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Metal complexes of perimidine and Schiff base ligands bearing both naphthalene and chromone moieties: synthesis and catalytic activity

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A new perimidine and a new Schiff base compounds were prepared by the condensation of visnagin derivative containing a carbonyl group with 1,8-diaminonaphthalene (1,8-DAN) and 2,3-diaminonaphthalene (2,3-DAN), respectively. Metal complexes of these chromone type ligands were also isolated by using the Cu(II) and Fe(II) ions. The synthesized compounds were characterized by UV-Vis, FT-IR, ^{1}H&^{13}C NMR, mass spectrometry, elemental and AAS analyses and also magnetic susceptibility and molar conductivity measurements. Catecholase activity of the complexes was investigated in methanol medium using 3,5-di-*tert*-butylcatechol (3,5-DTBC) as model substrate and the results showed that all complexes are active for catalyzing the oxidation of 3,5-DTBC to the corresponding quinone with first order reaction kinetics. Fe(II) complex of Schiff base ligand has been found to exhibit the best catecholase activity with a turnover number value of 890.1 h^{-1}.

Keywords: Schiff base, perimidine, metal complexes, catecholase activity

1.INTRODUCTION

Coordination chemistry has received a great deal of attention for a long time of period with the synthesis and characterization of a large number of transition metal complexes with various ligand systems containing nitrogen and oxygen donor atoms owing to their wide applications in various fields such as biological [1], analytical [2], material science [3] and catalysis [4]. Among these ligand systems, while Schiff bases have been studied extensively for decades [5,6], in recent years considerable attention has been drawn to perimidines as they have electron affinity, reduction potential and also exhibit diverse range of biological activities [7]. Synthetic method for the preparation of perimidines is the condensation reaction of 1,8-diaminonaphthalene (1,8-DAN) with various carbonyl groups, which requires a special reagent or force reaction conditions. Usually the product of this condensation is Schiff base, however when 1,8-DAN is used as primer diamine it can be obtained perimidine or its derivatives [8]. Although it is well-documented that metal complexes of salen type Schiff bases can be easily prepared [9], only a few studies dealt with metal complexes of perimidine derivatives in which the metal is bound to one nitrogen and to another donor atom introduced on a ring present on C-2 [10-14].

In this paper, we present the synthesis of a Schiff base and a 2,3-dihydro-1*H*-perimidine derivative obtained from the condensation of visnagin based carbonyl compound with 2,3-diaminonaphthalene (2,3-DAN) and 1,8-diaminonaphthalene (1,8-DAN), respectively. The synthesis, characterization and catecholase-like activity investigations of their mononuclear copper (II) and iron(II) complexes were also reported. Catecholase-like activity of metal complexes via oxidation of 3,5-di-*tert*-buthylcatechol (3,5-DTBC) to 3,5-di-*tert*-buthylquinone (3,5-DTBQ) was performed.

2.EXPERIMENTAL

2.1. Material

2,3-diaminonaphthalene, 1,8-diaminonaphthalene, copper(II) chloride ($CuCl_2$), iron(II) chloride tetrahydrate ($FeCl_2.4H_2O$), hydrogen peroxide (H_2O_2) solution (30 wt. % in H_2O), 3,5-di-*tert*-butylcatechol (3,5-DTBC) were purchased from Sigma-Aldrich and used without further purification. Solvents for the synthesis and analysis were commercially available and used as received.

2.2. Physical measurements

Melting points were determined on a Thermo Scientific 9100 apparatus using open capillary and the reported values are uncorrected. Elemental analyses (carbon, hydrogen and nitrogen) were carried out using a THERMO SCIENTIFIC Flash 2000 CHNS/O Analyzer, and the results agree with the calculated values. The FT-IR spectra of the samples were recorded on a Perkin Elmer Spectrum Two with U-ATR FTIR spectrometer in the wavenumber range of 4000–400 cm^{-1}. Electronic spectra were recorded in a OPTIZENα UV-Vis Spectrometer. ^{1}H NMR (600 MHz) and ^{13}C NMR (600 MHz) spectra were recorded in $CDCl_3$ on a Bruker Advance III HD spectrometer using TMS as

