

Synthesis spectroscopy and computational Studies of Manganese (II) Complexes incorporating (N,O)(O,O') ligands and their biological activity

ABSTRACT (ARIAL, BOLD, 11 FONT, LEFT ALIGNED, CAPS)

Manganese (II) complexes were synthesized via the reaction equimolar quantity of Manganese(II) chloride-hydrate ($\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$) with Chiral saccharides such $\{(\text{OH})_5(\text{CH}_2)(\text{C}_5\text{H}_5)\text{O}\}$ or $\{(\text{OH})_6(\text{CH}_2)(\text{C}_5\text{H}_5)\text{O}\}$ and ($\text{C}_9\text{H}_7\text{NO}$) as secondary ligands $[\text{Mn}(\text{C}_9\text{H}_7\text{NO})\{(\text{OH})_5(\text{CH}_2)(\text{C}_5\text{H}_5)\text{O}\}]\text{Cl}_2$ (**C1**), $[\text{Mn}(\text{QH})\{(\text{OH})_6(\text{CH}_2)(\text{C}_5\text{H}_5)\text{O}\}]\text{Cl}_2$ (**C2**), respectively where ($\text{C}_9\text{H}_7\text{NO}$) is 8-hydroxyquinoline, $\{(\text{OH})_5(\text{CH}_2)(\text{C}_5\text{H}_5)\text{O}\}$ Dextrose (Dex), $\{(\text{OH})_6(\text{CH}_2)(\text{C}_5\text{H}_5)\text{O}\}$ fructose (fru). These complexes were characterized by UV-vis, IR spectroscopy, tandem mass spectrometry and elemental analysis.

The complexes have been found to have square planer geometry as the optimization method. The molecular geometries obtained from XRD data.

The pre-optimized to standard convergence criteria using the basis Minimize Energy to Minimum.

The isolated compounds were screened for its antibacterial activity against six standard human pathogens (*Staphylococcus aureus*, *Streptococcus* spp., *Escherichia coli*, *Klebsiella* spp., *Pseudomonas* spp. and *Protues* spp.). and the results were obtained. About 10 to 70% for complex (C1) and about 10 to 60 % for complex (C2) of the activity.

Keywords: *Manganese (II) complexes; Chiral saccharides; optimization; geometries; Minimize Energy; Dextrose; fructose ; 8-hydroxyquinoline.*

1. INTRODUCTION

Mixed ligand complexes containing amino acid as coligand are potential biomimetic models for metal-protein interaction [1]. The metal complexes have wide applications in various fields of human interest that depend on the nature of the metal and type of the ligand [2,3]. Transition metals play a vital role in biological systems such as respiration, nitrogen fixation, photo- synthesis and cell division [4]. Light catalyzed inversion and diastereoisomeric equilibration [5] in chiral metal complexes have been studied extensively. Schiff base metal complexes based research works have been widely carried out from 1930, because of their biological and industrial applications [6]. The use of metal complexes as pharmaceuticals has shown promise in recent years particularly as anticancer agents [7]. So far various Schiff base complexes have been employed to catalytic oxidation of olefins to epoxides and aldehydes, and it has been proved that many Schiff base complexes gave improved results as catalysts for these kinds of oxidation reactions [8–9]. Amino acids are form complexes with metal atoms and exhibit significant enzymatic and biological activities [10]. Ternary complexes containing an amino acid as a secondary ligands are of significance as they are potential models for enzyme-metal ion substrate complexes. Antimicrobial activities of Ni(II) and Zn(II) ions have been reported [11]. Mixed ligands complexes are established to be biologically active against pathogenic microorganisms [12, 13], further, metal complexes, which include 8-hydroxyquinoline as primary ligands exerts biological activity, ternary complexes containing an amino acid as a secondary ligands are of significance as they are potential models for enzyme-metal ion substrate complexes. [14]

Mixed ligands Zr(IV) complexes prepared with 8-hydroxyquinoline as a primary ligand and amino acids such as L-alanine/L-serine/glycine as a secondary ligands. Zr(II) was used due to its high coordination number and ability to form stable complexes. These complexes were characterized and screened for their antibacterial, antifungal and cytotoxic properties [15]. The present work comprises of synthesis and characterization of chiral mixed ligands Mn(II) complexes by using (HQ) as a primary ligand and various chiral saccharides as secondary ligands were prepared as complexes and they found to be biologically active against pathogens such as (Staphylococcus-aureus, Streptococcus spp., Escherichia coli, Klebsiella spp., Psuedomonas spp. and Protues spp.).

