Catalytic oxidation of polyphenol trihydroxybenzene by Manganese (II) Complex of Methoxyphenyl Benzopyran derivative

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Abstract- The Manganese (II) complex of 2-Amino-4-(4-methoxyphenyl)-5, 6, 7, 8-tetrahydro-7, 7-dimethyl-5-oxochromene-3-carbonitrile (AMC) was synthesized. The organic ligand AMC was previously synthesized using an environment friendly method using microwave irradiation. The Manganese complex Mn^{II}AMC was characterized by different tools such as IR, electronic spectroscopy, elemental analysis, Thermal analysis and mass spectroscopy. The mode of metal binding shows that the Manganese binds to the ligand through the nitrogen atoms of the amino and cyanide groups. The Manganese complex Mn^{II}AMC was used in the homogenous oxidation of the polyphenol 1,2,3-trihydroxybenzene in presence of the green oxidant H_2O_2 to produce a first-order rate constant $k_{cat}= 6.3\times10^{-3}s^{-1}$. The catalysis shows catalytic efficiency of 2.49×10^3 times compared to the autooxidation of THB.

Index Terms- Benzopyran derivative; microwave; oxidation; trihydroxybenzene.

I. INTRODUCTION

The increasing demand for water has caused considerable attention to be focused towards recovery and reuse of waste waters [1]. Treatment of highly toxic organics in waste waters attracts more attention due to their harmful effects to the environment. Phenol is among the most common water pollutants[2,3], because it is present in the effluent of numerous industrial processes such as oil refineries, petrochemical, coal processing, Pulp and paper and pharmaceutical industries [4,5].
The study of the phenol oxidation catalyzed by peroxidase mimics is significantly important for not only providing useful information for the elucidation of the reaction mechanism but also applying in analytical clinical chemistry, in the synthesis of phenolic polymers and in the protection of the environment [6-9].

Complexes containing electroactive centralmetals are preferred catalysts for the oxidation of phenol since these complexes have a wide range of readily available oxidation states[10,11]. Iron and manganese complexes have been extensively studied as biomimetic catalysts for the oxidation of phenol in the presence of an environmentally clean hydrogen peroxide oxidant [12,13].

The use of microwave radiation to enhance organic reactions in environmentally benign solvents such as water, which is inexpensive and not dangerous, represents very powerful green chemical technology both from economic and synthetic points of view. This not only reduces the burden of organic solvent disposal but also enhances the rate of the reaction.

The synthesis of compounds having benzopyran rings has attracted great interest, since they have diverse pharmacological activities. [14,15].
In addition, a large number of benzopyran derivatives possess potent relaxant activity on blood vessels, cardiac muscle and other smooth muscles.[16,17].

In this study the manganese complexes of the bezopyrane derivative was prepared as an environment friendly catalyst and fully characterized. The catalyst was used to oxidize the polyphenolic compound trihydroxybenzene with the clean oxidant H_2O_2.

II. EXPERIMENTAL SECTION

2.1. Materials and Methods.

4-methoxybenzylaldehyde was purchased from Aldrich Chemical Co. Dimedone was purchased from Across Organics Co. (Belgium). Malononitrile, manganese acetate were obtained from Merck Co., Germany.

2.2. Synthesis of 2-Amino-4-(4-methoxy-phenyl)-5, 6, 7, 8-tetrahydro-7, 7-dimethyl-5-oxochromene-3-carbonitrile (AMC) using microwave irradiation)

The organic ligand AMC has been prepared as described in literature [18,19] in aqueous medium under microwave irradiation. A mixture of 4-methoxybenzaldehyde (5mmol) and malononitrile 2 (0.33 g, 5mmol) were mixed together in water (2 ml) in a tightly closed tube, and subjected to microwave irradiation for 0.5 min. until completion of the reaction (monitored by TLC). The precipitate formed was filtered, washed with water to give the pure arylidene malononitrile (90% yield) with melting point 114.5-115°C. An equimolar amounts of arylidene malononitrile (5mmol) and dimedone (0.7 g, 5mmol) were mixed together in water (2 ml) in a tightly closed tube, and subjected to microwave irradiation for 4.0 min. until completion of the reaction (monitored by TLC). The precipitate formed was filtered and washed with water several times to give the pure ligand AMC in 96% yield (m.p.= 194-195°C).