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an internal standard. Molar ionic conductance of the complexes were determined in dimethyl sulphoxide using a solution of about 10^{-3} M concentration on a Jenway Model 4070 conductivity meter. The magnetic susceptibilitiy measurements on powder form of the complexes were carried out with a Sherwood magnetic susceptibility balance (Model MK1) using $MnCl_2.4H_2O$ as calibrant at room temperature. Mass spectra were obtained either on an Agilent LC/MSD spectrometer using the ESI technique or on a Thermo Finnigan LCQ Advantage MAX using the ESI technique. Thin-layer chromatography (TLC) was performed on Merck silicagel plates ($60F_{254}$), and detection was carried out with ultraviolet light (254 and 366 nm).

2.3. Synthesis of free ligands, L^1 and L^2

Visnagin derivative starting material, *6-formyl-7-hydroxy-5-methoxy-2-methylbenzopyran-4-one* **(1)**, was prepared according to the reported method by our group [15]. For the synthesis of **L^1**, a mixture of **1** (0.47 g, 2 mmol) and 2,3-DAN (0.16 g, 1 mmol) in 95% ethanol (50 mL) was refluxed for 2h. For preparing of **L^2**, 0.23 g (1mmol) of **1** and 0.16 g (1 mmol) of 1,8-DAN was refluxed for 2h in 95% ethanol (50mL). The precipitates were filtered off, recrystallized from hot ethanol and dried.

L^1. (Yellow solid) Yield 81%; M.p.: 296-297ºC. Calculated for $C_{33}H_{26}N_2O_8$ (590.17): C, 69.15; H, 4.44; N, 4.74. Found C, 68.97; H, 4.72; N, 4.91. Selected IR data (ATR, cm^{-1}): 3045 (Aromatic C-H), 2843 (Aliphatic C-H), 1660 (C=O), 1605 (C=N). UV-Vis in DMSO (nm): 280, 350, 480. ^{1}H NMR (600 MHz, $CDCl_3$): δ, ppm 2.32 (s, 6H, Chromone-CH_3), 4.03 (s, 6H, Chromone-OCH_3), 6.00 (s, 2H, H-3 and H-3'), 6.75 (s, 2H, H-8 and H-8'), 7.54 (*dd*, 2H, Naph-H), 7.66 (s, 2H, Naph-H), 7.92 (*dd*, 2H, Naph-H), 9.23 (s, 2H, CH=N), 14.53 (s, 2H, Ar-OH). ^{13}C NMR (600 MHz, APT, $CDCl_3$): δ, ppm 19.95(CH_3), 64.27(OCH_3), 101.00 (CH), 110.45 (C), 111.44 (CH), 111.79 (C), 117.24 (CH), 126.86 (CH), 127.91 (CH), 132.88 (C), 142.00 (C), 159.74 (CH=N), 161.63 (C), 162.85 (C), 163.90 (C), 165.76 (C), 176.43 (C=O). MS (+ESI): *m/z* 591.3 [M+H]$^+$.

L^2. 6-(2,3-dihydro-*1H*-perimidin-2-yl)-7-hydroxy-5-methoxy-2-methyl-4H-chromen-4-one. (Gray solid) Yield 68%; M.p.: 170-171ºC. Calculated for $C_{22}H_{18}N_2O_4$ (374.13): C, 70.58; H, 4.85; N, 7.48. Found C, 70.07; H, 4.97; N, 7.63. Selected IR data (ATR, cm^{-1}): 3329 (N-H), 3251(N-H), 3048 (Aromatic C-H), 2925 (Aliphatic C-H), 1650 (C=O). UV-Vis in DMSO (nm): 290, 330, 350. ^{1}H NMR (600 MHz, $CDCl_3$): δ, ppm 2.32 (s, 3H, Chromone-CH_3), 3.89 (s, 3H, Chromone-OCH_3), 5.07(s, 2H, N-H), 5.98(s, 1H), 6.06 (s,1H), 6.51 (s, 1H, H-8), 6.75-7.35 (m, 6H, Naph-H), 10.33 (s, 1H, Ar-OH). ^{13}C NMR (600 MHz, APT, $CDCl_3$): δ, ppm 19.95(CH_3), 61.74(CH), 63.86(OCH_3), 101.05(CH), 107.79(CH), 110.44(C), 111.36(CH), 114.14(C), 115.42(C), 119.20(C), 126.84 (CH), 134.66(C), 141.12(C), 158.47(C), 159.47 (C), 162.73(C), 164.01(C), 176.78 (C=O). MS (+ESI): *m/z* 375.1 [M+H]$^+$.

