



## Synthesis, Characterization and Antibacterial Study of New Glyoxylic Acid and Its (N<sub>2</sub>O<sub>4</sub>) Mn<sup>II</sup> Ion Complex



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THE Schiff base reaction played an important role of the condensation reaction between 2-aminophenol and Glyoxylic acid in the presence of calculated amounts of KOH as a catalyst. The reaction has been carried out in ethanol under reflux and stirring condition for 3.5 hrs. All syntheses were carried out under hydrogen gas forming a new *potassium (E)-1-hydroxy-2-(2-hydroxyphenylimino)ethanolate* ligand type [NO<sub>2</sub>]. The ligand of the general formula K<sub>2</sub>[Mn(L<sub>2</sub>)] type and its Mn<sup>n</sup> complex K<sub>2</sub>[Mn(N<sub>2</sub>O<sub>4</sub>)] type, has been characterized by spectroscopic methods (F.T-I.R. and U.V-Vis.), elemental analysis (C.H.N) metal content, magnetic susceptibility measurement, Thin-layer chromatography (T.L.C), X-RD powder diffraction, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR molar conductance and Biological activity (The ligand and its Mn<sup>n</sup> complex were exposed to two types of bacteria (Staphylococcus aureus and Bacillus subtilis), using the agar disc diffusion method, and the ligand and its Mn<sup>n</sup> complex exhibited significant activities against these two types of bacteria). The X-RD of the Mn<sup>n</sup> ion complex revealed that the complexes are 100 % crystalline. The F.T-I.R. measurements, U.V-Vis. and mass spectrum for the ligand and its complex reveal the exact peak for each of the compounds functional groups.

The study revealed the formation of a new ligand type [NO<sub>2</sub>] with study the formation of new crystal complex and six-coordinate octahedral structure around Mn<sup>n</sup> metal ion in the ratio of 1:2 (metal:ligand) stable compounds which can be used in many fields (medicine & industry).

**Keyword:** Crystal ligand, 2-aminophenol and 2-oxoacetic acid (Glyoxylic acid), Manganese (II) acetate 4hydrate-99+%, Six-coordinate octahedral complex, Structural study, Schiff bases.

### Introduction

2-aminophenol is an organic compound with the formula | C=6 | H=4 (OH)| H=2 . Along with its isomer 4-aminophenol, it is an amphoteric molecule and a reducing agent. It is a useful

reagent for the synthesis of dyes and heterocyclic compounds. [1] Reflecting its slight hydrophilic character, white powder is moderately soluble in alcohols and can be recrystallized from hot water. 2-Aminophenol (and its isomer,

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4-aminophenol) is industrially synthesized by reducing the corresponding nitrophenol by hydrogen in the presence of various catalysts. 2-Aminophenol has a variety of uses. As a reducing agent, it is marketed under the names of Atomal and Ortol to develop black-and-white photographs. 2-Aminophenol is an intermediate in the synthesis of dyes. It is particularly useful in yielding metal-complex dyes when diazotized and coupled to a phenol, naphthol, or other aromatic or resonant dye species. [2,3]. Aminophenols and their derivatives are of commercial importance, both in their own right and as intermediates in the photographic, pharmaceutical, and chemical dye industries[4]. **Glyoxylic acid** is an organic compound. Together with acetic acid, glycolic acid, and oxalic acid, glyoxylic acid is one of the C<sub>2</sub> carboxylic acids. It is a colorless solid that occurs naturally and is useful industrially. Glyoxylic acid is usually described with the chemical formula OCHCO<sub>2</sub>H, i.e. containing an aldehyde functional group. Glyoxylate is the byproduct of the amidation process in biosynthesis of several amidated peptides. Glyoxylic acid was prepared from oxalic acid electrosynthetically[5, 6]. In organic synthesis, lead dioxide anodes were applied for the production of glyoxylic acid from oxalic acid in a sulfuric acid electrolyte. [7]. *Glyoxylate* is an intermediate of the glyoxylate cycle, which enables organisms, such as bacteria, [8] fungi, and plant [9] to convert fatty acids into carbohydrates. The glyoxylate cycle is also important for induction of plant defense mechanisms in response to fungi. [10]. **Manganese(II) acetate tetrahydrate-99+%** It is used as a mordant in dyeing, drier for paints and varnishes, an oxidation catalyst, It is also used in the manufacture of fertilizer. It is used for the production of high purity manganese dioxide, manganese oxide hydrate, oxide-based catalysts, and catalysts for oxidation. Crystalline Manganese source that decomposes to Manganese oxide on heating. It is generally immediately available in most volumes. All metallic acetates are inorganic salts containing a metal cation and the acetate anion, a univalent (-1 charge) polyatomic ion composed of two carbon atoms ionically bound to three hydrogen and two oxygen atoms (Symbol: CH<sub>3</sub>COO) for a total formula weight of 59.05. [11, 12]. **Schiff bases** have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. The chemistry of Schiff base ligands species has been gaining considerable

