

Military Technical College
Kobry El-Kobbah,
Cairo, Egypt



7th International Conference
on
Chemical & Environmental
Engineering
27 - 29 May, 2014.

CEEB-3

Spectral and Thermal Studies of Mo and Mn d-glucose Complexes.

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Abstract

The complexes of d-glucose with Mo (VI) and Mn (II) were prepared. The structures of the prepared complexes were characterized; the stoichiometry was determined by the elemental analysis, mode of bonding by IR and geometry by electronic spectroscopy. Thermal studies were carried out for the prepared complexes. The mechanisms of the thermal decomposition for the prepared complexes were studied by TGA. Thermodynamic and kinetic studies of the complexes were determined by DTA, and DSC techniques.

Keywords :

D-glucose, IR spectra, Nujol mull spectra, DTA, TGA, DSC , Mo- and Mn complexes

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Introduction:

Carbohydrates represent a very important class of compounds in biological systems and play a key role in many processes important to life ⁽¹⁻³⁾. Hydration of carbohydrates is an important point of research ⁽⁴⁻⁵⁾. Glucose is a simple monosaccharide found in plant. It is one of the three dietary monosaccharides, along with fructose and galactose that are absorbed directly into the bloodstream during digestion. An important carbohydrate in biology, cells use it as a secondary source of energy and a metabolic intermediate. Glucose is one of the main products of photosynthesis and fuels for cellular respiration. Glucose exists in several different molecular structures, but all of these structures can be divided into two families of mirror-images (stereoisomers). Only one set of these isomers exists in nature, those derived from the "particular chiral form" of glucose, denoted D-glucose, or D-glucose.

Molybdenum is a second-row transition metal ion that is involved in any sort of biological activity. In particular, through its +4, +5 and +6 oxidation states, it plays an important role in various oxidoreductase enzymes ⁽⁶⁾. Saccharide units in biological systems and their possible interactions with metal ions has been a promising field in the area of bioinorganic chemistry ⁽⁷⁾. Solution studies have clearly demonstrated complex formation between transition metal ions and saccharides ⁽⁸⁾; however, the isolated complexes in case of alkali and alkaline earth metal ions were mostly found to be adducts ⁽⁹⁾.

The coordination chemistry of manganese(II) has attracted considerable interest due to the crucial role played by the metal in redox and non-redox proteins. Studies involving the synthesis and characterisation of manganese complexes are useful towards the understanding of the structure and reactivity of manganese sites in biological systems ⁽¹⁰⁻¹²⁾.

Aim of the work

The aim of this manuscript:

- 1) Synthesis of Mo- and Mn- complexes with D-glucose in solid state.
- 2) Elemental analyses of complexes.
- 3) Structural determination of the complexes based on spectral results.
- 4) Thermal studies of some of the prepared complexes using DTA, TGA and DSC techniques

Experimental:

a) Preparation of Mo (VI)-Mn (II) d-glucose metal complexes

A hot clear solution of 0.01 mole of the $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ salt in 25 ml water was added to 0.01 mole solution of D-glucose dissolved in 25 ml of water for preparation of $\text{Mn}_3(\text{HL})_2(\text{OH})(\text{H}_2\text{O})_6\text{Cl}$ complex and hot clear solution of 0.01 mole of ammonium molybdate salt in 25 ml water was added to 0.01 mole solution of D-glucose dissolved in 25 ml of water for preparation of $\text{MoO}_2(\text{L}_1)_2$ complex. The reaction was done in presence of 5 ml concentrated ammonia solution. The reaction mixture was refluxed for 45 min and the precipitated complexes were filtered, washed several times by water and dried in a desiccator over CaCl_2 . The elemental analyses are given in Table (1).

Table (1): Elemental analyses of D-glucose (HL) complexes, calculated and experimental results ()

Complex	M	C	H	Cl	Colour	m.p. C°
MoO ₂ (HL) ₂	Mo				brown	>300
	(20.12)	(30.02)	(4.38)			
	19.81	29.77	4.16			
Mn ₃ (HL) ₂ (OH)(H ₂ O) ₆ Cl	Mn				reddish brown	>300
	(24.18)	(21.47)	(4.45)	(5.62)		
	24.00	21.14	4.88	5.20		

Chemical Analyses:a) Carbon, Hydrogen and halogen analyses:

The measurements have been carried out at the micro-analytical laboratory at the Chemistry Department Faculty of Science, Cairo University.

b) Metal analyses:

Mn complex was digested in aquaregia and the digested product determined by the atomic absorption technique at the Central Laboratory, Faculty of Science, Alexandria University. Mo was digested in aquaregia then determined by ICP/MS technique at The Main Laboratory of the Chemical War.

Spectrophotometric measurements:Ultraviolet and visible spectra:

The electronic spectral measurements in the visible and ultraviolet regions of the solid complexes (Nujol mull spectra) were measured at the Central Laboratory, Faculty of Science, Alexandria University.

Infrared spectra

The data have been carried out by KBr dick technique at the Central Laboratory, Faculty of Science, Alexandria University.

Thermal analyses measurements:

The measurements have been carried out at nitrogen atmosphere, rate of heating 10 C°/min at the micro-analytical laboratory at the Chemistry Department Faculty of Science, Cairo University.

Results and discussion**1- IR spectra of glucose complexes.**

The IR spectra of free glucose, MoO₂ (HL)₂ and Mn₃(L)₂(OH)(H₂O)₆Cl (LH₂ = d-glucose) were compared, Figure (1).

Table (2) collects the assignment of the main characteristic absorption bands for each of two molecules. The vibrational spectra that indicated in both, Figure (1) and Table (2), can be classified into two main groups of spectra. The region from 600 cm⁻¹ to 1500 cm⁻¹ in which C-O and C-C groups vibration modes are present and the carbohydrates generally shows their characteristic bands. On the other hand the bands from 2900 cm⁻¹ to 3450 cm⁻¹ assigned to CH and OH vibrations groups⁽¹³⁾. The broad band at 3400 cm⁻¹ for free d-glucose upon complexation converted into sharp band at (3418-3384 cm⁻¹) with a shoulder at (3250-3275 cm⁻¹) for Mo and Mn complexes respectively indicates the involving of OH in complexation⁽¹⁴⁻¹⁵⁾. Small sharp bands at 1375 cm⁻¹, 1333 cm⁻¹, 1250 cm⁻¹ and 1210 cm⁻¹ which characterized the bending moods for CCH, OCH, CH and OH in plane and the shift of

the band at 1429 cm⁻¹ in free glucose to (1402 -1396 cm⁻¹) in complexation indicates the involving of some OH groups in complication .Sharb band at 1638 which characterized the (C=O) carbonyl group in the free ligand shifted to (1632-1590 cm⁻¹) upon complexation indicates the participation of the OH group adjacent to the carbonyl group in complexation. The appearance of new broad bands at 901 cm⁻¹ with high frequency shoulder at 913 cm⁻¹ in case of Mo complex indicating the presence of the cis-MoO₂²⁺ moiety⁽¹⁶⁾. The appearance of new band at 597 cm⁻¹ in the complexes may refer to ν MnO⁽¹⁷⁻¹⁸⁾.

Table (2): The IR spectra in cm⁻¹ of D-glucose, MoO₂ (HL)₂ and Mn₃(L)₂ (OH)(H₂O)₆Cl

d-glucose	MoO ₂ (HL) ₂	Mn ₃ (L) ₂ (OH)(H ₂ O) ₆ Cl	assignment
	3418, 3250	3384,3275	ν OH
3400	2925	2924	ν CH ₂ CH ₂
2937	1632	1590	ν C=O
1638	1402	1396	δ OCH + δ COH + δ CCH
1429	-	-	δ OCH + δ COH + δ CCH
1375	-	-	
1333	-	-	δ OCH + δ CCH
1250,1210	-	-	δ CH + δ COH in plane
1154	1167	1075	ν CO + ν CC
1111,1094,1049,1031,1013	1072	-	ν CO + ν CCH
916	913-901	-	ν MoO ₂
837	-	-	ν CO + ν CCH+ δ CH
776,716	618	597	δ CCO + δ CCH
			ν MnO

2-Nujol mull spectra

The electronic spectrum for the prepared complexes were given at Figure (2), Table (3).

The electronic spectrum of MoO₂ (HL)₂ shows three bands at (230, 274 and 330 nm). The absorption bands between 200 and 400 nm can be assigned to ligand to metal charge transfer (CT) transitions

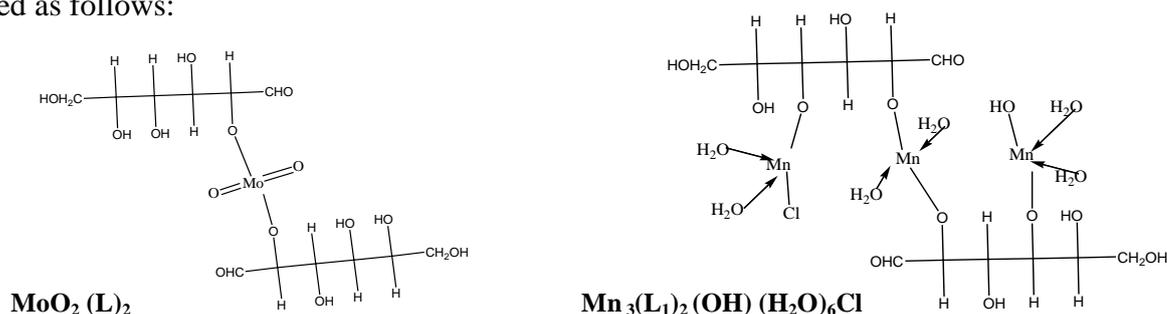
(O²⁻→Mo⁶⁺)⁽¹⁹⁾, while the absorption band at 330 nm has been assigned to an octahedral geometry of isolated molybdenum oxide centers⁽²⁰⁻²¹⁾.

