

Thermogravimetric Study of Some Schiff base Metal Complexes

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Abstract

Three ligands were prepared from Condensation of *o*. Vanillin and amino phenols and *p* – Toluidine . All ligands were characterized by IR , HNMR and mass Spectrometry . The metal complexes were prepared by refluxing the ligands with metal chloride salt . The Complexes were characterized by IR , HNMR, molar Conductance and thermal analysis . The values of Kinetics parameter were determined by Coats – Redfern method .

Keywords: Schiff base , Coats – Redfern , metal complexes, thermodynamic parameters .

I. Introduction

Schiff bases and their metal complexes have a wide range of application in different field, in organic synthesis , anticorrosion material . in medicine as biological active materials , etc ...^(1,2,3) . Schiff bases exhibit cases of chelation or metal complex formation , where the lone pair of electrons on nitrogen atom of azomethine behave as a Lewis base in donating an electron pair to a metal in the formation of stable coordination complexes ^(4,5) .Saline type of Schiff bases which contain OH group near to imine group allow the formation of six member ring when coordinated with metal ions and this phenomena increase the stability of resulted complexes ^(5,6) .

II.Experimental

A. Materials, instrumentation and spectral measurements

Materials:*o*. vanillin was obtained from Sigma company , 3 – aminophenol and 2 – aminophenol was purchased from Merck company and all other Solvents used were of analytical grade of purity. Instrumentation and Spectral measurement :

Melting points was determined on Thermo Fisher . The reactions was monitored by TLC using aluminium sheet type Silica gel 60 F 254 and the Spots were visualized by u . v lamp or iodine vapour IR spectra were recorded as KBr disc by using Shimadzu FT- IR 8300 spectrophotometer in the region 4000- 500 cm⁻¹ . The mass spectra were scanned by the EI technique at 70 eV with an Agilent Technologies 5975C spectrometer . The HNMR spectra were scanned on a Bruker (500 MHZ) spectrophotometer , TMS as the internal standard and DMSO - d₆ was used as solvent . Thermal degradation of complexes have been investigated by using Tg / DTg analysis by using Rheometric Scientific instrument the data were connected in the rang 25 – 700 °C with heating rate (10 °C / min) . Molar conductance was

Thermogravimetric analysis at a constant rate is a good technique for determination of the thermodynamic parameters in addition to study the stability of complexes and confirmed the presence of lattice and coordinated water molecules ⁽⁷⁻¹⁰⁾ There are many methods that are use to study the Kinetics of decomposition and determination of thermodynamic parameters depend on the Tg data , Coats – Redfern is a one of a popular methods ^(11,12)

measured as 10⁻³ M solution in DMF by using W . T . W - Conductivity meter .

2 : 2 : preparation of (L₁)

o. vanillin (1.52 g , 10 m mole) was dissolved in 30 ml of worm ethanol and mixed with 1.09 g (10 m mole) of 3- aminophenol in a 50 ml R . B . F . The mixture was refluxed for 1 hour . The reaction was monitored by TLC using ethylacetate : Benzene (3 : 7) as eluent . The solvent was evaporated and the solid orange was recrystallized from heptane (yield 82 %) m . p 137 – 138 °C

Preparation of(L₆)

o. vanillin (1.52 g , 10 m mole) was dissolved in 30 ml of worm ethanol and mixed with 1.09 g (10 m mole) of 2- aminophenol in a 50 ml R . B . F . The mixture was refluxed for 3 hours and the mixture was poured on crushed ice and the orange precipitate was recovered by Buchner filtration , washed with water and then dived at ~ 50 °C, and recrystallized from ethyl acetate , to give orange crystals (yield 78 %) , m. p 194 – 195 °C .

Preparation of (L₁₁)

3.04 g , 20 m mole of *o*. vanillin dissolved in 300 ml of warm absolute ethanol , and 2.14 g , 20 m mole of *p*-

toluidine dissolved in 30 ml warn absolute ethanol , was mixed in a 100 ml R . B . F and the mixture was refluxed for two hours and then poured on cursed ice and the precipitate . was recovered by Buchner filtration , the solid orange was recrystallized from heptane to give orange crystals dried at ~50 °C , (yield 83 %) m . p 98 – 100 °C .

General Procedure for preparation of metal complexes :

A Solution of $MCl_2 \cdot XH_2O$ ($M = Cu , Ni , Co$ and Zn) dissolved in hot ethanol , was added slowly with stirring to a hot solution of ligand (molar ratio 1 : 1) , and the resulted mixture was refluxed for 1- 2 hours . A dark brown precipitate which formed in case of Cu , Ni and Co and pale yellow precipitate in case of Zn complexes were recovered by Buchner filtration ,

washed with ethanol and diethyl ether and dried at ~ 50 °C . The yield and physical properties listed in Table 1 .

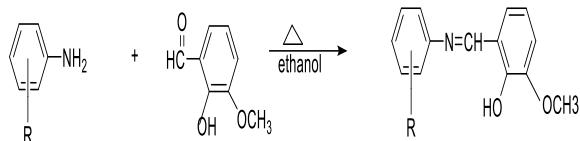
III. Results and discussion

A. Spectral characterization

This article presents the preparation of ligands containing azomethine group and two phenol groups in case L_1 and L_2 and one phenol group in case of L_3 , Divalent metal complexes were prepared from these ligands . The following scheme represent the ligands preparation and the physical properties and yield are presented in Table 1 .