interest primarily because of their fascinating structural diversities [13-15]. The electrophilic carbon atoms of aldehydes and ketones can be targets of nucleophilic attack by amines. The end result of this reaction is a compound in which the C=O double bond is replaced by a C=N double bond. This type of compound is known as an imines, or Schiff base with the general formula R<sub>1</sub>R<sub>2</sub>C=NR<sub>3</sub>, where R is an organic side chain. In this definition, Schiff base is synonymous with Azomethine. Many Schiff base complexes show excellent catalytic activity in various reactions and in the presence of moisture [16]. The condensation of salicylaldehyde with various aromatic amines in water under microwave irradiation. A judicious choice of the solvent and reaction conditions allowed the final products to be generated in excellent yields in a one-step procedure, whereas experiments under thermal conditions led to lower yields with tedious work-up [17]. The Schiff bases are widely used for industrial purposes and also exhibit a broad range of biological activities. This short review compiles examples of the most promising antimalarial, antibacterial, antifungal, and antiviral Schiff bases. An overview of synthetic methodologies used for the preparation of Schiff bases is also described [18].

The manuscript includes the description of the synthesis and physical characterization of *potassium (E)-1-hydroxy-2-(2-hydroxyphenylimino) ethanolate* type [NO<sub>2</sub>]<sub>2</sub> ligand in the ratio of 1:1 (2-aminophenol and Glyoxylic acid), and its new octahedral Mn<sup>II</sup> metal ion complex with the ratio of 1:2 metal ligand, forming new compound of (Mn-N and Mn-O) new bands by condensation reaction, and it has been supported by the most important techniques (F.T-I.R. and U.V-Vis.), elemental analysis (C.H.N) metal content, magnetic susceptibility measurement, Thin-layer chromatography (T.L.C), X-RD powder diffraction, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR molar conductance and study the Biological activity for the ligand and its complex..

## **Materials and Technique**

### **A. Materials**

Chemical reagents were commercially available and used without purification. Solvents were distilled from appropriate drying agents immediately before to use.

### **B. Physical Measurements**

Reagents were purchased from Fluka and Redial- Dehenge Chemical Co. Melting points

were obtained on a Buchi SMP-20 capillary melting point apparatus and are uncorrected. Fourier transform (FT-IR) spectra were recorded as FT-IR spectrophotometer in the range 4000- 400  $\text{cm}^{-1}$ . Electronic spectra of the prepared compounds were measured in the region 200-900 nm for  $10^{-3}\text{M}$  solutions in Dimethyl Sulfoxide (DMSO) and distilled water at  $25^\circ\text{C}$  using a Shimadzu 160 spectrophotometer with  $1.000 \pm 0.001$  cm matched quartz cell. Elemental microanalyses were performed on a C.H.N. analyzer. While metal contents of the complexes were determined by atomic absorption (A.A.) technique using a Shimadzu A.A. 680G A.A. spectrophotometer. Electrical conductivity measurements of the complexes were recorded at  $25^\circ\text{C}$  for  $10^{-3}\text{M}$  solutions of the samples in DMSO and distilled water using a PW 9526 digital conductivity meter. Magnetic measurements were recorded on a Bruker BM6 instrument at 298 K following the Faraday's method. The mass spectrum for the ligand was obtained by electron-impact on (Shimadzu GCMSQPA 1000), and proton one-nuclear magnetic resonance ( $^1\text{H-NMR}$ ) spectrum were acquired in (DMSO- $d_6$ ) solutions using (Jeol Lambda 400 MHz) spectrometer with tetramethylsilane.

