Synthesis of Schiff bases of Isatin and 5-bromoisatin with 2-aminobenzyl amine and their complexes

***Alaa M .Ali* Saher A. Ali , Ibrahim A.FliflandHaider A.M**

Department of chemistry ,College of Science,Thi-QarUniversity ,Iraq

Sahir_21211@yahoo.com

Abstract

The present work include preparation of two new Schiff bases formed from the condensation of2-aminobenzylamine with isatin and 5-Bromoisatin. Complexes of Nickel(II),Cobalt(II) and Chrome(III)with these Schiff bases were prepared .these compounds and theirs Complexes were characterized by elemental analyses and FT-IR ,^{1}HNMR and Mass spectra .the analyses of Ni(II),Co(II), Cr(III)Complexes are six-coordinate and have octahedral structure.

Keywords: Schiff base ,isatin,2-AminoBenzayl amine, complexes Schiff bases

Introduction: Schiff bases are condensation products of primary amines with carbonyl compounds and they were first reported by Schiff [(1)]in 1864.Schiff base ligand is a compound that contains a carbon-nitrogen double bond, with the nitrogen atom connected to an aryl or alkyl group. The general formula of Schiff base is R-CH=N-R' where R and R' is an alkyl or aryl group[(2)] .The most common way to get the rules of disclosure is a method of Condensation reaction between carbonyl compounds (Aldehydes or ketones) aliphatic or aromatic with primary amines (aliphatic or aromatic) and using reflux distillation process with a suitable solvent and for a period of time and which stimulates the interaction in the presence of drops of acid [(3)] such as (CH_3COOH) .has been studied mechanical interaction by many researchers have interpreted that the acid gives Proton to set the carbonyl in order to form ion Alcarboneom then amine added to the ion carboneom by very quick step and the speed selected step is the step of removal of the proton (Deprotonation) from the compound of the Central formation Alcarpinol amine and who is unstable and quickly lose water molecule to form Schiff base[(4)] .Schiff bases Characterized by susceptibility on the composition of metallic complexes and complexes Schiff bases are of great importance as a result of the many applications in many areas including industrial areas [(5)].In the pharmaceutical industry for this used as antidepressants for many diseases work being anti-spasm and as well as blood pressure reducers[(6)] and as anti-inflammatory [(7)] And anti-TB [(8)]

Physical Measurement and analysis:-

Melting point on(point/SMP31Melting) .

FT-IR spectro were recorded using(ShimadzuFTIR-spectrometer).

Micro analytical data for(C.H.N) were obtained using(Thermofinigan flash) .

MolarElectricalconductivitywere obtained using(Inolabcond720).

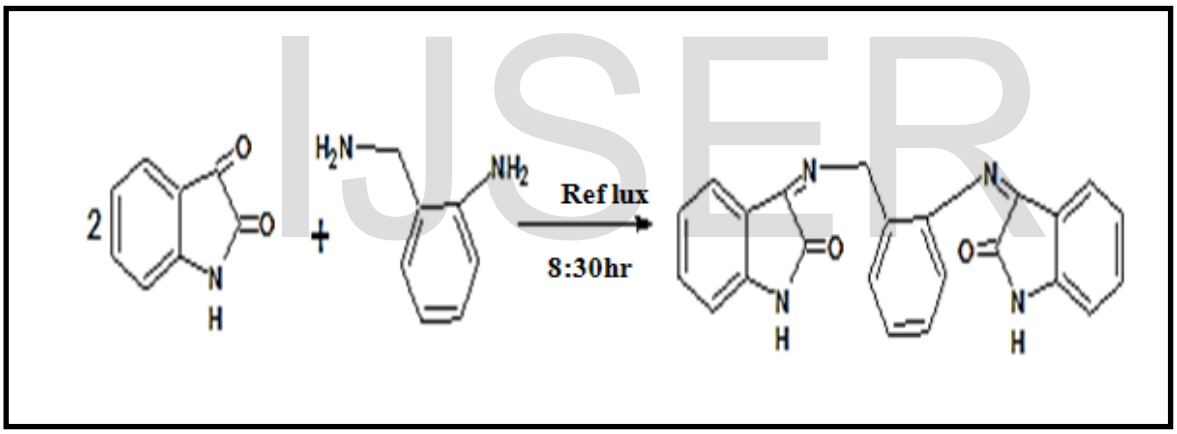
Nuclear Magnetic Resonance Spectra were obtained usingBruker DRX System AL500(500MHZ)
.

Mass Spectra were obtained using (Work mass selective Detector) 5973.

Electronic Spectra Measurement were obtained using(Uv-1650PC [Uv-visble] Spectrophotometer] .

Synthesis of Schiff base(L_1)

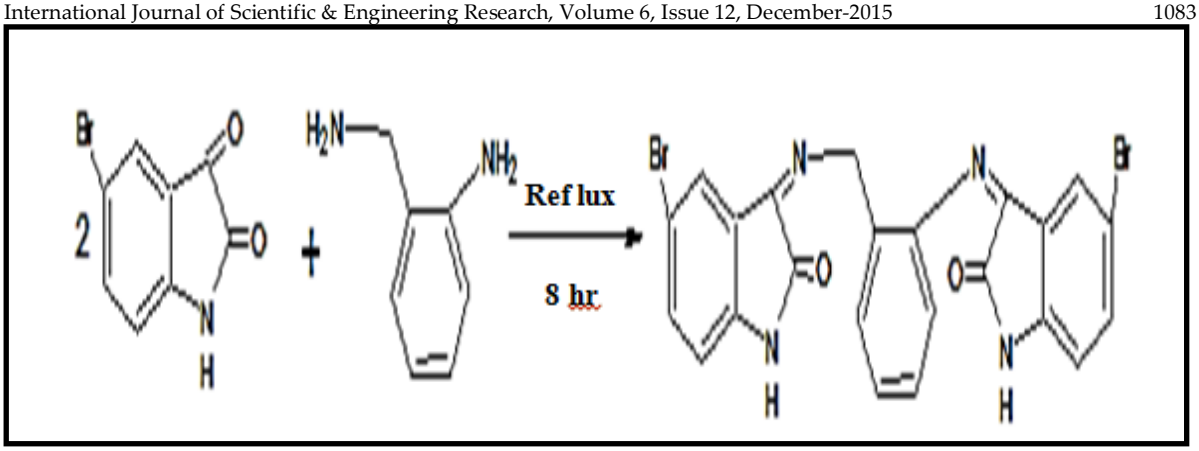
"(z)-3-(2-((z)-2-oxoindolin-3-ylideneamino)benzylimino)indolin-2-one"
In round bottomed flask with capacity of (250 ml). (0.002mole-0.3gm)of isatin was dissolved by 30ml of ethanol.with adding of 2-3 drops of glacial acetic acid .then gradually adding (0.001mole -0.12gm)of2-aminoBenzylamine dissolved in 10ml of ethanol . The reaction mixture was refluxed for (8-9)an hour at the refluxing temperature. and the product obtained was recrystallized from ethanol[9] .and the result of reaction (61.13%) the synthesis of Schiff base is schematically present at scheme 1 .



