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Synthesis and Characterization of a Novel Aminoketooxime Ligand and Enzymatic Efficiencies of Its Metal Complexes

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A novel aminoketooxime ligand and its mononuclear Cu(II) and Mn(II) complexes were synthesized. The structures of the synthesized compounds were illuminated by elemental analysis, inductively coupled plasma optical emission spectrometry, the Fourier transform infrared, ^{1}H- and ^{13}C-NMR, UV-Vis, magnetic susceptibility and conductivity measurements. According to the characterization studies ligand to metal ratio was found to be 2:1 with strong binding affinity of the ligand to the metal ions. In addition, complexes have been tested for their catecholase and phenoxazinone synthase-like activities. Kinetic studies were also carried out yielding $V_{\max}$, k_{cat} and K_M values of both complexes for catecholase and phenoxazinone synthase-like activities. Both complexes efficiently catalyzed the reactions of the enzymes they mimicked.

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PACS/topics: oxime, metal complex, spectroscopy, catecholase, phenoxazinone synthase

1. Introduction

Metal ions have been found to play a crucial role in many biological systems. At least one-third of all proteins appear to contain metal ions and even the nucleozymes such as ribozymes (RNA enzymes) appear to be metalloenzymes [1]. These metal ions can modify electron flow in a substrate or enzyme, thus effectively controlling an enzyme-catalyzed reaction. It is not possible to use the natural enzyme as a drug due to its delivery problems and instability in solution. Therefore, synthetic compounds able to mimic natural enzymes have been designed and studied by researchers [2, 3].

Oxime containing compounds are extensively synthesized and characterized due to their coordinating capability [4], besides their applications in chemical, pharmaceutical, biological, biochemical, and environmental fields [5, 6]. In addition to these properties of oximes and oxime containing metal complexes, they have the ability to mimic a natural enzyme. Higher capability of oxime metal complexes for oxidation and reduction reactions make them prominent candidates to mimic oxidoreductase family of enzymes that catalyze the electron transfer from one molecule to another.

In this study, we synthesized and characterized a new aminoketooxime ligand and studied the enzymatic activity of its metal complexes. Two enzymes from oxidoreductase family were chosen namely, catecholase and phenoxazinone synthase, regarding the mimicking capacity of the Cu(II) and Mn(II) metal complexes synthesized. Both enzymes carry varying number of copper ions as cofactor in their active sites, besides being metabolically important as well as the substrates and the products.

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2. Experimental

2.1. Physical measurements

All chemicals and solvents were of analytical grade and used as received, without any further purification. The ^{1}H- and ^{13}C-NMR spectra of the ligand were recorded on a JEOL NMR-400 MHz spectrometer, using TMS as an internal standard and $CDCl_3$ as a solvent. The IR spectra of the free ligand and its metal complexes were measured using a Schimadzu IRPrestige-21 FT-IR spectrophotometer within the range 4000–400 cm^{-1}, using KBr discs. In addition, spectrophotometric measurements were performed with a PG T80+ UV–Vis spectrometer. LECO 932 CHNS analyzer was used to determine C, H, and N proportions of the compounds. Perkin Elmer Optima 5300 DV ICP-OES spectrometer was used to obtain metal contents of the same complexes. Molar conductance of the complexes in DMF (10^{-3} M solution) were measured on an Optic Ivymen System conductivity meter at room temperature. Melting points were determined with an Electrothermal model IA 9100 digital instrument. Magnetic moment value measurements were carried out at room temperature on a Sherwood Scientific Magnetic Susceptibility Balance (model MX1).

2.2. Preparation of the ligand

2 mmol, 0.51 g of 1-(biphenyl)-2-chloro-2-hydroxy imino-1-etanone was dissolved in 20 ml EtOH and the mixture was cooled to –5 °C. Then, ethanol solution of 4 mmol 0.616 g 2-amino-4-nitrophenol was added dropwise to the solution of chloroketooxime over 15 min with cooling. Precipitation and colour change were observed in the reaction medium immediately. After that period, the reaction mixture was stirred for 2 h at the same temperature. Then it was allowed to stir at ambient temperature for 2 more hours. The resulting precipitated powder was filtered off, washed by aqueous sodium bicarbonate (1%), distilled water, ethanol and dried on P_2O_5.

