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Synthesis and Characterization of Salicylaldazine and Its Metal (II) Complexes Derived from Metal (II) Chlorides

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***Abstract*—** The salicylaldazine (ligand) and its metal (II) complexes like copper (II), nickel (II), zinc (II), cobalt (II) and manganese (II) complexes has been synthesized and characterized by different techniques using FTIR, UV-VIS spectroscopy. The ligand (salicylaldazine) is synthesized by the condensation reaction of salicylaldehyde and hydrazine sulfate. The salicylaldazine metal (II) complexes like Cu (II) , Ni(II), Zn (II), Co(II), Mn(II) were prepared by using metal (II) chloride in dioxane. The ratio of salicylaldazine and metal (II) chloride was 2:1 mole ration respectively. The resultant complexes having general formulae M+2 [L]2X2.xH2O.

The resultant compound was characterized by UV-VIS analysis and FTIR analysis. Their suggested formulae showed that Cu (II) , Ni(II), Co(II), Mn(II) salicylaldazine complexes acted as tridentate ligands and have octahedral geometry while Zn(II) salicylaldazine complex acted as bidentate ligand and has tetrahedral geometry. All of them acted as coordination ligands via nitrogen atom of phenolic hydroxyl group. Their molar conductivities showed that all of them are insulators at room temperature while at high temperature they can act as semiconductors.

Keywords—: L=salicylaldazine X= chlorides

I. INTRODUCTION

Azines are the functional class of organic compound formed by the condensation reaction of two equivalents of an aldehyde or ketone with one equivalent of hydrazine[1-2].The azines are polar species and usually solids which are slightly soluble in water[3-4].They are the class of compound AZOMETHINE which have been receiving increasing attention in recent years for their anti-bacterial, anti-fungal and anti-tumor properties. They are also used in bond formation reactions, polymerizations and in design of liquid crystal. Azines exhibit interesting optical biological and conductive properties and all extensively used as intermediates [5]. Many studies shows that azines are good synthones for obtaining hetrocyclic compounds such as pyrazole, pyridine ,purine and pyrimidine [6].Azines are also potential ligands owing to the two imine groups. Therefore, they have recently been used as ligands in coordination chemistry [7]. Azines are known to function as chelating agent [8-9]. The interest in such studies aroused from the fact that these compounds can display an tubercular effect [10], based on their tendency to form metal chelates with transition metal ions.[11-12]Azine contain an azomethine group. In transition metal chemistry azomethines are known as ligand forming co-ordination bonds.By the development of the coordination chemistry, azomethine compounds are getting used in coordination chemistry for the identification of geometrics of the complexes isomerisation of complex and for other many applications. [13- 14].

The metal ions play a vital role in vast number of biological processes the ions with biologically active ligands are a subject of considerable interest. Some of the biological active compounds like azines act via chelation but for most of them little is known about how metals binding influences their ability some heterocyclic azines are known to inhibit marine tumor growth and act as fluorescent brightening agent and are photo-sensitizer. Azines are developed for ion selective optical sensors. Mixed azines between opioid antagonist and steroidal ketones have show various metal complexes so their anti microbial and anti fungal properties[15].

Azine complexes with most transition metal ions serves as models for biologically important species. Polynuclear complexes derived from multidentate ligand have documented intresting structural feature. Litrature survey reveal that number of O,O ,O,N,N and O,N,O donor sequences resulted in the formation of polynuclear metal chelate [16-17]. Azine group (R2C=N-N=CR2) has lone pair containing electrons on nitrogen atom, if it is linked with aromatic ring carrying an additional donor site is well suitable for chelation. Azine have N, O donor system, which are an important class of ligand and have an important applications for making complexes. Azine have properties to form complexes with different metals depending upon their nature. [18-20].Azine metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications. Chelating ligands containing N and O donor atom show broad biological activity and are of special interest because of variety of ways in which they are bonded to metal ions. Metal ions bound to biologically active compounds may enhance their activities.

Like other azines, salicylaldazine forms chelates with a variety of transition metals. While extensive work has been devoted on the crystal and molecular structures of ligand, less work has been dedicated to the structure of its metal complexes. In the present paper, IR and UV analyses of salicylaldazine and its Cu(II), Ni(ll), Zn(ll), Co(ll) and Mn(ll) are reported. Also, the Melting Point, pH, and molar conductance are investigated.

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II. EXPEREMENT

A. Material

Metal salts, salicylaldehyde, hydrazine hydrate and solvents used were purchased from BDH, Unichem and E.Merck.

