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Metal Complexes of Mn(II) and Ni(II) with a SCHIFF Base LIGAND: Preparation, Characterisation and Biological Activity

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ABSTRACT: The new Schiff base ligand, sal-leucine (L) has been synthesized by the reaction of ethanolic solution of salicylaldehyde with leucine. The corresponding metal complexes were obtained by refluxing the chlorides of manganese (II) and nickel (II) with the prepared Schiff base in an ethanolic medium. The chemical structures of the synthesized ligand and its corresponding complexes were established by IR, EI-mass spectra, elemental analysis, solubility, molar conductance measurement and melting point/decomposition temperature. The conductivity measurement indicated the complexes to be non electrolyte. The solubility tests carried out showed that the complexes are soluble in most common organic solvents but insoluble in water, indicating that the compounds are not ionic. The antibacterial test of the ligand and the complexes showed that the complexes were found to be more active than the ligand against the organisms used.

KEYWORDS: Schiff base, Leucine, Metal complexes, azomethine, Salicylaldehyde and Antibacterial activity.

I.INTRODUCTION

The field of Schiff base complexes has been fast developing on account of the wide variety of possible structures for the ligands depending upon the aldehydes and amines. Schiff bases contained azomethine group (-RC=N-) and are usually formed by the condensation of a primary amine with an active carbonyl compound. Metal Schiff base complexes have been known since the mid nineteenth and even before the report of general preparation of the Schiff base ligands (Sebastian, 2010). Schiff bases are considered as a very important class of organic compounds, which have wide applications in many biological aspects (Jianning *et al.*, 2007). Transition metal complexes of Schiff bases are one of the most adaptable and thoroughly studied systems. These complexes have also applications in clinical, analytical and industries. They also play important roles in catalysis and organic synthesis (Sharghi and Nasseri, 2003). Studies of a new kind of chemotherapeutic Schiff bases are now attracting the attention of biochemists (Katia *et al.*, 1996). Schiff base metal complexes can now be considered as widely studied subject due to their industrial and biological applications (Mounika *et al.*, 2010). Ben Saber *et al.*, (2005) synthesized Fe(III) and Os(III) complexes with Schiff base derived from unsubstituted salicylaldehyde and 2-amino benzoic acid and characterized them by various methods like IR, NMR, UV etc. Aliyu and Ado (2010), synthesized Ni(II) and Mn(II) complexes with Schiff base derived from salicylaldehyde and 2-amino benzoic acid and characterized it by various methods.

Transition metal Schiff base complexes are used in various fields, such as medicine, agriculture, industries etc. For example, [Co(acac$_2$-en)] in dimethylformamide, pyridine and substituted pyridines proved to be involved in oxygen metabolism (Hanna and Mona, 2001). Transition metal complexes with 1,10 – phenanthroline and 2,2– bipyridine are used in petroleum refining (John *et al.,* 1976). Schiff base formed by the condensation of 1-formyl-2-hydry-3-naphtholic arylamide with O-hydroxyl or O-methoxy aniline complexes of Co(II), Ni(II), Cu(II) and Zn(II) are useful as figments (Gupta *et al.*, 2002). Oxovanadium complexes have been found strongly active, against some type of Leukemia (Dong *et al.*, 2002). Transition metal complexes derived from a number of amino acids have been reported to have biological activity (Zahid *et al.*, 2001). Popora and Berova (1981) reported that copper is good for liver function, its level in blood and urine has influence in pregnancy disorders, nephritis, hepatitis, leprosy, anemia and leukemia in

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children. This work reported the synthesis, characterization and antibacterial activity of Mn(II) and Ni(II) complexes with Schiff base derived from leucine and Salicylaldehyde due to their enormous importance.

II.MATERIALS AND METHODS

All reagents used in this work were obtained from BDH and are of Analar Grade. The reagents were used without further purification. All weighing were carried out using pw184 model electronic weighing balance aeADAM, molar conductance measurement was carried out using EC conductivity meter model 215. Mass spectroscopy was done using electron impact ionization mode DI- 50 unit of Shimadzu GCMS-QP5050A and the elemental analysis of the complexes and the schiff base ligand were carried out using elementar Vario EL III at the Regional Center for Mycology and Biotechnology (RCMB) at Al- Azhar University. While the infrared spectral analysis was recorded using IR MB3000 Infrared Spectrophotometer at the research laboratory of the Energy Research Centre Usmanu Danfodiyo University Sokoto. Melting Point and Decomposition temperatures were obtained using a BI Barnstead Electrothermal melting apparatus model IA9100.

