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Synthesis, Characterization and Biological activities of Schiff base Ligands and its Metal Complexes.

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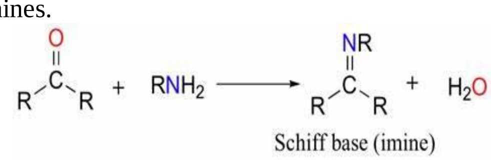
Abstract:

Salicylaldehyde-hexamine Schiff base ligands were synthesized by using conventional ,grinding and green method and characterized by using UV and FTIR spectroscopy. From the synthesized Schiff base ligands, Copper(II) and Nickel(II) complexes were prepared and characterized by FTIR, UV and Cyclic voltammeter. Antibacterial and antioxidant activities of complexes were also studied.

***Keywords**: Schiff base, FTIR, UV, Cyclic voltammeter*

1.Introduction

Schiff bases have been known since 1864 when Hugo Schiff reported the condensation of primary amines with carbonyl compounds. Schiff bases are condensation products of primary amines with carbonyl compounds and they were first reported by Schiff in 1864. The common structural feature of these compounds is the azomethine group with a general formula RHC=N-R1, where R and R1 are alkyl, aryl, cyclo alkyl or heterocyclic groups which may be variously substituted. These compounds are also knows as anils, imines or azomethines.



A large number of Schiff base complexes are characterized by an excellent catalytic activity in a variety of reactions at high temperature (>100ºC) and in the presence of moisture. In recent years, there have been numerous reports of their use in homogeneous and heterogeneous catalysis [1].

Transition mtal complexes with Schiff base as ligand have been amongst the widely studied co-ordination compounds in the past few years, since they are found to be widely applicable in many fields such as biochemical, analytical and antimicrobial fields [2] . It is well known from the literature that much work have been done on the synthesis and characterization of this compounds with Schiff base ligand formed from salicylaldehyde or substituted salicylaldehyde and various aromatic amines[3]. Heterocyclic ring containing sulphur, nitrogen, and oxygen impart special biological activity to these Schiff bases and their metal complexes[4] .In view of the above applications, the present work describes the results of our investigations on the synthesis, structural studies and antibacterial studies of nickel (II) complexes of Schiff base ligand.

2.Materials And Method

Synthesis of Hexammine-Salicylaldehyde derived Schiff base ligands and their metal complexes:

2.1. Synthesis of Salicylaldehyde-Hexamine Schiff base ligands

a)Conventional method:

Salicylaldehyde (3mmol) dissolved in ethanol(25cm^3) is mixed with Hexamine(3mmol) dissolved in ethanol(25cm^3).To this a few drops of acetic acid is added and the mixture is refluxed for (1-1$^{1/2}$) hour. Then it is cooled , filtered off, washed with water and dried under vacuum. The crude product thus obtained is recrystallized from ethanol.

b)Grinding method:

Salicylaldehyde (3mmol) dissolved in 10mL ethanol (25cm^3) is mixed with Hexamine(3mmol) dissolved in 10mL of ethanol (25 cm^3).To this a few drops of citric acid is added and the mixture is grinded for 20minutes.Pestle and Mortar are used for grinding to attain the powdered form. And then cooled water is added .The Precipitate was obtained.

c) Stirring method:

Hexammine(3mmol) in 10mL of water is mixed with Salicylaldehyde (3mmol) and then stirred for 10minutes.The precipitate was obtained.

The yields of the above said three methods were compared and the conventional method was found to be a better method with maximum yield. Since the yields of the other two methods are meger , they were not used for the further studies.

2.2Synthesis of Schiff base transition metal complexes:

The following general procedure was carried out for the preparation of Schiff base complexes with transition metals Cu(ll) and Ni(ll).

2.2.1Synthesis of Schiff base Nickel(ll) complex :

To the 10 ml ethanolic solution add 1 gm of $NiCl_2$ $(H_2O)_6$ complex. Take 2 gm of Schiff base ligand in 10 ml ethanol. Heat the solution. Add solution of Schiff base ligand in solution of $NiCl_2(H_2O)_6$. Few drops of ammonium solution where added until pH 6-8 was obtained. And then the reaction mixture is stirred at room temperature for 1 hour. The obtained product washed were filtered and washed with ethanol. Dried well and the Schiff base metal complex were formed. Greenish yellow colour complex were obtained and the yield is 66.26%.