Scheme 1: **Condensation reactions for the preparation of the L_1**

Synthesis of Schiff base(L_2)

(z)5-bromo-3-(2-((z)-2-oxoindolin-3-ylideneamino)benzylimino)indolin-2- one
In round bottomed flask with capacity of (250 ml) the isatin (0.002mole-0.45gm)was dissolved by 30ml of ethanol.with adding of 2-3 drops of glacial acetic acid.then gradually adding (0.001mole -0.12gm)of2-aminoBenzylamine dissolved in 10ml of ethanol . The reaction mixture was refluxed for (8-9)an hour at the refluxing temperature. and the product obtained was recrystallized from ethanol[9] .and the result of reaction (61.13%) the synthesis of Schiff base is schematically present at scheme 2.



Scheme 2: Condensation reactions for the preparation of the L_2

Synthesis of complexes :-

To 20 mL of ethanolic solution of Schiff base ligands (0.001 mol) was added drop wise to (10mL)of ethanolic solution of(0.001mol){(Nikle(II) ,cobalt(II),chrom(III)} chlorides and refluxed for(8-9 h). and the product obtained was recrystallized from ethanol[10] .

Table(1): Some physical properties of the prepared complexes (L_1)

number	FormulaMolecular	M.Wt	Color	M.P(C°)	Yield(%)
1	$C_{23}H_{16}N_4O_2$	380	Brown Red	156-154	65
2	$[Ni(L_1)CL_2]$	510	Darkbrown	180-182	64
3	$[Co(L_1)CL_2]$	510	Dark brown	165-163	68
4	$[Cr(L_1)CL_2]CL$	538	Black	175-177	61

Table(2): Some physical properties of the prepared complexes (L_2)

number	FormulaMolecular	M.Wt	Color	M.P(C°)	Yield(%)
1	$C_{23}H_{14}Br_2N_4O_2$	538	Light brown	160-162	70
2	$[Ni(L_2)CL_2]$	667	Black	181-182	72
3	$[CO(L_2)CL_2]$	668	Light brown	172-174	68
4	$[Cr(L_2)CL_2]CL$	696	Dark brown	188-189	65

Results and discussion

Elemental Analysis*:*

Selected Schiff bases were analyzed for carbon, hydrogen, nitrogen and. The results of the C.H.N. analysis were in a good agreement with the suggested formula Table (3).

Table3*:* Elemental microanalysis Data of Schiff bases (L_1 ,L_2)

Compound	Theoretical Data			practical Data		
$(L_1)C_{23}H_{16}N_4O_2$	N %	H %	C %	N %	H %	C %
	14.73	4.24	72.62	14.92	4. 41	73.08
$(L_2)C_{23}H_{14}Br_2N_4O_2$	10.41	2.62	51.33	10.37	2.75	51.66

IR Spectra: The IR spectra for the Schiff base ligand and its metal complex are shown in Table (4).

Table 4. Infrared data of the Schiff bases and metal complexes

symbol	Compound	N-H	C-H Alipha (Ar)	C=O	C=N	C-O	C=C	M-N	M-O	M-Cl
L_1	$C_{23}H_{16}N_4O_2$	3244	2959 3059	1735	1616	1188	1473	.....	.....	.....
A	$Ni(L_1)Cl_2$][	3227	2959 3059	1740	1623	1192	1465	567	455	281
B	$(L_1)Cl_2$]Co[	3297	2950 3059	1748	1627	1192	1469	570	455	258
C	$(L_1)Cl_2]ClCr$[	3247	2909 3051	1748	1620	1199	1454	520	455	293
L_2	$C_{23}H_{14}Br_2N_4O_2$	3267	2904 3056	1732	1616	1195	1469	.....	.....	.....
A	$Cl2]Ni(L_2)$[	3278	2900 3057	1740	1626	1195	1462	570	459	285
B	$Co(L_2)Cl_2]$ [	3278	2959 3052	1740	1619	1195	1465	563	455	279
C	$[Cr(L_2)Cl_2]cl$	3232	2960 3052	1741	1621	1195	1458	524	462	293

