

## Synthesis, Characterization, Thermal Behavior and Biological Properties of Zn (II) Schiff Base Complexes

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### Abstract

In this research, *N, N'*-bis ((E)-3-(4-dimethylamine) phenyl allylidene)-phenylen-1,2-diamine as a bidentate Schiff base ligand, was synthesized in ethanol and purified and then was identified by physical and spectral methods. Using this ligand, compounds with the general formula of  $ZnLX_2$  in which X is  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $N_3^-$ ,  $SCN^-$  and/or  $NO_3^-$ . Different techniques such as FT-IR, UV-Vis,  $^1H$ -NMR, thermal analysis (TG, DTA, DTG), melting point and molar conductivity were used for characterization of the coordination compounds. The IR spectrum of the ligand shows the group (C=N) vibration frequency at  $1604\text{ cm}^{-1}$  as main peak. However, the relevant frequency changed after complex formation which indicates coordination of the Schiff base ligand to the Zn metal ion. The data obtained from the UV-Vis spectra and the  $^1H$ -NMR of the ligand and its coordination compounds confirm their synthesis. Ultimately thermal behavior of the ligand and its metal compounds in the temperature range of  $20\text{-}900^\circ\text{C}$  was studied and their decomposition steps were evaluated along with some thermo-kinetic parameters of thermal decomposition of the complexes in each decomposition step.

**Keyword:** Complex, Zinc, Thermal behavior.

## 1. Introduction

These compounds are synthesized as organic polychelate ligands, the Schiff bases (C=N-) are unsaturated compounds [1-3]. Used in the field of coordination chemistry. Recently, several types of Schiff bases ligands with N, O, S and P atoms have been made available for structural analysis and biological applications [4-6]. In addition, Schiff bases have wide applications in several fields of life sciences as catalysts [6-8] and photochromic sensors [9,10]. these compounds also have fluorescence [11, 16,17,18], nonlinear optical, magnetic properties [19]. Schiff bases are considered significant ligands for metal ion coordination complexes due to their ease of synthesis, variability in structural design and range of applications [11, 20-22]. These ligands have been widely used as polychelator ligands and have shown high performance in terms of steric properties and therm – electronic regulation of their metal complexes [23-25]. Chemists design Schiff bases as polyunsaturated ligands their complexes and these have provided different fields of chemistry [7-23,24]. In this way we have focused on the synthesis, characterization, thermal behavior of Zn(II) Schiff base complexes using IR, NMR, UV-Vis, TG, DTA, TGA and molar conductivity of melting point methods.

## 2. Experimental

### 2. 1. Material and methods

All material for the synthesis of these compounds were purchased from Merck, Aldrich and/or BDH companies in high purity and used as received. the spectrum of IR ligand and synthesized complexes was taken by FT-IR type spectrometer (JASCO-680) in KBr disks and the spectrum of NMR these compounds taken by DPX FT-NMR-400 type spectrometer in DMSO solvent in range of 4000-400  $\text{cm}^{-1}$ . The UV-visible spectra of all compounds were taken by a 730-JASCO-V type spectrometer in range of 800-200 nm in DMF solvent. Melting point temperature ( $^{\circ}\text{C}$ ) of all compounds were recorded by the Kruse instrument. Molar conductance's all compounds of ( $1.0 \times 10^{-4}$  M in DMF solution) were determined using a Met Rohm 712 conduct meter at 298 K) the behavior of all compounds in thermal analysis was investigated by Perkin-Elmer type Piers Diamond type in the presence of  $\text{N}_2$  gas at a temperature range of 30-900 ( $^{\circ}\text{C}$ ) with a heating rate of 10 ( $^{\circ}\text{C}$ )/min were used.

## 2. 2. Synthesis of compounds

### 2. 2. 1. Synthesis of Schiff bases ligand

0.25mmol of 2,1-phenylenediamine dissolved in 3 mL ethanol was slowly added in room temperature with string, to a solution of 2mmol 4-dimethyl amin Cinnam aldehyde, which was dissolved in 10 mL of ethanol by ultrasonic for 30mn, and after four hours form a brownish orange precipitate. Then it was smoothed and washed with a little ethanol.

### 2. 2. 2. Synthesis of ZnL (Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub>) complexes

0,5mmol of Zinc salts dissolved in 3mL of ethanol and then the synthesized ligand was gradually added dropwise with it and stirring vigorously at 25<sup>0</sup>C temperature for four hours. finally, complexes in solution of reactions was precipitated a different colors and was washed smoothly with a little ethanol.

### 2. 2. 3. Synthesis of ZnL((SCN)<sub>2</sub>, (N<sub>3</sub>)<sub>2</sub> and (NO<sub>3</sub>)<sub>2</sub>) complexes

The synthesized ligand was gradually added dropwise over 30 minutes to 0,25mmol of Zinc salts, newly prepared in 3mL ethanol and after four hours of stirring at 25<sup>0</sup>C temperature complex in solution of reactions was precipitated a different colors and was washed smoothly with a little ethanol.

**TABLE (1) Vibrational spectral (cm<sup>-1</sup>) and electronic (nm) data of the Schiff base ligand and tis Zn (II) complexes**

Compounds	Color	M.P (° C)	Yield (%)	$\Lambda_M$ (cm <sup>2</sup> Ω <sup>-1</sup> M <sup>-1</sup> )
Ligand	Orange	164 – 167	25	0.60
ZnLCl <sub>2</sub>	crimson	260 – 263	70	0.53
ZnLBr <sub>2</sub>	brown- crimson	169 – 171	68	0.82
ZnLI <sub>2</sub>	brown- crimson	234 – 236	63	1.17
ZnL(SCN <sub>3</sub> ) <sub>2</sub>	brownish-black	206 – 208	66	0.54
ZnL(N <sub>3</sub> ) <sub>2</sub>	black-blood	193 – 196	32	0.50
ZnL(NO <sub>3</sub> )	black-blood	164 – 167	48	0.55