Table 1 : Physical properties of prepared ligands and complexes

Comp.	Molecular weight	Physical state	Time of reaction (hrs)	m. p °C	Yield %
L_1	$C_{14}H_{13}NO_3$ 243	Orange powder	1	137	82
L_2	$C_{14}H_{13}NO_3$ 243	Orange crystals	3	194-195	78
L_3	$C_{14}H_{13}NO_3$ 241	Yellow crystals	2	98-100	83
L_1Cu	$C_{14}H_{18}ClCuNO_6$ 394	Dark brown powder	1	>300	63
L_1Ni	$C_{14}H_{18}ClNiO_6$ 389	Brown powder	2	>250d	67
L_1Co	$C_{14}H_{18}ClNiO_6$ 388	Brown powder	2	175-176	70
L_1Zn	$C_{14}H_{18}ClNiO_6$ 396	Palle yellow powder	1	>260d	62
L_2Cu	$C_{14}H_{16}CuNO_{5.5}$ 349	Black powder	1	>300	60
L_2Ni	$C_{14}H_{21}NNiO_8$ 389	Grensh yellow powder	1	276d	64
L_2Co	$C_{14}H_{25}CoNO_{10}$ 424	Brown powder	1	168d	61
L_2Zn	$C_{14}H_{13}NO_4Zn$ 324	Palle yellow powder	$\frac{1}{2}$	>300	68
L_3Cu	$C_{15}H_{16}ClCuNO_3$ 356	Black powder	1	236d	62
L_3Ni	$C_{15}H_{19}ClNiO_{3.5}$ 360	Brown powder	3	116	67
L_3Co	$C_{15}H_{24}ClCoNO_7$ 422	Brown powder	4	180d	66
L_3Zn	—————	Orange powder	1	198-201	—————



Scheme 1

L₁ R : meta OH , L₂ R : ortho OH , L₃ R : meta CH₃

B. Spectroscopic Characterization

a) FT – IR Spectra :

The IR Spectrum of L₁ show a brood band at 3383 cm⁻¹ attributed to stretching vibration of OH group , a very strong band at 1620 cm⁻¹ which attributed to stretching vibration of azomethine group (C=N) which confirm the formation of Schiff base⁽¹³⁾ . when compared the IR spectral data of the ligand with their metal complexes , the azomethine band shifted to lower frequency ($\Delta\nu = -23 \dots\dots -14 \text{ cm}^{-1}$) . which confirm the participation of the ion pair of nitrogen atom of azomethine in the formation of coordinated bond with

the central metal ions⁽¹⁴⁾ , in addition the changing of bands in the ligand IR spectrum especially that attributed to C-O and C-N as see in the Table 2 . The presence of lattice and coordinated water molecules confirmed by the brood band at the region ~3444 – 3448cm⁻¹ .

The IR spectrum of L₂ show the azomethine band at 1631 cm⁻¹ which shifted to lower frequency in the corresponding Cu complexes ($\Delta\nu = -23 \text{ cm}^{-1}$) and 1616 cm⁻¹ ($\Delta\nu = -15 \text{ cm}^{-1}$) in Zn complexes ($\Delta\nu = -19 \text{ cm}^{-1}$) . L₃ IR spectrum show the stretching vibration band of azomethine at 1597 cm⁻¹ as a very strong band which shifted to higher frequency in Cu , Ni and Co complexes ($\Delta\nu = +11 \rightarrow +19 \text{ cm}^{-1}$) while in Zn complexes this band shifted to lower frequency ($\Delta\nu = -3 \text{ cm}^{-1}$) . all other bands are tabulated in Table 2 .

