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RESEARCH ARTICLE

Synthesis, Characterization, Analytical ,Thermal Analysis Studies of Schiff Base And Their Metal Ion Complexes

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Abstract

The research includes preparation of Schiff bases of salicylidene[4-Bromo aniline & 3—Bromo aniline] derived from condensation reaction of substituted aniline with salicylaldehyed .

. The identity of this ligand and its metal (Ni^{+2} &Co^{+2}) ions complexes have been characterized by elemental analysis ,UV –Vis. ,FTIR&thermal analysis .The IR &UV-Vis.spectral data suggest that ,the ligand behaves as didentate ligand towards the central metal ion with nitrogen donor atoms .From UV –Vis. Data the stoichemsitry of complexes (1:2)(M:L) was found .The thermal behaviour (TGA)of complexes was studied and thermodynamic parameters were determined by Horowitz –Metzger

INTRODUCTION

In recent years ,there have been chanced interest in synthesis and importance as catalysts in many reactions .[1-2]Several studies showed that the presence of lone pair of electrons in Nitrogen atom of the azomethine group is of considerable chemical and biological importance .Because of the relative easiness of preparation .[3-4]Schiff base are generally excellent chelating agents especially when a functional group like –OH- or SH- is present[5-6]close to the azomethine group so as to form a five or six member ring with the metal ion .Schiff base resulted from aromatic aldehyedes ortho-substituted with a hydroxyl group have initially arouse the researchers interest because of their ability to act as didentate ligand for transitional metal ions[7-8].In studies concerning quantitative structure antitumor activity relationship of a series of Schiff bases derived from variously substituted aromatic amine and aldehyedes .It has been shown that azomethine from salicylaldehyedes gave the best correlation .[9-10]The aim of our study is to prepare organometallic compounds from Schiff bases and measure from thermal analyesis (TGA) studies, thermodynamic parameters were calculated .

2-1-Material &Instrumental:-

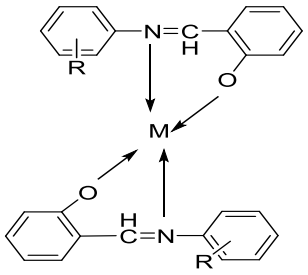
All chemical and solvent were purchased from (Fluka &B.D.H)
Chemical companies metal salt as Acetate, The dehydration 0f salts carried out by during in oven for several hours at (100 -110)^0 C .Apparatus for analysis and physical measurement used *Melting point were recorded on Vec .GVP igitial model VMP –D (Jenway) .*FTIR spactra were recorded using SHIMADZU –FTIR -8400S- Gapan. *Elemental analysis CHN carried out by Perkin Elmer -2400 series II USA. *UV –Vis. Spectra were recorded on UV-Vis 9200BI OTECH ENGINEERING .MANA GEMENT Co. LTD (UK)single beam .*Thermal analysis (TGA) carried out by Perkin Elemer TGA-7 (USA).*dddDSC /PERKIN –ELEMER DSC-6 (USA).

2-2 **General procedure for synthesis of Salicylidene[** 4-**Bromo-aniline(I)& 3-Bromo aniline(II)]** :- The Schiff bases (I&II) was prepared by condensation of equimole of (0.344 g / 0.02 mmole) of substituted aniline and Salicyialdehyed (0.244 g / 0.02 mmole).Each reactant (was dissolved in warm (10 ml) ethanol. Then mixed together

followed by adding two drops of glyacial acetic acid , Refluxed for 2h. Then solid product was collected through filtration and then the product was recrystallized by ethanol and then dried [11].

2-3-1 **Preparation of Schiff base transition metal complexe**s :- An ethanolic solution of (1mmole) of salicyldene[4 –Bromo-aniline (I) &3-Bromo- aniline (II)] was added to ethanolic solution of (0.5 mmole)of $Ni(Ac)_2$,The mixture was stirred ,refluxed for 2h. The solid crystal was obtained ,filtered ,washed with ethanol then dried.[12]

2-3-2:- An ethanolic solution of (1mmole)of salicyldene **[** 4- Bromo –aniline (**I**) & 3-Brom-aniline (**II)]** was added to ethanolic solution of (0.5mmole) of $Co(Ac)_2$,The mixture was stirred ,refluxed for 2h. The solid product was obtained, filtered , washed with ethanol then dried.

