ChemSearch Journal 6(2): 35 – 41, December, 2015
Publication of Chemical Society of Nigeria, Kano Chapter

Received: 06/10/2015 Accepted: 08/12/2015
http://dx.doi.org/10.4314/csj.v6i2.7

Synthesis, Characterization, Antimicrobial Activity and Antioxidant Studies of Metal (II) Complexes of Schiff Base Derived from 2 – Hydroxy - 1- Naphthaldehyde and Hydrazine Monohydrate

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ABSTRACT

Transition metal complexes of Co(II) and Ni(II) with Schiff base ligand (HL) derived from condensation of 2-hydroxy-1-naphthaldehyde and hydrazine monohydrate were successfully synthesized and separated. The Schiff base ligand and the metal (II) complexes prepared were characterized by melting point/decomposition temperature, solubility, conductivity, FT-IR spectra and elemental analysis results. IR spectra of the free ligand showed a band at 1655cm^{-1} which is assigned to the (-C=N-) stretching vibration of the azomethine. This band was observed at lower frequencies in the spectra of the metal (II) complexes which indicate complexation. Low (5.00 – 7.00Ohm^{-1}cm^{2}mol^{-1}) conductivity measurement obtained showed that the complexes are non electrolyte while elemental analysis result revealed 1:1 Metal-Schiff base ratio. The in vitro antimicrobial assay showed that the compounds are active against most of the bacterial isolates (*E. coli, Kleb pneumonia, P. mirabilis, P. aeruginosa,* and *S. aureus*) as well as fungal isolates (*C. albicans, F. solani, A.* and *fumigates*). Antioxidant activity of the phenolic Schiff base against 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radicals was ascertained by employing probit analytical method using SPSS 16.0 software. The IC_{50} for the phenolic Schiff base revealed its promising use as an antioxidant.

Keywords: Antioxidant, Complex, DPPH, Schiff base, 2-hydroxy-1-naphthaldehyde

INTRODUCTION

Schiff bases are the condensation products of primary amines with carbonyl compounds **(**Kalaivani *et al*., 2012**)**. They are compounds containing azomethine group (-N = C-). The coordination chemistry of these bases has been considerably enriched due to the synthesis of metal complexes in which the metal is coordinated through sulphur, nitrogen and/or oxygen atom. Metal complexes with ligands containing N, O or S donor have been found to be useful as potential drugs (Chandra *et al.*, 2012 Similarly, phenolic Schiff bases have been found to have various applications in different spheres, ranging from inorganic chemistry, physical chemistry and analytical chemistry to biochemistry and biology (Vicini *et al*., 2003; Tarafder *et al*., 2003). They have also been reported as effective corrosion inhibitors on mild steel such as copper and aluminium (Solmaz *et al*., 2011). They are known for their antibacterial (Khan *et al*., 2009, Chohan *et al*., 2004, Kabeer *et al*., 2001), antifungal (Cohan *et al*., 2006, Guo *et al*., 2007) and anticancer activities (Vicini *et al*., 2003). Due to the presence of phenolic –OH group, Schiff bases are reported as powerful antioxidants and good radical scavengers (Mohammed *et al.*, 2012). In general, the free radical scavenging activity of phenols is mainly attributed to the hydrogen atom transfer of the -OH, -NH and -SH groups (usually attached to aromatic rings) to the free radicals.

MATERIALS AND METHOD

Materials

2-hydroxyl-1-naphthaldehyde and hydrazine monohydrate were obtained from Sigma – Aldrich. Metal (II) chloride (Analar grade) were used to synthesize the complexes. WSR -1B micro processor MPA and Gallen Kemp apparatus were used for melting /decomposition temperature determination for schiff base and metal (II) complexes respectively. Scan Go Micro Plate Reader (Thermo-scientific model) and SPSS 16.0 software was used for the analysis of the data obtained in determining the antioxidant property of the compounds. All solvents were used as purchased without further purification. Elemental analysis was carried out at the centre for catalysis and energy research (PUTRA – CAT) Malaysia.
Bacterial and fungal isolates were obtained and identified at the Department of Microbiology, Faculty of Sciences, Bayero University, Kano.

Nutrient agar (NA) and potato dextrose agar (PDA) were used as bacterial and fungal media respectively.

METHODS

Preparation of the Schiff base

A solution of 0.5mole hydrazine monohydrate in 25cm^3 ethanol was added slowly to a solution of 0.1mole 2-hydroxy-1-naphthaldehyde in 25cm^3 ethanol to form the reaction mixture. The mixture was then refluxed with magnetic stirrer for one hour. The pale yellow crystals obtained on cooling the reaction mixture was filtered, washed successively with ethanol and diethyl ether, recrystallized from methanol and then dried over $CaCl_2$ for one week (Byeong-Goo *et al*., 1996).