The electronic spectra for The electronic spectrum of the complex MoO₂ (HL)₂ and [Mn₃(L)₂ (OH)(H₂O)₆Cl] presents a shoulder at 653 nm . It can he assigned to the ⁶A₁ → ⁴T₁ transition for tetrahedral fields⁽²²⁾.

Table (3): λ max (nm) of the complexes

Complex	λ max (nm)
MoO ₂ (L) ₂	230(s), 274(b), 330(b)
Mn ₃ (L) ₂ (OH) (H ₂ O) ₆ Cl	375(s),539(b), 653(b)

From the previous studies,MoO₂ (L)₂ and Mn₃(L)₂ (OH) (H₂O)₆Cl complexes can be assigned as follows:



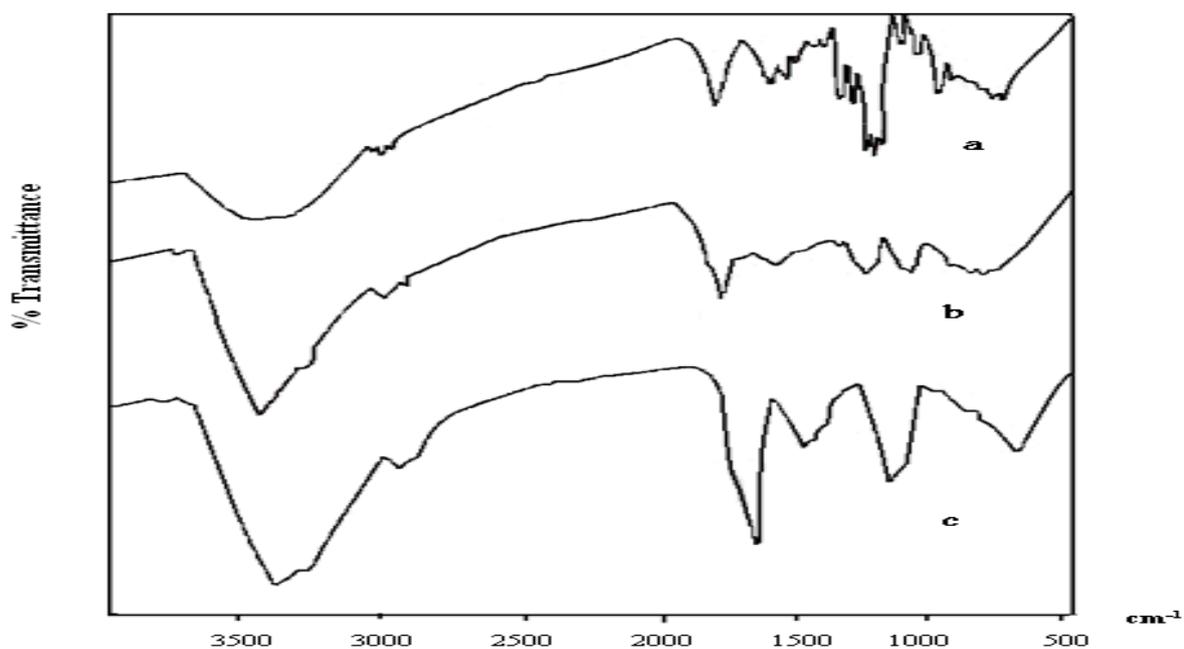


Figure (1): IR spectra cm^{-1} for:

a) d-glucose

b) $\text{MoO}_2(\text{HL})_2$

c) $\text{Mn}_3(\text{L})_2(\text{OH})(\text{H}_2\text{O})_6\text{Cl}$

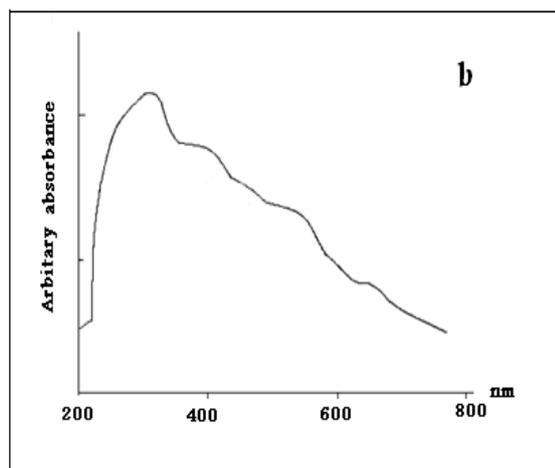
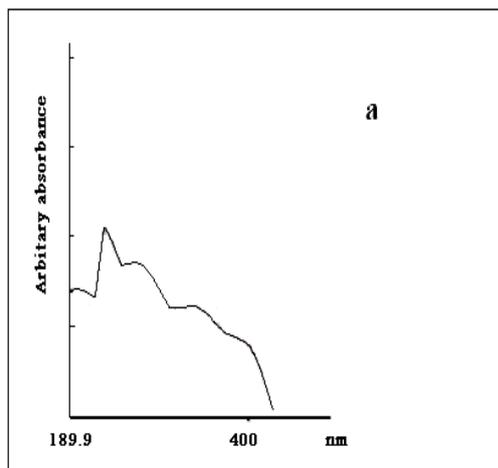


Figure (2): Electronic spectra in nm for:

a) $\text{MoO}_2(\text{HL})_2$

b) $\text{Mn}_3(\text{L})_2(\text{OH})(\text{H}_2\text{O})_6\text{Cl}$

3-Thermal analysis:

Thermal studies (DTA, TGA and DSC) were carried out for prepared complexes Figures (3-4)

