



SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF MN(II), CO(II) AND NI(II) COMPLEXES WITH SCHIFF BASE DERIVED FROM 4-CHLOROANILINE AND SALICYLALDEHYDE

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ABSTRACT

Transition Metal Complexes of Mn(II), Co(II) and Ni(II) with Schiff base derived from 4-chloroaniline and Salicylaldehyde were synthesized and characterized by conductivity measurement, magnetic susceptibility, infrared spectra, metal-ligand ratio determination and solubility test. The Schiff base and its metal complexes were tested for antibacterial activity against Staphylococcus aureus and Escherichia coli and fungal activity against Aspergillus flavus and Mucor species. The low molar conductance values range ($16-28.10\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) indicated that all the complexes are non electrolytes. The magnetic susceptibility revealed that all the complexes are paramagnetic in nature. 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 antimicrobial studies revealed moderate activity against the tested organism 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 chelation.

Key words: Salicyldehyde, 4-chloroaniline, Mn(II), Co(II), Zn(II) complexes, antimicrobial activity.

INTRODUCTION

Schiff bases are the condensation products of an amine and carbonyl compounds, and are important class of ligand that coordinates to metal ions via azomethine nitrogen. (Bhausahab *et al.*, 2013); Schiff base is a ligand that contained 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 non bonding electrons of the nitrogen. They also have many other hetero-elements like Oxygen and Sulphur which provided binding sites through non bonding electrons (Aliyu and Zayyan, 2013). They are crystalline solids which are feebly basic, but at least some form insoluble salts with strong acids. They also offer a versatile and flexible series of Ligand capable of binding with various metal ions to gives complexes with suitable properties for theoretical or practical applications (Javed, 2006). The Schiff bases are known to be neoplasm inhibitors, antiviral, and antibacterial, anticancer and plant growth regulator (Bhausahab *et al.*, 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 and Kumar, 2006).

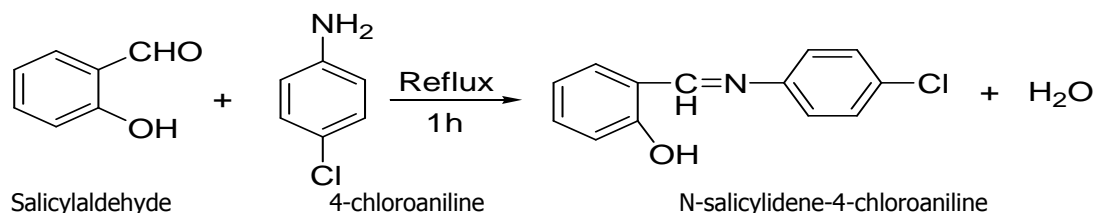
Transition metal complexes with Schiff base as a ligand have been amongst the widely studied coordination compound in the past few years, since they are found to be widely applicable in many fields (Dhivya, *et al.*, 2012). It is well known that some drugs have higher activity when administered as metal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

This research work is focusing on synthesis, characterization and antimicrobial studies of some transition metal complexes with Schiff base derived from 4-chloroaniline and Salicylaldehyde.

General Procedure

All chemicals used in this work were analytical grade and were used without further purification. 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 Melter 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 points 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.



Scheme 1: Preparation of the Schiff base

Preparation of Schiff base metal complexes

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 at room temperature, on cooling, colored precipitates were formed, which were filtered, washed with cold ethanol, dried at room temperature and re-crystallized with ethanol to obtain required complexes. The metal salts used include Mn(II), Co(II) and Ni(II) salts respectively. (Javed *et al.*, 2006)

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 were 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 10 ml of each solvent. The results obtained were shown in table .2 (Kawkab and Al-Ali, 2010)

Determination of Water of Hydration in the Complexes

Exactly 0.2g of each prepared complex was placed in a weighted clean glass beaker which was then placed in an oven at 110°C 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)

$$\% \text{ water of hydration} = \frac{\text{weight loss}}{\text{initial weight of sample}} \times 100\% \quad (1)$$

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 cold ethanol, dried at room temperature and re-crystallized with ethanol to obtain the required Schiff base (Dhivya *et al.*, 2012)

Molar conductance measurements

Exactly 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 and Ibrahim, 2011)

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.

$$\text{Molar conductance} = \frac{100 \times \text{specific conductance}}{\text{ionic concentration}} \quad (11)$$

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, 2006).

$$X_g = CL \frac{(R-R_0)}{10^9 M} \quad (111)$$

Where X_g = Mass susceptibility, C = 1 (Constant), L = Sample length in the tube (whose range should be set between 1.5 to 3.5cm, R = Reading obtained from the sample packed in the tube, R₀ = Reading obtained from preweight empty tube, M = mass of the sample in the tube (measured in gram).

