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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDIES OF SCHIFF BASE DERIVED FROM 4-METHYL-o-PHENYLENEDIAMIE AND 2-HYDROXNAPTHALDEHYDE AND ITS METAL (II) COMPLEXES

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ABSTRACT
Schiff base of 4-methyl-o-phenylenediamine and 2-hyroxy-1-napthaldehyde was synthesized and was used to prepare some metal (II) complex by refluxing with Metal (II) chloride ions. The ligand and its complexes were characterized by melting point and decomposition temperature, FTIR, solubility, magnetic susceptibility, conductivity measurement and elemental analysis. The IR spectral data revealed that, the Schiff base coordinated to the respective metal(II) ion through the azomethine nitrogen and phenolic oxygen due to the shifting of the azomethine band υ(C = N) from 591cm^{-1} to 1603 and 1581cm^{-1} in the spectra of the complexes. The band at 567 and 563cm^{-1} were due to υ(M–N), and 729-752cm^{-1} due to υ(M–O) and the infrared spectra of the metal(II) complexes showed strong bands 3443 and 3363cm^{-1} suggesting the presence of coordinated water in the metal complexes. Molar conductance values determined 9.17 and 10.04Ω^{-1}cm^{2}mol^{-1} showed that, the complexes were non-electrolytes. The ligand and its metal (II) complexes are not soluble in water and most organic solvents except DMF and DMSO. The melting point of the ligand and the decomposition temperatures of the metal (II) complexes were 243 and 224^{o}C, which indicated their good thermal stability. The magnetic moment values of the metal (II) complexes obtained were 5.65 and 5.22BM for Mn(II) and Fe(II) complexes. This positive values indicated that they were paramagnetic. The elemental analysis suggested a metal to ligand ratio of 1:2. The antibacterial and antifungal test carried out on the ligand and its metal(II) complexes sowed moderate activity.

Keywords: Schiff words, metal (II) complexes, antimicrobial activity, molar conductance

INTRODUCTION

A Schiff base (also known as imine or azomethine) is a chemical compound containing carbon and nitrogen double bond (-HC=N-) in which the nitrogen atom is connected to aryl or alkyl group. These compounds were named after Hugo Schiff, A German scientist, who first reported them in 1864 (Khetani, 2015).Structurally a Schiff base is a nitrogen analogue of an aldehyde or a ketone, in which the carbonyl group (C=O) is replaced by an imine or azomethine group. Schiff bases of aliphatic aldehydes are unstable and readily polymerized while those of aromatic aldehydes have an effective conjugation system, making them more stable (Abbas *et al.,* 2010). Schiff bases are considered versatile pharmacophores for various pharmacological activities where the azomethine group has been demonstrated to be critical to the bioactivity. For example, Schiff bases, whether of natural or non-natural origin, have exhibited promising antibacterial, anti-tubercular, anti-fungal, anti-parasitic, anti-viral, anti-oxidant, anti-cancer, analgesic, anti-inflammatory properties (Da-silver *et al.*, 2011). Transition metals are known to form complexes and Schiff bases have often been used as chelating ligands in the field of coordination chemistry. Their metal complexes have been of great interest for many years. It is well known that N, O and S atoms play a key role in the coordination of metals at the active sites of numerous Schiff bases (Brown and Smith, 1990). Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer, antiviral and herbicidal applications (Cozzi, 2004). They serve as models for biologically important species and find applications in biomimetic catalytic reactions. It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities (Chandra and Sangeetika, 2004).

