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THERMAL INVESTIGATION OF IRON(III) AND MANGANESE(II, III) COMPLEXES OF DIANILS DERIVED FROM 6-FORMYLKHELLIN

Synthesis, characterization

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Abstract

Manganese and iron complexes of Schiff bases derived from 6-formylkhellin were prepared and characterized. Complexes of *o*-phenylenediamine derivative (ligand (I)) are monomeric or dimeric whereas those of *p*-phenylenediamine derivative (ligand (II)) are polymeric. The complexes obtained are characterized by a lower magnetic moment values. The complexes also have different solvent of crystallization with different nature of interaction. The thermal behaviour of the ligands and their metal complexes was investigated by means of DTA, TG, IR and X-ray diffraction spectroscopy. Ligand (I) shows different thermal behaviour from that of ligands (II) and (III). The complexes of ligand (II) give abnormal oxides as a final product during their thermal decomposition.

Keywords: DTA, 6-formylkhellin, IR spectroscopy, manganese and iron complexes of Schiff bases, *o*-phenylenediamine, *p*-phenylenediamine, TG, X-ray diffraction

Introduction

Since the days of the ancient Egyptians, physicians emphasized on the utility of naturally occurring drugs. Furochromones can be used in relieving the pain of renal colics and urterial spasms and in facilitating the passage of urterial stones. Later, it became well known that some furochromone derivatives possess coronary vasodilating activity [1, 2]. Several substituted furochromones show potential spasmolytic activity [3, 4]. This pronounced activity stimulated the interest in the synthesis of heterocyclic compounds derived from 3-formylkhellin for medicinal chemistry programs. For example, chromone-3-carboxaldehyde (I) occupies a unique position because it contains O–C=C–C=O group which is being responsible for its biological activity [5].

On the other hand, furobenzopyrones occupy a position of considerable significance as a result of their widespread occurrence in the plants and their potential as pharmaceuticals [6–9]. One of the members of that important category is 6-

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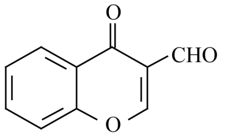
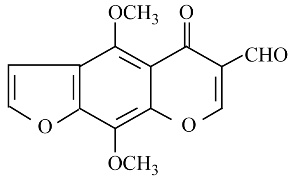


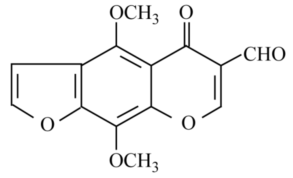
(I)

formylkhellin (II), which can be obtained from the chemical treatment of the naturally occurring furochromones (khellin).



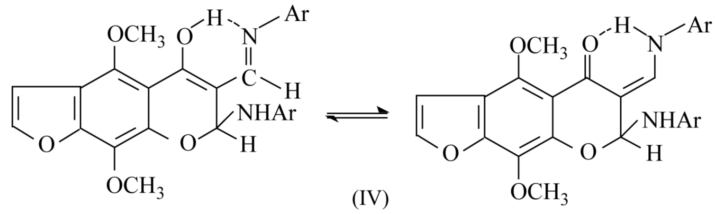
(II)

The carboxaldehyde group in 6-formylkhellin occupies a unique position. So, a number of heterocyclic compounds can easily be obtained through the chemical reactions with it. For example, when compound (II) was treated with primary aromatic or heterocyclic amines in (1:1) mole ratio, it gives the corresponding anils (III).



(II)

But on treatment with an excess of amines the corresponding 6-(aminomethylene)-7-amino derivatives (IV) were obtained [10–12].



(IV)

Literature survey shows no work have been done on the metal complexes of those anils or their dianils. In the present work, a number of dianils ligands of 6-formylkhellin and their metal complexes with iron and manganese ions were prepared and characterized. The thermal behaviour of the compounds obtained is also studied by means of DTA/TG, IR and X-ray, diffraction spectroscopy.