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).

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:

$$\bar{n} = \frac{\sum X_i}{X_i - 1} \dots\dots\dots (iv)$$

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

Antimicrobial Activity Test

The antimicrobial activity test was carried out against two bacterial strains; namely *Staphylococcus aureus* (Gram-positive) and *Escherichia coli* (Gram-negative), and also two 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°C and the inhibition zone was measured after 24 hours for bacterial strain and 48 hours for fungal isolates and compared with standards. (Dhivya *et al.*, 2012)

RESULTS AND 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
[MnL ₂]	Yellow	68.2	203.4	-
[CoL ₂]	Brown	67.8	210.3	-
[NiL ₂]	Light green	72.0	212.0	-

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
[MnL ₂]	IS	S	SS	S	S	S	S
[CoL ₂]	IS	S	SS	S	S	S	S
[NiL ₂]	IS	S	S	S	S	S	S

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

Table.3: Conductivity Measurement of Complexes in DMSO

Complex	Concentration Moldm ⁻³	Specific Conductance Ohm ⁻¹ cm ⁻²	Molar Conductance Ohm ⁻¹ cm ² mol ⁻¹
[MnL ₂]	1.0×10 ⁻³	16.3×10 ⁻⁶	16.3
[CoL ₂]	1.0×10 ⁻³	23.1×10 ⁻⁶	23.1
[NiL ₂]	1.0×10 ⁻³	28.1×10 ⁻⁶	28.1

Key: L= Ligand, DMSO= Dimethylsulfoxide

Table.4: 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	-	-	3404
[MnL ₂]	1597	514	389	-
[CoL ₂]	1612	506	392	-
[NiL ₂]	1588	514	396	-

Key: L= Ligand

Table.5: Magnetic Susceptibility of the Complexes

Complex	Xg(gmol ⁻¹)	Xm(gmol ⁻¹)	µ _{eff} (BM)	Property
[MnL ₂]	6.42×10 ⁻⁶	3.3×10 ⁻³	2.81	Paramagnetic
[CoL ₂]	4.26×10 ⁻⁶	2.2×10 ⁻³	2.29	Paramagnetic
[NiL ₂]	6.87×10 ⁻⁶	3.6×10 ⁻³	2.98	Paramagnetic

Key: L = Ligand

Table.6: Metal-Ligand ratio using Job's method

Complex	L.mole Frac. At max.Absorbance (Xi)	No. of Coordinate ligand ($\bar{n}) = \frac{Xi}{1-Xi}$
[MnL ₂]	0.68	2.1
[CoL ₂]	0.67	2.0
[NiL ₂]	0.69	2.2

Key: L = Ligand, \bar{n} = Number of coordinated ligand, Xi = Ligand mole fraction

Table.7a: Antibacterial activity of Schiff base and Metal (II) Complexes

Compound	Diameter of Inhibition zone(mm)/concentration						
	<i>S.aureus</i>			<i>E.coli</i>			Control
	15µg	30µg	60µg	15µg	30µg	60µg	30µg
Schiff base	06	07	09	07	09	10	Ciprofloxacin 22
[MnL ₂]	10	11	14	08	09	13	
[CoL ₂]	09	10	13	09	11	14	
[NiL ₂]	10	12	15	11	13	16	

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

Table.7b: Antifungal activity of Schiff base and Metal (II) Complexes

Compound	Diameter of Inhibition zone(mm)/concentration						
	<i>A.flavus</i>			<i>M.species</i>			Control
	15µg	30µg	60µg	15µg	30µg	60µg	30µg
Schiff base	08	07	10	06	08	09	Ketoconazole 28
[MnL ₂]	09	11	13	08	10	13	
[CoL ₂]	09	10	12	09	10	12	
[NiL ₂]	11	14	16	09	12	14	

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 *et al.*, (2013).

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

The decomposition temperature Mn(II), Co(II) and Ni(II) Complexes fall in the range of 203.4°C-212.0°C respectively. (Table.1), these temperatures are relatively high indicating the good stability of the complexes due to the formation of large rings, this is closer to the results reported by Aliyu and Zayyan, (2013).

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 and Al-Ali, (2013).

The molar conductance values obtained in (Table.3) ranges from 16-28.10 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ indicating non electrolytic nature of the complexes. The values obtained fall within the range of 10-50 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ reported by Dhivya *et al.*, (2012).

The values obtained in the spectra of the Schiff base showed a band at 1609 cm^{-1} which is assigned to V (>C=N-) stretching vibration and another band at 3408 cm^{-1} which is assigned V(O-H) stretching vibration (Table.4). 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, et al., (2013).