2.4. Synthesis of the metal complexes

A hot solution of MCl_2 (M = Fe or Cu) (1 mmol) in ethanol (30 mL) was added dropwise to a refluxing solution of **L^1** (0.59 g, 1 mmol) or **L^2** (0.37 g, 1 mmol) in chloroform (50 mL). The synthesis process of Fe(II) complexes was performed under nitrogen atmosphere. After refluxing for 2 hours, the resulting solution was concentrated to 10 mL. In case of no precipitation, pure water was added into the final solution dropwisely until precipitation occurs. The precipitates were collected by filtration and dried in vacuum under pressure to obtain metal complexes.

[CuL^1(H$_2$O)$_2$]. The product isolated as light brown powder was obtained after recrystallization from DMSO. Yield 63%. Calculated for $C_{34}H_{28}CuN_2O_{10}$ (687.1): C, 59.34; H, 4.10; N, 4.07; Cu, 9.23. Found C, 59.01; H, 4.32; N, 4.19; Cu, 9.07. Selected IR data (ATR, cm^{-1}): 2828 (Aliphatic C-H), 1650 (C=O), 1600 (C=N), 567-466 (M-O and M-N). UV-Vis in DMSO (nm): 280, 300, 350, 520. MS (+ESI): *m/z* 711.2 [M+H+Na]$^+$. Λ(DMSO) 7.3 Ω^{-1} cm^2 mol^{-1}; μ_{eff} : 1.79 B.M.

[FeL^1(H$_2$O)$_2$]. The product isolated as dark brown powder was obtained after recrystallization from DMSO. Yield 70%. Calculated for $C_{34}H_{28}FeN_2O_{10}$ (680.11): C, 60.01; H, 4.15; N, 4.12; Fe, 8.21. Found C, 59.87; H, 4.39; N, 4.32; Fe, 8.55. (Selected IR data (ATR, cm^{-1}): 2840 (Aliphatic C-H), 1650 (C=O), 1598 (C=N), 567-447 (M-O and M-N). UV-Vis in DMSO (nm): 280, 300, 350, 520. MS (+ESI): *m/z* 681.4 [M+H]$^+$. Λ(DMSO) 7.8 Ω^{-1} cm^2 mol^{-1}; μ_{eff} : 4.77 B.M.

[CuL^2(H$_2$O)$_4$]. The product isolated as light brown powder was obtained after recrystallization from DMSO. Yield 55%. Calculated for $C_{22}H_{24}CuN_2O_8$ (507.08): C, 52.02; H, 4.76; N, 5.51; Cu, 12.51. Found C, 51.86; H, 4.92; N, 5.69; Cu, 12.09. Selected IR data (ATR, cm^{-1}): 3272 (N-H), 3056 (Aromatic C-H), 2923 (Aliphatic C-H), 1653 (C=O), 564-400 (M-O and M-N). UV-Vis in DMSO (nm): 270, 290, 350, 410, 450, 680. MS (+ESI): *m/z* 529.54

$[M+Na]^+$. Λ(DMSO) 5.6 Ω^{-1} cm^2 mol^{-1}; μ_{eff} : 1.89 B.M.