MATERIALS AND METHODS

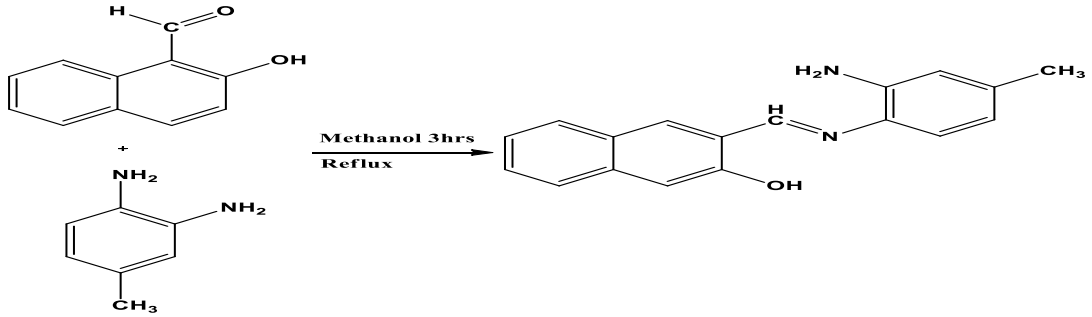
Materials

All the reagents used in this work were of analytical grade and were used without further purification. The glass wares were washed thoroughly with detergent, rinsed with distilled water and dried in an oven at 110^{o}C before used. Magnetic susceptibility measurement of the complexes were measured using Sherwood MK1 magnetic susceptibility balance. Melting point of the Schiff base as well as the decomposition temperature of the complexes were determined using Gallenkamp melting point apparatus. Infrared spectral analyses were recorded using Agilent Technologist FTIRcary 630 spectrophotometer. Molar conductance of the complexes were measured using Jenway 4010 conductivity meter. Elemental Analysis was conducted at Micro Analytical Centre OEA labs, United Kingdom, using CE Instrument (Thermo) EA1110 Elemental Analyser. The antimicrobial activity of ligand and metal complexes were tested *in vitro* against bacteria such as *Staphylococcus aureus,Escherichia coli* and*klebsiela pneumonia* by paper disc plate method and compared with known antibiotics,Gentamycin. For the fungicidal activity, compounds were screened *in vitro* against *Aspergillus fumigates, Aspergillusflavus*and*Aspergillus*

Niger by the same method which compared with Ketaconazole; in which the antimicrobial activity studies were carried out at the Department of Microbiology, Bayero University, Kano.

2.2 Preparation of the Schiff base

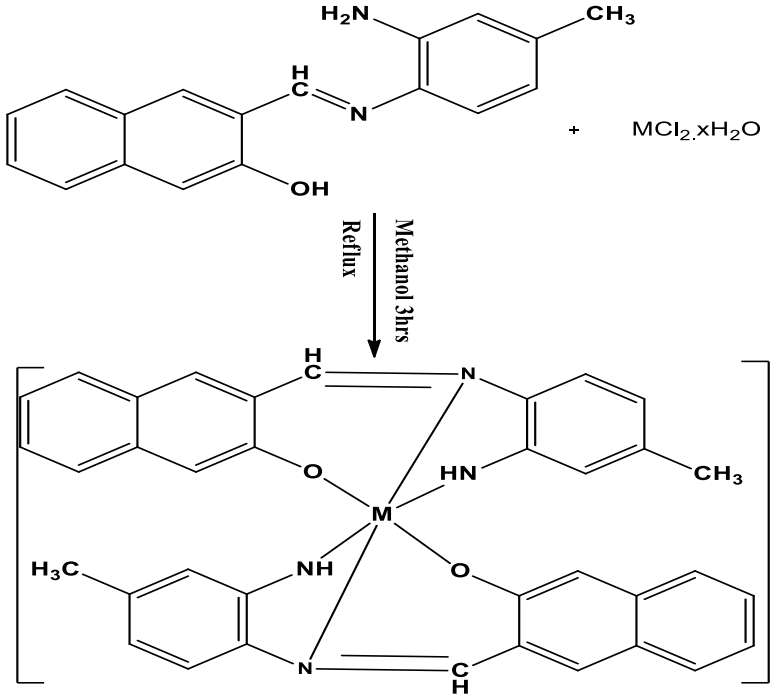
4-methyl-o-phenylenediamine (0.258g, 0.001mol) solution in ($25cm^3$) methanol was added to the ($25cm^3$) methanolic solution of 2-hydroxy-1-napthaldehyde (0.172g; 0.002mol) with stirring and the reaction was refluxed for 3 hours. The solid product formed was separated by filtration, purified by crystallization from methanol, washed with diethyl ether, and then dried in a dessicator over an hydrous calcium chloride (Gehad *et al.*, 2004)



Schame 3.1 synthesis of the Schiff base.