The shifting of the bands of V(C=N) stretching vibration in the spectra of the metal complexes in the region 1588 cm^{-1} -1612 cm^{-1} (Table.4) indicated the complexation has taken place.

The new bands appeared in the spectra of the metal complexes at 506-514 cm^{-1} and 389-396 cm^{-1} which are assigned to V(M-O) and V(M-N) stretching vibration respectively, (Table.4) also indicating the coordination of the Schiff base ligand to the metal(II) ion. This is similar to the report of Dhivya, et al., (2012).

The values obtained from magnetic susceptibility measurement of all the complexes at room temperature shows that all the complexes are paramagnetic. (Table.5)

The metal-ligand ratio for each complex was determined using job's method as 1:2. (Table.6) the finding is similar to the report of Ignat, (2012).

The antimicrobial activity of the Schiff base and its metal complexes were tested against bacterial strains (*Staphylococcus aureus* & *Escherichia coli*) and fungal isolates (*Aspergillus flavus* and *Mucor species*).The diameter of the inhibition zones were measured and recorded as shown in Table 7a 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 chelation. The findings are similar to that reported by Achut *et al.*, (2010)

Conclusion

The Schiff base derived from 4-Chlorroaniline and Salicylaldehyde and its corresponding transition metal complexes of Mn(II), Co(II) and Ni(II) were synthesized and characterized successfully. The molar

conductance values range 16-28.1 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ indicated the non electrolytic nature of the complexes. The metal-ligand ratio was found to be 1:2 in all the prepared complexes. All The complexes are paramagnetic in nature. 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 activity of the Schiff base and its metal complexes 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.

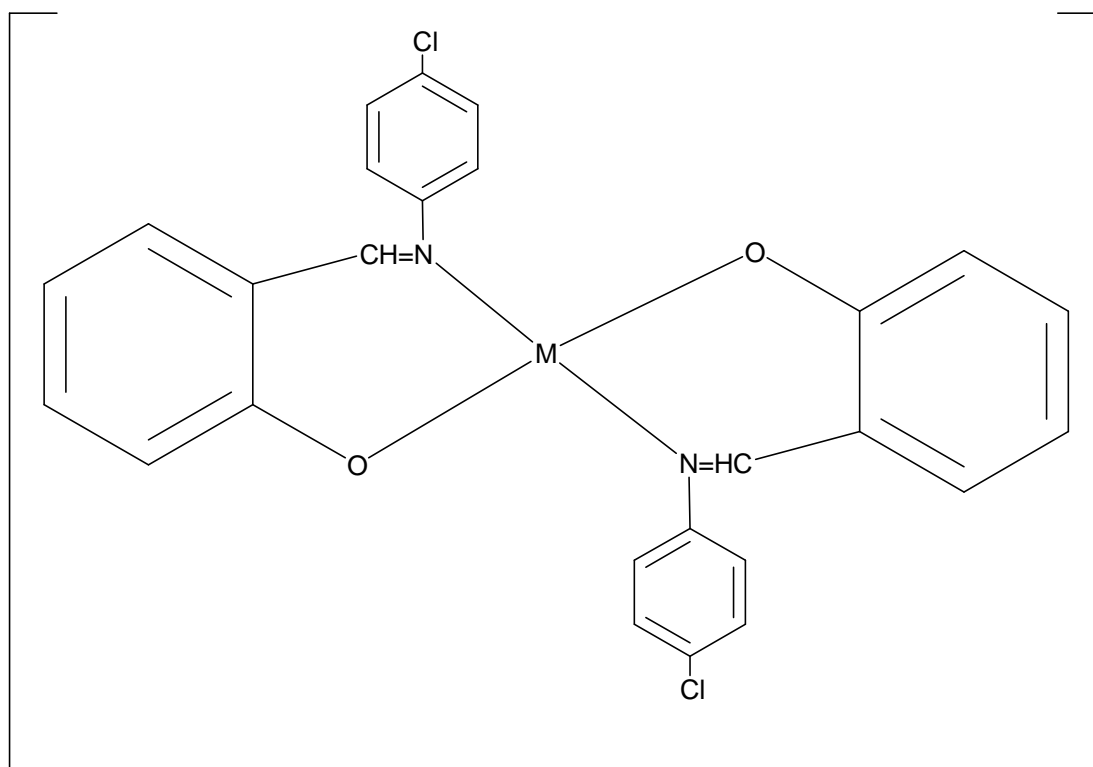


Fig.4.1: Proposed structure of the metal complexes
Key: M= Mn(II), Co(II), Ni(II)

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