2.3. Synthesis of Mn^{II}AMC complex.

Manganese (II) acetate (0.1 mole) dissolved in ~ 40 ml absolute ethanol was added to 0.1 mole of the ligand AMC dissolved in ~ 40 ml absolute ethanol. The mixture was heated under reflux for ~ 2 h. The bluish precipitate was formed, filtered off and finally washed by hot ethanol several times and dried in an open air.

2.4. Physical methods.

Carbon, hydrogen and nitrogen contents were determined at the Microanalytical Unit, Cairo University, Egypt. IR spectra of the ligand and its solid complex were measured in KBr on a Mattson 5000 FTIR spectrometer. The electronic spectra and kinetic measurements were performed using Varian Cary 4 Bio UV/VIS spectrophotometer.

^{1}H- NMR spectrum of the ligand was recorded on Joel-90Q Fourier Transform (200 MHz) spectrometers in [D$_6$] DMSO. The mass spectra of the ligand and its metal complex were recorded on a Shimadzu GC-S-QP 1000 EX spectrometer using a direct inlet system. Thermal analysis measurement (TGA) was recorded on a Shimadzu thermo-gravimetric analyzer model TGA-50 H, using 20 mg samples. The flow rate of nitrogen gas and heating rate were 20 cm^3 min^{-1} and 10°C min^{-1} respectively. The magnetic susceptibility measurement for the manganese (II) complex was determined by the Gouy balance using $Hg[Co(NCS)_4]$ as a calibrant at room temperature.

2.5. Kinetic reactions for Trihydroxy-benzene (THB) oxidation

The catalytic activity of the Mn^{II}AMC complex toward the homogenous oxidation of trihydroxybenzene (THB) in ethanol solution at 25 °C was determined by measuring the initial rate of THB oxidation. The increase of the absorption at 420 nm (ε = 4.583 M^{-1}cm^{-1}) due to the oxidation product [20] with time was obtained on a Varian Cary 3E spectrophotometer. A plot of the formation of the product with respect to time gives the initial rate. To study the effect of the catalyst concentration on the rate of the reaction, various amounts of the Manganese (II) complex (20 - 700 µM) have been used with 150 µM H_2O_2 for oxidation of 1.0 mM THB at 25^{o}C. At the same time, 140 µ M of the catalyst has been used in the oxidation of different concentrations of the substrate (10 –4000 µM) in presence of 150 µM H_2O_2 to study the effect of THB concentration on the reaction. The rate laws were determined and rate constants obtained. The dependence of H_2O_2 on THB oxidation by 140 µM Mn^{II}AMC was determined by measuring the oxidation rate at different concentrations of hydrogen peroxide (10 – 300 µM) in presence of 1.0 mM THB in ethanol at 25^{o}C. The auto-oxidation rate of THB was determined under the same conditions in the absence of Mn^{II}AMC.

III. RESULTS AND DISCUSSION

3.1. Characterization of AMC.

The organic ligand AMC has been prepared using microwave irradiation method which enhances organic reactions in environmentally benign solvents such as water representing very powerful green chemical technology both from economic and synthetic points of view. This not only reduces the burden of organic solvent disposal but also enhances the rate of the reaction. The ^{1}H-NMR spectrum revealed peaks attributed to δ = 1.03 (s, 3H, CH_3), 1.19 (s, 3H, CH_3), 2.23 (d, 1H, J_{AB} = 16 Hz, H-8a), 2.31 (d, 1H, J_{AB} = 16 Hz, H-8b), 2.45 (s, 2H, C_6-H), 3.79 (s, 3H, OCH_3), 4.02 (s, 1H, C_4-H), 4.95(s, 2H, NH_2, D_2O exchangeable) and 7.11-7.29 (m, 4H, Ar-H).

The IR spectral data (Fig. 1) and ^{1}H-NMR spectroscopy together with the molecular weight from the mass spectrum (m/z = 324) confirm the structure of the ligand.

