

**SYNTHESIS, CHARACTERISATION AND ANTIMICROBIAL STUDIES OF SCHIFF  
BASE LIGAND DERIVED FROM SALICYLALDEHYDE AND  
2,4-DINITROPHENYLHYDRAZINE AND ITS METALS COMPLEXES**

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**ABSTRACT**

Schiff base ligand derived from salicylaldehyde and 2,4-dinitrophenylhydrazine and its metal (II) complexes were synthesized and characterized on the basis of melting point/decomposition temperature, solubility, molar conductance, magnetic susceptibility infrared and UV/visible spectrophotometry. The composition of the complex has been found to be 1:2 (metal-Ligand) ratio. The complex has low molar conductance values 5.29 -5.49 5.30 5.31 5.43 5.44  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  showing non-electrolytes. The synthesized ligand and its metal (II) complexes were screened for antibacterial activity against bacterial isolates using well method. The results of these studies revealed that all the compounds and the ligand showed significant antibacterial and antifungal potency. The ability of these compounds to show antimicrobial activity indicates that they can be further evaluated for medicinal and environmental applications.

**Keywords:** Salicylaldehyde, Schiff base, antibacterial, antifungal.

**INTRODUCTION**

Schiff bases play a significant role in coordination chemistry [1]. They have been widely studied because of their industrial and biological applications. Schiff bases are usually formed by the condensation of aliphatic, aromatic aldehydes or ketones with primary aliphatic or aromatic amines, e.g. hydrazides. The significance of schiff base like those of hydrazones lies in the fact that these compounds not only possess antimicrobial activities but also show greater tendency to form complexes. Schiff bases prepared by using variety of aldehydes and amines possessed antituberculosis, anticancer, bacteriostatic, fungicidal, medicinal and pesticidal activities [2].

Schiff bases have appeared to be an important intermediate in a number of enzymatic reactions involving interaction of enzyme with amino or carbonyl group of the substrate. In the lysine class, represented by fructose diphosphate aldolase, an intermediate schiff base is formed

between  $\alpha$ -amino group of lysine of enzyme and a carbonyl group of substrates [3]. Hydrazide schiff base,  $RR'C=N-NR''R'''$ , are used as intermediates in synthesis [4], as functional groups in metal carbonyls and in organic compounds [5] and in particular in hydrazine schiff base ligands [6], which are among others employed in dinuclear catalysts [7]. Furthermore, hydrazones exhibit physiological activities in the treatment of several diseases such as tuberculosis. This activity is attributed to the formation of stable chelates complexes with transition metals which catalyse physiological processes [8]. They also act as herbicides, insecticides, nematocides, rodenticides, plant growth regulators, sterilants for houseflies, among other applications.

This paper reports the studies on manganese(II), iron(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of schiff base derived from salicylaldehyde and 2,4-dinitrophenylhydrazine due to paucity of the information.

## MATERIALS AND METHODS

All the reagents used were analytical grade. Salicylaldehyde and 2,4-dinitrophenylhydrazine were obtained from Sigma-Aldrich. All the solvents were used without further purification. The glass used were washed with detergent, rinsed with distilled water and dried in an oven at 110 °C before use. Electric meter balance model H30AR was used for weighing. Melting/decomposition temperature was determined using Gallen-Kamp melting point apparatus. The molar conductivity measurement was carried out in DMSO using Denver Instrument model 20 pH/conductivity meter. Jenway 6305 UV-Visible spectrophotometry was used for UV-analysis. The IR spectra of the ligand and its metal complexes were recorded using Agilent Technology FT-IR 8500s Fourier transform spectrophotometry with the of range 400-4000  $\text{cm}^{-1}$ . Microbial and fungal identification as well as studies were carried out at the Department of Microbiology, Federal Polytechnic, Mubi, Nigeria.

### Preparation of the schiff base

Equimolar mixture of salicylaldehyde (10 mmol) and 2,4-dinitrophenylhydrazine (10mmol) in ethanol (30 ml) were refluxed on a hot plate with stirring for 3 h. The orange crystalline solid

obtained was filtered, washed with ethanol and then recrystallized from methanol and dried in a desiccator over calcium chloride ( $\text{CaCl}_2$ ) for three days [10, 11].

### **Preparation of the complexes**

Metal complexes were prepared by addition of a solution of the appropriate metal (II) chloride (3 mmol) in an ethanol (20 ml) to a solution of the ligand (6 mmol) in same solvent (20 ml). The mixture was refluxed on a hot plate with stirring for 3 h. The product obtained was concentrated to half its volume, filtered, washed with distilled water, diethyl ether and dried in desiccator over ( $\text{CaCl}_2$ ) [10, 12].

### **Determination of metal to ligand ratio**

The number of ligands coordinated to the metal ion was determined using Job's method of continuous variation [13]. Dimethyl sulphoxide (DMSO) solution, 3 mmol of the ligand and the metal chlorides were prepared. The following ligand to metal salt ratio (ml); 1:15, 3:13, 5:11, 7:9, 9:7, 11:5, 13:3, 15:1 were taken from the ligand solution and each of the metal chloride solution respectively. A total volume of 16 ml was maintained (in that order) throughout the process and the mole fraction of the ligand was calculated in each mixture.

### **Molar conductivity measurement of the complex**

The molar conductance of the complexes was determined by preparing a solution of each metal (II) complex ( $0.001 \text{ mol/dm}^3$ ) in DMSO in test tube and the electrode was inserted and the reading was recorded.

