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Mass and Thermal Gravimetric Study of some Novel complexes of 3,5-dichloro Salicylaldehyde.

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Abstract:

The novel complexes of Co(II) Ni(II) Cu(II) and Zn(II) from Schiff base synthesized from 3,5-dichlorosalicylaldehyde and 2-aminopyridine. Mass spectra of ligand and complexes give the accuracy in molecular weight. The fragmentation of molecular ion peaks of compounds further gives the conformation of parent compounds. Thermal decomposition of the ligands and all the complexes shows the release of gases like NH_3, H_2O, CO, and CO_2 at different temperatures**.**

Keywords: - 3,5-dichlorosalicylaldehyde, Schiff base Mass spectra, Thermal Gravimetric analysis.

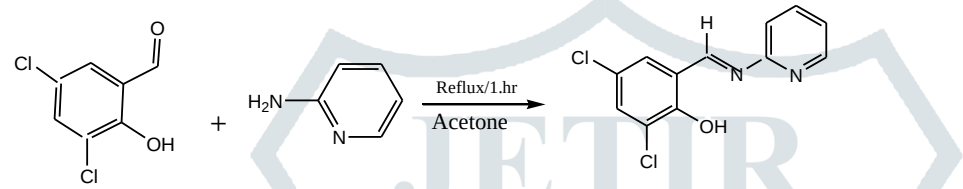
Introduction:

Schiff bases and their metal complexes of Co(II), Ni(II), Cu(II), and Zn(II) show biological activity[1]. The Schiff, bases are generally bi- or tridentate[2]forming stable complexes[2], N(3,5-dichloro-2-hydroxybenzylidine) pyridine-amine is a bidentate ligand. Chemotherapeutic studies of new kinds of Schiff bases and complexes are now attracting the attention of researchers[3]. The interest in the coordination chemistry of 3d metal increases in the chemical and biological functions[4]. Many Schiff base complexes show high catalytic activity[4,19]. Despite these benefits, like other natural essential bio-actives, used for Ayurvedic food processing[5]. The capable biological responses of aminopyridine derivatives have made them an important class of substituted N-heterocycles[6]. Schiff base compounds are versatile and synthesized by condensation of carbonyl compound and amine, Schiff base compounds can coordinate with different metal ions[7,18]. Schiff base metal compounds have attracted much more attention in the curative area due to their distinctive ligation behavior, effective physiochemical properties, and significant application in medicinal agent[8]. A range of biological activities like antimicrobial[9,19], DNA binding[10], antituberculosis [11,15] anticancer[12,16]. A Nickel (II) Schiff base complex of 3,3 dichlorosalicylaldehyde and 4,4-Dimethyl-3-thiosemicarbazide in DMF was found potential inhibitor for SARS-CoV-2 virus[13,17]. The mass fragmentation pattern in ligand n(3,5-dichloro-2-hydroxybenzylidine) pyridine-2-amine, and its metal complexes have been synthesized successfully [14,20.]

Synthesis of Schiff base Ligand N(3,5-dichloro-2-hydroxybenzylidine) pyridine-2-amine from 3,5-dichlorosalicylaldehyde and 2-aminopyridine.

A saturated solution of 3,5-dichlorosalicylaldehyde (0.08mol,15.29g) in acetone was mixed with 2-aminopyridine(0.08mol,7.52g) in 10ml water. The solution was exposed to sunlight for half an hour with constant stirring and further. Then the solution was left undisturbed for half hour. After the solution was cooled down, a bright orange-colored precipitate was obtained. This Schiff base was further filtered and washed with ethanol. Afterward, it was dried and then recrystallized. The solvent used here for recrystallization was acetone. The purity of the Schiff base and the completion of the reaction were tested by TLC. The solvents used for TLC were n-hexane and acetone in a ratio of 8:2.