3.2. Characterization of Mn^{II}AMC.

The IR spectral data of the Mn (II) complex compared with the ligand showed that the manganese (II) binds to AMC through the NH_2 and C≡N nitrogen atoms. This suggestion was supported by reducing in the intensity and shifting of the cyanide band from 2220 cm^{-1} in the ligand to 2205 cm^{-1} in the complex spectrum [16-21]. At the same time, the NH_2 bands were shifted from 3372 and 3280 cm^{-1} in the ligand to 3450 and 3300 cm^{-1} in the complex spectrum. The coordination of the nitrogen atoms to the metal is also consistent with the presence of a new band at 473 cm^{-1} due to νMn–N. The broadening in the band at 3450 cm^{-1} is due to overlapping of the νOH stretching vibration of water molecule with νNH_2 group. The band corresponding to νCO band appears at the same position in the ligand and complex spectra, indicating to not participation in the coordination. The proposed structure is also supported by the presence of a new band at 522 cm^{-1} attributed to Mn–O[22].

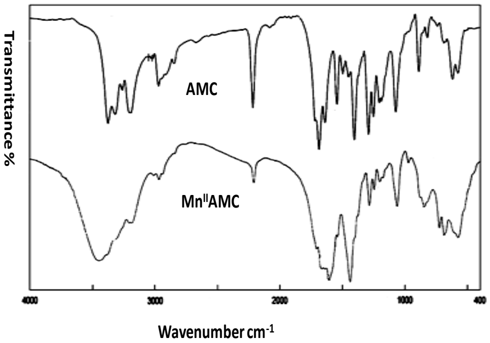


Figure 1. FTIR spectra of the AMC and Mn^{II}AMC complex

3.2.1.Electronic spectral data of Mn^{II}AMC.

The electronic spectrum of the metal complex Mn^{II}AMC (Figure 2) exhibited three absorption bands at 230 nm, 305 nm due to n → π* and π → π* and the other one at 350 nm due to d → d transitions, respectively, suggesting an octahedral geometry around Mn ion[23]. The magnetic moment of Mn (II) complex is 5.31 BM. This value suggests the presence of five unpaired electrons and supports the octahedral geometry around the Mn ion.

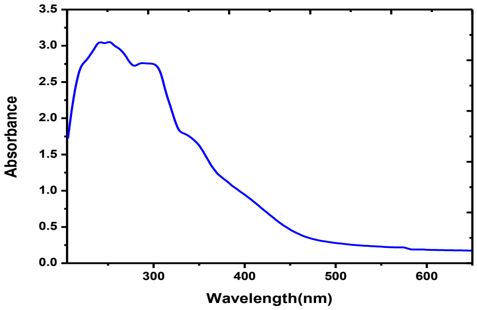


Figure 2. Electronic spectrum of Mn^{II}AMC.

3.2.2.Thermal analysis of Mn^{II}AMC

The majority of compounds including complexes suffer physical and chemical changes when subjected to heat energy. Under defined experimental conditions, these changes are characteristic of such substances and can be used for its qualitative and quantitative analysis.

Manganese complex showed three stages of decomposition (Figure 3). The first stage at 155-180 °C corresponds to removal of two water molecules inside the coordination sphere with weight loss (calc. = 6.75%, found = 6.80%). The second peak in the temperature range of 195-350 °C corresponds to removal of two CO_2 molecules, two NH_3 molecules and $PhOCH_3$ with weight loss (cal. = 43.15%, found = 43.25%). The third inflection point in the range of 365-470 °C corresponds to $(CH_3)_2CHCH_2CHO$ with weight loss (cal. = 16.13%, found =16.31%).