A. Preparation of the Schiff base:

The Schiff base was prepared by the reaction of salicylaldehyde and leucine amino acid in which $25cm^3$ ethanolic solution of salicylaldehyde (1.22g, 0.01mol) was added to the same volume of ethanolic solution of the leucine amino acid (1.31g, 0.01mol). The mixture was then refluxed for about 2 hrs with gradual addition of sodium hydroxide solution (0.4g, 0.01mol) after every 30 minutes. The final mixture was left for about 15 minutes to cool, the product formed was then collected by filtration, washed several times with ethanol and recrystallized from hot ethanol. The product was dried in a dessicator over phosphorous (V) oxide (Azzouz and Ali, 2010).

B. Preparation of Schiff base Metal Complexes:

The metal complexes were prepared by refluxing $25cm^3$ of ethanolic solution of metal (II) salts (0.01mol) (MX_2, where M= Ni (II) and Mn(II) ; X=Cl) with ethanolic solution of the prepared Schiff base (0.01mol) for about 2 hrs. The metal complexes that precipitate out was collected by filtration and then washed repeatedly with hot ethanol until the washing was colourless. The product was then air dried over phosphorus (V) oxide (El-Ajaily, 2006).

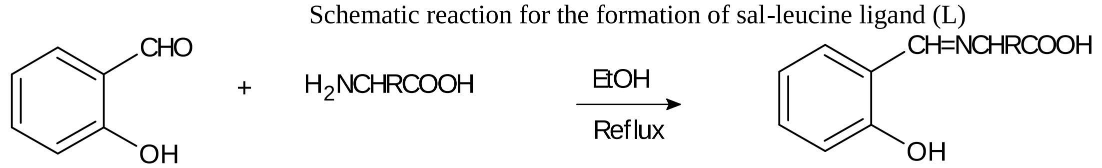
C. Antibacterial Test:

The antibacterial activity test was studied against two gram-positive bacteria *Staphylococcus aureus* and *Bacillus cereus* and two gram-negative bacteria *Escherichia coli* and *Vibrio cholera* respectively. Each of the compounds was dissolved in DMSO at a concentration of 1 mg/ml. Paper discs of Whatman filter paper no. 1 were cut and sterilized in an autoclave. The paper discs were saturated with 10 µl of the compounds dissolved in DMSO solution or DMSO as negative control and was placed aseptically in the Petri dishes containing Nutrient agar media inoculated with the above mentioned four bacteria separately. The petridishes were incubated at 37 °C and the inhibition zones were recorded after 24 hrs of incubation (Mounika *et al.*, 2010).

III.RESULTS AND DISCUSSION

The condensation of salicylaldehyde and leucine amino acid in ethanol yields a single product according to the following reaction:

Schematic reaction for the formation of sal-leucine ligand (L)



Salicylaldehyde Leucine Schiff base (L)