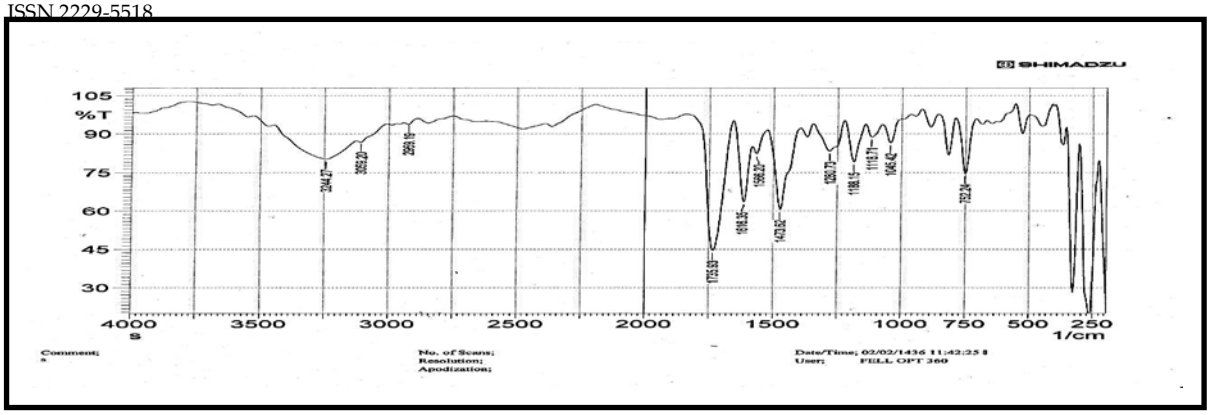


Figure 1: IR spectrum of $L_1(C_{23}H_{16}N_4O_2)$

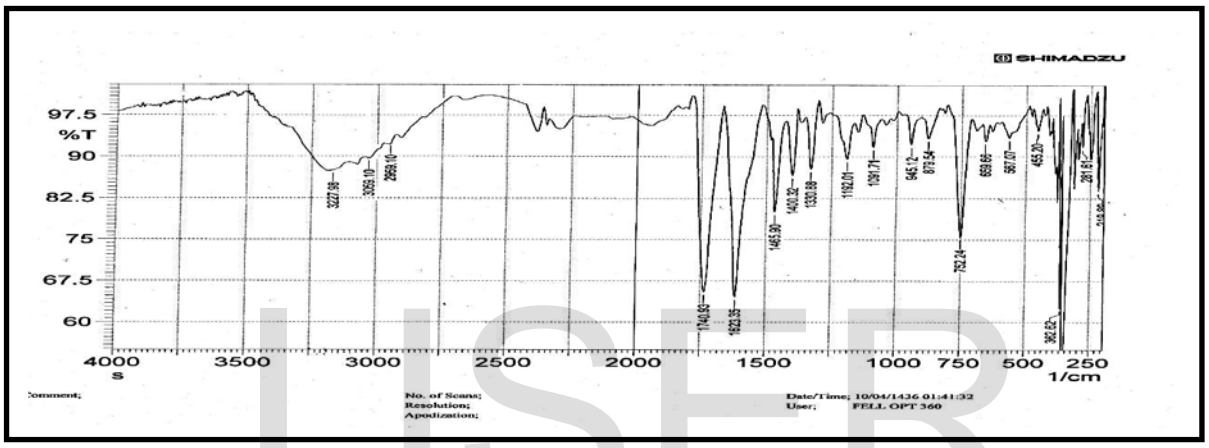


Figure 2:IR spectrum of$[Ni(L_1)Cl_2]$

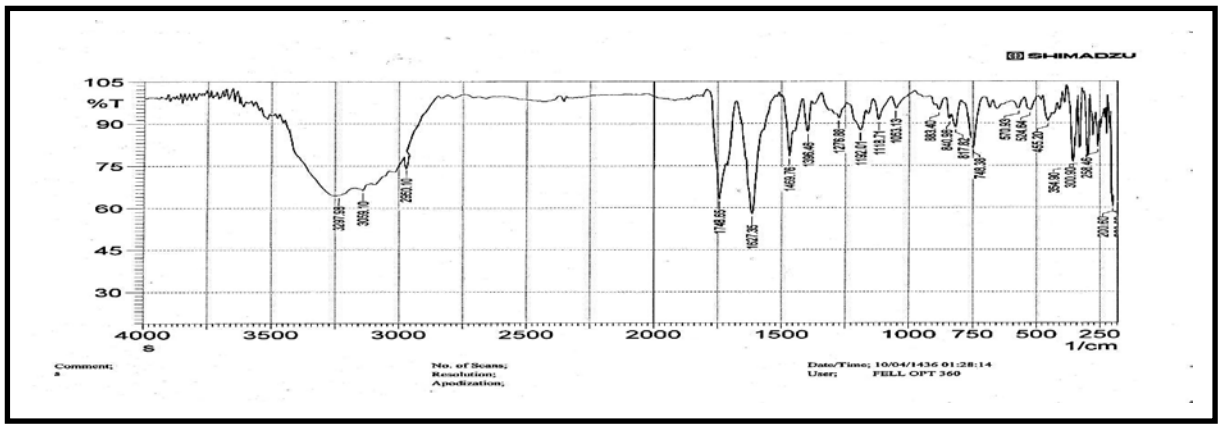


Figure 3: IR spectrum of$[Co(L_1)Cl_2]$

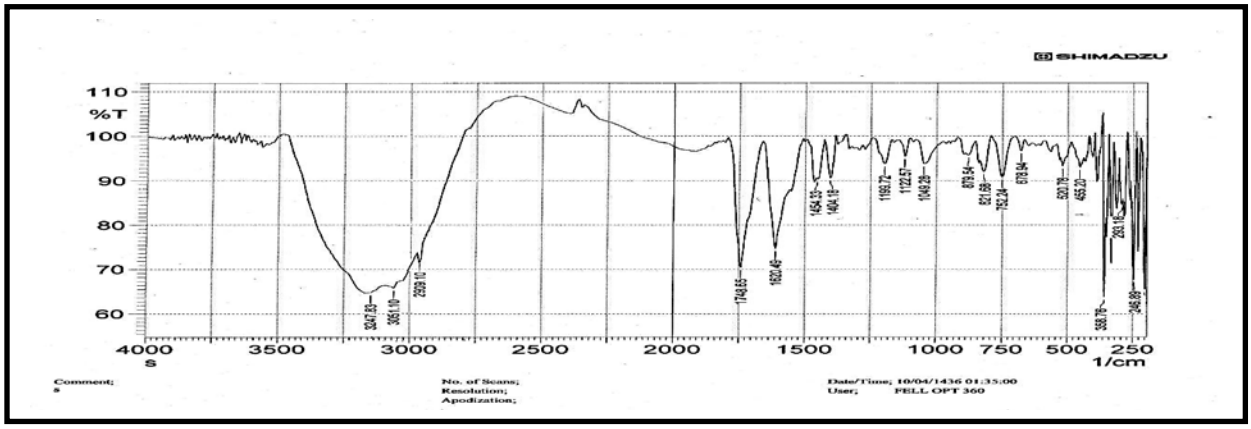


Figure 4: IR spectrum of[$Cr(L_1)Cl_2]Cl$

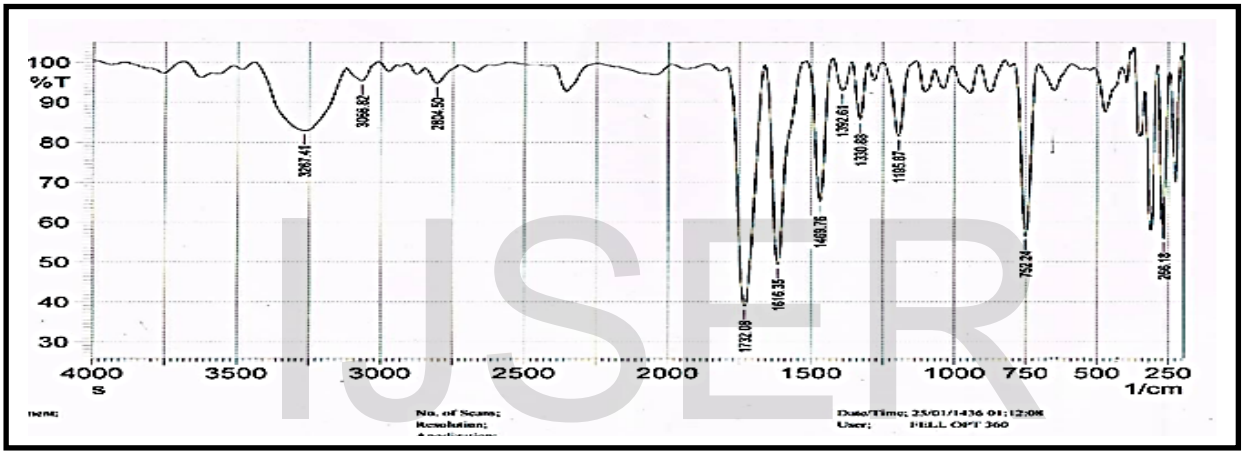


Figure 5: IR spectrum of($C_{23}H_{14}Br_2N_4O_2$

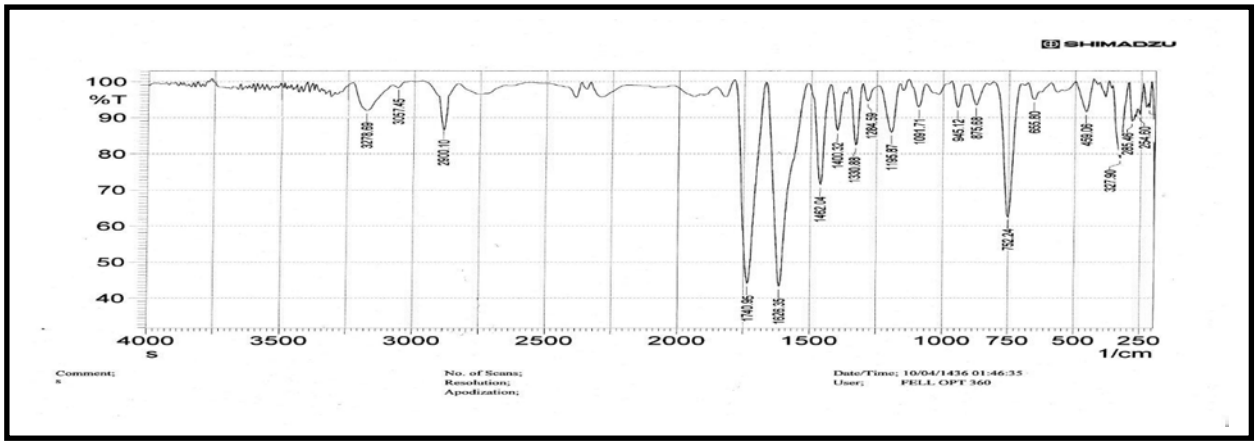


Figure 6: IR spectrum of $Ni(L2)Cl_2$

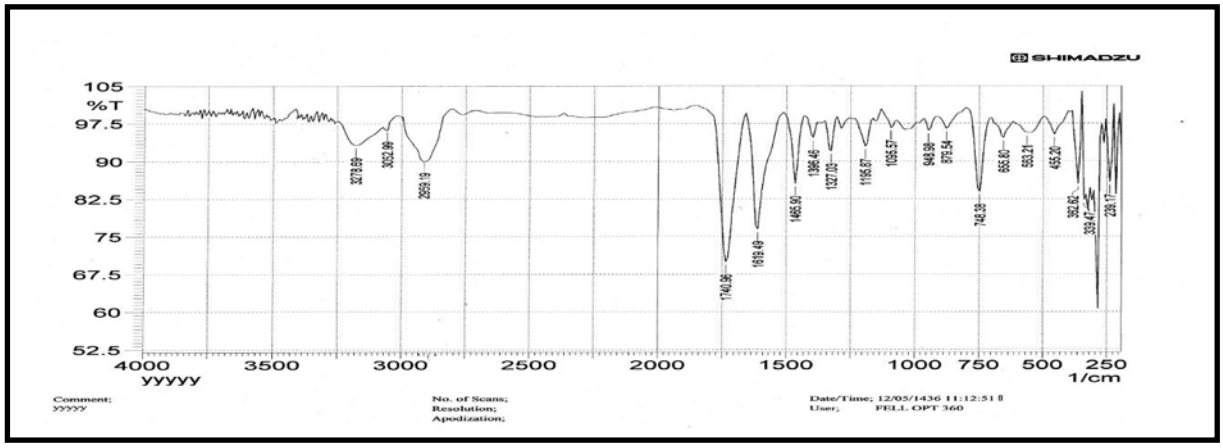


Figure7:IR spectrum of $[Co(L2)Cl_2]$