#### Synthesis of $[\text{NO}_2]$ Ligand & its $\text{Mn}^n$ complex

**A. Preparation of potassium (E)-1-hydroxy-2-(2-hydroxyphenylimino)ethanolate type  $[\text{NO}_2]$  ligand. Fig.1.**

All syntheses were carried out under hydrogen gas. To a solution of 2-aminophenol (0.10 g, 1 mmol) in ethanol (15 mL) was added Glyoxylic acid (0.07 g, 1 mmole) in (15 mL) ethanol in one portion. The solution was stirred for (3.5 hrs.) at  $100^\circ\text{C}$ , let it at room temperature for a while. After this time the Brown precipitate was filtered off, recrystallized from methanol and dried in vacuum. Yield: (85 %) m.p. ( $103^\circ\text{C}$ ).

#### **B. General Synthesis of the Complex**

$[\text{NO}_2]$  ligand complex were prepared by the general methods Fig. 2, and as follows:-

A suspension of Manganese (II) acetate tetrahydrate (0.30 g, 1.20 mmol) and  $[\text{NO}_2]$  ligand (0.5 g, 2.43 mmol) in methanol (20 mL) with calculated amount of KOH, was heated at reflux for (2 hrs.) After cooling, a deep Brown precipitate was obtained that was collected, washed with 1:1 mixture of ethanol: methanol (5 mL) and dried in vacuum. Yield: (0.32 g, 64 %). m.p. ( $155^\circ\text{C}$ ). The complex have been prepared in the ratio of 1:2 metal-ligand. Elemental analysis data, colors, and yields for the complex are given in Table 1.

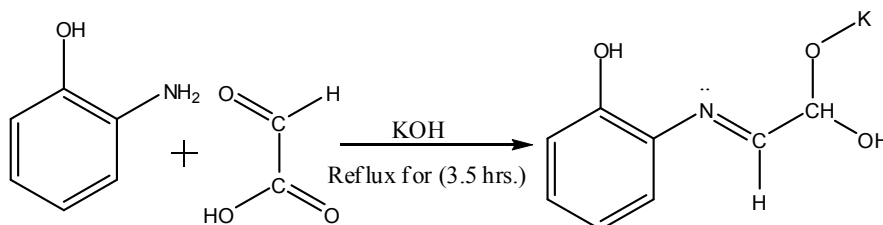


Fig. 1. Synthetic route for ligand  $[\text{NO}_2]$ .

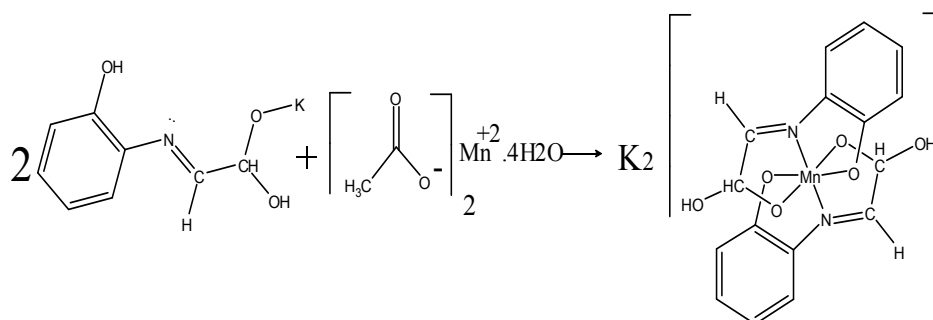


Fig. 2. The general structure for suggested metal ion complex.

**TABLE 1.** The Physical Properties of the Ligand and its Mn<sup>n</sup> Complex.

Molecular formula	M.Wt	Yield%	colour	m.p.c°	Found, (calc%)						$\epsilon_M(\Omega^{-1} \text{cm}^2 \text{mol}^{-1})$
					Mn	C	H	N	O	K	
[NO <sub>2</sub> ]- C <sub>8</sub> H <sub>8</sub> KNO <sub>3</sub>	205.25	85	Brown	103	-	46.77	3.89	6.82	23.38	19.05	-
					-	44.21	3.01	6.07	20.98	18.70	-
K <sub>2</sub> [Mn(N <sub>2</sub> O <sub>4</sub> )]	463.43	64	Deep Brown	155	11.85	41.47	3.04	6.04	20.71	16.87	100
					10.30	40.11	2.50	5.12	18.90	16.00	

## Results and Discussion

[NO<sub>2</sub>] ligand was achieved from the reaction of 2-aminophenol and Glyoxylic acid in the ratio of 1:1 in alkaline medium. The general synthetic method for the preparation of the ligand and its complexes involves the reaction of the Manganese(II) acetates according to Fig. 2. The ligand was obtained in almost a quantitative yield, and the metal complex of the ligand with Mn<sup>n</sup>, metal ion were obtained in moderate yields. The compounds were characterized by Elemental analysis, F.T-I.R., Ultraviolet-visible (U.V-Vis.), Magnetic susceptibility, Melting point, Thin-layer chromatography (T.L.C.), X-RD, <sup>13</sup>C-NMR and <sup>1</sup>H-NMR

