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Synthesis, Characterization and Antifungal Studies on Metal (II) Complexes of Tetradentate Schiff Base Derived from Ethylenediamine and 4-(Benzeneazo) Salicylaldehyde

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ABSTRACT
The tetradentate Schiff base obtained in high yield (86.77%) from condensation of 4-(Benzeneazo) salicylaldehyde and Ethylenediamine was used for the synthesis of metal (II) complexes of Cu, Ni and Zn. Both the tetradentate Schiff base and its metal (II) complexes were characterized on the basis of FTIR, melting point/decomposition temperature, solubility test, and elemental analysis. The ligand melted at 200^{0}C while the complexes decompose at 225^{0}C, 240^{0}C 260^{0}C for Zn(II), Ni(II) and Cu(II) complexes respectively. The solubility test for both Schiff base and the metal (II) complexes. The compounds were found to be soluble in DMF and DMSO and insoluble in water and slightly soluble in nitrobenzene. The results for elemental analysis indicated that there is close relationship between the calculated values and the obtained values using. The result for antifungal studies indicates that the compounds have low activity compared to the control sample.

Keywords: Elemental analysis, Metal complexes, Schiff base, Solubility test

INTRODUCTION

German Chemist Hugo Schiff developed a new form of organic compounds which was named after him in 1864, theses group of compounds; imines are often referred to as Schiff base in his honour. (Cozzi, 2004). In reality, Schiff base ligands are able to stabilize metals in various oxidation states in the periodic table and controlling the activity of metals in a large variety of useful catalytic reactions

Schiff base compounds and their metal complexes have been widely investigated because of their wide range of applications including catalysis, antimicrobial, corrosion inhibitor (Gupta and Sutar, 2007) and (Li, *et al.*, 1999). Moreover, transition metal (II) complexes, which emerged from the derivatives of salicylaldehyde and diamine, gained considerable recognition. This is due to their potentials as catalyst for the insertion of oxygen into an organic substrate.

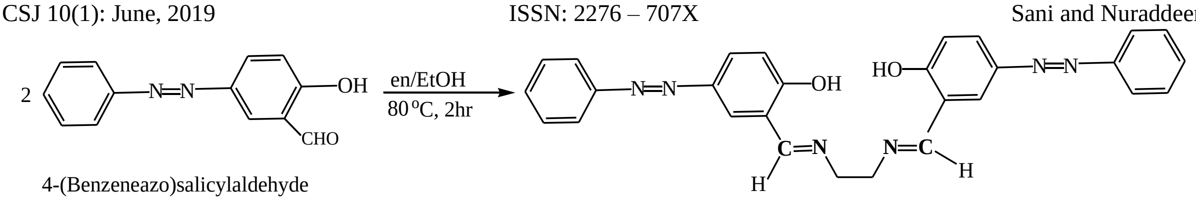
The interest in metal complexes in which the Schiff bases play a role as the ligands are increasing as evidenced by the number of publications appearing annually (approximately 500) (Brodowska and Lodyga-Chruscinska, 2014). This research was aimed to synthesized ligand from 4-benzeneazo salicylaldehyde and ethylenediamine which was subjected to complexation with chlorides of Ni, Cu and Zn in their +2 oxidation states. The compounds were also characterized by FTIR, solubility tests and elemental analysis and finally their antifungal potentials were investigated.

MATERIALS AND METHODS

All chemicals and solvents used in this research were of Analytical grade and were used as purchased without further purification. The glass wares used were washed with detergent and then rinsed with distilled water and dried in an oven at 110^{0}C. Infrared spectral analysis was carried out using Shimadzu FTIR-8400S spectrophotometer in the range of 500- 4000cm^{-1}, Melting point and decomposition temperatures were determined using BUCHI510 melting point machine.

Synthesis of Schiff base

The Schiff base was synthesized by a following a procedure adopted from Ajibade and Ikechuku, (2015) in which ethylenediamine (0.01mol) was slowly added to a solution of 4-(Benzeneazo) Salicylaldehyde (0.02mol) (intermediate) in 30cm^3 ethanol. The mixture was refluxed for two hours, the precipitate obtained was washed several times with ethanol and dried at 50 °C overnight (Scheme 1).