Synthesis of the Complexes

Schiff base (1.32 g; 0.01 mol) solution in hot methanol (25 cm^3)and aqueous solution of the metal(II) chloride (0.01 mol), were mixed, stirred and refluxed for 2 hours. The product obtained was then reduced to nearly half its volume and left overnight which resulted in the formation of a solid precipitate. The coloured precipitate obtained was then filtered, recrystallised in methanol, washed with cold ethanol and dried (Munde *et al*., 2009).



Schame 3.2 Synthesis of the complexes

Where $1 \leq n \leq 3$ and M = Mn(II) and Fe(II)

Physical measurements

IR spectra of the Schiff base and its metal(II) complexes were recorded on FTIR Carry Agilent Technologies model 630 spectrophotometer. C, H and N were estimated by using CE instrument (Thermo) EA1110 elemental analyzer .Jenway 4010 conductivity meter was used in conductivity measurement using DMSO as solvent. Gallenkamp melting point apparatus was used to obtained Melting point and decomposition temperature. Magnetic measurements of the complexes were performed on Gouy's balance at room temperature.

Antibacterial and Antifungal Test

The method used by (Yushau and Salisu, 2011)was used in antibacterial test, in which the schiff base and its metal(II) complexes were assayed by ager disc diffusion method using cultures of *staphylococcus aureus, Escherichia coli,* and *Klebsiella pneumonia*. The samples were separately dissolved in

dimethylsulfoxide (DMSO) to have three different concentrations (15, 30 and 60) µg/disc. Each of these was separately placed on the surface of the culture and incubated at 37°C for 24 hours. The diameter of zone of inhibition produced by the Schiff base ligand and its metal(II)complexes were taken and recorded. Similar procedure was applied in antifungal by using *Aspergillusflavus*, *Aspergillusniger*and *Aspergillusfumigatus*fungal isolates.

Results and Discussion

Physical Properties of the Schiff base and its Metal(II) Complexes

The ligand and its meta l(II) complexes were prepared in good yield, and their physical properties were analyzed and presented in table 1. The percentage yield of the Schiff base was 89.14 % while that of the complexes were 668.70 and 74.73 %. The ligand was yellow while the Mn(II) and Fe(II) complexes were brown and dark brown respectively. It was found that the melting point of the Schiff base was 195 ^{O}C and the decomposition temperature of the metal(II) complexes were 243 and 225 ^{O}C, this is an indication of their thermal stability. The molar conductance of the metal(II) complexes were 9.17 and 10.04 Ω-1 $cm^2mol^{-1}$for Mn(II) and Fe(II) complexes. These low values suggest their non-electrolytic nature as reported by (Spinu; 2008). The effective magnetic moments of the

complexes were 5.65 and 5.22 B.M showing their paramagnetic nature.

Table 1: Physical Properties of the Schiff base and its Metal(II) Complexes

Compounds	Colours	% yield	M.P. (^{0}C)	D.Temp (^{o}C)	μ_{eff}(BM)	M.L ($\Omega^{-1}cm^2mol^{-1}$)
L(Ligand)	Yellow	89.14	195	-	-	-
[MnL2].(H_2O)	Brown	68.70	-	243	5.65	9.17
[FeL2].2(H_2O)	Dark brown	74.73	-	224	5.22	10.04

Solubility Test

Water and some common organic solvents were used to determine the solubility of the ligand and its metal(II) complexes. From the result of solubility test presented in table 2, it can be seen that, the ligand and its metal(II) complexes were soluble in dimethylsulfoxide (DMSO) and dimethylformamide (DMF), slightly soluble in methanol and insoluble in n-hexane and insoluble in acetonitrile.