### A. The IR Spectrum of the Ligand

The two bands at (3373.5 and 3305.9 cm<sup>-1</sup>) due to the  $\nu(\text{NH}_2)$  primary amine group [19, 20] of 2-aminophenol Fig. 3-a, and the strong band at (1745.5 cm<sup>-1</sup>) of Glyoxylic acid Fig. 3-b which is attributed to  $\nu(\text{C}=\text{O})$  are disappeared in the spectrum of the free ligand and replaced by  $\nu(\text{C}=\text{N})$  new band at (1598.9 cm<sup>-1</sup>) as a consequence of the coordination between 2-aminophenol and Glyoxylic acid indicating Schiff base reaction [21, 22] Fig. 3-c. The bands at (3361.9 cm<sup>-1</sup>) and (3051 cm<sup>-1</sup>) Fig. 3-a and Fig. 3-b which are due to the  $\nu(\text{O}-\text{H})$  of the 2-aminophenol and Glyoxylic acid are shifted to lower and higher frequencies respectively as a result of the coordination and the effect of the neighboring groups of the starting materials in comparison with that of the spectrum of the free ligand at (3061 cm<sup>-1</sup>) Fig. 3-c. While the band at (2758 cm<sup>-1</sup>) of the  $\nu(\text{C}=\text{C})$  of the ring of 2-aminophenol [23] is shifted to higher frequency at (2964.5 cm<sup>-1</sup>) as a result of the delocalization of electron *Pi* density of the ring. Table 2.

### B. The UV-Vis Spectrum of the Ligand

The UV-Vis spectrum of the ligand Fig. 4, exhibit two intense absorption peak at (230 nm) (43478 cm<sup>-1</sup>) ( $\epsilon_{\text{max}}=3800 \text{ molar}^{-1} \cdot \text{cm}^{-1}$ ) and (250 nm) (40000 cm<sup>-1</sup>) ( $\epsilon_{\text{max}}=2800 \text{ molar}^{-1} \cdot \text{cm}^{-1}$ ), assigned for ( $\pi \rightarrow \pi^*$ ) and ( $n \rightarrow \pi^*$ ) transitions [24]. Table 3.

### C. The IR Spectrum of the Mn Complex

In the spectrum of the free ligand Fig. 3-c there is an important bands at (3061 cm<sup>-1</sup>), (2729 cm<sup>-1</sup>) and (1598.9 cm<sup>-1</sup>) due to the  $\nu(\text{O}-\text{H})$  ring,  $\nu(\text{C}-\text{H})$  and  $\nu(\text{C}=\text{N})$  respectively all these bands has been shifted to higher and lower frequencies respectively in comparison with that of the spectrum of Mn<sup>n</sup> complex Fig. 3-d, as a consequence of the coordination of the ligand with the metal ion. While the characteristic new formed bands at (530 cm<sup>-1</sup>) and (570 cm<sup>-1</sup>) range assigned to the  $\nu(\text{Mn}-\text{N})$  and  $\nu(\text{Mn}-\text{O})$  [25] respectively for the formed complex Table 2.

### D. The UV-Vis Spectrum of the Mn<sup>n</sup> Complex

The UV-Vis spectra of Mn<sup>n</sup> complex Fig. 4 showed two intense absorption peaks in the range at (240 nm) (41666 cm<sup>-1</sup>) ( $\epsilon_{\text{max}}=4000 \text{ molar}^{-1} \cdot \text{cm}^{-1}$ ) and (275 nm) (36363 cm<sup>-1</sup>) ( $\epsilon_{\text{max}}=2100 \text{ molar}^{-1} \cdot \text{cm}^{-1}$ ), range assigned to the ( $\pi \rightarrow \pi^*$ ) and ( $n \rightarrow \pi^*$ ) respectively [26]. The third peak detected in the visible region at (510 nm) (19607 cm<sup>-1</sup>) ( $\epsilon_{\text{max}}=200 \text{ molar}^{-1} \cdot \text{cm}^{-1}$ ), range attributed to the electronic transition ( ${}^6A_{1g} \rightarrow {}^4T_{1g(4G)}$ ) [27]. The electronic spectra of Mn<sup>II</sup> complex is depicted in Fig. 4. The electronic spectral data of Complex is listed in Table 3. For the Mn<sup>II</sup> complex, there is only one configuration for five unpaired electrons, which corresponds to the half-filled *d-shell* and is spherically symmetric. The ground state term is  ${}^6S$  and belongs to the  ${}^6A_{1g}$  group. The *d-d* transitions for the high-spin manganese (II) complexes are spin-forbidden. The intensity of the electronic transition from ground state  ${}^6S$  to the states of fourfold multiplicity are very weak and since Mn<sup>II</sup> ion has a *d5* configuration the same type of energy level diagram is applied whether the metal ion is in octahedral or in tetrahedral environments [28]. The electronic spectra of the complexes display the absorption bands in the range (19607 cm<sup>-1</sup>). The transition may be assigned to the ( ${}^6A_{1g} \rightarrow {}^4T_{1g(4G)}$ ), this transition reveal the octahedral geometry for the complexes. [29].

