

Synthesis, Characterization and Antimicrobial Studies on Schiff Base Derived from o-Aminopyridine and o-Anisaldehyde and its Manganese(II) and Copper(II) Complexes

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ABSTRACT

The antimicrobial activities of new Schiff base complex was studied. The Schiff base ligand was synthesized by refluxing o-aminopyridine and o-anisaldehyde in ethanol. Metal(II) complexes of the synthesized Schiff base were prepared by refluxing a mixture of the metal(II) chlorides of manganese and copper. The ligand, its manganese and copper complexes were found to be off white, pale brown and dark green respectively. From the FTIR spectra, 1577 cm⁻¹ is assigned to the azomethine bond of the Schiff base and was found to shift to 1614 cm⁻¹ and 1618 cm⁻¹ in manganese(II) and copper(II) complexes respectively. A plot of Job's method of continues variation suggested 1:2 metal-ligand ratio, while magnetic susceptibility data is consistent with tetrahedral arrangement. The complexes were found to be non-electrolytic with high spin configuration as obtained from molar conductance property, and were best soluble in DMSO and DMF but insoluble in water. The ligand was found to melt at 168 °C and while the decomposition temperatures of the manganese and copper complexes are 238 °C and 240 °C respectively indicating thermal stability. Antimicrobial activity using Agar well diffusion method against two bacterial and two fungal isolates, suggests a promising activities at all concentrations with increasing activity as concentration increases. The new complexes were suggested to be potential pharmaceuticals, but toxicity test and further characterization such as MS to accurately identify their structures, are recommended

Key words: o-anisaldehyde, 2-aminopyridine, Ligand, Characterization, Antimicrobial

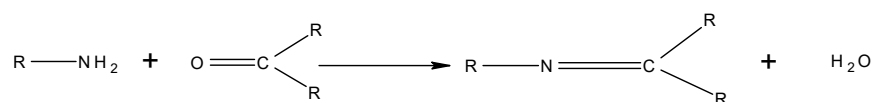
INTRODUCTION

The emergence of resistant strains during treatment greatly increases the risk of treatment failure and that pathogens that have become resistant to drug treatment are a growing public health problem and unless cases of drug resistance are followed up when they arise and then the necessary measures are taken to contain them, therefore, due to the increasing resistance

of drugs treatment by the microbes, despite their role in biological system, there is the need to synthesize as many compound with antimicrobial activities as possible to address the problem [1]. This is because antimicrobial resistant captured special attention in the medical field and therefore, various health organizations have prioritize the need for the discovery of new antimicrobial compounds with high therapeutic values, having greater effectiveness against the resistant microbial strains [2]. This shows that, in spite of the number of available reports by different scholars in the field, the need for the synthesis of antimicrobial compounds such as metal complexes cannot be overemphasized.

This research is aimed at producing new metal complexes with promising therapeutic value through the synthesis and characterization of new Schiff base complexes of Manganese and Copper. Metal complexes are compounds which contain a central metal, acting as a Lewis acid, surrounded by electron pair donors called ligands, acting as a Lewis base. Ligand can bind to the central metal to form various types of compounds. Ligands having more than one donation site (bidentate or polydentate) form ring around the central metal atom or ion and these types of complexes are called chelates. Compounds containing carbon nitrogen double bond, called imines, forms a good ligand and their activity is in most cases enhanced by the presence of functional groups such as amine, thiols, or hydroxyl [3]. Similarly, Sikarwar et al. [4] reports that, chelating ligands containing O and N donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. It was reported recently that compounds containing cyclic imines, which act as a ligand, form stable complexes with transition metals and have biological applications, and are also potential pharmaceuticals that act as antitumor, antibacterial antifungal as well as antiviral. [5]

Imines, also known as Schiff bases, are very good organic ligand. The synthesis of Schiff base and their metal complexes have gained researchers interest due to their interesting biological activity. Schiff bases are the compounds containing azomethine group (-HC=N-), they are condensation products of ketones or aldehydes with primary amines and were first reported by Hugo Schiff in 1864. Scheme 1 give the general preparatory method for Schiff bases



Scheme 1: General preparation of Schiff base

In recent time, Schiff bases are used as intermediates for the synthesis of amino acids or as ligands for preparation of metal complexes having a series of different structures [6].