**TABLE (2) Analytical and Physical data of the Schiff base ligand and tis Zn (II) complexes**

Compounds	$\nu$ CH arom	$\nu$ CH alkene	$\nu$ CH aliph	$\nu$ CH imine	C=N	-N <sub>3</sub> , -SCN -O <sub>3</sub> N	C=C	Zn-N	$\lambda_{max}$ (nm)
Ligand	3464	3367	2958	2850	1604	-	1490,1439	—	399
ZnLCl <sub>2</sub>	3446	3219	2992	2856	1592	-	1490,1438	499	386
ZnLBr <sub>2</sub>	3441	3158	2930	2853	1598	-	1442	527	313, 386
ZnLI <sub>2</sub>	3447	3256	2986	2886	1592	-	1488, 1438	517	354, 385
ZnL(SCN <sub>3</sub> ) <sub>2</sub>	3445	3150	2906	2856	1593	2067	1480,1438	506	388
ZnL(N <sub>3</sub> ) <sub>2</sub>	3446	3085	2912	2853	1593	2066	1480,1437	499	387
ZnL(NO <sub>3</sub> ) <sub>2</sub>	3447	3081	2916	2856	1548	1195,1228	1480,1439	501	388

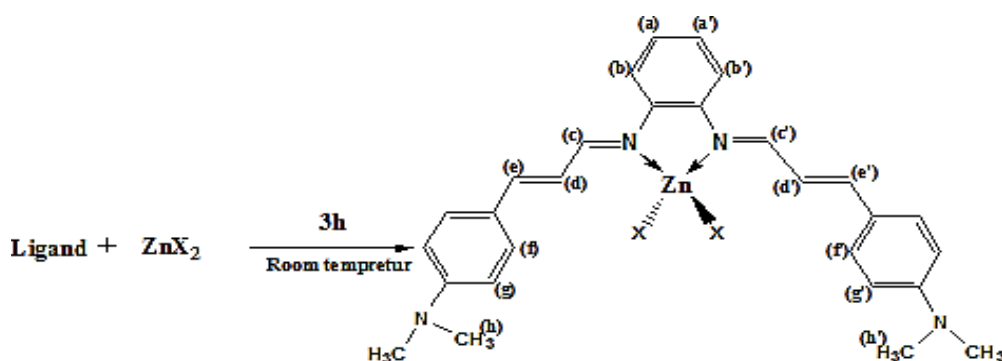
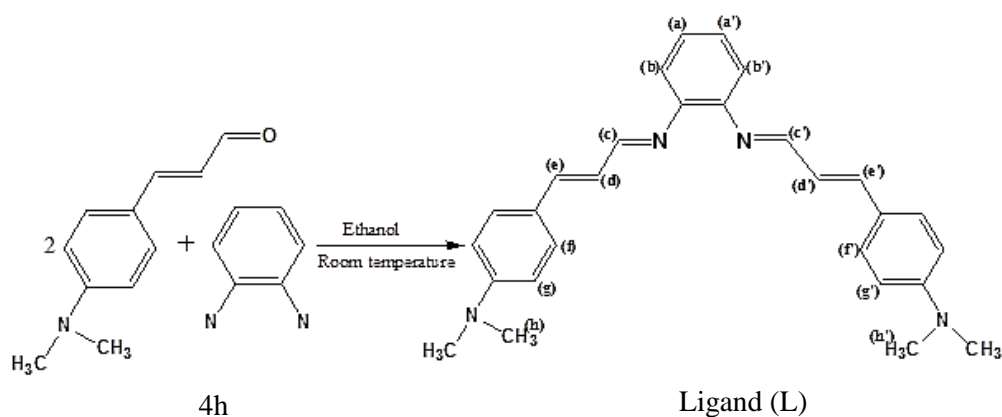
**TABLE (3) <sup>1</sup>HNMR Spectral data of the ligand and its Zn (II) Schiff base complexes in DMSO**

Compounds	<sup>1</sup> HNMR data ( $\delta$ , ppm)
Ligand	7.71 (bs, 2H <sub>cc'</sub> ), 7.43 (d, 4H <sub>ff'</sub> , J=8.70Hz) 7.23 (d, 2H <sub>bb'</sub> , J=8.9 Hz), 7.21 (d, 2H <sub>aa'</sub> , J=8.9 Hz), 6.71 (d, 4H <sub>gg'</sub> , J=8.7 Hz), 6.62 (dd, 2H <sub>dd'</sub> , J <sub>1</sub> =15.7 Hz, J <sub>2</sub> =8.0 Hz), 6.51 (d, 2H <sub>ee'</sub> , J=15.5 Hz), 3.00 (s, 12H <sub>hh'</sub> ).
ZnLCl <sub>2</sub>	7.80 (bs, 2H <sub>cc'</sub> ), 7.47 (d, 4H <sub>ff'</sub> , J=8.9Hz) 7.3 (d, 2H <sub>bb'</sub> , J=7.6 Hz), 7.30 (d, 2H <sub>aa'</sub> , J=6.1 Hz), 6.78 (d, 4H <sub>gg'</sub> , J=8.9 Hz), 6.69 (dd, 2H <sub>dd'</sub> , J <sub>1</sub> =15.7 Hz, J <sub>2</sub> =8.0 Hz), 6.57 (d, 2H <sub>ee'</sub> , J=15.3 Hz), 3.00 (s, 12H <sub>hh'</sub> ).
ZnLBr <sub>2</sub>	8.26 (bs, 2H <sub>cc'</sub> ), 7.45 (d, 4H <sub>ff'</sub> , J=7.46Hz) 6.76 (d, 2H <sub>bb'</sub> , J=8.8 Hz), 6.67 (t, 2H <sub>aa'</sub> , J=6.68 Hz), 7.23 (d, 4H <sub>gg'</sub> , J=7.23 Hz), 6.18 (dd, 2H <sub>dd'</sub> , J <sub>1</sub> =15.80 Hz, J <sub>2</sub> =6.9 Hz), 6.32 (d, 2H <sub>ee'</sub> , J=15.9 Hz), 2.99 (s, 2H <sub>hh'</sub> ).
ZnLI <sub>2</sub>	8.01 (d, 2H <sub>cc'</sub> , J=9.0 Hz), 7.48 (d, 4H <sub>ff'</sub> , J=8.70Hz) 7.26 (d, 2H <sub>bb'</sub> , J=7.3 Hz), 7.23 (t, 2H <sub>aa'</sub> , J=7.23 Hz), 6.77 (d, 4H <sub>gg'</sub> , J=8.9 Hz), 6.60 (dd, 2H <sub>dd'</sub> , J <sub>1</sub> =18.7 Hz, J <sub>2</sub> =8.30 Hz), 7.12 (d, 2H <sub>ee'</sub> , J=16.1 Hz), 2.99 (s, 12H <sub>hh'</sub> ).