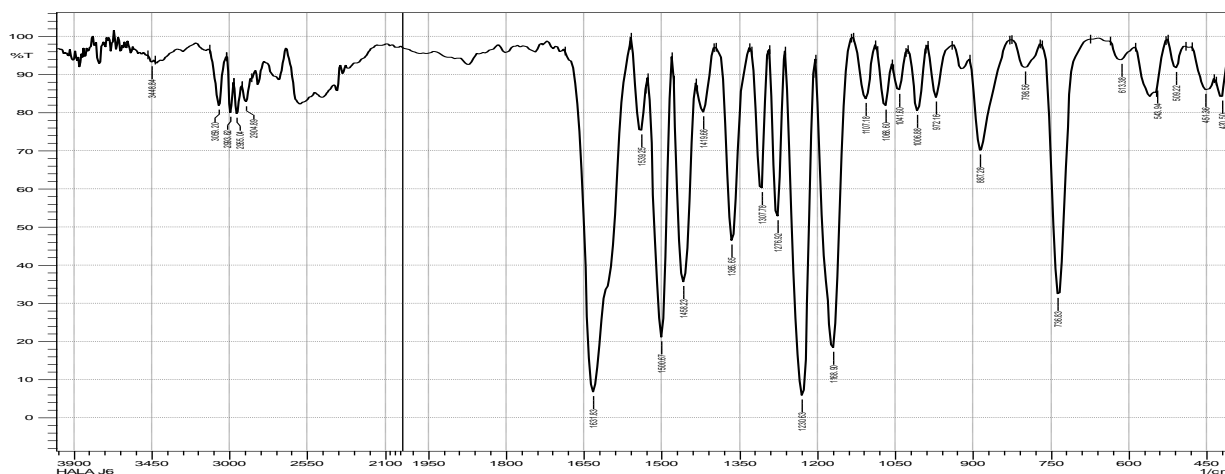


Fig 1 : IR Spectrum of Ligand L₂

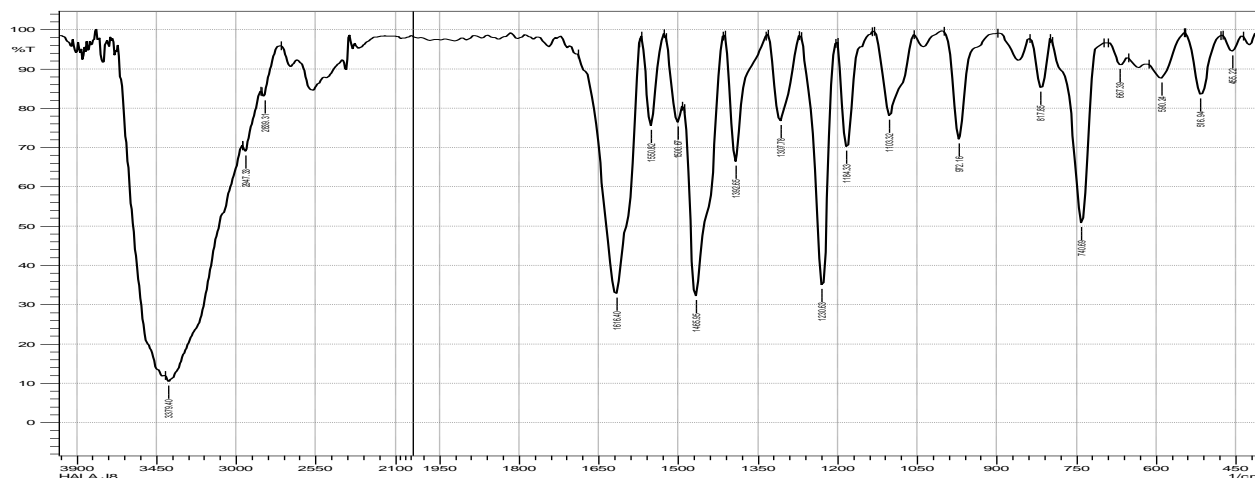


Fig 2 : IR Spectrum of L₂Ni

Table 2 : IR Spectra data of ligands and complexes (KBr , cm⁻¹)

Comp.	OH	CH Aromatic	CH Alph.	-HC=N- azomethine	C=C	C-N	C-O phenolic	M-O	M-N
L ₁	3383	3001 3059	2931	1620	1454 1519	1361	1219 1261	—	—
L ₁ Cu	3363	—	2943	1608	1550	1446	1222 1276	543	462
L ₁ Ni	3365	—	—	1606	1392	1361	1220 1242	642	609
L ₁ Co	—	3383	2939	1604	1469	1384	1222 1246	540	466
L ₁ Zn	— -	3059	2939	1593	1442	1396	1215 1242	567	462
L ₂	3448	3059	2955	1631	1458 1500	1365	1168 1230	—	—
L ₂ Cu	3448	3163	2935	1608	1458	1354	1253	528	493
L ₂ Ni	—	—	2947 2839	1616	1465	1307	1230	516	455
L ₂ Co	—	3063	2835	1616	1500	1388	1176	536	459
L ₂ Zn	3417	3055	2924 2831	1612	1477	1388	1107	513	424
L ₃	3483 3344	3047	2935 2839	1597	1481	1249	1068 1165	—	—
L ₃ Cu	3448	3032	2928 2835	1608	1508 1550 1462	1246	1080	574	497
L ₃ Ni	—	3055	2924 2831	1612	1508 1465	1234	1188	520	420
L ₃ Co	—	3063	2943 2839	1616	1465	1384	1249	505	424
L ₃ Zn	—	3001	2924	1589	1438	1330	1230 1188	501	459

b) ¹HNMR Spectra :

The HNMR Spectrum of L₁ in DMSO – d₆ show the following signals (Fig 3) δ 3.8 (S , 3H , OCH₃) , 6.7 – 7.2 (m , 7H , Ar-H) , 8.8 (S , 1H , Azomethine) 9.6 (br , 1H , OH amine moiety) , 13.2 (br , 1H , OH , vanillin moiety) . when compared these data with the HNMR of diamagnetic complex (L₁ Zn) and the disappearance of OH proton around 13.2 ppm has suggested the OH group of vanillin moiety in ortho position and close to azomethine group was deprotonated and binding with Zn⁺⁺ ion . Also the signal of azomethine proton was shifted to down field (δ = 8.8 ppm Δδ = -0.1 ppm) which indicated the participation of lone pair on nitrogen atom in formation of the complexes via a coordination bond also a new signal at δ 8.4 ppm was observed this may be attributed

to the OH proton of amine moiety and shifted to high field and involvement in complex formation .

The HNMR Spectrum of L₂ Show the following signals 3.8 (S , 3H , OCH₃) , 6.8 – 7.3 (M , 7H , Ar – H) 8.95 (S , 1H , HC=N) and 9.7 (br , 1H , OH) , While the HNMR spectrum of the Co responding Zn Complex show the following signals 3.7 (S , 3H , OCH₃) , 6.8 – 7.6 (m , 7H , Ar- H) , AND 8.9 (S , 1H , HC=N) . These results indicate that the both L₁ and L₂ behave as tridentate ligands .

The HNMR spectrum of L₃ show the following signal 2.3 (S , 3H , CH₃) , 3.8 (S , 3H , OCH₃) , 6.8 – 7.3 (m , 7H , Ar-H) 8.9 (S , 1H , HC=N) , 13.3 (S , 1H , OH) . The disappearance of the signal at 13.3 ppm in the L₃Zn complex . HNMR and the shifted of signal that of the azomethine proton from 8.9 ppm to 8.7 ppm confirm the complex formation .

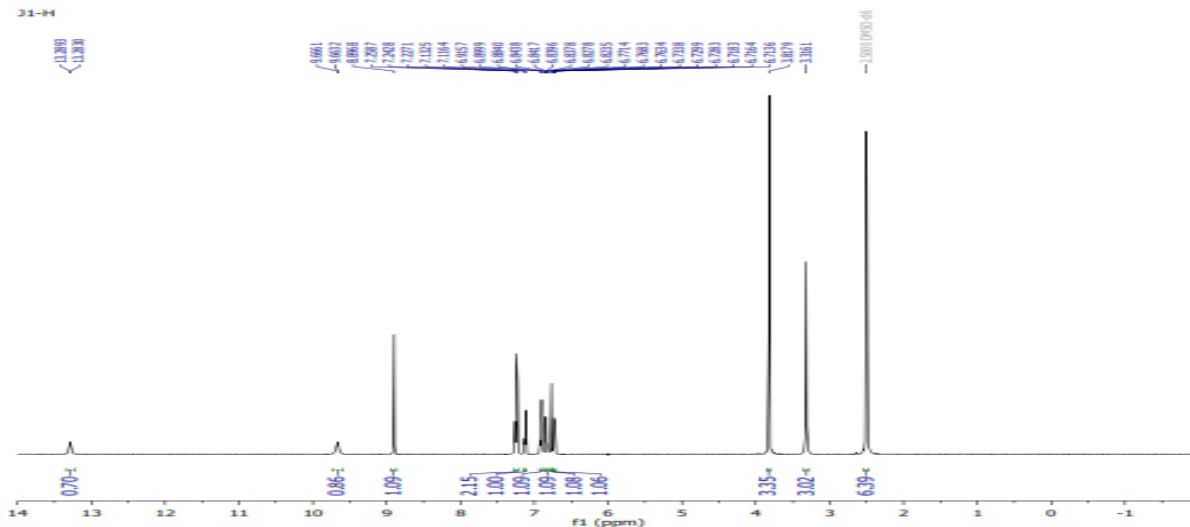


Fig 3 : ^1H NMR Spectrum of L_1 ($\text{DMSO} - \text{d}_6$)

