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Synthesis, Physicochemical Characterization and Microbial Activity of N, N' Bis(2 – hydroxyl – 1- Naphthalyl)propylenediiminato Metal (II) Complexes

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Abstract

The ligand, N, N'- bis(2 – hydroxyl – 1 – naphthalyl)propylenediimine was prepared from the reaction of 2-hydroxy- 1 – naphthaldehyde and propylenediamine. The prepared ligand was used to synthesize complexes with Mn(II), Mn(II), Co(II), Ni(II) and Cu(II), respectively. Their solubility, melting/decomposition temperature, molar conductance, elemental analysis, infrared were carried out. Elemental analysis of the complexes for C, N and H revealed 1:1 metal to ligand ratio. The ligand and its divalent metal complexes were screened for their antibacterial activity against *E. Coli, Kleb, proteus* and *Salm. Sp.* as well as *Rhizopus sp.* and *Mucur sp. fungal* isolates. It has been found that all the complexes show different activity on the isolates and that the complexes show higher activity than the free ligand.

Introduction

N, N'- bis(2 – hydroxyl – 1 – naphthalyl)propylenediimine is a Schiff base named after Hugo Schiff (1864). Schiff bases are those compounds containing the azomethine group, -RC=N-. They are usually prepared by the condensation of a primary amine with an active carbonyl compound. The carbonyl functional group can be from an aldehyde or from a ketone. The former gives the aldimines and the latter the ketoimines. The resulting bases can only be effective as coordinating ligands if they bear a functional group, usually the hydroxide group, sufficiently near the site of condensation so that a five or six – membered chelate ring can be formed upon reaction with a metal ion (Pierre, 1987). The family of Schiff bases is important intermediates for the synthesis of some bioactive compounds such as β-lactam (Thomas, 2007). Furthermore, they are reported to show a variety of interesting biological actions including antibacterial (Jarrahpour *et al*., 2004; Bahija *et al*., 2006) and antifungal (Dhakery and Saxena, 2007; Dash *et al*., 1987; Patel and Jejurka, 1994) and catalysts (Nashinaga *et al*., 1998).

A new synthetic procedure for the preparation of some copper (II) complex compounds from condensation of copper (II) acetate and prepared Schiff bases derived from 2-hydroxy-1-naphthaldehyde and some aliphatic diamines was reported, however were not fully characterized (Byeong-Goo *et al*., 1996). This paper presents the synthesis, physicochemical characterization and microbial activity of N, N' bis(-2 – hydroxyl – 1- naphthalyl)propylenediiminato metal (II) complexes.

Experimental

All chemicals and solvents used were of analytical grade (AnalaR or BDH) while propylenediamine and 2-hydroxy-1-naphthaldehyde were obtained from Sigma-Aldrich and were used without further purification. Molar conductance measurements were carried out using Jenway 4010 conductivity meter. Elemental analyses for carbon, nitrogen and hydrogen were carried out at the Micro-analytical Laboratory at the University of Bristol, United Kingdom. Four pathogenic bacteria viz: *Klebsiella sp., Escherchia coli, Proteous sp.* and *Salmonella sp.* and two fungi *Rhizopus sp., Mucor sp.* were collected from Microbiology unit of the Department of Biological Sciences, Bayero University, Kano, Nigeria. Nutrient agar and Potato Dextrose agar were used as bacteriological and fungal media respectively.

Preparation of the Schiff Base

The Schiff base was prepared as reported and then filtered, washed with ethanol and dried over Phosphorus pentoxide for a week (Ahmed and Akhtar, 1983; Byeong-Goo *et al*., 1996).

Preparation of the Metal(II) Schiff Base Complexes

All the N, N' bis(2 – hydroxyl – 1-naphthalyl)propylenediiminato metal (II) complexes were prepared as reported and were separated, washed with ethanol and dried over Phosphorus pentoxide for a week (Ahmed and Akhtar, 1983; Byeong-Goo *et al*., 1996).

Antibacterial and Antifungal Activity Tests

The Schiff base and its divalent metal complexes were dissolved separately in DMSO to have three different concentrations (500µg, 1000µg and 2000µg) per disc. They were placed on the surface of the culture and incubated at 37^{o}C for 24hrs (Ramon *et al*., 2003; Yeamin *et al*., 2003). The in vitro antibacterial activity was carried out by disc diffusion method. The diameter of zone of inhibition produced by the Schiff base and its metal (II) complexes were compared with Augumentin (30µg) and Ketoconozole (600µg) for bacterial and fungal standard respectively.

