



Synthesis, characterization, kinetic and thermodynamic parameters evaluation from TG-DTA analysis of Cu(II), Co(II) and Mn(II) complexes with two phenol Schiff bases

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ABSTRACT

Complexes of Cu(II), Co(II) and Mn(II) with two Schiff base ligands {[2-carboxyphenyl]imino]methyl} phenol (HL_A) and {[2-hydroxyphenyl]imino]methyl} phenol (HL_B) were synthesized and characterized by FT-IR, UV-Visible, ¹H NMR spectroscopy and elemental analysis. All the synthesized complexes have been evaluated for their thermal degradation studies using TG-DTA analytical methods in static air. Thermodynamic and kinetic parameters were evaluated from the TG-DTA curves using Arrhenius equation.

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1. Introduction

Coordination chemistry of transition metal complexes of iminophenol ligands derived from Schiff base condensation of substituted aniline and salicylaldehyde have been extensively studied over the last decades [1-8]. Schiff bases and their metal complexes have a variety of biological, clinical, analytical and industrial applications and they are playing an important role in catalysis organic synthesis [9-13]. Transition metal complexes with Schiff bases as ligands have been structurally characterized and used to study phenolic oxidation, antibacterial and antifungal activity [14,15]. The presence of nitrogen and oxygen donor atoms gives special properties to coordination compounds and they can be used effectively and stereo specifically in catalysis for oxidation, reduction and hydrolysis [16].

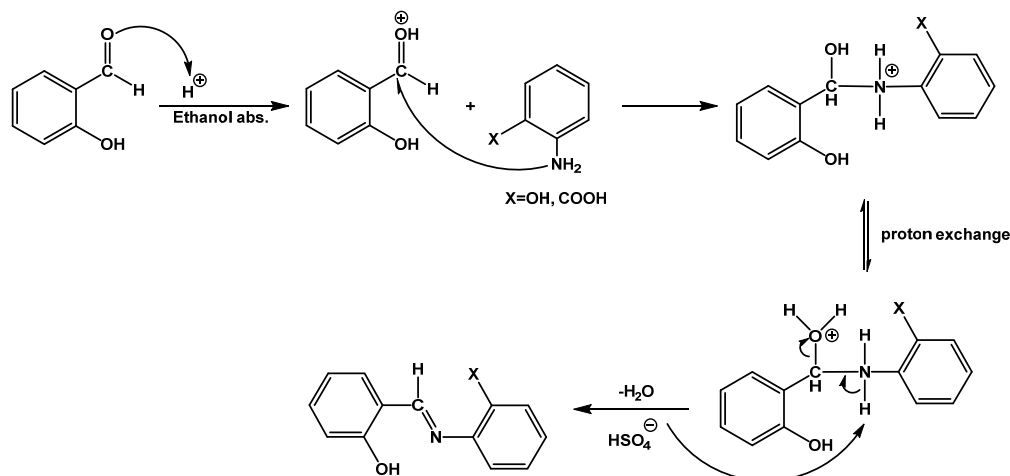
In view of the interesting in chelating behavior of salicylaldehyde derived Schiff bases ligands, we prepared the coordination complexes of Cu(II), Co(II) and Mn(II) with such a class of new ligands having C=N, COOH and OH groups to support and evaluated the chelation behavior. A comparative thermal degradation study of these ligands and their metal complexes are investigated by using TG-DTA analytical

methods in static air. Thermodynamic and kinetic parameters were evaluated from TG-DTA curves using Arrhenius equation, plot between the rate of decomposition (ln k) and 1/T.