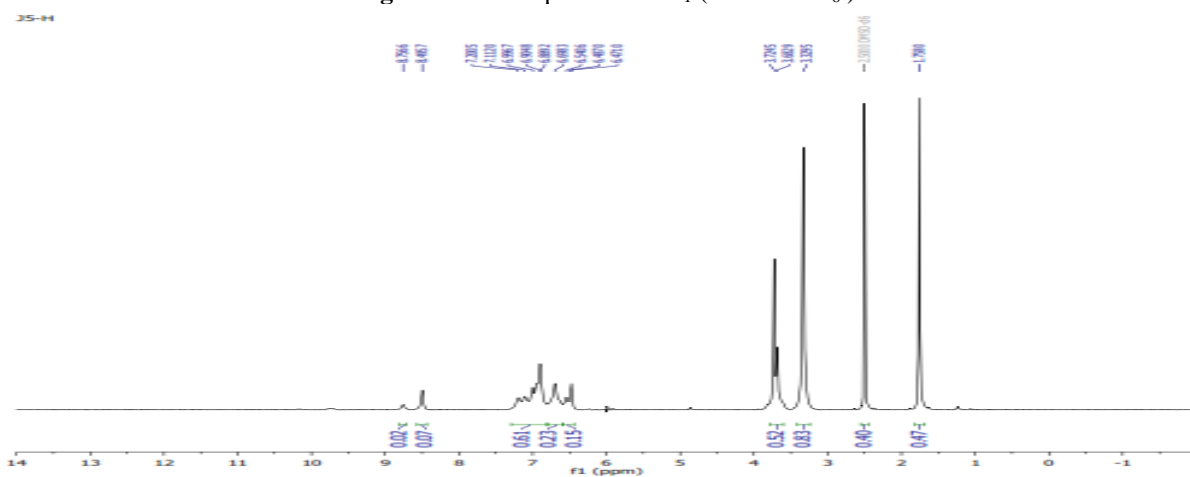


Fig 4 : ^1H NMR Spectrum of $\text{L}_1 \text{Zn}$ ($\text{DMSO} - \text{d}_6$)

Table 3 : ^1H NMR Spectral data (δppm)

Comp.	Chemical schift (δ ppm)
L_1	3.8 (s , 3H , OCH_3) , 6.7 – 7.2 (m , 7H , Ar-H) 8.8 (s , 1H , $\text{HC}=\text{N}$) , 9.6 (br , 1H , OH) 13.2 (br , 1H , OH)
L_1Zn	3.7 (s , 3H , OCH_3) , 6.4 – 7.2 (m , 7H , Ar-H) 8.7 (m , 1H , $\text{HC}=\text{N}$) , 8.4 (m , 1H , OH)
L_2	3.8 (s , 3H , OCH_3) , 6.8 – 7.3 (m , 7H , Ar-H) 8.9 (s , 1H , $\text{HC}=\text{N}$) , 9.7 (br , 1H , OH)
L_2Zn	3.7 (s , 3H , OCH_3) , 6.4 – 7.6 (m , 7H , Ar-H) 8.9 (br , 1H , $\text{HC}=\text{N}$)
L_3	2.3 (s , 3H , CH_3) , 3.8 (s , 3H , OCH_3) 6.8 – 7.3 (m , 7H , Ar-H) , 8.9 (s , 1H , $\text{HC}=\text{N}$) 13.3 (m , 1H , OH)
L_3Zn	2.2 (s , 3H , CH_3) , 3.7 (s , 3H , OCH_3) 6.5 – 7.3 (m , 7H , Ar-H) , 8.7 (s , 1H , $\text{HC}=\text{N}$)

Mass Spectrometry :

Mass spectrometry technique as a powerful structural characterization has been successfully used to confirm the molecular ion of the resulted Schiff bases . All ligands shows the peak of molecular ion of each

ligand as a base peak in all three ligands where the ligand L₁ show the peak at 243 m / z , L₂ at 243 m / z and L₃ at m / z 241 these results confirm the condensation of amines and o- vanillin in 1 : 1 molar ratio . The major fragments of L₁ and L₃ are presented in schemes 2 and 3 .