$[FeL^2(H_2O)_4]$. The product isolated as dark brown powder was obtained after recrystallization from DMSO. Yield 72%. Calculated for $C_{22}H_{24}FeN_2O_8$ (500.9): C, 52.82; H, 4.84; N, 5.60; Fe,11.16. Found C, 52.22; H, 5.1; N, 5.72; Fe, 11.01. Selected IR data (ATR, cm^{-1}): 3299 (N-H), 3063 (Aromatic C-H), 2924 (Aliphatic C-H), 1655 (C=O), 561-460 (M-O and M-N). UV-Vis in DMSO (nm): 270, 340, 360, 600. MS (+ESI): *m/z* 501.39 $[M+H]^+$. Λ(DMSO) 5.1 Ω^{-1} cm^2 mol^{-1}; μ_{eff} : 4.83 B.M.

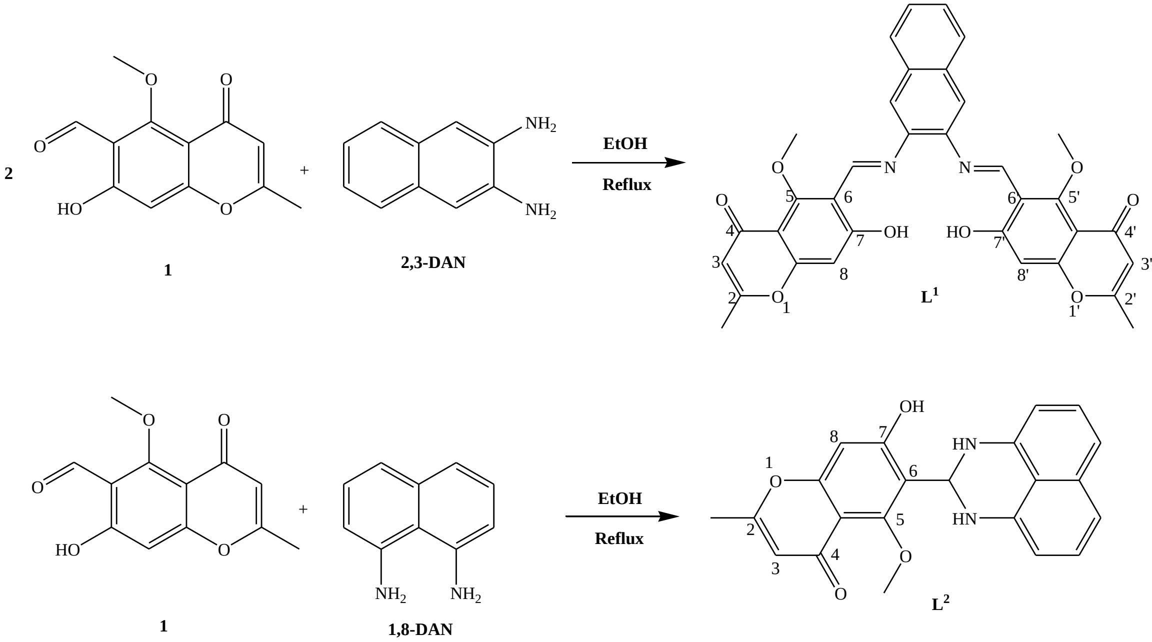
2.5. Catecholase activity

The catecholase activity of the prepared metal complexes was evaluated by using 3,5-DTBC as the substrate. The reactions were monitored spetrophotometrically by following the absorption increase at c.a. 400 nm of the corresponding quinone (3,5-DTBQ). To measure the ability of complexes to oxidize 3,5-DTBC, 2.10^{-5} M methanolic solution of complexes were treated with 2.10^{-3} M of 3,5-DTBC at room temperature in the presence of H_2O_2 (as an oxygen source). Absorbance *vs* wavelength plots were recorded for the resultant reaction mixture at a regular time interval of 2 min in the range 300–500 nm. To determine the dependence of the rates and kinetic parameters such as V_{max}, K_m and k_{cat}, the kinetics measurements were performed by using the initial rate method at 25°C for all complexes.