Preparation of the Schiff base metal complexes

The two Schiff base metal (II) complexes were prepared by addition of the mixture of the Schiff base (0.1mole) and sodium hydroxide (0.2mole) in hot ethanol (50cm^3) into an aqueous solution of the metal (II) chloride (0.1mole). The mixture was refluxed for 2hours while stirring magnetically. The yellow crystals obtained were washed with ethanol and diethyl ether, recrystallised from methanol and then dried over $CaCl_2$ for a week. (Byeong-Goo *et al*., 1996).

Antibacterial Activity Test

The *in vitro* antibacterial studies of the Schiff base ligand and its Co(II) and Ni(II) complexes were assayed using four gram negative (*E. coli, K. pneumonia, P. aeruginosae* and *P. mirabilis*) and one gram positive (*S. aurius*) bacterial (clinical) isolates by Disc Diffusion Technique (Sharma *et al.*, 2009).

The suspension of each microorganism was rubbed using sterile swab on a solidified nutrient agar in Petri dishes. Three different concentrations (500 µg, 250 µg and 125 µg) per disc of the test compounds in DMSO were prepared and placed on the culture media before incubation at 37^{0}C for 24hrs. Activities were determined by measuring (in mm) the diameter of the zone showing complete inhibition. The results obtained were compared with the activity of Augumentin (30 µg) as a standard antibacterial drug.

Antifungal Activity Test

The *in vitro* antifungal property of the Schiff base ligand and its Co(II) and Ni(II) complexes were assayed using three fungal isolates (*C. albicans, F. solani* and *A. fumigates*) by Disc Diffusion Technique (Sharma *et al*., 2009).

Potato Dextrose Agar was used to prepare the culture media and incubated at room temperature for seven days. The results obtained were compared with the activity of Ketoconozole (600 µg) as a standard antifungal drug.

Antioxidant Activity Test

The free radical scavenging activity of the phenolic Schiff base and its metal (II) complexes against 2,2-diphenyl-1-picrylhydrazyl (DPPH) radicals was studied according to the procedure described by Aktumsek *et al*, 2013 and Lu *et al*., 2013.

Each sample of stock solution (1.0 mg/ml) of the test compounds was diluted through the final concentration; 1000, 500, 250, 125, 62.5, 31,30, 15,63 and 7.81 µg/ml. A total of 50µM DPPH methanolic solution (3.8ml) was added to the sample solution (0.1ml each) and allowed to react at room temperature for 30mins in the dark. The reduction capability of the DPPH radicals was determined from the decrease in its absorbance at 517nm which can be induced by antioxidants.

Inhibition of DPPH radical (I %) was calculated using the relation

$$I\% = \frac{(A_{Blank} - A_{Sample})}{A_{Blank}}$$

Where A_{blank}= Absorbance of the reagents without the test compound

A_{sample}= Absorbance of the reagents with the test compound

The concentration corresponding to the 50% inhibition (IC_{50}) was determined using Probit Analysis by means of SPSS 16.0 software. The IC_{50} values obtained are compared with that of ascorbic acid as a standard antioxidant. Lower IC_{50} value indicates higher activity.

Determination of Number of Coordinated Ligand

The ligand to metal ratio in the complexes was determined using continuous variations method (Job's method) (Agelici, 1971). 0.003moldm-3 solution of each of the metal(II) salt was prepared and absorbance measured from the uv-visible spectrophotometer. A solution mixtures having total volume of 16cm3 in which the mole fraction of each Schiff base is 0.1, 0.4, 0.5, 0.6, 0.8, 0.9 and 1.0. The absorbance of each of these solution mixtures was measured at a λ_{max} of 620nm and 700nm for Co(II) and Ni(II) respectively.

RESULTS AND DISCUSSION

The Schiff base (L) was obtained as yellow crystalline product of condensation of 2-hydroxy-1-naphthaldehyde and hydrazine monohydrate in good yield (Table 1). It was complexed with Nickel (II) chloride and Cobalt (II) chloride to obtain the corresponding Schiff base metal (II) complexes as presented in Table 1.Sharp melting /decomposition temperatures indicated that the compounds are pure

while the magnetic measurement result showed that all the complexes are paramagnetic (Table 1). Conductivity measurement of the complexes revealed the non electrolytic nature of the compounds (Table 1) and 1:1 metal to ligand ratio as supported by the elemental analysis results (Gary 1971).

Solubility test revealed the compounds are soluble in protonic solvents such as methanol and ethanol, insoluble in distilled water, ether, nitrobenzene and carbon tetrachloride while slightly soluble in acetone, acetonitrile and dimethylformamide (Table 2).