### **Antibacterial activity**

The antibacterial activity of schiff base ( $\text{C}_{13}\text{H}_{10}\text{O}_5\text{N}_4$ ) and its metal(II) complexes were assayed against five bacterial isolates (*Escheria coli*, *Proteus. l*, *Klebsiella pneumoniae*, *Pseudomonas aureginosa* and *Staphylococcus aureus*) by the reported method [14]. The suspension of each microorganism was rubbed onto the surface of solidified nutrient agar (N.A.) already poured into petri dishes with swap stick. The stock solution was suitably diluted to get dilution of 4000, 2000 and 1000  $\mu\text{g/well}$  of the Schiff base and the metal complexes. Wells (6 mm in diameter) were dug in the agar media with the help of a sterile metallic borer. Ciprofloxacin ( $5\mu\text{g/disc}$ ) was used as control. The wells were incubated immediately at  $37^\circ\text{C}$  for 24 h. Activity was determined by

measuring the diameter of zones showing complete inhibition (mm) and comparing the values with the standard.

### **Antifungal activity**

The antifungal activity of schiff base ( $C_{13}H_{10}O_5N_4$ ) and its metal (II) complexes was assayed against three fungal species (*Fusarium solani*, *Aspergillus fumigate* and *Candida albicaus*) by the reported method [14]. The suspension of each microorganism was rubbed onto the surface of solidified potato dextrose agar (PDA) already poured into petri dishes with swap stick. The stock solution was suitably diluted to get dilution of 4000, 2000 and 1000  $\mu\text{g}/\text{well}$  of the schiff base and the metal complexes. Wells (6 mm in diameter) were dug in the agar media with the help of a sterile metallic borer. Manozef  $\mu\text{g}/\text{well}$  was used as the control. The wells were incubated immediately at 37 °C for 48 h. Activity was determined by measuring the diameter of zones showing complete inhibition (mm) and comparing the values with the standard.

## **RESULTS AND DISCUSSION**

The solubility test of the ligand and the complexes was carried out. The ligand is soluble in DMF and DMSO, slightly soluble in ethanol, methanol and acetone but insoluble in chloroform and water as shown in (Table 1). The solubility of the complexes shows that all the complexes are soluble in DMSO, DMF, chloroform, acetone and ethanol except for Zn (II) and Co (II) which are slightly soluble in ethanol and acetone respectively, all the complexes are insoluble in water as shown in Table 2.

The molar conductivities of the complexes were measured in DMSO. The values of these conductance of the complexes in  $10^{-3}$  M DMSO at room temperature determined are in the range 5.18-11.0  $\text{ohm}^{-1}\text{CM}^2\text{Mol}^{-1}$ . These indicate that the complexes dissociate very slightly in this solvent as shown in Table 1.

IR spectra analysis of the free ligand shows band at 3268  $\text{cm}^{-1}$  assigned to  $\nu(\text{O-H})$  stretching vibration. The strong peak at 1616  $\text{cm}^{-1}$  is attributed to azomethine  $\nu(\text{C=N})$  group [15]. The band in the range 1611-1624  $\text{cm}^{-1}$  are all observed in the metal complexes prepared, which indicate the participation of the azomethine nitrogen in coordination to the metal ions [16]. Two absorption bands in the range 608-620 and 405-470  $\text{cm}^{-1}$  in the metal (II) chelates, were observed

respectively [17], indicating the formation of M-N and M-O bonds confirming coordination of the ligand to the metal (II) ions respectively as shown in Table 4.

Magnetic susceptibility measurements provide the magnetic property of the metal complexes. The magnetic moment value of Mn(II) complexes is 0.96 BM. The magnetic moment value of Fe(II) complexes is zero. These indicate that the Mn(II) complexes is paramagnetic while Fe(II) is diamagnetic as shown in Table 3.

Table 1: Physical properties of the ligand and its metal(II) complexes

Compound	% Yield	Colour	Melting/ Decomposition Temperature (°C)
L	67.22	Pale Orange	220
[CoL <sub>2</sub> ]	89.67	Orange	250
[NiL <sub>2</sub> ]	81.68	Deep Orange	246
[MnL <sub>2</sub> ]	83.98	Orange	255
[FeL <sub>2</sub> ]	77.27	Orange	270
[CuL <sub>2</sub> ]	73.42	Pale Orange	250
[ZnL <sub>2</sub> ]	79.30	Pale Orange	249

Where L = C<sub>13</sub>H<sub>10</sub>O<sub>5</sub>N<sub>4</sub>

Table 2: Solubility of ligand and metal (II) complexes

Compound	H <sub>2</sub> O	MeOH	EtOH	Acetone	Chlorof orm	DMF	DMSO
L	IS	SS	SS	SS	IS	S	S
[CoL <sub>2</sub> ]	IS	SS	S	SS	S	S	S
[NiL <sub>2</sub> ]	IS	SS	S	SS	S	S	S
[MnL <sub>2</sub> ]	IS	SS	S	S	S	S	S
[FeL <sub>2</sub> ]	IS	SS	S	S	S	S	S
[CuL <sub>2</sub> ]	IS	S	S	S	S	S	S
[ZnL <sub>2</sub> ]	IS	SS	SS	S	S	S	S