Key: R= $CH_2CH(CH_3)_2$

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The Mn(II) and Ni(II) complexes formed are pale yellow and green different from the color of the ligand (i.e milky), indicating that the colors formed depend on the number of electrons and their transition in the d-orbitals of the metal (II) ions. They have decomposition temperatures between 236°C – 308°C. These high decomposition temperatures revealed the stability of the complex compounds (Table 1). The solubility test (Table 2), carried out showed that the metal (II) complexes formed using sal-leucine are soluble in most organic solvents but insoluble in water, indicating that the compounds are not ionic. The molar conductance measurement showed that the complexes determined in 10^{-3}M DMSO solution are in the range of 0.04 - 0.13 $Ohm^{-1}cm^2mol^{-1}$, which are low indicating that the complexes are non-electrolytic in nature. A band appearing at 3450cm^{-1} assigned to *v*(O-H) in the Schiff base compound (L) was not found in the spectra of the corresponding metal complexes indicating deprotonation and coordination of the hydroxyl oxygen to the metal atom. Again the IR spectral data of the ligand (L) showed a band at 1650cm^{-1}, which is assigned to *v*(C=N) stretching vibration, a feature found in Schiff bases. The shifting of this group to frequency ranging from (1590$cm^{-1}$and 1620cm^{-1}) in the metal complexes when compared to free ligand, suggest that the ligand is coordinated to the respective metal ions through the nitrogen atom of azomethine group. New bands, which are not present in the spectrum of ligand (L) appeared in the spectra of complexes in the range of 540-590 cm^{-1}, corresponding to *v*M-N and 510-570 cm^{-1} to *v*M-O vibrations respectively. The appearance of *v*M-N and *v*M-O vibrations supported the involvement of N and O atoms in complexation with metal ions under investigation. The results of elemental analysis for the composition of C, H and N carried out on the complexes are consistent with similar work in the literature which is an indication of successful synthesis, as shown in the Table 4. The electron ionization (EI) mass spectra of the metal (II) complexes recorded at room temperature are used to compare their stoichiometric compositions. The mass spectra of Mn (II) complex shows a molecular ion peak at m/z =288 and Ni (II) complex at m/z=292 which corresponds to molecular weight of the respective compounds and are listed in Table 5. However, other different molecular ion peaks appeared in the mass spectra of the complexes are attributed to the fragmentation of the metal complex molecule obtained from the rupture of different bonds inside the molecule by successive degradation leading to many more important peaks due to formation of various radicals. The spectra of complexes show molecular ion peaks in good agreement with the structure suggested by elemental analysis earlier reported.

The antibacterial test was carried out against two gram +ve and two gram –ve bacterial isolates namely: *staphylococcus aureus, Bacillus cereus* and *Escherichia coli spp, Vibrio cholera.* The tests carried out on the free schiff base (L) revealed that it has no significant effect on all the bacterial isolates with a diameter of 6mm per 3000µg, 2000µg and 1000µg concentrations. The metal complexes on the other hand showed higher activities against all the bacterial isolates particularly at 3000µg and 2000µg concentrations. The results are presented in Tables 7 & 8.

Table 1: Physical Properties of Sal-leucine ligand (L) and its Metal (II) Complexes

Compound	**% yield**	**Colour**	**Decomposition Temp.(°C)**
[$C_{13}H_{17}NO_3$]	79.1	Yellow	
[$NiC_{13}H_{15}NO_3$]	69.8	Pale blue	236
[$MnC_{13}H_{15}NO_3$]	73.4	Gray brown	308

Table 2: Molar Conductance of L and its Metal (II) Complexes in 10^{-3} DMSO Solution

Compound	**Electrical conductivity ($Ohm^{-1}cm^{-1}$)**	**Molar conductivity ($Ohm^{-1}cm^2mol^{-1}$)**
[$NiC_{13}H_{15}NO_3$]	0.13 x 10^{-6}	0.13
[$MnC_{13}H_{15}NO_3$]	0.04 x 10^{-6}	0.04

Table 3: The Infrared Spectral Data of L and its Metal (II) Complexes.

Compound	**vOH(cm^{-1})**	**vC=N(cm^{-1})**	**vM-N(cm^{-1})**	**vM-O(cm^{-1})**
[$C_{13}H_{17}NO_3$]	3450	1620		
[$NiC_{13}H_{15}NO_3$]		1620	590	570
[$MnC_{13}H_{15}NO_3$]		1590	540	510

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Table 4: Solubility of L and its Metal (II) Complexes in common some organic solvents.

Compound	Water	Ethanol	Acetone	DMSO	Ether	Chloroform	Tetra chloro methane
[$C_{13}H_{17}NO_3$]	-	-	-	-	-	-	-
[$NiC_{13}H_{15}NO_3$]	IS	S	SS	S	SS	SS	IS
[$MnC_{13}H_{15}NO_3$]	IS	SS	S	S	IS	S	IS

Key: **S**= Soluble, **SS**= Slightly soluble, **IS**= Insoluble

Table 5: Elemental Analysis of L and its Metal (II) Complexes

	Calculated/(found)%		
Compound	**C**	**H**	**N**
[$NiC_{13}H_{15}NO_3$]	53.48(53.56)	5.18(5.22)	4.80(4.89)
[$MnC_{13}H_{15}NO_3$]	54.18(54.31)	5.23(5.21)	4.86(4.94)

Table 6: Mass Spectral Data of L and its Metal (II) Complexes.

