ChemSearch Journal 8(2): 68 – 74, December, 2017
Publication of Chemical Society of Nigeria, Kano Chapter

Received: 27/10/2017 Accepted: 13/12/2017

Synthesis, Characterization and Antimicrobial Studies of Cu(II) and Zn(II) Complexes with the Schiff base N-salicylidene-4-chloroaniline.

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ABSTRACT

Transition Metal Complexes of Cu(II) and Zn(II) with Schiff base N-salicylidene-4-chloroaniline were synthesized and characterized by solubility test, infrared spectra, conductivity measurement, magnetic susceptibility, metal-ligand ratio determination, and antimicrobial activity. The low molar conductance values range (16.-27Ohm^{-1}cm^{2}mol^{-1}) indicated that all the complexes are non-electrolytes. The magnetic susceptibility revealed that the Cu(II) complex is paramagnetic while Zn(II) complex is diamagnetic. The metal-ligand ratio was found to be 1:2 in all the complexes. The infrared spectra suggested that the Schiff base behaves as a bidentate ligand. The Schiff base and its metal complexes were tested for antibacterial activity using *Staphylococcus aureus and Escherichia coli* and fungal activity using *Aspergillus flavus and Mucor species*. The results of the tests indicated moderate antimicrobial activity against the tested organism when compared with the standards (Ciprofloxacin and Ketoconazole), and this activity increases by increasing concentration. The Metal Complexes showed higher activity than free Ligand due to chelation.

Keywords: Salicylaldehyde, 4-chloroaniline, Schiff base, Complexes, antimicrobial activity.

INTRODUCTION

The chemistry of carbon-nitrogen double bond plays a vital role in the reactivity of the Schiff base. (Devesh *et al.*, 2014). Schiff bases are the condensation products of an amine and carbonyl compounds, and are important class of ligand that coordinate to metal ions via azomethine nitrogen. (Chaudhary, 2013). Schiff base is a ligand that contains carbon- nitrogen double bond in which the nitrogen atom is connected to an aryl group or alkyl group but not hydrogen. The carbonyl group of the aldehyde gives aldimines while that of Ketone gives ketoimines, and these provided binding site for the metal ions through nonbonding electrons of the nitrogen. They also have many other hetero-elements like Oxygen and Sulphur which provided binding sites through nonbonding electrons. (Aliyu and Zayyan, 2013)

Schiff base compounds represent one of the most employed classes of ligand in coordination chemistry due to convenient synthetic preparation and versatility. These aspects influence their ability to form stable complexes with large number of transition metal ions (Ignat, 2012*)*. They have been widely studied because of their industrial and biological applications (Tariq, 2010). They are also useful in catalysis and in medicine as antibiotics and antitumor agents. (Achut *et al.*, 2010) Schiff bases are used as intermediate for the synthesis of amino acid or as ligand for preparation of metal complexes having series of different structures (Trangadia, 2006).

Schiff base metal complexes play a significant role in the development of chelation chemistry. The chelation makes these compounds effective and stereo specific catalyst for oxidation, reduction and hydrolysis, and they also show biological activity and other transformation of organic and inorganic chemistry. (Kawkab, 2012)

Transition metal complexes with Schiff base as a ligand have been amongst the widely studied coordination compound in the past few years, since they are found to be widely applicable in many fields. (Dhivya, 2012) It is well known that some drugs have higher activity when administered as metal complexes than as a free ligand, and they have potential applications in many fields such as antibacterial, antiviral, anticancer drugs and electrochemistry. (Kawkab, 2010)

Schiff base metal complexes have important application in medicinal chemistry. Medical science demands such types of drugs which are more potent, biologically active, easily absorbable and nontoxic, and show fast action for treatment of diseases. Extensive studies revealed that chelation makes the complex more stable and biologically more active in the presence of bio-metal. Metal ions fix the complexes at the specific site of the proteins and enzymes of the host and show their potentiality (Chaudhary, 2013).