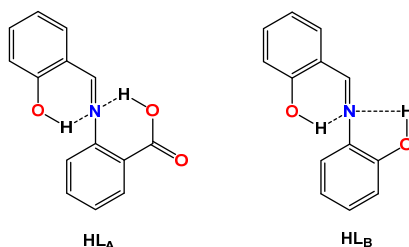
2. Experimental

2.1. Materials and methods

All chemicals and solvents used in the present work were of analytical reagent grade supplied Merck and BDH and used without further purification. Carbon, hydrogen and nitrogen analysis were carried out by using CE440 Elemental Analyzer-Exeter Analytical, Inc. USA. The ¹H NMR spectra of the ligands were measured at room temperature by using NMR Spectrometer (Bruker, 300 MHz). The absorption spectra in the UV-Visible range 200-800 nm were studied with UV-9200 Biotech Engineering Management Co. Ltd. (UK) UV Spectrophotometer. FT-IR spectra by KBr pellets were recorded with a FT-IR 8400s Spectrophotometer model 2000 from Shimadzu, Japan. Thermogravimetric measurements were carried out under nitrogen atmosphere using a TGA Q50 V20.13 Build 39. Universal V4.5A TA Instruments.



Scheme 1. The synthesis route of Schiff bases ligands (HL_A , HL_B).



Scheme 2. The suggested hydrogen bonds of the prepared Schiff bases (HL_A , HL_B).

2.2. Synthesis of ligands

The ligands (HL_A and HL_B) were synthesized according to the previous reported procedure [17,18]. By magnetically stirring of an equimolar of salicylaldehyde in 10 mL of ethanol with 2-carboxy aniline, 2-hydroxyl aniline and adding of 2-3 drops of concentrated sulphuric acid. The mixture was refluxed for 2-3 hours then an orange and reddish-brown product were separated out after cooling in ice bath, filtered off, washed with cold ethanol and dried in vacuumed desiccator, Scheme 1 and 2.

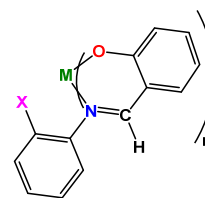
[[2-Carboxyphenyl] imino]methyl]phenol (HL_A): Color: Orange. Yield: 85%. M.p.: 172-175 °C. FT-IR (KBr, ν , cm^{-1}): 3473, 3375 (OH) (br, alcohol and acid), 1676 (C=O) (acid), 1631 (CH=N) (azomethine), 1246 (C-O) (phenolic), 1564 (C=C) (Ar). ^1H NMR (300 MHz, $\text{DMSO}-d_6$, δ , ppm): 13.77 (s, 1H, OH), 9.75 (s, 1H, COOH), 8.96 (s, 1H, N=CH), 7.64-6.84 (m, 8H, Ar-H). Anal. calcd. for $\text{C}_{14}\text{H}_{11}\text{NO}_3$: C, 69.70; H, 4.60; N, 5.81. Found: C, 69.65; H, 4.62; N, 5.28%. UV/Vis (CHCl_3 , λ_{max} , nm, ϵ): 255 (4.42), 330 (4.23), 435 (4.12).

[[2-Hydroxyphenyl] imino]methyl]phenol (HL_B): Color: Reddish brown. Yield: 88%. M.p.: 190-192 °C. FT-IR (KBr, ν , cm^{-1}): 3450, 3414 (OH) (br, alcohol and acid), 1631 (CH=N) (azomethine), 1274 (C-O) (phenolic), 1591 (C=C) (Ar). ^1H NMR (300 MHz, $\text{DMSO}-d_6$, δ , ppm): 10.70 (s, 2H, OH), 10.25 (s, 1H, N=CH), 6.53-7.65 (m, 8H, Ar-H). Anal. calcd. for $\text{C}_{13}\text{H}_{13}\text{NO}_2$: C, 73.23; H, 5.20; N, 6.57. Found: C, 73.15; H, 5.27; N, 6.67%. UV/Vis (CHCl_3 , λ_{max} , nm, ϵ): 250 (4.22), 325 (4.43), 420 (4.18).

2.3. Synthesis of complexes

The copper(II) and cobalt(II) complexes were synthesized in similar manner using a method described elsewhere [19].