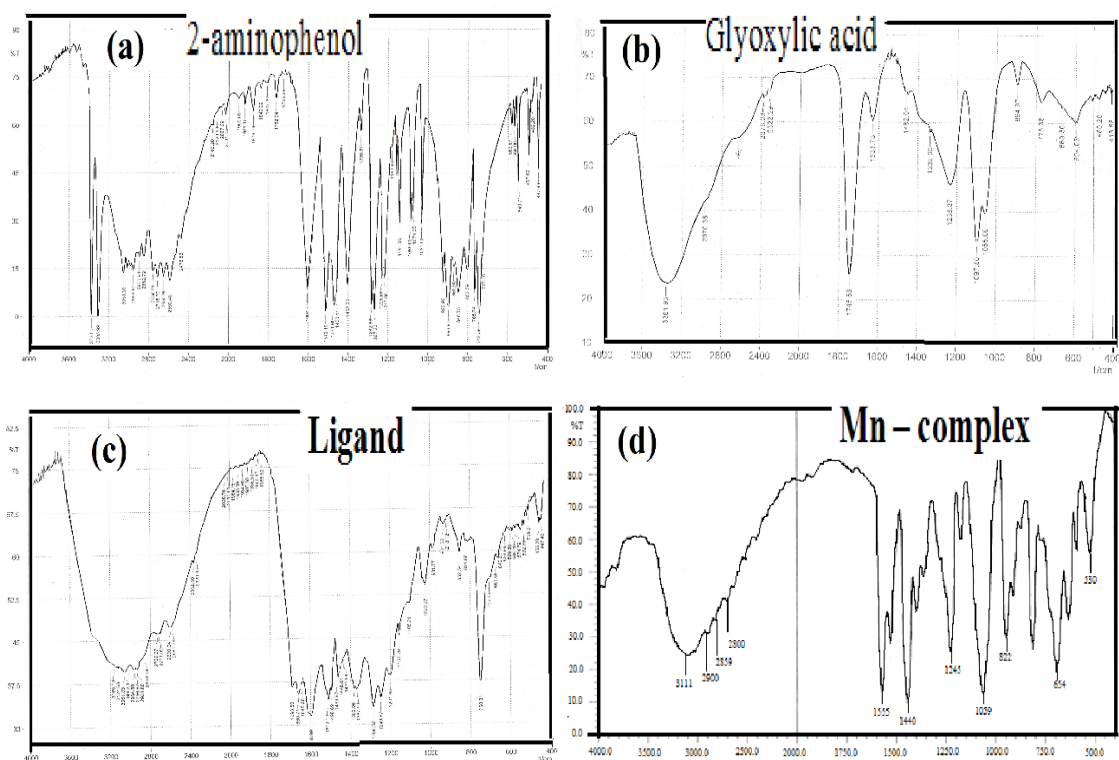


Fig. 3. The F.T-I.R spectrum for the [NO<sub>2</sub>] ligand and its starting materials with its Mn<sup>II</sup> complex.

TABLE 2. FT-IR spectra for the ligand and its precursors with its Mn<sup>II</sup> complex.

