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SYNTHESIS, ANTIBACTERIAL AND ANTIFUNGAL INVESTIGATIONS OF MN (II) COMPLEXES WITH SCHIFF BASES DERIVED FROM 2 – HYDROXY – 1 – NAPHTHALDEHYDE AND SOME ALIPHATIC DIAMINES

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ABSTRACT
Schiff base ligands derived from 2-hydroxy-1-naphthaldehyde and some aliphatic diamines were synthesized and characterized. Each of the ligands was used to form complex with Mn (II). Solubility, elemental analyses and IR spectra were carried evaluated. Elemental analyses of the complexes for C, N and H revealed 1:1 metal to ligand ratio. Antibacterial and antifungal activities were determined. Disc diffusion method was employed for these antimicrobial assays against four pathogenic bacteria (Escherichia coli, Salmonella typhi, Proteus sp. and Klebsiella pneumonae) and two fungi (Mucor sp. and Rhizopus sp.). It was found that the ligands and the complexes showed different activities against the isolates. The complexes showed higher activity than the free ligands.

Keywords: Schiff base, diamine, ligand, complex, isolates, analysis

INTRODUCTION

Addition of an amine to a compound containing a carbonyl functional group aldehyde or ketone, produces an imine, which is also known as a Schiff base. The former gives an aldimine while the latter produces a ketoimine. The resulting Schiff base can be an effective coordinating ligand if it bears an additional group usually a hydroxyl group near the site of condensation. A Schiff base acts as a ligand because it usually contains –N and –O donor atoms (Cotton and Wilkinson, 1972).

The earliest systematic synthetic study of Schiff bases was initiated by Pfeiffer *et al.* (1931). They prepared a variety of complexes derived from salicyldehyde and pyrrole -2- aldehyde. Much work has been reported on transition metal complexes of Schiff bases derived from suitably substituted aromatic carbonyl compounds and a number of amines (Alev *et al*, 2004, Jeong- Geun and Yong – Koo, 1999). However, exhaustive literature search revealed paucity of information on transition metal complexes of aromatic Schiff bases derived from aliphatic diamines and aromatic compounds such as 2-hydroxy-1-naphthaldehyde. One of the available works suggested the formation of N, N`-bis (2-hydroxy-1-naphthyl) ethylenediiminato copper (II) complex during attempted preparation of copper (II) mixed chelates from dibasic Schiff base (Ahmed and Akhtar, 1986).

Chelate compounds obtained from Schiff bases are convenient for the study of change in structure and associated biological activity, since varying the substituents in the metal ring permits variation in the three dimensional structure of the molecule (Eman *et al.*, 2008). It has been demonstrated through several studies that biological activity of chelating compounds is enhanced on chelation with metal ions. Some of the inactive ligands have been found to develop such properties upon chelation (Eman *et al.*, 2008). The antitumor activity of some Schiff bases has been attributed to their ability to chelate with transition metals. Several explanations have been suggested for this enhancement. Generally, it has been observed that certain transition metal complexes have greater activity and less toxic effects than the free ligand (Eman *et al.*, 2008). The azomethine linkage is a significant feature that makes Schiff base ligands interesting candidate for biological activity as well as coordination/chelation with the metal ions (Sari *et al.*, 2003, Cimerman *et al.*, 2000, Spinu and Kriza, 2000). The interaction between metal ions and such biologically active ligands represents an important route in designing new metal-based antibacterial, antifungal and anticancer therapies against different kinds of bacteria, fungi and viruses that are resistant to the conventional drugs.

Schiff base aldehydes have a wide variety of applications in many fields e.g. biological, industrial and analytical (Ibrahim and Sherif, 2007). Schiff bases derived from acetylacetone and p-methoxyaniline showed great activity against some bacteria like *Staphylococus aureus, Bacillus sutilis, Escheriachia coli* and fungi, *Aspergillus niger* (Ramon *et al.*, 2003). They can as well be used as fluorimeric analytical reagents (Ibrahim and Sherif, 2000, Cimerman *et al.*, 2000). Transition metal Schiff base complexes play very vital roles as they are known to possess biological activities such as anticonvulsant, antibacterial, antiviral and antidiabetic (Mimose *et al.*, 1991). Sudo *et al.* (1997) reported that rhodonine derivatives acted as hepatitic C virus (HCV) protease inhibitor. It was reported that transition metal Schiff base complexes could be used as corrosion inhibitors as well as antifungal and antifouling agents (Bhatia *et al.*, 1993).

Moreover, 2-hydroxy-1-naphthaldehyde thiosemicarbazone complexes with Co(II), Ni(II), Zn(II) and Cu(II) were reported to be biomimic enzyme catalysts (Ming *et al.*, 2000). Byeong – Goo *et al.* (1996) reported 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.
However, microbial activity of the Schiff bases and their complexes were not studied, which this paper presents.

