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# SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL STUDIES ON IRON (II) COMPLEX OF SCHIFF BASE DERIVED FROM ORTHOPHENYLENEDIAMMINE AND 2-NITROBENZALDEHYDE

***Sani, M., Bashir, A. and Saeed, A.**

Department of Chemistry, Federal University of Dutsin-ma, P.M.B 5001, Katsina State.

*Corresponding authors' email: smuhammad4@fudutsinma.edu.ng Phone: +2348063962618

## ABSTRACT

The synthesis and characterization of Schiff base derived from Orthophenylenediammine and 2-Nitrobenzaldehyde and its Iron (II) complex were undertaken. It was prepared by the condensation reaction of Orthophenylenediammine and 2-Nitrobenzaldehyde. Its Iron (II) metal complex was synthesized by coupling Iron (II) chloride with the formed ligand. These ligands and their complexes were characterized on the basis of their melting point and Decomposition temperature of the Schiff base and metal(II) complexes respectively, infrared spectral analysis, Solubility test, conductivity Test and magnetic susceptibility measurement. The ligand was found to be yellow in colour with a percentage yield of 50% and melting point of 265ºC, The Iron (II) complex was found to be Redish brown in colour with 55% percentage yield and 300ºC decomposition temperature, The ligand and the Iron (II) complex were found to be insoluble in water, n-hexane and Acetone and slightly soluble in methanol and ethanol and completely soluble in Dimethyl sulphoxide, The Iron (II) complex was found to be paramagnetic in nature, A band at 1525cm$^{-1}$ of the ligand showed that the Aldehyde coordinated with the primary amine.

**Keywords**: Ligand, Complexes, Orthophenylenediammine, 2-Nitrobenzaldehyde

## INTRODUCTION

The synthesis and characterization of transition metal complexes of Schiff bases containing nitrogen and oxygen donor's atoms has increased manifold in the recent past (Pouralimardan *et al*, 2007, Krishnapriya *et al*, 2005). The Schiff base ligands are considered to be good chelating agents (Ooysena *et al*, 2013), Schiff bases are a special class of ligands with a variety of donor atoms exhibiting interesting coordination modes towards transition metals (Chandra *et al,* 2009) and azomethine linkage is responsible for the biological activities (Sinha *et al* 2008). The Schiff bases derived from various amines have been widely investigated (Ansary *et al,* 2002) and find applications in biomimetic catalytic reactions, materials chemistry and industry (Celik *et al,* 2002). Schiff base complexes have also gained attention as stereo chemical models in transition metal coordination chemistry due to their structural variety (Biswas *et al,* 2010).

Coordination Chemistry gave the beautiful chance to Schiff bases and their metal complex to emerge as a diverse field of chemistry. Now-a-days these metal complexes play an important role in the development and progress of coordination chemistry (Shoichiro, Yamada. 1999). The literature clearly shows that the study of this diverse ligand system is linked with many of the key advances made in inorganic chemistry (Bella, *et al* 2008) although the magnetic, spectroscopic and solubility properties of these Schiff-base complexes are well documented (Kilic, *et al* 2007). Presently, the coordination chemistry of structurally modified bio-ligands and the transition metal complexes with potential biological activity are the focus of extensive investigations in front of inorganic chemists. Schiff base ligands have received special attention because of their mixed softhard donor character, versatile coordination behaviour (Tyagi *et al* 2011). Structural factors such as ligand rigidity, the types of donor atoms and their disposition have shown to play significant roles in determining the binding features of these ligands toward metal cations. The chelating ability of Schiff bases gives them the place in the coordination chemistry and is used as chelating agents (Grünwald, *et al* 2010). The preparation of Schiff bases containing >C=N groups with potential ligating ability has drawn a lot of attention because of their use as chelating agents, analytical reagents, metal indicators in complexometric titrations and calorimetric reagents, in addition to biochemical research (Singh, *et al* 2012). The behaviour of the >C=N bond is strongly dependent on the structure of the amine moiety, which in turn controls the efficiency of the conjugation and may incorporate structural elements able to modulate the steric crowding around the coordination (Lassaletta, *et al* 2004). In view of above applications, in this present paper we report synthesis and characterization of Fe (II) complex derived from 2-Nitrobenzaldehyde and o-phenylenediamine. Besides the characterization of complexes by standard technique like IR, Solubility test and magnetic susceptibility of the complex have been examined