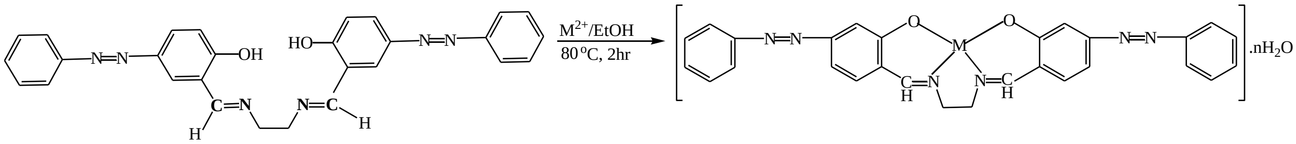


4-(Benzeneazo)salicylaldehyde

Scheme 1: Synthesis of the Schiff base

Synthesis of Metal Complexes

The ethanolic solution of the ligand (0.01mol) was slowly added into ethanolic solution of $NiCl_2$ (0.01mol) and refluxed for two hours at 80°C. The product obtained was washed severally with ethanol and dried at 50°C overnight. The procedure was repeated for $CuCl_2$ and $ZnCl_2$. (Scheme 2)



Where M = Zn (II), Cu (II) and Ni (II) and n= number of mole

Scheme 2: Synthesis of Metal (II) Complexes

RESULTS AND DISCUSSION

The Physical properties of the ligand and its corresponding Metal (II) Complexes were summarized in Table 1 in which the Schiff base prepared was orange yellow crystalline solid with percentage yield of 86.77% and melting point of 200°C which is high indicating high stability. The prepared metal (II) complexes were of different colours and were obtained in very good yields ranging from (77.00 - 97.00) (Table1). The decomposition temperature values 240, 260°C and 225 for Ni (II), Cu (II) and Zn (II) respectively and were found to be much higher than the melting point of the ligand (200°C) thus served as evidence suggesting for metal complexes formation (Fugu *et al*., 2013).

Table1: Physical Properties of the Ligand and its Metal (II) Complexes

Compound	Colour	Melting Point (⁰C)	Decomposition Temperature (⁰C)	Percentage Yield (%)
L	Orange Yellow	200	___	86.77
[Ni L].$2H_2O$	Sandy Brown	___	240	90.78
[CuL].$2H_2O$	Greenish Yellow	___	260	77.00
[ZnL].$2H_2O$	Milky	___	225	97.00

L =Ligand/Tetradentate Schiff base.

The solubility tests were carried out on the ligand in water and some organic solvents. The results showed that it is soluble in methanol, ethanol, Benzene, Acetic acid, acetonitrile, DMF, DMSO and Nitrobenzene but insoluble in water and carbon tetrachloride as shown in Table 2. The solubility test of the complexes showed that all the complexes are soluble in DMSO, insoluble in distilled water and carbon tetrachloride (Table 2)

Table 2: Solubility Test for the Ligand and its Metal (II) Complexes

Solvents	Compounds			
	Ligand	[NiL].$2H_2O$	[CuL].$2H_2$ O	[ZnL] .$2H_2O$
Dis. H_2O	SS	SS	IS	IS
Methanol	SS	S	SS	S
Ethanol	SS	SS	SS	SS
Benzene	SS	S	SS	IS
Nitrobenzene	SS	SS	SS	IS
Acetic Acid	S	SS	SS	S
CCl_4	SS	IS	SS	SS
Acetonitrile	SS	S	SS	IS
DMF	SS	S	S	S
DMSO	S	S	S	S

Key: S = Soluble, SS = Slightly Soluble, IS = Insoluble and L = Ligand/Tetradentate Schiff base.

The FTIR spectra of the ligand (Table 3) showed the characteristic band at 1633cm^{-1} is due to the formation of azomethine group (>C=N-) which is a key evidence for ligand formation. The shifting of this band in the spectra of the complexes indicates the coordination of metal ion through nitrogen atom of the azomethine group (Monika and Sulekh, 2012). The appearance of new bands in the spectra of the metal (II) complexes which were absent in the spectra of the ligand showed that there is coordination between the metal and the lone pair of electrons on the azomethine nitrogen (Hamrit *et al*., 2000) (Table 4). 4-(Benzeneazo salicylaldehyde) and ethylenediamine. The (C-O) group of the Schiff base shows band at 1283cm^{-1},the band shifted toward the lower frequency of the spectra of the complexes indicates coordination through the oxygen atom In the lower frequency region, some new bands have been observed in the complexes between 574-592cm^{-1} that are attributed to (M-N) and 422-481cm^{-1}attributed to (M-O).

Table 3: FTIR Results for the Ligand and its Metal (II) Complexes

Compound	v(C=N) cm^{-1}	v(C-O)cm^{-1}	v(M-N)cm^{-1}	v (M-O) cm^{-1}
L	1633	1283	___	____
[NiL].2H_2O	1626	1242	574	437
[CuL].2H_2O	1629	1240	592	452
[ZnL].2H_2O	1637	1253	559	456

L = Ligand/Tetradentate Schiff base.

The results of the elemental analysis of the Schiff base and divalent metal complexes for H, C and N determined showed that the observed and calculated percentages of the elements are in good agreement with proposed formulation and also the results suggested 1:1 metal-Schiff base ratio in all the complexes. The results are summarized in Table 4.