3. RESULTS AND DISCUSSION

3.1. Syntheses

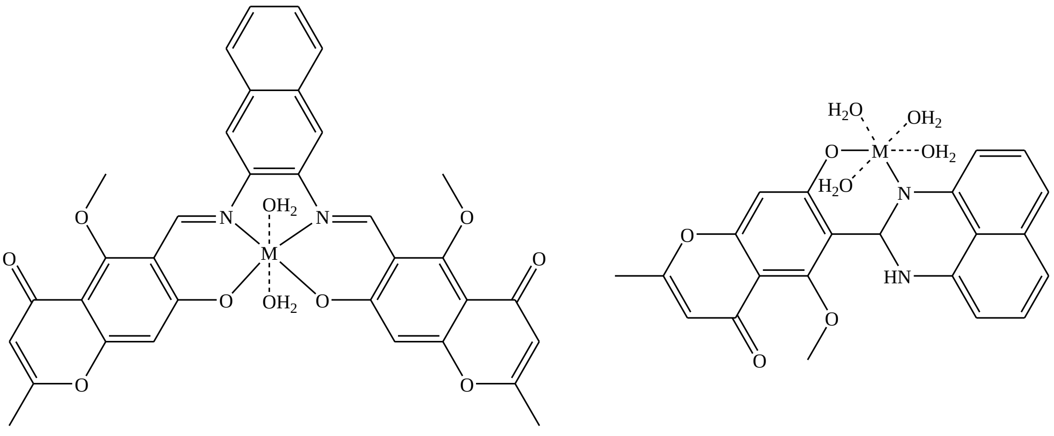
A new 2,3-dihydro-1*H*-perimidine derivative, a new Schiff base ligand and their Cu(II) and Fe(II) complexes were prepared and the structures have been confirmed by studying their physical and spectral properties. The synthetic routes for ligands are given in Scheme 1. The obtained results of micro-analysis, molar conductivity and magnetic susceptibility measurements for the synthesized compounds are consistent with the calculated results from empirical formula of all molecules. The lower molar conductance values (5.1-7.8 Ω^{-1} cm^2 mol^{-1}) in DMSO support the non-electrolytic nature of all the metal complexes, indicating that there are no counter ions in the proposed structures [16]. Magnetic measurements were recorded at room temperature and they were in the range of 1.79-1.89 and 4.77-4.83 B.M. for Cu(II) and Fe(II) complexes, respectively, suggesting octahedral geometry [17]. The proposed structures of the complexes are given in Figure 1.



Scheme 1. Synthesis of free ligands.

3.2. Electronic spectra

The electronic absorption spectra in the UV-Visible region of the ligands and their metal complexes were measured using freshly prepared 10^{-4} M solutions in DMSO. In the 270-350 nm region, the spectra exhibit the strong broad absorption bands for both perimidine and Schiff base ligands, indicating π-π* and n-π* transitions of azomethine groups and aromatic rings. In the spectra of all metal complexes, the weak bands at longer wavelengths (450-680 nm) might be attributed to d-d transitions of metal ions [18].



M = Cu or Fe

Figure 1. The proposed structures of Schiff base and perimidine metal complexes.

3.3. FT-IR spectra

In the FT-IR spectrum of **L**^{2}, two bands with medium intensity were observed at 3329 and 3251 cm^{-1} attributing to two N-H stretching vibrations of perimidine ring. The strong bands appeared at 1650 and 1594 cm^{-1} can assigned to carbonyl absorption of chromone ring and C=C stretching vibrations, respectively. The FT-IR spectra of perimidine Cu(II) and Fe(II) complexes revealed a medium, broad band at 3272 and 3299 cm^{-1}, respectively, attributing to a N-H stretching vibration and this indicates that one of the N-H groups of perimidine ring is not coordinated to the metal ion. Furthermore, the coordination of perimidine ring to the metal ion is supported by the existence of medium intensity bands in the region 460-564 cm^{-1} due to M-N and M-O stretching vibrations [10]. In the FT-IR spectrum of **L**^{1}, two sharp peaks observed at 1660 and 1605 cm^{-1} are due to carbonyl and azomethine groups, respectively. The absorption bands of carbonyl and azomethine groups have been shifted to lower frequencies in Cu(II) and Fe(II) complexes of Schiff base, indicating the involvement of oxygen and nitrogen atoms in complexation with the metal ions. This is further confirmed by appearance of the new bands in the region 466-567 cm^{-1} attributing to M-N and M-O stretching vibrations [19].