Figure-1 reaction of Schiff base synthesis



3,5-dichlorosalicylaldehyde 2-aminopyridine N-(3,5-dichloro-2-hydroxybenzylidene)pyridin-2-amine

Synthesis of Co(II) complex:

The metal complex of cobalt was synthesized by mixing 0.002M (0.534 g) Schiff base with the metal salt $CoCl_2.4H_2O$(0.242g, 0.001M) in a 20 ml aqueous solution of methanol in the ratio of 2:1. This reaction mixture was then heated on a sand bath at 40-50^{0}C and the reaction mixture was continuously stirred. This mixture was allowed to stand for half-hour. A solid precipitate having red-brown color was obtained. This precipitate itself was the complex of cobalt. Further, this complex was filtered and purified and then washed with hot ethanol. The completion of the reaction and the purity of the complex formed were tested by using TLC. The solvents used for TLC were n-hexane and acetone in a ratio of 8:2.

Synthesis of Ni(II) complex:

The metal complex of nickel was synthesized by adding Schiff base [L5] (0.002M, 0.534g) to the metal salt of $NiCl_2.7H_2O$(0.240g,0.001M) in 20 ml methanol in the ratio of 2:1. The reaction mixture was heated at 40-50^{0}C and was stirred continuously. Then it was allowed to stand for half-hour. This precipitate itself was the complex of nickel. Further, the complex was filtered and purified and then washed with hot ethanol. The completion of the reaction and purity of the complex formed were tested by using TLC.

Similarly, the other complexes of Cu and Zn were synthesized, by using $CuCl_2$.and $ZnCl_2$

Mass Spectra of ligand and Complexes:

Mass spectra of all compounds were recorded on mass spectrometer by dlc_ms50-1200mz_2500v_12min_0.120ml flow_95b.m method on instrument impact HD 1819696.00184. The source type is an ESI scan between a range of m/z 50-1200 The molecular weight of the compound is derived from the mass

spectrum of a compound. The m/z value of the ion is the molecular weight of the compound. The molecular ion peak is sometimes the base peak. The base peak is the most intense peak in the spectrum. In the mass spectrum of Schiff base, the positive ion peak at m/z=267 represents the intact N(3,5-dichloro-2-hydroxybenzylidene) pyridine-2-amine molecule(M+*). The peak at m/z=269 shows the isotopic peak in which one of the chlorines should be Cl^{37}. The abundance of isotopes is nearly equal. The molecular ion subsequently undergoes a series of fragmentation occurs when 70ev energy bombardment on the molecule which is shown in the spectrum clearly at 223,186 and 95. Also, peaks observed at 270, 273, and 276 indicate the presence of isotopes of O^{18}, $Cl^{37}$and C^{13}, with small abundance**.**

Mass spectra of complexes:

The Co(II) complex shows a molecular ion base peak at 757.50 for the complex $[CoL_2Cl_2]$ $Cl_2.2H_2O$. The m/z value is 554,507 with small intensities 325 and 327, 338 and 340, 322, and 324, these peaks show the fragmentation of complex some of them show isotopic peaks. The mass spectrum of the Ni(II) complex shows a molecular ion peak at m/z at 656, which is equivalent to the molecular weight of $[NiL_2Cl_2]$. Other peaks at m/z655 and 652,650 are due to fragmentation. Both the complexes after demetallation form $[L]^+$.The mass spectrum of Cu(II) indicates the m/z value at 573.25 for the molecular ion peak. The m/z values at 409.16, 267,217, and 95 show the fragmentation in the complex. suggesting the $[Cu(L)_2]$ Cl complex. In the Zn complex, the molecular ion peak value is at 757.50 exactly equal to Co(II) complex. other m/z value at 685,663, 485,267.215, and 95 for fragmentations. Initially, fragmentation of small molecules like H2O, Cl, etc removes. Each complex shows an m/z value at 267 confirming the presence of ligand in the complex The mass spectrum of ligands and complexes is given in Figures 2-5. The fragmentation of the Schiff base is given in figure 6.

Fig. -2 Mass spectra of Schiff base

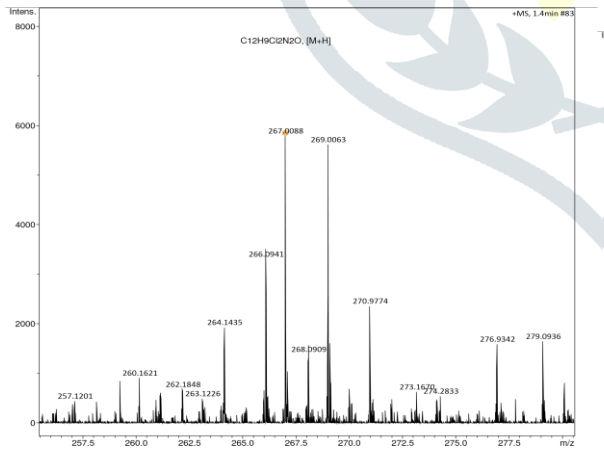


Fig. -3 Mass spectra of Co(II)