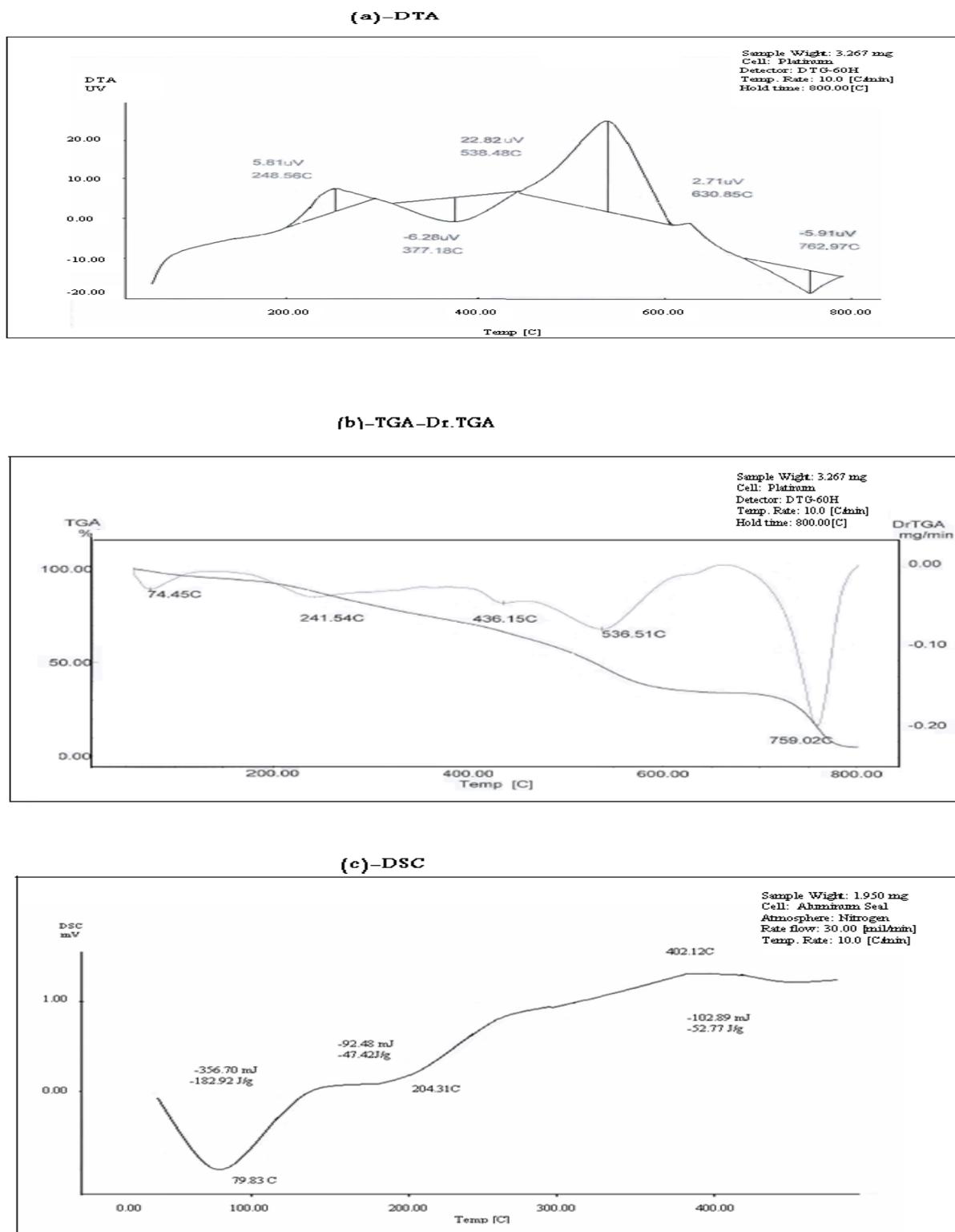


Figure (3): Thermal analysis data DTA, TGA, Dr. TGA and DSC of MoO₂ (HL)₂

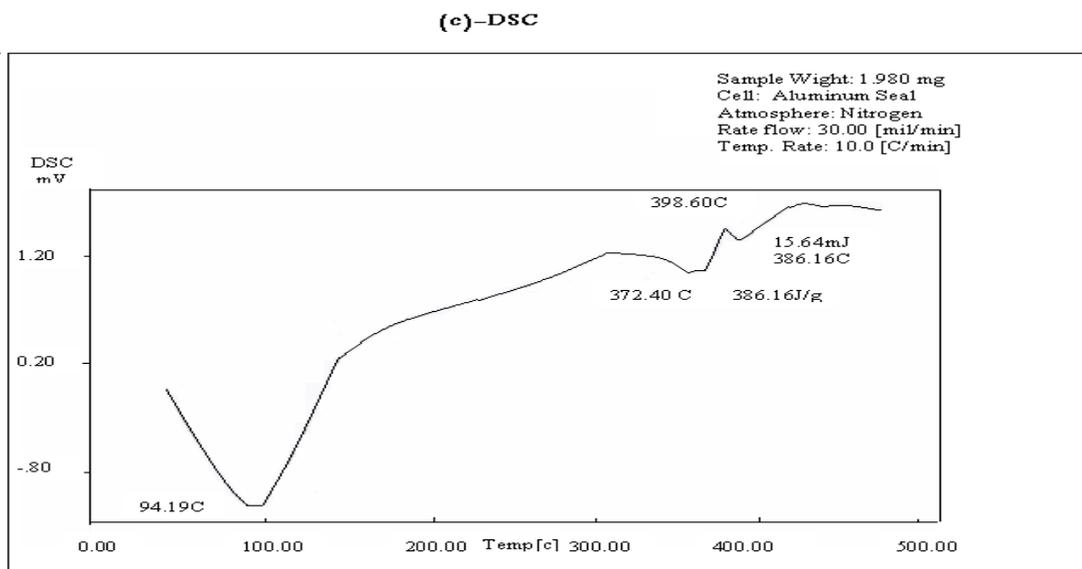
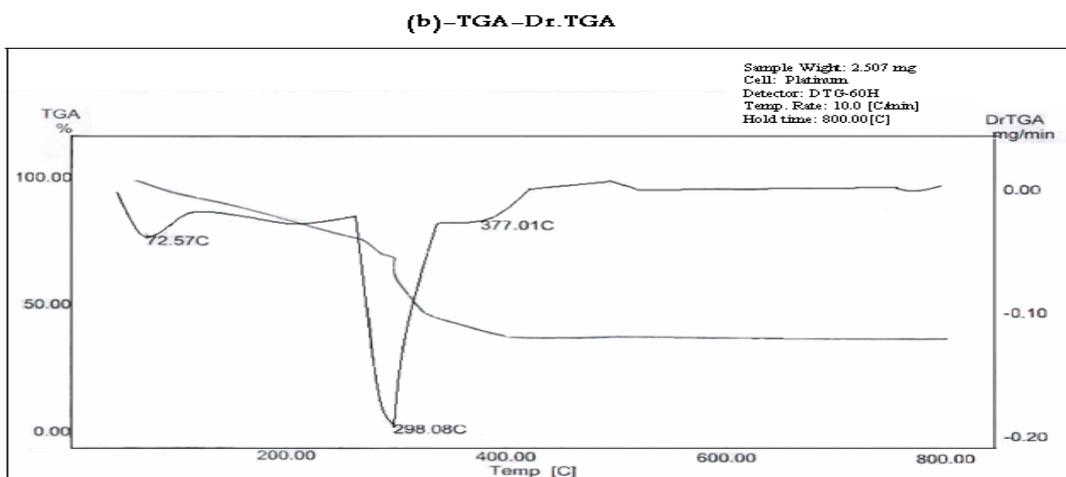
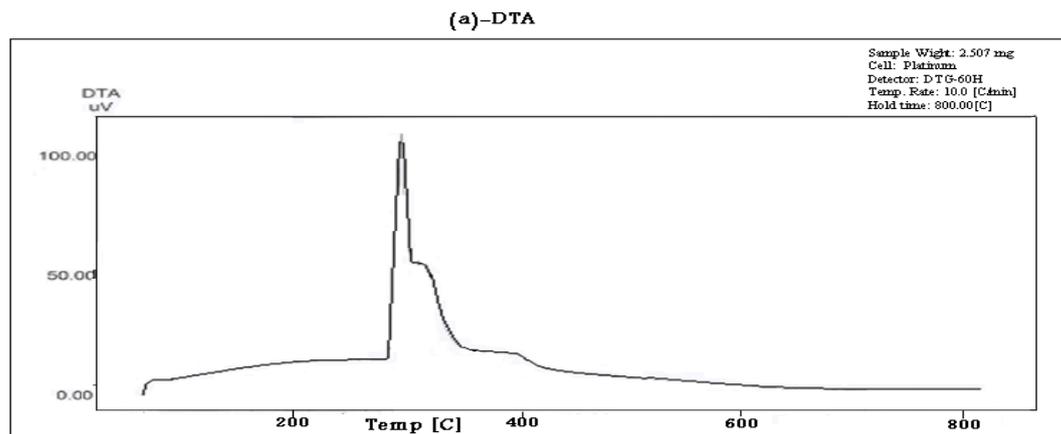
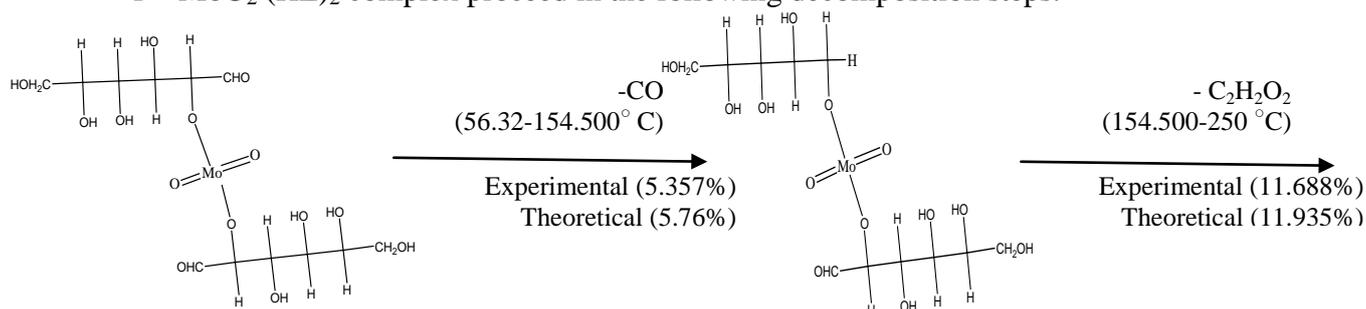


Figure (4): Thermal analysis data DTA, TGA, Dr. TGA and DSC of $Mn_3(L)_2(OH)(H_2O)_6Cl$

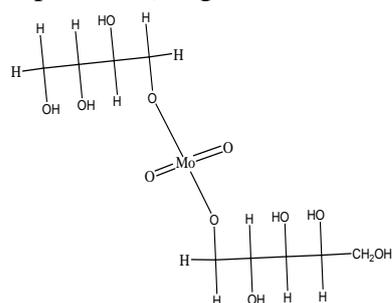
Summarizing the obtained TGA measurements for the selected complexes of d-glucose (LH_2) with Mo and Mn, Figures (3b-4b), where fruitful conclusions for the mechanism of decomposition are given:

1- MoO₂ (HL)₂ complex proceed in the following decomposition steps:



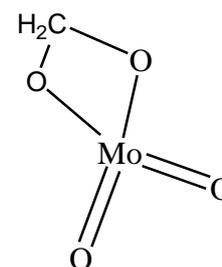
Dioxo molybdenum bis glucose tri-ol-pentanol d-glucose

2 - (Dioxo molybdenum mono 5 - O - 2, 3, 4



- C₈H₁₆O₇
(250-599.77 ° C)