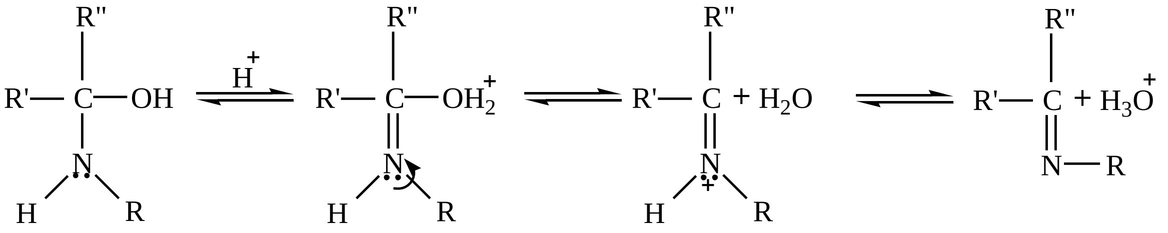
Schiff bases, named after Hugo Schiff, are formed when primary amines react with aldehydes or ketones under specific conditions (Cimerman, Miljanić, *et al*, 2000). Structurally, a Schiff base is a nitrogen analogue of an aldehyde and ketone in which the carbonyl group (C=O) has been replaced by an imine or azomethine group.

Schiff base compounds and their metal complexes have been extensively investigated due to their wide range of applications including catalysts, medicine (Sridhar et al., 2002), anti-corrosion agent (Meerana et al., 2015). Schiff bases are studied widely due to their synthetic flexibility, selectivity and sensitivity towards the central metal atom; structural similarities with natural biological compounds and also due to presence of azomethine group (-N=CH-) which is important in elucidating the mechanism of transformation and racemization reaction biologically (Chohan et al., 2010; Karia and Parsania, 1999; Amir et al., 2002; More et al., 2002).

Schiff bases are widely employed as ligands in coordination chemistry (Andruh *et al* 2005). This is because they are readily available, versatile and have tunable properties which depend on the starting materials (primary amine and carbonyl precursors). They exhibit various reactivities and functionalities. Moreover, the number, the nature and the relative position of the donor atoms of a Schiff base ligand allow a good control over stereochemistry of the metallic centres, as well as the number of the metal ions within homo and heteropolynuclear complexes. All these advantages make Schiff bases very good ligands to form metal complexes that are of interest in bioinorganic chemistry, catalysis, encapsulation, transport and separation process (Akmal *et al* 2007)

The acid/base catalysis or heating is employed for the synthesis of Schiff bases as their reactions are mostly reversible. The formation of Schiff base does not follow a simple nucleophilic addition, but give an unstable additional compound called carbinolamine (Gopu and Xavier, 2015).

The compound thus obtained is unstable and loses water molecule. The dehydration step during formation of Schiff base is actually the rate determining step and the reaction shown in scheme 1 is catalyzed by acid.



Scheme 1: Mechanism of Schiff base formation

**Aim of the research**

This research work is aimed at synthesizing and characterizing Schiff base and its Iron (ii) complex derived from ortho phenylenediamine and 2- Nitrobenzaldehyde.

## MATERIALS AND METHODS

### Materials

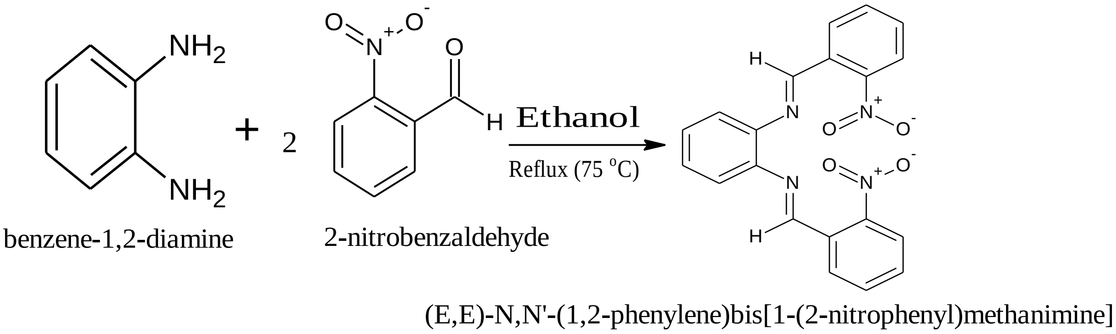
The chemicals and reagents used were of AR (Analytical reagents) grades. List of chemicals and reagents used includes: Absolute ethanol (CH3COOH), 2–Nitrobenzaldehyde for synthesis ($C_7H_5NO_3$), O –phenylenediamine, Iron (II) Chloride (hexahydrate) (Fe (II) $Cl_2.6H_2O$).