H_2L, dark yellow compound; yield: 45%; m.p.: 137 °C. Anal. calc. for $C_{20}H_{15}N_3O_5$: C, 63.66; H, 4.01; N, 11.14; found: C, 63.32; H, 4.13; N, 11.02%; ^{1}H-NMR ($CDCl_3$, ppm): 9.47 (s, 1H, O–H_{oxime}), 6.97–8.32 (m, 12H, Ar–H), 6.74 (s, 1H, O–H_{phenol}), 3.93 (s, 1H, N–H); ^{13}C-NMR ($CDCl_3$, ppm): 186.60 (carbonyl), 149.11 (oxime), 110.14–128.97 (aromatic); FT-IR (KBr, cm^{-1}): 3597 w (O–H_{phenol}), 3327 b (N–H), 3083 w (O–H_{oxime}), 1604 m (C=N), 1523 s (C–N), 1395 w (N–O) (b, broad; s, strong; m, medium; w, weak); UV-Vis (DMF solution, nm): 295, 393, 431.

2.3. Preparation of the complexes

Mononuclear Cu(II) and Mn(II) complexes of the ligand were prepared similarly. 0.3 mmol metal salts of Cu(II) or Mn(II) dissolved in ethanol was added to a hot ethanol solution of 0.6 mmol ligand and was continuously stirred. A distinct change in colour and decrease in pH (pH = 3.0–3.5) was observed, an equivalent amount of ethanolic solution of KOH (0.1 M) was added dropwise to adjust a pH value of about 5–6, solid product precipitated. The complex precipitated, was kept on a water bath at 80 °C for one hour in order to complete the precipitation. The mixture was cooled to +4 °C and kept overnight. The solid product was filtered, washed with water and ethanol, respectively and dried on P_2O_5.

For $Cu(HL)_2$, dark brown complex; yield: 54%; m.p.: > 300 °C. Anal. calc. for $C_{40}H_{28}CuN_6O_{10}$: C, 58.86; H, 3.46; N, 10.30; Cu, 7.79; found: C, 58.51; H, 3.35; N, 10.06; Cu, 7.53%; Λ_M (DMF solution, Ω^{-1} cm^2 mol^{-1}): 9.40; μ_{eff} = 1.68 B.M.; FT-IR (KBr, cm^{-1}): 3397 b (N–H), 3079 w (O–H_{oxime}), 1600 m (C=N), 1517 s (C–N), 1434 w (N–O), 526 w (M–O), 439 w (M–N) (b, broad; s, strong; m, medium; w, weak); UV-Vis (DMF solution, nm): 290, 340, 439, 514.

For $Mn(HL)_2$, black complex; yield: 52%; m.p.: > 300 °C. Anal. calc. for $C_{40}H_{28}MnN_6O_{10}$: C, 59.49; H, 3.49; N, 10.41; Mn, 6.80; found: C, 59.34; H, 3.61; N, 10.15; Mn, 6.95%; Λ_M (DMF solution, Ω^{-1} cm^2 mol^{-1}): 7.20; μ_{eff} = 5.82 B.M.; FT-IR (KBr, cm^{-1}): 3352 b (N–H), 3074 w (O–H_{oxime}), 1601 m (C=N), 1508 m (C–N), 1454 w (N–O), 524 w (M–O), 445 w (M–N) (b, broad; s, strong; m, medium; w, weak); UV-Vis (DMF solution, nm): 296, 339, 420, 547.

2.4. Enzymatic activities

Synthesized complexes were tested for their catecholase (catechol oxidase: EC 1.10.3.1) and phenoxazinone synthase (o-aminophenol oxidase: EC 1.10.3.4) activities. Catecholase enzyme catalyzes the conversion of 3,5-di-*tert*-butylcatechol to 3,5-di-*tert*-butylquinone [7, 8] while phenoxazinone synthase catalyzes the formation of 2-aminophenoxazine-3-one (APX) from 2-aminophenol (OAPH) [9].

2.5. Catecholase-like activity

Catecholase-like activity of the complexes was spectrophotometrically evaluated by the oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) to 3,5-di-*tert*-butyl-o-benzoquinone (3,5-DTBQ) which gives a characteristic band at 400 nm. The complexes (1 10^{-4} M) were dissolved in dioxygen saturated methanol and the substrate (5×10^{-3} M) was added to the medium. The measurements performed by following the increase in absorbance at 400 nm corresponding to the formation of the product. The initial reaction rates also determined from the slope of the trace at 400 nm during the first 5 min of the reactions, when the absorption at 400 nm increases linearly. Initial rates of catechol oxidation were determined by the modified method reported by Reim and Krebs [7].