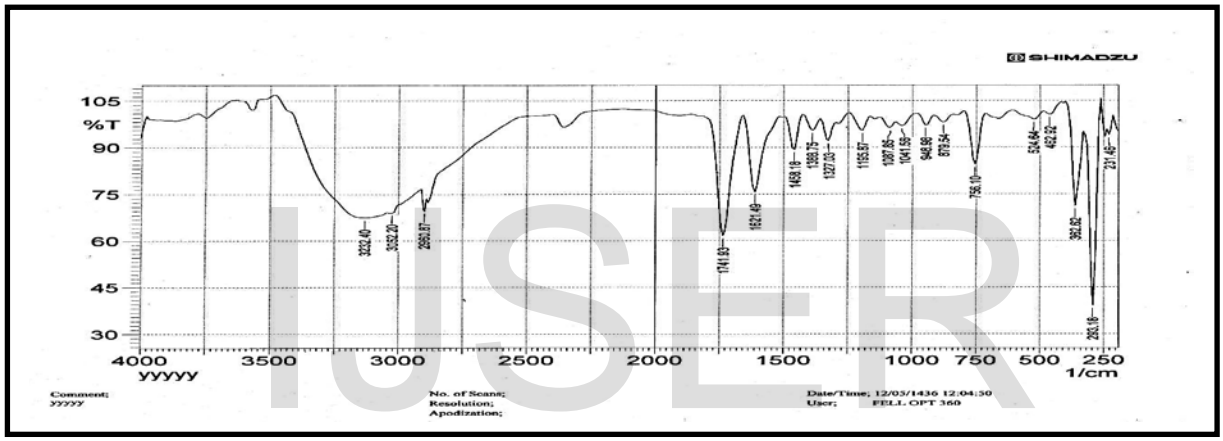


Figure8: IR spectrum of $[Cr(L2)Cl_2]Cl$

Nuclear Magnetic Resonance Spectra (^{1}H-NMR):

The 1H-NMR Spectra of **L_1**showed absorption band at (7.521-8.036) ,(4.731),(2.972) regions resulting from aromatic protons, NH protons, CH2 protons, respectively.

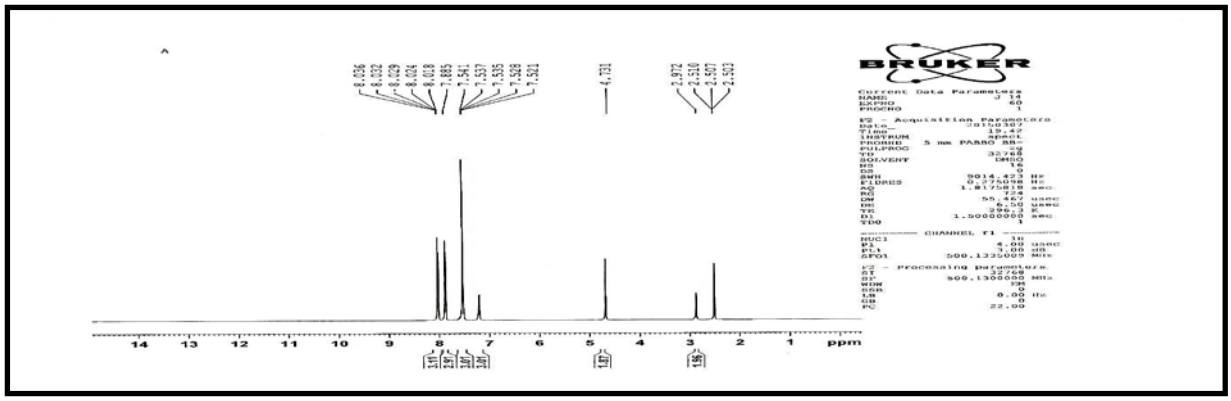


Figure 9. ^{1}H NMR analysis for L_1 ($C_{23}H_{16}N_4O_2$)

The 1H-NMR Spectra of **L_2** showed absorption band at (7.520-8.035) ,(4.729),(2.969) regions resulting from aromatic protons, NH protons, CH2 protons,respectively.