All glass ware used were washed with tap water and detergent and rinsed with distilled water. The compounds were synthesized by the use of Reflux condenser, magnetic hot plate, weighing balance and round bottom flask. Melting points were recorded in open capillaries, the IR spectra of the Schiff base ligand and its metal (II) complex were record by Fourier-Transform spectrophotometer (Agelent tech) in the range 400-1000 $cm^{-1}$ for the lower Region and 650-4000 $cm^{-1}$ for the upper Region.

### Methods

***Synthesis of the Schiff Base***

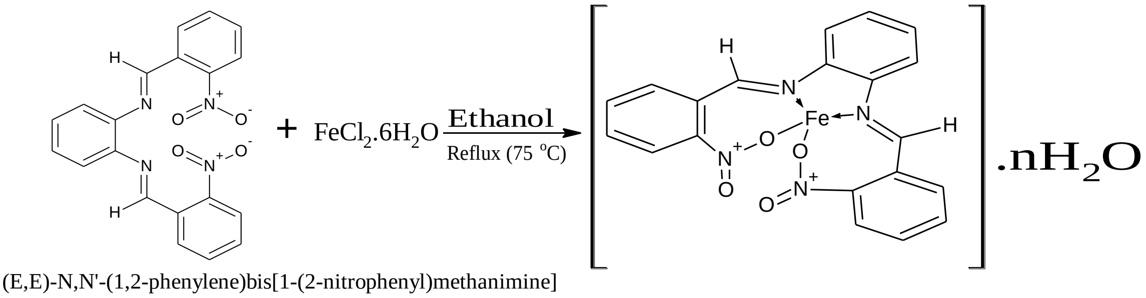
The ethanolic solution of 2–Nitrobenzaldehyde (0.60g) was added to an ethanolic solution of O–phenylenediamine (0.28g) and the mixture was left to reflux for 2 hours. On cooling, a solid product was formed which was filtered, washed with ethanol and dried. Recrystallization from hot ethanol gave the pure form of the ligand.



Scheme 2: Formation of the Schiff Base

***Preparation of the metal (II) complex***

A warm ethanolic solution of the Schiff base (0.22g) was added to a magnetically stirred solution of Iron (II) chloride (0.26g). The mixture was refluxed for 2hours. On cooling, brown precipitate was formed which was filtered, washed with ethanol and dried. Recrystallization from aqueous ethanol gives the desired metal (II) complex.



Scheme 3: Formation of the Metal (II) complex

### *Solubility test*

Solubility of the Schiff base and its Metal (II) complex were checked in Ethanol, Methanol, Acetone, n-Hexane and dimethylsulfoxide (DMSO) which was done by shaking a small amount of each Compound in a test tube.

### *Melting point and Decomposition Temperature*

The melting point of the ligand and the decomposition temperature of the complex were determined by placing a sample in glass capillary tube and heated in SMP10 melting point machine, where by the temperatures were recorded by the thermometer inserted inside the machine.

### *Infrared Spectroscopy*

The infrared spectra of the ligand and the complex were recorded on the Cary FT-IR-630 model spectrometer using KBr disc in the region 4000–650 cm$^{-1}$ at upper region and 400-1000 cm$^{-1}$ at lower Region.

