# Synthesis and identification of polymeric phenolic Schiff bases containing azobenzene, of Mn (II) complex

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**Abstract**

Modern phenolic polymer metal (II) complex have been synthesized by using polymeric Schiff base ligand, synthesized by the polymerization intensification reaction of 4-aminoazobenzen and 4-hydroxybenzalehyde. The polymer at metal (II) complex and ligand have been characterized by micro-analytical, UV–vis, FT-IR spectrum–Vis and CHN elemental analyser. The results detected the formation of 1:1 (L:M) complex. The effect of volume, pH and time on the absorbance values of the complex was calculated. Absorption spectra show the λ max of ligand is clear at 415 nm and complex at 385 nm this mean red shift and complex formation. These spectral and thermal studies provide very valuable information about the structural features, stability and crystallinity of the Schiff bases.

**Keywords**: polymer phenolic Schiff base and Mn ( Ⅱ ) complex.

## 1. Introduction

Schiff base components and their metal compounds have been widely scanned due to their broad domain of implementations involving catalysts crystal engineering [1, 2], anti-corrosion agent [6], medicine [3, 4]. Schiff bases are Schiff bases having chelation with nitrogen, oxygen etc. donors and their complexes have been utilized as medicine and reported to possess a wide diversity of biological activities against microorganism's bacteria fungi and certain type of tumours also, they have many clinical, biochemical and pharmacological properties [9]. The Formation for Schiff base mostly

takes place down acid or base catalysis or together with heat. The combined Schiff bases are crystalline solids, which are feebly basic however at least several form unsolvable salts together with strong acids. Schiff base ligands have considerable importance in chemistry field. numerous Schiff base compound offer stellar catalytic action in different reactions for high temperature >100 °C and in the existence of the humidity [14]. From the beginning of point for synthesis of many installation involve sulphur drugs, fungicides, biocides and chemical reaction. ligands, they also supply numerous possibility binding sites for complexation of varied metal ions like Co(II), Cu(II), Ni(II), and Zn(II) among others with well-determined biological roles [15, 16]. numerous metal complexes of Schiff bases with heterocyclic compound are, then, process as a significant category for new drug evolution, in fact, the implementation as possibility medicine because the existence of multi-functional groups such as -NHN=CH- or C=N linkage which is very fundamental in drug cooperation [17]. The Schiff base ligands are created by the intensification of a fundamental amine and an active group of carbonyls and contain the azomethine group (−CH=N− or >C=N−:). Schiff bases can act as mono-, di-, tri-, depending on the number of superscript atoms current in molecule and form mostly five - six membered chelate circle with an iron metal [18].

between numerous Schiff bases dithiocarbazate ($NH_2NHCS_2$) have been studied as ligands for long time.

## *2. Experimental*

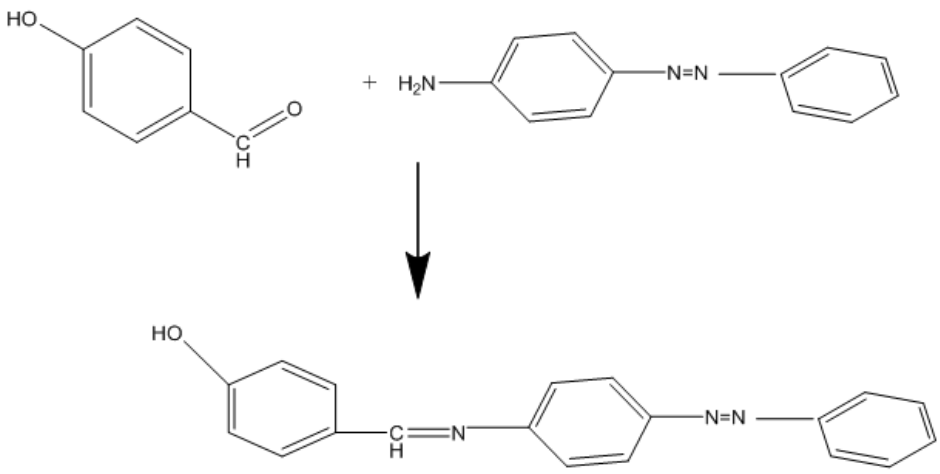
### *2.1. Materials and Instrumentation*