2. MATERIAL AND EXPERIMENTAL DETAILS:

2.1 Materials

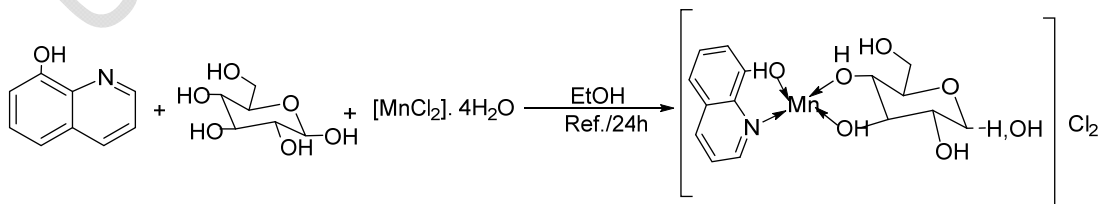
2.1.1 Chemicals and instruments

All chemicals were used as received from supplied. The metal salt Manganese (II) Chloride was produced by Laboratory Reagent chemical company. saccharides were obtained from chem-King company and 8-hydroxyquinoline produced by BHD chemical company, sodium hydroxide produced by Riedel-dehean chemical company. Ethanol and methanol production company PSPARK chemical company. Used Solvents were purified by distillation. The UV spectra were recorded on a Shimadzu UV-2010 double-beam Spectrophotometer spec-thermometer, with samples in 1 cm quartz cuvettes. The Fourier Transform-Infrared Spectroscopy (FTIR) (Perkin-Elmer) was carried out over the range of 4000–400 cm^{-1} with resolution of 1 cm^{-1} on diamond. Mass spectrometry used by tandem mass spectrometry methods and x-ray powder with elemental analysis. CHN analyses were on BROKER company.

2.2 Excremental suction:

2.2.1 Synthesis of [(8-hydroxyquinoline)(Dextrose)Manganese(II)] $[\text{Mn}(\text{HQ})(\text{Dex})]\text{Cl}_2$ (C1)

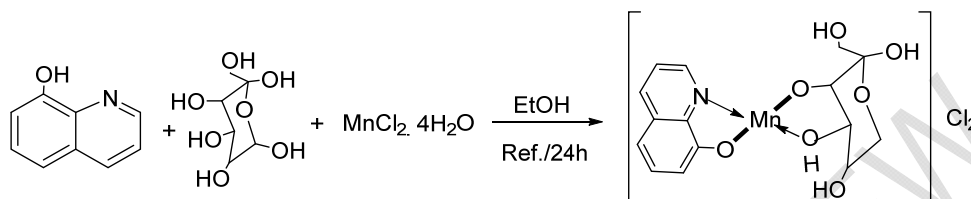
This complex was synthesized as previously reports [16] with certain modifications. Manganese (II) Chloride $[\text{MnCl}_2 \cdot 4\text{H}_2\text{O}]$ (396mg, 0.2mmol) in 10 ml of ethanol and then an equimolar quantity of 8-hydroxyquinoline $\{\text{C}_9\text{H}_7\text{NO}\}$ (290 mg, 0.2mmol) in 10 ml of ethanol was added a dropwise at room temperature with stirring. The temperature was gradually increased and the reaction mixture was refluxed for 10 minutes, during that time the color was turned to brown. After that aqueous solution of Dextrose (396mg, 0.2mmol) was added to the mixture. The reaction was refluxed in water bath for more than four hours. During that time the color was observed yellow. The complex was obtained by raising the pH of the reaction mixture by adding (0.01 ml) of NaOH solution. The yellow solid was separated from the cold solution by filtration. Then the solid compound was washed with cold water followed by mixture of ethanol: water (1:1). The final solid was dried under vacuum, after purification of the product was acquired with (380 mg, 50%), CHN analysis calculated (found) C = 43.5 (44) & H = 5 (6.6) & N = 3.4 (3.7) & M = 13.2 (11.2) (Scheme 1).



