of $[MnL_2]^+$ (1⁺) and $[CuL_2]$ (2).

Figure 4. Electronic spectra (acetonitrile medium) of (a) complex 1 and (b) complex 2.

Figure 5. Electronic transitions in complex 1 in DMSO solution.

Figure 6. Electronic transitions in complex 2 in DMSO solution.

Figure 7. (a) Rate *versus* substrate concentration plot for the oxidation of 3,5-DTBCH₂ in acetonitrile catalyzed by complex 1 at 25 °C. (b) Lineweaver-Burk plot for the oxidation of 3,5-DTBCH₂.

Figure 8. Electronic spectrum of I_{3} (catecholase activity by complex 1).

Figure 9. (a) Rate *versus* substrate concentration plot for the oxidation of o-aminophenol in methanol catalyzed by complex 2 at 25 °C. (b) Lineweaver-Burk plot for the oxidation of o-aminophenol.

Figure 10. ESI mass spectrum (+ve) of 1:100 mixture of complex 1 and 3,5-DTBCH₂ in methanol recorded after 15 min of mixing.

Figure 11. Cyclic voltammograms of ligand, complex 1 and complex 2 recorded in acetonitrile solution with TEAP supporting electrolyte and glassy carbon working electrode at a scan rate 100 mV/s^{-1} .