ZnL(SCN<sub>3</sub>)<sub>2</sub> 7.90 (d, 2H<sub>cc'</sub>, J=8.9 Hz), 7.43 (d, 4H<sub>ff'</sub>, J=8.80H) 7.23 (d, 2H<sub>bb'</sub>, J=6.1 Hz), 7.24 (t, 2H<sub>aa'</sub>, J=6.8 Hz), 6.66 (d, 4H<sub>gg'</sub>, J=8.9H), 6.09 (dd, 2H<sub>dd'</sub>, J<sub>1</sub>=17.2 Hz, J<sub>2</sub>=7.3 Hz), 6.22 (d, 2H<sub>ee'</sub>, J=15.5 Hz), 2.91 (s, 12H<sub>hh'</sub>).

ZnL(N<sub>3</sub>)<sub>2</sub>. 8.55 (bs, 2H<sub>cc'</sub>), 7.59 (d, 4H<sub>ff'</sub>) 7.34-7.28 (4H<sub>bb'</sub>, aa') 6.78-6.58 (m, 8H<sub>gg'</sub>, dd', ee'), 3.03 (s, 12H<sub>hh'</sub>).

ZnL(NO<sub>3</sub>)<sub>2</sub> 8.52 (d, 2H<sub>cc'</sub>, J=8.1 Hz), 7.48 (d, 4H<sub>ff'</sub>, J=9.0 Hz) 7.12 (d, 2H<sub>bb'</sub>, J=6.1 Hz), 7.13 (d, 2H<sub>aa'</sub>, J=6.2 Hz), 6.45 (d, 4H<sub>gg'</sub>, J=9.0 Hz), 6.51 (dd, 2H<sub>dd'</sub>, J<sub>1</sub>=15.6 Hz, J<sub>2</sub>=7.9 Hz), 6.58 (d, 2H<sub>ee'</sub>, J=15.9 Hz), 2.99 (s, 2H<sub>hh'</sub>).



ZnLX<sub>2</sub> Where in X=Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, SCN<sup>-</sup>, N<sub>3</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>

Scheme (1) Synthetic route from ligand to zinc(II) complexes

### 3. Results and Discussion

#### 3.1 Physical and analytical data

The physical and analytical data of bidentate Schiff base ligand and its Zn(II) complexes are given in Table 1. The proposed structures of the compounds, as seen in (scheme. 1), have been validated by spectroscopic, physical and other methods. Examination of the analysis data of these compounds with the general formula  $ZnLX_2$  (L=ligand) and (X=  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $N_3^-$ ,  $SCN^-$ ,  $NO_3^-$ ) for the complexes shows seen in (Scheme. 1) the ligand melts in the range 164-167°C, while the melting temperature of the complexes is in the range of 260-263°C. these coordination compounds do not dissolve in water and common organic solvents such as alcohol, but are soluble in DMSO and DMF solvents. The Yield of ligand are 25% and the Yields of metal complexes are 32-70% respectively. As shown in the Table 1, all synthesized compounds are solid and colored, insensitive to moisture, stable at 25 °C, and degraded in further heating. The molar conductivity of these compounds in DMF solvent ( $10^{-4}$ mol) was in the range of  $0.50-1.17\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$ , which is confirmed their non- electrolytic nature at 25°C [27]. The Low molar conductivities indicate that the halide/ pseudo halide ions and Schiff base ligand have been bonded to the zinc ion in an inner-sphere coordination mode.

#### 3.2. FT/IR spectra

The IR spectrum of free ligand and its synthesized Zn(II) complexes were recorded in range of 4000 to 400  $\text{cm}^{-1}$ . As shown in (Figure. 1). Table. 2 summarizes the important vibrational frequencies of these complexes compared to the free Schiff base ligand. in the IR ligand spectrum one absorption band at  $1604\text{cm}^{-1}$  belongs to the cinnamaldehyde carbonyl group and two absorption bands in the range of  $3464\text{cm}^{-1}$  and  $3434\text{cm}^{-1}$  belong to the amine group of the 1,2-phenyl diamine, which confirms the synthesis of purity and the formation of an imine functional group (C=N) of the desirable ligand. The IR spectra of the synthesized compounds shown ligand-related vibration, but with the difference that the ligand absorption bands change with alignment with the metal. Modifications include displacement of vibration absorption bands, the ligand compound, which is used as a by-dentate ligand in the synthesis of desirable complexes, has several specific bands.

1- A strong absorption band in the range of  $1604\text{cm}^{-1}$  corresponding to (C=N), which is the displacement of this absorption band towards lower energies, indicating the coordination of ligand from towards the N imine to the zinc metal ion coordination complexes.