Scheme (1) preparation of $[\text{Mn}(\text{HQ})(\text{Dex})]\text{Cl}_2$

2.2.2 Synthesis of [(8-hydroxyquinoline) (fructose)Manganese(II)] $[\text{Mn}(\text{HQ})(\text{fru})]\text{Cl}_2$ (C2)

This complex was synthesized by the same method described before [16] with certain modification. The preparation was via the equimolar quantity of Manganese (II) Chloride, 8-hydroxyquinoline $\{C_9H_7NO\}$ and fructose with the mole ratio of 1:1:1 or 396mg, 290 mg and 360mg respectively. The final yellow product was collected and then purified with (360 mg, 47%) CHN analysis calculated (found) C = 43.5 (44) & H = 5.1 (6.6) & N = 3.4 (3.7) & M = 13.3 (11.3) (Scheme 2).



Scheme (2) preparation of $[Mn(HQ)(Fru)]Cl_2$

2.2.3 Preparation of Bacterial Suspensions

One ml aliquots of 24 hours broth cultures of test organisms were aseptically distributed onto nutrient agar slopes and incubated at 37°C for 24 hours. The bacterial growth was harvested and washed off with sterile normal saline, to produce a suspension containing about 10^8 - 10^9 colony forming units per ml. The average number of the viable organism per ml of saline suspension was determined using surface counting technique. The suspension was stored in the refrigerator at 4°C till used. Serial dilution of the stock suspension were made in sterile normal saline in tubes and adjustable volumes micropipette transferred one drop (0.02 ml) volumes of the appropriate dilution onto the surface of dried nutrient agar plates. The plates were allowed to stand for two hours at room temperature for the drop to dry and then incubated at 37°C for 24 hours. After incubation, the number of developed colonies in each slide was counted. The average number of colonies per drop (0.02 ml) was multiplied by 50 and by the dilution factor to give the viable count of the stock suspension, expressed as the number of colonies forming units per ml suspension. Each time new stock suspension was prepared. All the above experimental condition were maintained constant so that suspension with very close viable counts would be obtained.

2.2.4 Testing for Antibacterial Activity

The cup –plate agar diffusion method was adopted with some minor modification, to assess the antibacterial activity. 20 ml aliquots of incubated agar were distributed into sterile Petri dishes, the agar was left to set in each of these plates which were divided into two groups, each group has six cups in each (10 mm in diameter) were cut using a sterile cork- borer (No 4). Each of the halves was designed for one of the test compounds. Separate Petri- dishes were created for the standard antibacterial chemotherapeutic agent. The agar discs were removed, Alternated cups were filled with 0.1 ml sample of each of the extracts and pure complexes using adjustable volume micro titer pipette, and allowed to diffuse at room temperature for two hours. The plates were then incubated. In the upright position at 37°C for 24 hours.

The above procedure was repeated for different concentrations of the complexes and the standard antibacterial chemotherapeutic. After incubation, the diameter of the resultant growth inhibition zones was measured and averaged.

3. RESULTS AND DISCUSSION

3.1 FT-IR Spectral Study:

Studying complexes $[\text{Mn}(\text{HQ})(\text{Dex})]\text{Cl}_2$, $[\text{Mn}(\text{HQ})(\text{fru})]\text{Cl}_2$ in Fourier transform Infrared (FT-IR) spectroscopy, to confirm the appearance of some function to be observed in the complex. Absorption peak at 1108 cm^{-1} indicated strong absorption of $\nu(\text{C}-\text{O})$ stretching frequency and also appearance absorption at $1496\text{--}1495\text{ cm}^{-1}$ indicates the presence of $\nu(\text{C}=\text{N})$ stretching frequency, interacted within the complexes, the free ligand normally occurs at higher region $\nu(1582\text{ cm}^{-1})$. A negative shift in this vibrational mode on complexation indicates the coordination through the tertiary nitrogen donor of HQ. The plane and out of plane ring deformation modes are observed at 785 cm^{-1} , confirming coordination through the nitrogen atom of HQ with metal. while the appearance absorption at 783 cm^{-1} and 507 cm^{-1} which indicated the presence of association $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ stretching respectively. The shifts of these frequencies are due to the coordinate bonding of nitrogen to the metal [17-18].