EXPERIMENTAL

Apparatus

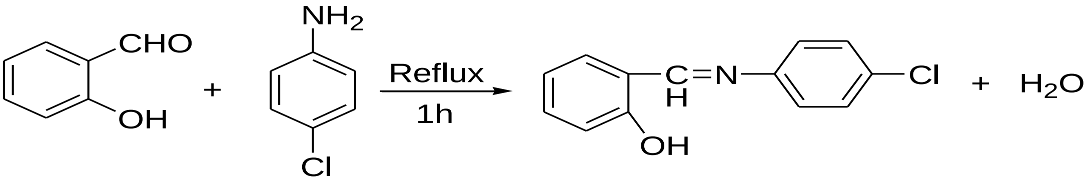
All glass wares used in this work were washed with detergent after soaking in conc. HNO_3 rinsed with distilled water and dried in an oven. Weighing was conducted using electrical Metler balance model AB54. Infrared spectral analysis was recorded using Fourier transform infrared spectrophotometer (FTIR-8400S) range 4000-400cm^{-1}. Electrical conductance was measured using Jenway conductivity meter model 4010 range 20-200µs. Melting point and decomposition temperature were determined using microprocessor melting point apparatus (WRS-IB) and Gallenkamp melting point apparatus. Magnetic susceptibility was determined using magnetic susceptibility balance MKI Sherwood scientific ltd.

Reagents

All chemicals used in this work were Aldrich grade and were used without further purification.

Preparation of Schiff base

The Schiff base was prepared by mixing ethanolic solution of 4-chloroaniline (1.28g, 0.01mol) with that of ethanolic solution of salicylaldehyde (1.22g, 0.01mol). The resulting solution was refluxed for one hour, and then cooled at room temperature; on cooling the bright yellow crystalline solid was formed. Then the solid was filtered, washed with ethanol, dried at room temperature and re-crystallized with ethanol to obtain the required Schiff base (Dhivya *et al.*, 2012).



Salicylaldehyde 4-chloroaniline N-salicylidene-4-chloroanilin

Scheme 1: Preparation of Schiff base

Preparation of Schiff base metal complexes

The metal complexes were prepared according to procedure reported by (Javed *et al.*, 2006). The complexes were obtained by mixing hot ethanolic solution (4.62g, 0.02mol) of Schiff base ligand with hot ethanolic solution of 0.01mol of metal salts. The reaction mixture was refluxed for 3hrs, and then cooled to room temperature, on cooling, colored precipitates were formed, which were filtered, washed with ethanol, dried at room temperature and re-crystallized with ethanol to obtain required complexes. The metal salts used include Cu(II) and Zn(II) salts respectively.

Determination of Melting point of Schiff base and Decomposition Temperature of the metal complexes

The melting point of Schiff base and the decomposition temperature of metal complexes were determined using microprocessor melting point apparatus (WRS-IB) and Gallenkamp melting point apparatus. The results obtained are shown in Table 1. (Aliyu and Zayyan, 2013).

Solubility Test

The solubility test of Schiff base and metal complexes were carried out in water, ethanol, methanol, acetone, chloroform, Dimethylsulfoxide and Dimethylformamide in which 0.2g of each sample was tested in 10ml of each solvent. The results obtained are shown in table 2. (Kawkab, 2010).

Determination of Water of Hydration in the Complexes

The 0.2g of each prepared complexes was placed in a weighted clean glass beaker which was then placed in an oven at 110ºC for 3hrs, until a constant weight was obtained.

The weight loss if any recorded as water of hydration from the constant weight of anhydrous complex; the percentage water of hydration was calculated for each complex using the expression below. (Aliyu and Ado, 2010)

$$\%\ \text{water of hydration} = \frac{\text{weight loss}}{\text{initial weight of sample}} \times 100\%$$

Molar conductance measurements

The 0.001mol of each complex was dissolved in 10ml of Dimethylsulfoxide (DMSO) and the corresponding specific conductance values were recorded using Jenway conductivity meter model 4010. (Moamens, 2013).From the specific conductance value recorded, the molar conductance of each metal complex was calculated using the expression below. The results obtained are shown in Table 3.

$$\text{Molar conductance} = \frac{100 \times \text{specific conductance}}{\text{ionic concentration}}$$

Magnetic Susceptibility Measurement

The magnetic susceptibility of complexes was determined using magnetic susceptibility balance MKI Sherwood science ltd via the expression below. The results obtained are shown in Table.5. (Javed *et al.*, 2006).

$$\text{Xg} = \text{CL}\,\frac{(\text{R} - \text{Ro})}{10^9\text{M}}$$

Estimation of Metals in the Complexes

The 0.2g of each complex was treated with 25cm^3 distilled water and 5cm^3 of nitric acid. The resulting mixture was heated to about dryness, before allowed to cool to room temperature, 25cm^3 of distilled water was then added and the mixture was stirred and filtered. The filtrate which contains the metal ions was collected and diluted to 100cm^3. (Vogel, 1972) The solution was used to determine the metal ions present.