3.4. NMR spectra

The ^{1}H NMR spectrum of **L**^{1} in $CDCl_3$ showed two significant singlets at 9.23 and 14.53 ppm, corresponding to the azomethine (CH=N) and phenolic protons (Ar-OH), respectively. The signals in the range of 6.00-7.92 ppm were assigned to the aromatic protons on the naphthalene and chromone rings. Two sharp singlets were observed at 2.32 and 4.03 ppm due to methyl and methoxy protons, respectively. In the ^{13}C APT NMR spectrum of **L**^{1}, the total count of the carbon peaks matched well with the composition of the compound. The positive signal at 159.74 ppm clearly indicates the presence of methine carbon at imine (CH=N) group. The negative signal at 176.43 ppm was attributed to the quaternary carbon of carbonyl group in the chromone ring. The quaternary carbon atoms belong to the chromone ring and adjacent to the oxygen atoms were appeared as four negative signals in the region 161.63-165.76 ppm in the APT spectrum of **L**^{1}. In the ^{1}H NMR spectrum of **L**^{2}, the singlets appear at 2.32, 3.89 and 10.33 ppm were attributed to $–CH_3$, $-OCH_3$ and Ar-OH groups in the chromone ring, respectively. The aromatic protons were observed in the range of 6.75-7.35 ppm. The singlet observed at 5.07 ppm were assigned to –NH protons of perimidine structure. The signals corresponding to Ar-OH and –NH protons were disappeared after addition of D_2O (Figure 2).

The ^{13}C NMR spectrum (with the aid of APT and DEPT techniques) in $CDCl_3$, were found to agree with the proposed structure of **L**^{2}. The negative signal at 176.78 ppm clearly indicates the presence of quaternary carbonyl carbon. The positive peaks observed at 19.95 and 63.86 ppm were assigned to methyl and methoxy carbons of chromone ring, respectively. Another positive signal appeared at 61.74 ppm was likely to be assigned to the aliphatic methine carbon in the perimidine ring.