Table 4: Elemental Analysis for the Ligand and Metal (II) complexes

Formulae	**Found% (Calculated)%**		
	H	**N**	**C**
L	70.46(70.57)	5.91(5.08)	17.84(17.64)
[NiL].2H_2O	58.95(59.08)	4.26(4.60)	15.00(14.76)
[CuL].2H_2O	58.02(58.58)	4.23(4.56)	14.73(14.63)
[ZnL].2H_2O	59.05(58.39)	4.53(4.55)	13.99(14.59)

The antifungal test of the ligand and its metal (II) complexes were carried out against *Aspergillus flavus and Candida albican* using Agar well diffusion technique. The ligand showed no activity on both fungal isolates at 15µg/disc for both the fungal specie and 60µg/disc for *Aspergillus flavus* also [NiL] and [ZnL] are being resisted by *Aspergillus flavus* and *Candida albanica* at 15 µg/disc and 60µg/disc concentrations. The metal complexes were found to be active against all the organisms than the ligand as indicated in Table 5. The enhanced antifungal activity of the metal chelates over their corresponding chelating agent may be explained on the basis of Overtone's concept (Anjaneyulu *et al*., 1986) and the Tweedy's chelation theory. 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 (Chacrabarti 1993). The compounds were found less active compared to the tested standard.

Table 5: Antifungal Profile of the Ligand and Complexes

Compound	Zone of Inhibition (mm)/Concentration (μg/disc)					
	Aspergillus flavus			*Candida Albicon*		
	15	**30**	**60**	**15**	**30**	**60**
Ligand	06	12	06	06	11	12
[NiL].2H_2O	11	13	06	06	14	10
[CuL].2H_2O	10	12	13	10	14	16
[ZnL].2H_2O	06	12		10	14	16
Standard						
(Ketoconozole)	25	30		16	33	18

L =Ligand/Tetradentate Schiff base. NZI =No Zone of Inhibition

CONCLUSION:

The chemistry of Schiff bases and their metal complexes have a very long history and a lot of applications in today's world. The ligand and its metal (II) complexes were prepared and characterized using some analytical and spectroscopic methods. The compounds were found active against fungal sample.

REFERENCES:

Ajibade Peter A. and Ikechukwu P. Ejidike., (2015). Synthesis, Characterization and Biological Studies of Metal (II) Complexes of (3E)-3-[(2-{(E)-[1-(2,4-Dihydroxyphenyl) ethylidene] amino}ethyl)imino]-1-phenylbutan-1-one Schiff Base. *Journal of Chemical* and *Pharmaceutical Science Research* 2:11-12.

Anjaneyulu, Y., Murthy, L. N. and Rao, R. P. (1986). Prepation , characterization and antimicrobial activity studies on some ternary complexes of Cu(II) with acetylacetone and various salicylic acids," Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry,. *Research Journal of Pharmaceutical, Biology and Chemical Sciences*:2:257–272.

Cozzi P., G. (2004): Metal Salts Schiff base Complexes in Catalysis: *Practical Aspects Chemistry Society* 33: 410-421.

Chacrabarti, P. (1993). Synthesis, characterization and antimicrobial studies of Cu (II) complexes with semicarbazone and salicylaldehyde. *Journal of Molecular Biology:* Pp.463.

Fugu, M. B., Ndahi, N.P.. Paul, B.B. and Mustapha, A.N., (2013). "Synthesis, characterization, and antimicrobial studies of some vanillin Schiff base metal(II) complexes" *Journal of Chemical and Pharmaceutical Research* 5(4):22-28

Gupta, K. C. and Sutar, A. K. (2007): Catalytic Activities of Schiff Base Transition Metal Complexes. *Coordination chemistry Review* 252(12-14):1420 - 1450.

Li, S. Chen S.; Ma H.; Yu R. and Liu D. (1999): Corrosion inhibition of copper and some Schiff bases *Corrosion Science* 41:1273.

Monika, T., and Sulekh, C., (2012). Synthesis, Characterization and Biocidal Properties of latinum Metal Complexes Derived from 2,6-diacetylpyridine(bis thiosemicarbazone. *open Journal of Inorganic Chemistry* 3(1):41–48.

Muhammad, A., A., Karamat, M. and Abdul W. (2011). Synthesis, characterization and biological applications of Schiff bases. *International Conference on Chemistry and Chemical Process:* 10: 1-7.

Nief, O.A., (2013). Photostabilization of Poly (Vinyl Chloride) by Some Schiff Base Derived from 2-amino pyridine Chemicals : *Journal of Al-Nahrain University*, 16(4):18–28.

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. Chemical Society Japan* 76: 137-142.