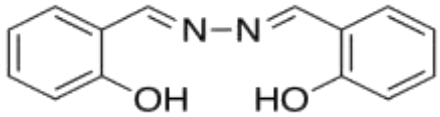

Figure 1: Structure of the ligand

SYNTHESIS OF THE LIGAND

EQUATION

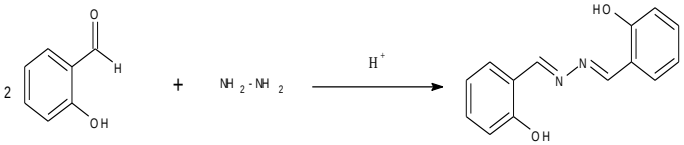

Figure 2: Salicylaldehyde hydrazine salicylaldazine

B. Procedure

Take about 3.1g (0.025mole) of powdered hydrazine sulphate into 250ml of beaker . Add 48.75ml of distilled water and then add 3.0ml (0.025mole) of concentrated liquid ammonia (density about 0.88) and then add 6.3ml (0.05mole,6.5g) of salicylaldehyde drop by drop with constanat stirring the mixture. Yellow soft layer was formed on constant stirring of about 30 – 60 minutes at room temperature. Then shake the mixture for further an hour and collect the yellow solid .The yellow cubed shape solid is filtered off and washed with water to remove its impurities.After washing, dried the solid in air and crushed it in order to get the powdered form. Recrystallized it with acetone or rectified spirit.

III. SYNTHESIS OF METAL (II) COMPLEXES

Dissolved 3g(0.0125mole) of salicylaldazine in 15ml of dioxane solution in a round bottom flask. After that, made another solution in 0.811g (0.00625 mole) of metal (ll) chloride (MCl2) in 17ml of buffer solution . The ratio of the both mixture is in 2:1 for azine solution and metal (ll) chloride solution respectively.A coloured solution was formed at the junction. The mixture was not separated at that time, settled it on reflux condenser for 2–3 hours. The mixture became concentrated which showed the formation of complex. Remove them from reflux condenser, allowed to cool at room temperature and filtered out. The residue contain the metal(ll) complex of salicylaldehyde azine. Washed it with water in order to removed the impurities, dried and weighted.Took the melting point, molar conductivity and percentage yield

IV. RESULTS AND DISCUSSION

The azine are a class of compound azomethine group which have been receiving increasing attention for their antibacterial, antifungal and antitumor properties. Salicylaldehyde azine had been synthesized by the condensation of salicylaldehye with hydrazine sulphate 2:1 mole ratio. The formation of yellow cube like solid indicated that the salicylaldazine was formed. Filtered it,the residue contained the desired ligand. Dried the solid and crushed into powdered form. The salicylaldazine was recrystallized from ethanol in ordered to remove impurities. The synthesized compound named salicylaldehyde azine was a solid which had bright yellow color containing molecular formulae C14H12N2O2, having molecular weight 240.29 g. its solubility and other properties are described in tables.

The metal (II) complexes were prepared by the condensation of their metal (II) chlorides with salicylaldehyde azine in the dioxane solvent in a reflux condenser. The resultant complexes were Ni(ll), Cu(ll), Zn(ll), Co(ll), and Mn(ll) complexes of salicylaldazine. After that all of them were characterized by UV-visible spectrophotometer and FTIR. All these complexes were of different colors, percentage yields, melting points and structures. All of them showed different molar conductivity. They were insulators at room temperature and on high temperature they acted as semi conductors. During the observation of melting point it was noted that most of them were decomposed on heating without being melt. Table. 1,2.

Table no. 1: Physical properties of the ligand and its metal (ll) complexes

Table no. 2: Analytical data of the ligand and it metals (ll) complexes

Name	Mol. formula and weight	Color and phase	Melting points	Percentage yield	Geometry
Salicylaldazine	$C_{12}H_{22}O_2N_2$ 240.2	Lemon yellow solid	213 º	80.8%	
Ni (ll) salicylaldazine	$C_{28}H_{26}NiN_4O_6$ 573.2	Green-yellow solid	101º	81.6%	Octahedral
Cu (ll) salicylaldazine	$C_{28}H_{27}CuN_4O_6$ 579.0	Pale yellow solid	120 º	76.6%	Octahedral
Co (ll) salicylaldazine	$C_{28}H_{26}CoN_4O_6$ 573.46	Brown yellow solid	220 º	83.3%	Octahedral
Mn (ll) salicylaldazine	$C_{28}H_{26}MnN_4O_6$ 569.4	Yellowish green solid	210 º	71.6%	Octahedral
Zn (ll) salicylaldazine	$C_{28}H_{24}ZnN_4O_5$ 561.93	Bright yellow solid	212 º	80.0%	Tetrahedral

