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Synthesis, Characterization and Antimicrobial Studies of Schiff base Derived from Salicyldehyde and 2,4-dinitrophenyl hydrazine and its Metal (II) Complexes

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Abstract: *Schiff base ligand derived from salicylaldehyde and 2,4-dinitrophenylhydrazine were synthesized. Cu(II) and Zn(II) complexes (CuL_2 and ZnL_2) were synthesized. The compound were characterized on the basis of melting point/decomposition temperature, solubility, molar conductance, magnetic susceptibility infrared analysis and UV visible spectrophotometry. The complexes have been found to be 1:2 (Metal-Ligand) ratio. All the complexes have low molar conductance values, between (6.39-6.59) indicating non-electrolytic nature. The synthesized ligand 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 isolate (Fusarium solani, Aspergillus fumigate and Candida albicans) using well method. The results revealed that the complexes show more activity against the microorganisms compared to the Schiff base.*

Keywords: *Schiff bases, Metal complexes, 2,4-Dintrophenylhydrazine, Salicylaldehyde Microorganisms.*

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I. Introduction

The chemistry of metal complexes including ordinary complexes, chelates and mixed ligands complexes has been extensively studied till date for their bioinorganic relevance as well as a wide range of physicochemical properties [Bhatt, 2008 & Keskioglu, 2008]. Inclusion of varieties of ligands in complexes has enable the tailor making of the properties of the complexes originating due to metal ions, polynuclear complexes with inclusion of different metals is imperatives [Dul, 2010 & Venegas-Yazigi 2010]. Mixed metal complexes are a class of compounds which can have properties that are not present in ordinary complexes (Murugavel, 2008, Paschke, 2003, Masoud, 2005 and Paital, 2007). However, synthetic route leading to heteropolynuclear complexes with pre-established structures and properties has always remained a challenge for synthetic chemists. Numerous homopolynuclear complexes have been characterised so far (Prushan, 2007 and Lemaire, 2006). These complexes are generally obtained using polydentate ligands in which some of the donor atoms are unable to coordinate with the same metal ions due to stearic factors. This utilised functionality drawn on another metal ion forming polynuclear complex (Deepalatha, 2006, Bhatt 1998, 2001). A one pot procedure for template synthesis of hetero metallic complexes has not been well established yet. This difficulty has been overcome to some extent using an approach complexes as ligands Murugavel, 2008, Paschke, 2003 and Dobrokhotova, 2011). Here, a complex with some unutilized functionality on ligand is considered as a ligand and name as metal organic ligand (MOL). This MOL when allowed to react with metal ions result in formation of mixed metal complexes.

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

II. Materials and Methods

All the reagents used were analar grade and salicyldehyde and 2,4 – nitrophenyl hydrazine were obtained from Sigma-Aldrich. All the solvents were used without further purification. The glassware used were washed with detergent, rinsed with distilled water and dried in an ovum at 110^{o}C before used. 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 Scimadzu FT-IR Fourier transform

spectrophotometer in the range 4000 – 400cm^{-1}. Microbial and fungal identification as well as studies were carried out at the department of Microbiology, Bayero University Kano Nigeria.

Preparation of Schiff base

The Schiff base ligand was obtained by the condensation of equimolar mixture of salicylaldehyde (10mmol=1.08cm^3) with 2,4-dinitrophenylhydrazine (10mmol=1.198g) in ethanol and then refluxed on a hot plate with 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.(Salawu *et al* 2011 and Monfared*et al* 2007).

Preparation of Complexes

3mmol hot ethanolic solution of metal(II) chloride was added to ethanolic solution of the ligand (6mmol) in drops while stirring. The mixture was refluxed on a hot plate 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 ($CaCl_2$)(Salawu *et al* 2011 and Hassan *et al* 2007).

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. (Angelici, 1973).

Molar Conductivity Measurement of the Complex

Solution of each metal(II) complex (0.001mol/dm^3) was prepared in DMSO and molar conductance was measured.

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 the reported 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 controls. The wells were incubated immediately at 37°C for 24hrs. Activity was determined by measuring the diameter of zones showing complete inhibition (mm) and comparing the values with the standard. (Atta-ur-Rahman, 2001).

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 albicans*) 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 48hrs. Activity was determined by measuring the diameter of zones showing complete inhibition (mm) and comparing the values with the standard.(Atta-ur-Rahman, 2001).