The starting materials represented by, 4-hydroxybenzalehyde, 4-aminoazobenzen were of Aldrich (USA). The standard stock solution was prepared by dissolving an appropriate amount of Metal salt [$MnCl_2.4H_2O$] salts in ethanol. Acetic acid, ethanol and formalin (Merck) were used as received. Absolute ethanol was used for the preparation of the solutions. FT-IR spectra by KBr pellets were recorded with a FT-IR 8400S spectrophotometer model 2000 from shimadzu Japan (4000 - 400 $cm^{-1}$). The absorption spectra by usingUV- Visible range (200-800) nm were studied Uv-visible Spectrophotometer-160, Shimadzu, Japan.

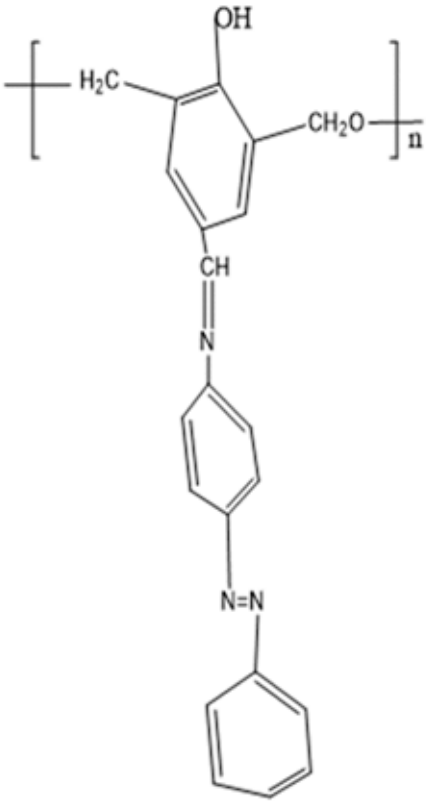
### *2.2 Synthesis*

*2.2.1 Synthesis of Schiff base*

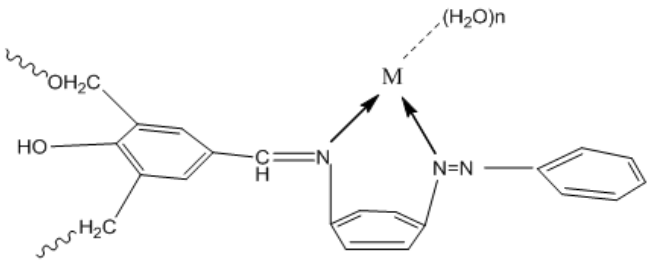
The Schiff base were prepared by reacting (0.01 mole and 3.944 gm) of the 4-hydroxybenzalehyde (0.01M and 1.22gm) 4- aminoazobenzen dissolved in 35 mL ethanol. The solution was then refluxed for 4 hours at 76°C in the existence of a few drops of glacial acetic acid and the contents teeming into cold water to stand for 24 hours. The solid precipitated then filtered and dried. The Schiff base have been isolated as solids orange crystalline. The yields were more than 70% (**Scheme 1, compound 1**). phenolic polymeric Schiff-base were prepared through polymerization intensification of compound 1 with formalin in alkaline medium 10% NaOH for 3 hours to till full the polymerization. The product was cooled at room temperature, coloured residue was created a dusky orange powder applied for analytical research and a component with Mn (**Scheme 2, compound 2**). Metal salt with hydrate [$MnCl_2.4H_2O$] ($Mn^{2+}$ $1x10^{4-}$)] mole) was dissolved in free ethanol. The phenolic polymeric Schiff-bases -compound 2- added to the metal solution applied for the analytical study.