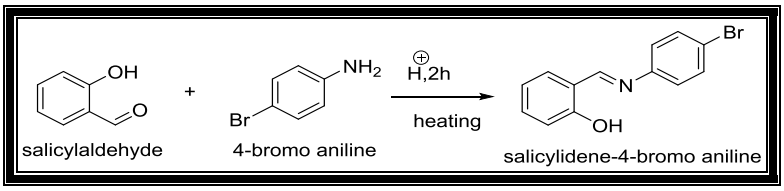


M = Ni , Co

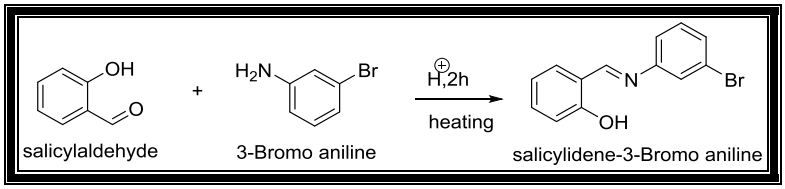
R= **I** = P-Br & **II**=m -Br

The Suggest Structure of Schiff Base Metal Ion Complexes

3- Result &Discussion :-



Equation (1) preparation of Schiff base **I**



Equation (2) preparation of Schiff base **II**

All the synthesized compounds were purified by successive recrystallization using ethanol .The structures of these compounds were determined by the basis of their FTIR –spectra ,CHN analysis & UV-Vis. Spectra .

3-1:-**IR-SPECTRA** :-The IR spectra of the Schiff base showed the presence of (C= N) stretching band at (1606-1610) and disappearance of aldehyed grouo (HC=O)which appear at position (1700-1720)cm^{-1}& disappearance of amine group at position (3100-3300)cm^{-1} for (I&II). Complexes are compared with that of the Schiff base ligand to determine the changes that might have taken place during complexation. The most important bands are shown in Table (1) for the ligand and their (Ni &Co)metal ion complexes [13]

compound	color	Yield %	m.p	K stability	% founded (calculated)			
					%C	%H	%N	%res.
LI	yellow	82	73	-	57.91 (57.95)	4.29 (4.14)	4.90 (4.93)	31.96 (32)
$Co(LI)_2$	purple	67	243	1.7×10^8	51.5 (51.75)	3.56 (3.45)	4.44 (4.39)	39.46 (39.41)
$Ni(LI)_2$	green	86.7	>300	3.4×10^8	52.63 (52.75)	3.32 (3.45)	4.5 (4.39)	39.58 (39.41)
LII	orange	89.3	93	-	73.05 (73.00)	5.858 (5.73)	6.20 (6.10)	13.932 (14.1)
$Co(LII)_2$	gray	64	240	2.6×10^8	65.6 (65.75)	4.75 (4.70)	5.5 (5.48)	24.15 (24.07)

Ni(LII)$_2$	Sprig green	80.6	178	1.2×10^8	64.62 (64.75)	4.65 (4.70)	5.45 (5.48)	24.28 (24.07)

Note: L_1 = $C_{13}H_{10}ONBr$, N1=C_7H_8NBr

Table (2) The most significant IR-band of ligand and its metal com

compound	NH_2	C-H alphatic	C=N	C=O	C=C	C-H aromatic
S	-	-	-	1735	1575	3130
N1	3473&3381	2850	-	-	1590	3059
L_1	-	2830	1616	-	1610	3188

Note: L_1 = $C_{13}H_{10}ONBr$, N1=C_7H_8NBr , S=Salicylaldehyde

3-2: **Spectrophotametrically** study obtain the clue about the stability &stiochemistry of Schiff base complexes with (Ni&Co) ions .using the concentration of Schiff base ($1x10^{-4}$)M in ethanolic solution was kept constant [14] .And the UV-Vis. Spectra using mole ratio & continuous variation methods were recorded until desired mole ratio was reached the data are consistent with the empirical formula of each compound. And the analytical data of complexes confirm formation of stable (1:2)(M:L) and corresponds well with the general formula [15].

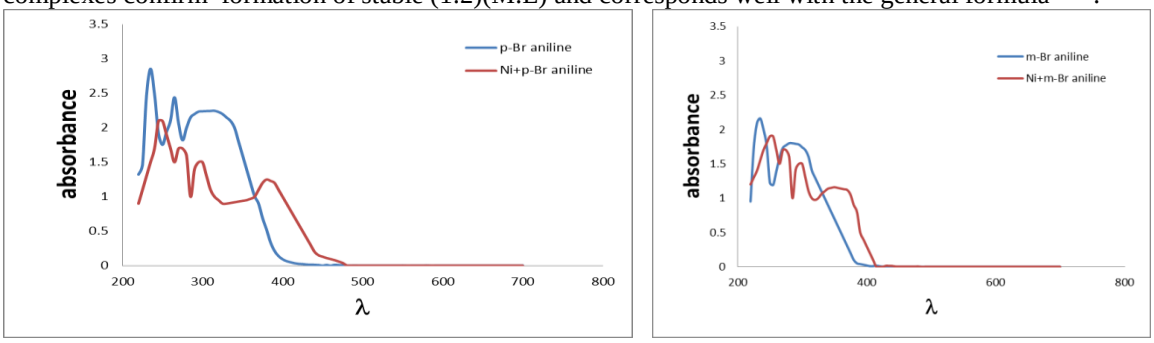


Fig (1&2) UV-Vis. Spectra for Schiff base(II&I) their Ni metal ion complexes.