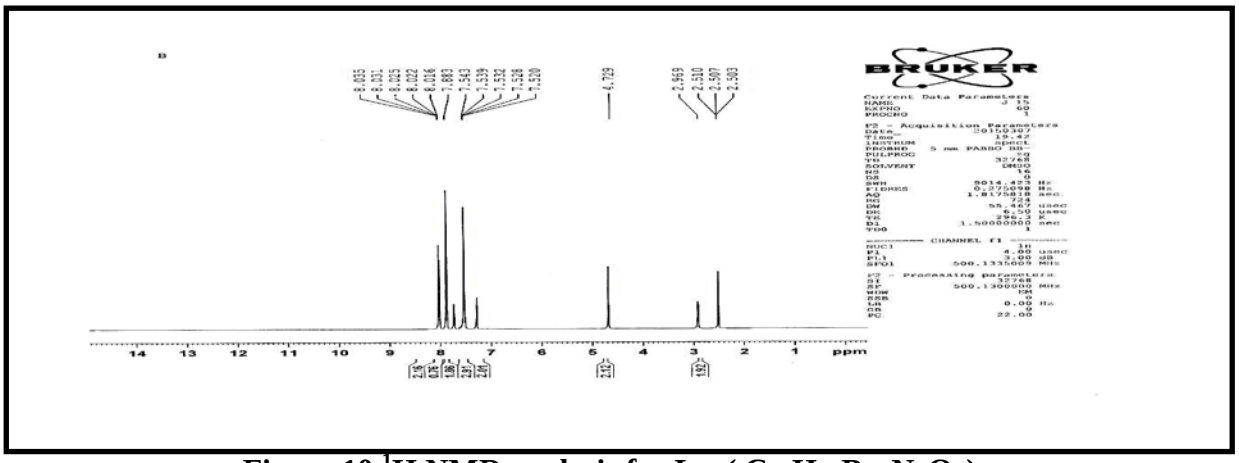


Figure 10.^{1}H NMR analysis for L_2 ($C_{23}H_{14}Br_2N_4O_2$)

Mass Spectra of Schiff bases and complexes:

The mass fragmentation of the free Schiff bases ()and theirs complexes are shown in scheme(3,4) and figures (11-18) .the base peaks at m/e+ 380 and 538 are corresponding to the original molecular weights of the two schiff bases (L_1,L_2)respeetively.

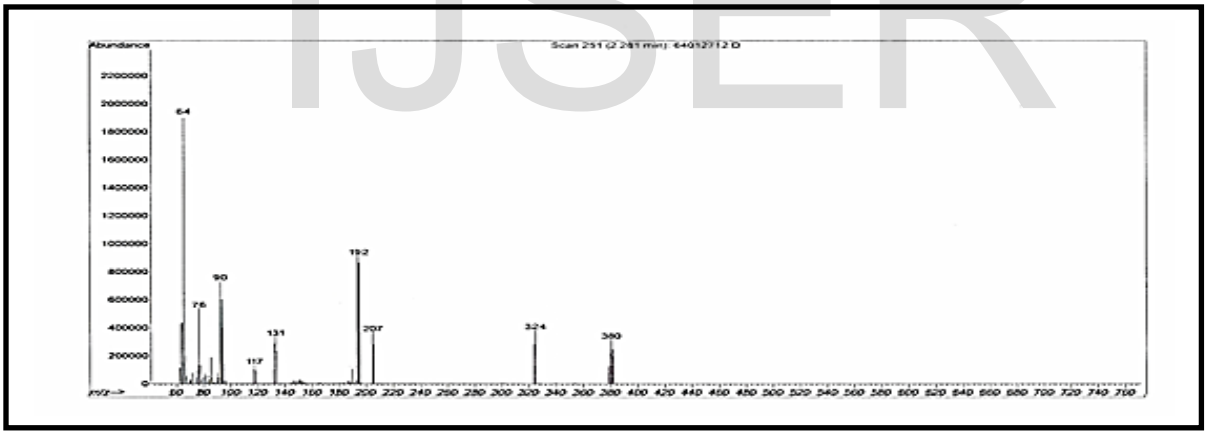


Figure 11:Mass spectrum of L1 :($C_{23}H_{16}N_4O_2$)

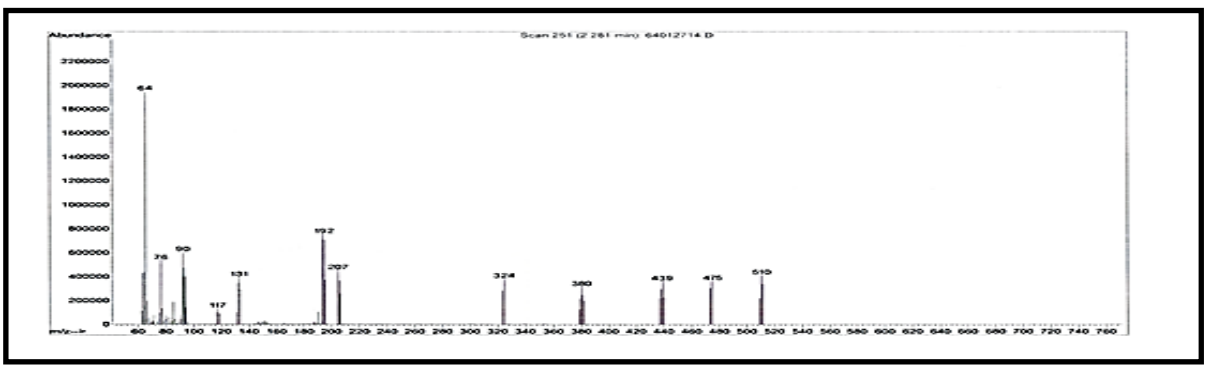


Figure 12:Mass spectrum of [Ni(L1)Cl2]