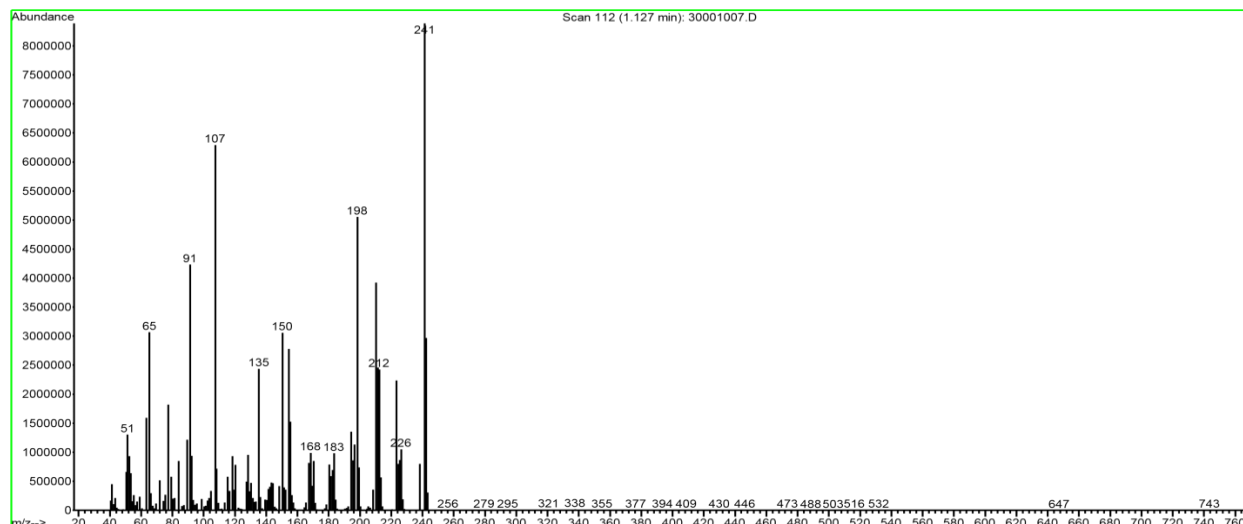
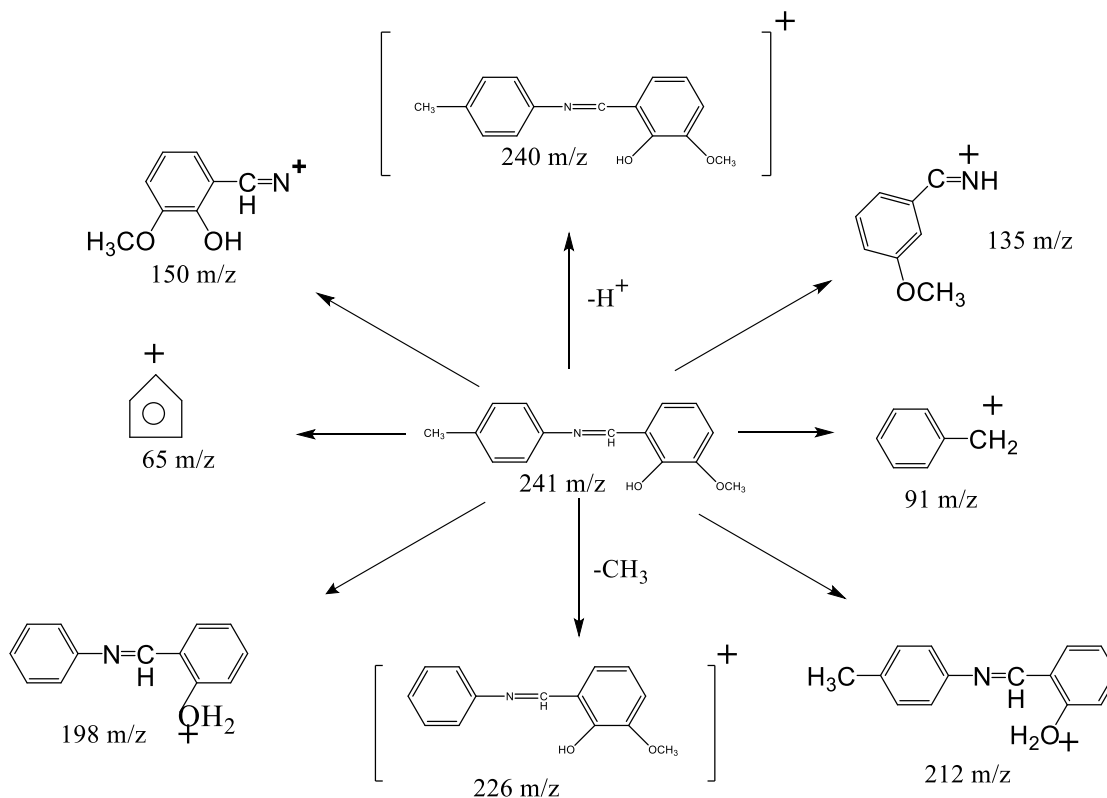


Fig 5 : EI – Mass Spectrum of L₃



Scheme 2 : Fragmentation diagram of L₃

Molar conductance :

The molar conductance of all complexes is measured at 25 °C for 10⁻³ M solution in DMF . it is concluded from the results that the molar conductance values or too low(5-18 ohm⁻¹ cm² mol⁻¹) indicated the non – electrolytic nature of the complexes .

Thermal analysis :

Thermal analysis (Tg , DTg) of all complexes is a good to get information a bout the stability as well as to verify the presence or a absent of lattice water molecules and the presence of coordinated water^(17, 18). The decomposition temperature and weight losses of all complexes are presented in Table 4 .

The first decomposition step in all complexes except L₂Zn is represent to the loss of lattice water molecules ,

in some cases the loss of lattice water , molecules shows two endothermic peak in DTg curve in the rang < 100 °C and indicates that the lattice water molecules are energetically non equivalent⁽¹⁹⁾ Fig 6 . The second steps in all complexes at the rang 120 – 200 °C represents the loss of coordinated water molecules a lone or together with HCl . The third decomposition step represent the removal a parts of organic moiety from the complexes and seems to be over lap with the fourth step as indicated by DTg Curves . The final product remaining in all complexes at ~ 600 ~ 700 °C is defined as metal oxide or metal oxide containing some carbon⁽²⁰⁾.