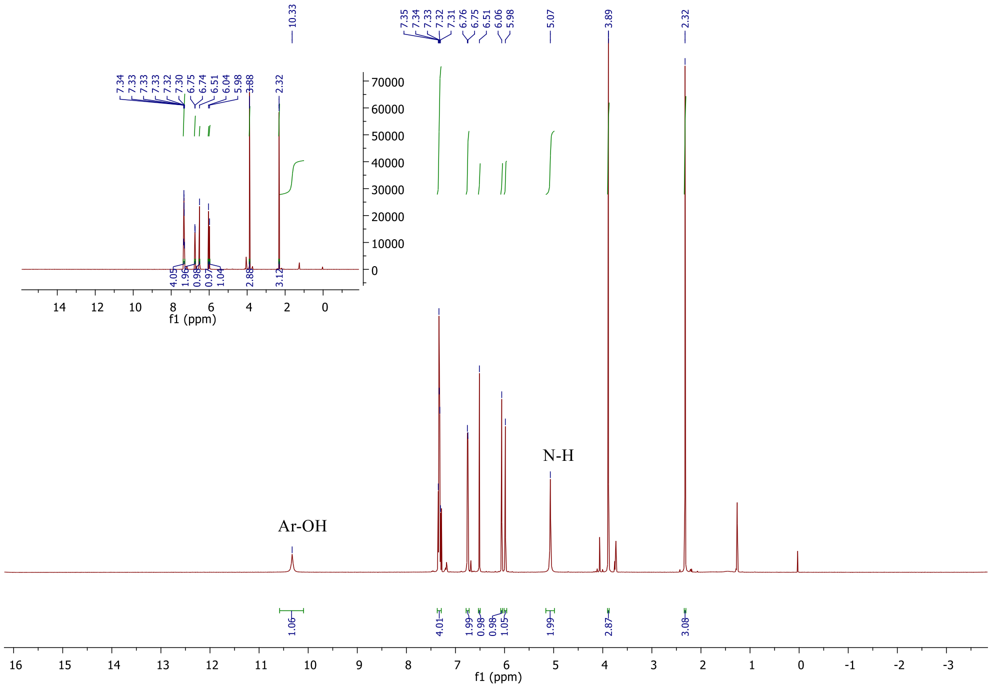


Figure 2. ^{1}H-NMR Spectrum of $\mathbf{L^2}$ ligand in $CDCl_3$ (Inset shows D_2O exchange spectrum of $\mathbf{L^2}$)

3.5. Mass spectra

In the mass spectra of the ligands, the molecular ion peaks for $\mathbf{L^1}$ and $\mathbf{L^2}$ can be seen at m/z = 591.3 and at m/z = 375.1 corresponds to $[M+H]^+$, respectively. Also, the formation of complexes was further confirmed by mass spectroscopy. The mass spectra for mononuclear complexes, $[CuL^1(H_2O)_2]$, $[FeL^1(H_2O)_2]$, $[CuL^2(H_2O)_4]$, $[FeL^2(H_2O)_4]$, show peaks at m/z = 711.2, 681.4, 529.54, 501.39 related to fragments of $[M+H+Na]^+$, $[M+H]^+$, $[M+Na]^+$ and $[M+H]^+$, respectively.

3.6. Catecholase activiy

2.11.1. Spectrophotometric study. In order to investigate the catecholase activity of all prepared complexes, 3,5-DTBC with low quinone-catechol reduction potential has been chosen as substrate. The oxidised product, 3,5-DTBQ is remarkably stable and shows a maximum absorption around 400 nm [20]. Methanol solution of the complexes was added in 100 equivalents of 3,5-DTBC in the presence of H_2O_2 and the repetitive UV-Vis spectral scan was recorded at a regular time interval of 2 min in the range 300-500 nm. After addition of 3,5-DTBC and H_2O_2, the time dependent spectral scan shows very smooth growing band at 400 nm (Figure 3) for all complexes, indicating the formation of the corresponding quinone (3,5-DTBQ).

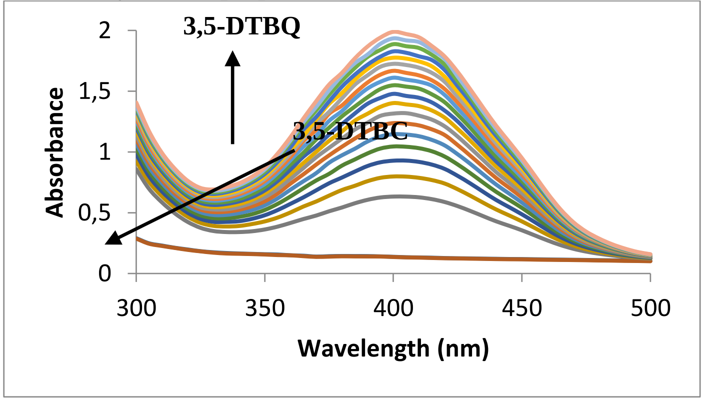


Figure 3. UV–Vis spectral changes of $[CuL^2(H_2O)_4]$ complex in methanol upon addition of 100-fold excess of 3,5-DTBC, observed at two minute intervals of time.

2.11.2. Enzyme kinetics study. Enzymatic kinetic experiments were performed by using UV–Vis spectrophotometry thermostated at 25 °C. To understand the kinetic aspects of catalysis, the rate constant for a catalyst complex was determined by traditional initial rate methods. The pseudo-first-order condition was maintained by using substrate solutions ranging between 10 times and 100 times larger than that of the synthesized complexes. The Michaelis-Menten approach of enzyme kinetics was applied to analyze the rate versus concentration of the substrate data. In all cases, a first-order kinetic dependence was observed at low concentrations of 3,5-DTBC, whereas a saturation kinetics was observed at higher concentration (Figure 4).