2.6. Phenoxazinone synthase-like activity

1.67×10^{-4} M of each complexes and 12.5×10^{-3} M of substrate 2-aminophenol (OAPH) were dissolved in DMF and completed to 25 ml as the final volume, separately. They were proportionally mixed and measured immediately in a quartz cuvette. Spectrum scan was carried out between 300 and 600 nm with 30 s intervals for 25 repeats. The oxidation reaction of OAPH was monitored by following the increase in absorbance at 433 nm, which is a typical band for 2-aminophenoxazine-3-one (APX). The initial reaction rates determined from the slope of the trace at 433 nm during the first 5 min of the reactions, when the absorption increases linearly [9].

3. Results and discussion

Synthetic route for the synthesis of aminoketooxime ligand can be seen from Fig. 1. Firstly, 4-(chloroacetyl)biphenyl was obtained from chloroacetyl chloride and biphenyl in the presence of aluminum chloride according to Friedel-Crafts acylation. 1-(biphenyl)-2-chloro-2-hydroxyimino-1-etanone was obtained by reacting 4-(chloroacetyl)biphenyl with isopentyl nitride in the presence of dry HCl gas [10]. 2-(biphenyl-4-yl)-N'-hydroxy-N-(2-hydroxy-5-nitrophenyl)-2-oxoacetimidamide was synthesized reacting 1-(biphenyl)-2-chloro-2-hydroxyimino-1-etanone with 2-amino-4-nitrophenol.

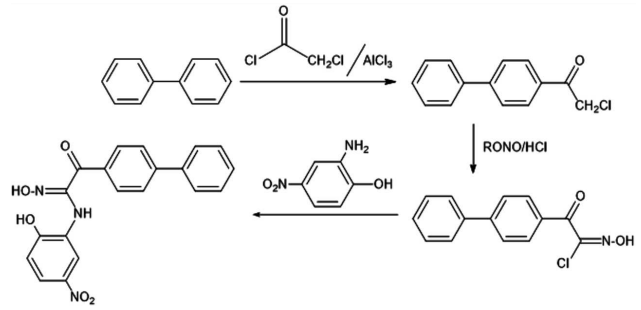

Fig. 1. Route for the synthesis of the ligand (H_2L).

At the last step of synthetic process, the reaction of ligand with proper metal salts, Cu(II) and Mn(II) complexes were obtained by precipitation.

3.1. ^{1}H- and ^{13}C-NMR spectra

^{1}H- and ^{13}C-NMR spectra were obtained by using $CDCl_3$ solvent (Fig. 2 and Fig. 3). From the ^{1}H-NMR

spectrum of the ligand, a singlet peak at 9.47 ppm corresponding to oxime group and multiple peaks corresponding to aromatic C–H protons between 6.97 and 8.32 ppm were seen while phenolic O–H proton signal was observed at 6.74 ppm as a singlet peak. Signal belonging to N–H proton was observed at 3.93 ppm as a singlet peak.

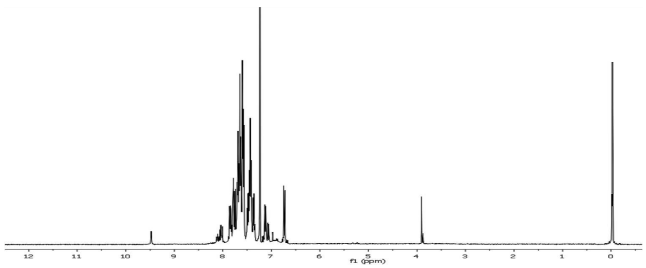

Fig. 2. ^{1}H-NMR spectrum of the synthesized ligand.

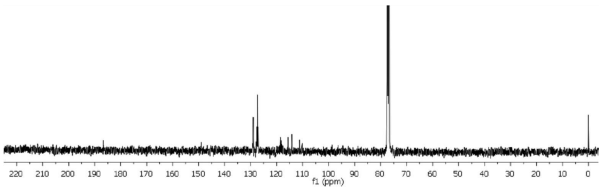

Fig. 3. ^{13}C-NMR spectrum of the synthesized ligand.

