SYNTHESIS, PHYSICO-CHEMICAL AND ANTIMICROBIAL STUDIES ON METAL (II) COMPLEXES WITH SCHIFF BASE DERIVED FROM SALICYLALDEHYDE AND 2,4-DINITROPHENYLHYDRAZINE

ABSTRACT

Schiff base derived from salicylaldehyde and 2,4-dinitrophenylhydrazine was synthesized. Its Mn(II) and Fe(II) complexes (MnL_2 and FeL_2) were synthesized by reflux the metal (II) chlorides with the Schiff base. All the compounds were characterized on the basis of melting point/decomposition temperature, solubility, molar conductance, magnetic susceptibility infrared analysis and uv - visible spectrophotometry. The composition of the complexes has been found to be 1:2 (Metal-Ligand) ratio. The complexes have low molar conductance values 6.39 -6.59 ohm^{-1} cm^{2} mol^{-1} indicating non-electrolytes. The Schiff base and its metal (II) complexes were screened for antibacterial activity against five bacterial isolates *Escherichia coli*, *Proteus mirabilis*, *Klebsiella pneumoniae*, *Pseudomonas aureginosa and Staphylococcus aureus* and three fungal isolates *Fusarium solani*, *Aspergillus fumigate* and *Candida albicaus* using well method. The results revealed that the complexes showed higher activity against the microorganisms compared to the Schiff base.

Keywords: Schiff base, Salicylaldehyde, Hydrazides, Antibacterial, Antifungal.

Introduction

Schiff bases play a significant role in the area of 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 or aromatic aldehydes or ketones with primary amines, hydrazides, etc. The significance of Schiff bases like azomethines, hydrazones, semicarbazones, thiosemicarbazones, etc. lies in the fact that the compounds not only possess antimicrobial activities but also show greater tendency to form complexes.

Hydrazones (RR’C=N–NR’’R’’’) are used as inter- mediates in synthesis[2] as functional groups in metal carbonyls[3], in organic compounds[4] and in particular hydrazine Schiff base ligands[5] which are among others employed in dinuclear catalysis[6]. Furthermore, hydrazones exhibit physiological activities in the treatment of several diseases such as tuberculosis. This activity is attributed to the formation of stable chelate complexes with transition metals which catalyse physiological processes[7]. They also act as herbicides, insecticides, nematocides, rodenticides, plant growth regulators, sterilants for houseflies, among other applications[7]. In analytical chemistry, hydrazones find applications as multidentate ligands for transition metals in colorimetric or fluorimetric determinations[8].

This paper reports the studies on manganese (II) and Iron (II) complexes of Schiff base derived from salicylaldehyde and 2,4-dinitrophenylhydrazine due to paucity of information.

Materials and Method

All the reagents used were analar grade. Salicyldehyde and 2,4–nitrophenyl hydrazine were obtained from Sigma-Aldrich. All the solvents were used without further purification. The glasswares used were washed with detergent, rinsed with distilled water and dried in an ovum at 110^{o}C before use. Electric metler balance model H30AR was used for weighing. Melting/decomposition temperature were determined using Gallen Kamp melting point apparatus. Molar conductance measurements were carried out in DMSO using Denver instrument model 20. Jenway 6305 uv-visible spectrophometer was used for uv-visible analysis. IR spectra of the Schiff base and metal (II) complexes were recorded using Schimadzu FT-IR Fourier transform spectrophotometer in the range 4000 – 400cm^{-1}. Bacterial and fungal identification as well as studies were carried out at the Department of Microbiology, Bayero University Kano Nigeria.

Preparation of Schiff base

Equimolar mixture of salicylaldehyde (10mmol) and 2,4-dinitrophenylhydrazine (10mmol) in hot ethanol (30ml) were refluxed with contant stirring for 3hrs. The orange crystalline solid obtained was filtered, washed with ethanol and then recrystallized from methanol and dried in a desiccator over calcium chloride ($CaCl_2$) for three days[9][10] .