Estimation of Copper in Copper (II) Complex

The percentage composition by weight of copper in complex was calculated using gravimetric factor.

$$\text{G.F} = \frac{\text{Relative atomic weight of cupper}}{\text{Molecular weight of } [\text{CU}(\text{C}_5\ \ \text{H}_5\,)_2(\text{SCN})_2}$$

Estimation of Zinc in Zinc (II) Complex

The percentage composition by weight of zinc in the complexes was calculated using gravimetric factor.

$$\text{G.F} = \frac{\text{Relative atomic weight of Zinc}}{\text{Molecular weight of } [\text{Zn}(\text{C}_5\text{H}_5\text{N})_2]\ (\text{SCN})_2}$$

Determination of Metal to Ligand Ratio

The number of ligand coordinated to the metal ion was determined using Job's method of continuous variation (Angelici, 1977).

The 3mmol aqueous solution of the ligand and the metal salt were prepared. The following ligand to metal salt ratio (ml); 0:10, 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2 and 9:1 were taken from the ligand solution and each of the metal salts solutions respectively. A total volume of 10ml was maintained (in that order) throughout the process and the mole fraction of the ligand was calculated in each mixture. The solutions of the metal salts were scanned (as blank) to find the wavelength of maximum absorption (λ_{max}) for that particular metal ion (Angelici, 1977). The machine was fixed at λ_{max} (in each case) before taking the absorbance values. The absorbance values were extrapolated against mole fraction of the Ligand and the number of coordinated ligand (coordination number) was determined using the relation below:

$$\bar{\text{n}} = \frac{\text{Xi}}{\text{Xi} - 1}$$

Where n= number of coordinated ligand, Xi = ligand mole fraction at maximum absorbance.

Antimicrobial Activity Test

The antimicrobial activity test was studied against bacterial strains, namely *Staphylococcus aureus* (Gram-positive) and *Escherichia coli* (Gram-negative), and also fungal isolates *Aspergillus flavus* and *Mucor species* respectively. The Schiff base ligand and metal complexes were dissolved separately in Dimethylsulfoxide (DMSO) at three different concentrations (15µg, 30µg and 60µg) per disc. The discs were saturated with compounds dissolved in Dimethylsulfoxide (DMSO) and then placed in petridishes containing culture media (nutrient agar for bacteria) and (sabouroud dextrose agar for fungi). The petridishes were incubated at 37^{o}C and the inhibition zone was measured after 24hours for bacterial strain and 48hours for fungal isolates and compared with standards. (Dhivya *et al.*, 2012)

Results Discussion

Table 1: Percentage yield, Colour, Decomposition Temperature and Melting point of the Schiff base and the Complexes.

Compound	Colour	%yield	Decomposition Temp. (°C)	Melting point Temp. (°C)
Schiff base	Bright yellow	78.9	-	115.6
[CuL_2]	Dark green	65.0	207.9	-
[ZnL_2]	White	59.8	209.7	-

L = Ligand

Table 2: Solubility of the Ligand and the Complexes in some common Solvents

Compound	Water	Methanol	Ethanol	Chloroform	Acetone	DMF	DMSO
Schiff base	IS	S	S	S	S	S	S
[CuL_2]	IS	S	SS	S	S	S	S
[ZnL_2]	IS	S	SS	S	S	S	S

L = Ligand, DMSO = Dimethylsulfoxide, DMF = Dimethylformamide, IS = Insoluble,
SS = Slightly soluble, S = Soluble

Table 3: IR Spectra of the Schiff base and Complexes

Compound	V(C=N) cm^{-1}	V(M-O) cm^{-1}	V(M-N) cm^{-1}	V(O-H) cm^{-1}
Schiff base	1609	-	-	3408
[CuL_2]	1601	583	408	-
[ZnL_2]	1598	502	388	

Key: L= Ligand

Table 4: Conductivity Measurement of Complexes in DMSO

Complex	Concentration Moldm^{-3}	Specific Conductance Ohm^{-1} cm^{-1}	Molar Conductance Ohm^{-1} cm^{2} mol^{-1}
[CuL_2]	1.0×10^{-3}	27.0×10^{-6}	27.0
[ZnL_2]	1.0×10^{-3}	24.9×10^{-6}	24.9

Key: L= Ligand, DMSO= Dimethylsulfoxide

Table 5: Magnetic Susceptibility of the Complexes

Compound	Xg(gmol^{-1})	Xm(gmol^{-1})	$\mu_{eff\ (BM)}$	Property
[CuL_2]	3.14×10^{-6}	1.7×10^{-3}	1.98	Paramagnetic
[ZnL_2]	-1.62×10^{-6}	-8.5×10^{-3}	-	Diamagnetic