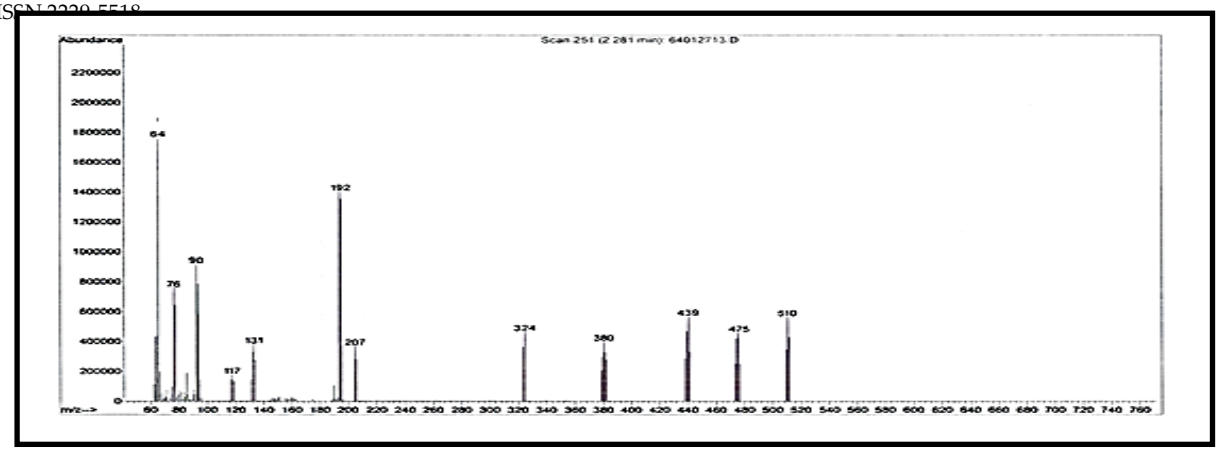


Figure 13:Mass spectrum of- [Co(L_1) CL_2]

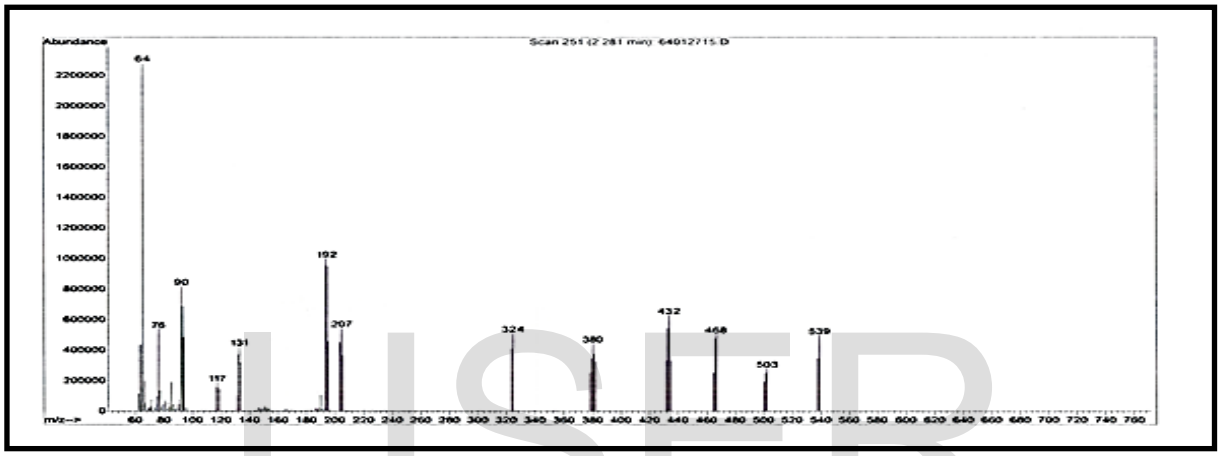
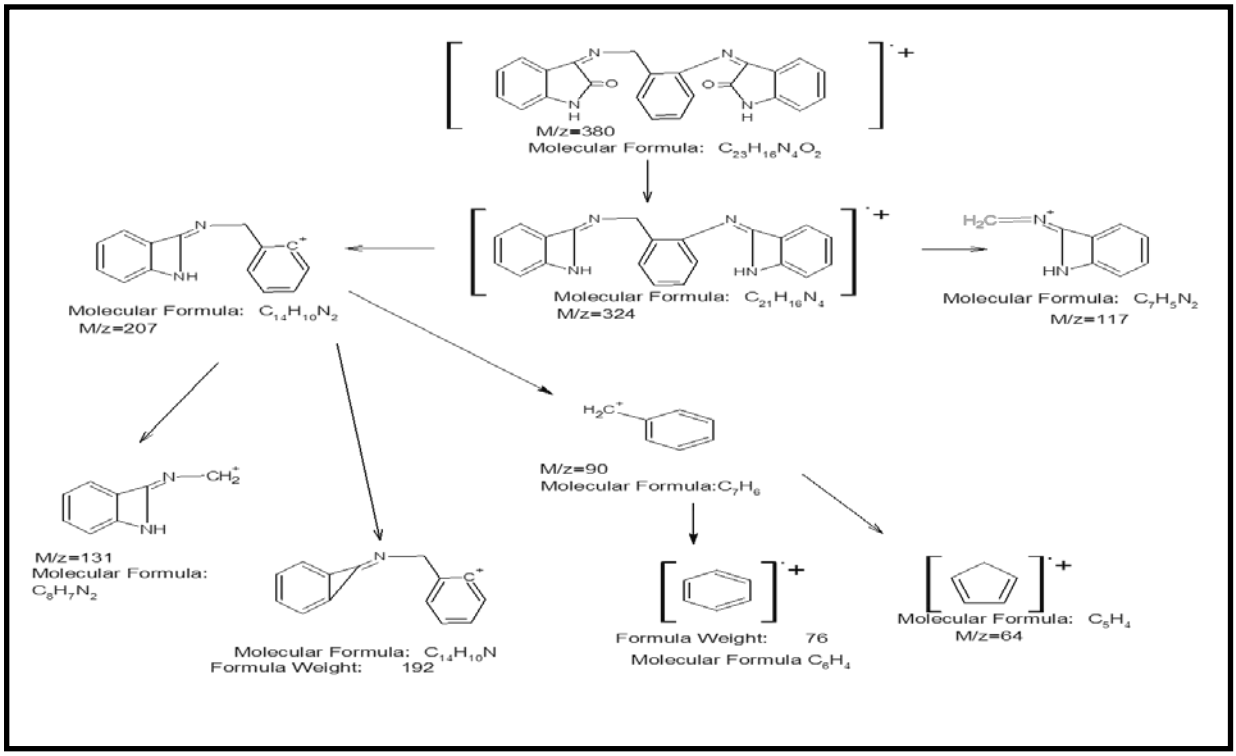


Figure 14 Mass spectrum of: -[Cr(L_1)C l_2] Cl



Scheme(3) :Fissions path mass spectrometer for the(L_1)