Preparation of Complexes

Metal complexes were prepared by addition of a solution of metal (II) chloride (3mmol) in an ethanol (20ml) to a solution of the ligand (6mmol) in same solvent (20ml). The mixture was refluxed with stirring for 3hrs. The product obtained was concentrated to half its volume, filtered, washed with distilled water, diethyl ether and dried in desiccator over ($CaCl_2$) [9][11].

Determination of Number of Coordinated Ligand

3mmolar dimethyl sulphoxide (DMSO) solution 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 16ml was maintained (in that order) throughout the process and the mole fraction of the ligand was calculated in each mixture. The solution of the metal chlorides were scanned (as blank) to find the wavelength of maximum absorption (λ_{max}) for that particular metal ion. The machine was fixed at λ_{max}(in each case) before taking the absorbance values. The absorbance values were extrapolated against mole fraction of the ligand and the number of coordinated ligand (coordination number) was determined[12].

Molar Conductivity Measurement of the Complex

The molar conductance measurement of the complexes was carried out by preparing a solution of each metal(II) complex (0.001mol/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 ($C_{13}H_{10}O_5N_4$) and its metal(II) complexes were assayed against five bacterial isolates (*Escheria coli, Proteus mirabilis, Klebsiella pneumoniae, Pseudomonas aureginosa and Staphylococcus aureus*) by well method. 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 µg/well of the Schiff base and the metal complexes. Wells (6mm in diameter) were dug in the agar media with the help of a sterile metallic borer. Ciprofloxacin 5µg/disc was used as control. The wells were incubated immediately at 37°C for 24hr. Activity was determined by measuring the diameter of zones showing complete inhibition (mm) and comparing the values with the standard[13].

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. 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 µg/well of the Schiff base and the metal complexes. Wells (6mm in diameter) were dug in the agar media with the help of a sterile metallic borer. Manozef µg/well was used as the control. The wells were incubated immediately at 37°C for 48hr. Activity was determined by measuring the diameter of zones showing complete inhibition (mm) and comparing the values with the standard[13].

Results and Discussion

The ligand prepared is orange crystalline solid. The manganese (II) and iron (II) Schiff base complexes prepared are crystalline orange and have decomposition temperatures 255^0C and 270^0C respectively (Table 1). These high decomposition temperatures revealed the stability of the complexes. The solubility tests carried out on the ligand and its metal(II) complexes revealed that they are soluble in most common organic solvents but insoluble in water (Table 2). The molar conductance measurements of the complexes in 10^{-3}M dimethyl sulphoxide (DMSO) is in the range 6.39 – 6.59 ohm^{-1} cm^{-2} mol^{-1}, which are relatively low, indicating non electrolytic nature (Table 3). IR spectra analysis of the free ligand shows broad band at 3268cm^{-1} assigned to v(O-H) stretching vibration. The strong peak at 1616cm^{-1} is attributed to azomethine v(C=N) group[14]. The band at 1617cm^{-1} observed in the metal complexes indicate the participation of the azomethine nitrogen in coordination to the metal ions[15]. Two absorption bands in the range 615-617 and 412-470cm^{-1} in the metal(II) chelates indicate the formation of M-N and M-O bonds in the metal (II) ions respecticely as shown in Table 4.

The magnetic susceptibility measurements provide magnetic property of the metal complexes. The magnetic moment value of Mn (II) complex is 0.96 BM. The magnetic moment value for Fe(II) complexes is zero. These indicate that the Mn(II) complex is diamagnetic while Fe(II) is diamagnetic.

The number of coordinated ligands per metal ion was also determined using Jobs method of continuous variation. For each metal(II) complex, absorbance versus mole fraction of the ligand was plotted. The mole fraction of the ligand at maximum absorbance was used in calculating the number of ligand coordinated to respective metal ions (Mn^{2+}, Fe^{2+}). The results obtained show that the metal to ligand ratio is 1 : 2 also as shown in figure 1 and 2 respectively.