Keys: S=SOLUBLE, SS=SLIGHTLY SOLUBLE, IS=INSOLUBLE

Table 3: Magnetic moment values of the Metal (II) complexes

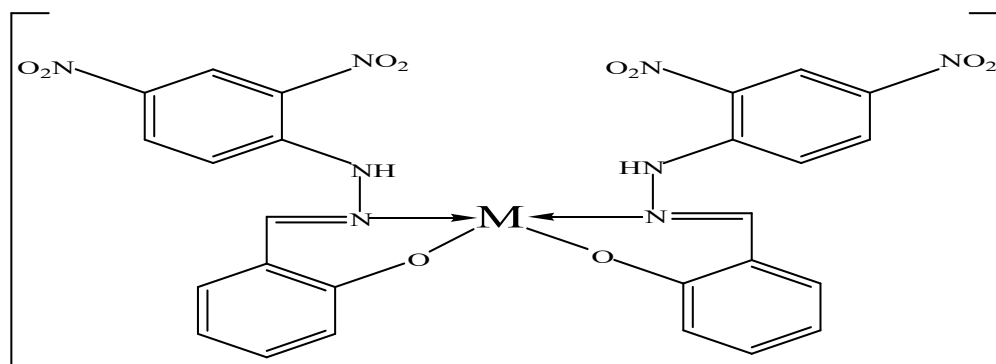
Complexes	Xg(g <sup>-1</sup> )	Xm(mol <sup>-1</sup> )	μ <sub>eff</sub> (BM)
[CoL <sub>2</sub> ]	1.44x10 <sup>-6</sup>	944x10 <sup>-6</sup>	1.50
[NiL <sub>2</sub> ]	-	-	Dia
[MnL <sub>2</sub> ]	5.83x10 <sup>-7</sup>	386x10 <sup>-6</sup>	0.96
[FeL <sub>2</sub> ]	-	-	Dia
[CuL <sub>2</sub> ]	8.33x10 <sup>-7</sup>	555x10 <sup>-6</sup>	1.15
[ZnL <sub>2</sub> ]	-	-	Dia

Where L = C<sub>13</sub>H<sub>10</sub>O<sub>5</sub>N<sub>4</sub>; χ<sub>g</sub> = mass susceptibility; χ<sub>m</sub> = molar susceptibility; μ<sub>eff</sub> = effective magnetic moment

Table 4: Infrared Spectral Data of Ligand and its Metal (II) Complexes

Compound	OH (cm <sup>-1</sup> )	C = N (cm <sup>-1</sup> )	M – N (cm <sup>-1</sup> )	M – O (cm <sup>-1</sup> )
L	3268	1616		
[CoL <sub>2</sub> ]		1618	608	405
[NiL <sub>2</sub> ]		1615	620	412
[[MnL <sub>2</sub> ]		1611	615	470
[FeL <sub>2</sub> ]		1620	608	412
[CuL <sub>2</sub> ]		1618	617	409
[ZnL <sub>2</sub> ]		1615	616	415