3.2 UV-Vis. Spectral Study:

$[\text{Mn}(\text{HQ})(\text{Dex})]\text{Cl}_2$, $[\text{Mn}(\text{HQ})(\text{fru})]\text{Cl}_2$ were examined in spectrally by using a ultraviolet and visible radiation UV-Vis. Peaks absorption of initial at 285 nm , 342 nm , a sharp peak at 401 nm and a broad peak at 443 nm which demonstrates the transmission of the types $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, d-d transition and C-T (Charge Transfer) transition respectively for the complex $\text{Mn}(\text{HQ})(\text{Dex})\text{Cl}_2$ whereas the complex $[\text{Mn}(\text{HQ})(\text{fru})]\text{Cl}_2$ showed absorption at 260 nm , 340 nm and 440 nm in frequency (3846 cm^{-1} , 2941 cm^{-1} and 2272 cm^{-1}) respectively which is demonstrates the transmission of the types $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and C-T (Charge Transfer) transition respectively. These are identical with those reported in previously work. where the complex $[\text{Mn}(\text{HQ})(\text{fru})]\text{Cl}_2$ showed absorption at 260 nm , 340 nm and 440 nm which is demonstrates the transmission of the types $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and C-T (Charge Transfer) transition respectively. These are identical with those reported in previously [19-22] as shown in Figure 1.

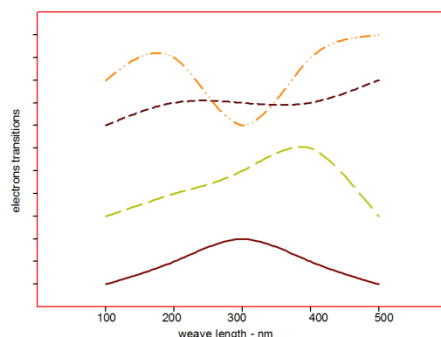


Fig. 1. Uv-Vis spectrum of complexes $[\text{Mn}(\text{HQ})(\text{Dex})]\text{Cl}_2$, $[\text{Mn}(\text{HQ})(\text{fru})]\text{Cl}_2$ $\pi \rightarrow \pi^*$ (brown dots), $n \rightarrow \pi^*$ (brown line), d-d transition (light green dots) and C-T (orange dots)

3.3 X-ray powder diffraction (XRD):

As chitosan present strong interaction bonding between ligands and metal ions, it usually presents more crystalline character than other carbohydrates [23]. In the XRD spectrum for characteristic peaks at $2\theta = 10.4$, 14.2 and 24 were observed for $[\text{Mn}(\text{HQ})(\text{Dex})]\text{Cl}_2$, at the meantime complex $[\text{Mn}(\text{HQ})(\text{fru})]\text{Cl}_2$ found peaks at $2\theta = 10.4$, 19.2 and 21 were observed

in agreement with the previous reports [24,25]. Figure 2 presents XRD diffract to grams of manganese complexes with Dextrose or fructose and 8-hydroxyquinoline as a ligands and co-ligands representative example and in the XRD diffract to grams of all metal complexes a widening and an intensity decrease were observed in peaks as well as in crystallinity values.

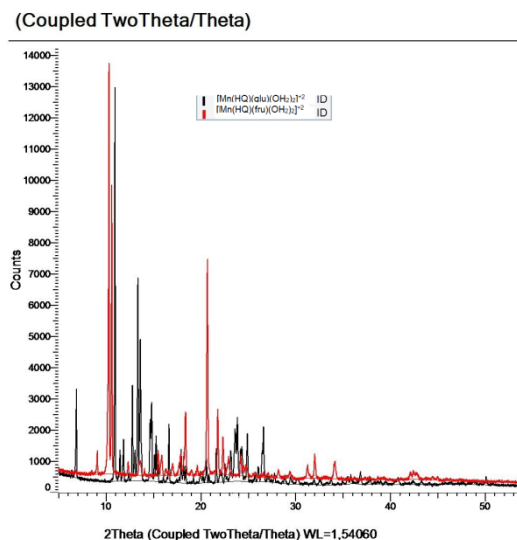


Fig. 2. XPRD spectra of $[Mn(HQ)(Dex)]Cl_2$ in Black and $[Mn(HQ)(fru)]Cl_2$ in red