Compound	Expected m/z	Found m/z	Peak assigned
Ni(II) complex	292.0	292	[M]
Mn(II) complex	288.2	288	[M]

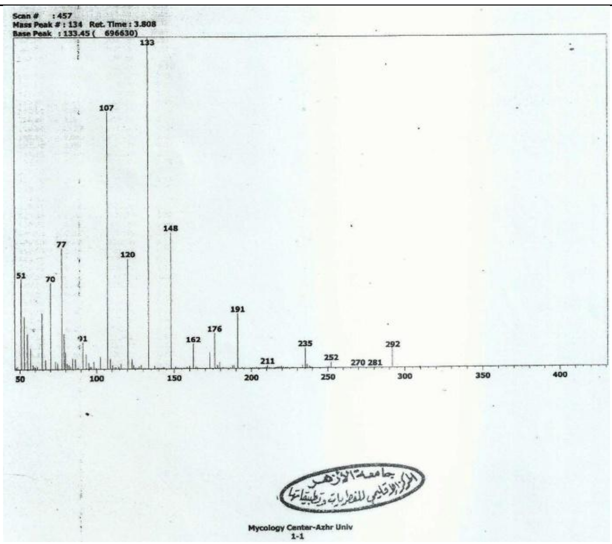

Fig. 1: Mass spectrum of Ni(II) complex

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Table 7: Antibacterial Activity of L and its Metal (II) Complexes on gram -ve bacterial isolates

Compound	Clinical isolate	Zone of inhibition/ concentration (μg)			Clinical isolate	Zone of inhibition/ concentration (μg)			Control (DMSO)
	E. coli spp	**3000**	**2000**	**1000**	***Vibrio cholera***	**3000**	**2000**	**1000**	
Ligand (L^1)		6mm	6mm	6mm		6mm	6mm	6mm	6mm
Ni(II) Complex		11mm	6mm	6mm		11mm	10mm	6mm	6mm
Mn(II) Complex		14mm	9mm	6mm		6mm	6mm	6mm	6mm

Table 8: Antibacterial Activity of L and its Metal (II) Complexes on gram +ve bacterial isolates

Compound	Clinical isolate	Zone of inhibition/ concentration (μg)			Clinical isolate	Zone of inhibition/ concentration (μg)			Control (DMSO)
	Staph spp	**3000**	**2000**	**1000**	***Bacillus cereus***	**3000**	**2000**	**1000**	
Ligand (L^1)		6mm	6mm	6mm		6mm	6mm	6mm	6mm
Ni(II) Complex		8mm	10mm	8mm		8mm	8mm	7mm	6mm
Mn(II) Complex		6mm	14mm	6mm		12mm	8mm	6mm	6mm

From the analyses of the complexes, the general molecular structure has been proposed below:

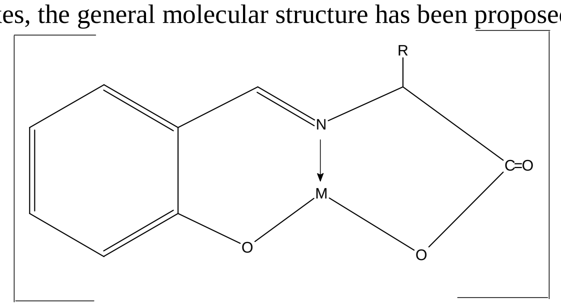

Fig. 2: The molecular structure of the complexes where M is Mn(II) or Ni(II) and R is $CH_2CH(CH_3)_2$

IV.CONCLUSION

The sal-leucine ligand and its metal complexes of Ni(II) and Mn(II) have been structurally characterized. The various tests and analyses with supporting existing literature have confirmed the synthesized complexes. The complexes are all stable due to chelation and the antibacterial studies of the complexes showed that they have positive effect on the bacterial isolates tested on them with better activity when compared to that of the free schiff base ligand.