Schiff bases of aliphatic aldehydes are unstable and readily polymerizable while those with aromatic aldehydes having effective conjugation are more stable [7]. Chelating ligands containing O and N donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to the metal. The synthesis of schiff base ligands and their metal complexes have been extensively studied because of their interesting biological activities [4]. Schiff bases are versatile metal complexing agents that can coordinate with metals especially the transition metals to form complexes. The complexes of Schiff base are thermally stable with vast therapeutic applications. They are used in pharmaceutical industry because of their wide spectrum of biological activities, including antibacterial, antifungal, antidiabetic, antitumor, antiproliferative, anticancer, herbicidal, and anti-inflammatory activities [8].

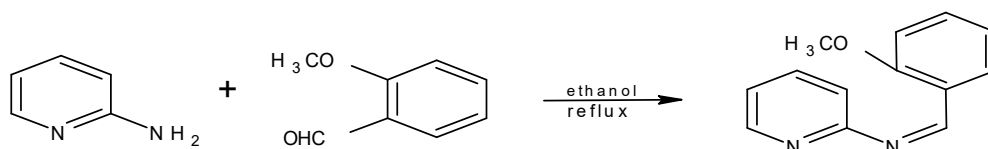
The antimicrobial studies of o-aminopyridine and o-anisalbenzaldehyde Schiff base complexes of Mn(II) and Cu(II) was not reported and therefore in the present work, the synthesis, characterization, antibacterial and antifungal studies of a Schiff base derived from o-aminopyridine and o-anisalbenzaldehyde and its complexes are reported.

MATERIALS AND METHODS

The reagents used in this work are of analytical grade and were used as purchased without purification. Glass wares were washed and dried in an oven at 110 °C overnight before use. FTIR was carried out using Fourier Transform Infrared spectrophotometer (Cary 630 by Agilent Technology) from 400 to 4000 cm^{-1} , melting point of the Schiff base and decomposition temperature of the complexes were determined using Stuart (SMP 110) melting point apparatus, Conductivity of the complexes was determined using Jenway 4010 conductivity METER, UV visible was conducted using Parkin Elmer λ -35 for the Job's method and magnetic susceptibility was determined using Sherwood Scientific Magnetic Susceptibility Balance MK1. Bacterial and fungal isolates were obtained from Malam Aminu Kano Teaching Hospital Kano (AKTH) and identified at THE Microbiology Department, Bayero University Kano. Nutrient Agar and Potato Dextrose Agar were used as media for the bacterial and fungal isolates respectively.

Preparation of the Schiff base

Equimolar ratio (0.03 mol) of o-aminopyridine (2.8236 g) and o-anisaldehyd (3.63 mL) were dissolved in ethanol (50 mL). The mixture was refluxed at 70 °C for 3 h. The reaction mixture was concentrated, cooled to room temperature to afford the crystalline product (Scheme 2) which was re-crystallized from hot ethanol and collected by filtration, and dried in a dessicator over CaCl₂ for 18 hours [9].



Scheme 2: preparation of the Schiff base

Synthesis of the complexes

The complexes were prepared by dissolving 0.003mol of the Schiff base in 25 mL hot ethanol and 0.0015 mol of MCl₂.nH₂O (where M = Co or Ni) in 25 mL hot ethanol solution. The two solutions were mixed together and refluxed with constant stirring for 2 h at 70 °C. On cooling, coloured solids were precipitated out. The products were filtered, washed with cold methanol, cold ethanol and pet. ether, and then dried in a dessicator over CaCl₂ for 18 hours [6].

Antimicrobial activity

The antimicrobial activity of the Schiff base and its complexes were studied using two bacterial isolates: *S. aureus* and *E. coli* and two fungi: *Mucor specie* and *C. albicans* using Agar well diffusion method. The solidified culture media were inoculated with the test microorganisms and wells were dug in the nutrient agar (NA) medium for bacteria and potato dextrose agar (PDA) medium for fungi with the help of a sterile cork-borer. The compounds were dissolved (0.06 g) in DMSO (1.0 mL) to give a stock solution (60,000 µg/mL). Various concentrations of the test compounds were made (60,000 µg/mL, 30,000 µg/mL and 15,000 µg/mL) and introduced into the well by means of a micro syringe and incubated for 24 hours at 35 °C. The zones of inhibition were measured in mm [10].