Results and Discussion

The Schiff base, N, N' bis(2 – hydroxyl – 1-naphthalyl)propylenediimine was prepared as yellow crystalline solid. The percentage yield recorded was 89.17 as shown in Table 1. Solubility test (Table 2) carried out on the ligand in some common solvents showed that, it is soluble in methanol, ethanol and DMSO but insoluble in water, ether and carbon tetrachloromethane while in nitrobenzene and acetonitrile slightly soluble. The N, N' bis(2 – hydroxyl – 1- naphthalyl)propylenediiminato metal (II) complexes prepared are readily soluble in DMSO only. The very low molar conductance values (6 – 11) $Ohm^{-1}cm^{2}mol^{-1}$ of the metal (II) Schiff base complexes in 10^{-3}M DMSO solution, revealed them to be non-electrolytes (Geary, 1971).

The Schiff base and its divalent metal (II) complexes were characterized by infrared analysis (Table 3). The sharp bands at 1631 and 3400 cm^{-1} in the Schiff base are attributable to *ν*(C==N) and *ν*(O—H) stretching vibrations, respectively (Boucher and Faulkner, 1980). The band at 3400 cm^{-1} disappeared due to deprotonation of the hydroxyl group on coordination, the *ν*(C==N) stretching vibration (1610 – 1634) was shifted to lower frequency side on complexation which indicated the involvement of the azomethine nitrogen in coordination. The appearance of the two new bands in the regions 501 – 525 and 730 – 740 cm^{-1} in the metal chelates suggests the formation of M—O and M—N bonds, respectively (Saleen *et al*., 2003).

The result obtained from elemental analysis of the divalent metal complexes (Table 4) to determine percentage of C, N and H established 1:1 metal to Schiff base ratio.

The ligand and its metal (II) complexes have been screened for the antibacterial activity (Tables 5 – 10) against four bacteria, via., *E. Coli, Kleb, Proteus and Salm.* by dissolving them separately in DMSO to have three different concentrations (500µg, 1000µg and 2000µg) per disc. They were placed on the surface of the culture and incubated at 37^{o}C for 24hours. Then in vitro antibacterial activity of the Schiff base and its metal (II) complexes was carried out by disc diffusion method. The diameter of zone of inhibition produced by the Schiff base and its metal (II) complexes was compared with the standard (Plates 1 and 2) (Boucher and Faulkner, 1980; Ramon *et al*., 2003). Similarly, the Schiff base and its divalent metal complexes were screened for antifugal activity (Table 11 – 16) against two fungi, via., *Rhizopus sp. And Mucur sp.* as observed for antibacterial activity. It was found that the inhibition by the metal (II) complexes is more than that by the free ligand as shown in plate 3.

From the results of the analyses carried out on the N, N' bis(2 – hydroxyl – 1-naphthalyl)propylenediiminato metal (II) complexes and the earlier reports on similar work, the general molecular formula below is suggested.

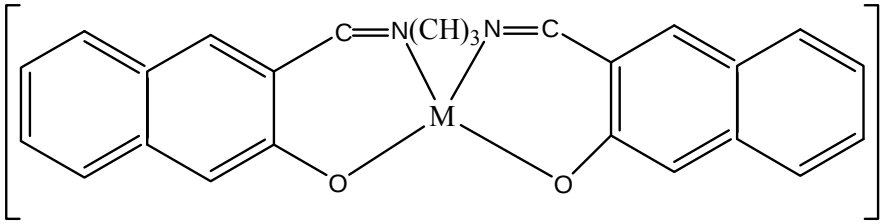

Fig. 1: The proposed general structure of N, N' - bis(2-hydroxy -1- naphthalyl)propylenediiminato metal(II) complexes

Where M = Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)

TABLE 1: Physical properties of the Schiff base and its metal (II) complexes

Ligands/Complexes	Colour	% Yield	Melting Point (^oC)	Decomposition Temp. (^oC)
Ligand	Yellow	89.17	226	-
[MnL]	Green	87.43	-	302
[FeL]	Brown	75.15	-	300
[CoL]	Brown	81.16	-	304
[NiL]	Brown	86.10	-	306
[CuL]	Blue	82.32	-	307

L = N, N` - bis (2-hydroxy-1-naphthyl)propylenediiminato
[MnL] = N, N` - bis (2-hydroxy-1-naphthyl)propylenediiminato manganese (II)
[FeL] = N, N` - bis (2-hydroxy-1-naphthyl)propylenediiminato iron (II)
[CoL] = N, N` - bis (2-hydroxy-1-naphthyl)propylenediiminato cobalt (II)
[NiL] = N, N` - bis (2-hydroxy-1-naphthyl)propylenediiminato nickel (II)
[CuL] = N, N` - bis (2-hydroxy-1-naphthyl)propylenediiminato copper (II)