Table 2: Solubility test of the Schiff base and its metal(II) complexes

Compound	Water	Ethanol	Methanol	Acetonitrile	Ether	DMSO	DMF	nHexane
Ligand (L)	IS	IS	IS	IS	IS	S	S	IS
[MnL_2].H_2O	IS	IS	SS	IS	IS	S	S	SS
[FeL_2].2H_2O	IS	IS	SS	IS	IS	S	S	IS

Key: IS= insoluble, SS= Slightly Soluble, S= Soluble

FTIR Analysis

The infrared spectra of the Schiff base showed a prominent band at 1611cm^{-1} due to ν(C=N) linkage appeared indicating that condensation between 2-hydroxy-1-napthaldehyde and 4-methyl-o-phenylenediamine has taken place resulting into formation of the Schiff base. The azomethine band of the Schiff base at 1611cm^{-1} was observed to shift down field to a range of 1581 – 1640$cm^{-1}$for all the metal(II) complexes which is attributed to the participation of the azomethine nitrogen (C=N) in the co-ordination to the metal ions similar observation on some related metal(II) complexes was reported by (Byong-Goo, 1996). The absorption bands in the range of 563-567 cm^{-1} and 748 – 752 cm^{-1}observed for all the complexes suggested the formation of (M – N) and (M – O) bond respectively. Also, the infrared spectra of the metal(II) complexes showed strong band in 3368 and 3443cm^{-1} region, suggesting the presence of coordinated water in the metal complexes (Nakmoto *et al*; 2003)

Table 3: Infrared spectral data of the Schiff base and its metal(II) complexes

Complex	ν(OH) cm^{-1}	ν(C=N) cm^{-1}	ν(M–N) cm^{-1}	ν(M–O) cm^{-1}
Ligand (L)	_	1611	–	–
[MnL_2].H_2O	3443	1603	567	748
[FeL_2].2H_2O	3368	1581	563	752

Elemental analysis

The elemental analysis for C, H and H for all complexes determined showed an excellent agreement between the calculated and observed values and the result suggested 1:2 metal to Schiff base.

Table 4: Microanalysis Data of the Schiff base and its metal (II) complexes

Compound	M.wt. (g/mol)	% Calculated (Found)		
		C	H	N
L	276	39.13(39.58)	2.89(3.21)	5.07(4.79)
$[MnL_2].H_2O$	622.94	34.67(35.01)	2.57(2.20)	4.49(3.85)
$[FeL_2].2H_2O$	641.85	33.66(33.01)	2.49(2.21)	4.36(4.89)

Antimicrobial Activity

The antimicrobial actvity results of the screened Schiff base ligand and its metal(II) complexes are given in the table 5 and 6. The ligand and its complexes were screened for their antibacterial activities against the selected bacteria isolates of *Staphylococcus aureus, Eschirichia coli,* and *Klebsiella pneumonia* by disc diffusion method. It was found that metal(II) complexes have more effect in inhibiting the microbial growth. This may be due to the interaction of the metal(II) complexes with lipoproteins of the cell. Therefore, the metal(II) complexes may restrict the normal functioning of the microbial cell. Similar result was reported by yushau and Sadisu. Furthermore, their higher stability at higher temperature may also allow them to use them as a potential antimicrobial agent. Similar result was also recorded in table 6 for antifungal activity shown by selected fungi isolates of *Aspergillus fumigates,Aspergillusflavus*and *Aspergillus Niger*

Table 5:Antibacterial activities of the Schiff base and its metal(II) complexes against bacterial species

Test Organism Used	Ligand(μg/mm)			$[MnL_2].H_2O$(μg/mm)			$[FeL_2].2H_2O$(μg/mm)			Control (mm) antibiotic used
	15	30	60	15	30	60	15	30	60	Gentamycin (80mg)
Staphylococcus aureus	8	10	12	6	9	14	10	13	18	24
Escherichia coli	19	6	6	12	16	19	8	11	15	18
Klebsiella pneumonia	6	6	6	6	6	6	6	10	14	20

Table 4.6: Antifungal activities of metal (II) complexes against bacterial species