Table 1: Physical and Analytical Data of the Schiff base and the Metal (II) Complexes

Compounds	Colour	Yield (%)	Melting Temp. (^{0}C)	Elemental Analysis Calc. (Found) %C	%H	%N	Magnetic (μ_{eff}) Temp. (K)	Molar Conductance(Ohm^{-1}cm^{2}mol^{-1})
Schiff base (L)	Yellow	78	260	77.64 (77.21)	4.70 (4.53)	8.23 (8.11)	—	-
CoL	Light Brown	61	310	66.52 (66.01)	3.53 (3.40)	7.05 (7.00)	3.14	7.00
NiL	Dark Brown	75	278	66.55 (65.99)	3.53 (3.11)	6.97 (6.88)	3.05	5.00

L = N,N'-Bis(2-hydroxy-1-naphthyl)hydrazine

Table 2: Solubility of the Schiff base and the Metal (II) Complexes

Solvents	Schiff base (L)	CoL	NiL
Distilled Water	IS	IS	IS
Methanol	S	S	S
Ethanol	S	S	S
Ether	IS	IS	IS
Acetone	SS	SS	SS
Nitrobenzene	IS	IS	IS
Carbon tetrachloride	IS	IS	IS
Acetonitrile	SS	SS	SS
Dimethylsulfoxide	S	S	S
Dimethylformamide	SS	SS	SS

L = N,N'-Bis(2-hydroxy-1-naphthyl)hydrazine
S = soluble, SS = slightly soluble, IS = insoluble

The IR spectra of the Schiff base and the metal complexes were recorded on Shimadzu 8400S FT-IR spectrophotometer in the range 4000-400cm^{-1}. The spectra of the ligand showed sharp bands at 1655cm^{-1} and 3434 cm^{-1} attributed to v(-HC=N-) and v(-OH) stretching vibrations respectively (Table 3). The 3434 cm^{-1} v(-OH) disappeared in the spectra of the metal (II) complexes indicating deprotonation of the phenolic –OH of the Schiff base (Aliyu and Sani 2011). The v(-HC=N-) vibration in the metal complexes shifted to lower frequencies (1611-1599cm^{-1}) which indicates the formation of coordinate bond between the metal ions and the azomethine nitrogen. Two new bands (532-512 cm^{-1} and 771-721 cm^{-1}) appeared in the far infra red region in the spectra of the complexes, which suggests the formation of M-O and M-N bonds, respectively (Aliyu and Sani 2012).

Table 3: IR Vibration Frequencies of the Schiff base and its Metal (II) Complexes

Compound	ν(OH) cm^{-1}	ν(C=N)cm^{-1}	ν(M-O)cm^{-1}	ν (M-N)cm^{-1}
Schiff base (L)	3434	1655	—	—
CoL	—	1611	532	721
CuL	—	1602	505	743
NiL	—	1599	512	771

L = N,N'-Bis(2-hydroxy-1-naphthyl)hydrazine

The *in vitro* antimicrobial activity of the Schiff base and its Co(II) and Ni(II) complexes were assayed using Disc Diffusion Technique (Sharma et al., 2009). Diameter of the zones of inhibition by the Schiff base and its metal (II) complexes at concentrations of 500, 250 and 125 µg/disc, against the five bacterial and three fungal isolates used are presented in Tables 5 and 6 respectively. The antibacterial activity results (Table 4) revealed that all the test compounds are active against, *S. aurius* at all concentrations, *P. mirabilis*, *E. coli* and *P. aeruginosa* at high concentrations. The results obtained were compared with activity of a standard antibacterial drug (Augumentin), and the test compounds showed potential antibactericidal activity.

The antifungal activity results (Table 5) revealed that all the test compounds are active on the tested fungal isolates namely *C. albicans, F. solani* and *A. fumigates*. These results are compared with that of Ketoconozole as a standard antifungal drug.

The enhanced antimicrobial activity of the metal chelates over their corresponding chelating agent may be explained on the basis of Overtone's concept (Anjaneyula and Rao, 1986), and the Tweedy's chelation theory (Maruvada *et al*., 1994 and Thangadurai *et al*., 2001). According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favors the passage of only lipid-soluble materials due to which, lipophilicity is an important factor which controls the antimicrobial activity. 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 the positive charge of the metal ion with donor groups. Furthermore, it increases the delocalisation of π-electrons over the whole chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity enhances the penetration of the complexes into lipid membranes and thus blocking the various metabolic activities of microorganisms. The higher activity of the metal complexes can be attributed to the involvement of a metal ion in the normal cell processes (Robertson 1995).