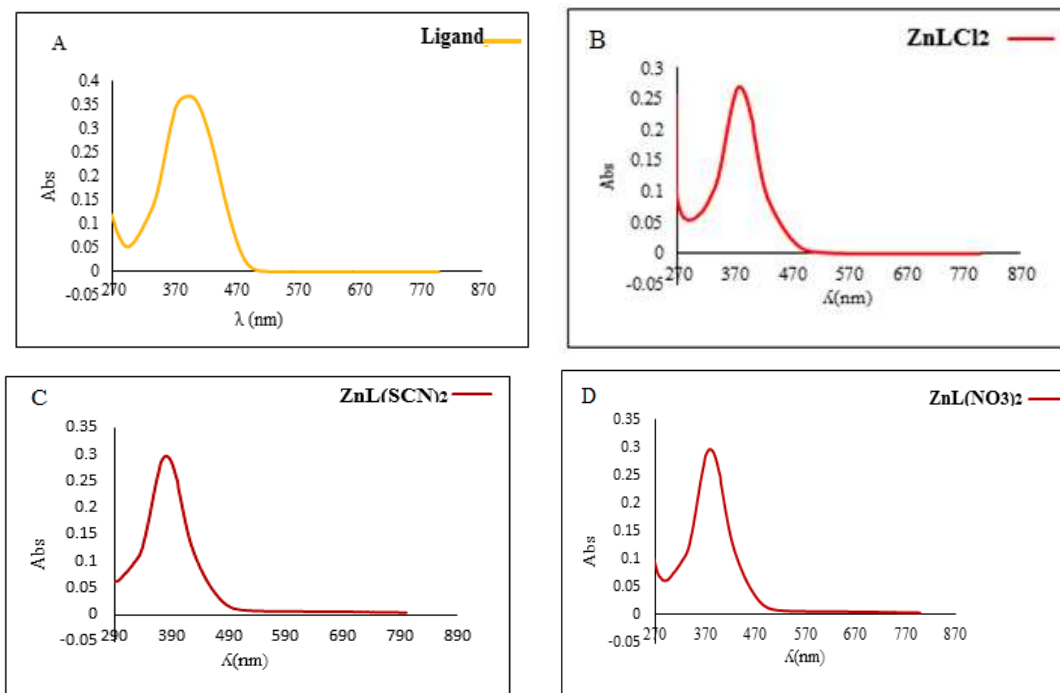
2- vibrational bands in the range of  $1336\text{cm}^{-1}$  and  $1323\text{cm}^{-1}$  depend on the group C=C, which is placed at different frequencies when ligand coordinated with zinc metal.

3- vibrations belonging to the C-H amine that are seen in the range of  $2958\text{cm}^{-1}$  and  $2850\text{cm}^{-1}$ , which are displaced after coordinated.

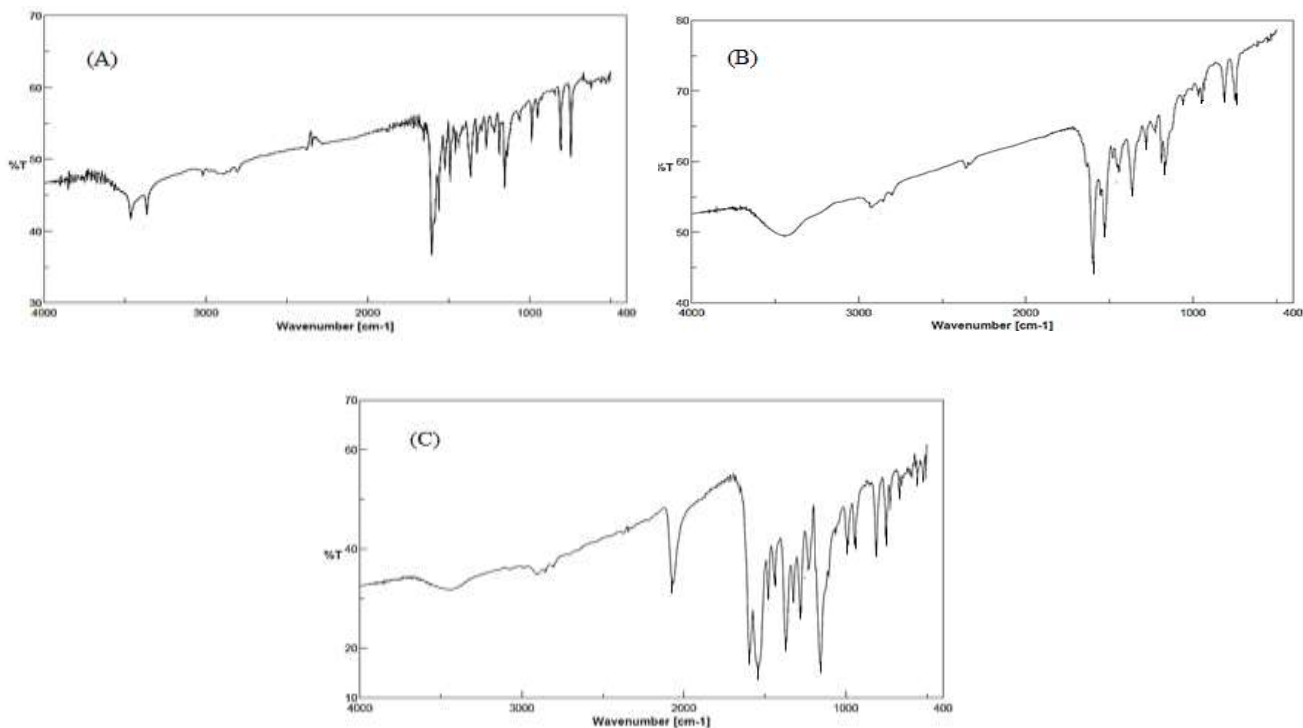
The vibrational bond of imine in this synthesized compounds shows the desired displacement relative to the ligand free, this type of displacement is due to the  $\pi$ -back bone of the zinc metal, which reduces the length of iminic bond and as a result, cause it strengthens the iminic bond which has shifted to larger frequencies and this displacement indicates coordinated of ligand to the zinc metal. In the new zinc (II) synthesized complexes, the absorptions bands in the range of  $1592\text{cm}^{-1}$  to  $1598\text{cm}^{-1}$  depend on the imine group (C=N), these absorptions bands placed at lower frequencies then the ligand (Table. 2). For the thiocyanate zinc complex, an absorption band in range of  $2067\text{cm}^{-1}$  belong to  $\text{SCN}^-$  and for the azide zinc complex an absorption band in range of  $2066\text{cm}^{-1}$  belong to  $\text{N}_3^-$ , both which are coordinated form nitrogen head, and an absorption band in range of  $2066\text{cm}^{-1}$  belong to and an absorption band corresponding to the zinc nitrate complex appeared in the range of  $211\text{cm}^{-1}$  the displacement of these absorption bands corresponds to a slight change from the free state to them. The nitrate group is attached to the zinc metal atom via oxygen. The ligand and several samples zinc synthesized complexes spectra are shown in (Figure. 2)

### 3. 3. Electron spectra description

The electronic spectra of the ligand and its zinc(II) complexes are shown in (Figure. 3) MDF ( $10^{-4}\text{mol}$ ) solvent at room temperature was used to record these spectra, ligand field transitions are not seen in the constructed complexes, for these synthesized complexes, charge transfer and intra-ligand transfer are also not seen in the UV range (Table. 1). In the ligand electron spectrum of the ligand, a transfer in the range of  $399\text{nm}$ , which belongs to the azometin  $\pi \rightarrow \pi^*$  group, appears as a peak. For zinc bromide and zinc iodide complexes, another peak appeared in the range of  $313\text{nm}$  and  $354\text{nm}$  which is related to the transfer of electrons d to the complexes  $\pi^*$ .