III. Results and Discussion

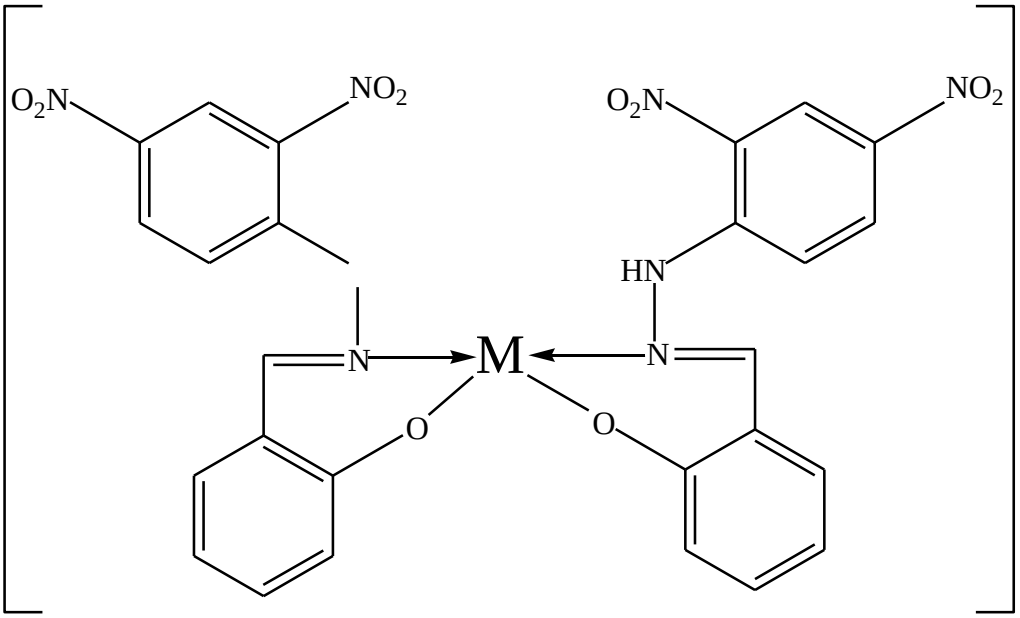
The ligand prepared is orange crystalline solid, it is soluble in common organic solvents but insoluble in water. The copper(II) and zinc(II) Schiff base complexes prepared are crystalline orange and have decomposition temperatures 250^{0}C and 249^{0}C, respectively. These high decomposition temperatures, revealed the stability of the complex compounds (Table 1). The solubility tests carried out on the ligand and its nickel(II) complex 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 dimethylsulphoxide is in the range 5.18 – 6.04 ohm^{-1}CM^{-2}Mol^{-1}, which are relatively low, indicating their 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 (Bhatt, 2001). The band in the range 1611-1624cm^{-1} are all observed in the metal complexes prepared, which indicate the participation of the azomethine nitrogen in coordination to the metal ions [Ahmed, 1983]. Two absorption band in the range 616-617 and 409-415cm^{-1} in the metal(II) chelates, respectively , indicating the formation of M-N and M-O bonds confirming coordination of the ligand to the metal(II) ions as shown in Table 4.

The magnetic susceptibility measurements provide information regarding the structure of the metal complexes. The magnetic moment values of Cu(II) complex is 1.15 BM. The magnetic moment values Zn(II) complexes are zero. These indicates the diamagnetic character of Fe(II) complexes.

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 5 and 6 below.

From the analyses of the complexes the general molecular structure has been proposed below:



Key; M=Cu, Zn.

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
[CuL_2]	73.42	Pale Orange	250
[ZnL_2]	79.30	Pale Orange	249

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

Complexes	Xg(g^{-1})	Xm(mol^{-1})	μ_{eff}(BM)	Property
[CuL_2]	8.33x10^{-7}	555x10^{-6}	1.15	Paramagnetic
[ZnL_2]	-	-	Dia	Diamagnetic

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

Compound	**H O** $_2$	**MeOH**	**EtOH**	**Acetone**	**DMF**	**DMSO**
L	IS	SS	SS	SS	S	S
CuL_2	IS	SS	S	SS	S	S
ZnL_2	IS	SS	S	SS	S	S

Table 4 Infrared Spectral Data

Compound	**$^{-1}$ - OH (cm)**	**$^{-1}$ - C = N (cm)**	**$^{-1}$ M – N (cm)**	**$^{-1}$ M – O (cm)**
L	3268	1616		
CuL_2		1617	615	409
ZnL_2		1617	608	415

Table 5 Antibacterial Activity Profile of the Compounds

Isolates / Conc. (ug/ml)		L			$[CuL_2]$			$[ZnL_2]$	
	1000	2000	4000	1000	2000	4000	1000	200	4000
Proteus mira.	11	14	14	NZI	NZI	07	09	10	10
E. Coli	NZI	NZI	NZI	NZI	NZI	NZI	14	14	15
P. aureginosa	NZI	NZI	12	NZI	NZI	NZI	NZI	NZI	NZI
kleb. Pneumonie	09	10	11	NZI	NZI	NZI	NZI	NZI	NZI
Stap. Aureus	12	14	14	19	20	21	14	15	20

L= $C_{13}H_{10}O_5N_4$
NZI=No Zone of Inhibition

Table 6 Antifungal Activity Profile of the Compounds

Isolates / Conc. (ug/ml)		L			$[CuL_2]$			$[ZnL_2]$	
	1000	2000	4000	1000	2000	4000	1000	2000	4000
C. albicans	NZI	NZI	NZI	NZI	NZI	NZI	09	10	17
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

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