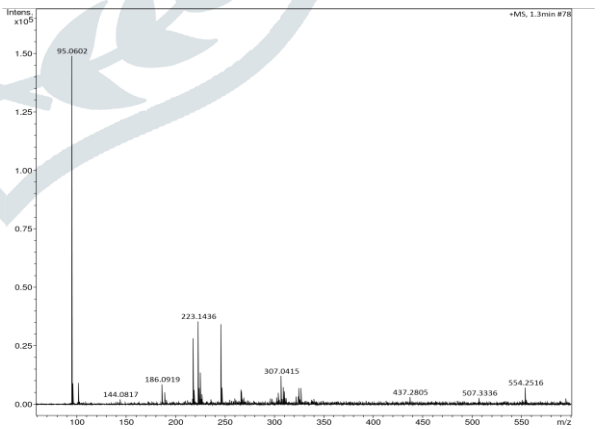


Fig. 4 Mass Spectra of Ni(II)

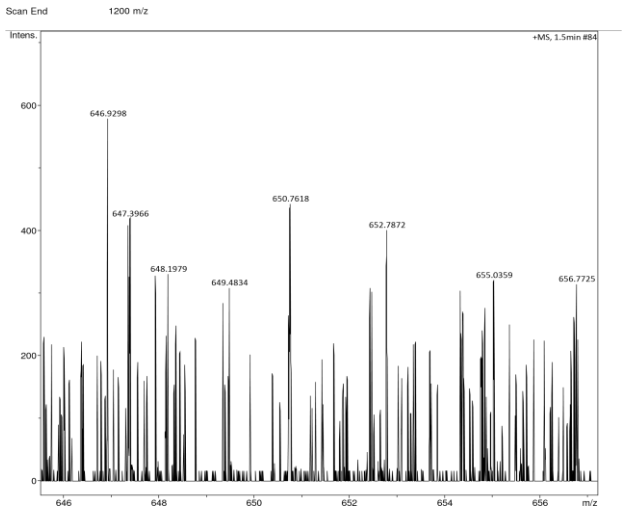


Fig.-5 Mass spectra of Cu(II) complex

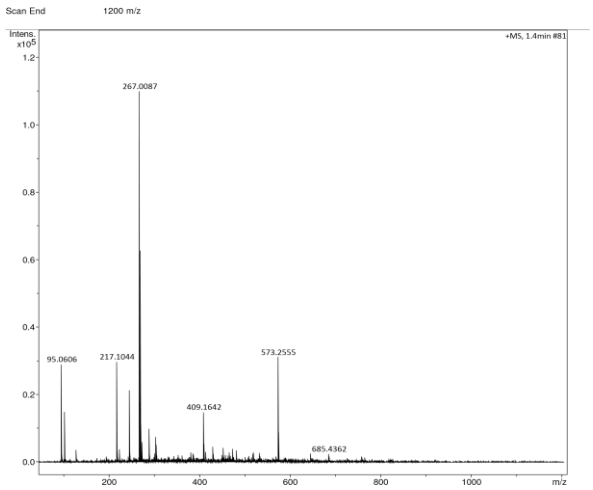


Fig.-6 fragmentation of Schiff bases

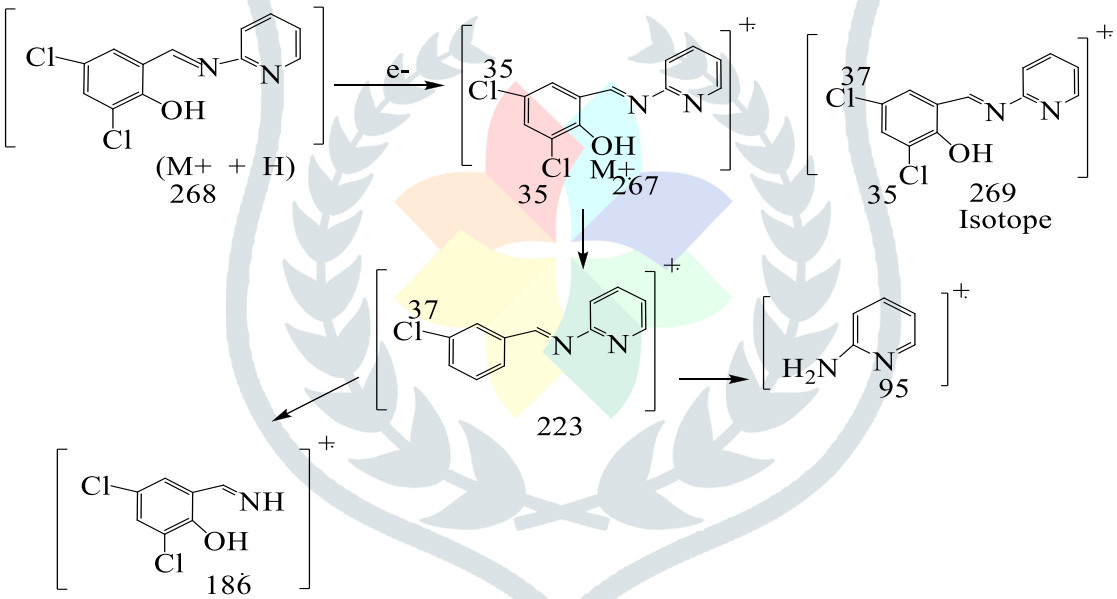


Table-1 Thermal Gravimetric Analysis (TGA)

Complexes	Mol(Wt.)	TG range(^{0}C)		Mass loss (%)	Total mass loss (%)	Assignment
1) Ligand	267	60-150 297.87-318.83 460-770 770-1160	Exothermic	0.40 95.64 2.64 3.74	96%	H_2 Organic compound ($C_{12}H_7N_2Cl_2$) 0.5 H2O H2O
2) Co(II)	757.57	56-280 280-630 630-850 850-1160	Exothermic Endothermic - -	8.16 36.19 28.56 24.47	97.39	Cl_2, $2H_2$ Organic compound (C12H7N_2Cl_2) $4CO_2+4NH_3+2H_2O$ $Co+CoO+CO_2$
3) Ni(II)	757.50	74-220 220-430 430-780 780-1160	Exothermic Endothermic - -	15.07 20.35 30.15 15.26	80	CO_2+2H_2O+CO $CO_2+2NH_3+H_2O+2CO$ Organic compound ($C_8H_2Cl_4$) Mix. Ni+NiO
4) Cu(II)	573	160-370 370-650 550-880 880-1170	Exothermic Exothermic Endothermic -	31.69 21.79 5.10 9.66	69.38	$2NH_3+2CO_2+2CO$ $CuO+CO_2$ CO $2NH_3+H_2O$
4) Zn(II)	757.50	90-230 230-460 460-720	endothermic	10.13 21.52 34.43	98	$2CO+H_2O$ $2CO_2+2H_2O+2NH_3$ $3CO_2+3CO+2NH_3$

		720-1150		35.32		$Zn+ZnO+2H_2O$