To a hot solution of 1 mmol in 10 mL ethanol of each Schiff bases ligands, 1 mmol of $\text{Cu}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ which dissolved in about 5-10 mL of ethanol, were added drop-wise with constant stirring. The contents were refluxed on water bath for two hours. The product was cooled to room temperature. Upon cooling, colored precipitates were formed, which were filtered and washed with ethanol and then diethyl ether followed by drying overnight at 50 °C. While, Mn(II) complexes were synthesized by followed [20], a hot ethanolic solution of 1 mmol of $\text{MnCl}_2 \cdot \text{H}_2\text{O}$ in 10 mL of ethanol was added, drop-wise with constant stirring, to a hot ethanolic solution of 2 mmol in 40 mL ethanol of each ligands. The mixture was refluxed on a water bath for two hours. Then, 2 mmol of sodium acetate was added the mixture and refluxing was continued for two hours. The formed complexes were filtered and washed with ethanol and dried in vacuumed desiccator [Scheme 3].



Scheme 3. The participation of O and N groups in coordination M: Co(II), Cu(II) and Mn(II), n: 1, 2, X: OH, COOH.

3. Results and discussion

All the results of the elemental analysis for the prepared ligands and their metal complexes are very close to the expected formulas as shown in Table 1.

Table 1. Elemental analysis of the ligands and their metal complexes.

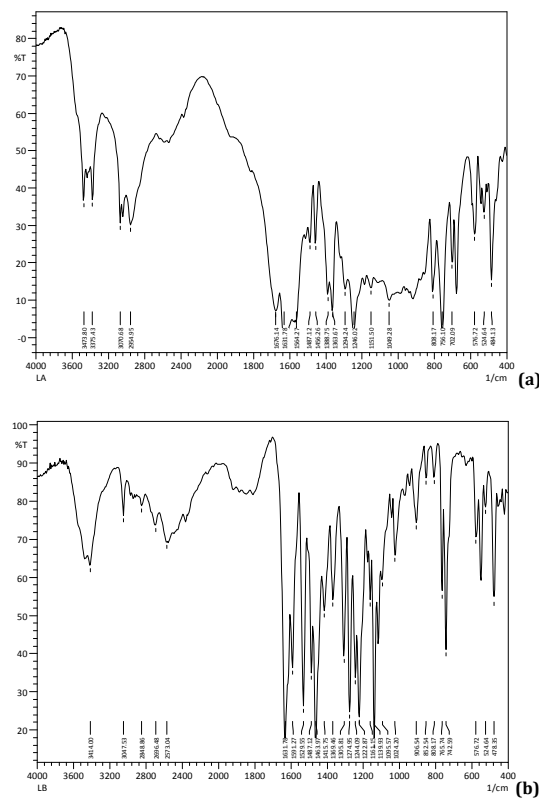
Expected formula	Color	Elemental analysis (calculated / found)		
		C	H	N
HL _A	Orange	69.70 / 69.65	4.60 / 4.62	5.81 / 5.28
CuL _A (H ₂ O) ₄	Pale green	44.74 / 45.55	4.83 / 4.61	3.73 / 3.57
CoL _A (H ₂ O) ₄	Pale soil color	45.30 / 45.37	4.89 / 4.48	3.77 / 3.64
[Mn(L _A) ₂ (H ₂ O) ₂]Cl ₂ ·2H ₂ O	Soil color	49.57 / 49.52	4.16 / 4.63	4.13 / 4.11
HL _B	Reddish brown	73.23 / 73.15	5.20 / 5.27	6.57 / 6.67
CuL _B (Ac) ₂	Olive	56.43 / 55.94	4.46 / 4.52	3.87 / 3.97
CoL _B Ac	Pale brown	54.39 / 54.52	4.26 / 4.29	4.23 / 4.29
[Mn(L _B) ₂ (H ₂ O) ₂]Cl ₂ ·2H ₂ O	Soil color	50.18 / 50.19	4.53 / 4.37	4.50 / 4.74

Table 2. FT-IR spectra data (cm⁻¹) of the prepared compounds.