**Scheme 1.** Synthetic route for the preparation of Schiff bases.




**Compound 1** —formalin, 10% NaOH/ refl 3hr→ **Compound 2**




**Scheme 2:** Synthetic routes of the polymeric phenolic metal complex (M=Mg).

**3. Results and discussions**

### 3.1. FT-IR spectra

The FT-IR spectra supply precious notification related to the quality of functional group connected to the ion metal. In demand, the study of the bonding style of polymeric Schiff base ligand and the polymeric metal complex, the FT-IR spectrum of the polymeric Schiff base was contrast to the spectrum for the corresponding ligand and their (FT-IR spectral) data are Figure 1(a, b). The FT-IR spectra of the free ligands shows a broad band at 3600 cm−1 attributed to phenolic group OH. [1], broad band in the area of 3005–2980 $cm^{-1}$ suggest the presence the water molecule in coordinate sphere [20]. The C– H aromatic stretch appeared at 750 $cm^{-1}$ [2]. Stretching vibration of C=C of aromatic ring evidence at 1595–1597 $cm^{-1}$ for ligand. The (FT-IR spectra) of the ligand offer a band at 1609 $cm^{-1}$ due to C=N (group of azomethine) [3]. Band observed at 1138 to1152 and 1213-to1273 $cm^{-1}$ are assigned to C–N of phenolic C–O stretching vibrations of ligand polymers [2, 3]. The C=N stretch appeared as a severe band at 1614 cm-1 along with the C=C at 1497[1], 1516 cm-1 respectively. The strong bands at 1612 and 927 cm-1 are assigned to vibrations (C-N) and vibrations (N=N) modes.