By the investigation of ^{13}C-NMR spectrum of the ligand, signal obtained from the chemical shift corresponding to the carbonyl carbon was observed in the lowest area of the spectrum at 186.60 ppm and oxime group carbon at 149.11 ppm. Peaks originating from the chemical shifts of aromatic carbons can be seen between 110.14 and 128.97 ppm.

Data obtained were coherent with the previous similar molecules' NMR data and other analytical results carried out for characterization [11–16].

3.2. FT-IR spectra

FT-IR spectra of the synthesized ligand and its metal complexes were shown in Fig. 4–6. Investigation of characteristic bands belonging to the ligand and its Cu(II) and Mn(II) complexes has given such results. The band observed at 3083 cm^{-1} which corresponds to the oxime group of the ligand neither disappeared, nor shifted in the spectra of the complexes revealing that the oxime proton still exists in both complexes. The weak band at 3597 cm^{-1} corresponding to the phenolic O–H group of the ligand has disappeared by the formation of the complex indicating that the phenolic oxygen was involved in the coordination with metal ions. The vibrational frequency of the band originating from N–H group of the ligand was observed at 3327 cm^{-1} as a broad band. This band has been shifted to higher frequencies by the complex formation which shows that the N–H group of aromatic amine moiety was involved in the complexation process [17].

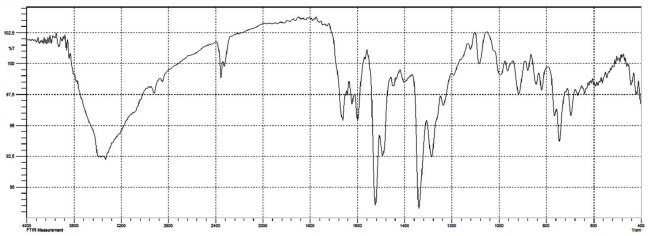

Fig. 4. FT-IR spectrum of the ligand.

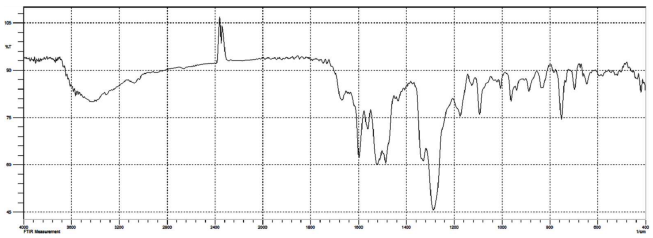

Fig. 5. FT-IR spectrum of the $Cu(HL)_2$.

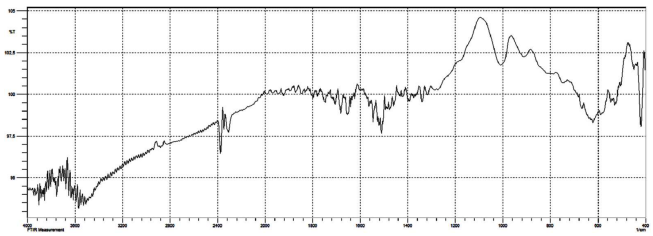

Fig. 6. FT-IR spectrum of the $Mn(HL)_2$.

Although the band observed at about 1600 cm^{-1}, corresponding to the C=N bond of the oxime group of the ligand, has been affected by complex formation, the shifts at the vibrational frequency are not significant in both spectra of the complexes. These insignificant shifts may result from the coordination of oxygen atom neighbouring the C=N group.

Characteristic band at 1395 cm^{-1} which corresponds to the N–O bond of the oxime group of the ligand is shifted noticeably to higher frequency values (39 and 59 cm^{-1}) in complexes spectra indicating that oxygen atom of the oxime group has taken part in coordination.

Coordination mode of the ligand to the metal ion in the complexes are supported by the appearance of new bands at about 525 and 445 cm^{-1} which are assigned to ν(M–O) and ν(M–N), respectively.

3.3. UV-Vis

To acquire and compare the spectral pattern and electronic behavior of the ligand and the complexes, 1×10^{-5} M of each compound dissolved in DMF and completed to a final volume of 25 ml. Spectral scan was recorded between 200 and 600 nm. From the spectra,

electronic transitions and wavelengths corresponding to the maximum absorbance were recorded.

From the UV-Vis spectrum of the ligand, $\pi \rightarrow \pi^*$ transitions corresponding to the benzene group, the $\pi \rightarrow \pi^*$ transitions corresponding to C=N group of oxime, the $n \rightarrow \pi^*$ transitions belonging to the same C=N group are observed at 295, 393, and 431 nm, respectively.