Compound	$\nu(\text{-NH}_2)$	$\nu(\text{O-H})$	$\nu(\text{C-H})$ Ring	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
2-oxoacetic acid	-	3361.9	-	1745.5	-	-	-
2-aminophenol	3373.5-3305.9	3051	2758	-	-	-	-
[NO <sub>2</sub> ]-C <sub>8</sub> H <sub>8</sub> KNO <sub>3</sub>	-	3061	2729	-	1598.9	-	-
K <sub>2</sub> [Mn(N <sub>2</sub> O <sub>4</sub> )]	-	3111	2900	-	1555	530	570

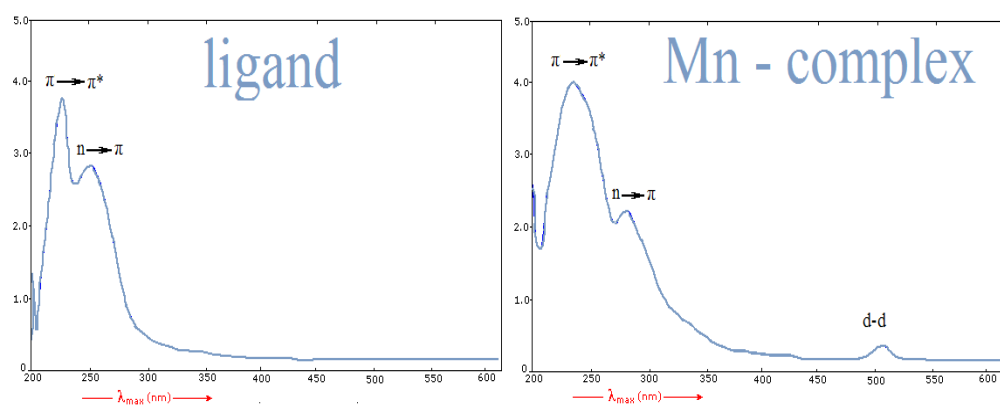


Fig. 4. The U.V-Vis spectrum for the [NO<sub>2</sub>] ligand and its Mn<sup>II</sup> complex



**TABLE 3.** The Electronic Spectral data for the Ligand and its Mn<sup>n</sup> Complex.

Compound	Band Position $\lambda_{nm}$	Wave number (cm <sup>-1</sup> )	$\epsilon_{max}$ (dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> )	Assignment	Magnetic Moment (B.M)	Suggested configuration
[NO <sub>2</sub> ]-C <sub>8</sub> H <sub>8</sub> KNO <sub>3</sub>	230	43478	3800	$\pi \rightarrow \pi^*$	-	-
	250	40000	2800	$n \rightarrow \pi^*$	-	-
	240	41666	4000	$\pi \rightarrow \pi^*$	-	-
K <sub>2</sub> [Mn(N <sub>2</sub> O <sub>4</sub> )]	275	36363	2100	$n \rightarrow \pi^*$	-	-
	510	19607	200	${}^6A_{1g} \rightarrow {}^4T_{1g}(4G)$	3.7	Octahedral

**E.** The magnetic moment value is 5.6 B.M [30], demonstrates that the Mn<sup>n</sup> complex are paramagnetic and has high spin octahedral geometry Table 3.

**F.** Molar Conductance:- The prepared complex found to be solids, it is soluble in some organic solvents like Dimethylformamide and Dimethylsulfoxide. The higher value observed of molar conductivities in DMSO in the range of (100) indicates the electrolyte behavior of the Mn<sup>n</sup>metal ion complex [31-33].

**G.** Elemental analysis (C.H.N) and metal determination were in good agreement with general formula given for the Mn<sup>n</sup>metal ion complex. Table 1. gives in details the physical properties of the complexes.

**H.T.L.C.** Measurement for the derivative [NO<sub>2</sub>] ligand and its Mn<sup>n</sup>complexare showed in Fig.5. The appearance of new spots with different  $R_f$  compared with the  $R_f$  of the ligand. Table 4. for Mn<sup>n</sup> indicated the formation of the complex. Since the spot position belong to Mn<sup>n</sup> ion complex are differ from the position of the ligand spot.

**I.** The biological activity of the [NO<sub>2</sub>] ligand and its Mn<sup>n</sup> complex was tested on two types of pathogenic bacteria using inhibition method [34-37]. The two types of bacteria were Gram-positive *Staphylococcus aureus* and *Bacillus subtilis*. The [NO<sub>2</sub>] ligand and its complex showed inhibition diameter against the two types of bacterial after 24 hrs., and this inhibition diameter was increased after 48 hrs. Fig. 6.

**J.** The X-ray powder diffraction (X-RD) pattern of Mn<sup>n</sup>complex shows well-defined crystalline peaks indicating that the sample is 100 % crystalline in nature [38, 39]. An X-RD powder diffraction

pattern of Mn<sup>n</sup> complex has been given in Fig. 7. The sample has been dried and then scanned in the 2 $\theta$  range of 10-80<sup>o</sup> confirming octahedral geometry around Mn<sup>n</sup> ion complex [40, 41].