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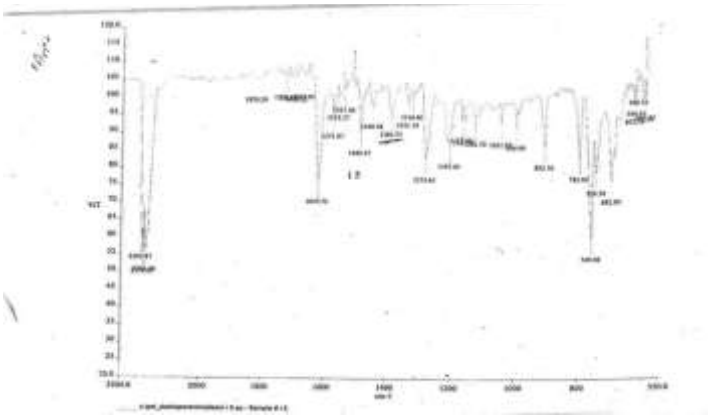
Compound	pH	λ_{max} (nm)	Molar Conductance	λ_{max} (nm)
Salicylaldazine	7.0	392	5.7 µS	392
Ni (ll) salicylaldazine	7.5	414	4.4 µS	414
Cu (ll) salicylaldazine	7.1	414	5.5 µS	414
Co (ll) salicylaldazine	6.6	409	3.4 µS	409
Mn(ll) salicylaldazine	7.7	413	3.1 µS	413
Zn (ll) salicylaldazine	6.8	414	1.9 µS	414

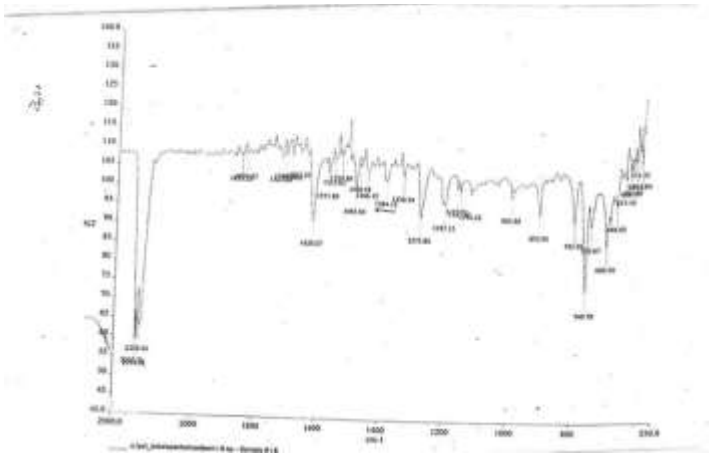
Table no.3 : FTIR spectra of ligand and its complexes

Sr. No	COMPOUND	C=N Bands	C – O Bands	N – N Bands	C – C Bands	M – O Bands	M – N Bands
1	Salicylaldazine	1623	1316	980	1159	Nill	Nill
2	Ni (ll)salicylaldazine	1611	1195	985	1148	571	601
3	Cu (ll) salicylaldazine	1617	1196	983	1147	571	601.7
4	Co (ll) salicylaldazine	1620	1197	983.95	1148	576	601.5
5	Mn (ll) salicylaldazine	1619	1197	984	1147	572	602.1
6	Zn (ll) salicylaldazine	1620	1197	983.8	1147	571	601.7