Key: L = Ligand

Table 6: Percentage Composition of the Metal in the complexes using Gravimetric Method

Complex	% metal	%.ligand
[CuL_2]	10.15	89.85
[ZnL_2]	12.6	87.4

Key: L= Ligand

Table 7: Empirical Formula Calculation for Copper Schiff base Complex

	Copper	Schiff base ($C_{13}H_{10}ONCl$)
%Composition	10.15	89.95
Mole = %Composition/Atomic wt or Molecular wt	10.15/63.5 = 0.160	89.95/231.5 = 0.388
Divide through by 0.160	0.160/0.160	0.388/0.160
Mole ratio =	1	2

Key: wt = weight

The same procedure was used to calculate the empirical formula of Zn(II) complex. As shown in table 7.

Table 8: Metal-Ligand ratio using Job's method

Complex	L.mole Frac. At max.Absorbance (Xi)	No. of Coordinate ligand $(\bar{n}) = \frac{Xi}{1-Xi}$
[CuL_2]	0.68	2.1
[ZnL_2]	. 0.70	2.3

L = Ligand, n̄ = Number of coordinated ligand, Xi = Ligand mole fraction

Table 9a: Antibacterial activity of Schiff base and Metal (II) Complexes

Compound	Diameter of Inhibition zone(mm)/concentration						
	S.aureus			*E.coli*			Control
	15µg	**30µg**	**60µg**	**15µg**	**30µg**	**60µg**	**30µg**
Schiff base	06	07	09	07	09	10	
[CuL_2]	08	10	13	09	10	14	Ciprofloxacin 22
[ZnL_2]	09	10	12	09	12	15	

Key: S = *Staphylococcus*, E = *Escherichia*, L = Ligand

Table 9b: Antifungal activity of Schiff base and Metal (II) Complexes

Compound	Diameter of Inhibition zone(mm)/concentration						
	A.flavus			*M.species*			Control
	15µg	**30µg**	**60µg**	**15µg**	**30µg**	**60µg**	**30µg**
Schiff base	08	07	10	06	08	09	
[CuL_2]	09	11	14	09	11	13	Ketoconazole 28
[ZnL_2]	08	10	13	08	19	12	

Key: A = *Aspergillus*, M = *Mucor*, L = Ligand

Discussion

The reaction between 4-chloroaniline and salicylaldehyde yielded Schiff base ligand (N-salicylidene-4-chloroaniline) which is bright yellow crystalline solid with the percentage yield of 78.8% and melting point temperature of 115.6°C. (Table 1) This is in agreement with the colour and closer in melting point reported by Usharani, 2013.

The interaction between Schiff base and metal (II) salt of (copper and zinc) formed complexes with different colours. (Table 1) The colours may be due to charge transfer or nature of the ligand.

The decomposition temperature Cu(II) and Zn(II) complexes fall in the range of 207°C-209.7°C respectively. (Table 1), these temperatures are relatively high indicating the good thermal stability of the complexes due to the formation of large rings.

The Schiff base and its metal complexes are soluble in some common organic solvents such as Dimethylsulfoxide (DMSO), Dimethylformamide (DMF), methanol, acetone and chloroform, slightly soluble in ethanol and insoluble in water. (Table 2) this is in agreement with the solubility of similar complexes reported by Kawkab, 2013.

The values obtained in the spectra of the Schiff base showed a band at 1609cm^{-1} which is assigned to ν (>C=N-) stretching vibration and another band at 3408cm^{-1} which is assigned ν(O-H) stretching vibration (Table 3). The broad band disappeared in the spectra of the metal complexes, indicating deprotonating on coordination to the metal (II) ion. This is closer to the finding reported by Usharani, 2013.

The shifting of the bands of ν(C=N) stretching vibration in the spectra of the metal complexes in the region 1601cm^{-1}-1598cm^{-1} (Table 3) indicated that the complexation has taken place. The new bands appeared in the spectra of the metal complexes appeared within the ranges of 583-502cm^{-1} and 408-388cm^{-1} are assigned to ν(M-O) and ν(M-N) stretching vibration respectively, (Table 3) also indicating the coordination of the Schiff base ligand to the metal(II) ion. This is similar to the report of Dhivya, 2012.