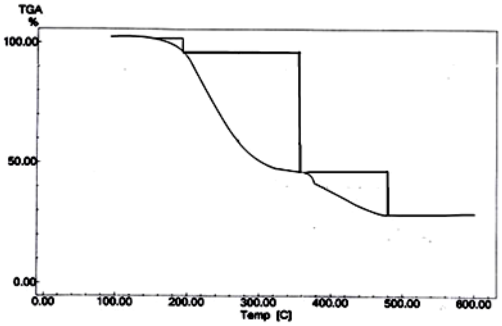


Figure 3. TGA of the manganese complex of Mn^{II}AMC

Thermodynamic parameters

The thermodynamics activation parameters of the decomposition process were evaluated using the well known Coats –Redfern equation [24]. The activation energy Ea, the activation entropy ΔS, the activation enthalpy ΔH, and the free energy (Gibbs function ΔG) for all decomposition stages were calculated (table 1). The entropy ΔS gives information about the degree of disorder of the system. The enthalpy ΔH gives information about the total thermal motion and Gibbs or free energy gives information about the stability of the system.

3.2.3. Mass spectroscopy of Mn^{II}AMC.

The mass spectrum of manganese complex ($C_{23}H_{29}N_2O_9Mn$) Figure 4, shows a molecular ion peak at m/z = 531 corresponding to the Mn complex moiety.

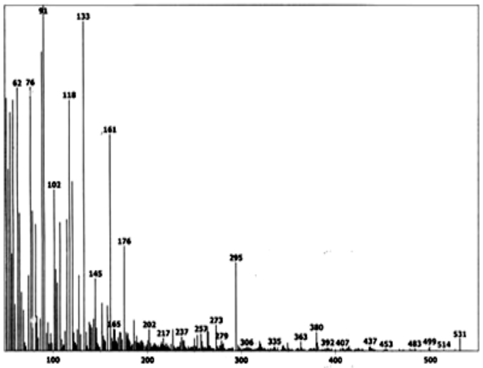


Figure 4. Mass spectrum of Mn^{II}AMC complex

The elemental analysis in table 2, together with the IR, electronic spectral data , mass spectroscopy, thermal analysis and magnetic moment suggest that the structure of the manganese complex is [Mn L$(AC)_2$.$2H_2O$] where L = AMC, as shown in the structure(1).

3.3.Catalytic activity study

3.3.1. Oxidation of trihydroxybenzene (THB).

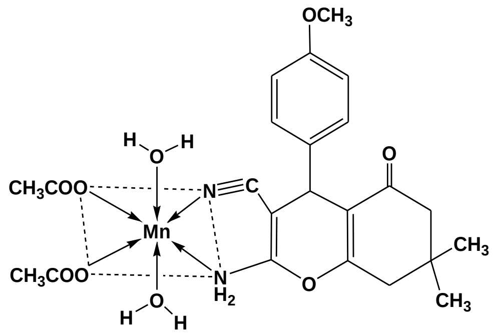
Environmental and economic factors make the use of harmful oxidants increasingly unacceptable except on a small scale, hydrogen peroxide is used in the oxidation of 1,2,3-trihydroxybenzene (THB). Mn^{II}AMC complex was used to activate the green oxidant H_2O_2 in the oxidation of THB affording an effective catalyst.

Table 1. Thermodynamic parameters for Mn^{II}-AMC complex

Decomposition temperature K	E (kJ mo^{-1})	ΔS (J K^{-1} mo^{-1})	ΔH (kJ mo^{-1})	ΔG (kJ mo^{-1})
428-453	81.1	-38.1	77.4	94.3
468-623	87.8	-38.3	83.5	103.5
638-743	125.5	-38.5	119.8	146.5

Table 2. Elemental analysis of the complex Mn^{II}AMC.

Complex M.wt.	% C		% H		% N		%Mn	
	Cal.	Foud	Calc.	Foud	Calc.	Foud	Calc	Foud
531	51.97	51.94	5.46	5.41	5.27	5.30	10.33	10.29



Structure 1. the manganese complex Mn^{II}AMC.