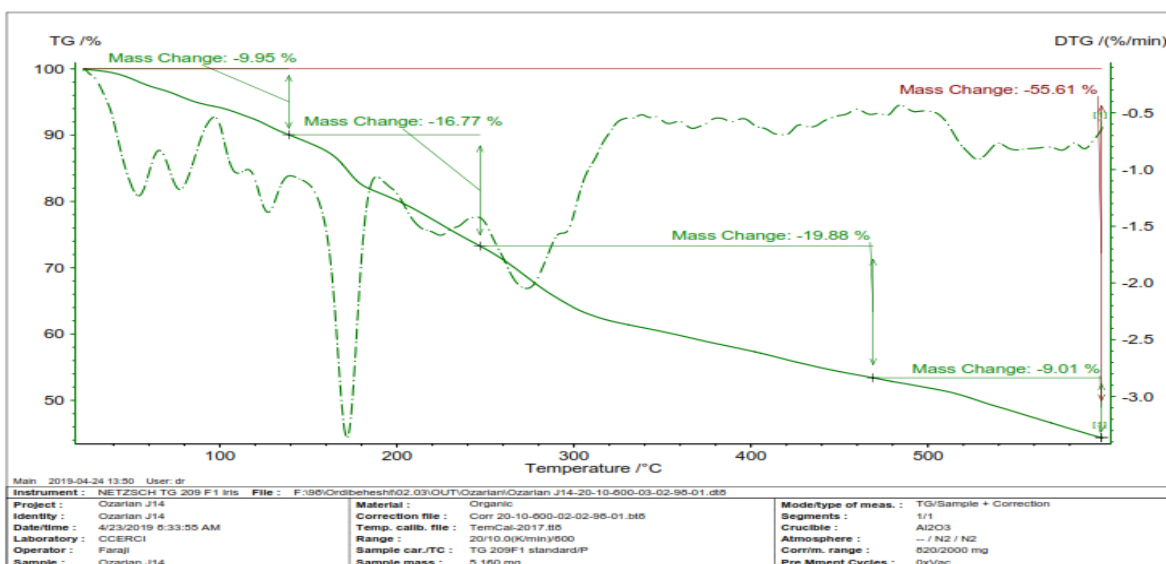


Fig 6 : Tg / DTg Curves of L₃Co

Table 4 : Thermal analysis data of Complexes

Comp.	Step	T ₁ °C	T ₂ °C	Mass Loss% (Therotal)	Assignment
L ₁ Cu	I	25	110	4.65 (4.56)	1H ₂ O (lattice)
	II	115	320	18.90 (18.88)	1H ₂ O + 1HCl (coord)
	III	320	548	23 (20.17)	CuO
L ₁ Ni	I	53	120	13.43 (13.88)	1H ₂ O (lattice)
	II	125	253	10.70 (10.74)	1HCl
	III	260	700	41.49 (28)	NiO+C
L ₁ Co	I	25	100	4.46 (4.63)	1H ₂ O (lattice)
	II	98	293	18.93 (19.18)	2H ₂ O + 1HCl (lattice)
	III	300	700	32.85 (18)	CoO + C
L ₁ Zn	I	25	105	4.66 (4.54)	1H ₂ O (lattice)
	II	110	700	(37. 73)	ZnO
L ₂ Cu	I	29	105	7.89 (7.73)	1.5H ₂ O (lattice)
	II	120	175	5.69 (5.59)	1H ₂ O(coord)
	III	179	479	50.75	_____
	IV	480	700	25	CuO
L ₂ Ni	I	26	121	18.5 (18,36)	H ₂ O ₄ (lattice)
	II	125	176	5.63 (5.67)	1H ₂ O (coord)
	III	180	700	28.9 (19.2)	NiO

L ₂ Co	I	25	135	16.84 (16.98)	1H ₂ O (lattice)
	II	135	209	15.23 (15.34)	3H ₂ O (coord)
	III	210	700	17.25 (17.21)	CoO
L ₂ Zn	I	25	190	5.46 (5.55)	1H ₂ O(coord)
	II	190	400	-----	-----
	III	400	700	21 , 16 (46)	-----
J ₃	I	220	600	98.69	C
L ₃ Cu	I	25	190	5.1 (5.05)	1H ₂ O (coord)
	II	190	264	50	1H ₂ O (coord)
	III	270	600	34.61	-----
L ₃ Ni	I	25	90	2.39 (2.5)	1/2H ₂ O (lattice)
	II	120	600	49.56 (50.14)	1H ₂ O(coord)+methanol+ Toluene + 1HCl
L ₃ Co	I	25	90	8.3 (8.5)	2H ₂ O (lattice)
	II	100	190	13.59 (13.98)	3H ₂ O(coord)
	III	200	250	35.04 (37.76)	1HCl
	IV	250	600	35.04 (37.76)	methanol + Toluene + 1HCl

Kinetic and thermodynamic data analysis :

The thermal decomposition of all complexes were studied Kinetically using Coats – Redfern method . Activation energy (E) , enthalpy change (ΔH) , entropy change ΔS and Gibbs free energy change are evaluated graphically from Tg data by employing the Coats – Redfern relation in the following from

$$\log \left[\frac{\log \frac{w_f}{w_f - w_t}}{T^2} \right] = \log \left[\frac{AR}{\theta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{2.303 RT}$$

Where wf , wt are weight loss at the end of stage and weight loss at temperature (t) respectively. E , R , A ,

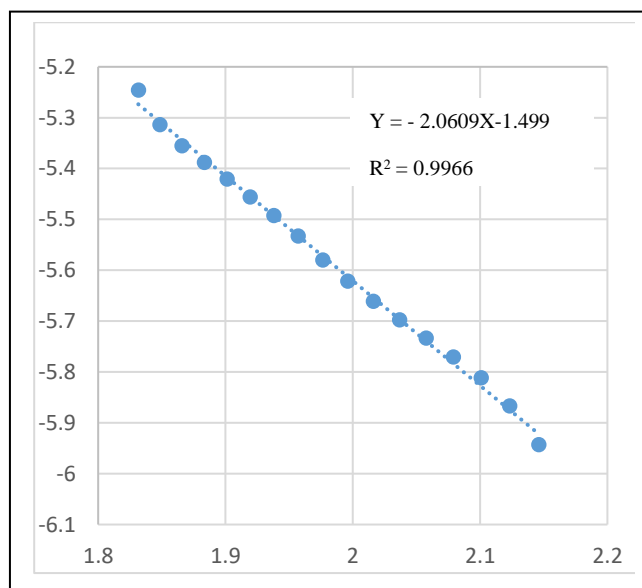
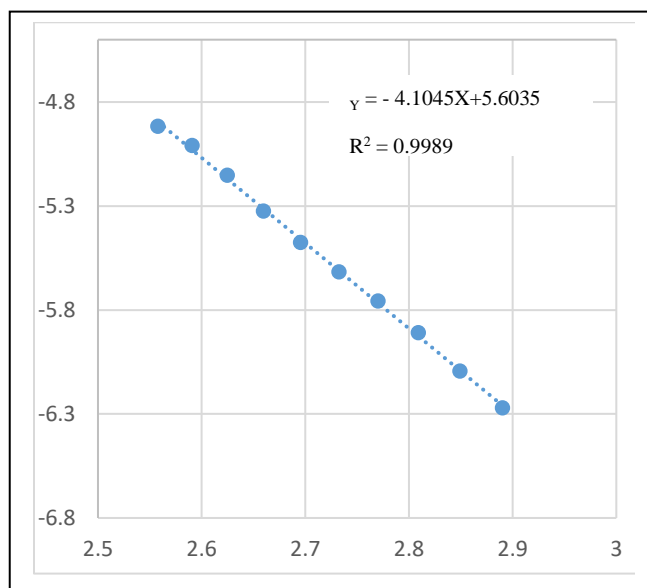
θ are the activation energy , the gas constant (8.31 J mol⁻¹ k⁻¹) pre – exponential factor and heating rate (10 °C/ min) respectively . The results of all steps are summarized in Table 5

