ChemSearch Journal 7(2): 28 – 33, December, 2016
Publication of Chemical Society of Nigeria, Kano Chapter

Received: 17/10/2016 Accepted: 23/11/2016
http://dx.doi.org/10.4314/csj.v7i2.6

Synthesis, Characterization and Antimicrobial Studies of Mn(II) Complex With N-Salicyl-O-Hydroxyphenyleneiminato Schiff Base Ligand

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ABSTRACT
The complex of Mn(II) with schiff base derived from 2-aminophenol and 2-hydroxybenzaldehyde has been synthesised and characterized by molar conductance, elemental analysis, FT-IR, solubility test and potentiometric studies. The elemental analysis data suggested the stoichiometry to be 1:1 [M:L]. Solubility test carried out in some common solvents showed that it is soluble in methanol, DMSO, acetone and diethylether but insoluble in benzene and ether, while in toluene is slightly soluble and these suggested the polar nature of the complex. The molar conductance measurement of the complex is 2.5 Ω^{-1} cm^2 mol^{-1} which is very low suggesting that the complex is non-electrolyte. Evidence from Infrared spectral study indicated a strong band in the spectra of free ligand occurring at 1600cm^{-1} which assigned to $v_{(C=N)}$. It shifted to lower frequency region 1520cm^{-1} in the complex indicating the involvement of nitrogen atom of azomethine group. The coordination of Schiff base with the metal ion as showed by the appearance of low frequency band at 430cm^{-1} due to metal-oxygen $v_{(M-O)}$ vibration thus confirming participation of oxygen in the coordination. Further coordination of metal to azomethine nitrogen $v_{(M-N)}$ is confirmed by a new band at 580cm^{-1}. The synthesized ligand, and metal complex were screened for its antibacterial activity using gram positive (*Staphylococcus aurous*) and gram negative (*Escherichia coli*) and antifungal activity using *Aspergillum niger* and *Candida albican* as potential antimicrobials and showed moderate activity.

Keywords: Schiff base; Mn(II) complex; Antimicrobial study

INTRODUCTION

Metal complexes of Schiff base have played a vital role in the development of coordination chemistry (Shibuya *et al*., 2008). Various Schiff base complexes have been widely studied because of their antimicrobial, anticancer, analgesic, anti-inflammatory, antifertility, and herbicidal applications (Gangani and Parsania 2007). Chelating ligands containing N, and O donor atoms showed broad biological activity and are of special interest because of the ways in which they are bonded to the metal ions (Thankamony and Mohanan 2007). It is known that existence of metal ions bonded to biologically active compounds may enhance their activities (Raman *et al*., 2007; Halli and Patil 2011; Shivakumar and Halli 2006). Schiff base metal complexes had been widely studied due to their industrial applications (Halli and Patil 2011).

Schiff base are easily prepared by the condensation of aldehydes and amines. Stereogenic centers or other elements of chirality (planes, axes) can be introduced in the synthetic design. Schiff base ligands are able to coordinate many different metals (Osman, 2006). Complexes have been used in catalytic reactions and as models for biological systems (Chen and Martel 1987; Costamagna *et al.*, 1992). During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donors. This may be attributed to their stability, biological activity and potential applications in many fields such as oxidation catalysis, and electrochemistry (Hamada 1997).

Some class of complexes obtained from transition and non-transition metals are active and stereo specific catalysts for oxidation, reduction and hydrolysis and they show biological activity, and other transformations of organic and inorganic chemistry (Ramesh and Sivagamasundari 2003). It is well known that some drugs have higher activity when administered as metal complexes than as free ligands (Ramesh and Sivagamasundari 2003).

The present aim of the work is to synthesize a schiff base derived from 2-hydroxybenzaldehyde and 2-aminophenol and its Mn(II) complex, and study their antibacterial and antifungal activities.

MATERIALS AND METHODS.

All the reagents used in this study were of the analytical grade, purchased from Sigma Aldrich and were used without further purification.

Elemental analysis of the metal complex was carried out using precipitation gravimetric analysis. Melting point (MP) or decomposition temperature was determined on a Gallenkamp apparatus AA3235. pH measurements were performed using a Jenway pH meter model 3320. Molar conductance measurement was carried out using Jenway conductivity meter model 4010. Infra-red spectral analyses were recorded using Perkin Elmer spectrum 100Fourier transform IR spectrometer within the range of 400- 4000cm^{-1}. The *in vitro* antimicrobial activities were studied using disc diffusion method, the two pathogenic bacteria viz *Escherichia coli* and *Staphylococcus aurous* and two fungi *Aspergillum niger* and *Candida albican* were obtained from Microbiology unit of Department of Biological Science Bayero University Kano Nigeria.