MATERIALS AND METHOD

All chemicals and solvents used were of analytical grade (AnalaR or BDH) while 2-hydroxy-1-naphthaldehyde and diamines 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 Ligands

All the ligands were prepared as described by Ahmed and Akhtar (1986), Beong – Goo *et al.* (1996). The ligands formed were then filtered, washed with ethanol and dried over phosphorus pentoxide for a week.

Preparation of the complexes

All the complexes were prepared as described by Ahmed and Akhtar, (1986); Beong – Goo *et al*, (1996). They were separated, washed with ethanol and dried over phosphorus pentoxide for a week.

Antibacterial Activity Test

The ligands and complexes were dissolved separately in Dimethylsulphoxide (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 following the method Bukhari *et al.*, 2005; 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 ligands and complexes were compared with Augumentin (30µg) and Ketoconozole (600µg) for bacterial and fungal standard respectively.

RESULTS AND DISCUSSION

The resulting ligands appeared crystalline solids. The percentage yield recorded was 75.50 – 89.17 as shown in Table 1. Solubility test carried out on the ligands in some common solvents showed that, they were soluble in methanol, ethanol and DMSO but insoluble in water, ether and carbon tetrachloromethane while slightly soluble in nitrobenzene and acetonitrile. The complexes are readily soluble in DMSO only. Molar conductivity values of the complexes in DMSO solution were in the range 9 – 12 $\Omega^{-1}mol^{-1}$ cm^2 confirmed the non-electrolytic nature of the complexes.

All the ligands and complexes were characterized by elemental analyses to determine percentage of C, N and H. The observed and calculated compositions (%) of the elements were in good agreement and supported the one ligand to a metal ion complexation as shown in Table 1 and Fig. 2.

The antibacterial activity test for the ligands and the complexes were determined. The diameter of inhibition zone (mm) was measured for each treatment. The ligands showed minimal activity against the entire organisms (Table 3) with no activity recorded against *Klebsiella pneumonae*. However, *Salmonella typhi*. is resistant to [MnL`] at all the concentrations L` is N, N` - bis (2-hydroxy-1-naphthyl) ethylenediiminato. while [MnL``] resistant at 1000 and 20000 $\mu$g where is L``N, N` - bis (2-hydroxy-1-naphthyl) propylenediiminato . [MnL```] is found to be active at all the concentrations where L```is N, N` - bis (2-hydroxy-1-naphthyl) butylenediiminato. The complexes showed stronger activity on the isolates. Highest zone of 10 mm was recorded on *Protueus sp.* while *E. coli* showed 8 – 10 mm, with no activity on *Kleb.* In the case of [MnL``] *kleb* was resistant to it with some activity between 8 – 15mm. Moreover, [MnL```] showed similar result on the isolates as in the case of [MnL``] as shown in Table 4. All results were better than that obtained with the standard. This showed that the ligands and the complexes were more active than the standard.
Antifungal activities of ligand Schiff bases were studied and results presented in Fig1. The ligand L`` recorded activities in three different concentrations against *Mucor sp*. with no activity on *Rhizopus sp*. while other ligands L`` and L``` recorded some activity at 2000µg only on *Rhizopus* and *Mucor sp*. Antifungal activity for the complexes (Table 6) showed that [MnL`] was active on *Rhizopus sp*. and *Mucor sp*. at 1000µg and 2000µg respectively while [MnL``] gave no zone of inhibition. But for [MnL```], it was active on *Rhizopus. sp.* at all concentrations while *Mucor sp*. produced some activity at 1000µg and 2000µg.The results indicated that the complexes showed more activity than the ligands under similar experimental conditions. This would suggest that the chelation could facilitate the ability of a complex to cross a cell membrane which can be explained by Tweedy's chelation theory (Fehmi *et al.*, 1998). Chelation considerably reduces the polarity of the metal ion mainly because of partial sharing of its positive charge with the donor groups and possible electron delocalization over the whole chelate ring. Such chelation could also enhance the lipophilic character of the central metal atom, which subsequently favors its permeation through the lipid layer of the cell membrane (Tumer *et al.*, 2007)

Table 1: Some Physical Properties of the Ligand and Mn(II) Schiff Base Complexes

Ligands/Complexes	Colour	% Yield	Melting Point (°C)	Decomposition Temp. (°C)
L`	Yellow	78.50	215	-
L``	Yellow	89.17	226	-
L```	Yellow	79.84	263	-
[MnL`]	Green	87.43	-	295
[MnL``]	Green	64.29	-	302
[MnL```]	Green	64.84	-	340