And the Figs are listed in supplementary data . The E values of the first steps for all complexes ranging from 26 – 78 kJ . mol⁻¹ which represent the dehydration of lattice water . The positive values of ΔH to all steps mean that the process are endothermic and the negative values of ΔS indicated that decomposition process are very slow .

Table 5 : Kinetic Parameters for decomposition stages of complexes using Coats – Redfern equation

Comp.	stage	A (s ⁻¹)	E (KJ.mol ⁻¹)	ΔH (KJ.mol ⁻¹)	ΔS (KJ.mol ⁻¹ K ⁻¹)	ΔG (KJ.mol ⁻¹)
L ₁ Cu	I	1.52x10 ⁸	62.28630698	59.31133	-0.96993	406.548
	II	2.35x10 ²	38.61460136	33.76987	-1.08518	666.4325
	III	5.62x10 ⁷	90.35016753	84.84064	-0.98334	736.794
L ₁ Co	I	3.79x10 ¹⁰	78.55182506	75.46882	-0.92438	418.4126
	II	1.5x10 ³	39.44135994	35.5689	-1.0679	533.2106
	III	9.4x10 ⁷	106.1213529	101.0855	-0.97831	693.9414
	IV	6.89x10 ⁵	102.9191944	96.51218	-1.02116	883.8285
L ₁ Ni	I	4.5x10 ⁶	50.3337128	47.45845	-0.99876	393.0285
	II	6.4x10 ⁴	55.6322401	51.67668	-1.03687	545.2248
	III	1.8x10 ³	57.17724519	51.97519	-1.06885	721.0769
	IV	3.15x10 ⁹	165.1082807	158.4104	-0.9515	925.3163
L ₁ Zn	I	3.5x10 ⁵	44.050539	41.1919	-1019.97	350910.9
	II	7.6 x 10 ¹	32.61466893	27.96938	-1094.21	611690.1
	III	2.1x10 ⁴	69.42437211	64.36358	-1048.13	638375.7

L₂Cu	I	3.7x10 ⁶	51.31778516	48.26802	-1.00102	415.641
	II	3.5x10 ⁶	60.44830018	56.69218	-1.00304	510.0645
	III	4.1x10 ⁵	68.01773425	63.63836	-1.02229	602.3849
	IV	1.9x10 ³	60.49863294	55.16361	-1.06859	741.1978
L₂Co	I	4.3x10 ⁷	55.33579356	52.45222	-0.98014	392.5599
	II	3.2x10 ⁷	69.83086174	66.39052	-0.98393	473.7363
	III	1.8x10 ⁶	76.53813207	72.01749	-1.00999	621.451
	IV	2.7x10 ⁴	77.59052684	71.44944	-1.04757	845.6046
	V	1.3 x 10 ¹¹	193.5399723	186.5263	-0.92048	963.4075
L₂Ni	I	1.03x10 ⁶	46.6955923	43.86188	-1.01104	388.6254
	II	9.2x10 ⁵	63.18808624	59.23253	-1.01471	542.2332
	III	3.3x10 ⁹	36.04724805	31.50999	-1.10079	632.5387
	IV	7.24 x10 ¹¹	204.4849545	197.33	-0.90687	978.1436
L₂Zn	I	1.8x10 ³	32.6546672	29.69631	-1.06412	408.522
	II	0.11378955	14.28856992	8.54636	-1.15008	803.2543
	III	2.6x10 ¹⁰	184.1688935	177.5541	-0.93385	920.8985
L₃	I	1.6x10 ⁴	66.04844126	62.00978	-1.04802	571.3459
	II	1.17x10 ¹⁸	214.2395574	209.6192	-0.78412	645.5893
L₃Cu	I	4.8x10 ³	34.36540676	30.57605	-1057.95	482453.7
	II	4.8x10 ¹²	137.7670684	133.3129	-887.2	475672.5
L₃Co	I	2.6x10 ³	26.57358994	23.94763	-1.05989	358.8735
	II	5.3x10 ⁷	69.89650484	66.27334	-0.98021	493.6431
	III	1.9x10 ⁷	82.72274553	78.43479	-0.99006	589.3051
	IV	2.2x10 ⁶	111.8659853	105.1681	-1.01158	920.5005
L₃Ni	I	1.6x10 ⁵	42.0766529	39.20139	-1.02636	394.3203
	II	1.8x10 ⁴	47.83257672	43.79392	-1.04742	552.8421
	III	1.10x10 ⁸	19.82938341	15.29212	-1.12917	631.8202
	IV	5.6x10 ⁹	169.2935546	162.604	-0.94661	924.6238