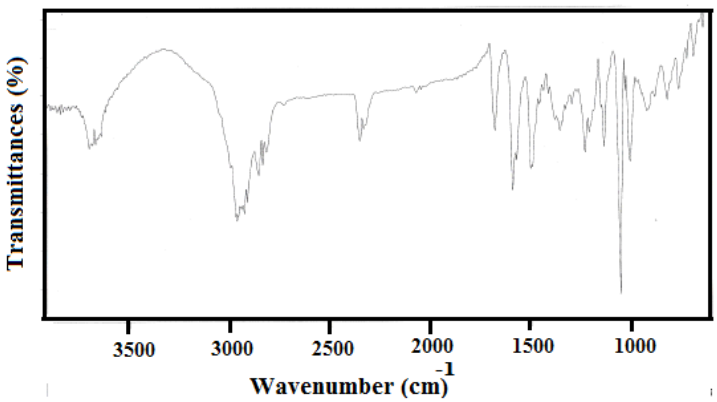



**Figure1**(**a**). FTIR spectrum of polymer Schiff base (ligand).

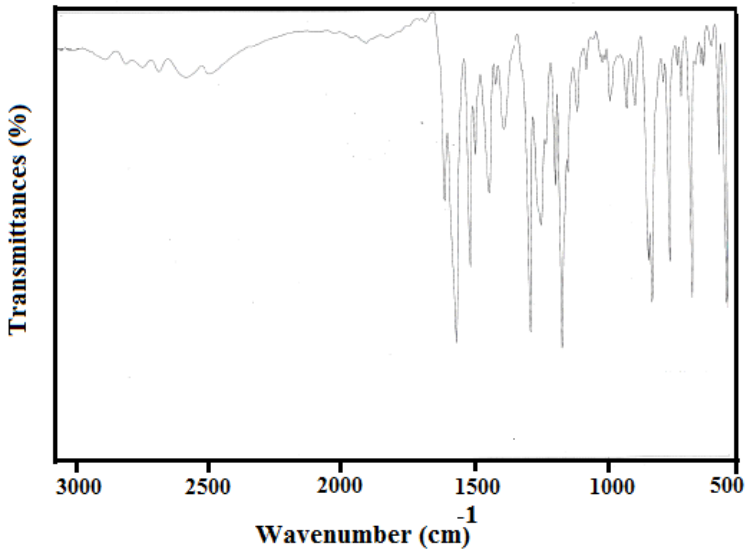



**Figure 1(b).** FTIR spectrum of Schiff base

### *3.2 UV-vis spectrum of Schiff base metal complex*

The spectrum of compound and the ligand shows in the (fig. 3) beneath optimum situation Absorption spectra show the ($\lambda_{max}$) of ligand ispure at 415 nm and 385 nm that mean the red shift and formation complex.

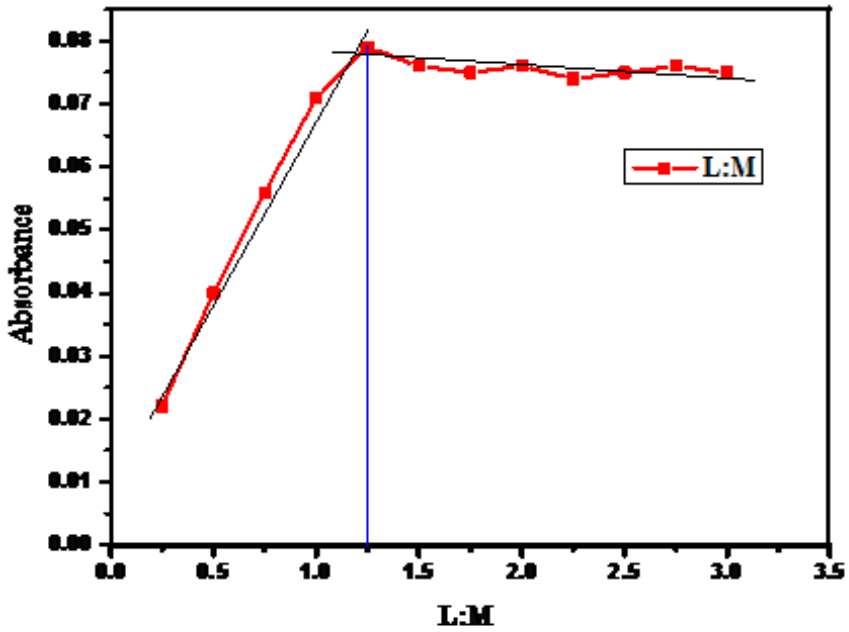



**Figure.3:**

Show the mole-ratio (M:L) at ($\lambda_{max}$) of complex

***3.3 Composition of the complex***

The composition of complex was evaluated by continuous variation and mole ratio methods. To determine the metal- ligand ratio, it has been used the molar ratio method by preparation a series solution for complex by the fix concentration of the metal and change the ligand concentration then measurement of absorbances (fig. 2), it found that the ratio between metal and ligand for complex is 1:1 [4].

To determination of the stability of complex, it was calculated the stability the complex as following equation (1):

$M_{\alpha c} + L_{\alpha c}$ $M_{(1-\alpha)\,C}$ 1

Where α= decomposition degree, c= molar concentration, stability constant can be calculated by the equation (2):

K= [ML]/[M][L] 2

Decomposition degree (α) can be calculated according of the equation (3)

$\alpha = A_m - A_s / A_m$ 3

Where $A_s$= Absorption when concentration of the ligand and metal is equal (equivalent point) absorption their access of ligand, $A_{m\ =}$ concentration applied the equation (3) in (2) is result equation (4):

$K=(1-\alpha)/\alpha^2 C$ 4

Calculated molar absorptivity ($\varepsilon_{max}$) according of the equation (5)

$Am= \varepsilon_{max}bc$ 5

b: cell constant (b=1 cm), c=molar concentration ($1x10^{-4)}$)

The (table:1) and (fig:2) below shows that the value of the stability constant K is high, ie, the complex has a high stability, which enhances the possibility of using the polymer detector recorded in the spectral estimation of this element Mn [4].