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

Solvent	Ligand	[MnL]	[FeL]	[CoL]	[NiL]	[CuL]
Water	IS	IS	IS	IS	IS	IS
Methanol	S	S	S	S	S	S
Ethanol	S	S	S	S	S	S
Ether	IS	IS	IS	IS	IS	IS
Acetone	S	S	S	S	S	S
Nitrobenzene	SS	SS	SS	SS	SS	SS
Acetonitrile	SS	SS	SS	SS	SS	SS
Carbon tetrachloride	IS	IS	IS	IS	IS	IS
Dimethylsulphoxide	S	S	S	S	S	S

KEY: S – Soluble
IS – Insoluble
SS – Slightly Soluble

Table 3: IR of the Schiff base and its metal (II) Complexes

Compound	ν (O—H) (cm^{-1})	ν(C==N) (cm^{-1})	ν(M—O) (cm^{-1})	ν(M—N) (cm^{-1})
Ligand	3400	1631	-	-
[MnL]	-	1624	525	733
[FeL]	-	1610	501	730
[CoL]	-	1621	510	736
[NiL]	-	1634	503	736
[CuL]	-	1616	525	740

Table 4: Elemental Analysis Results of the metal(II) Schiff base complexes

Compound	% Calculated (found)		
	C	H	N
Ligand	78.61(78.48)	5.81(5.54)	7.33(7.13)
[MnL]	69.04(68.01)	4.64(4.55)	6.44(6.44)
[FeL]	68.90(67.21)	4.63(4.60)	6.43(6.25)
[CoL]	68.41(66.62)	4.59(4.33)	6.38(5.43)
[NiL]	68.45(67.10)	4.60(4.63)	6.39(5.43)
[CuL]	67.70(65.53)	4.55(4.55)	6.32(6.48)

Table 5: Sensitivity of clinical isolates to the Schiff base (µg)

Isolates	500	1000	2000
E. coli	-	-	-
Kleb	8	9	9
Prot.	7	9	9
Salm.	-	-	-

Table 6: Sensitivity of clinical isolates to manganese(II) Schiff base complex (µg)

Isolates	500	1000	2000
E. coli	-	-	-
Kleb	8	9	9
Prot.	7	9	9
Salm.	-	-	-

Table 7: Sensitivity of clinical isolates to iron(II) Schiff base complex **(µg)**

Isolates	500	1000	2000
E. coli	-	-	-
Kleb	-	-	-
Prot.	9	10	9
Salm.	-	-	-

Table 8: Sensitivity of clinical isolates to copper(II) Schiff base complex **(µg)**

Isolates	500	1000	2000
E. coli	9	11	12
Kleb	8	12	14
Prot.	21	22	23
Salm.	-	-	-

Table 9: Sensitivity of clinical isolates to nickel(II) Schiff base complex (µg)

Isolates	500	1000	2000
E. coli	-	-	-
Kleb	-	-	-
Prot.	-	-	-
Salm.	-	-	-

Table 10: Sensitivity of clinical isolates to copper(II) Schiff base complex (µg)

Isolates	500	1000	2000
E. coli	-	-	-
Kleb	-	-	-
Prot.	-	-	-
Salm.	-	-	-

Table 11: Sensitivity of fungal isolates to Schiff base

Isolates	Standard		Schiff Base	
Conc. **(µg)**	500	500	1000	2000
Rhizopus sp.	8	6	6	8
Mucur sp.	8	6	6	8

Table 12: Sensitivity of fungal isolates to manganese(II) Schiff base complex **(µg)**

Isolates	Standard		Schiff Base	
Conc. **(µg)**	500	500	1000	2000
Rhizopus sp.	7	6	8	8
Mucur sp.	7	6	6	6

Table 13: Sensitivity of fungal isolates to iron(II) Schiff base complex **(µg)**

Isolates	Standard		Schiff Base	
Conc. **(µg)**	500	500	1000	2000
Rhizopus sp.	8	6	7	8
Mucur sp.	8	6	6	13

Table 14: Sensitivity of fungal isolates to cobalt(II) Schiff base complex **(µg)**

Isolates	Standard		Schiff Base	
Conc. **(µg)**	500	500	1000	2000
Rhizopus sp.	7	6	7	8
Mucur sp.	7	6	7	7

Table 15: Sensitivity of fungal isolates to nickel Schiff base complex **(µg)**

Isolates	Standard		Schiff Base	
Conc. **(µg)**	500	500	1000	2000
Rhizopus sp.	7	6	6	6
Mucur sp.	7	6	6	6

Table 16: Sensitivity of fungal isolates to copper(II) Schiff base complex **(µg)**

Isolates	Standard		Schiff Base	
Conc. **(µg)**	500	500	1000	2000
Rhizopus sp.	8	6	6	6
Mucur sp.	8	6	6	6

Plate 1: Antibacterial result against Prot. Sp.

Plate 2: Antibacterial result against the standard (Augumentin)

Plate 3: [FeL] with Rhizopus and Mucor

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