3.4 Mass spectrometry

These compounds were clearly indicated by mass spectra. The most interested peaks in the EI-mass spectra of compounds at 451 and 418 a corresponded to $[Mn(HQ)(Dex)]Cl_2$ and $[Mn(HQ)(Dex)]^+Cl$ or $[Mn(HQ)(fru)]Cl_2$ and $[Mn(HQ)(fru)]^+Cl$ ions receptivity as shown in Figure 3.

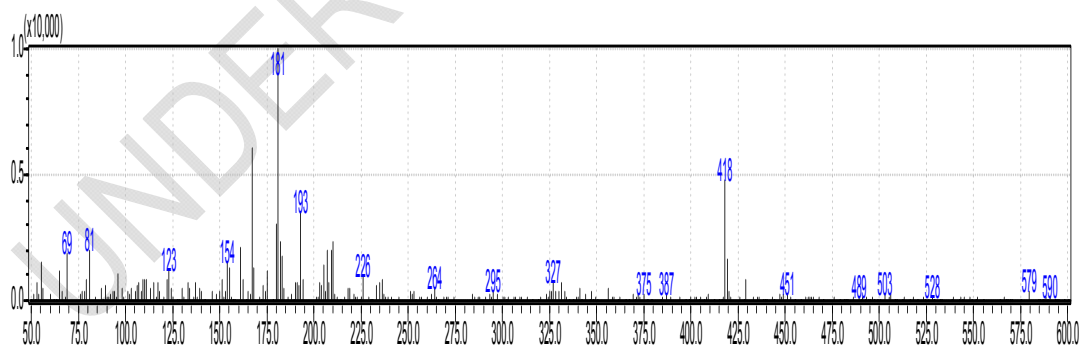


Fig. 3. Mass spectra of $[Mn(HQ)(Dex)]Cl_2$

3.5 Computational study:

The molecular geometries obtained from XRD data and were drowning via ChemBio3D Ultra-14. The pre-optimized to standard convergence criteria using the basis Minimize Energy to Minimum RMS Gradien to examine their properties at the minimum energy. The

calculated structural parameters of compounds **C1** and **C2** compare well with the analog experimentally complexes determined parameters (Table1).

Table 1. Parameter Optimization of [Mn(HQ)(Dex)]Cl₂ and [Mn(HQ)(fru)]Cl₂

Parameters Optimization	[Mn(HQ)(Dex)]Cl ₂	[Mn(HQ)(fru)]Cl ₂
Stretch:	3.9699	4.2121
Bend:	62.6648	50.3041
Stretch-Bend:	-2.1175	-1.7481
Torsion:	35.7864	7.6040
Non-1,4 VDW:	-7.9603	-9.1738
1,4 VDW:	28.7849	25.1011
Dipole/Dipole	3.0127	3.5019
Total Energy	124.1409	79.8012
	kcal/mol	kcal/mol

The Mn(II) atom displays a distorted square-planar coordination geometry, with one N atom and three O atoms from four the ligand in the equatorial plane position. Mn–N, Mn–O(1), and Mn–O(2) and Mn–O(4) bond lengths are 1.848Å, 1.836Å, 1.808Å and 1.595Å, respectively, and are within the average values found in a Cambridge structural database search [26-28] for compounds having two carbon atoms in the imines bridge. These bond lengths detailed are shown in Table2 and Figure 4.

The chelate bite angle, defined by the < N-Mn-O(1) bond angles of 95.04° and the < O(1)-Mn-O(2) for the complexes **C1** at meantime the **C2** showed bond angles < N-Mn-O(1) of 95.035° and < O(2)-Mn-O(3) of 93.00° derives from the short two-carbon phenyl bridge.