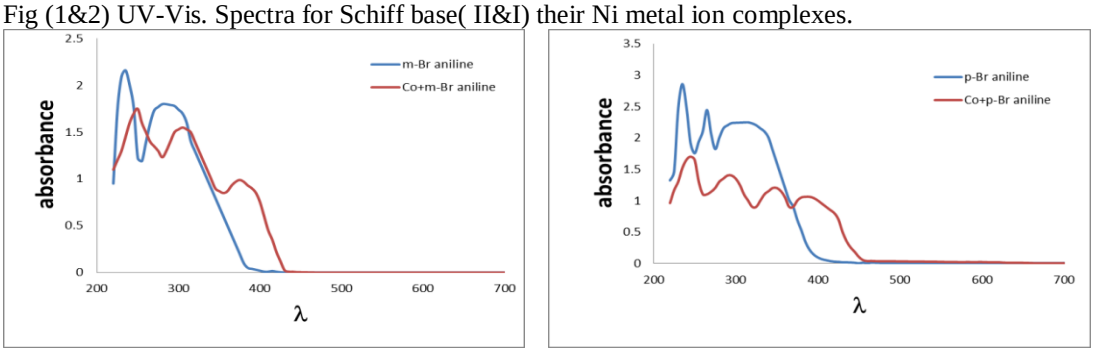
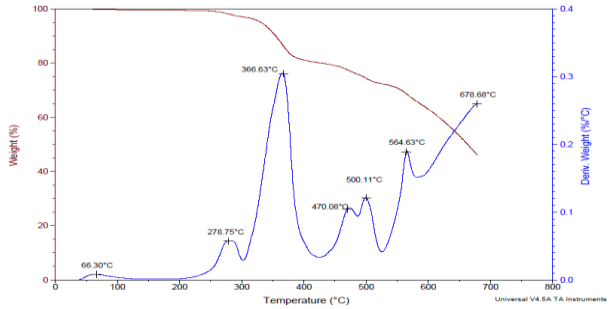


Fig (3&4) UV- Vis. For Schiff base (II &I)their Co metal ion complexes.

:-The elemental analytical data of the compounds shown in table (2) **3-3: CHN analysis** Indicate that Schiff base formation has occurred in 1:1 ratio as in structure (1) and they formed stable complexes with (Ni & Co) . The result data of CHN analysis good support for the structure of prepared Schiff base and it is very near to the calculated values .

3-4 : -Thermogravimetric Analysis:- The dynamic TGA with the percentage mass loss at different steps have been recorded. The simultaneous TG analysis of [Ni^{+2}&Co^{+2}]complexes was studied from ambient temperature to 1000C^0in nitrogen atmosphere [16]. The analysis of the thermogram of complexes indicated that Co-complexes shows five-step decomposition with Schiff base **I** ,The decomposition is completed leading to the formation of stable residue of metal oxide (CoO).Where as with Schiff base **II** shows four-step decomposition .On othere hand Ni-complexes shows three step decomposition with Schiff base**I** .Same as Ni-complexes with Schiff base **II** shows four step decomposition .

The thermal degradation of Co(L**I**)$_2$:-



Fig(5):thermal degradation of Co-P-br

$C_{26}H_{18}O_2N_2Br_2Co + O_2 \longrightarrow C_{25}H_{18}0_2N_2Br_2Co + CO$

$C_{25}H_{18}O_2N_2Br_2Co + O_2 \longrightarrow C_{24}H_{16}O_2N_2Br_2 + CO_2 + H_20$