Compound	Ar-CH	CH=N	C=O	C-O	C=C
HL _A	3070	1631	1676	1246	1564
CuL _A (H ₂ O) ₄	3124	1606	1587	1384	1552
CoL _A (H ₂ O) ₄	3138	1614	1591	1408	1537
[Mn(L _A) ₂ (H ₂ O) ₂]Cl ₂ ·2H ₂ O	3142	1614	1589	1408	1544
HL _B	3047	1631	-	1274	1591
CuL _B (Ac) ₂	3057	1614	-	1377	1531
CoL _B Ac	3057	1606	-	1292	1543
[Mn(L _B) ₂ (H ₂ O) ₂]Cl ₂ ·2H ₂ O	3061	1598	-	1301	1537

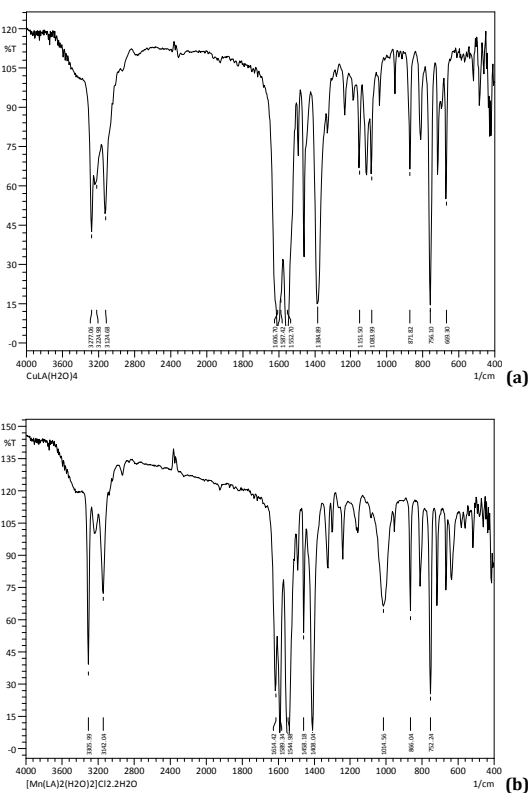
3.1. FT-IR spectroscopy

The chemical structure of the two iminophenol ligands and some of their transition metal Cu(II), Co(II) and Mn(II) complexes were identified by comparing with the FT-IR analysis data in the literature [20,21]. The main functional groups and their FT-IR frequencies of Schiff bases and their complexes are listed in Table 2, Figure 1 and 2. They were recorded in wavenumber range 4000-400 cm⁻¹.

**Figure 1.** FT-IR spectra of HL_A (a) and HL_B (b).

The FT-IR spectra of the two iminophenol ligands (HL_A and HL_B) show no C=O (1665 cm⁻¹) bond of salicylaldehyde. The FT-IR spectra of the two aminophenol ligands (HL_A and HL_B) exhibit a strong bands at 1631 cm⁻¹ due to the -C=N-

azomethine group, which indicate that the Schiff base ligands have been produced [22,23].

**Figure 2.** FT-IR spectra of CuL_A(H₂O)₄ (a), and [Mn(L_A)₂(H₂O)₂]Cl₂·2H₂O (b) complexes.

The appearance of -C=N- azomethine in all the metal complexes at a lower frequencies 1598-1614 cm⁻¹ compared to the iminophenol ligands, suggesting that, this group has been coordinated to the central metal ions Cu(II), Co(II) and Mn(II). In the iminophenol ligands (HL_A and HL_B) the frequency of hydroxyl group was observed at about 3473-3375 and 3480-3414 cm⁻¹, respectively, due to intramolecular hydrogen bonding between OH and the imines groups in the ligands (Scheme 2), which was disappeared in the metal complexes [24,25], this indicates that the OH group has been deprotonated and coordinated to the central metal [26].