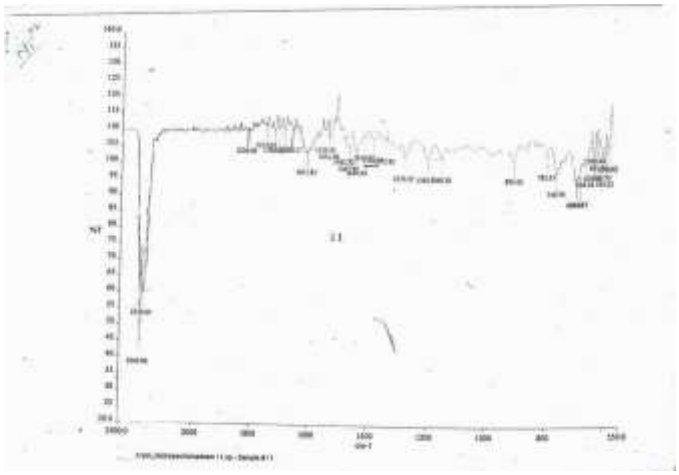
FTIR spectra of Mn (ll) salicylaldazine



FTIR spectra of Zn (ll) salicylaldazine



FTIR spectra of Ni (ll) salicylaldazine



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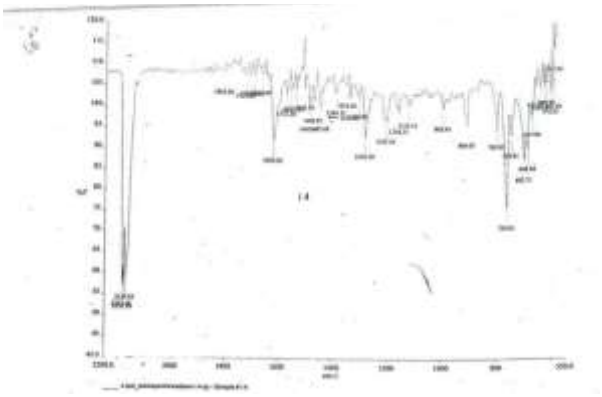
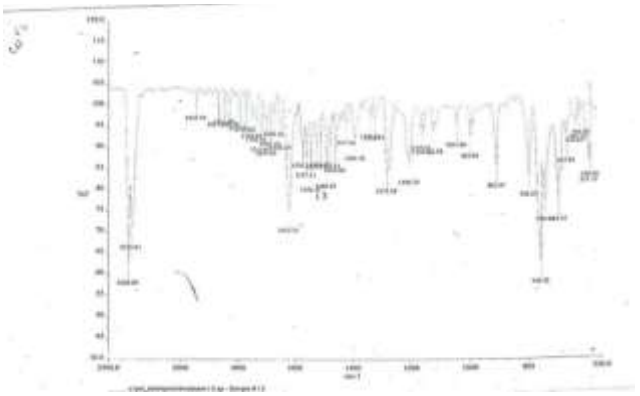
FTIR spectra of Co (ll) salicylaldazine



FTIR spectra of Cu (ll) salicylaldazine



V. RESULTS AND DISCUSSION

The azine are a class of compound azomethine group which have been receiving increasing attention for their antibacterial, antifungal and antitumor properties. Salicylaldehyde azine had been synthesized by the condensation of salicylaldehye with hydrazine sulphate 2:1 mole ratio. The formation of yellow cube like solid indicated that the salicylaldazine was formed. Filtered it,the residue contained the desired ligand. Dried the solid and crushed into powdered form. The salicylaldazine was recrystallized from ethanol in ordered to remove impurities. The synthesized compound named salicylaldehyde azine was a solid which had bright yellow color containing molecular formulae C14H12N2O2, having molecular weight 240.29 g. its solubility and other properties are described in tables.

The metal (II) complexes were prepared by the condensation of their metal (II) chlorides with salicylaldehyde azine in the dioxane solvent in a reflux condenser. The resultant complexes were Ni(ll), Cu(ll), Zn(ll), Co(ll), and Mn(ll) complexes of salicylaldazine. After that all of them were characterized by UV-visible spectrophotometer and FTIR. All these complexes were of different colors, percentage yields, melting points and structures. All of them showed different molar conductivity. They were insulators at room temperature and on high temperature they acted as semi conductors. During the observation of melting point it was noted that most of them were decomposed on heating without being melt. Table. 1,2.

Their UV analysis showed that the ligand(salicylaldazine) has a λmax value 392nm at the absorbtin 2.240 in carbon tetra chloride. The nickel(ll) salicylaldazine has a λmax value 414nm at the absorbtion 3.382 in carbon tetra chloride. The zinc(ll) salicylaldazine has a a λmax value 414nm at the absorbtion 2.337 in carbon tetra chloride. The copper(ll) salicylaldazine has a a λmax value 414 nm at the absorbtion 2.332 in carbon tetra chloride.The cobalt (ll) salicylaldazine and manganese (ll) salicylaldazine have a λmax values 409nm and 413nm respectively at the absorption 2.443 and 2.022 in carbon tetra chloride. Table.2

The geometry of the complexes when noted, we found that all of them have octahedral geometry except nickel(ll) Salicylaldazine it showed tetrahedral geometry. The ligand which form four bonds with ligand is bidentate. All others Cu,Zn,Co,Mn(ll) salicylaldazines were tridentate and all of them have octahedral geometries they form four bonds with ligand.

The IR analysis showed different peaks in different regions. The chemical structural analysis of ligand and its Cu(ll) , Ni(ll) , Co(ll) , Mn(ll) , Zn(ll) complexes were done by FTIR. The spectrum of them shown in Figures.Frequency range and other details of characteristic absorption peaks of spectra are given in Table.