$C_{24}H_{16}O_2N_2Br_2 + O_2 \longrightarrow C_{23}H_{16}O_2Br_2Co + N_2 + CO$

$C_{23}H_{16}O_2Br_2Co + O_2 \longrightarrow C_{22}H_{14}O_2Br_2Co + H_2 + CO$

$C_{22}H_{14}O_2Br_2Co + O_2 \longrightarrow C_{22}H_{10}O_2Br_2Co + 2H_2O$

The thermal degradation of $Co(LII)_2$:-

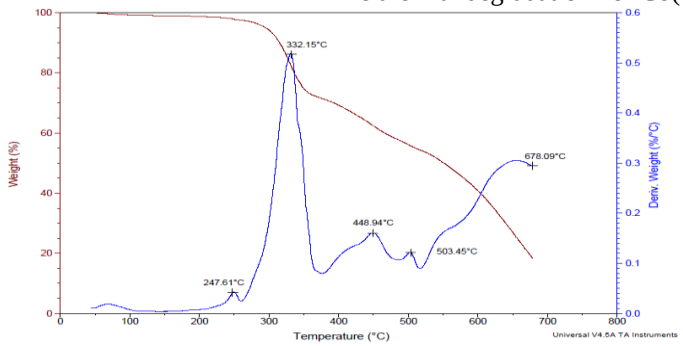


Fig (6): thermal degradation of Co +m Br

$C_{26}H_{18}O_2N_2Br_2Co + O_2$ ------- $C_{25}H_{18}O_2Br_2Co + CO_2 + N_2$

$C_{25}H_{18}O_2Br_2Co + O_2$ --------- $C_{22}H_{16}O_2Br_2Co + H_2O + CO_2 + 2CO$

$C_{22}H_{16}O_2Br_2Co + O_2$ -------- $C_{22}H_{12}O_2 O Br_2Co + 2H_2$

$C_{22}H_{12}O_2Br_2Co + O_2$ ------- $C_{20}H_{10}O_2Co + CO + CO_2 + 2HBr$

The thermal degradation of $Ni(LI)_2$:-

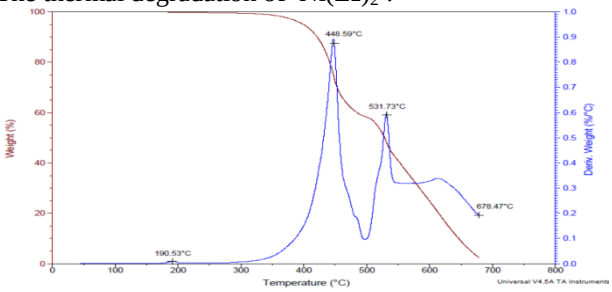


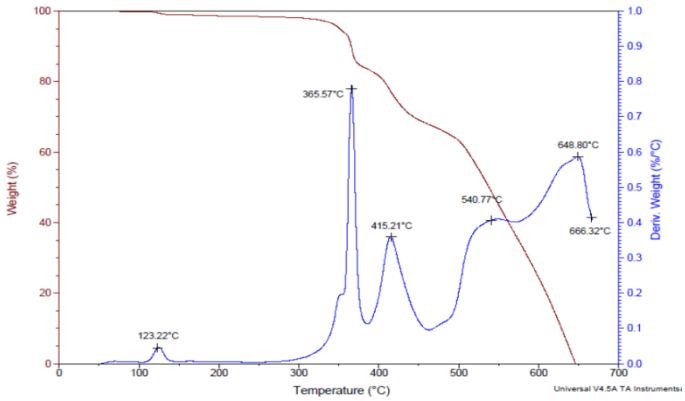
Fig (7) : thermal degradation of $Ni(LI)_2$

$C_{26}H_{18}O_2N_2Br_2Ni + O_2$ -------- $C_{25}H_{18}O_2Br_2Ni + N_2 + CO$

$C_{25}H_{18}O_2Br_2Ni + O_2$ -------- $C_{25}H_{15}O_2Br_2NI + HBr + H_2O$

$C_{25}H_{15}O_2BrNi + O_2$ -------- $C_{23}H_{14}O_2Ni + 2CO_2 + HBr$

The thermal degradation of $Ni(LII)_2$:-



Fig(8) : thermal degradation of $Ni(LII)_2$

$C_{26}H_{18}O_2Br_2Ni + O_2$ -------- $C_{25}H_{18}O_2Br_2Ni + N_2 + CO$

$C_{25}H_{18}O_2Br_2Ni + O_2$ -------- $C_{23}H_{14}O_2Br_2Ni + 2CO + 2H_2O$

$C_{23}H_{14}O_2Br_2Ni + O_2$ --------- $C_{21}H_{13}O_2BrNi + HBr + 2CO$

$C_{21}H_{13}O_2BrNi + O2$ ---------- $C_{18}O_2Ni + 4H_2 + 2CO + 2H_2O + HBr$

The thermodynamic parameters { ΔG , ΔS , ΔH } for the decomposition have been determined by Horowitz – Metzger methods,[17]The values are given in table (3).

Table (3) Thermodynamic parameters of metal complexes.

	K	**ΔH(J)**	**ΔG(J)**	**ΔS(J.K^{-1})**
Ni + II	0.074	38244	16709	**27.9**
Co + II	0.049	19953	19280	**0.9**
Ni + III	0.090	11877	15424	**-4.6**
Co + III	0.055	60692	18573	**54.5**

CONCLUSION :-

In the light of above discussion we have proposed on the basic of the physic- chemical and spectral data discussed above one can assume that the ligand behave as very stable didentate ligand .

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