Synthesis of Schiff base

Schiff base was prepared by mixing 1.7g of 2-hydroxybenzaldehyde in 20cm^3 absolute ethanol and 1.5g of 2-aminophenol in 30cm^3 absolute ethanol. The solution was reduced to one-half of its original volume by heating and then cooled in an ice-bath resulting in the formation of orange polycrystalline product. The product was then washed thoroughly with hot ethanol and recrystallized with same solvent and dried in vacuum desiccators over phosphorus pentoxide for two days (Saidul *et al.*, 2001).

Synthesis of the complex

A 25cm^3 of ethanolic solution of $MnCl_2.4H_2O$ was added to 30cm^3 of ethanolic solution of the prepared Schiff base. The resulting mixture was boiled on a water bath for 5 min and cooled. The precipitate that formed was separated from the solvent, washed several times using hot ethanol and recrystallized with ethanol and dried in desiccators over P_4O_{10} for two days. (Saidul *et al.* 2001).

Estimation of Manganese in the Complex

The estimation of Mn(II) in the complex was carried out by precipitation gravimetric method as reported by Vogel (1972) and the product obtained was dried in an oven at 110^{0}C to constant weight (Vogel, 1972).

Microbial activity

The antimicrobial activities of the ligand and its metal complex in dimethylsulfoxide (DMSO) were performed *in vitro* by disc diffusion method. The ligand and the complex were dissolved separately in dimethylsulfoxide to produce three different concentrations (1000µg, 2000µg and 3000µg) per disc, which were placed on the surface of the culture and incubated at 37^{o}C for two days. The diameter of the zone of inhibition produced by the ligand and complex were compared with that of the referenced drugs (Augumentin) for bacteria standard and (Ketoconozole) for fungal standard (Ramon *et al.*, 2003; Yeamin *et al.*, 2003).

Determination of Dissociation Constant of the Schiff Base

To a 400cm^3 beaker 90cm^3 of distilled water was added followed by 100cm^3 of 0.2moldm^{-3} KNO_3, 10cm^3 of 0.4moldm^{-3} solution of schiff base and solution of NaOH (0.48moldm^{-3}) was added gradually and the corresponding pH value was taken after each addition. The acid dissociation constant pKa of the Schiff base was also calculated. (Gregory *et al.*, 1978)

RESULTS AND DISCUSSION.

The ligand has an orange colour with 81.3% yield and melting point of 96^{0}C. The interaction of prepared schiff base and manganese (II) chloride gave N-Salicyl-O-hydroxyphenyleneiminatomanganese(II) complex. The complex has a brown colour with 70.94% yield and decomposition temperature of 135^{0}C.

Table 1: Physical characteristics and percentage composition.

Compound	Colour	% yield	Melting point(^{0}C)	Decomposition Temp. (^{0}C)	Percentage composition		
					Mn(%)	Ligand(%)	H_2O(%)
Ligand	Orange	81.38	96	-	-	94.7	-
[Mn(L)].2H_2O	Brown	70.94	-	135	16.78	77.72	5.50

Table 2: Solubility test.

Compound	Methanol	Benzene	Ether	Toluene	Acetone	DMSO	Diethyl ether
Ligand	S	IS	IS	SS	S	S	S
[Mn(L)].2H_2O	S	IS	IS	S	S	S	S

Key: S = Soluble, IS = Insoluble, SS= Slightly Soluble and L=Ligand.

Table 3: IR Spectral data(cm^{-1}) of ligand and its Mn(II) complex.

Compound	$v_{(0H)}$ cm^{-1}	$v_{(C=N)}$ cm^{-1}	$v_{(M-O)}$ cm^{-1}	$v_{(M-N)}$ cm^{-1}
Schiff base	3510	1600	-	-
[Mn(L)].2H_2O	3540	1520	430	580

Table 4: Conductance measurement (10^{-3}M), Stability constant and Gibb's free energy.

Compound	Electrical conductance (Ω^{-1})	Molar conductance (Ω^{-1} cm^2 mol^{-1})	Stability constant	Gibb's free energy ($KJmol^{-1}$)
$[Mn(L)].2H_2O$	2.46 x 10^{-6}	2.5	1.4454 x 10^{10}	-5.7933 x 10^{-1}

Table 5: Antibacterial activities of the investigated ligand and its complex.