Test Organism Used	Ligand (μg/mm)			$[MnL_2].H_2O$(μg/mm)			$[FeL_2].2H_2O$(μg/mm)			Control (mm) Ketoconazole(200mg)
	15	30	60	15	30	60	15	30	60	-
Aspergillus fumigates	6	9	10	6	9	11	9	10	13	23
Aspergillusflavus	6	7	11	6	9	11	6	6	9	19
Aspergillus Niger	7	9	13	9	9	10	8	10	11	19

CONCLUSION

The Schiff base and its Mn(II) and Fe(II) complexes were prepared and characterized. Conductivity measurement showed that the complexes are non-electrolyte. The decomposition temperature of these Schiff base complexes revealed high values which is an indication of high stability. The solubility test carried out in various solvents showed they are all soluble in DMSO and DMF. IR spectroscopy shows the Schiff base are co-ordinated to the central metal ion through the N-atom of the azomethine. The positive values of the magnetic susceptibility of the complexes shows that the complexes are paramagnetic in nature. The elemental analysis of Schiff base and their metal complexes shows 2:1 ligand to metal ratio. Anti-microbial activity of the ligand and its metal complexes indicate that the metal(II) complexes were more active than the free Schiff base on one or more isolates. Even though the metal complexes were found to be more active than the free Schiff base, they were lower than the standard drugs (*gentamycin* and *ketoconazole* for bacterial and fungal isolate respectively) used.

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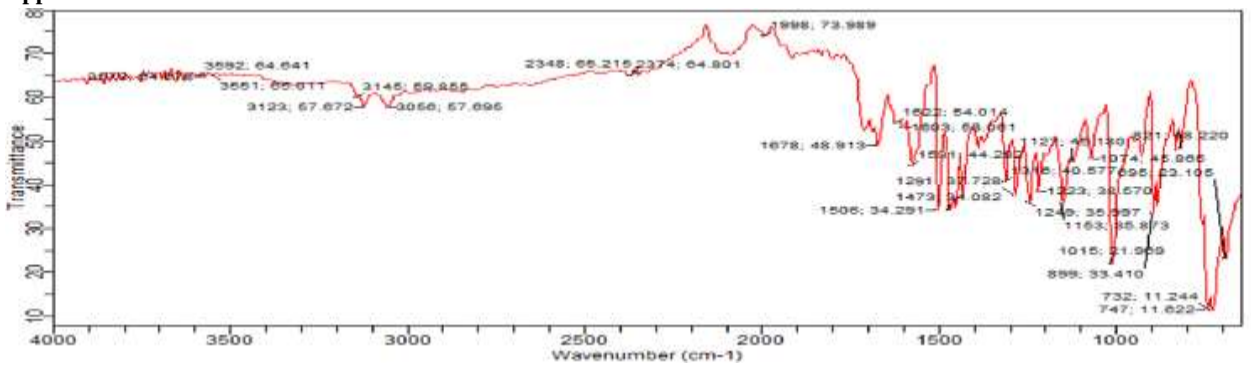
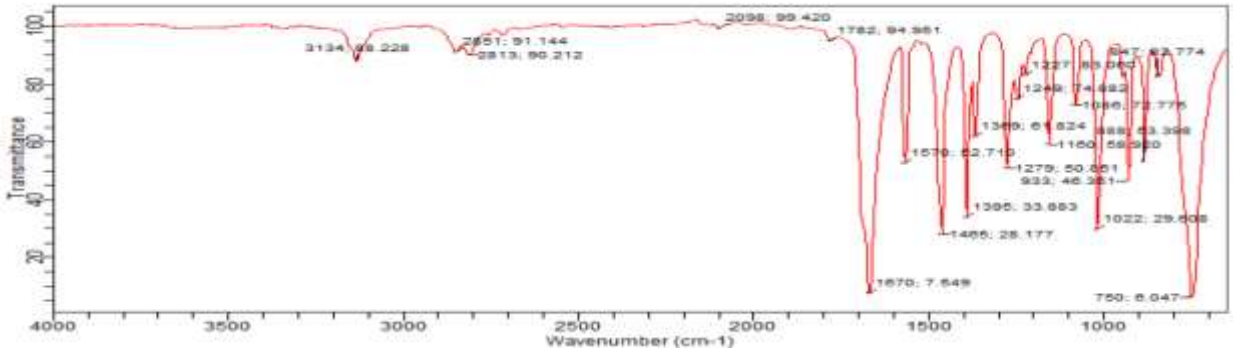
APPENDICES