Where L = C<sub>13</sub>H<sub>10</sub>O<sub>5</sub>N<sub>4</sub>



M=Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup>

Fig. 1: Proposed structure of the metal(II) complexes

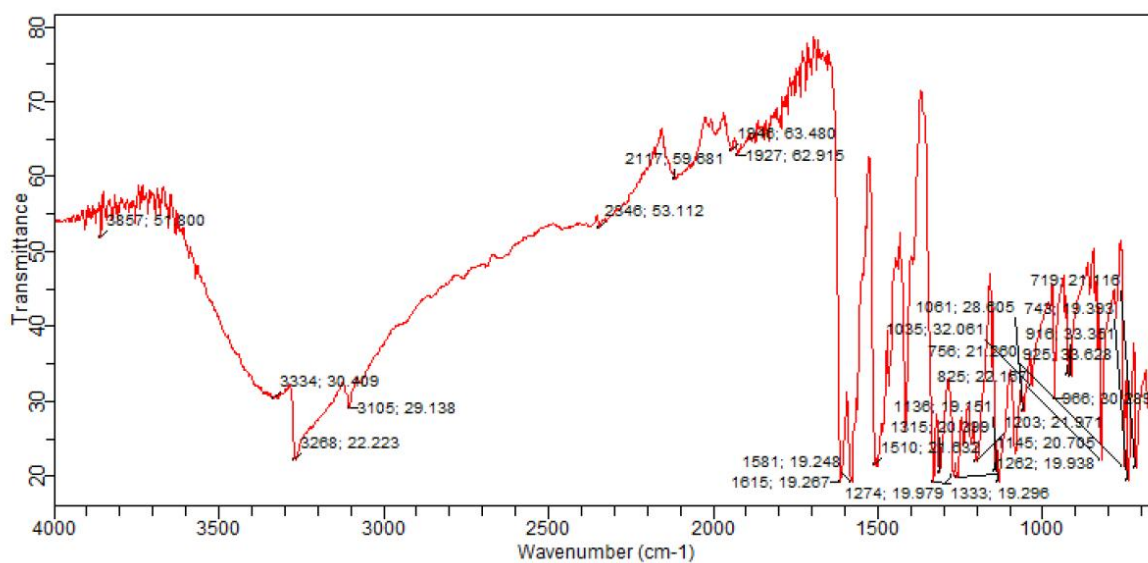


Fig. 2: Infrared spectral of Ni(II) complex

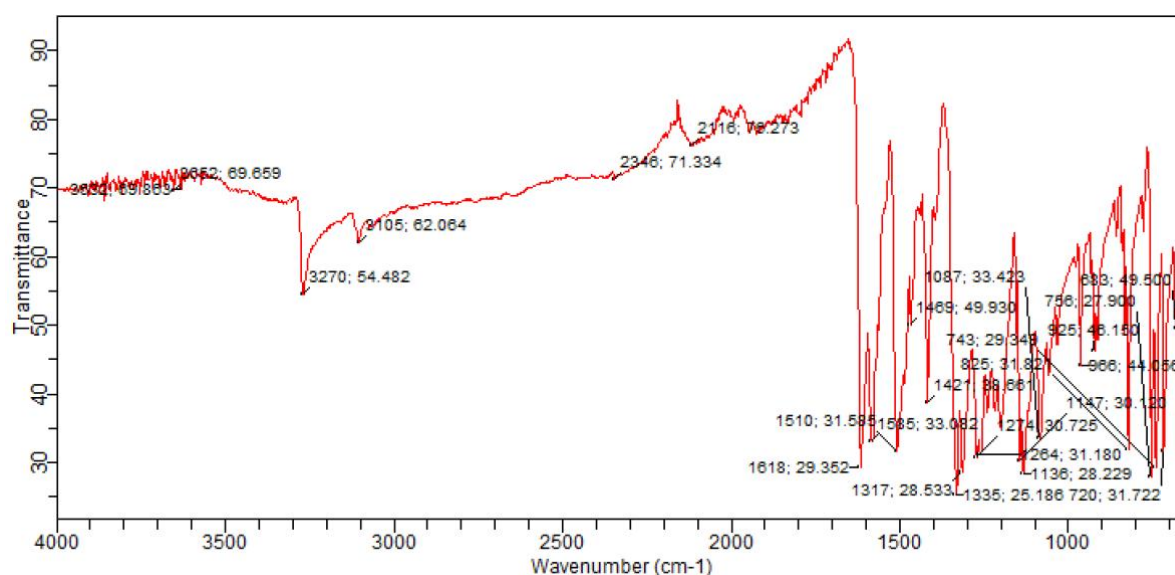


Fig. 3: Infrared spectral of Cu(II) complex



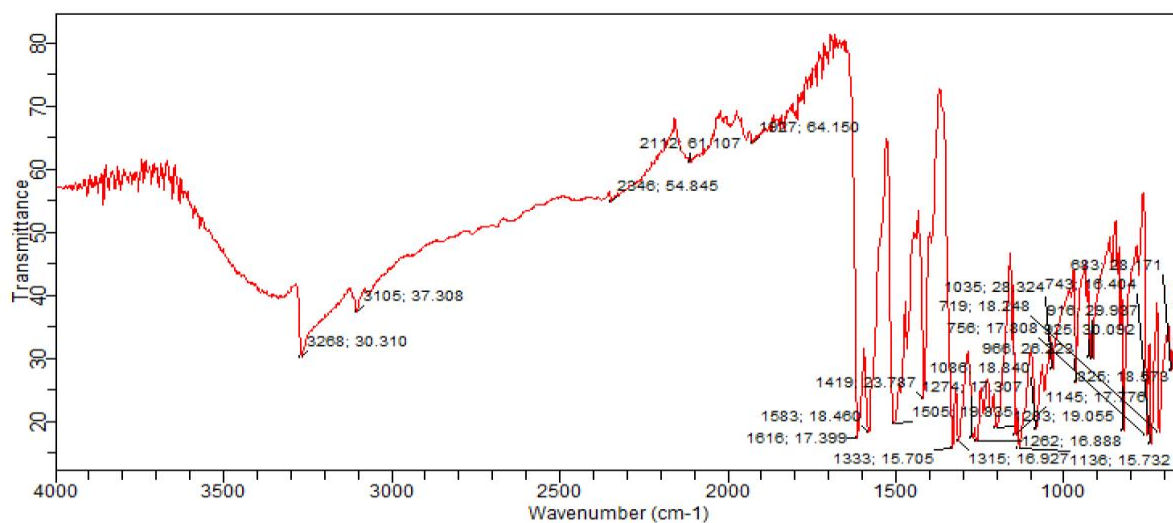


Fig. 4: Infrared spectral of Co(II) complex