**Figure (1) Electronic spectra of (A) ligand, (B) ZnLCl<sub>2</sub>, (C) ZnL(SCN)<sub>2</sub> and (D) ZnL(NO<sub>3</sub>)<sub>2</sub> complexes**



**Figure (2) infrared spectra of (A) ligand, (B) ZnLCl<sub>2</sub> and (C) ZnL(SCN)<sub>2</sub> complexes**



### 3. 4. NMR spectra

In continuation of FT/IR and UV-visible spectral analyses, the ligand and its Zn (II) complexes were subjected to  $^1\text{H}$ NMR spectroscopy. The  $^1\text{H}$ NMR spectral data have been tabulated as Table 3. The  $^1\text{H}$ NMR spectra of the ligand and the zinc iodide complex are giving Figure 3 as examples. A comparison of the  $^1\text{H}$ NMR signals of the complexes with respect to free ligand according to Scheme 1 can well confirm their formation. A specific signal from the Schiff base ligand related to the hydrogen azometin cc' appeared as a broad signal in the range of 7.71 ppm. In the range of complexes, the signals in the range of 7.80- 8.55 ppm can be compared with the hydrogens of the azometin group. This is a strong evidence for the coordination of Schiff base ligand with zinc metal. The aromatic signal of the free ligand hydrogens ff', gg' and bb' appear as doublet and aa' as multiplet appear in the range of 7.43, 6.71, 7.23 and 7.21 ppm, respectively. These peaks come up or down to the metal center after the ligand is coordinated and are seen in the range of 7.43-7.59, 6.65-7.34, 6.26-7.34 and 6.34-7.31ppm, respectively. The alkene hydrogens signal ee' appear in the ligand structure as double peaks of 6.51 ppm and peak hydrogens dd' appear as double and double in the peaks of 6. 62 ppm regions. But in their complexes, the signals of these hydrogens after ligand coordination are seen in the range of 6.22-7.12 ppm as double and 6.09-6.78 ppm as double and double respectively. The aliphatic hydrogen peaks of the ligand, hh' in the range of 3.00 ppm appear as single and these signals appear in the peaks of zinc complexes in the range of 2.99-3.03 ppm seen.

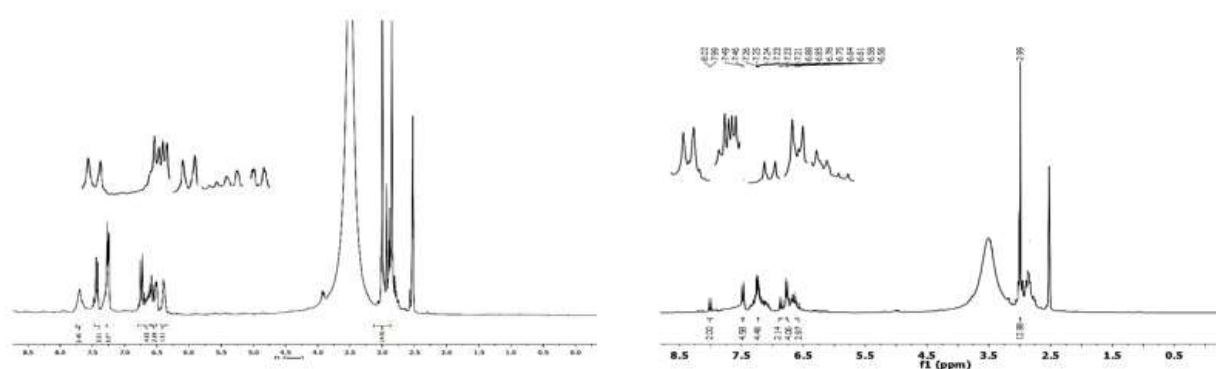
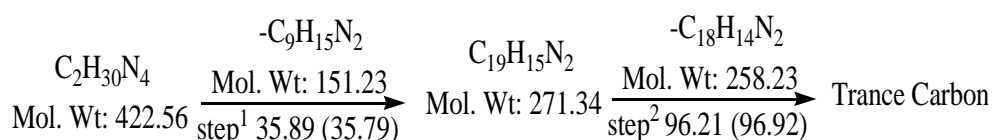


Figure (3)  $^1\text{H}$ NMR spectra of ligand and  $\text{ZnL}_2$  complex

### 3. 5. Thermal investigation (TG/DTA)

In addition to determining the stability of the related compounds, the presence or absence of coordinated or free water molecules in the structure of these complexes can be determined by the thermal study data of the ligand and the compound synthesized on zin. The water molecule normally separates from the composition structure at temperature below 200 °C, which ultimately reveals a mass deficiency in the TG/DTG diagram as a definite peak. Also, the study of the temperature decomposition behavior of the above compounds can be studied at different temperatures and at different stages. The Schiff base ligand decomposes in two temperature steps on the study of the thermal composition diagram. In the first stage, thermal composition of C<sub>9</sub>H<sub>15</sub>N<sub>2</sub> components in the range of 148-400 °C is removed from this compound. The reduced mass in the second stage is related to the C<sub>18</sub>H<sub>14</sub>N<sub>2</sub> fragments which are removed from the composition in the range of 400-700 °C. Finally, the final residue of this compound is the amount of carbon. Table 4 shows the data depending on the proposed steps and components. The heat degradation stages of the ligand are shown in Scheme 2.