The spectra of Cu(II) and Mn(II) complexes have the same signal for $\pi \rightarrow \pi^*$ transitions at about 295 nm which correspond to benzene group. On the other hand, $\pi \rightarrow \pi^*$ transitions observed at 393 nm for ligand were shifted to 340 nm for complexes. These blue shifts may be due to the involvement in coordination of oxygen atom adjacent to the imine nitrogen. The $n \rightarrow \pi^*$ transitions appeared at 431 nm for ligand were shifted to 439 nm for $Cu(HL)_2$ and 420 nm for $Mn(HL)_2$. These shifts to higher and lower values revealed that the oxime group has been involved in the coordination. Also, $d \rightarrow d$ transitions were observed at 514 and 547 nm due to the participation of Cu(II) and Mn(II) metal ions in the coordination, which respectively have an electronic configuration of d^9 and d^5 [18].

The molar conductance values of the complexes in DMF (10^{-3} molar solutions 25 °C) indicated that $Cu(HL)_2$ and $Mn(HL)_2$ complexes are non-electrolytes [19]. In addition, magnetic moment measurements at room temperature showed that both complexes are paramagnetic. $Cu(HL)_2$ complex has a magnetic susceptibility value of 1.68 B.M. which fits d^9 metal while $Mn(HL)_2$ complex has 5.82 B.M. which fits d^5 metal ion in a octahedral geometry.

3.4. Enzymatic activities

Selected enzymes belong to oxidoreductase family which catalyzes the oxidation reduction reactions throughout the living organisms from the simplest to the most complex ones. Both catecholase and phenoxazinone synthase enzymes contain Cu(II) as a cofactor in their active sites. They were picked up due to their biochemical importance and imitability by the synthesized complexes.

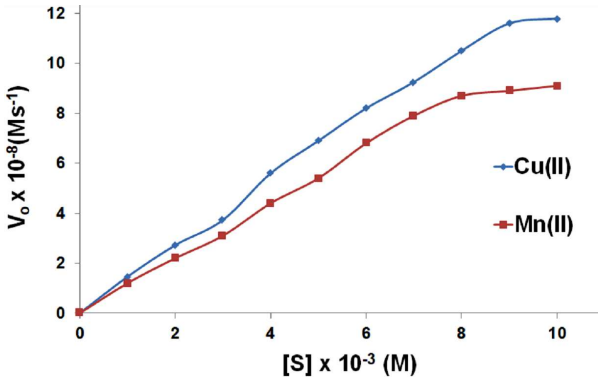

Fig. 7. Michaelis–Menten plot of the synthesized Cu(II) and Mn(II) complexes catecholase-like activity.

Synthesized complexes were tested for their catecholase and phenoxazinone synthase enzymatic activities. After

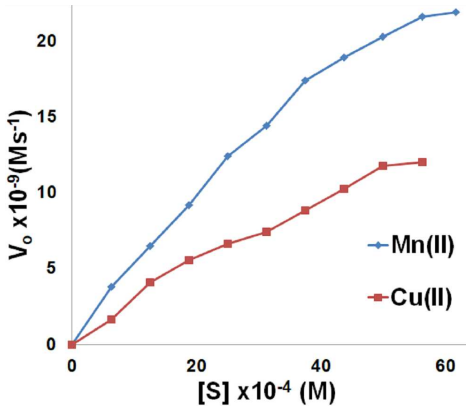

Fig. 8. Michaelis–Menten plot of the synthesized Cu(II) and Mn(II) complexes phenoxazinone synthase-like activity.

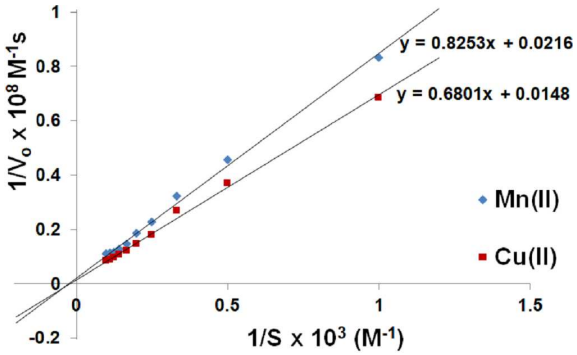

Fig. 9. Lineweaver–Burk plot shows the reciprocal of both velocity vs. substrate concentration of the synthesized Cu(II) and Mn(II) complexes catecholase-like activity.