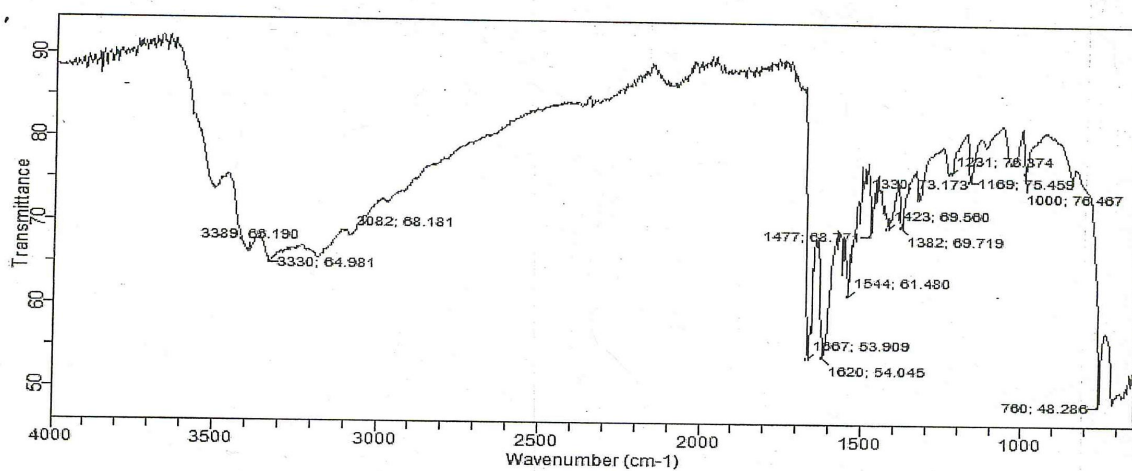


Fig. 5: Infrared spectral of Fe(II) complex

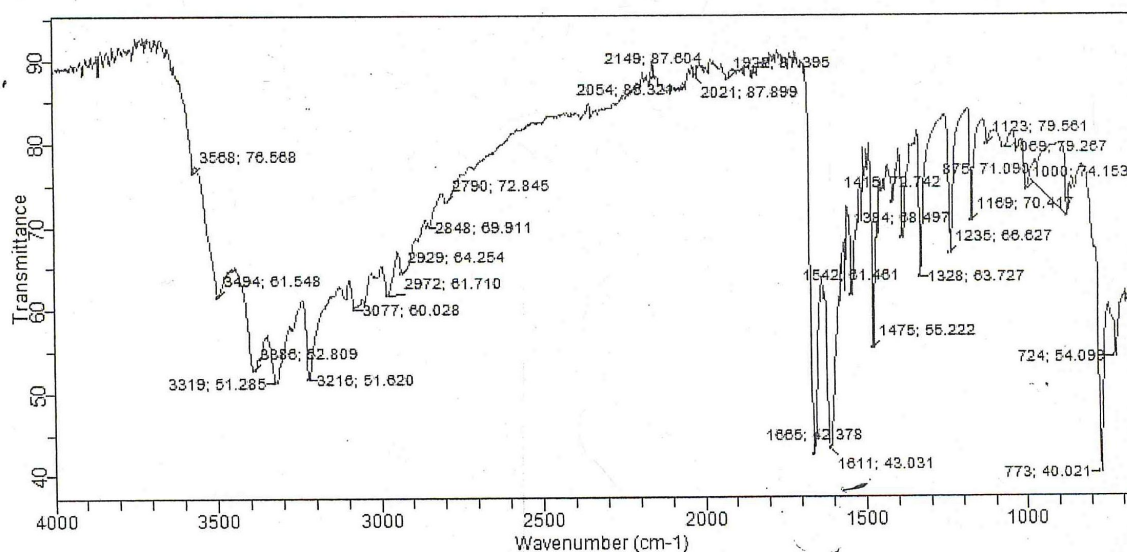


Fig. 6: Infrared spectral of Mn(II) complex

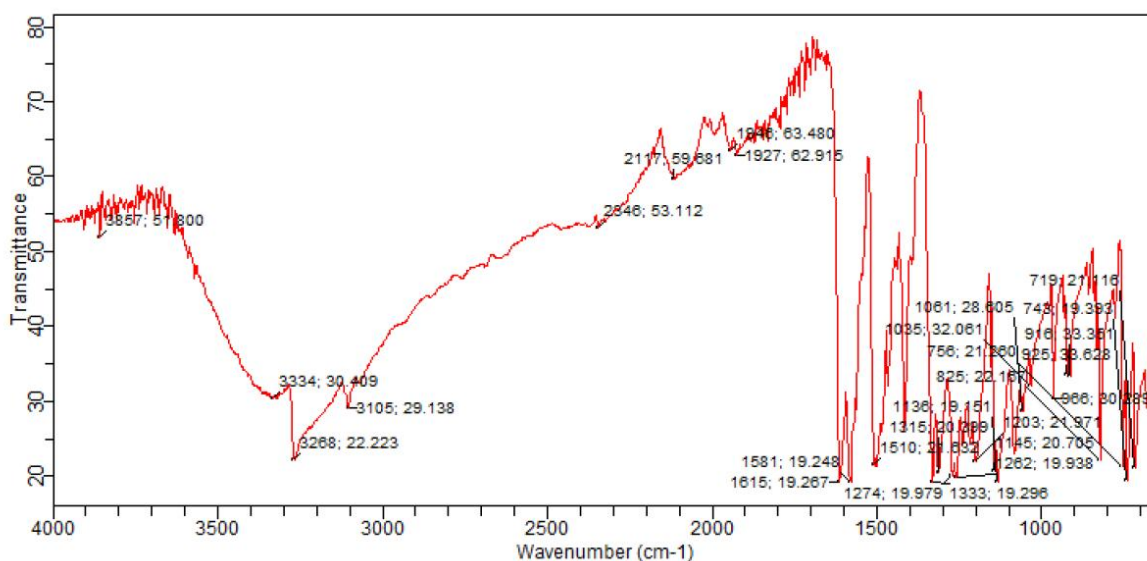


Fig. 7: Infrared spectral of Zn(II) complex

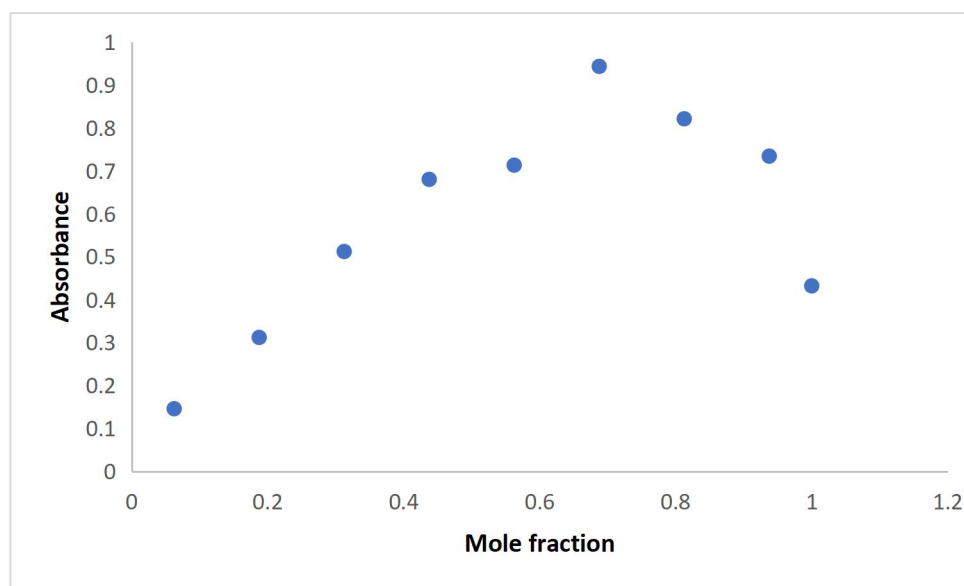


Fig 7: Plot of absorbance of Cobalt(II) chloride solution with L against mole fraction at  $\lambda_{\max}=400\text{n}$