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

Compound	% Yield	Colour	Melting/ Decomposition Temperature (^oC)	Molar Conductance Ohm^{-1} cm^2 mol^{-1}
L	67.22	Pale Orange	220	
$[MnL_2]$	89.67	Orange	250	6.39
$[FeL_2]$	81.68	Deep Orange	246	6.59

Table 2 Magnetic moment values of the Metal (II) Complexes

Complexes	$Xg(g^{-1})$	$Xm(mol^{-1})$	μ_{eff}(BM)	Property
$[MnL_2]$	$5.83x10^{-7}$	$386x10^{-6}$	0.96	Paramagnetic
$[FeL_2]$	-	-	Dia	Diamagnetic

Table 3 Solubility of Schiff base and its Metal (II) Complexes

Compound	H_2O	MeOH	EtOH	Acetone	DMF	DMSO
L	IS	SS	SS	SS	S	S
$[MnL_2]$	IS	SS	S	SS	S	S
$[FeL_2]$	IS	SS	S	SS	S	S

Key: S = soluble, SS = slightly soluble, IS = insoluble

Table 4 Infrared Spectral Data

Compound	v(- OH) cm^{-1}	v(- C = N) cm^{-1}	v(M – N) cm^{-1}	v(M – O) cm^{-1}
L	3268	1616		
$[MnL_2]$		1617	615	470
$[FeL_2]$		1617	608	412