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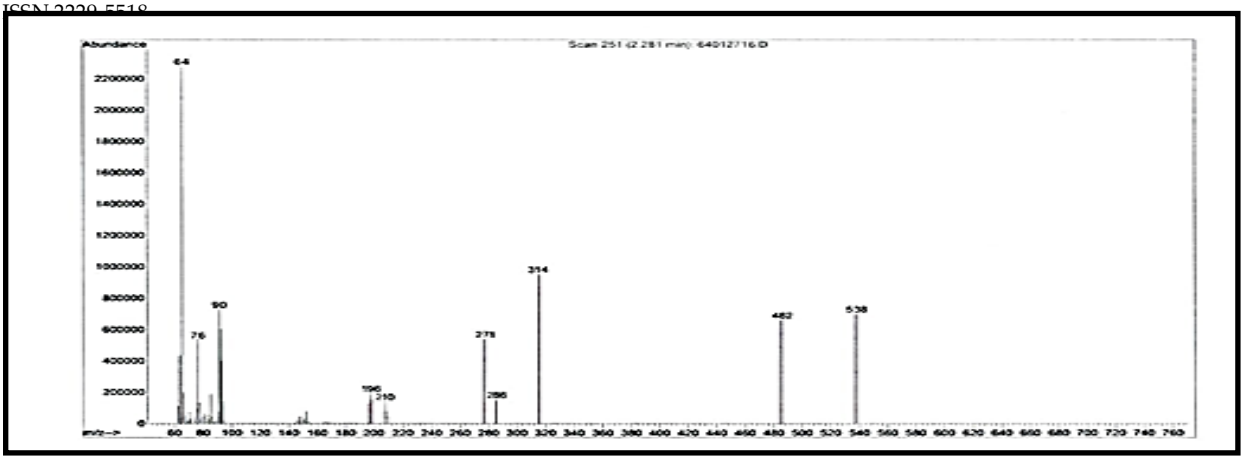


Figure 15: Mass spectrum of L2:($C_{23}H_{14}Br_2N_4O_2$)

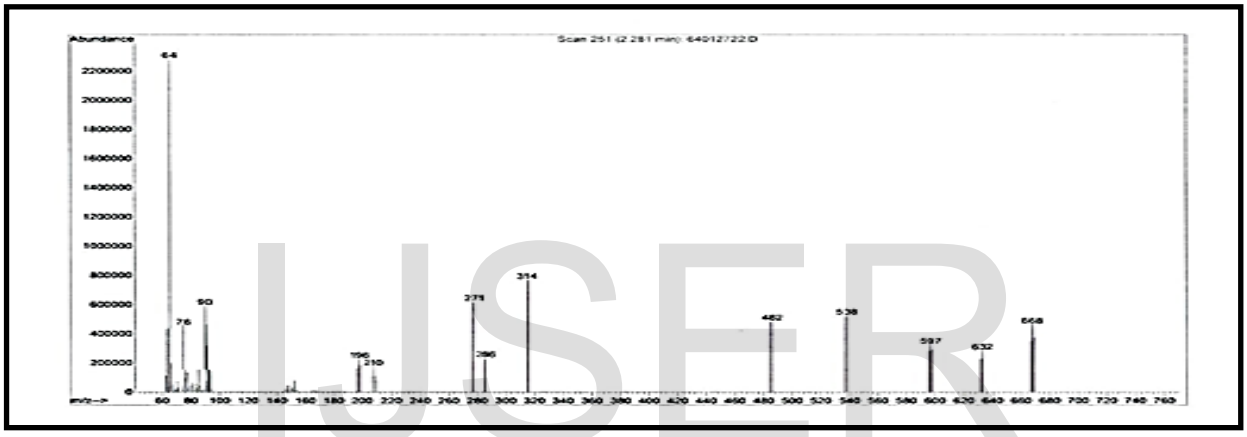


Figure 16:Mass spectrum of: - [Ni(L_2)Cl_2]

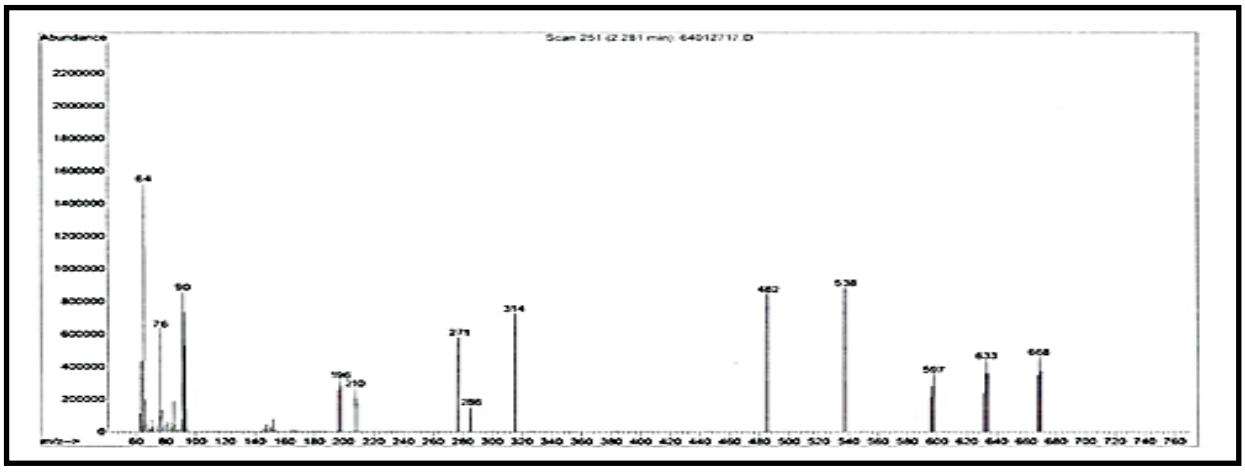


Figure 17:Mass spectrum of : - [CO(L_2)Cl_2]