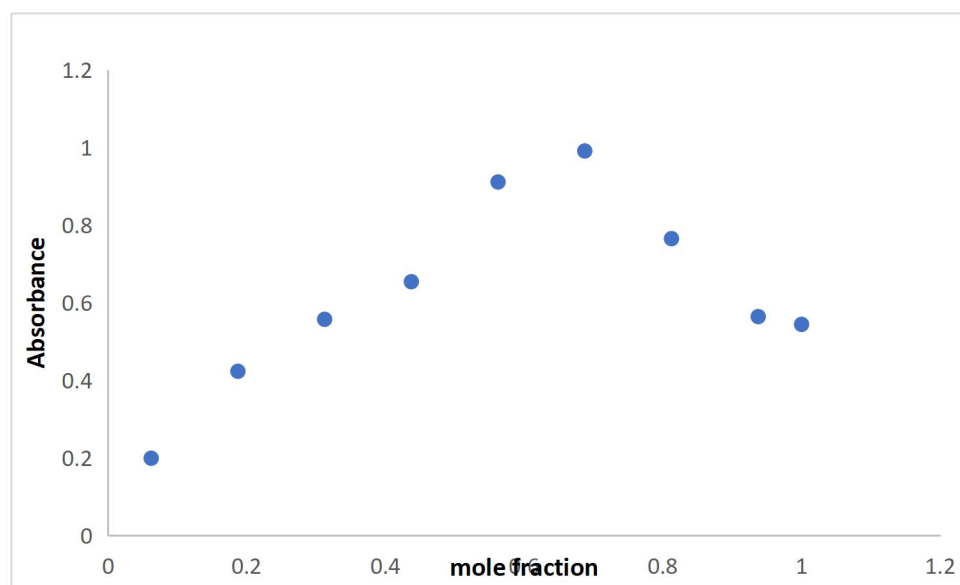


Fig. 8: Plot of absorbance of Copper (II) chloride solution with L against mole fraction

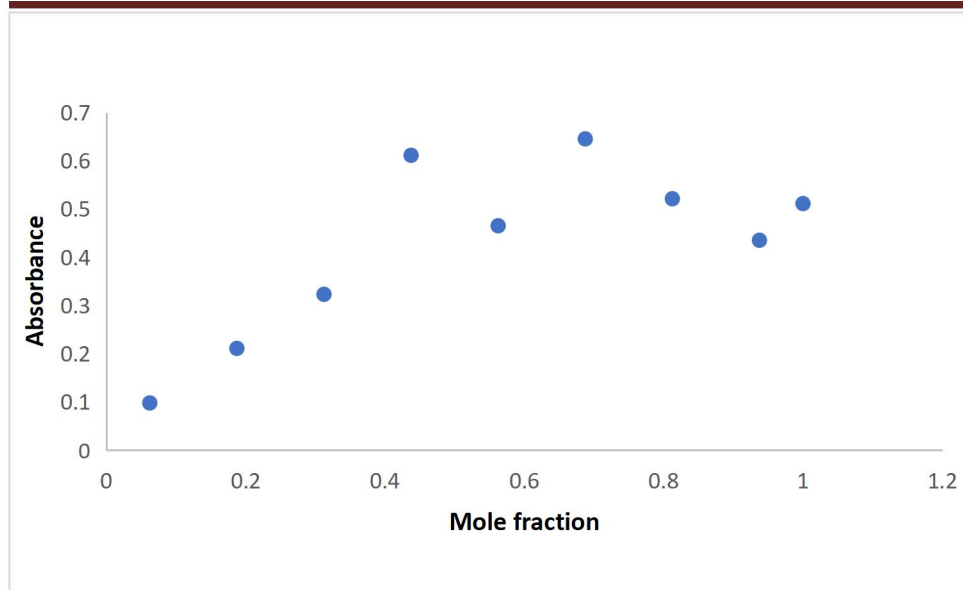


Fig. 9: Plot of absorbance of Iron (II) chloride solution with L against mole fraction