2.2.2Synthesis of Schiff base Copper(ll) complex:

To the 10 ml ethanolic solution add 1 gm of $CuCl_2(H_2O)_6$ complex. Take 2 gm of Schiff base ligand in 10 ml ethanol. Heat the solution. Add solution of Schiff base ligand in solution of $CuCl_2(H_2O)_6$. Few drops of ammonium solution where added until pH 6-8 was obtained. And then the reaction mixture is stirred at room temperature for 1 hour. The obtained productd washed were filtered and washed with ethanol. Dried well and the Schiff base metal complex were formed. Greenish yellow colour complex were obtained and the yield is 66.26%.

2.3. Antimicrobial activity

2.3.1 Preparation of test micro organisms:

A loopful of the test organism was transferred to already sterilized 10 ml Nutrient agar and incubated overnight at 37^0C for bacteria and 30^0C for fungi. *Aspergillusniger* was cultured as a slant culture in an acidified PDA (Potato Dextrose Agar) media. 25 ml of sterilized Muller-Hinton Agar (MHA) (Hi Media, Mumbai, India) was poured in petriplates and allowed to solidify at room temperature on which the test organisms were inoculated.

2.3.2 Antimicrobial assay

The antimicrobial activity was measured by Disc Diffusion method. The sterile discs were impregnated with the known concentration of the various extracts (15 µl) and standard drugs. The discs were then placed on the already inoculated petridishes containing the inoculum of test microbes in such a way that there is no overlapping of the zones of inhibition. The seeded plates were then incubated at 37^0C for 24 hours and 48 hours for bacteria and fungi respectively. The antimicrobial activity of the animal extracts was recorded as the mean diameter of the resulting inhibition zone of growth measured in millimetres.

From the results, the Active Index (AI) and Proportion Index (PI) were calculated using the following formulae,

$$\text{Active Index (AI)} = \frac{\text{Inhibition zone of the test sample}}{\text{Inhibition zone of the standard}}$$

$$\text{Proportion Index (PI)} = \frac{\text{Number of positive results obtained for individual extract}}{\text{Total number of tests carried out for each extract}}$$

2.4.Antioxidant Activity DPPHradicalscavengingactivity:

The DPPH is a stable free radical and is widely used to assess the radical scavenging activity of antioxidant component. This method is based on the reduction of DPPH in methanol solution in the presence of a hydrogen donating antioxidant due to the formation of the non-radical form DPPH-H [5].

The free radical scavenging activity of all the extracts was evaluated by1,1- diphenyl-2-picryl-hydrazyl (DPPH) according to the previously reported method.Briefly,an0.1mM solution of DPPH in methanol was prepared and1ml of this solution was added to 3ml of the solution of all various solvent extracts at different concentration(50,100,200,400&800µg/ml). The mixtures were shaken vigorously and allowed to stand at room temperature for 30min. Then the absorbance was measured at 517 nm using a UV-VIS spectrophotometer (Genesys10s UV, Thermo Electron Corporation).Ascorbic acid was used as the reference. Lower absorbance values of reaction mixture indicate higher free radical scavenging activity. The capability to scavenging the DPPH radical was calculated by using the following formula.

DPPH scavenging effect(%inhibition)=$\{(A_0–A_1)/A_0)*100\}$

Where, A_0 is the absorbance of the control reaction and A_1 is the absorbance in presence of all of the extract samples and reference .All the tests were performed in triplicates and the results were averaged.

3. Results and Discussion

The characterization results of the synthesized Schiff base ligands and its metal

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complexes are described below by various techniques. The results obtained are discussed in detail as follows

3.1UV Spectral studies:

The UV-Visible spectrum of the synthesized Schiff base and its metal complexes are represented below.