**Table:1** value of the stability constant K

| Complexes | $\lambda_{max}$ (nm) | **Value $A_s$** | **Value $A_m$** | **α** | **K** | $\varepsilon_{max}$ **L.mol$^{-1}$.cm$^{-2}$** |
|---|---|---|---|---|---|---|
| L:Mn | ٤١٥ | ٠,٠٧١ | ٠,٠٧٦ | ٠,٠٦٥٧ | ١٠$^{٦}$2.167 x | ٧٦٠ |

### *3.4. Effect of pH*

The influence of pH on absorbance amount of compound was calculated as in (fig. 1) show the explain for the absorbance of the compound in the range (pH 5-8) was adopted, the reduction in absorbance in value of pH below (4) is due to forming of azolium cation, however pH higher than (8) has reason a reduction in the absorbance because the formation of $Mn(OH)_2$.

**Figure:4.** Effect of pH on the absorbance of the complex at room temp.

### *3.5: Stability of the chromogenic system with time*

The stabilization of chromogenic regulation with time is shown in the (fig. 2). This Figure explain the complex system reach for a maximum amount for absorbance with in one hr. and residue fixed up to 24 hrs.

**Figure:5.** Absorbance of complex at different (18-50°C).

### *3.6: Determine the optimal conditions for the complex*

The influence of several volumes was calculated 0.5-7 ml of ligand condensation ($1x10^{-4}$ M) at fixed volume of metal (1 ml) at concentration, the absorbance in $\lambda_{max}$ for compound (415 nm) set that the better volume of the reagent for full the reaction is 3 ml, which it has the highest absorption for complex.

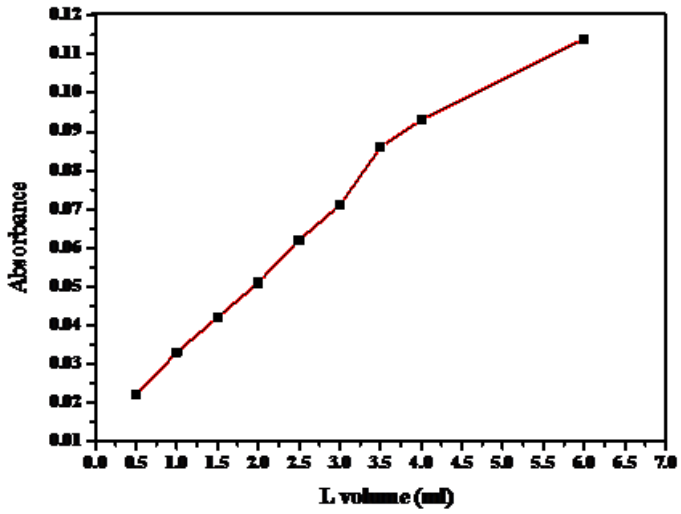



**Figure:6** Absorbance of complex at different volume of ligand

**Table 2: C.H.N values of the ligand**

| N% | H% | C% | |
|---|---|---|---|
| 11.63 | 5.30 | 69.79 | Theoretical value |
| 12.82 | 5.35 | 66.05 | Practical value |

### *4. Conclusion*

In the present study, new Schiff base polymer were synthesized by the condensation polymerization of Schiff base monomer in good yield. ligand staring from 4-hydroxybenzalehyde and4- aminoazobenzen in high yields. This ligand was then reacted with formalin in alkaline medium to give polymeric Schiff base ligand. The phenolic polymeric Schiff-bases was added to the metal solution used for analytical study. The polymeric Schiff base ligand, have been characterized on the basis of FT-IR, spectra in the UV- Visible and CHN elemental analyser. FTIR studies indicate that in the course of polycondensation the C = N bonds remained intact to a large extent. The spectroscopic data, physical properties, molar conductivity and molar ratio method indicated that the prepared ligand as polymeric phenolic forming complex metal ion.

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