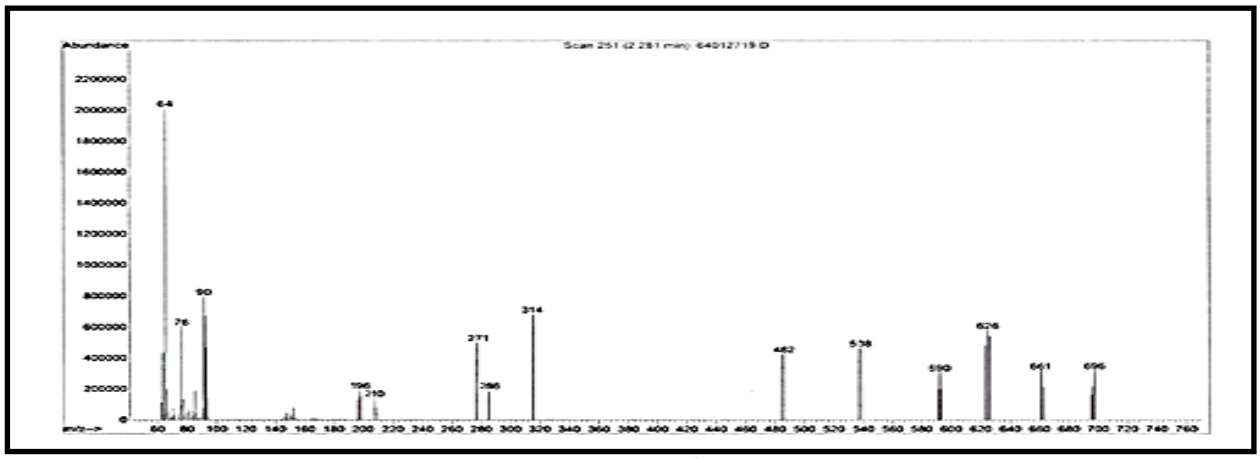
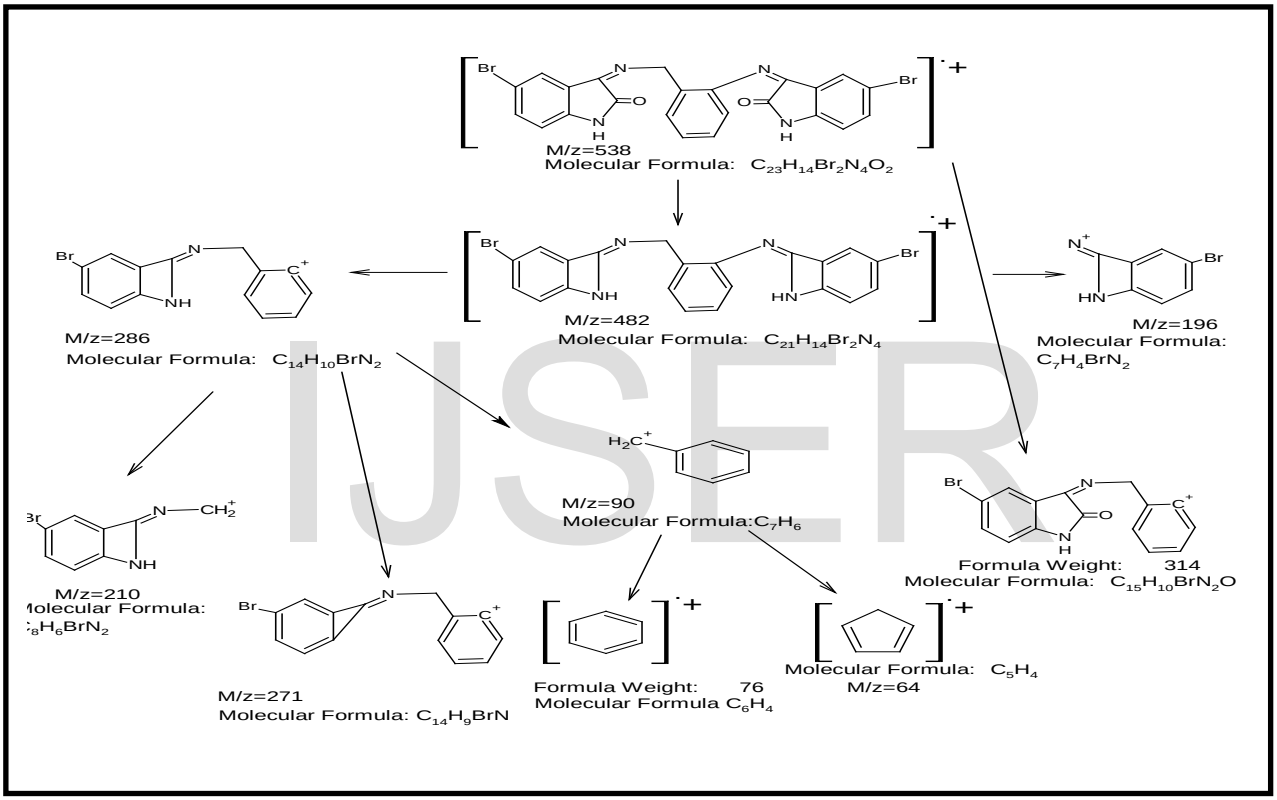


Figure 18:Mass spectrum of : - Cr(L_2)Cl2]Cl



Scheme(4) :Fissions path mass spectrometer for the(L_2)

Molar Conductivity:-

The measurement of molar conductivity for the ionic form of a compound in solution is completed for [Ni(II),Co(II) ,Cr (III)] with the ligand(L_1 ,L_2) and the result is reported in the two table(5,6).

Table(5):Conductivity measurement values of ligand'scomplexes(L_1)at298K. and by using DMSO as solvent.

Complex Number	Complexes	Λm (S .cm^2 .mole^{-1})	Electrolyte
1	[Ni(L_1)Cl2]	12	Non Electrolyte
2	[Co(L_1) Cl_2]	9	Non Electrolyte
3	[Cr(L_1) CL_2]Cl	40	1:1

Table(6): Conductivity measurement values of ligand's Complexes(L_2)at298K^0. and by using DMSO as solvent.

Complex Number	Complexes	Λm (S .cm^2 .mole^{-1})	Electrolyte
1	[Ni(L_2) Cl_2]	18	Non Electrolyte
2	[Co(L_2) Cl_2]	15	Non Electrolyte
3	[Cr(L_2) CL_2]CL	37	1:1

References

1- H. Schiff , Ann , 131 (1864) Citedim , R. W. Layer , *Chem. Rev.*Vol (63) ,pp. 489 **, (1963)**

2- K .Krishnankutty, M. Basheer and P .Ssayudev, *J . Argentine.Chem*Socity. , Vol(96),pp 13 -21 **(2008)**.

3-Mohamed G G .synthesis, characterization and biological activity of bis(phenylamine) Schiff base liqands and their metal complezes,Spectrochim. Acta A Vol(64),pp 188 **(2006).**

4- M.R. Maurya, S.J.J. Titinchi and S.Chand ;"*J.Mol. Catal. (A). Chem.*;" Vol(193),pp165-176, **(2003)**.

5- M. Harikumaran and V. Siji, *J. Indian Chem. Soc.*,Vol(86), pp. 441-448,**(2009).**

6- S. Sengupta, O.Pandey, A.Srivastava, M. Mishra andC. Tripathi, *J. Indian Chem. Soc.*,Vol(85), pp. 247-251,**(2008).**

7- D. Prakash, C. Kumar, A. Gupta, S. Prakash and K. Singh, *J. Indian Chem. Soc.*, Vol(85), , pp. 252-256**,(2008).**

8- N. Perveen,Thesis,Condenced Heterocyclic from aminoazoles,Aslamia University, **(1996).**

9-Al.Mukhtar and I. A- Mustafa, "Inorganic and coordination chemistry ", Arabic version, Univ.ofMousl, **(1988).**

10- E. Ispir, S. Torog˘lu , A. Kayraldız,"Syntheses, characterization, antimicrobial and genotoxicactivitiesof new Schiff bases and their complexes", Vol 10, pp 953-960,**(2008).**