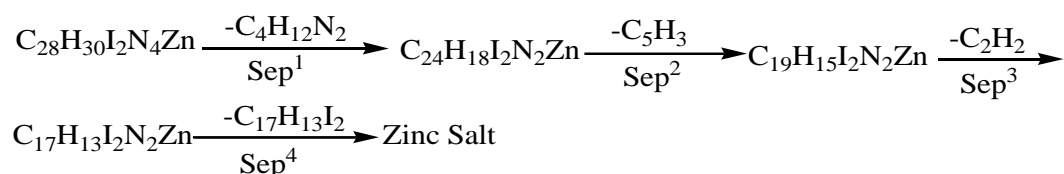


#### Scheme (2) thermal decomposition steps of ligand

The study of thermal composition of these compounds concludes that not all synthesized complexes decompose completely. Thermal composition of synthesized compounds is lost in three to four stages without the composition of water at temperatures below 200 °C. In the following, the thermal behavior of ZnLI<sub>2</sub> is studied as an example. The compound does not lose almost all of the relevant ligand during the four steps undergoing thermal composition. In the first stage, the thermal composition of component with molecular formula C<sub>4</sub>H<sub>12</sub>N<sub>2</sub> loses in the temperatures range of 200-320 °C. the reduced mass in the second stage corresponds to a piece of molecule with the molecule formula C<sub>5</sub>H<sub>3</sub> removed from the composition in the temperature range of 320-428 °C. In the third stage, the lowest mass reduce is related to the removal of Sam particle with the molecular formula C<sub>2</sub>H<sub>2</sub> which takes place in the temperature range of 428-519 °C.

During the fourth stage of the thermal analysis in the thermal range of 519-762 °C pieces with molecular formula  $C_{17}H_{13}I_2$  are separated from this complex, which are the most molecular mass related to this piece. Table 3 shows the data related to the proposed phases and components of the decomposed complex and other complexes. The thermal decomposition phases related to this complex can be seen in Scheme 3.

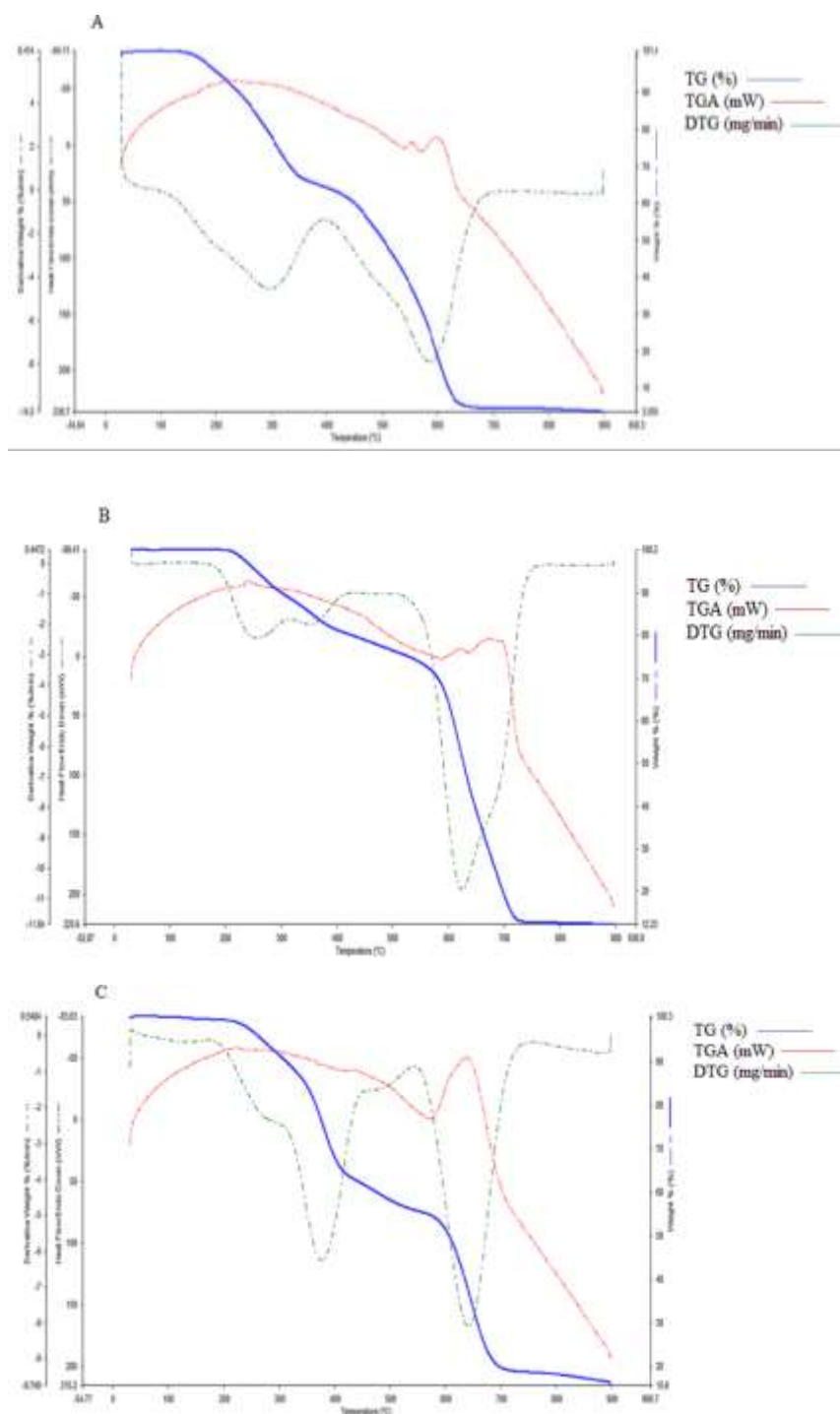
Composition of the data depending on the thermal analysis of the synthesized zinc compounds show that the zinc chloride complex starts to decompose at higher temperatures, is more stable and zinc nitrate complex starts at lower temperatures than other compound. It decomposes and has less stability Table 4.