**K.** The <sup>1</sup>H-NMR spectrum for [NO<sub>2</sub>] ligand in DMSO-d<sup>6</sup> solvent Fig. 8, showed single signal peak appear at (9.7 ppm – 1(O-H) ) attributed to aromatic C-OH group. And multiple peaks at (6.5-7.2 ppm - 4 (C-H)) attributed to C-H benzene ring . Table 5, summarized the details of the other chemical shifts.

**L.** The <sup>13</sup>C-NMR spectrum for [NO<sub>2</sub>] ligand in DMSO-d<sup>6</sup> solvent Fig. 9, showed single signal peak appear at (65 ppm –CH aliphatic (1H)) attributed to methyl group. Table 6, summarized the details of the other chemical shifts.

## Conclusion

The reaction of 2-aminophenol and Glyoxylic acid gives the required [NO<sub>2</sub>] ligand. The reaction of this ligand with manganese (II) acetates resulted in the formation of the required complex with octahedral geometry around Mn<sup>n</sup> ion complex. Physical, chemical, and spectroscopic methods were used to investigate the mode of bonding and overall structure of the Mn<sup>n</sup> complex of [NO<sub>2</sub>] ligand which have been synthesized and characterized by elemental analyses and spectroscopic techniques, The X-RD of the Mn<sup>n</sup> ion complex revealed that the complexes are 100 % crystalline. The F.T-I.R. measurements, U.V-Vis. and mass spectrum for the ligand and its complex reveal the exact peak for each of the compounds functional groups. Moreover, the aims of this study are to:

1. The formation of new crystal complex by the reaction between 2-aminophenol and 2-oxoacetic acid with Mn<sup>n</sup> metal ion.

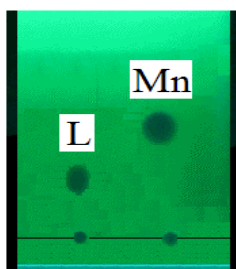


Fig. 5. The T.L.C. measurements for the  $[\text{NO}_2]$  ligand and its  $\text{Mn}^{\text{II}}$  metal ion complex

TABLE 4. The T.L.C. measurements for  $[\text{NO}_2]$  ligand and its  $\text{Mn}^{\text{II}}$  complex.

Compound	Range of $R_f$ (mm)
$[\text{NO}_2]\text{-C}_8\text{H}_8\text{KNO}_3$	2.3
$\text{K}_2[\text{Mn}(\text{N}_2\text{O}_4)]$	4.1

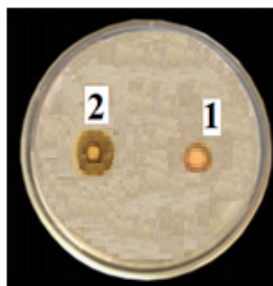


Fig. 6. The Biological Activity of  $[\text{NO}_2]$  ligand and its  $\text{Mn}^{\text{II}}$  metal ion complex after 48 hrs.

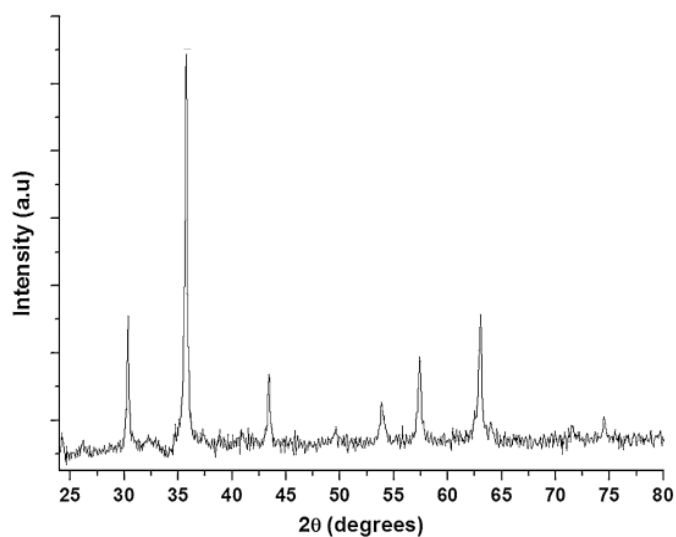


Fig. 7. The X-RD powder diffraction pattern for  $\text{Mn}^{\text{II}}$  complex.