the observation of the complexes catalytic function, they were subjected to kinetic studies to acquire data comparable with other researchers' results. Both complexes showed the Michaelis–Menten kinetics for both enzymes (Fig. 7 and 8). To obtain and exhibit more precise results, reciprocal of both axes was calculated and shown in a Lineweaver–Burk plot in Fig. 9 and 10. Interception of the best lines from the y axis gives $1/V_{\max}$ and x axis

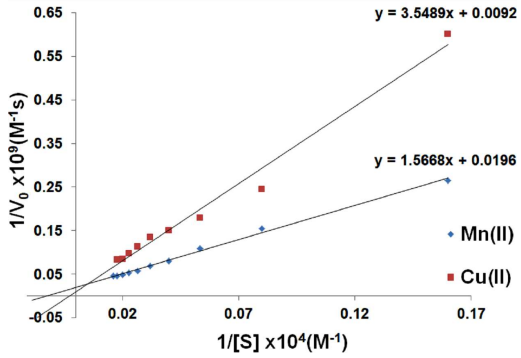

Fig. 10. Lineweaver–Burk plot shows the reciprocal of both velocity vs. substrate concentration of the synthesized Cu(II) and Mn(II) complexes phenoxazinone synthase-like activity.

gives $-1/K_M$. From the data k_{cat} is obtained by dividing $V_{\max}$ to $[E]_{total}$.

3.4.1. Catecholase activity

Catecholase-like activity of the synthesized complexes was measured by following the increase in absorbance at 400 nm, which indicates the increase in the concentration of the product 3,5-di-*tert*-butylquinone. Figure 11 shows the overall reaction catalyzed by catecholase. Spectral scan of the reaction mixture between 300 and 600 nm with 30 s intervals gave the spectra in Fig. 12. The absorbance, activity and product increased gradually at 400 nm. Both complexes showed similar spectral patterns which revealed that they are actively catalyzed the oxidation of 3,5-di-*tert*-butylcatechol in a similar manner with different rates.

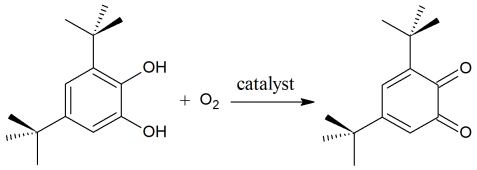

Fig. 11. Oxidation reaction of 3,5-di-*tert*-butylcatechol to 3,5-di-*tert*-butylquinone by catecholase in the presence of O_2.

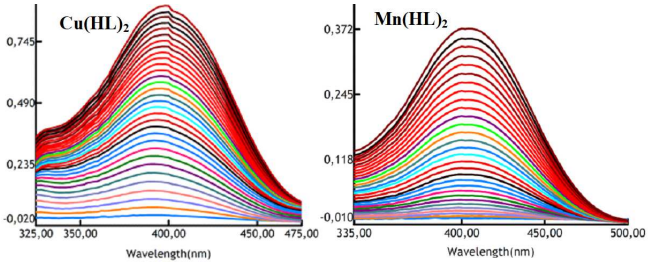

Fig. 12. Catecholase-like activity of the complexes shown by the spectral scan between 300 and 600 nm with 30 s intervals.

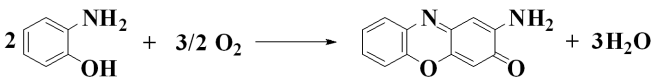

Fig. 13. Formation of 2-aminophenoxazine-3-one (APX) in several steps from 2-aminophenol (OAPH) catalyzed by phenoxazinone synthase.

Both complexes catalytic behavior follows the Michaelis–Menten kinetics. Figures 7 and 8 show the plot of substrate concentration versus V_0 of the reactions. K_M is the substrate concentration corresponding the value of $V_{\max}/2$ which is inversely proportional to the affinity of enzyme to the substrate.

$Mn(HL)_2$ seemed to have a higher affinity for 3,5-di-*tert*-butylcatechol than $Cu(HL)_2$ but, $Cu(HL)_2$ has a higher k_{cat} value (50.40 1/h) compared to $Mn(HL)_2$ (33.48 1/h) from Table I, since the overall reaction rate depends on the size of the enzyme and substrate, proximity and orientation of the substrate to the active site of the enzyme and other factors [20, 21].