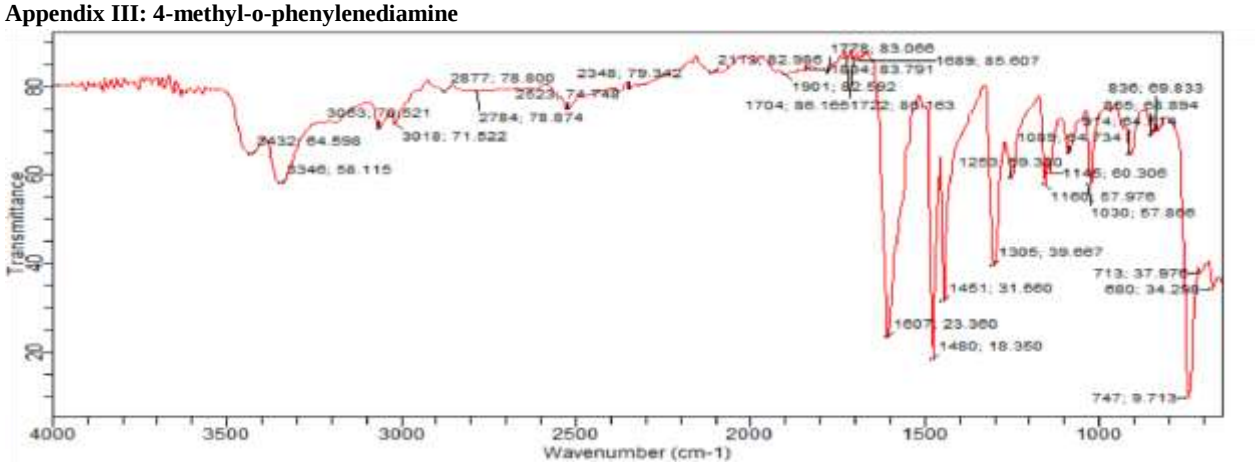
Appendix I: Schiff base



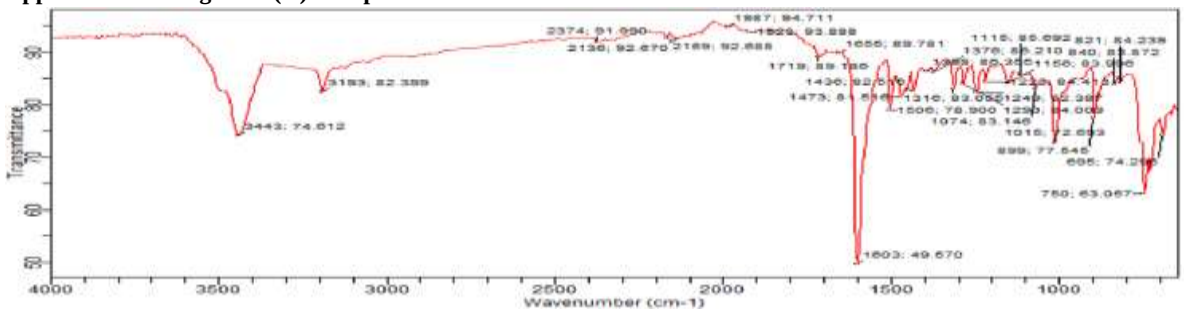
Appendix II: 2-hydroxy-1-napthaldehyde



Appendix III: 4-methyl-o-phenylenediamine



Appendix IV: Manganese (II) Complex



Appendix V: Iron (II) Complex