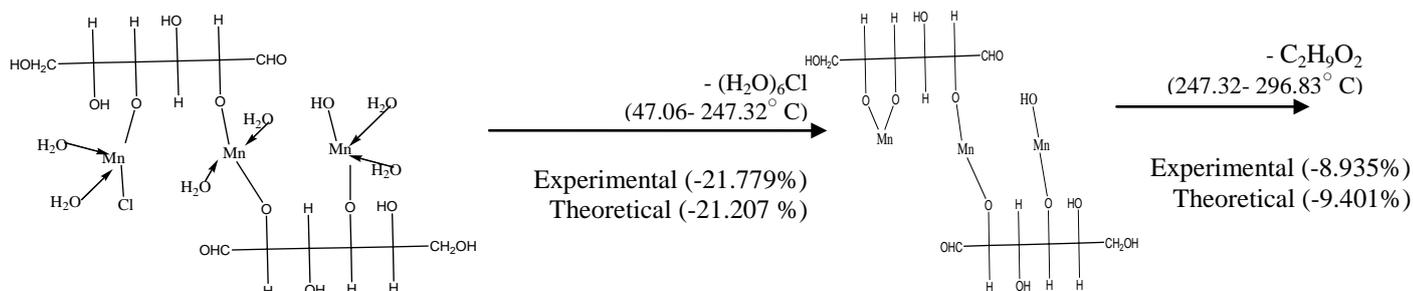
Experimental (46.378%)
Theoretical (46.527%)



Dioxo

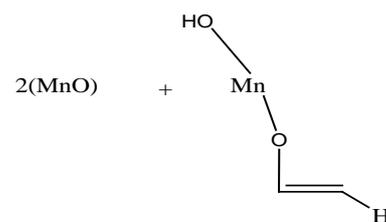
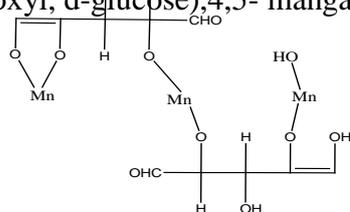
5-(Dioxo molybdenum-1-O-2, 3 di-ol propanol)-2, 3, 4 tri-ol -pentanole molybdenum O-O-methan

2- Mn₃(L)₂(OH)(H₂O)₆Cl complex proceed in the following decomposition steps:



Tri manganese hydroxyl chloro hexa hydro bis glucose hydroxyl, d-glucose),4,5- manganese-, d-glucose

2 (2-manganese, 4- manganese



-C₈H₈O₇
(296.83- 423.56 ° C)

Experimental (-31.432%)
Theoretical (-31.710%)

2-(2-O-manganese, 4- manganese hydroxyl, 3,5 di-ol, 4-5 en, penatanal) 4,5-O, O-manganese 3-ol, 4-5 en, penatanal

Bis manganese manganese + hydroxyl O-ethylene

DTA studies:

DTA thermal analysis were studied for the glucose complexes Figures (3a,-4a) MoO₂ (HL)₂ and Mn₃(L)₂ (OH)(H₂O)₆Cl . MoO₂ (HL)₂ gave three exothermic peaks and two endothermic peaks and Mn₃(L)₂ (OH)(H₂O)₆Cl gave two exothermic peaks.

The ln ΔT versus 10³/T plots for the complexes: MoO₂ (L)₂ and Mn₃(L)₂ (OH)(H₂O)₆Cl respectively are given, where, Figures (5-6) gave best fit straight lines from which the activation energies (E_a) were calculated . The order of chemical reactions (n) were calculated via the peak symmetry method ⁽²³⁻⁻²⁷⁾. The reaction orders are 1, 1.5 and 2. The fractions appeared in the calculated order of the thermal reactions, (n), Table (4), confirmed that the reactions proceeded in complicated mechanisms.

The maximum and the minimum T_m values are 1034 and 522 °K, respectively. The value of the decomposed substance fraction, α_m, at the moment of maximum development of reaction (with T=T_m) being determined from the relation ⁽²⁸⁾

$$(1 - \alpha_m) = n \frac{1}{1-n}$$

It is of nearly the same magnitude and lies within the range 0.500-0.649.

The calculated values of the collisions number, Z, showed a direct relation to E_a. The maximum and minimum Z values are 2 and 0.152, respectively, let to suggest different mechanisms with variable speeds.

The change of entropy values, ΔS[#], for all complexes, are nearly of the same magnitude and lie within the range -0.263 to -0.286 kJK⁻¹mol⁻¹, all are with -ve signs, Table (4). So, the transition states are more ordered, i.e. in a less random molecular configuration, than the reacting complexes.

The heat of transformation, ΔH[#], can be calculated ⁽²⁹⁾ from the DTA curves, Figures (3a, 4a). All the ΔH[#] values are with -ve signs, Table (4). In general, the change in enthalpy (ΔH[#]) for any phase transformation taking place at any peak temperature, T_m, can be given by the following equation:

$$\Delta S^\# = \Delta H^\# / T_m$$

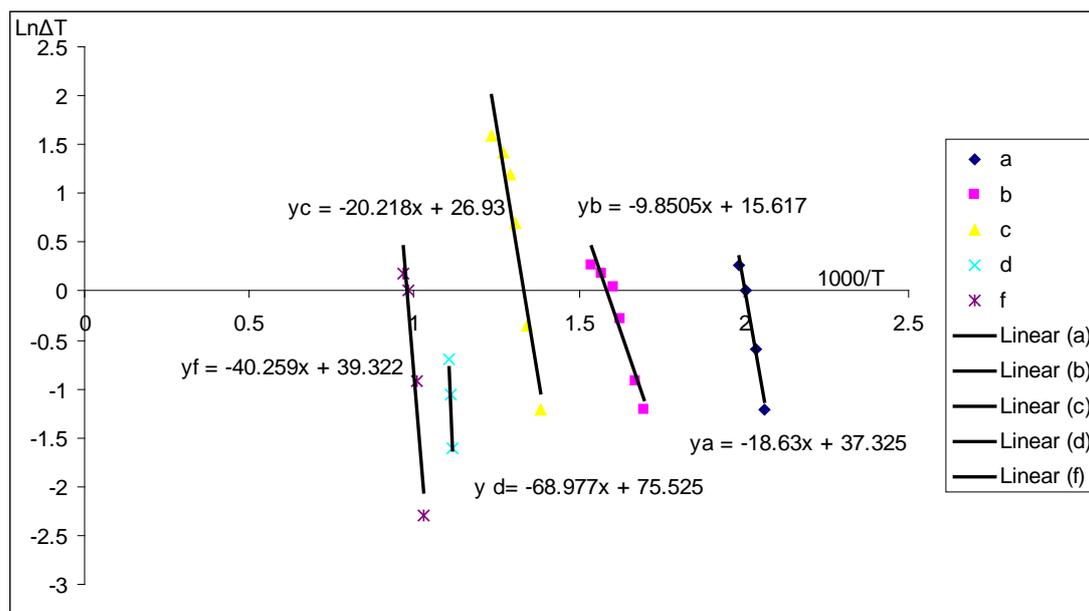


Figure (5): lnΔT-10³/T relationship for MoO₂ (HL)₂ complex

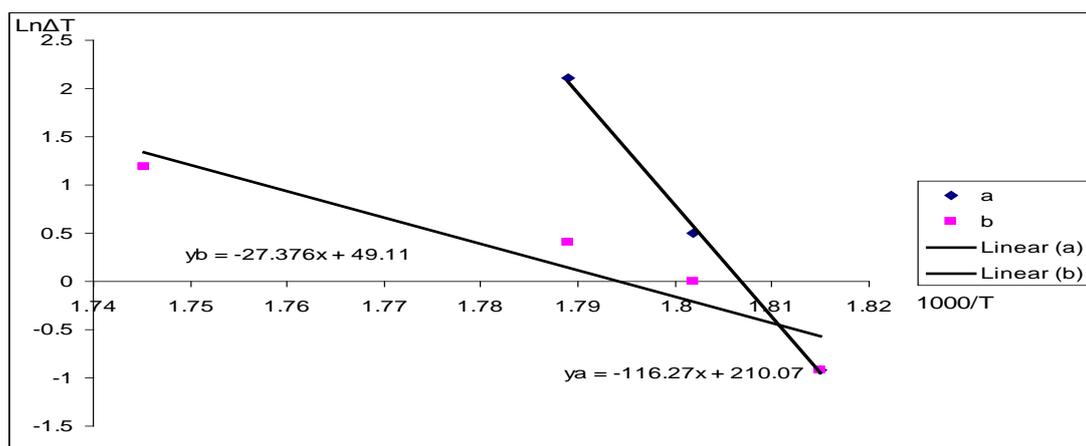


Figure (6): $\ln\Delta T-10^3/T$ relationship for $Mn_3(L)_2(OH)(H_2O)_6Cl$ complex

Table (4):DTA thermodynamic parameters of the complexes.