RESULTS AND DISCUSSION

Table 1 shows some physical properties of the Schiff base and its complexes. The Schiff base was crystallized as pale yellow crystal with a good yield of 64.5%, while the Mn(II) and Cu(II) complexes were obtained as pale brown and dark green crystal powder respectively

with a good yield of 76% and 81% for the cobalt and nickel complexes respectively. The Schiff base has a high thermal stability with a high melting point of 168 °C and the complexes show better stability to heat than the Schiff base with a sharp decomposition temperature of 238 °C and 240 °C for the Mn(II) and Cu(II) complexes respectively.

Table 2 shows the solubility of the Schiff base and its complexes, the Schiff base was found to be insoluble in water, petroleum ether, chloroform and acetone, but soluble in ethanol, DMSO, DMF and methanol, therefore, ethanol was used as solvent for the synthesis of the complexes. Similarly, the complexes were all found to be insoluble in water, petroleum ether, chloroform and acetone, but soluble in ethanol, DMSO and DMF.

Table 3 shows some selected Infrared spectral data of the ligand and its metal(II) complexes. In the FTIR spectra of the ligand and the complexes, vibration frequencies were assigned for the ligand and the complexes. A peak at 1577 cm^{-1} was assigned to azomethine [4] which shifted to 1614 cm^{-1} in Mn(II) complex and 1618 cm^{-1} in Cu(II) complex, this indicates the coordination of the azomethine nitrogen to the metal(II) ions [11]. Similarly, 678 cm^{-1} and 652 cm^{-1} vibrations which were absent in the spectra of the ligand are assigned to the metal-nitrogen bond [12]. Moreover, 430 cm^{-1} and 422 cm^{-1} which were also not found in the spectra of the ligand indicates the coordination of the methoxide oxygen to the Mn(II) and Cu(II) ions respectively. On a similar note, the peak at 1242 cm^{-1} which shifted to 1252 and 1238 cm^{-1} in Mn(II) and Cu(II) complexes respectively were assigned to C-O bond of the methoxy group [13].

Table 4 shows magnetic susceptibility measurement of the complexes, The effective magnetic moment of the complexes, as determined from the magnetic susceptibility, were 5.72 BM and 1.74 BM for the cobalt(II) and nickel(II) complexes respectively, which suggests high spin complexes with octahedral geometry [12].

Table 5 shows the molar conductance as determined from the electrical conductance in 0.003 mol dm^{-3} DMSO solution of the complexes which suggest a non-electrolytic nature.

Table 6 shows the percentage composition of the metals, chlorine and the ligand as obtained from gravimetric analysis. Within the limit of experimental error, the values obtained are consistent with the theoretical value and it suggest 1:2:2 M:L:Cl ratio.

Table 7 shows the percentage of water of crystallization in the complexes. All the complexes were found to be hydrated due to the presence of broad peak around 3200 cm^{-1} in the IR spectra of the complexes, indicating water of hydration where Mn(II) complex was found to be monohydrate and the Cu(II) complex dihydrate. To confirm the metal ligand

reacting ratio, Jobs method of continuous variation was applied [14]. From the Job's plot given in Figures 1 and 2, the number of coordinated ligand was determined which indicates a 1:2 metal ligand ratio for the two metal complexes.

Table 8 shows the antibacterial activity of the Schiff base and its metal(II) complexes as carried out against bacterial isolates (*Staphylococcus aureus* and *Escherichia coli*) using Ciprofloxacin as control. The Schiff base shows no activity against *Staphylococcus aureus* at all concentrations, but show activity against *Escherichia coli*. The two metal complexes show activity against the two bacterial isolates. The Cu(II) complex was found to be more active than Mn(II) complex, but less active than the control.

Table 9 shows the antifungal activity of the Schiff base and its metal(II) complexes as carried out against fungal isolates (*Mucor specie* and *Candida albica*) using Ketoconazole as control, which indicates that the Schiff base ligand and its metal(II) complexes shows no activity against *Mucor specie* at all concentrations with a control having 35 mm inhibition, but are active against *Candida albica* with a control having 37 mm inhibition. The Cu(II) complex shows more activity, and the activity increases with increasing concentration. The complexes show better activity than the free Schiff base in both antibacterial and antifungal sensitivity tests.