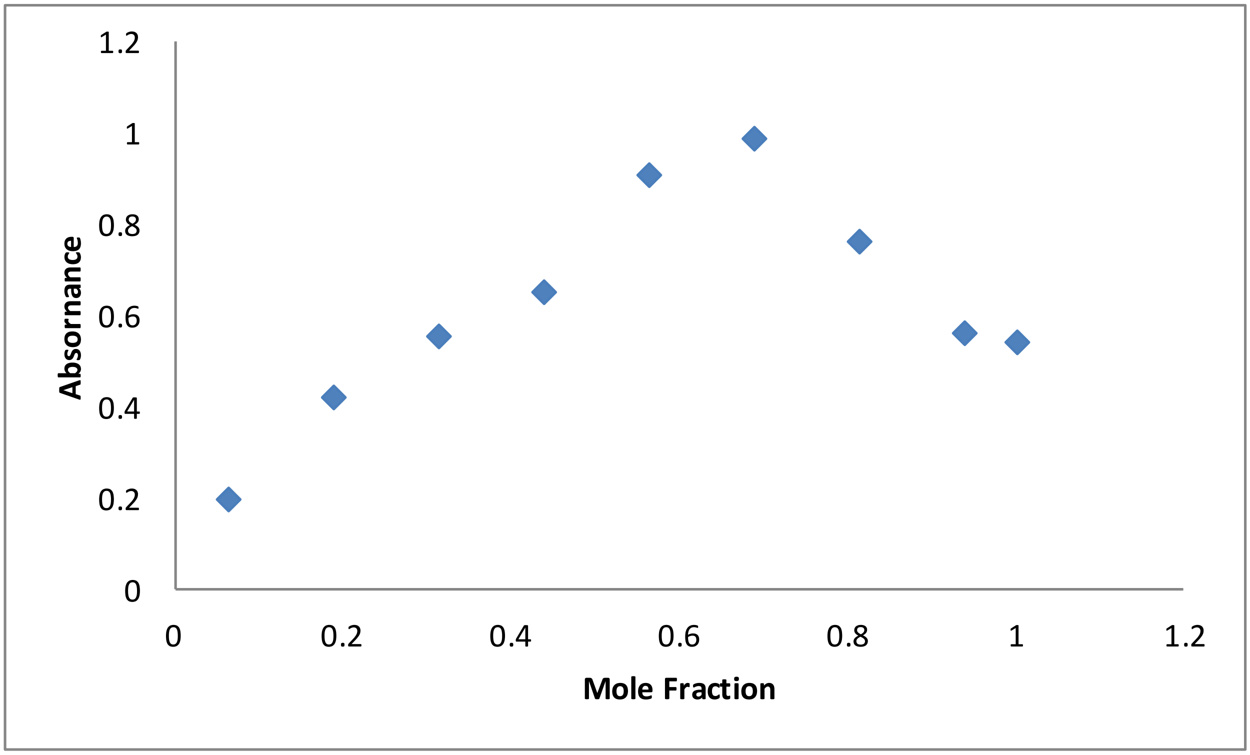


Figure 1: Plot of Absorbance of Mn^{2+} - Schiff base against Mole fraction

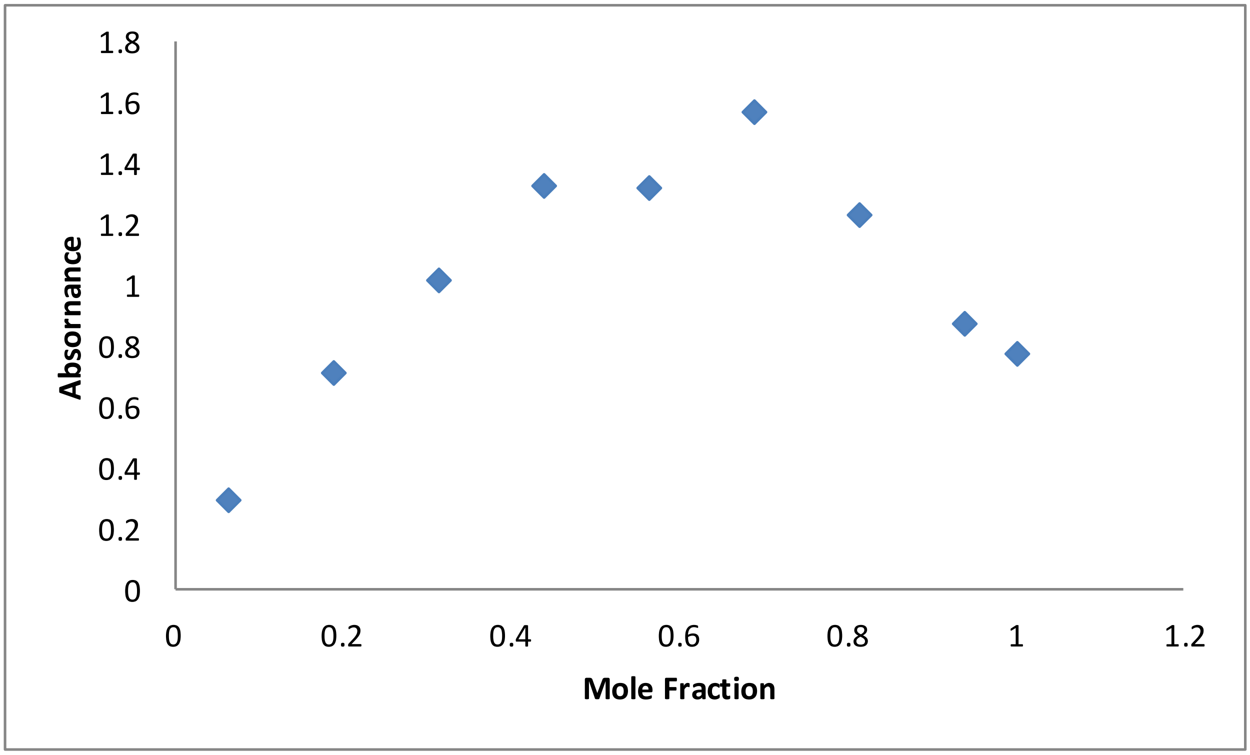


Figure 2: Plot of Absorbance of Fe^{2+} - Schiff base against Mole fraction

The metal (II) complexes have tetrahedral geometry. The synthesized ligands and its metal(II) complexes were screened for their antibacterial activity against five bacterial isolates viz; *E. coli*, *S. aureus*, *P. aureginosa and K. Pneumoniae* S. aureus and antifungal activity against three fungal species (*C. albicaus*, *F. solani and A. fumigates*). The results of these studies revealed that all the compounds and the ligand showed significant antibacterial and antifungal potency. The ligand showed lower activity against the isolates compared to the complexes. The result is shown in Table 7 and 8 respectively.