In order to study the catalytic activity of the Mn^{II}AMC complex and its interaction with H_2O_2 towards the homogenous oxidation of 1,2,3-trihydroxybenzene, THB has been used as a substrate to provide detailed kinetic information. The oxidation rates of THB by 140 µM Mn^{II}AMC at different concentrations of THB (Figure 5) have been determined in the presence of 150 µM H_2O_2. The rate of THB oxidation is found to be nonlinear, reaching saturation at high THB concentrations which suggest an enzyme-like pre-equilibrium kinetics. This kinetics can be described as the binding of THB with the catalyst Mn^{II}AMC to form an intermediate THB- Mn^{II}AMC complex, Followed by the conversion of the bound substrate (THB) into product[25]. The reaction in the presence of saturation amount of H_2O_2 (250 µM) (Figure 5) produces a first-order rate constant k_{cat} = 0.0063 s^{-1} ($t_{1/2}$ = 110 s) and dissociation constant K′ = 18 mM. The Mn^{II}AMC affords a significant catalytic efficiency k_{cat}/K'= 0.12 $M^{-1}s^{-1}$ as the second order rate constant[25]. The catalysis shows 2.49 × 10^3 times rate enhancement in terms of the first-order rate constant (k_{cat}/k_o, wherein $k_o = 2.53 \times 10^{-6}$ s^{-1} is the rate constant for the uncatalyzed reaction under the same reaction conditions. The oxidation of the trihydroxybenzene as a function of H_2O_2 also shows a saturation pattern at high concentrations (Figure 6), showing k_{cat} = 0.011 s^{-1} and K′= 28 mM , indicating direct binding of this oxidant to the active metal center. Therefore, both THB and H_2O_2 are considered to be substrates.

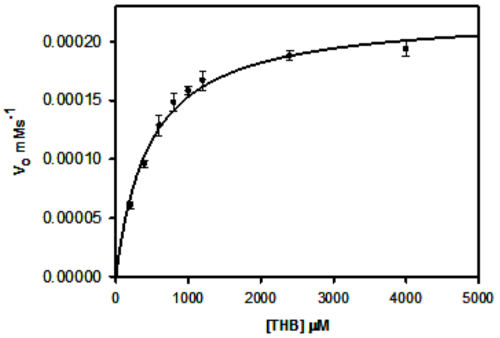


Figure 5. oxidation of different concentrations of THB using 140 µM Mn^{II}AMC with 250 µM H_2O_2 at 25°C.

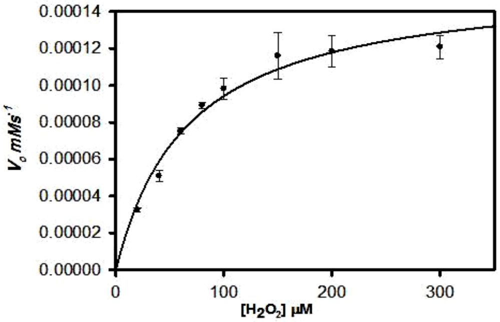


Figure 6. oxidation of 1.0 mM THB using 140 µM Mn^{II}AMC with different concentrations of H_2O_2 at 25°C.

To study the effect of the catalyst concentration on the oxidation of THB with 250 µM H_2O_2 (Figure 7), different concentrations of the Mn^{II}-AMC have been used in the oxidation of THB.

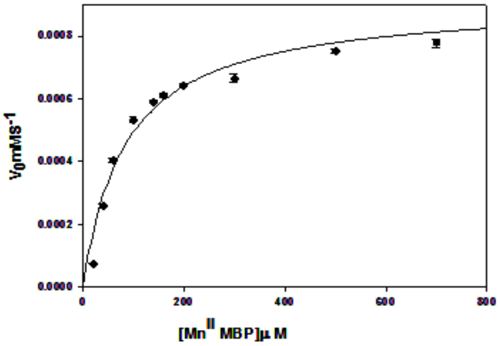


Figure 7. oxidation of 1.0 mM THB using different concentrations of Mn^{II}AMC.

The observed rate was found to be linear till 140 µM of manganese complex and then reach saturation indicating that the optimum concentration for the manganese complex to be used as a good catalyst is around 140 µM.

IV. CONCLUSION

The environment friendly Mn^{II}AMC complex was synthesized and fully characterized using different tools. The geometry around the manganese ion is found to be octahedral geometry. The Mn^{II}AMC complex has been used as a catalyst in the homogenous oxidation of polyphenol 1,2,3-trihydroxybenzene in presence of H_2O_2 as a green oxidant. The complex affords a significant catalytic activity towards the oxidation of THB compared to the uncatalyzed reaction.

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