Complex	Peak (type)	Slope	ΔE_a	a	b	n	α_m	T_m (°K)	Z	$\Delta S^\#$	$\Delta H^\#$
$MoO_2(L)_2$	a(exo)	-18.63	154.89	1.35	1.7	1.123	0.616	522	0.367	-0.277	-144.741
	b(endo)	-9.85	81.89	1.75	1.75	1.260	0.589	650	0.152	-0.286	-186.047
	c(exo)	-20.22	168.11	2.1	2.75	1.101	0.614	811	0.249	-0.284	-230.266
	d(exo)	-68.98	573.50	0.9	0.6	1.543	0.550	904	0.763	-0.276	-249.08
	e(endo)	40.23	334.47	1	1.9	0.914	0.649	1034	0.388	-0.282	-292.44
$Mn_3(L)_2(OH)(H_2O)_6Cl$	a(exo)	-116.27	925.097	1.25	0.5	1.99	0.500	558	2.00	-0.263	-146.20
	b(exo)	-27.37	277.604	0.75	1	1.09	0.616	584	0.469	-0.276	-161.154

DSC studies:

DSC thermal analysis studies for the glucose complexes Figures (2c, 3c) $MoO_2(HL)_2$ and $Mn_3(L)_2(OH)(H_2O)_6Cl$ gave the following.

The glass transition and crystallization temperatures were determined from DSC graph for the selected complexes, Figures (3c, 4c) and Table (5). The crystallization temperatures of $MoO_2(HL)_2$ was 402.12 °C and 398.60 °C for $Mn_3(L)_2(OH)(H_2O)_6Cl$ has gained enough energy to move into very order arrangements after that it gave off $Mn_3(L)_2(OH)(H_2O)_6Cl$ heat through an exothermic transition. DSC plot is used to carefully determine the melting temperature through melting transition, where, the complex should absorb heat until all the crystals have melted.

However the Debye model ⁽³⁰⁻³¹⁾ is applied to describe capacity change over a large temperature range. The C_p can be represented as the following empirical form:

$$C_p = aT + b$$

By plotting C_p versus T, a straight line is obtained, thus, "a" and "b" parameters can be determined from the slope and intercept of the line, respectively, Figures (6-7, a, b) and Table (6).

Further applications based on Debye model on the complexes are given from the scope of the following equations:

$$C_p \cong C_v = \alpha T^3 + \gamma T, \quad \frac{C_p}{T} = \alpha T^2 + \gamma$$

Where, γ and α are the coefficients of electronic and lattice heat capacities, respectively. C_v is the heat capacity at constant volume which is assumed to be equal to C_p . Plots of C_p / T versus T^2 should yield straight lines with slopes α and intercepts γ , Figures (6-7, c, d) and Table (7)

However, DSC studies for the selected $[\text{MoO}_2 (\text{HL})_2]$ and $\text{Mn}_3(\text{L})_2 (\text{OH})(\text{H}_2\text{O})_6\text{Cl}$ complexes are given, Figures (6,7).

The data of each complex comprised two Figures (6, 7)

(A) Full $C_p - T$ relation curve for the complexes, Figures (6a, 7a).

(B) $C_p - T$ relation for the straight lines deduced from Figure (b) is given. The straight lines are analyzed and their reasonable equations are given and the validity is calculated with higher R^2 values for each line, Figures (6b, 7b). However, the observations deduced from Figures (6-7, a, b) are based on the following equation: $C_p = aT + b$.

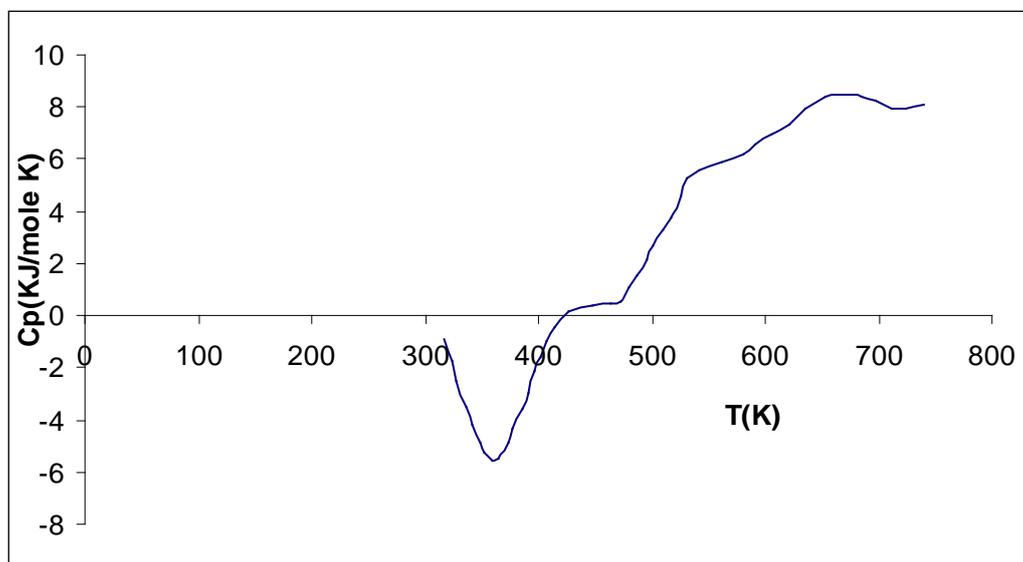
(C) $\frac{C_p}{T} - T^2$ relations are given, Figures (6c,7c).

(D) Similarly, $\frac{C_p}{T} - T^2$ relations analyzed in a similar way to (B), Figures (6d,7d). However, the following equation is applied:

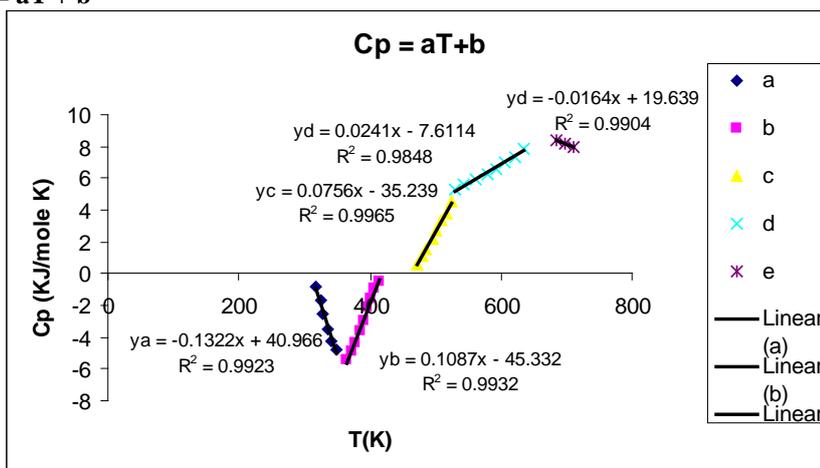
$$\frac{C_p}{T} = \alpha T^2 + \gamma$$

Based on the previous observations the barbitol complexes are given in $\text{Mo O}_2 (\text{HL})_2$ and

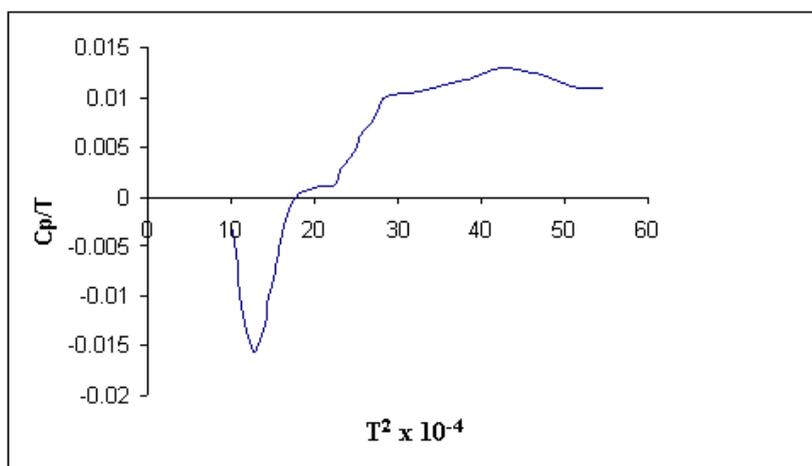
$\text{Mn}_3(\text{L})_2 (\text{OH})(\text{H}_2\text{O})_6\text{Cl}$ Figures (6,7), respectively, and the data were collected in Tables (6,8).