The molar conductance values obtained in (Table 4) ranges from 16-27Ohm^{-1}cm^{2}mol^{-1} indicating non electrolytic nature of the complexes. The values obtained fall within the range of 10-50 Ohm^{-1}cm^{2}mol^{-1} reported by Dhivya *et al*., 2012.

The values obtained from magnetic susceptibility measurement of the Cu(II) complex at room temperature shows that the complex is paramagnetic due to positive values, while Zn(II) complex is diamagnetic due negative value. (Table 5)

The metal-ligand ratio for each complex was determined using gravimetric factor and job's method as 1:2. (Table 7 and 8….) similar to the report of Ignat, 2012

From the empirical formula calculation of Cu(II) complex, the molecular structure [CuL$_2$] was proposed. Similarly the molecular structures of Zn(II) complex was obtained. (Table 7) as reported by Aliyu and Ado, 2011.

The antimicrobial activity of the Schiff base and its metal complexes were tested against bacterial strains *(Staphylococcus aureus and Escherichia coli)* and fungal isolates *(Aspergillus flavus and Mucor species).*The diameter of the inhibition zones were measured and recorded as shown in Table 9a and b. The results of the tests indicated moderate antimicrobial activity against the tested microorganisms when compared with the standards (Ciprofloxacin and Ketoconazole), and this activity increases by increasing concentration. And also the metal complexes showed higher activity than free ligand, due to the effect of metal ions on the normal metabolic function of the cell. The findings are similar to that reported by Achut *et al*., 2010

CONCLUSION

The Schiff base N-salicylidene-4-Chlorroaniline and its corresponding transition metal complexes of Cu(II) and Zn(II) were synthesized and characterized successfully. The molar conductance values range from 16-28.1 ohm^{-1}cm^{2}mol^{-1} indicated the non electrolytic nature of the complexes. The metal-ligand ratio was found to be 1:2 in all the prepared complexes. The Cu(II) complex is paramagnetic while Zn(II) complex is diamagnetic. The Schiff base and its metal complexes are soluble in some organic solvents such as Methanol, Acetone, DMSO and DMF e.t.c. Also the antimicrobial studies against some bacterial strains *Escherichia coli* and *Staphylococcus aureus* and fungal isolates *Aspergillus flavus* and *Mucor species* indicated some level of the activity when compared with the standards.

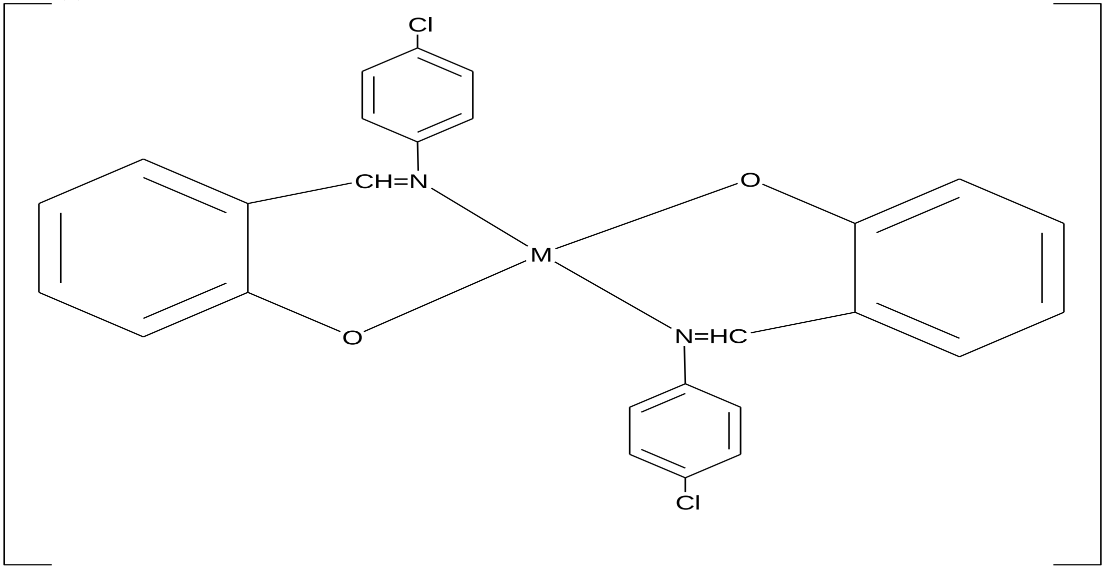


Fig.1: Proposed structure of the metal complexes

Key: M= Cu(II), Zn(II)

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