REFERENCES

[1]Aliyu, H. N. and Ado, I. (2010): studies of Mn (ii) and Ni (ii) complexes with schiff base derived from 2-amino benzoic acid and Salicylaldehyde. *Bayero Journal of Pure and Applied Sciences*, 3(1): 245-249.
[2]Azzouz, A.S.P. and Ali, R.T. (2010): Synthesis of Schiff Bases Derived From Benzaldehyde and Salicylaldehyde With Some Amino Acids by a New Develop Method. *National Journal of Chemistry*, 37: 158-168.
[3]Ben Saber, S.M, Mailub A.A., Hudere S.S, and El-ajaily, M.M (2005), complexation behavior of some Schiff base complexes toward transition metal ions. *Micro Chemical Journal.* 81: 191-194.
[4]Dong, Y., Narla, R.K. and Sudbeck, E. (2002): Synthesis, X-ray structure, and anti-leukemic activity of oxovanadium (IV) complexes, *Journal of Inorganic Biochemistry*, 78: 321-330.
[5]El-Ajaily, M.M., Maihub, A.A., Hudere, S.S. and Ben Saber, S. M. (2006): Nickel (II) chelate of Schiff base derived from 4-dimethyl-amino-benzaldehyde with cysteine. *Asian Journal of Chemistry society*, 18 (4): 2427-2430.
[6]Gupta, S.K., Hitchcock, R.H. and Kushwah, Y.S. (2002): Synthesis, Characterization and Crystal structure of a Ni (ii) shiff base complex derived from acetylacetone and ethylene diamine; *Journal of coord. Chem.*, 55 (12): 1401-1407.

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International Journal of Advanced Research in Science, Engineering and Technology
Vol. 5, Issue 5 , May 2018

[7]Hanna, W.G. and Mona, M. (2001): Synthesis, characterization and antimicrobial activity of Co (II), Ni (II) and Cu (II) with new asymmetrical Schiff base, *Transition metal chemistry*, 26(6): 644-651.
[8]Jianning, L., Bing, Z., Bowan W., Kejun, Z. and Shenli, H. (2007): The Direct Electrochemical Synthesis of Ti(II), Fe(II), Cd(II), Sn(II), and Pb(II) Complexes with N, N_-Bis(Salicylidene)-o-Phenylenediamine. *Turk J Chem.,* 623.
[9]John, J., Alexander, H.P. and Magret, J.S. (1976): *Chemistry with Laboratory*, Harcout Bruce, Johanovich, 63-64.
[10]Katia, B., Simon, L., Anne, R., Gerard, C., Francoise, D. and Bernard, M.M. (1996): Synthesis and Characterization of New Chiral Schiff Base Complexes with Diiminobinaphthyl or Diiminocyclohexyl Moieties as Potential Enantioselective Epoxidation Catalysts, *Inorganic Chemistry*, 35: 387-396.
[11]Mounika, K., Anupama, B., Pragathi, J. and Gyanakumari, C. (2010): Synthesis¸ Characterization and Biological Activity of a Schiff Base Derived from 3-Ethoxy Salicylaldehyde and 2-Amino Benzoic acid and its Transition Metal Complexes. *J. Sci. Res.*, 2 (3): 513-524.
[12]Popora, E. and Berova, S. (1981): "Copper as Coating for Ceramies" *Bulgarius Chemical Abstract*, 84: 184.
[13]Sebastian, M. (2010): Transition Metal Complexes of Quinoxaline based Schiff base Ligands: Synthesis, Characterization and Catalytic Study, Unpublished Ph.D Thesis. Submitted to the Department of Applied Chemistry, Cochin University of Science and Technology, Pp 1-38.
[14]Sharghi, H. and Nasseri, M. A. (2003): Schiff-Base Metal (II) Complexes as New Catalysts in the Efficient, Mild and Regioselective Conversion of 1,2-Epoxyethanes to 2-Hydroxyethyl Thiocyanates with Ammonium Thiocyanate. *Bull. Chem. Soc. Jpn.*, 76: 137-142.
[15]Zahid, H. C., Asifa, M. and Claudiu, T.S. (2001): Transition Metal ion complexes of schiff bases Synthesis, characterization and antibacterial properties. *Metal Based Drugs,* 8: 137-143.