L` = N, N` - bis (2-hydroxy-1-naphthyl) ethylenediiminato
L`` = N, N` - bis (2-hydroxy-1-naphthyl) propylenediiminato
L``` = N, N` - bis (2-hydroxy-1-naphthyl) butyllenediiminato
[MnL`] = N, N` - bis (2-hydroxy-1-naphthyl) ethylenediiminato Manganese (II)
[MnL``] = N, N` - bis (2-hydroxy-1-naphthyl) propylenediiminato Manganese (II)
[MnL```] = N, N` - bis (2-hydroxy-1-naphthyl) butylenediiminato Manganese (II)

Table 2: Elemental Composition of the Ligands and their Complexes

	Percentage Calculated (Found)		
Ligands/Complexes	**C**	**H**	**N**
L`	78.33 (78.15)	5.48 (5.40)	7.61 (7.33)
L``	78.61 (78.48)	5.81 (5.54)	7.33 (7.13)
L```	78.86 (78.81)	6.11 (6.10)	7.07 (7.01)
[MnL`]	68.42 (65.78)	4.31 (4.27)	6.65 (6.29)
[MnL``]	69.04 (6.01)	4.64 (4.55)	6.44 (6.44)
[MnL```]	64.21 (63.21)	4.94 (4.80)	6.24 (6.01)

Table 3: Sensitivity of Clinical Isolates to the Ligands

	L I G A N D S								
	L` (µg)			L`` (µg)			L``` (µg)		
Isolates	**500**	**1000**	**2000**	**500**	**1000**	**2000**	**500**	**1000**	**2000**
E. coli	NZI	NZI	NZI	NZI	NZI	NZI	8	8	9
Kleb	NZI	NZI	NZI	NZI	NZI	NZI	NZI	NZI	NZI
Proteus	9	9	10	NZI	NZI	NZI	NZI	NZI	NZI
Salmonella	10	11	11	9	10	11	10	11	13

NZI = NO ZONE OF INHIBITION = 0.0

Table 4: Sensitivity of Bacterial Pathogens on Mn(II) Schiff base Complexes

	C O M P L E X E S								
	MnL`(µg)			MnL`` (µg)			MnL``` (µg)		
Isolates	**500**	**1000**	**2000**	**500**	**1000**	**2000**	**500**	**1000**	**2000**
E. coli	NZI	NZI	NZI	11	8	NZI	NZI	10	10
Kleb	8	9	9	NZI	NZI	NZI	NZI	NZI	NZI
Proteus	7	9	9	9	NZI	NZI	8	9	9
Salmonella	NZI	NZI	NZI	10	11	11	10	10	10

Table 5: Sensitivity of Fungal Isolates to Ligands

	L I G A N D S											
	L` (µg)				L`` (µg)				L``` (µg)			
Isolates	**500**	**1000**	**2000**	**Ket.**	**500**	**1000**	**2000**	**Ket.**	**500**	**1000**	**2000**	**Ket.**
Rhizopus sp.	NZI	NZI	8	8	NZI	NZI	NZI	7	NZI	NZI	7	8
Mucor sp.	NZI	NZI	8	8	7	7	7	7	NZI	7	8	8

Ket. = Ketoconozole

Table 6: SensitivityTests of Fungal isolates to Cobalt (II) complexes

	C O M P L E X E S											
	MnL` (µg)				MnL`` (µg)				MnL``` (µg)			
Isolates	**500**	**1000**	**2000**	**Ket.**	**500**	**1000**	**2000**	**Ket.**	**500**	**1000**	**2000**	**Ket.**
Rhizopus sp.	NZI	8	8	7	NZI	NZI	NZI	7	15	16	17	8
Mucor sp.	NZI	NZI	8	7	NZI	NZI	NZI	7	NZI	11	12	12

Fig. 1: Antifungal Activity of the complexes against *Rhizopus* and *Mucor*

From the results of the analyses carried out on the complex compounds and the earlier report on similar work, the general molecular formula below is suggested.

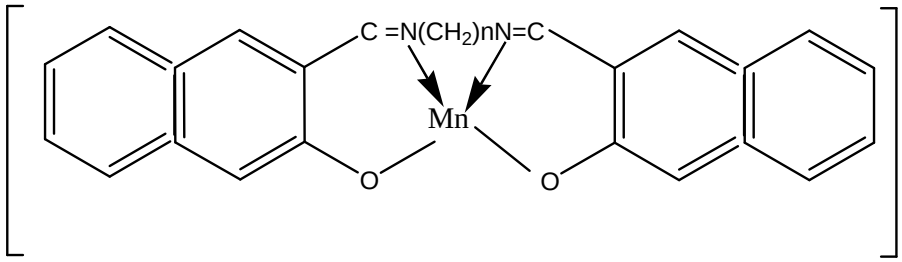

Fig. 2: Proposed General Molecular Structure of the Mn(II) Schiff Base Complex Compounds

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