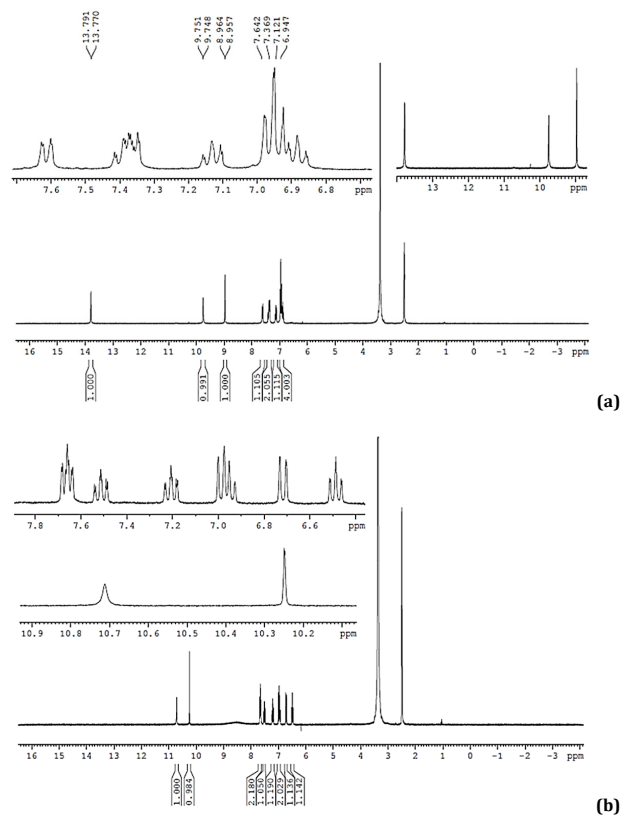


Figure 3. The ^1H NMR spectra of the Schiff bases ligands - (a) HLA and (b) HL_B.

A strong band was observed at 1246 and 1274 cm^{-1} in the iminophenol ligands (HL_A and HL_B), respectively, due to phenolic C-O stretching mode which was shifted to a higher frequency after complexation with the central metal ion, also the appearance of new bands at 500 and 538 cm^{-1} , which are refer to $\nu(\text{M-O})$ and $\nu(\text{M-N})$, respectively [27], indicating coordination through imine nitrogen and phenolate oxygen [28]. The strong sharp bands at 756 and 742 cm^{-1} indicate the presence of coordinated H_2O molecules with Cu(II), Co(II) and Mn(II) metal ions, respectively [29]. Many aromatic peaks for the ligands and complexes were appeared about 1531-1591 cm^{-1} .

The small band at 1676 cm^{-1} in the iminophenol ligand HL_A due to the carboxylic C=O stretching mode which was shifted to a lower frequency after complexation with the central metal ions [30]. In complexes $\text{Cu}(\text{L}_B)(\text{Ac})_2$ and $\text{Co}(\text{L}_B)\text{Ac}$, medium to sharp bands in the regions 1581-1471 cm^{-1} and 1377-1386 cm^{-1} have been assigned to asymmetric and symmetric vibrations of the coordinated acetate group. The large difference between ν_{asymOCO} and ν_{symOCO} of ~ 200 cm^{-1} or more is indicative of a monodentate coordination through the carboxylate groups [31]. Complex $\text{Cu}(\text{L}_B)(\text{Ac})_2$ shows strong symmetrical bands at 1581 cm^{-1} (ν_{asymOCO}) and at 1377 cm^{-1} (ν_{symOCO}) with $\Delta\nu$ 204 cm^{-1} , which indicates monodentate coordination through the carboxylate groups. The complex $\text{Co}(\text{L}_B)\text{Ac}$ shows strong symmetrical bands in the range 1471 cm^{-1} (ν_{asymOCO}) and 1386 cm^{-1} (ν_{symOCO}) with $\Delta\nu$ 85 cm^{-1} , which indicates bidentate chelating coordination through the acetate group [32], i.e. $\Delta\nu$ less than and more than 200 cm^{-1} indicates the presence of bidentate chelating coordination and monodentate coordination through an acetate group, respectively.