Table 1: Physical properties of the Schiff base and the complexes

Compound	Molecular formular	Colour	Percentage yield (%)	Melting Point (°C)	Decomposition Temperature (°C)
Ligand	C ₁₃ H ₁₂ N ₂ O	Pale Yellow	64.5	168	-
[MnL ₂]	MnC ₂₆ H ₂₄ N ₄ O ₂ Cl ₂	Pale brown	76	-	238
[CuL ₂]	CuC ₂₆ H ₂₄ N ₄ O ₂ Cl ₂	Dark green	81	-	240

L = Ligand, C₁₃H₁₂N₂O

Table 2: Solubility of the Schiff base in water and some organic solvents

Compound	Dist. water	Ethanol	Methanol	Pet.ether	Chloroform	Acetone	DMF	DMSO
Ligand	IS	S	SS	IS	IS	IS	S	S
[MnL ₂]	IS	S	S	IS	IS	SS	S	S
[CuL ₂]	IS	S	S	IS	IS	IS	S	S

L = Ligand, C₁₃H₁₂N₂O

Table 3: Selected Infrared spectral data of the ligand and its metal(II) complexes

Compound	$\nu(\text{C}=\text{N}) \text{ cm}^{-1}$	$\nu(-\text{OCH}_3) \text{ cm}^{-1}$	$\nu(\text{M}-\text{N}) \text{ cm}^{-1}$	$\nu(\text{M}-\text{O}) \text{ cm}^{-1}$
Ligand	1577	1242	-	-
[MnL ₂]	1614	1252	678	430
[CuL ₂]	1618	1238	652	422

L = Ligand, C₁₃H₁₂N₂O

Table 4: Molar magnetic susceptibility, gram magnetic susceptibility and effective magnetic moments of the complexes

Compound	$X_g (\text{ergG}^{-2}\text{g}^{-1})$	$X_m (\text{ergG}^{-2}\text{mol}^{-1})$	$\mu_{\text{eff}} (\text{B.M})$
[MnL ₂]	2.495×10^{-5}	1.373×10^{-2}	5.72
[CuL ₂]	22.595×10^{-7}	1.263×10^{-3}	1.74

L = Ligand, C₁₃H₁₂N₂O

Table 5: Conductivity Measurement of the complexes

Compound	Electrical conductance	Molar conductance
	(ohm ⁻¹ cm ⁻¹) x 10 ⁻⁶	(ohm ⁻¹ cm ² mol ⁻¹)
[MnL ₂]	1209	33.58
[CuL ₂]	303	8.41

L = Ligand, C₁₃H₁₂N₂O

Table 6: Percentage compositions of the metals and chlorine

Complex	% composition of metal		% composition of Cl ⁻		% composition of Ligand	
	calculated	Experimental	Calculated	Experimental	calculated	Experimental
[MnL ₂]	10.03	10.10	12.96	12.00	77.01	75.00
[CuL ₂]	11.41	9.90	12.76	12.90	75.83	73.80

Table 7: Percentage water of crystallization

Compound	Initial weight (g)	Weight loss (g)	% water of crystallization
Mn(II) Complex	0.2	0.0058	2.9
Cu(II) Complex	0.2	0.0068	3.4

Table 8: Antibacterial activity of the Schiff base and its metal(II) complexes

Compound	Zone of inhibition (mm)/concentration (µg/mL)					
	<i>Staphylococcus aureus</i>			<i>Escherichia coli</i>		
	60	30	15	60	30	15
Ligand	-	-	-	15	12	11
[MnL ₂]	14	12	09	18	15	12

[CuL ₂]	20	17	15	-	-	-
Standard(5,000 µg/mL)	31			27		

L = Ligand, C₁₃H₁₂N₂O Standard = Ciprofloxacin

Table 9: Antifungal sensitivity test of the Schiff base and its metal(II) complexes