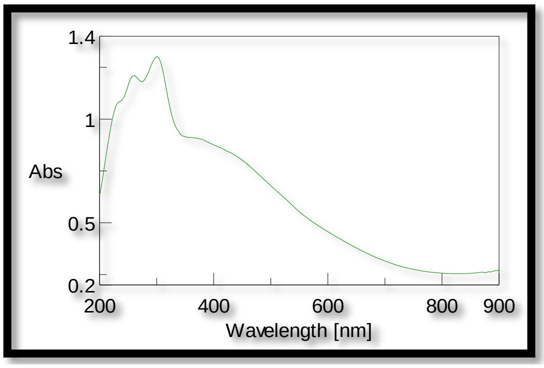

Fig: 1 UV Spectrum of Schiff base Ligand

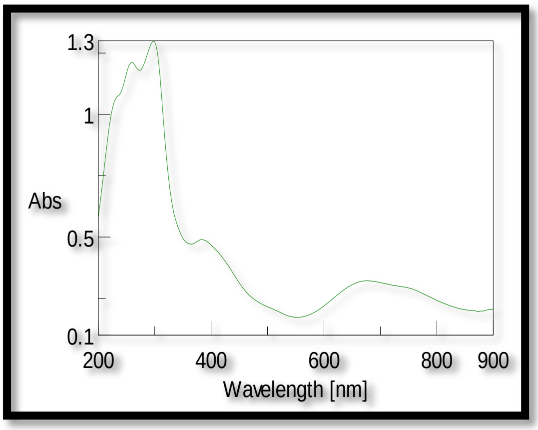

Fig: 2 UV Spectrum of Schiff base Ligand - Nickel complex

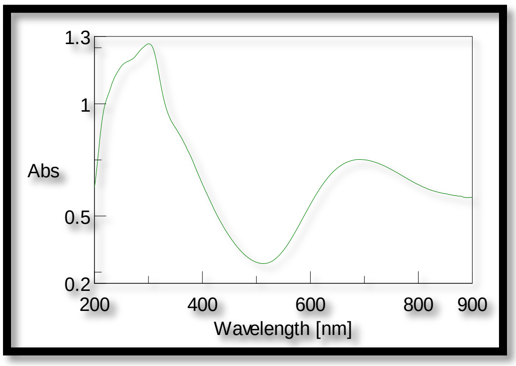

Fig: .3UV Spectrum of Schiff base Ligand – Copper complex

The λ max value of the synthesized Schiff base is found to be around 300 nm. λ max value of the synthesized Schiff base nickel complex is found to be around 310 nm. λ max value of the synthesized Schiff base is found to be around

FT-IR Studies

The IR spectrum was taken using a Nicolet iS5 FT-IR instrument operating at a resolution of 4000-400cm^{-1} in the percent transmittance mode. Generally all the Schiff base ligands give the FT-IR peaks at lower wave number ranging from 400 to 800cm^{-1}.

3.2FTIR Spectra of Schiff Base Ligand:

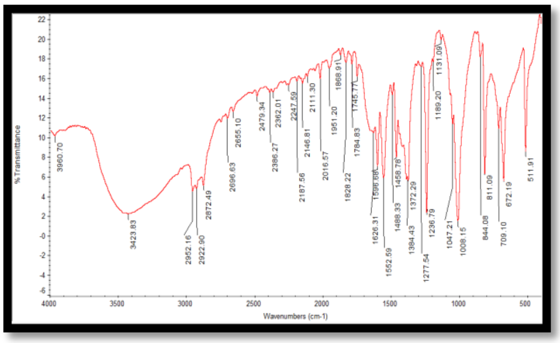

Fig: 4 FT-IR Spectrum of Schiff base Ligand

FTIR Spectra of Schiff Base nickel complex:

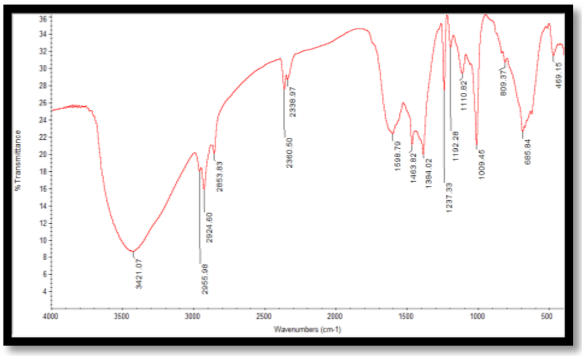

Fig: 5 FT-IR Spectrum of Schiff base Ligand - Nickel Complex.

The FTIR spectra of Schiff base ligand shows band resulting from OH stretching in the region 3422cm^{-1}. The band observed in the range 1626cm^{-1} is due to the azomethine (-HC=N) stretching frequency. The band around 1458 cm^{-1} which is assigned to C=C aromatic ring. In Schiff base ,the band appears at 1626cm^{-1} but in the complex the above band is shifted to lower frequency 1598cm^{-1} indicating the participation of azomethine group with metal ion. The new band at 469cm^{-1} was assigned to the metal nitrogen (M-O) vibrations. This band was observed in the spectra of metal complex and not in the spectra of uncomplexed schiff base ligand & thus confirming the participation of O& N atoms in the co-ordination.