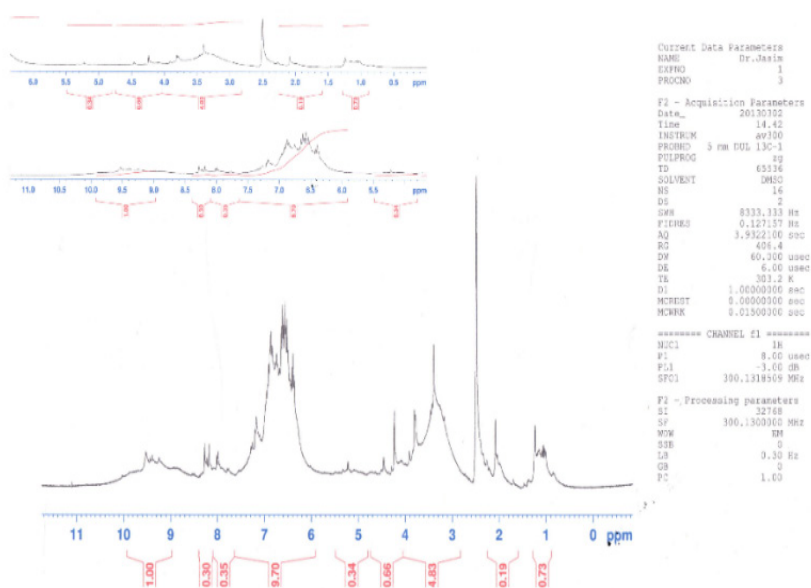


Fig. 8. The  $^1\text{H}$ -NMR spectrum for the  $[\text{NO}_2]$  ligand.

TABLE 5. The chemical shifts in  $^1\text{H}$ -NMR spectra of  $[\text{NO}_2]$  ligand.

Proton environment	H	$\delta$ (ppm)
O-H aromatic	1 (C-OH)	9.7
O-H alcohol	1 (O-H)	3.3
C-H benzene	4 (C-H)	6.5-7.2
C-H methine	1 (C-H)	5.3
H aldimine	1 (H)	7.9
DMSO solvent	-	2.4

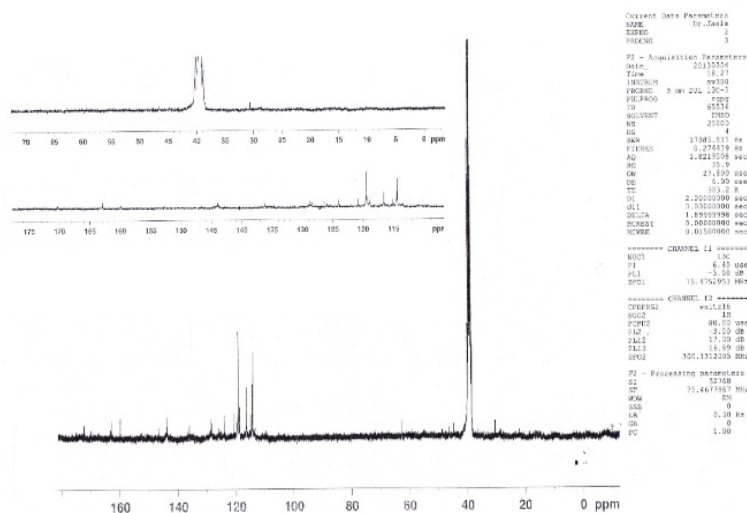


Fig. 9. The  $^{13}\text{C}$ -NMR spectrum for the  $[\text{NO}_2]$  ligand.



**TABLE 6. The chemical shifts in <sup>13</sup>C-NMR spectra of [NO<sub>2</sub>] ligand.**

Proton environment	H	δ(ppm)
C-H aliphatic methyl	(C-H)	65
C-H benzene	4(C-H)	115-120
C benzene	2(C)	135-144
C-H imine	(C-H)	160
DMSO solvent	-	39

- Determine the best some metal complexes for activating the multiple bonds in M-N and M-O.
- Syntheses of new crystal ligand from 2-oxoacetic acid
- Studying the characteristic properties of *potassium (E)-1-hydroxy-2-(2-hydroxyphenylimino) ethanolate* type [NO<sub>2</sub>] ligand.

#### Prospective Studies

Preparation of new Schiff Bases crystal complexes with first, second and third row transition metals of the periodic table

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