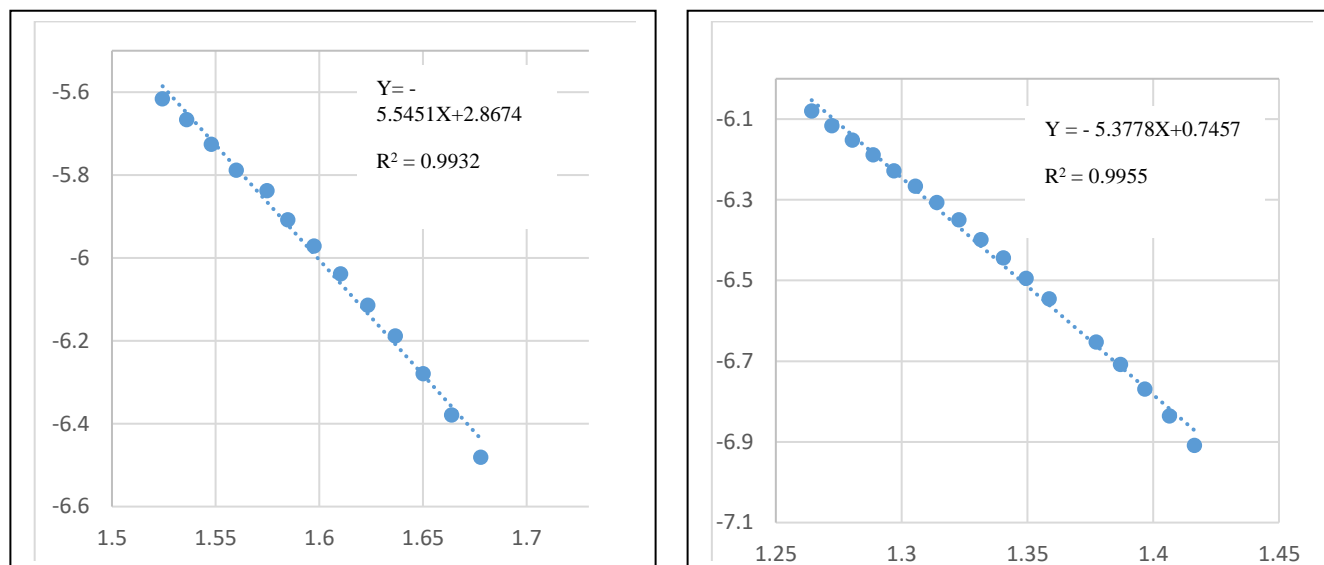
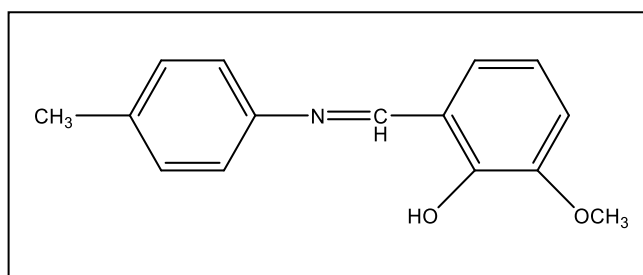
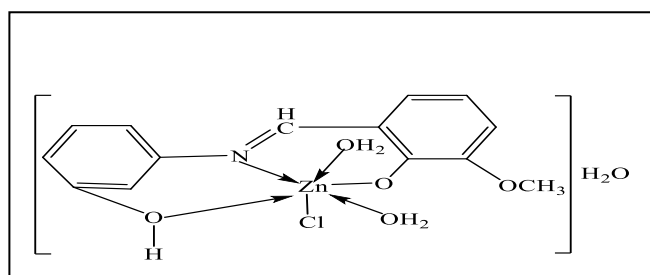
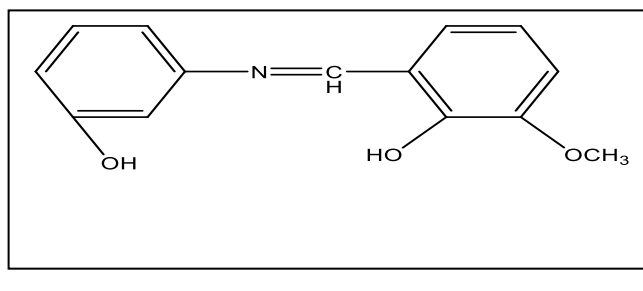
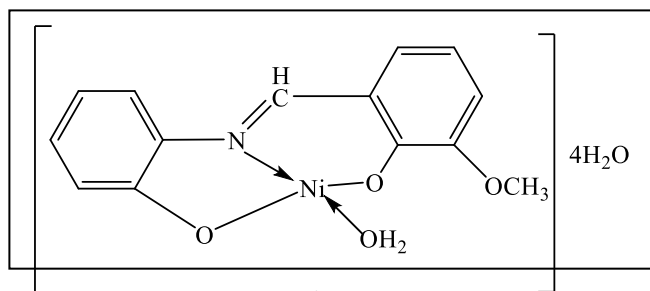
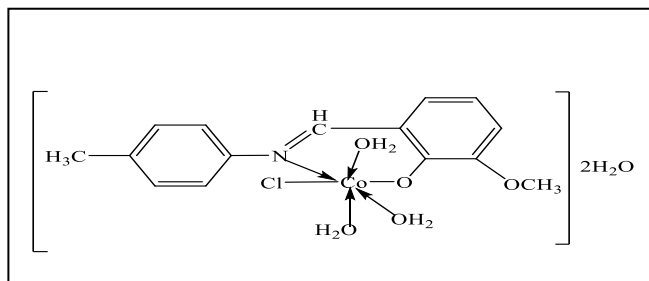


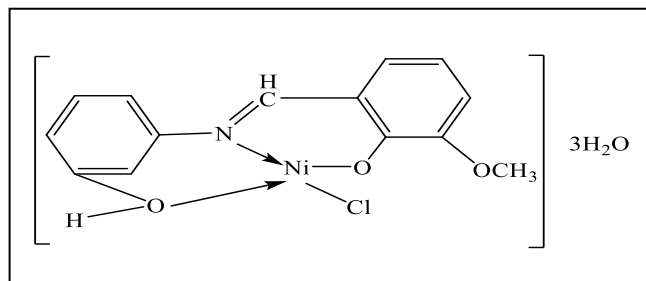
Fig 7 : Coats – Redfern Plots of L_1Ni stages

Structures ligands and complexes





L_3Co



L_1Ni

IV. References

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