Thermal gravimetric analysis (TGA) was carried out for all the synthesized Schiff bases and its complexes. This analysis was performed in a total nitrogen atmosphere. It was found that, the thermal decomposition of two complexes is not similar to that of the ligand. The thermal gravimetric analysis of the compounds was carried out starting from room temperature 27^0c to 1200^0c. The instrument used for this TGA of the compounds was SDT600. The analysis was done in Yashwant Mahavidyalay Nanded.

The ligand 267 is in a solid state. This is the cause which its thermal decomposition has been endothermic in its initial phase and then exothermic. The first thermal gravimetric temperature ranges from 60-150^0c and the thermal decomposition of this compound further releases an H_2 molecule. Here, the weight loss observed in the compound was 0.40%. The thermal decomposition continues further and another range of temperature for the compound is 210-460^0c. After its thermal decomposition, the weight loss observed in that compound is 95.64%. Thus here an organic compound is released whose molecular formula is $C_{12}H_7N_2Cl_2$. Further, at the temperature range between 460-770^0c loss of mass observed was 2.64% and elimination of an H_2O molecule took place. Similar to this, another water molecule was eliminated from the temperature range of 770-1160^0c. The loss of mass observed in this range is the range of 3.74%. The thermal decomposition of this compound is exothermic. This is decided according to the DTA value. The weight loss of the gases of the Schiff base ligands is shown in Figure 2 and Table 1.