3.2. ^1H NMR spectroscopy

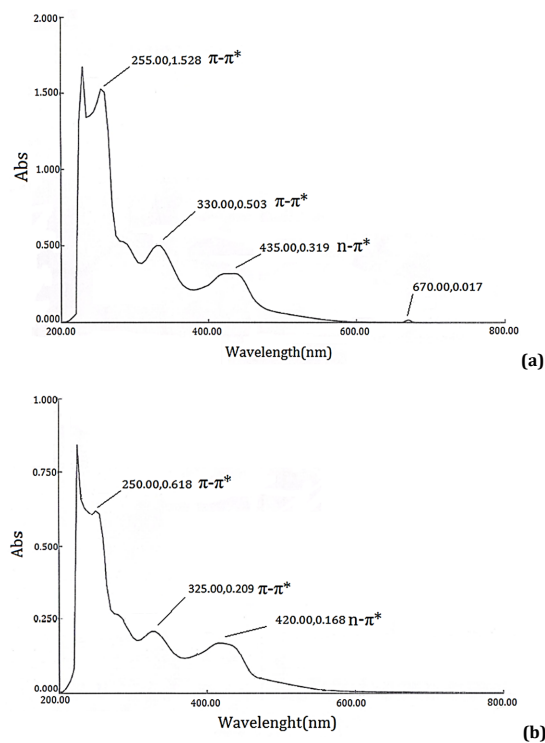
The ^1H NMR spectra for ligands (HL_A and HL_B) were measured in DMSO- d_6 at room temperature. The free ligands show proton resonance from δ 0 to 15 ppm, and the splitting pattern peak values for all protons are assigned unambiguously as shown in Figure 3. The chemical shift observed for phenolic -OH protons in the two ligands (HL_A, HL_B) at δ 13.77 and 10.70 ppm, respectively [33]. Which always have a given singlet in off-set at high δ values, thus confirming it's involvement in an intramolecular hydrogen bond with the neighboring nitrogen atom [34]. The multiple signals around δ 6.84-7.64 and δ 6.53-7.65 ppm are assigned to aromatic protons of both rings, which aren't affected by chelation. A sharp singlet, which is shifted downfield, and observed at δ 8.96 and 10.25 ppm are assigned to the azomethine protons in the ligands (HL_A, HL_B), respectively. The number of peaks and proton resonance of the free Schiff base ligands completely differ upon complexation [35]. The imine proton is shifted up-field by δ 0.2 ppm and the phenolic OH protons are absent in any of the metal complexes. This confirms the bonding of nitrogen and oxygen of the ligands to the metal ion. The same results were confirmed by the FT-IR spectra [36].

3.3. Electronic spectra

The electronic spectra data of the two Schiff base ligands (HL_A, HL_B) (Figure 4) have been generally exhibit in three main bands. The first absorption band at 255 and 250 nm which can be attributed to the π - π^* transition for the aromatic system while the second absorption band attributed to π - π^* transition of imines group which appeared at 330 and 325 nm [37].

Table 3. Thermal stability and thermodynamic parameters of ligands (HL_A, HL_B) and metal complexes.

Compound	T _s (K)	Temp. of 50% wt loss (°C)	Rate of decomp. (%/min)	Char content 625 °C, (%)	Activation energy (E _a) (kJ/mol)	Temp. range (°C)	ΔH* (kJ/mol)	ΔS* (J/mol K)	ΔG* (kJ/mol)
HL _A	559.58	295	13	12	35.99	89-220	31.34	-305.77	171.13
CuL _A (H ₂ O) ₄	553.92	288	46	8	43.83	76-288	39.25	-293.19	162.44
CoL _A (H ₂ O) ₄	636.82	388	23	-	19.57	33-336	13.85	-291.47	185.63
[Mn(L _A) ₂ (H ₂ O) ₂]Cl ₂ .2H ₂ O	607.50	362	34	20	38.27	191-320	33.22	-304.83	185.07
HL _B	609.80	342	32	11	55.53	108-263	64.37	-325.83	198.74
CuL _B (Ac) ₂	624.78	433	13	10	18.40	138-346	13.60	-209.65	130.82
CoL _B Ac	756.22	520	21	8	16.29	126-348	10.01	-271.83	205.57
[Mn(L _B) ₂ (H ₂ O) ₂]Cl ₂ .2H ₂ O	456.24	550	69	36	87.75	110-192	83.96	-346.82	158.32