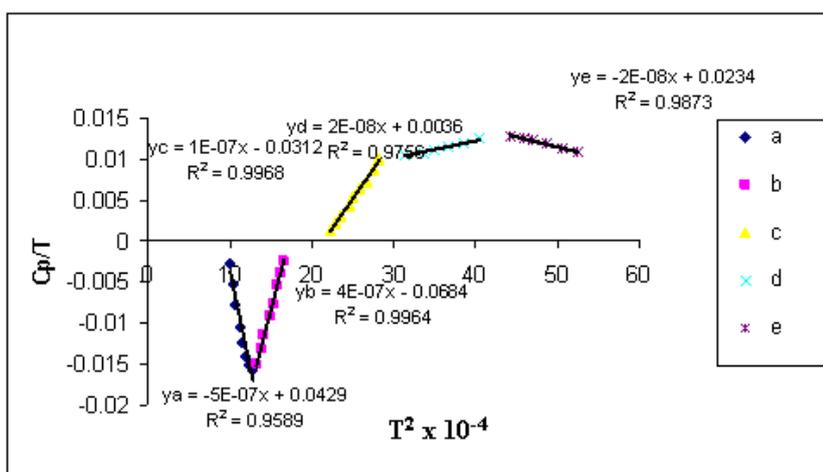
A) $C_p = aT + b$



B) $C_p = aT + b$

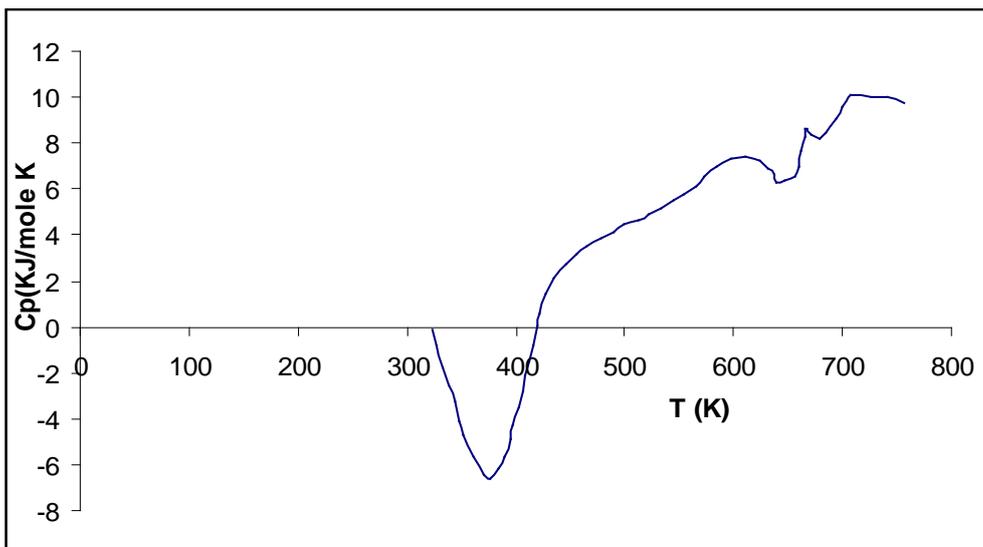


c) $C_p/T = \alpha T^2 + \gamma$

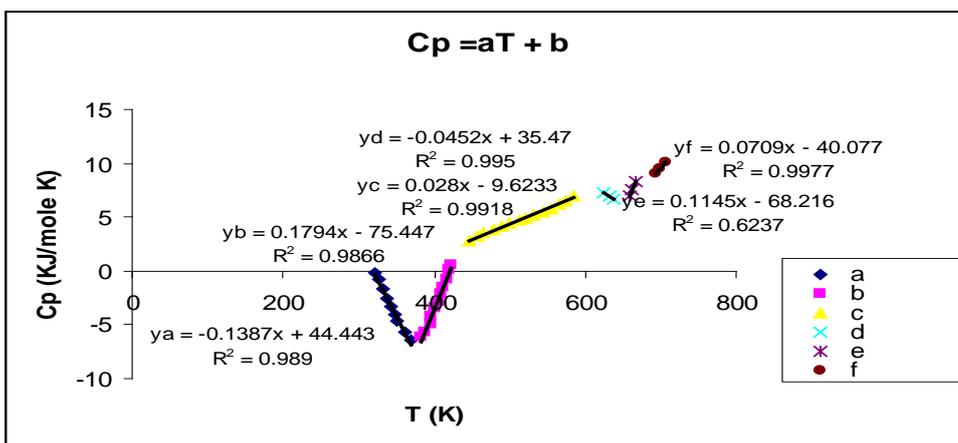


d) $C_p/T = \alpha T^2 + \gamma$

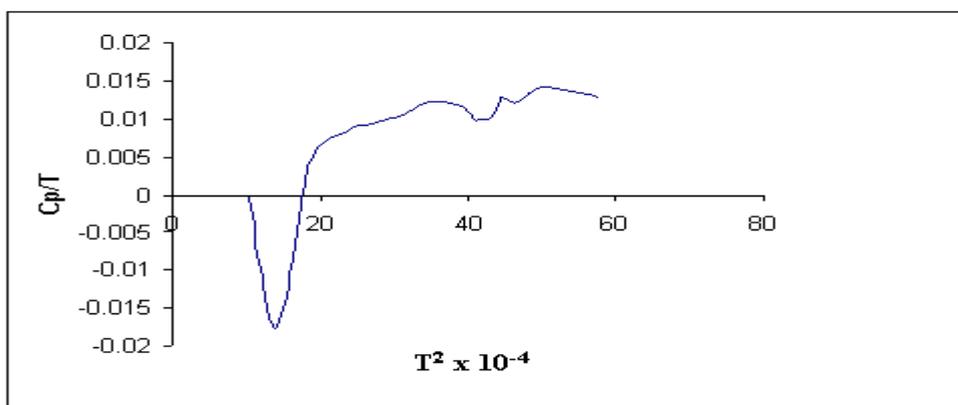
Figure (6) :DSC curves of MoO₂ (HL)₂ complex dependence of specific heat and temperature



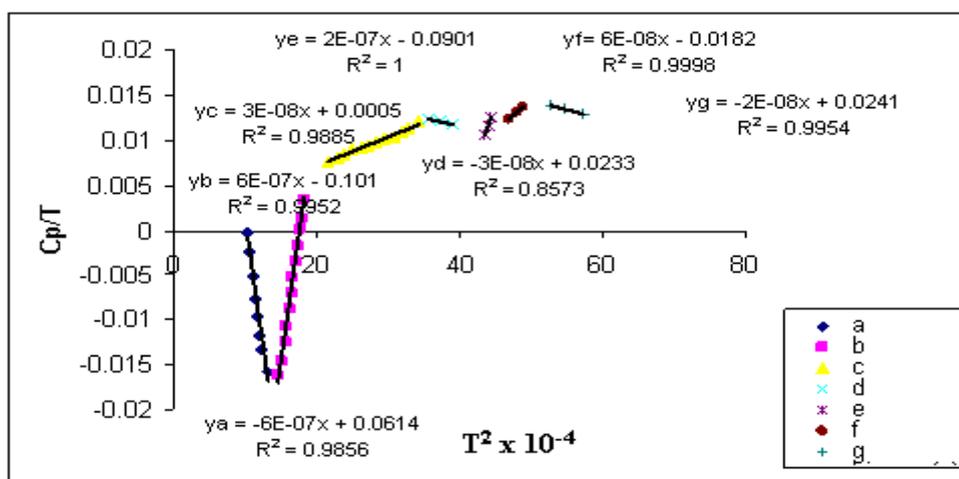
A) $C_p = aT + b$



b) $C_p = aT + b$



c) $C_p/T = \alpha T^2 + \gamma$



d) $C_p/T = \alpha T^2 + \gamma$

Figure (7): DSC curves of $Mn_3(L)_2(OH)(H_2O)_6Cl$ complex dependence of specific heat and temperature

Table(5): Thermal transitions of the selected complexes.

Complex	Peak (type)	Point of reaction (°C)	Tc (°C)	Tm (°C)	Tg (°C)	Enthalpy (ΔH) (J/g)
$MoO_2(HL)_2$	a(endo)	52.3	79.83	—	107.69	-182.92
	b(endo)	176.3	204.31	—	243.59	-47.42
	c(exo)	361.5	—	402.12	—	52.77
$Mn_3(L)_2(OH)(H_2O)_6Cl$	a(endo)	59	94.19	-----	114.29	----
	b(exo)	392	—	398.60	—	7.90

Table (6) : The slopes "a" and intercept "b" for DSC curves of selected complexes.

Complex	a ₁	a ₂	a ₃	a ₄	a ₅	a ₆
	[b ₁]	[b ₂]	[b ₃]	[b ₄]	[b ₅]	[b ₆]
$MoO_2(HL)_2$	-0.132	0.109	0.076	0.024	-0.016	
	40.7	-45.33	-35.34	-7.61	19.639	
	317-359 °K	374-414 °K	473-525 °K	531-653 °K	686-711 °K	
$Mn_3(L)_2(OH)(H_2O)_6Cl$	-0.166	0.19	0.029	-0.041	0.115	0.072
	50.44	-79.81	-9.85	32.98	-68.22	-41.11
	323-352 °K	389-422 °K	445-589 °K	624-647 °K	660-672 °K	685-708°K

• $C_p = a T + b$

From Dr. TGA diagram, Figure (3b,4b), the phase transition temperatures were calculated Table(7).

Table (7): The phase transition temperatures (K^o) of the selected complexes:

Complex	α	phase transition temperatures (K ^o)
MoO ₂ (HL) ₂	0.29	242
	0.33	436
	0.55	537
	0.89	759
Mn ₃ (L) ₂ (OH)(H ₂ O) ₆ Cl	0.256	73
	0.365	298
	0.642	377

Table (8): The slopes "α" and intercept "γ" for DSC curves of selected complexes.