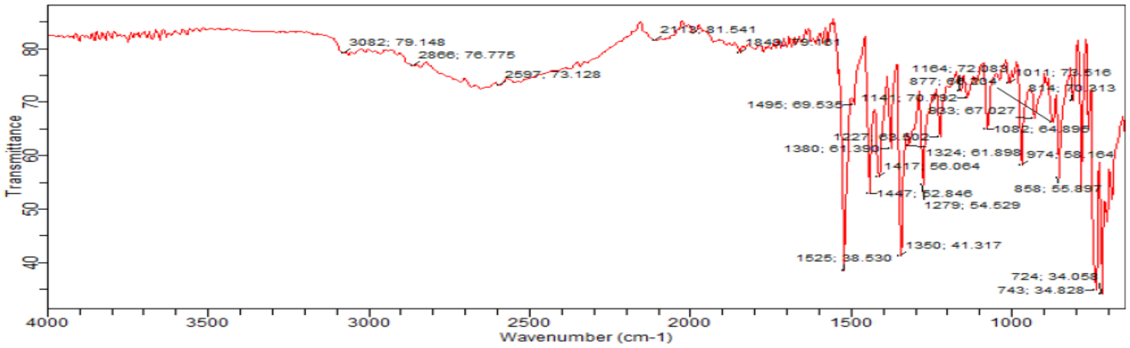


Figure 1: FT-IR spectra of the Schiff base

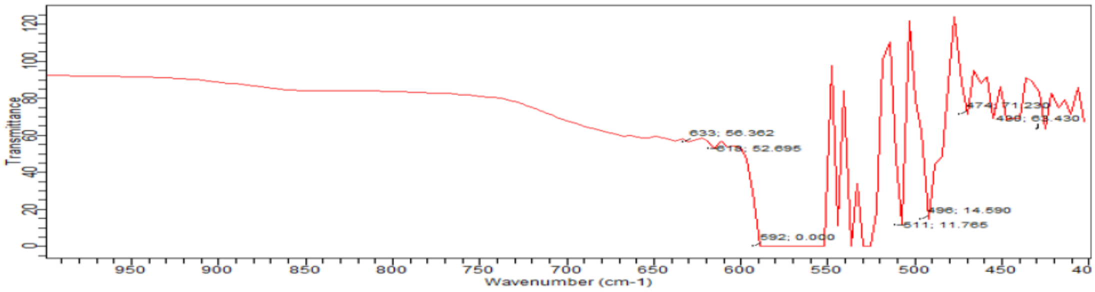


Figure 2: FT-IR spectra of the Fe (II) Complex at lower region

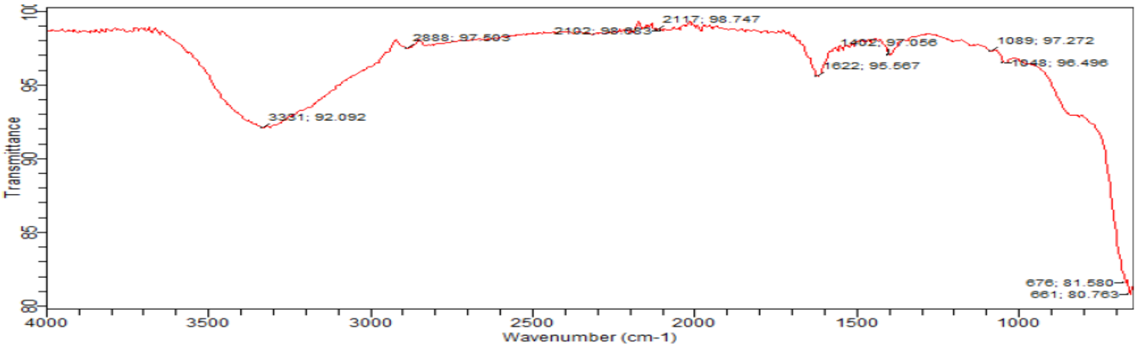


Figure 3: FT-IR spectra of the Fe (II) complex at Higher Region

### **Magnetic susceptibility measurements**

Magnetic susceptibility data of the Compound was collected at room temperature using MBS MK1 magnetic susceptibility balance.

Experimental method used to determine susceptibility balance is as follows

The contribution of the magnetic field produced by a substance is called its magnetic susceptibility. Magnetic susceptibility is measured using Gouy balance.

There is a relationship between the measured magnetic susceptibility and gram magnetic susceptibility (Xg) given by; $Xg = \frac{C_{Bal}\,(L)\,(R\text{-}R_o)}{10^9 M}$

Where; $C_{Bal}$ =Balance calibration constant =1.0

L= Height of the sample in tube (cm)

R = Reading for tube and sample

$R_0$ = Reading for empty tube

M = Mass of the sample (g)

From the knowledge of gram magnetic susceptibility ($X_g$), molar magnetic susceptibility ($X_m$) can be calculated using the relation. $X_m = (X_g) \times$ (Molar mass)

Where; Xg = Gram magnetic susceptibility

Xm = Molar magnetic susceptibility

Note that when ($X_g$) is negative, then it indicate that its diamagnetism likewise if ($X_g$) is positive, then it indicates that its Paramagnetism while $R_o$ is always negative because glass is diamagnetic in nature.

## RESULTS AND DISCUSSION

### Results

The results obtained from various analyses in this research are presented in the following Tables

**Table 1: Physical properties of the ligand and its Metal (II) Complex**

| Compound | Colour | %Yield | M.P ($^0$C) | D.T ($^0$C) |
|---|---|---|---|---|
| Ligand | Yellow | 50 | 265 | ___ |
| Fe (ii) Complex | Reddish brown | 55 | ___ | 300 |

**Table 2: Solubility of the ligand and its Metal (II) Complex in Water and some solvent**

| Solvent/Compound | Ligand | Fe (II) Complex |
|---|---|---|
| Distilled Water | IS | IS |
| n-Hexane | IS | IS |
| Methanol | SS | SS |
| Ethanol | SS | SS |
| Acetone | IS | IS |
| Dimethylsulfoxide (DMSO) | S | S |