**Figure 4.** The electronic spectra of the ligands - (a) HL_A and (b) HL_B.

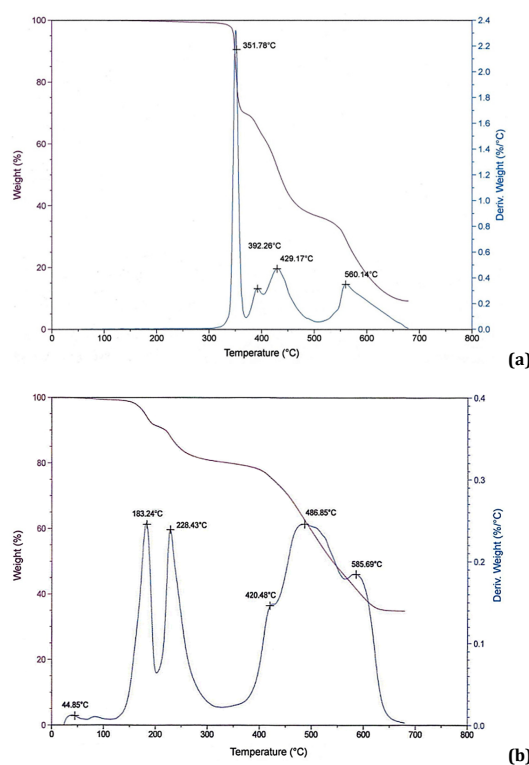
These bands weren't significantly affected by chelating. The third absorption band at 435 and 420 nm assigned to n-π* transition [38], which was shifted to a longer wavelength (red shift) upon formation of the complexes. This shift may be attributed to the donation of the lone pairs of nitrogen atoms of the Schiff bases ligands to the metal ion N:→ M.

3.4. Thermogravimetric study

The thermal stability characteristic parameters were obtained from analysis of the thermograms (Figure 5), which are listed in Table 3. The kinetic parameters such as activation energy (E_a) was calculated from Arrhenius plots between the rate of decomposition (ln K) and 1/T. Half weight loss temperature (T_{50%}) which is represents the temperature at which the sample loses half of its total weight. The rate of decomposition which was measured from the slopes of the TGA curves at decomposition temperature. The thermodynamic parameters of activated complexes, including the free energy ΔG*, the enthalpy ΔH* and the entropy ΔS* of the process were calculated using Freeman-Carroll equation [39,40].

The thermodynamic parameters of activated complexes are often calculated using the peak temperature T_s so that the value of ΔG*, ΔH* and ΔS* are related to the highest rate of the process. The negative values of ΔS* indicate that the activated

complexes have more ordered structures than the reactant [41]. The thermogram results show that some of these compounds have one decomposition temperature while the others have two, four and five. On the other side the char content of these compounds at 625 °C were less than 20% and some of those have more than 30%, which are indicate the thermal stability of these compounds.

**Figure 5.** Thermograms of the CuL_B(Ac)₂ and [Mn(L_B)₂(H₂O)₂]Cl₂.2H₂O.

4. Conclusions

Cu(II), Co(II) and Mn(II) complexes with two Schiff base ligands have been prepared and studied. The results of TG-DTA measurements showed to have enough resistance against thermal decomposition for the metal complexes than their parent ligands. According to the TG analysis, weight losses of the metal complexes changed at 625 °C as follows: [Mn(L_B)₂(H₂O)₂]Cl₂.2H₂O > [Mn(L_A)₂(H₂O)₂]Cl₂.2H₂O > CuL_B(Ac)₂ > CoL_BAc ≈ CuL_A(H₂O)₄. As result, [Mn(L_B)₂(H₂O)₂]Cl₂.2H₂O demonstrated higher thermal stability against thermal degradation than ligands and other metal complexes.

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