Compound	*Escherichia coli*: zone of inhibition (mm)			*Staphylococcus aureus*: zone of inhibition (mm)		
	1000μgml^{-1}	2000μgml^{-1}	3000μgml^{-1}	1000μgml^{-1}	2000μgml^{-1}	3000μgml^{-1}
Schiff base	-	-	5	5	10	12
$[Mn(L)].2H_2O$	14	15	16	-	13	15
Augmentin	17	18	20	15	16	18

Table 6: Antifungal activities of the investigated ligand and its complex.

Compound	*Aspergillus niger:* zone of inhibition (mm)			*Candida albican:* zone of inhibition (mm)		
	1000μgml^{-1}	2000μgml^{-1}	3000μgml^{-1}	1000μgml^{-1}	2000μgml^{-1}	3000μgml^{-1}
Schiff base	-	-	9	-	-	-
$[Mn(L)]. 2H_2O$	6	9	11	-	10	10
Ketoconozole	12	15	19	11	14	17

Table 7: Dissociation Constant (pka) of the Schiff Base

S/N	**Volume of NaOH (cm^3)**	pH	**[H^+]**	**[OH^-]**	**[Na^+]**	**A_{tot}**	pKa
1	0.5	9.85	9.4515x10^{-11}	7.7625x10^{-5}	1.1970x10^{-3}	1.9950x10^{-2}	11.2504
2	1.0	9.87	9.0261x10^{-11}	8.1283x10^{-5}	2.3881x10^{-3}	1.9900x10^{-2}	10.9268
3	1.5	9.91	8.2319x10^{-11}	8.9125x10^{-3}	3.5732x10^{-3}	1.9851x10^{-2}	10.7564
4	2.0	9.98	7.0065x10^{-11}	1.0471x10^{-4}	4.7525x10^{-3}	1.9802x10^{-2}	10.6678
5	2.5	10.05	5.9635x10^{-11}	1.2303x10^{-4}	5.9259x10^{-3}	1.9753x10^{-2}	10.6054
6	3.0	10.11	5.1940x10^{-11}	1.4125x10^{-4}	7.0936x10^{-3}	1.9704x10^{-2}	10.5476
7	3.5	10.14	4.8473x10^{-11}	1.5136x10^{-4}	8.2555x10^{-3}	1.9656x10^{-2}	10.4684
8	4.0	10.19	4.3202x10^{-11}	1.6982x10^{-4}	9.4118x10^{-3}	1.9608x10^{-2}	10.4143
9	4.5	10.26	3.6771x10^{-11}	1.9953x10^{-4}	1.1707x10^{-2}	1.9512x10^{-2}	10.4143
10	5.0	10.31	3.2772x10^{-11}	2.2307x10^{-4}	1.1707x10^{-2}	1.9512x10^{-2}	10.3322
11	5.5	10.38	2.7893x10^{-11}	2.6303x10^{-4}	1.2847x10^{-2}	1.9512x10^{-2}	10.2265
12	6.0	10.43	2.4860x10^{-11}	2.9512x10^{-4}	11.3981x10^{-2}	1.9417x10^{-2}	10.2265
13	6.5	10.47	2.2673x10^{-11}	3.2359x10^{-4}	1.5109x10^{-2}	1.9370x10^{-2}	10.1360
14	7.0	10.51	2.0678x10^{-11}	3.5481x10^{-4}	1.6232x10^{-2}	1.9324x10^{-2}	10.0211
15	7.5	10.54	1.9297x10^{-11}	3.8019x10^{-4}	1.7349x10^{-2}	1.9277x10^{-2}	9.8481
16	8.0	10.56	1.8429x10^{-11}	3.9811x10^{-4}	1.8462x10^{-2}	1.9231x10^{-2}	9.5448
17	8.5	10.59	1.7199x10^{-11}	4.2658x10^{-4}	1.9568x10^{-2}	1.9185x10^{-2}	8.1218

Average Dissociation Constant (pKa) = 10.27

The ligand and metal chelate are colored and stable in air at room temperature. The analytical results of the complex are consistent with the proposed molecular formula and confirmed the formation of 1:1 (M:L) ration in the complex (Table 1). Solubility test (Table 2) carried out on the ligand and its Mn(II) complex in some common solvents showed that, it is soluble in methanol, DMSO, acetone and diethylether but insoluble in benzene and ether, while in toluene is slightly soluble these suggested the polar nature of the complex.