The turnover rate 50.40 1/h we obtained for $Cu(HL)_2$ is higher to those values reported (k_{cat} = 23.58, 6.00 1/h) [22, 23], and comparable to those reported (k_{cat} = 63.72, 58.68 1/h) [24, 25] for mononuclear Cu(II) complexes. The turnover rate of 33.48 1/h obtained is comparable to the reported value of 48.96 1/h for mononuclear Mn(II) complex [9].

TABLE I

Catecholase and phenoxazinone synthase-like activities of metal complexes.

Enzymes mimicked	Compound	$V_{\max}$ [M/s]	K_M [M]	k_{cat} [1/ks]	k_{cat} [1/h]
catecholase	$Mn(HL)_2$	4.63×10^{-7}	3.82×10^{-2}	9.30	33.48
	$Cu(HL)_2$	6.76×10^{-7}	4.55×10^{-2}	14.00	50.40
phenoxazinone synthase	$Mn(HL)_2$	0.51×10^{-7}	0.80×10^{-2}	0.61	2.20
	$Cu(HL)_2$	1.09×10^{-7}	3.85×10^{-2}	1.30	4.68

3.4.2. Phenoxazinone synthase activity

The reaction catalyzed by phenoxazinone synthase was mimicked by both metal complexes (Fig. 13). The formation of APX was observed by following the increase in absorbance at 433 nm with spectral scans between 300 and 600 nm for 30 s intervals. The absorbance at 433 nm is a characteristic wavelength for the product APX (Fig. 14).

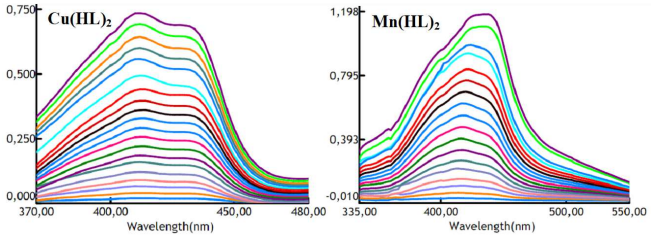

Fig. 14. Spectral scans between 300 and 600 nm with 30 s intervals show the increase in absorbance at 433 nm which is characteristic for APX.

Both complexes efficiently catalyzed the oxidation of OAPH to APX in the presence of O_2. DMF is used as a solvent and the proportion of OAPH to O_2 was found to be 2:1.5. The pattern of scan spectra were different for $Cu(HL)_2$ and $Mn(HL)_2$ suggesting that the two complexes may act different during catalysis. The proximity of the complexes with the substrate, or the percentage of fragmentation products may be the reason for the difference in patterns.

$Mn(HL)_2$ has a higher binding affinity for OAPH compared to $Cu(HL)_2$, but $Cu(HL)_2$ has a higher turnover rate (4.68 1/h) as in catecholase (Table I). In literature, vast majority of the enzyme mimicking studies comprise dinuclear complexes. Among those, in a rare study for mononuclear Cu(II) complex, the turnover rate has been

reported as 29.88 1/h which is higher than our result (2.20 1/h) [26]. For mononuclear Mn(II) complex, Kaizer et al. have been reported 2.92 1/h turnover rate which is comparable to our result (2.20 1/h) [9].

4. Conclusion

This study comprises the synthesis and characterization of a novel amine containing ketooxime ligand and its mononuclear Cu(II) and Mn(II) complexes. Ligand has a donor set in ONO form which enables the coordination with oxygen atoms of oxime and phenol groups plus the nitrogen of amine group. Obtained results revealed that the complexes have an octahedral geometry with a metal:ligand ratio of 1:2 (Fig. 15). According to the calculated k_{cat} values, $Cu(HL)_2$ showed higher catecholase and phenoxazinone synthase-like activity compared to $Mn(HL)_2$. The results suggest that the synthesized complexes are biomimetically active and have the potential to be used as model systems.

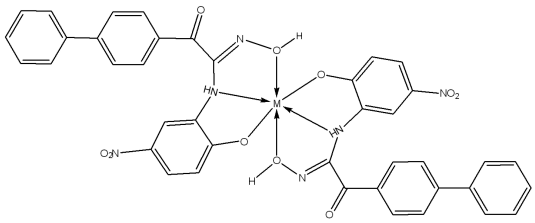

Fig. 15. Structure of the mononuclear complexes of H_2L (M: Cu(II) or Mn(II)).

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