Table 4: Sensitivity of Schiff base and Metal (II) Complexes on Bacterial Isolates

Isolates	**Schiff base (L) (µg/disc)**			**CoL (µg/disc)**			**NiL (µg/disc)**		
	500	**250**	**125**	**500**	**250**	**125**	**500**	**250**	**125**
E. coli	07	NZI	NZI	11	09	NZI	14	07	NZI
K. pneumoniae	NZI	NZI	NZI	NZI	NZI	NZI	NZI	NZI	NZI
P. aeruginosa	07	NZI	NZI	10	08	NZI	14	11	08
P. mirabilis	08	07	NZI	11	09	07	09	07	06
S. aureus	10	08	07	14	10	07	12	11	07

L = N,N'-Bis(2-hydroxy-1-naphthyl)hydrazine
KEY: NZI = No Zone of Inhibition

Table 5: Sensitivity of Schiff base and Metal (II) Complexes on the Fungal Isolates

Isolates	Schiff base (L) (µg/disc)			CoL (µg/disc)			NiL (µg/disc)		
	500	250	125	500	250	125	500	250	125
C. albicans	10	07	NZI	14	10	08	13	10	09
F. Solani	07	06	NZI	16	10	07	10	08	06
A. fumigates	12	10	08	14	12	08	15	13	08

L = N,N'-Bis(2-hydroxy-1-naphthyl)hydrazine
KEY**:** NZI = No Zone of Inhibition

The results for the antioxidant activity of the phenolic Schiff base ligand and the metal (II) complexes are presented in Table 6. The IC_{50} values showed that only the ligand possesses radical scavenging activity against DPPH radicals. Ascorbic acid was employed as the standard antioxidant for comparison. The IC_{50} value of the ligand was found to be 2.98 µg/ml whereas that of ascorbic acid was 4.11 µg/ml. The lower concentration value (IC_{50}) of the Schiff base indicates that the phenolic ligand has good antioxidant activity as compared to the Ascorbic acid standard used (El Hassane 2014). The metal complexes showed negative IC_{50} values which indicated the absence of phenolic –OH available for proton donation, and hence void of radical scavenging activity, since negative concentration values are not possible.

Table 6: Probit Concentrations of the Schiff base and the Metal (II) complexes for 50% Inhibition (IC_{50})

Compound	IC_{50} (µg/ml)
Schiff base (L)	2.98
CoL	-3.57
NiL	-5.93
Standard (Ascorbic Acid)	4.11

L = N,N'-Bis(2-hydroxy-1-naphthyl)hydrazine

CONCLUSION

A Schiff base derived from the condensation of 2-hydroxy-1-naphtahldehyde and hydrazine monohydrate as well as its Co(II) and Ni(II) complexes have been synthesized. Antimicrobial activity results indicated that the Schiff base ligand and its metal (II) complexes are promising antibacterial and antifungal agents. There was enhanced antimicrobial activity in the metal (II) complexes than the free ligand has been explained on the basis of chelataion theory. The antioxidant activity results obtained indicated that the metal(II) complexes are void of radical scavenging property as they have negative IC_{50} values. The Schiff base ligand , however, showed good radical scavenging activity with IC_{50} value of 2.98 µg/ml.

The proposed molecular structure of the Schiff base and its metal (II) complexes are presented as Fig. 1 and 2 respectively

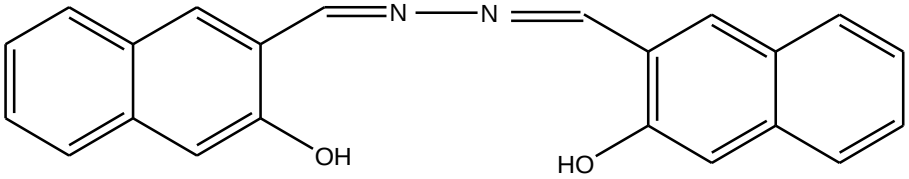
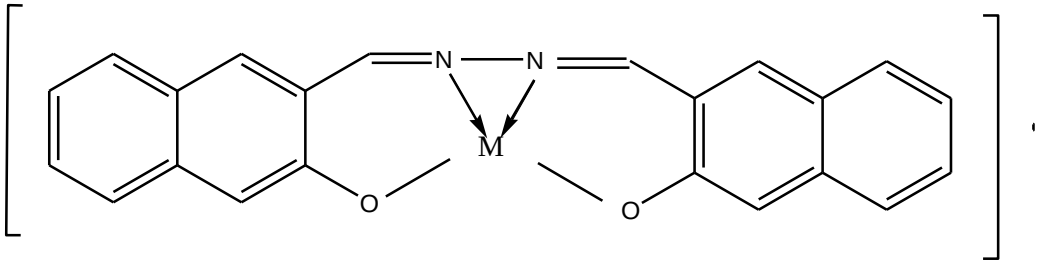


Fig. 1: Proposed Molecular Structure of the Schiff base



where M = Co^{2+} or Ni^{2+}

Fig. 2: Proposed Molecular Structure of Complexes

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