The complex of Co(II) has a molecular weight of 757.57 g. This complex starts to decompose at the temperature of 56^0c. The first temperature range for the TGA of the CO complex is 56-280^0c. In this range, it was found that the Cl_2 and H_2 gas were eliminated. The loss of mass was observed to be 8.16%. This decomposition of the complex is endothermic; as can be noticed from the graph. Further, the temperature range for TGA was 280^0-630^0c. The thermal decomposition of the CO complex in this temperature range releases an organic compound whose molecular formula was found to be $C_{12}H_7N_2Cl_2$. At the temperature range between 630-850^0c, three gases mainly, NH_3, CO_2, and hardly H_2O are released on thermal decomposition of the complex. The weight loss was 36.19% .This decomposition was found to be exothermic. The Co complex is broken between 850-1160^0c into metal and metal oxide. These are Co and CoO along with carbon dioxide (CO_2). This decomposition is also exothermic. The weight loss was 28.56%.

The molecular weight of the Ni(II) complex is 757.50. The thermal gravimetric analysis of Ni(II) complexes displayed the release of three gases initially at the temperature range 74-220^0c. The gases released were H_2O, CO_2, and CO a74-220^0c. This decomposition is found to be exothermic and the weight loss observed was 15.07%. Further, between the temperature range of 220-430^0c, the release of gases namely CO_2, CO, NH_3, and H_2O was seen and the weight loss observed was 20.35%. This thermal decomposition was found to be exothermic. Similarly, the temperature range between 430-780^0c was also found to be exothermic and the weight loss observed

was 30.15%. The thermal decomposition of the Ni complex in this range resulted in the elimination of an organic compound having the molecular formula $C_8H_2Cl_4$. The next temperature range was between 780-1160^{0}c. The weight loss observed was 15.26% and the thermal decomposition of the complex resulted in the release of a mixture of Ni and NiO.

The molecular weight of Cu(II) complex according to mass spectra is 573. The thermal decomposition of the complex initially at temperatures 160-370^{0}c shows 31.69% weight loss, which indicates the loss of NH_3, CO_2, and CO gases. This loss is endothermic. The Loss of CuO along with CO_2 takes place between temperatures 370-650^{0}c it is an endothermic process and weight loss is 21.79%. The temperature range between a 650-880^{0}c loss of CO takes place exothermically. At last, 9.66% weight loss at 880-1170^{0}c indicates the loss of NH_3 and H_2O molecules. The molecular weight of the Zn(II)complex according to mass spectra is 757.50. The thermal decomposition of the complex initially at temperatures 90-230^{0}C shows 10.13% weight loss, which indicates the loss of CO gas and H_2O. This loss is endothermic. The loss of CO_2, NH_3, and H_2O takes place between the temperature range of 230-460^{0}C. It is an endothermic process and weight loss is 21.52%. The temperature range between 460-720^{0}C, and the loss of CO_2, CO, and NH_3 takes place exothermically. At last, 35.42% weight loss at 720-1150^{0}C indicates the loss of Zn, ZnO, and H_2O molecules. All the data stated in Table 1 and figure 7-11

Fig- 7 TGA of Schiff base:

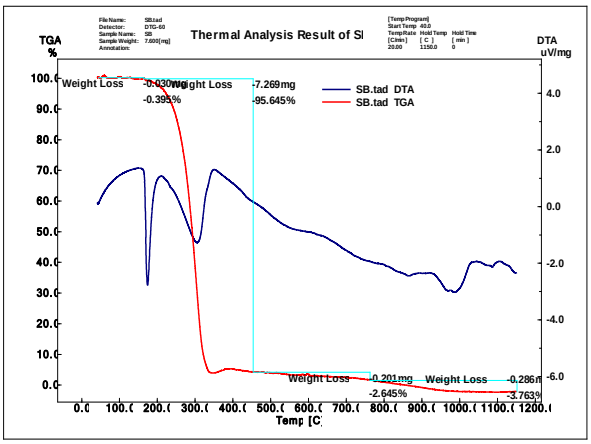


Fig.-8 TGA of Co(II) complex

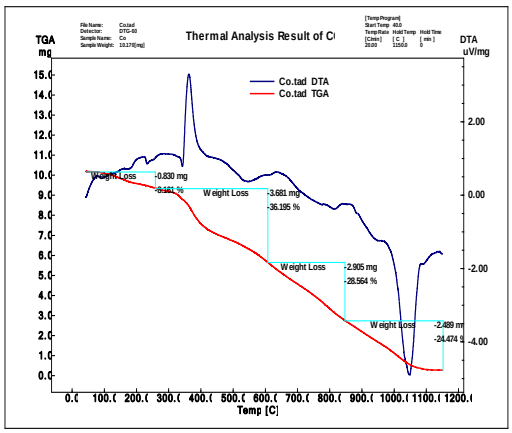


Fig.- 9 TGA of Ni(II) complex

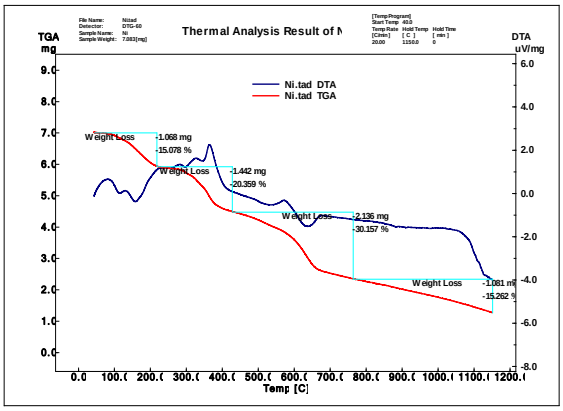


Fig.- 10 TGA of Cu(II) complex

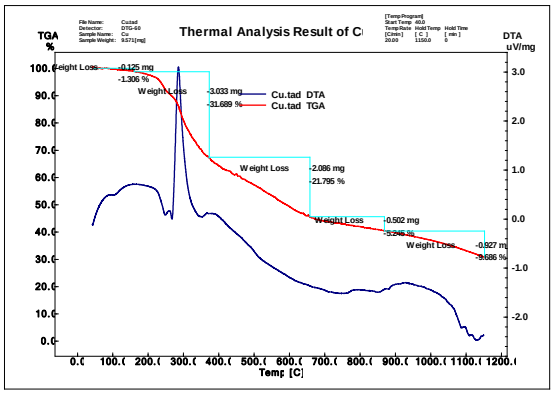
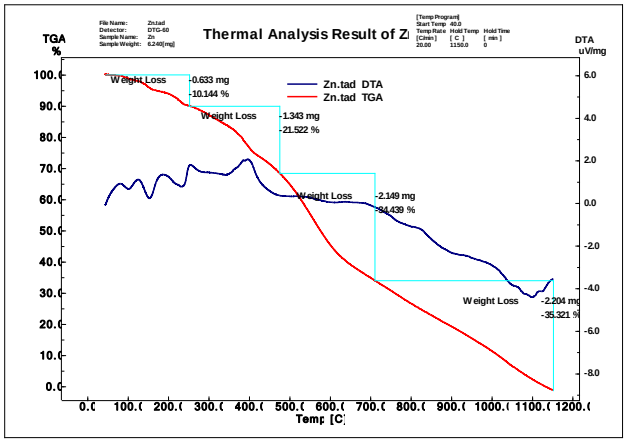


Fig.- 11 TGA of Zn(II) complex



Conclusion:

Salicylaldehyde Schiff base and its complexes were successfully synthesized by a simple condensation method. The yield of dark orange color of the Schiff base was directly proportional to the time of synthesis. The degree of completion. A high concentration of 3,5-dichlorosalicylaldehyde made the product more viscous and the color of the solution brighter. The structure of ligand and complexes had been confirmed with a mass fragmentation pattern. Two peaks at equal intensity in ligand mass spectra show isotopes at m/z 267 and 269. TGA gives the characterization regarding composition. A change in mass at a particular temperature removes a small gas molecule. DTA indicates the decomposition type whether it is endothermic or exothermic.

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