Complex	α_1	α_2	α_3	α_4	α_5	α_6	α_7
	[γ_1]	[γ_2]	[γ_3]	[γ_4]	[γ_5]	[γ_6]	[γ_7]
MoO ₂ (HL) ₂	-5*10 ⁻⁷ [0.043] (322-361) ² °K	4 *10 ⁻⁷ [0.067] (374-414) ² °K	1.0*10 ⁻⁷ [0.031] (473+525) ² °K	2.0*10 ⁻⁸ [0.0005] (542-636) ² °K	-2.0*10 ⁻⁸ [0.023] (665-739) ² °K		
Mn ₃ (L) ₂ (OH)(H ₂ O) ₆ Cl	-6.0*10 ⁻⁷ [0.0614] (323-361) ² °K	6*10 ⁻⁷ [-0.101] (383-428) ² °K	3.0*10 ⁻⁸ [0.0008] (465-574) ² °K	-4*10 ⁻⁸ [0.028] (598-640) ² °K	3*10 ⁻⁷ [-0.103] (660-666) ² °K	6.0*10 ⁻⁸ [0.0162] (685708) ² °K	-2.0*10 ⁻⁸ [0.0241] (727-757) ² °K

Thermodynamic and Kinetic Studies:

$$\frac{C_P}{T} = \alpha T^2 + \gamma$$

In order to assess the influences of the structural properties of the chelating agent and the type of the metal on the thermal behavior of the complexes, the order (n) and the heat of activation (E) of the various decomposition stages were determined from the TG and DTA using the Coats-Redfern⁽³²⁾ and Horowitz-Metzger⁽³³⁾.

(i) Coats-Redfern Method⁽³²⁾:

This depends on the following equation:

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \ln \left(\frac{AR}{\beta E} \right) - \frac{E_a}{RT} \quad (1)$$

Where $g(\alpha) = 1 - (1 - \alpha)^{1-n} / 1 - n$ for $n \neq 1$ and $g(\alpha) = -\ln(1 - \alpha)$ for $n = 1$, R is the universal gas constant. The correlation coefficient, r, can be computed using the least squares method for different values of n (n = 0, 0.5, ..., 1) by plotting $\ln \left[\frac{g(\alpha)}{T^2} \right]$ versus 1/T for the metal complexes, Figure (8). The n-value which gave the best fit (≈ 1) will be chosen as the order parameter for the decomposition stage of interest. The slope of the straight line equals (E_a / R) and the intercept the pre-exponential factor, A can be determined, Table (9).

(ii) Horowitz-Metzger Method⁽³³⁾:

This was used to evaluate the degradation kinetics as follows:

$$\ln[-\ln(1-\alpha)] = \frac{E_a \theta}{RT_s^2} \quad \text{for } n = 1 \quad (2)$$

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{1-n}\right] = \ln\left(\frac{A}{\beta} \frac{RT_s^2}{E}\right) - \frac{E_a}{RT_s} + \frac{E_a \theta}{RT_s^2} \quad \text{for } n \neq 1 \quad (3)$$

Where $\theta = T - T_s$, T_s is the DTG peak temperature, T the temperature corresponding to weight loss W_t . In this method a straight line should be observed between the left hand sides of equations (2) and (3) versus θ with a slope of $\frac{E_a}{RT_s^2}$, Figure (9) and Table (10):

The thermodynamic parameters of activation can be calculated by following equations ⁽²⁹⁾:

$$\Delta H^* = E_a - RT \quad (4)$$

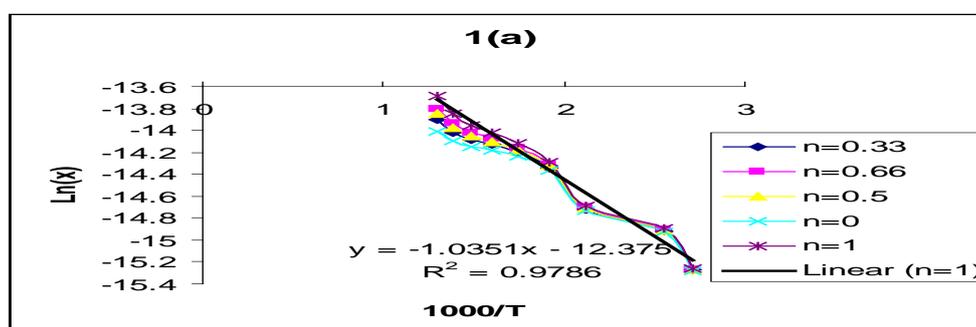
$$\Delta S^* = R \ln \frac{hA}{K_B T} \quad (5)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (6)$$

Where ΔH^* is the enthalpy of activation (KJ / mol), ΔS^* is the entropy of activation (KJ / mol.K), ΔG^* is the Gibbs free energy of activation (KJ / mol), h is the Plank's constant and K_B is the Boltzmann's constant.

The kinetic parameters evaluated by Coats-Redfern and Horowitz-Metzger methods are represented in Figure (8, 9) and Table (9,10), respectively, which reveals the following observations:

- All decomposition stages showed a best fit for $n = 1$, while the other values have no better correlation.
- The negative values of the entropy of activation, ΔS^* of the decomposition steps of the metal complexes indicate that the activated fragments have more ordered structure than the undecomposed complexes and/or the decomposition reactions are slow ⁽³⁴⁾.
- The positive sign of the enthalpy of activation, ΔH^* of the decomposition stages reveals that the decomposition stages are endothermic processes.
- The positive sign of free energy of activation, ΔG^* , indicates higher values of the final residue than that of the initial compound, all the decomposition steps are non-spontaneous processes.



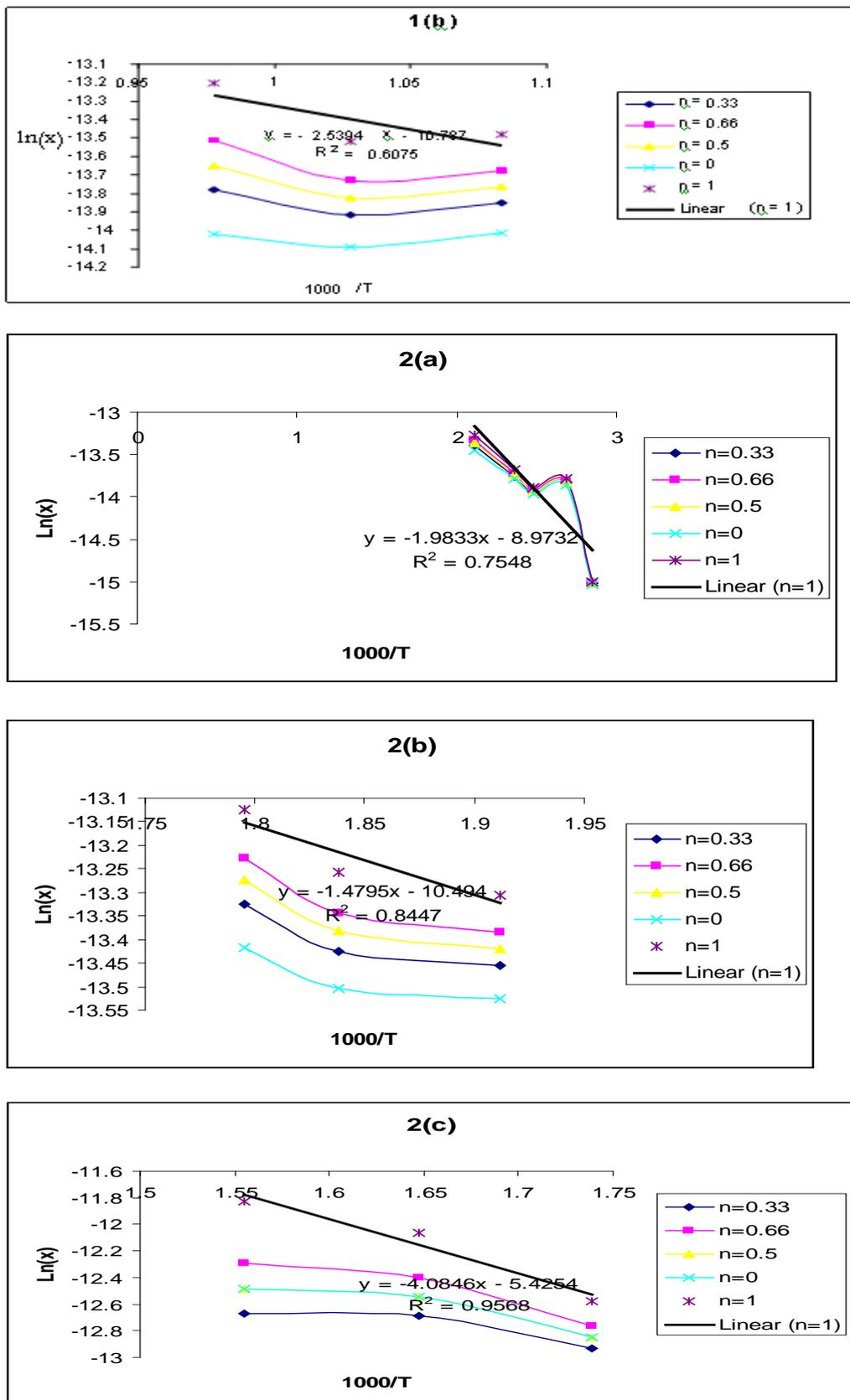
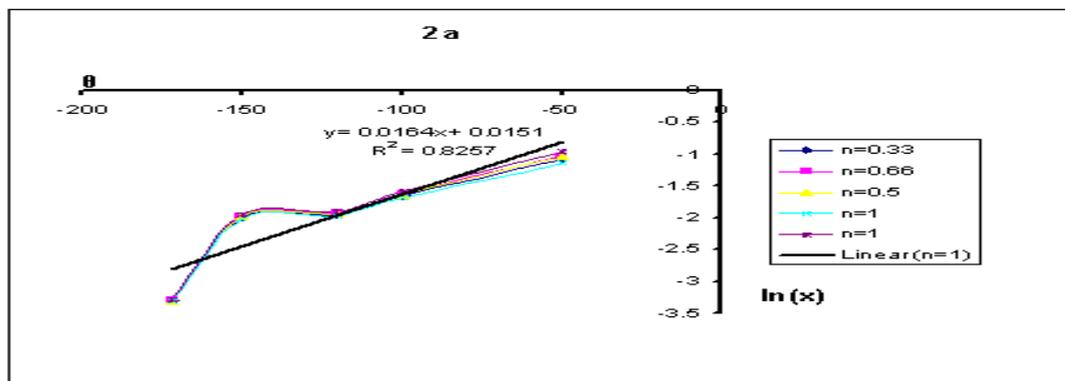
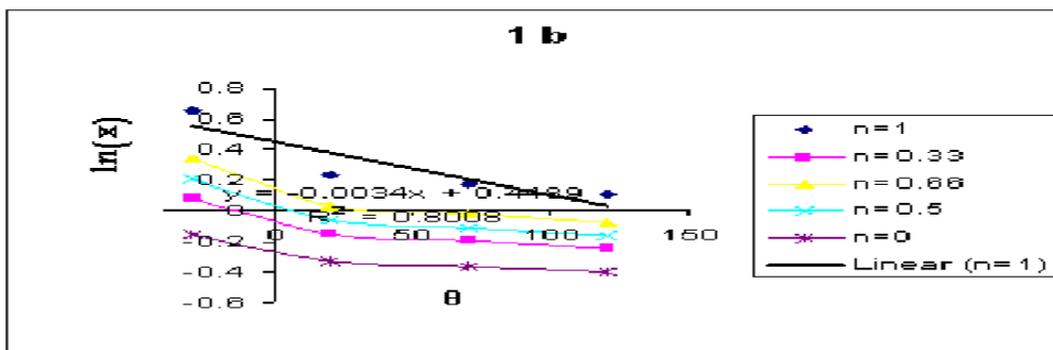
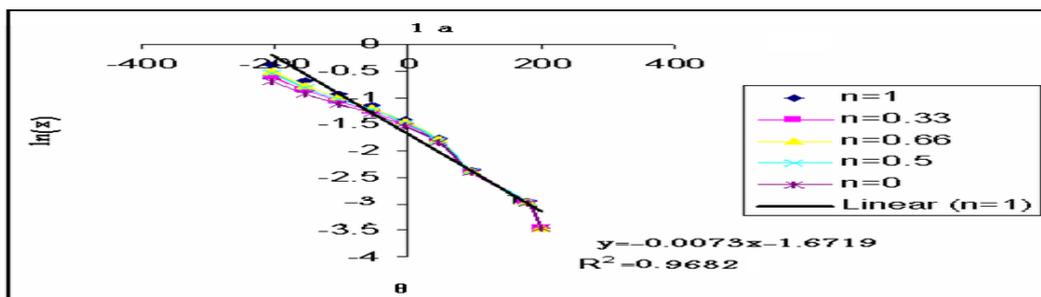