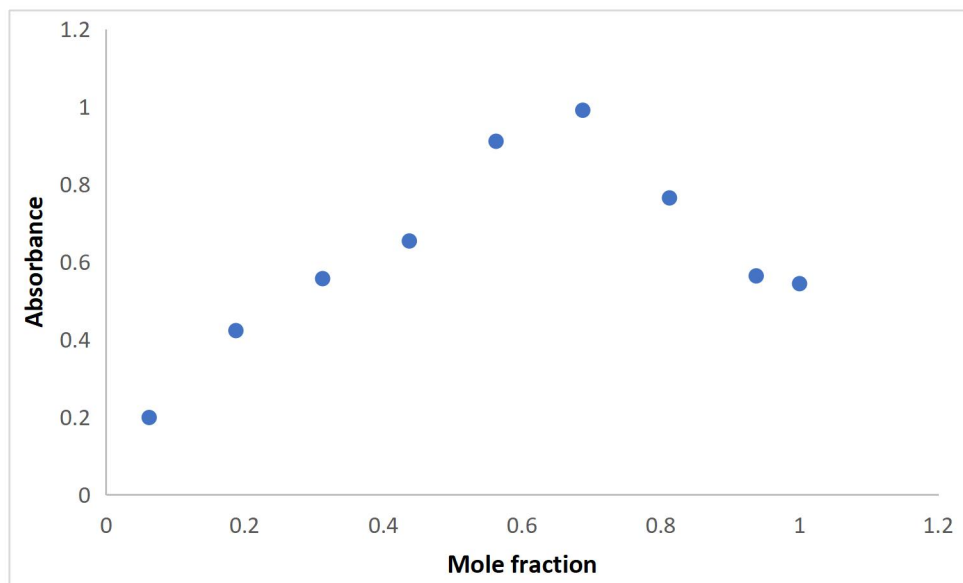


Fig.10: Plot of absorbance of Manganese (II) chloride solution with L against mole fraction

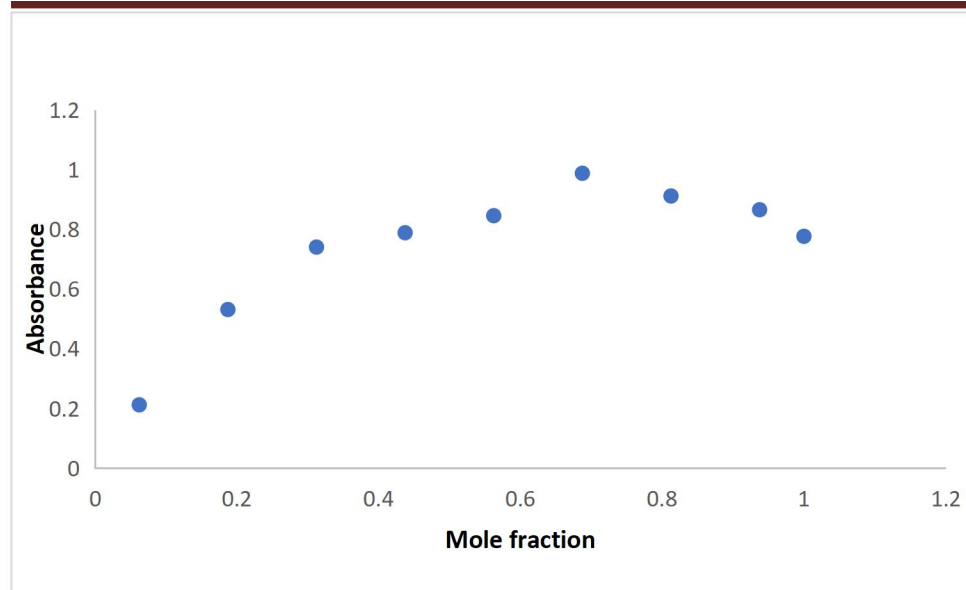


Fig.11: Plot of absorbance of ligands, Nickel (II) chloride solution against mole fraction

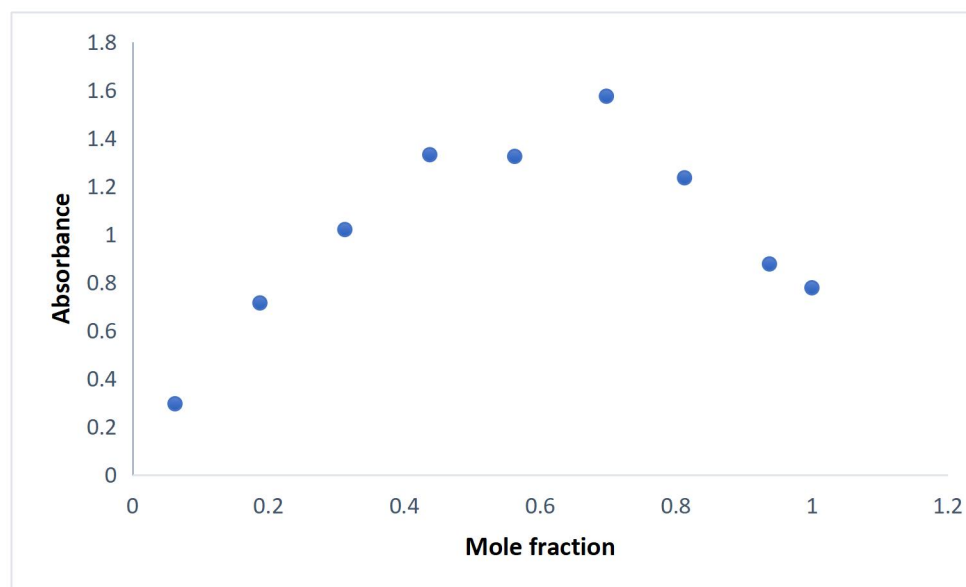


Fig.12: Plot of absorbance of Zn (II) chloride solution against mole fraction

From the analyses conducted the general molecular structure of the complexes is at this moment proposed in Fig. 1 and the IR chart is shown in Figs. 2, 3, 4, 5, 6 and 7 for Ni(II), Cu(II), Co(II), Fe(II), Zn(II) and Mn(II) complexes respectively, while the mole ratio between the metals and the ligand is shown in figs. 8, 9, 10, 11 and 12 .