3.3Cyclic Voltametry:

The cyclic voltammogram of Cu(II) and Ni(II) complexes were recorded with a BAS CV–50 instrument at room temperature and purge of N2 gas. The cyclic were recorded in the p^H 1.0. The background current was recorded for all sweep rates studied in the potential range from 0 to 0.5. Schiff base showed an oxidation peak in the particular condition.(Fig 6). Schiff base nickel complex showed an reduction peak in the particular condition.(Fig 7).Schiff base copper complex showed an oxidation peak in the particular condition.(Fig 8).

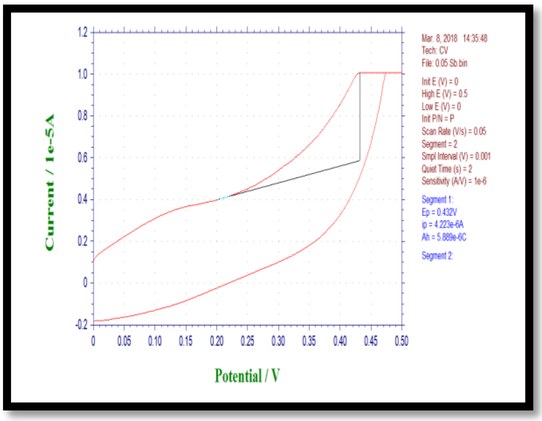

Fig:6 Cyclic voltagram of Schiff base Ligand- copper complex

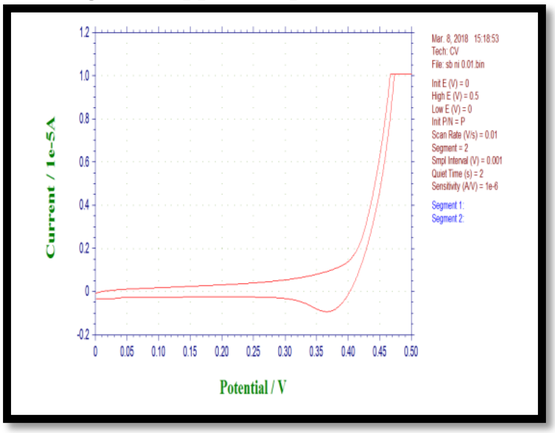

Fig: 7 Cyclic voltagram of Schiff base Ligand -Nickel complex

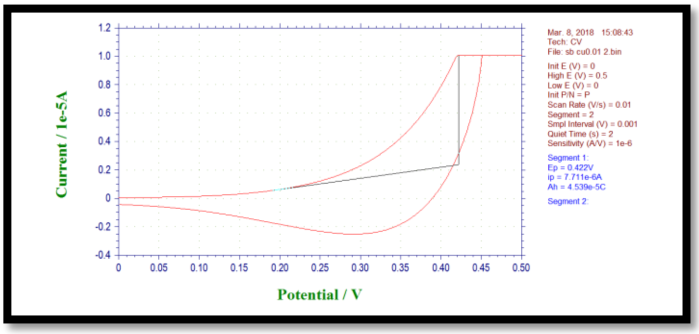

Fig: 8 Cyclic voltagram of Schiff base Ligand- copper complex

3.4Antimicrobial activity

The data pertaining to the antimicrobial potential of Schiff base ligand and its Cu & Ni complexes are presented in table below. The results indicate that the complexes show more activity against microorganisms under identical experimental conditions. This would suggest that the chelation could facilitate the ability of a complex to cross a cell membrane and can be explained by Tweedy‟s chelation theory. All the test compounds show lesser activity than the standard antibiotics.