The observed molar conductance values of the synthesized complex (Table 4) in DMSO solvent (1.0 x 10^{-3} mol) is 2.5 Ω^{-1} cm^2 mol^{-1} which is very low suggesting that the complex is non electrolyte (Geary. 1972).. Conductivity measurements are frequently been used in characterization of metal chelate (mode of coordination) within the limit of their solubility. They provide a method of testing the degree of ionization of the complex, the molecular ions that the complex librates in solution (in case of presence of anions outside the coordination sphere) the higher will be its molar conductivity.

The IR spectra of the schiff base and its metal complex are reported in Table 3. Shows that, the IR spectrum of the free ligand have a broad band at 3510cm^{-1} which can be assigned to phenolic OH group. A shift of frequency in the spectra of the complex indicates coordination through metal atom. The band appearing at 1600cm^{-1} is due to $v_{(C=N)}$ of azomethine group of the free ligand. This band was shifted to lower frequency (1520cm^{-1}) on complex formation. This shift is due to coordination of azomethine nitrogen to the central metal ion. The sharp band at 3540cm^{-1} for schiff based complex is due to $v_{(O-H)}$ stretching vibration, indicating the presence of coordinated water (Byeog-Goo *et al*., 1996). The appearance of the two new band at 430 and 580cm^{-1} in the metal chelates were tentatively assigned to the $\nu_{(M-O)}$ and $\nu_{(M-N)}$ vibrations, respectively (Saleem *et al*., 2003). The stability constants of the Mn(II) complex determine is 1.4454 x 10^{10} and the corresponding change in Gibb's free energy is -5.7933 x 10^{-1} $KJmol^{-1}$ (Table 4).

The synthesized Schiff base and the complex showed moderate to good microbial activity against the organisms tested. In case of bacterial strains *E. coli* showed least activity in the Schiff base and good activity in complex (Table 5) whereas *S. aureus* showed moderate to good activity in both Schiff base and complex compared to the reference drug (Augumentin), this is probably due to the greater lipophilic nature of complexes. Such increased activity of the metal chelates can be father explained on the basis of Overtone's concept and Tweedy's chelation theory (Tweedy 1964). On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charge of the metal ion with donor group (Kralova *et al.,* 2000, Parekh *et al.,* 2005) further, it increases the delocalization of π electrons over the whole chelate ring and enhances the penetration of the complexes into lipid membrane and those block the metal binding sites on enzymes of microorganisms (Vaghasia *et al.*, 2004).

Antifungal strains, *A. Niger* has zone of inhibition ranging between 6-11mm with the metal complex having higher zone of inhibition more than the derived Schiff base (Table 6). In case of *C. Albicans*, the effective antifungal activity was not observed against the schiff base, whereas the complex showed moderate activity compared to the reference drug (Ketoconozole). Thus, it can be said that, complexation or chelation increases antimicrobial activity as explained by Overton's concept and Tweedy's chelation theory. The mode of action of the compounds may involve formation of a hydrogen bond through the azomethine group with the active centers of the cell constituents, resulting in an interference with normal cell process (Dharamraj *et al.,* 2001).

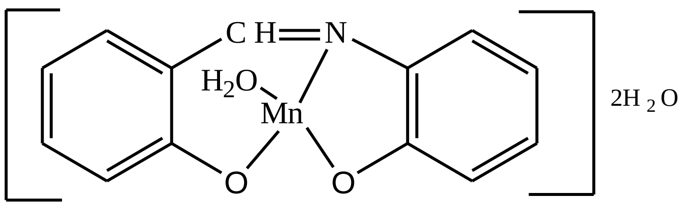

Figure 1: Proposed molecular structure of the complex.

CONCLUSION.

The schiff base and its Mn(II) complex have been synthesised. The analytical data show that the metal ligand stoichiometry is 1:1. The complex is non-electrolyte in DMSO solvent. The spectral data show that the ligand act as tridentate, coordinating through nitrogen atom of azomethine, oxygen atom of hydroxyl group of salicylaldehyde and oxygen atom of hydroxyl group of 2-aminophenol. Antimicrobial studies of the complex reveal that they show better activity when compared to that of the schiff base. From the spectral data and other analytical results, the proposed tentative structure of the metal complex is given as in Figure 1.

ACKNOWLEDGEMENTS

The Department of Microbiology, Bayero University Kano and Department of Science Laboratory Technology, Kano State Polytechnic are hereby acknowledged for their kind contribution and support.

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