**Scheme (3) thermal decomposition steps of  $ZnLI_2$  complex**

Kinetic parameters obtained from TG, DTG and DTA diagrams include activation energy ( $E^*$ ), enthalpy changes ( $\Delta H^*$ ), entropy changes ( $\Delta S^*$ ), Gibbs free energy changes ( $\Delta G^*$ ). It is listed in Table 4. These kinetic parameters are obtained at each step by Cartes Redfurn diagrams. According to the results, the activation energy ( $E^*$ ) is more indicative of thermal stability, most of the composition in each stage of thermal decomposition and covers the range of 29.52-128.28 °C, which the highest value is related to the first stage of the thermal decomposition of  $ZnLCl_2$  and the lowest value is related to the second stage of the thermal decomposition of  $ZnL(N_3)_2$ . positive enthalpy changes ( $\Delta H^*$ ) for all compounds indicate the calorific value of the decomposition phases and are in the range of 12.15-123.90 °C, most of which are related to the first phase. Thermal decomposition of  $ZnLCl_2$  complex and the lowest value is related to the second stage of thermal decomposition of  $ZnLCl_2$ . Negative entropy changes ( $\Delta S^*$ ) indicate compound accumulation and reduction of irregularity at each stage and range from  $-8.98 \times 10^{-2}$  -  $-1.14 \times 10^{-2}$  °C, the highest value is related to the first stage of thermal decomposition of  $ZnLI_2$  and the lowest value is related to the first stage of thermal decomposition of  $ZnLCl_2$ . Gibbs free energy ( $\Delta G^*$ ) positive energy changes indicate the non-spontaneity of these decomposition phases and range from  $1.68 \times 10^2$ -  $3.64 \times 10^2$

$^{\circ}\text{C}$ , the highest value is related to the fourth stage of thermal decomposition of  $\text{ZnL}(\text{SCN})_2$  and the lowest value is related to the first stage of thermal decomposition of  $\text{ZnLCl}_2$  compound.



**Figure (3) Thermo-gravimetric/differential thermal gravimetric (TG, DTG and TGA) plots of (A) ligand, (B)  $\text{ZnLI}_2$  and (C)  $\text{ZnL}(\text{N}_3)_2$  complexes**

TABLE (4) decomposition processes of ligand and its complexes

Compound	Temperature range/°C	Mass loss, found (calculated)/%	DTG peak/°C	Proposed segment	Final Residue
<b>Ligand</b>	148-400	35.89 (35.79)	299.05	C <sub>9</sub> H <sub>15</sub> N <sub>2</sub>	
	400-700	60.32 (61.13)	597.23	C <sub>18</sub> H <sub>14</sub> N <sub>2</sub>	Carbon
<b>ZnLCl<sub>2</sub></b>	215-320	17.35 (17.92)	253.22	C <sub>5</sub> H <sub>12</sub> N <sub>2</sub>	
	320-528	15.45 (13.82)	378.48	C <sub>6</sub> H <sub>5</sub>	
	528-660	28.02 (29.56)	633.13	C <sub>13</sub> H <sub>9</sub>	
	660-820	33.0 (27.0)	704.22	C <sub>4</sub> H <sub>4</sub> Cl <sub>2</sub> N <sub>2</sub>	Zinc Salt
<b>ZnLBr<sub>2</sub>. 0.39H<sub>2</sub>O</b>	100-235	1.11 (1.11)	-	0.39H <sub>2</sub> O	
	235-390	19.10 (19.11)	348.57	C <sub>7</sub> H <sub>13</sub> N <sub>2</sub>	
	390-530	12.59 (11.93)	423.98	C <sub>6</sub> H <sub>6</sub>	
	530-805	64.82 (64.96)	670.45	C <sub>15</sub> H <sub>11</sub> Br <sub>2</sub> N <sub>2</sub>	Zn0.016
<b>ZnLI<sub>2</sub></b>	200-320	11.64 (11.88)	256.82	C <sub>4</sub> H <sub>12</sub> N <sub>2</sub>	
	320-428	8.12 (8.5)	356.3	C <sub>5</sub> H <sub>3</sub>	
	428-519	4.48 (3.52)	466.38	C <sub>2</sub> H <sub>2</sub>	
	519-762	62.48 (63.5)	625.21	C <sub>17</sub> H <sub>13</sub> I <sub>2</sub>	Zinc Salt
<b>ZnL(SCN<sub>3</sub>)<sub>2</sub>. 0.096H<sub>2</sub>O.</b>	70-223	5.18 (5.18)	-	0.096H <sub>2</sub> O	
	223-294	7.32 (7.34)	271.22	C <sub>4</sub> H <sub>12</sub> N	
	294-441	29.81 (29.29)	353.33	C <sub>15</sub> H <sub>9</sub> N	
	441-750	35.64 (35.52)	644.82	C <sub>10</sub> H <sub>9</sub> N <sub>2</sub> S <sub>2</sub>	Zinc Salt
<b>ZnL(N<sub>3</sub>)<sub>2</sub>. 0.16H<sub>2</sub>O</b>	180-200	0.5 (0.5)	-	0.16H <sub>2</sub> O	
	200-313	7.32 (7.34)	285.4	C <sub>3</sub> H <sub>9</sub> N	
	313-450	29.81 (29.29)	376	C <sub>11</sub> H <sub>11</sub> N	
	450-555	35.64 (35.52)	489	C <sub>3</sub> H	
	555-730	5.18 (5.18)	643.55	C <sub>11</sub> H <sub>9</sub> N <sub>5</sub>	Zinc Salt
<b>ZnL(NO<sub>3</sub>)<sub>2</sub>. 0.91H<sub>2</sub>O</b>	50-202	2.72 (2.72)	-	0.91H <sub>2</sub> O	
	202-375	19.04 (19.82)	309.69	C <sub>8</sub> H <sub>14</sub> N <sub>2</sub>	
	375-525	14.74 (14.7)	440.92	C <sub>7</sub> H <sub>6</sub>	
	525-728	53.87 (52.57)	631.5	C <sub>13</sub> H <sub>10</sub> N <sub>4</sub> O <sub>6</sub>	Zn

**TABLE (5) thermodynamic parameters ( $\Delta E^*$ , ( $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$ ) of decomposition processes of ligand and its complexes**