From the point of view of catalysis this is encouraging as a monomeric complex could potentially be more active than a dimer.

Moreover, there is a good agreement between the analog experimentally complexes and our theoretical complexes values with consideration the fact, that the experimental data refer to the solid phase, whereas the theoretical calculations were performed in the gaseous state.

Table 2. Bond Lengths of [Mn(HQ)(Dex)]Cl₂ and [Mn(HQ)(fru)]Cl₂

[Mn(HQ)(Dex)]Cl ₂		[Mn(HQ)(fru)]Cl ₂		[Ni{C ₆ H ₄ N ₂ (C ₆ H ₃ OOH) ₂ }] [26]	
Bond	Length /Å)	Bond	Length /Å)	Bond	Length /Å)
Mn-O(1)	1.836	Mn-O(1)	1.836	Ni-N(1)	1.863
Mn-O(4)	1.595	Mn-O(2)	1.808	Ni-N(2)	1.858
Mn-O(5)	1.7	Mn-O(3)	1.768	Ni-O(3)	1.868
Mn-N	1.261	Mn-N	1.848	Ni-O(1)	1.844
O1-C(4)	1.457	O1-C(4)	1.457	N(1)-C(7)	1.33
N-C(5)	1.526	N-C(5)	1.261	N(1)-C(8)	1.414
O2-C(10)	1.151	O2-C(13)	1.479	O(1)-C(1)	1.302
O5-C(11)	1.434	O3-C(11)	1.434		

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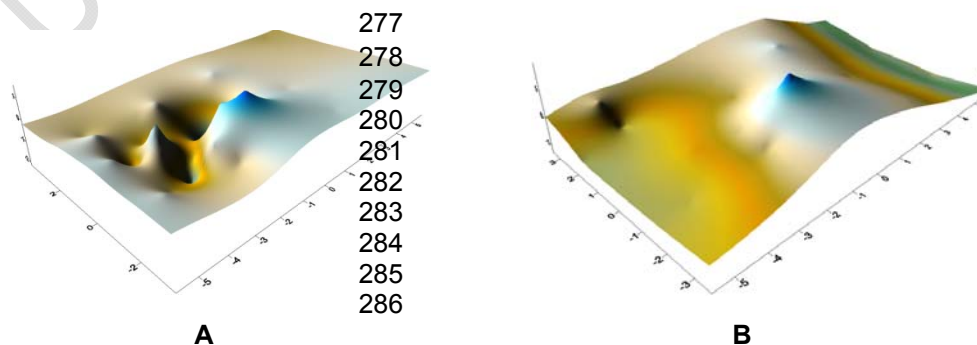
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Fig. 4. An Chemcraft view of the complex $[\text{Mn}(\text{HQ})(\text{Dex})]^{+2}$ (A) $[\text{Mn}(\text{HQ})(\text{fru})]^{+2}$ (B) shown at the 30% probability level

The dashed lines in three-dimensional (3D) of our complexes, that for electrons distribution is represented in [Figure 5](#), the molecular structures of compounds $[\text{Mn}(\text{HQ})(\text{Dex})]^{+2}$ and $[\text{Mn}(\text{HQ})(\text{fru})]^{+2}$ were obtained from single output files of theoretical complexes.



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Fig. 6. Antibacterial Activities in Concentration 0.001M (A), in Concentration 0.001M (B) and in Concentration 0.001M (C)

4. CONCLUSION

The computational chemistry presented in this paper shows that the investigation, molecular structure, molecular electrostatic analysis of $[\text{Mn}(\text{HQ})(\text{Dex})]\text{Cl}_2$ and $[\text{Mn}(\text{HQ})(\text{fru})]\text{Cl}_2$ complexes have been studied, by using the basis-set under Minimize Energy to Minimum RMS Gradient to pre-optimized to standard convergence criteria. Calculated geometric parameters of these complexes were compared with previous experimental structure. No significant differences were observed.

Moreover, experimental data of XRD showed these complexes were obtained via experimental work. The behavior of these complexes come affects in increased antibacterial activity under deferent concentrations. The behavior of these complexes come affects in increased antibacterial activity under deferent concentrations.

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