The azine ligand named salicylaldazine showed different peaks at different wavelength the C=N peak at 1623cm-1 , N – N peak at 980 cm-1 , C- C at 1159 cm-1 and C-OH peak at 1316 while this C- OH peak in their metal complexes disappeared and showed a peak of C – O at different wavelengths. The nickel (ll) salicylaldazine showed C=N peak at 1611.8 cm-1 , C-O peak at 1195 cm-1 , N – N peak at 985 cm-1 , C-C peak at 1148 cm-1 , M-O peak at 571 and M-N peak at 601 cm-1.The copper (ll) salicylaldazine showed C=N peak at 1617 cm-1 , C-O peak at 1196 cm-1 , N – N peak at 983 cm-1 , C-C peak at 1147 cm-1 , M-O peak at 571 and M-N peak at 601.7 cm-1. The cobalt (ll) salicylaldazine showed C=N peak at 1620 cm-1 , C-O peak at 1197 cm-1 , N – N peak at 983.9 cm-1 , C-C peak at 1148 cm-1 , M-O peak at 576 and M-N peak at 601.5 cm-1.The manganese (ll) salicylaldazine showed C=N peak at 1619 cm-1 , C-O peak at 1197 cm-1 , N – N peak at 984 cm-1 , C-C peak at 1147 cm-1 , M-O peak at 572 and M-N peak at 602.1 cm-1.The zinc (ll) salicylaldazine showed C=N peak at 1620 cm-1 , C-O peak at 1197 cm-1 , N – N peak at 983.8 cm-1 , C-C peak at 1147 cm-1 , M-O peak at 571 and M-N peak at 601.7 cm-1.

CONCLUSION

Based on the above observations of FTIR, UV-VIS , conductance measurements and insolubility in water and solubility in organic solvents like methanol , CCl4 etc and high melting points we proposed the octahedral structure of Mn(ll), Ni(ll) , Co(ll) ,Mn(ll) salicylaldazine complexes and Zn(ll) have tetrahedral geometries. All the ligand and its Mn(ll), Ni(ll) , Co(ll), Mn(ll) and Zn(ll) salicylaldazine complexes were insulator at room temperature. These complexes are widely use in industries, laboratories, and pharmaceutics.

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According to the analytical,physical and spectral studies the final structure and character of ligand and its metal(ll) complexes are concluded. The ligand was synthesized by the condensation of salicylaldazine with hydrazine sulfate. The metal complexes were also formed by the condensation reaction of salicylaldazine and metal(ll) chlorides in 2:1 mole ratio. The ligand acted as chelate which joined to metal ion through the azomethine nitrogen and one hydroxyl group of ligand. The ligand Salicylaldazine acted as bridging ligands joint through the one nitrogen of azomethine group of salicylaldazine.

They all were insoluble in water and slightly soluble in ethanol and methanol. The ligand is neutral in nature while its complexes are acidic and basic. Some of salicylaldazine complexes like cobalt and nickel(ll) salicylaldazine complexes were decomposed whithout being melt.

The ligand and its metal(ll) complexes were insulator at room temperature. This information was collected by molar conductivity measurement test. The UV.VIS and FTIR spectroscopy gave the suggested formula of the metal(ll) complexes of salicylaldazine. They showed that nickel (ll), copper (ll), manganese (ll), cobalt (ll) salicylaldazine complexes have octahedral geometry and zinc (ll) salicylaldazine complex have tetrahedral geometry.

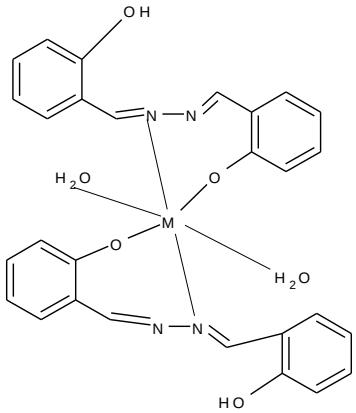

Figure 3: Structure of complex showing octahedral geometry

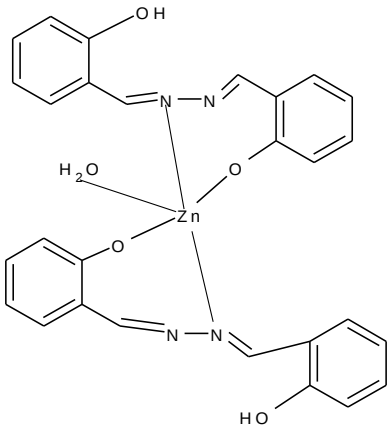

Figure 4: Structure showing the tetrahedral geometry

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