S= soluble, IS= Insoluble, SS= slightly soluble

**Table 3: FT-IR Spectral Data of the Ligand and its Metal (II) Complex**

| COMPOUND | V (C=N) cm$^{-1}$ | V (C-O) cm$^{-1}$ | V (OH) cm$^{-1}$ | V (M-N) cm$^{-1}$ | V (M-O) cm$^{-1}$ |
|---|---|---|---|---|---|
| LIGAND | 1525 | 1227 | 3082 | ___ | ___ |
| Fe (ii) Complex | ___ | 1402 | 3351 | 592 | 496 |

**Table 4: Magnetic measurement of the metal (II) Complex**

| Sample ID | $R_o$ | R | L (cm) | $W_o$ (g) | $W_1$ (g) | Xg | Result |
|---|---|---|---|---|---|---|---|
| Fe (II) Complex | -037 | 751 | 1.60 | 0.817 | 0.848 | 2.54 x $10^{-5}$ | Paramagnetic |

### Discussions

Condensation reaction of ethanolic solution of ortho phenylediamine and 2- Nitrobenzaldehyde give a Yellow solid product with a good yield of 50% and melting point of 265ºC.

The reaction of ethanolic solution of the Schiff base and its corresponding Metal (II) chloride forms complex of different colour and decomposition temperatures in the range above 300$^0$C as indicated in Table 1.

The solubility test carried out on the Compound showed that are insoluble in Distilled Water, n-hexane and Acetone while soluble in Dimethylsulfoxide (DMSO) and slightly soluble in Methanol and Ethanol as indicated in Table 2.

The FTIR spectra of the ligand determined showed a band at 1525cm$^{-1}$which is assigned to *v*(C=N) stretching vibration, a feature found in Schiff base. The shifting of this band to a lower frequency in the spectra of the complex indicates the coordination of the ligand to the metal (II) ion through the donor atoms.

The FTIR spectrum of the ligand exhibited a broad band in the range (3082-3351) cm$^{-1}$ and was assigned to *v*(OH) stretching vibration frequency. The band range (592) cm$^{-1}$and (496) cm$^{-1}$ are attributed to *v*(M-N) cm$^{-1}$and *v*(M-O)cm$^{-1}$ respectively Therefore, from the IR spectra, it is concluded that the ligand behaves as a neutral bidentat ligand coordinated to the metal ions via azomethine N and O these results are as shown in Table 3

The magnetic susceptibility result of the complex at room temperature was found to be paramagnetic as shown in table 4.

## CONCLUSION

The synthesis and characterization on iron (ii) complex of Schiff base derived from 2- Nitrobenzaldehyde and O–Phenylenediamine have been carried out successfully. The FTIR spectral data showed that the Schiff base was coordinated to the metal ions indicating the formation of azomethine (>C=N) band in the spectrum of the Schiff base and M-O, M-N bands in the spectra of the complex. Magnetic data showed that the complex is paramagnetic in nature. Melting point/decomposition temperatures were determined, Solubility in water and some common organic solvents carried out showed that the compounds behave differently. According to the available experimental data, the proposed structure of the Schiff base and its Iron (II) complex were shown below.

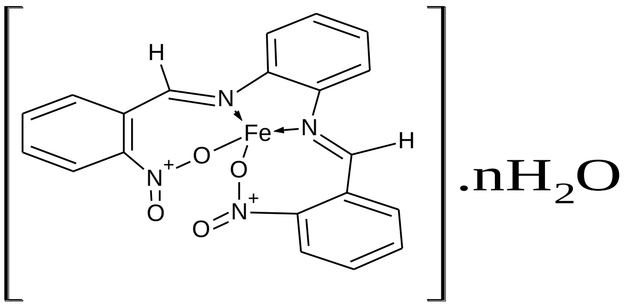


Figure 1: Propose structure of the metal (II) complex

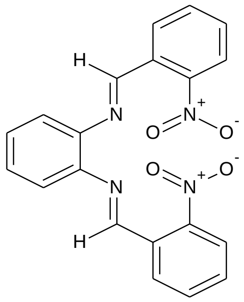


Figure 2: Propose structure of the Schiff Base

## RECOMMENDATIONS

The following are some recommendations for further investigations on the compounds synthesized:

1. X-ray crystallography for both the ligand and the complex.
2. X-ray Diffraction for both the ligand and the complex.
3. $^{1}$HNMRand $^{13}$C NMR should be conducted on the ligand and its metal (II) complex.
4. Anti microbial studies for both the ligand and its metal (II) complex

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