Compound	Decomposition step ( $^{\circ}\text{C}$ )	$E^*$ (KJ/mol)	$A^*$ ( $\text{S}^{-1}$ )	$\Delta S^*$ (KJ/mol.K)	$\Delta H^*$ (Kj/mol)	$\Delta H^*$ (Kj/mol)
<b>Ligand</b>	148-400	40.36	$1.34 \times 10$	$-3.11 \times 10^{-2}$	35.80	$2.06 \times 10^{+2}$
	400-700	93.17	$6.66 \times 10^{+2}$	$-2.62 \times 10^{-2}$	87.27	$2.37 \times 10^{+2}$
<b>ZnLCl<sub>2</sub></b>	215-320	128.28	$9.46 \times 11$	$-8.38 \times 10^{-1}$	123.90	$1.68 \times 10^{+2}$
	320-528	17.57	$1.32 \times 10^{-3}$	$-3.70 \times 10^{-2}$	12.15	$2.53 \times 10^{+2}$
	528-660	114.88	$1.77 \times 10^{+4}$	$-2.36 \times 10^{-2}$	107.38	$3.21 \times 10^{+2}$
	660-820	85.39	$1.03 \times 10^{+1}$	$-2.93 \times 10^{-2}$	77.27	$3.64 \times 10^{+2}$
<b>ZnLBr<sub>2</sub>.0.39H<sub>2</sub>O</b>	235-390	69.82	$1.53 \times 10^{+3}$	$-2.53 \times 10^{-2}$	64.66	$2.22 \times 10^{+2}$
	390-530	43.55	$4.51 \times 10^{-1}$	$-3.22 \times 10^{-2}$	37.76	$2.62 \times 10^{+2}$
	530-805	89.51	$4.13 \times 10^{+1}$	$-2.87 \times 10^{-2}$	81.66	$3.52 \times 10^{+2}$
<b>ZnLI<sub>2</sub></b>	200-320	102.16	$1.07 \times 10^{+9}$	$-1.41 \times 10^{-2}$	97.60	$1.75 \times 10^{+2}$
	320-428	71.01	$2.11 \times 10^{+4}$	$-2.33 \times 10^{-2}$	65.11	$2.30 \times 10^{+2}$
	428-519	83.54	$1.73 \times 10^{+4}$	$-2.36 \times 10^{-2}$	76.38	$2.80 \times 10^{+2}$
	519-762	29.52	$1.95 \times 10^{-2}$	$-3.50 \times 10^{-2}$	21.86	$3.45 \times 10^{+2}$
<b>ZnL(NCS)<sub>2</sub>.0.096H<sub>2</sub>O</b>	223-294	51.72	$1.40 \times 10^{+2}$	$-2.74 \times 10^{-2}$	45.82	$2.41 \times 10^{+2}$
	294-441	78.87	$4.99 \times 10^{+3}$	$-2.46 \times 10^{-2}$	71.72	$2.84 \times 10^{+2}$
	441-750	79.94	$2.19 \times 10^{+1}$	$-2.92 \times 10^{-2}$	72.29	$3.41 \times 10^{+2}$
<b>ZnL(N<sub>3</sub>)<sub>2</sub>.0.16H<sub>2</sub>O</b>	200-313	71.01	$2.11 \times 10^{+4}$	$-2.33 \times 10^{-2}$	65.11	$2.30 \times 10^{+2}$
	313-450	83.54	$1.73 \times 10^{+4}$	$-2.36 \times 10^{-2}$	76.38	$2.80 \times 10^{+2}$
	450-555	29.52	$1.95 \times 10^{+2}$	$-3.50 \times 10^{-2}$	21.86	$3.45 \times 10^{+2}$
<b>ZnL(NO<sub>3</sub>)<sub>2</sub>.0.91H<sub>2</sub>O</b>	555-730	100.67	$7.80 \times 10^{+2}$	$-2.62 \times 10^{-2}$	93.02	$3.35 \times 10^{+2}$
	202-375	66.03	$1.50 \times 10^{+3}$	$-2.53 \times 10^{-2}$	61.47	$2.00 \times 10^{+2}$
	375-525	38.55	$1.27 \times 10^{-1}$	$-3.33 \times 10^{-2}$	32.64	$2.69 \times 10^{+2}$
	525-728	78.87	$4.99 \times 10^{+3}$	$-2.46 \times 10^{-2}$	71.72	$2.84 \times 10^{+2}$

#### 4. Conclusion

In this study, a new bidentate Schiff base ligand of *N, N'*-bis [(E)-3-(4-dimethyl amine) phenylallylidene]-phenylen-1,2-diamine, in ethanol solvent was synthesized and then complexes Zn(II) was also made by the above ligand.

All of these compounds were identified by various physical and chemical methods including molar conductivity, melting point, FT-IR, UV-Vis,  $^1\text{H-NMR}$  and TG. Based on the results, the general formula of  $\text{MLX}_2$  in which X ions of chloride, bromide, iodide, azide, thiocyanate and nitrate were proposed for the complexes. In the IR spectrum, fast absorption at  $1604\text{cm}^{-1}$ , which belongs to the azometin group ( $\text{C}=\text{N}$ ) and this absorption band is transferred to lower energies in the complexes, which coordinated the ligand from the nitrogen said of the azometin group to  $\text{Zn(II)}$  ion confirms. In the UV-Vis spectrum of the ligand, a transition appears at  $402\text{nm}$  depending on the  $\pi \rightarrow \pi^*$  azometin group ( $\text{C}=\text{N}$ ). The results of  $^1\text{HNMR}$  nucleus magnetic resonance spectra show that hydrogen, depending on the  $\text{C}=\text{N}$  bond, olefin group hydrogen and aromatic rings in the synthesized compounds shifts to a lower level (weaker field) than the ligand. This also confirms the coordinated of the azometin group ( $\text{C}=\text{N}$ ) with  $\text{Zn(II)}$ . The thermal behavior of the synthesized compounds was studied using TG/DTG/TGA diagrams and based on the results, the ligand was completely decomposed and the zinc-related complexes were completely decomposed. In addition, a number of thermosynthetic parameters of ligand and complexes were calculated using TG/DTG diagrams.

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