Figure (8): Coats-Redfern plots of degradation steps of the selected complexes:
 1) $\text{MoO}_2(\text{HL})_2$ 2) $\text{Mn}_3(\text{L})_2(\text{OH})(\text{H}_2\text{O})_6\text{Cl}$

Table (9): Kinetic parameters evaluated by Coats-Redfern equation of the selected complexes.

Complex	Peak	Tm (°K)	A (s ⁻¹)	E _a KJ / mol	ΔH [#] KJ / mol	ΔS [#] KJ/mol.K	ΔG [#] KJ / mol
Mn ₃ (L) ₂ (OH)(H ₂ O) ₆ Cl	a	570	7.285×10 ⁻⁷	8.606	6.132	-0.362	112.944
	b	933	8.747×10 ⁻⁶	21.113	15.708	-0.348	242.055
Mn ₃ (L) ₂ (OH)(H ₂ O) ₆ Cl	a	390	4.19×10 ⁻⁵	16.483	15.516	-0.321	53.067
	b	540	6.81×10 ⁻⁶	12.301	10.081	-0.343	101.637
	c	609	8.147×10 ⁻³	33.954	31.161	-0.286	127.223



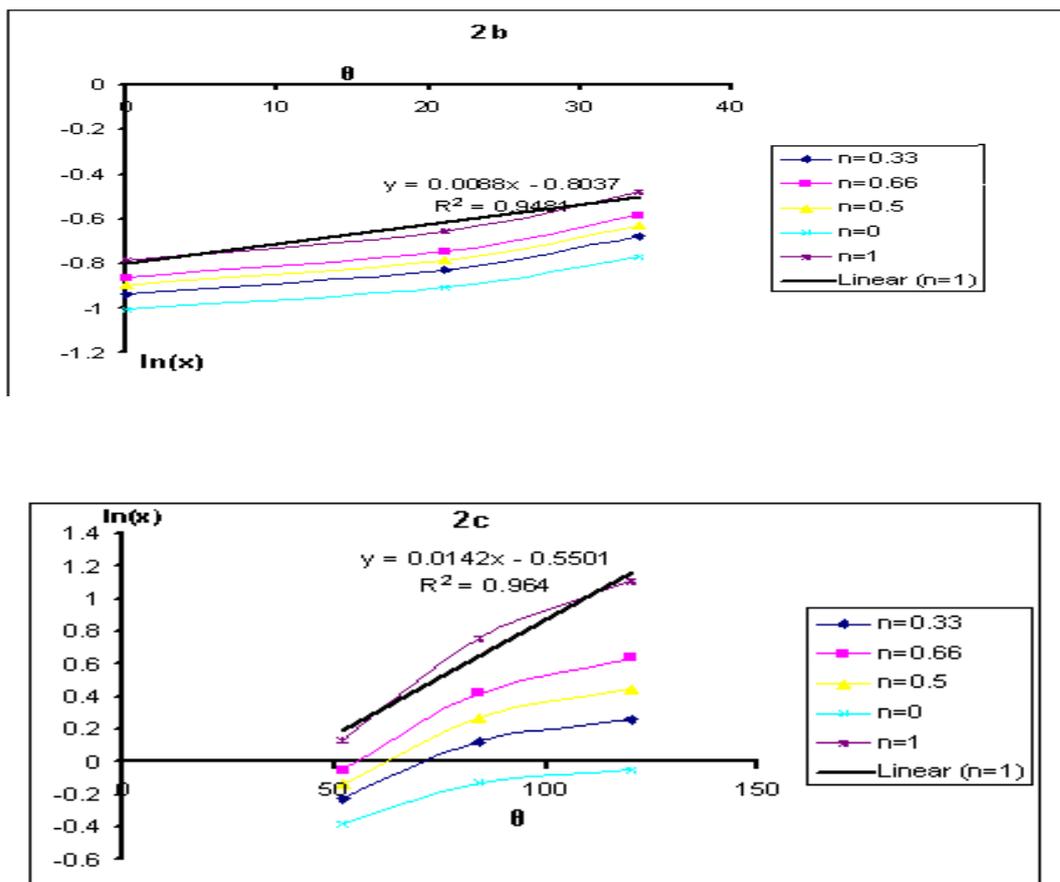


Figure (9): Horowitz-Metzger plots of degradation steps of the selected complexes:
 1) MoO₂ (HL)₂ 2) Mn₃(L)₂ (OH)(H₂O)₆Cl

Table (10): Kinetic parameters evaluated by Horowitz-Metzger equation of the selected complexes.

Complex	Peak	T _m (°K)	E _a KJ / mol	ΔH [#] KJ / mol	ΔS [#] KJ / mol.°K	ΔG [#] KJ / mol
MoO ₂ (HL) ₂	a	570	19.449	19.454	-0.368	19.244
	b	933	24.607	24.614	-0.351	24.287
Mn ₃ (L) ₂ (OH)(H ₂ O) ₆ Cl	a	390	20.739	20.736	-0.331	20.865
	b	540	21.334	21.330	-0.330	21.508
		609	43.786	43.781	-0.291	43.958

Conclusion:

From the previous studies we conclude:

- 1- The reactions proceeded in complicated mechanisms.
- 2- The transition states are more ordered than the reacting complexes
- 3- The kinetic parameters proved:
 - All decomposition stages showed a best fit for $n = 1$, while the other values have no better correlation.
 - The positive sign of the enthalpy of activation, ΔH^* of the decomposition stages reveals that the decomposition stages are endothermic processes.
 - The positive sign of free energy of activation, ΔG^* , indicates higher values of the final residue than that of the initial compound. All the decomposition steps are non-spontaneous processes.

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