Compound	Zone of inhibition (mm)/concentration (µg/mL)					
	<i>Candida albican</i>			<i>Mucor specie</i>		
	60	30	151	60	30	15
Ligand	23	20	13	-	-	-
[MnL ₂]	28	23	16	-	-	-
[CuL ₂]	27	25	22	-	-	-
Standard(2,000 µg/mL)	37			35		

L = Ligand, C₁₃H₁₂N₂O Standard = Ketoconazole

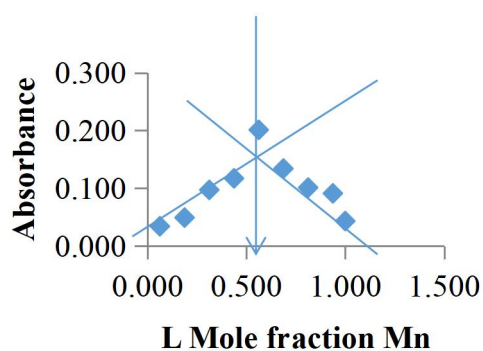


Fig. 1: Plot of absorbance against ligand mole fraction at 635 nm for Mn(II) complex

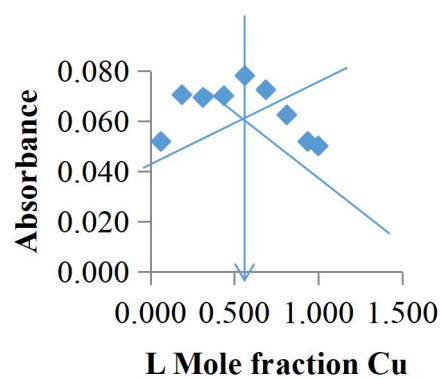
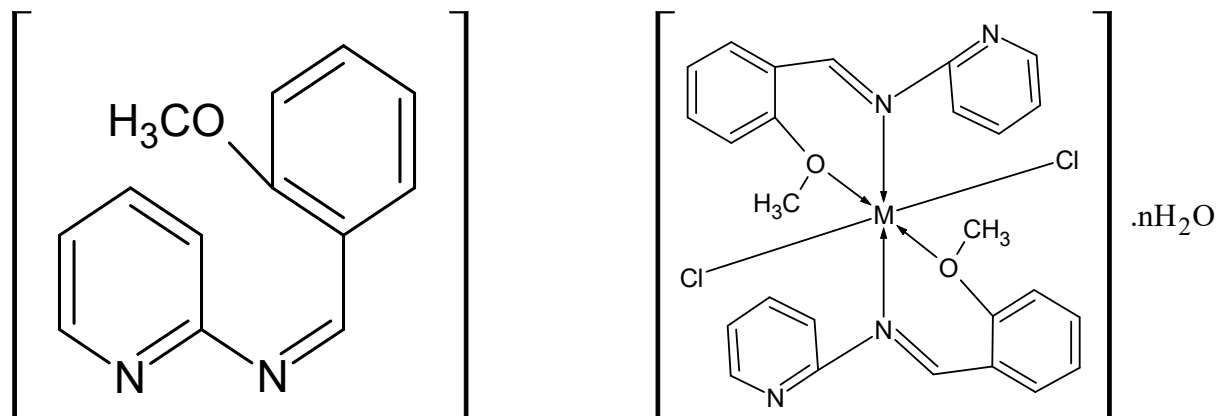


Fig. 2: Plot of absorbance against ligand mole fraction at 540 nm for Cu(II) complex

CONCLUSION

The Schiff base and its metal(II) complexes were synthesized, characterized, and tested for their antimicrobial activity. The Schiff base ligands were found to be bidentate and octahedral geometry was suggested for the two metal complexes. The complexes were found to be sensitive against the bacterial and fungal isolates used for the antimicrobial test, and the complexes shows better activity than the free ligand. However, it is recommended that the new compound should be subjected to cytotoxicity test to ensure it do not exert harmful effects on normal mammalian cells at effective antimicrobial concentrations. Moreover, NMR of the ligand and Mass spectroscopy (MS) of the ligand and the metal complexes are recommended for further research to fully identify the structure of the new compound. However, from the findings of this research, the following is proposed to be the most likely structure of the Schiff base and its complexes.



Where M= Mn or Cu

Fig. 3: Proposed structure of the Schiff Base Fig. 4: Proposed structure of the complexes

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