Linearization by using Lineweaver–Burk plot of 1/V versus 1/[S], provided the Michaelis–Menten constant (K_M), maximum initial rate (V_{max}) and turnover number (k_{cat}). The calculated kinetic parameters are listed in Table 2. According to their calculated turnover number values (k_{cat} values), the overall comparison of the complexes based on catecholase activity suggests that Fe(II) complex of Schiff base ligand has the best activity in catalyzing the oxidation of 3,5-DTBC to 3,5-DTBQ in methanol solution, with a turnover number (k_{cat}) of 890.1 h^{-1}. Also Fe(II) complexes have been found to show better catalytic acitivity than those of Cu(II) complexes for any ligand.

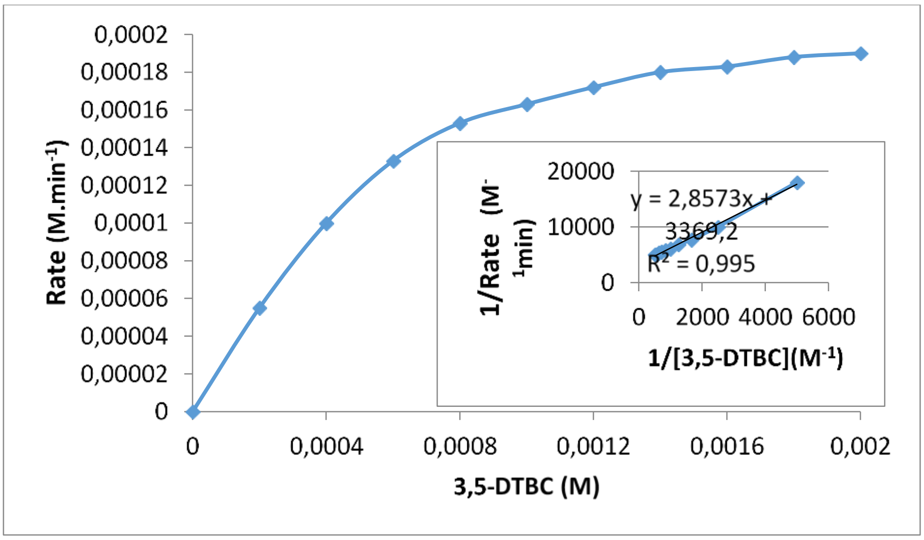


Figure 4. Michaelis–Menten and (inset) Lineweaver–Burk plots for $[FeL^1(H_2O)_2]$ with 3,5-DTBC in methanol.

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

Complex	V_{max} (M min^{-1})	K_M (M)	k_{cat}(h^{-1})
$[CuL^1(H_2O)_2]$	5.02×10^{-5}	7.6×10^{-4}	151.4
$[FeL^1(H_2O)_2]$	2.97×10^{-4}	8.5×10^{-4}	890.1
$[CuL^2(H_2O)_4]$	3.51×10^{-5}	5.4×10^{-4}	66.9
$[FeL^2(H_2O)_4]$	6.82×10^{-5}	9.1×10^{-4}	106.5

4. CONCLUSION

In this paper, we have described the synthesis and characterization of four new mononuclear metal complexes with a perimidine derivative and a Schiff base derivative ligand and their application in catalytic field. All prepared complexes have been evaluated for their catecholase activity potential and they have been observed to exhibit moderate catecholase activity with turnover number values ranging from 66.9 to 890.1 h^{-1}. To the best of our knowledge, metal complexes of perimidine ligand in this study are the first compounds which have been found to show catecholase acitivity. However, in comparison to metal complexes of perimidine ligand, Schiff base metal complexes have better catecholase activity towards the oxidation of 3,5-DTBC to the corresponding quinone.

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