Table 7 Antibacterial Activity Profile of the Compounds

Isolates / Conc. (ug/ml)		L			$[MnL_2]$			$[FeL_2]$		
	1000	2000	4000	1000	2000	4000	1000	200	4000	
Proteus mira.	11	14	14	13	13	14	09	10	10	
E. Coli	NZI	NZI	NZI	09	10	11	14	14	15	
P. aureginosa	NZI	NZI	12	NZI	NZI	NZI	08	10	10	
kleb. Pneumonie	09	10	11	10	13	14	10	15	15	
Stap. Aureus	12	14	14	09	12	16	12	12	13	

L= $C_{13}H_{10}O_5N_4$

NZI=No Zone of Inhibition

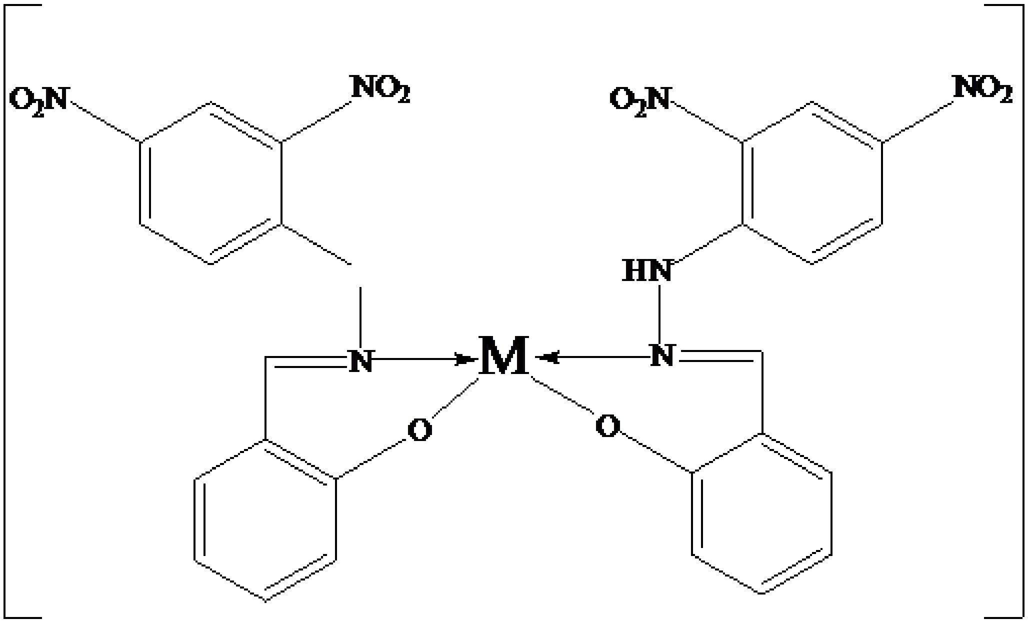
Table 8 Antifungal Activity Profile of the Compounds

Isolates / Conc. (ug/ml)		L			$[MnL_2]$			$[FeL_2]$		
	1000	2000	4000	1000	2000	4000	1000	2000	4000	
C. albicans	NZI	NZI	NZI	NZI	NZI	NZI	NZI	07	16	
F. solani	NZI	NZI	NZI	NZI	NZI	09	NZI	NZI	12	
A. fumigate	NZI	NZI	NZI	NZI	NZI	NZI	NZI	NZI	NZI	

L= $C_{13}H_{10}O_5N_4$

NZI=No Zone of Inhibition

From the analyses conducted the general molecular structure of the complexes is hereby proposed in figure 3 below:



Key; M=Mn, Fe.

Fig. 3: Proposed Molecular Structure of the Complexes

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