## CONCLUSIONS

A Schiff base ligand derived from salicylaldehyde and 2,4-dinitrophenylhydrazine and their Mn (II), Cu(II), Zn(II), Co(II), Fe(II) and Ni(II) complexes were synthesized successfully and characterized by melting point/decomposition temperature, solubility, molar conductance, magnetic susceptibility, infrared analysis and UV visible spectrophotometry. Characterization showed the complexes to be non-electrolyte with a variable degree of solubility in water and common organic solvent. The Schiff base behaves as bidentate ligand and is coordinated to the central metal ion through the azomethine and oxygen from the hydroxyl group. The metal(II) complexes have tetrahedral geometry. The synthesized ligand and its metal (II) complexes were screened for their antibacterial activity against five bacterial isolates and three fungal isolates. The result of the studies shows significant antibacterial and antifungal potency. The ligand show lower activity against the isolates compared to the complexes. The ability of these compounds to show antimicrobial activity indicates that they can be further evaluated for medicinal and environmental applications.

## REFERENCES

1. Kolede S.R., Mandlik, P.R. & Aswak, A.S. (2005), Synthesis of Hydrazones Schiff base and microbiological evaluation of Isonicotinoyl hydrazine with different acetophenone; *Oriental Journal of Chemistry*. 27, 1053-1062.
2. Hassan Hosseini Monfareda, Zahra Kalantaria, Mohammad-Ali Kamyabia & Christoph Janiak (2007). Synthesis, Structural Characterization and Electrochemical Studies of a Nicotinamide-bridged Dinuclear Copper Complex derived from a Tridentate Hydrazone Schiff Base Ligand. DOI:10.1002/zaac.00238
3. Subramanian, P. & Sakunthala, M. (2013). Antibacterial Activities of new Schiff base Metal Complexes Synthesized from 2-Hydroxy-1-Naphthaldehyde and 5-Amino-1-Naphthol. *World Journal of Pharmacy and Pharmaceutical Sciences*. 2, 2753-2764
4. Amr, A.E.G.E., Mohamed, A.M. & Ibrahim, A.A., (2003). Synthesis of Some New Chiral Tricyclic and Macrocyclic Pyridine derivatives as Antimicrobial Agents. *Z. Naturforsch.* 58b, 861.

5. Zeyrek, C.T., Elmali, A. & Elerman, Y. (2006). Super-Exchange Interaction on a Chair-piperazine Bridged Dicopper (II/II) Complex: Synthesis, Crystal Structure, Magnetic Properties and Molecular Orbital Calculation, *Naturforsch, Z.* 61b, 237-24.
6. Janiak, C., Lassahn, P.G. & Lozan, V. (2006): Metal Complexes for the Vinyl Addition Polymerization of Norbornene: *Macromol. Symposia* 236, 88.
7. Katyal, M. & Dutt, J. (1975). Analytical Application of Hydrazones. *Talanta.* 22, 151.
8. Krigas, T., Camp, L.V. & Rosenberg, B. (1965). Medicinal Properties of Transition Metal Complexes. *Nature*, 205, 698-699.
9. Elzahany, E.A., Hegab, K.H., Khalil, S.K.H. & Youssef, K.N.S. (2008). Synthesis of some Transition Metal Complexes with Schiff bases Derived from 2-formylindole, Salicylaldehyde and N-amino Rhodanine. *Australian Journal of Basic and Applied Science*, 2(2), 210.
10. Salawu, O.W. & Abdilsalam, A.O. (2011). Synthesis, characterization and biological activities of Cd(II) complexes with hydrazine ligands; *Scholars Research Library Der PharmaChemica.* 3(4), 298-304.
11. Monfareda, H.H., Omid, P. & Christophe, J. (2006). Synthesis and Spectral Characterization of Hydrazone Schiff bases Derived from 2,4-Dinitrophenylhydrazine. Crystal Structure of Salicylaldehyde-2,4-Dinitrophenylhydrazone. *Z.Naturforsch.* 62b, 717-720.
12. Aliyu, H.N. & Ado, I. (2011). Physicochemical Studies on Mn (II) and Ni (II) Complexes with Schiff Base Derived from 2- Amino Benzoic Acid and Salicylaldehyde. *Centrepont Journal (Science Edition)*, 17.2, 119 – 127
13. Angelici, R.J. (1973). Synthesis and Techniques in Inorganic Chemistry, 2<sup>nd</sup> edition, W.B Savders Company, New York, 115-125
14. Atta-ur-Rahman, Choudhary, M. I. & Thomsen, W. J. (2001). Bioassay techniques for drug development, Harwood Academic Publishers, Netherlands. 33b, 16.
15. Gomathi, V., Selvameena, R., Subbalakshmi, R. & Valarmathy, G. (2013). Synthesis, Characterization and Antimicrobial Studies of Schiff base Complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) Derived From 3-Aminophenol And 2-Hydroxynaphthaldehyde. *International Journal of Recent Scientific Research.* 4, 80-83.

16. Byeong-Goo, J., Chae-Dyong R, Hee-Name C, Ki-Hyung, C. & Yohng-Kook (1996). Synthesis and Characterization of Schiff base derived from 2-hydroxyl-1-naphthaldehyde and Aliphatic Diamines. *Bull. Korean Chemical Society*, 17(8), 687-693.
17. Ahmed, A. & Akhtar, F. (1983). Cu (II) and Ni (II) Complexes with a tetradentate Schiff base derived from 2-hydroxyl-1-naphthaldehyde and ethylenediamine. *Indian Journal of Chemical Science*, 20A, 737-758
18. Sunitha, S. & Aravindakshan, K.K. (2013). Syntheses, Characterisation and Antimicrobial studies on Transition Metal Complexes of Methylphenyl-4-[Phenyl (Phenylhydrazono) Methyl]-3-Pyrazolone. *International Journal of Pharmacy and Biological Sciences*, 3, 145-150.