The antibacterial activity of the Schiff base ligands and its soluble Cu(II) complexes was performed by the well diffusion technique. The zone of inhibition was measured against Staphylococcus aureus, *Bacillus Cereus, Bacillus subtilis, Escherichia coli, Klebsiella pneumonia, Salmonella typhi.* A clearing zone around the wells indicates the inhibitory activity of the compound on the organism. It indicate that the inhibition are much larger by metal complexes. The increased activity of the metal chelates can be explained on the basis of chelation theory . The chelation tends to make the ligands act as more powerful and potent bacterial agents, thus killing of the more bacteria than the ligand. It is observed that in complexes the positive charge of the metal partially shared with the donor atoms present in the ligand and there may be π- electron delocalization over the whole chelate ring. Schiff base Ligand -Copper Complex shows greater activity against *Staphylococcus aureus* in the ethanol extract and the nickel complex shows greater activity against etanol extract of *Klebsiella pneumonia.*

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Table: 1 Antimicrobial activity of Schiff base Ligand -CopperComplex

Name of the organism	Zone of Inhibition (mm)										
	Petroleum ether (40^0-60^{0}C)		Benzene		Chloroform		Ethanol		Water		Standards
	DIZ*	AI#	DIZ*	AI#	DIZ*	AI#	DIZ*	AI#	DIZ*	AI#	
Bacillus Cereus	-	0	-	0	-	0	5	0.42	6	0.50	7
Bacillus subtilis	-	0	-	0	-	0	-	0	1	0.06	8
Staphylococcus aureus	-	0	-	0	-	0	20	1.17	14	0.82	12
Escherichia coli	-	0	-	0	10	0.62	19	1.12	16	0.94	11
Klebsiella pneumonia	-	0	-	0	-	0	22	1.15	20	1.05	16
Salmonella typhi	-	0	-	0	6	0.38	19	1.19	22	1.38	14

*DIZ- Diameter of zone inhibition; #AI- Active Index - No inhibitory effect

Table: 2 Antimicrobial activity of Schiff base Ligand -CopperComplex

Name of the organism	Zone of Inhibition (mm)										
	Petroleum ether (40^0-60^{0}C)		Benzene		Chloroform		Ethanol		Water		Standards
	DIZ*	AI#	DIZ*	AI#	DIZ*	AI#	DIZ*	AI#	DIZ*	AI#	
Bacillus Cereus	-	0	-	0	-	0	8	0.82	-	0	7
Bacillus subtilis	-	0	-	0	-	0	7	0.62	-	0	8
Staphylococcus aureus	1	0.08	7	0.63	-	0	19	1.07	3	0.22	12
Escherichia coli	-	0	-	0	-	0	18	1.19	12	0.84	12
Klebsiella pneumonia	-	0	-	0	-	0	24	1.35	16	1.01	16
Salmonella typhi	-	0	-	0	6	0.38	19	1.19	21	1.28	14

3.5Antioxidant activity of Schiff Base Copper complex

DPPH is a stable free radical at room temperature and accepts an electron or hydrogen radical to become a stable diamagnetic molecule with an absorption maximum band around 515-528 nm and thus it is a useful reagent for evaluation of antioxidant activity of compounds[6].In the DPPH test , the antioxidants reduce the DPPH radical to a yellow-coloured compound, diphenylpicrylhydrazine, and the extent of the reaction will depend on the hydrogen donating ability of the antioxidants. Percentages of DPPH radical scavenging activity was tabulated in Table 3. The in vitro scavenging assay of DPPH radicals was performed spectrophotometrically with ascorbic acid as positive control.

The Schiff base –copper complex show a strong antioxidant activity of inhibiting DPPH radical when compared with standard ascorbic acid. Among the five solvents tested ethanol extract shows stronger antioxidant activity.

Absorbance of control at 517 nm 0.3846

Table: 3 Antioxicdant activity of Schiff base Ligand -CopperComplex

Concentration (µg/ml)	Petroleum ether	Benzene	Chloroform	Ethanol	Water	Standard Ascorbic acid
50	0.4944	0.5255	0.2124	0.1998	0.1122	0.3126
100	0.4876	0.4879	0.1918	0.0831	0.1080	0.2989
150	0.3922	0.4325	0.1989	0.0726	0.0767	0.2126
200	0.2345	0.4107	0.0976	0.0453	0.0621	0.1984

4. Conclusion

Yield of the Schiff base synthesized by using conventional method is found to be greater in amount compared with the other two methods. Schiff base ligands were used to synthesize Copper & Nickel complexes. Synthesized Schiff base ligands and metal complexes were amphorous in nature. UV ,IR spectra were used to characterize the prepared ligands and metal complexes. Cyclic voltagram shows presence of oxidation peaks in the Schiff base ligand and in the copper complex and reduction peak in the Schiff base nickel complex.Both the complexes were to exhibit strong antimicrobial activity. Schiff base copper complex shows a strong antioxidant activity (DPPH assay).Thus Schiff base is a ligand having biological activity.

5. References

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