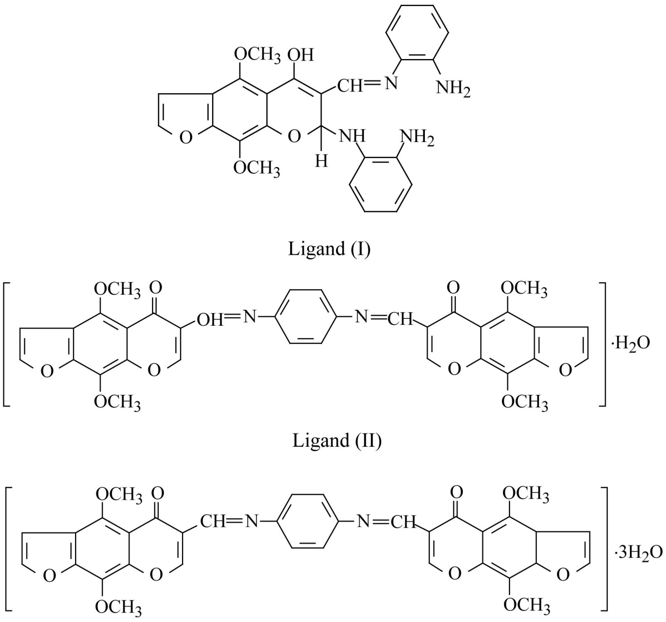
Experimental

All reagents were of pure grade and were used as submitted from Aldrich.

Preparation of ligands (Schiff bases)

A chloroform solution of 6-formylkhellin in appropriate molar ratio was added to *o*-phenylenediamine (ligand (I)) or *p*-phenylenediamine (ligands (II) and (III)) in chloroform. The molar ratios were (1:1) for ligands (I) and (II) and (2:1) for ligand (III). The reaction mixtures were stirred in air with warming for 3 h. The red or orange precipitates obtained were collected by filtration, washed by methanol several times and dried over, $CaCl_2/P_4O_{10}$ mixture for one week before measurements. In the case of ligand (III) diethylether was added to assist good precipitation.

The analytical and spectral data (Table 1) suggest the following structures for the compounds.



Ligand (I)

Ligand (II)

Ligand (III)

Scheme 1

Preparation of complexes

Complexes (1–4) were prepared by the addition of stoichiometric amount of hydrated metal chloride in methanol to a warm solution of 6-formylkhellin and the appropriate amine (1:1:1) molar ratio in chloroform. The reaction mixture was stirred in air for 3 h. Diethylether was added to assist good precipitation. The formed precipitates

Table 1a Elemental analysis, molar conductance of the investigated ligands and their complexes

No.	Compound	Colour	C/%		H/%		M/%		Λ^*/ Ω^{-1} mol^{-1} cm^2
			calc.	found	calc.	found	calc.	found	
	Ligand (I)	orange	66.1	66.2	5.0	4.8	–	–	–
	Ligand (II)	dark orange	63.9	63.8	4.0	4.0	–	–	–
	Ligand (III)	red	60.5	60.3	4.4	4.3	–	–	–
(1)	$[MnL^{I}Cl_2]_2\cdot 2C_2H_5OC_2H_5$	orange	55.6	55.8	4.2	4.2	6.6	6.2	20
(2)	$[FeL^{I}Cl_2]\cdot(2.5CH_3OH+0.5C_2H_5OC_2H_5+Cl)$	black	50.8	50.9	4.1	4.3	6.6	6.5	129
(3)	$[MnL^{II}_2Cl_4]_n\cdot(7CH_3OH+4H_2O+2Cl)_n$	dark brown	48.4	48.4	4.5	4.6	6.0	6.3	a
(4)	$[Fe_2L^{II}_2Cl_4]_n\cdot(2CH_3OH+10H_2O+2Cl)_n$	dark brown	46.4	46.6	4.2	4.5	6.2	6.2	a

*=molar conductance in 10^{-3} M DMF
a=insoluble
L^{I}, L^{II}=Schiff bases derived from 6-formylkhellin and *o*-phenylenediamine

Table 1b IR spectral data of the investigated ligands and their complexes

No.	Compound	IR ν/cm^{-1}									
		–OH	NH_2	$–CH_2$	$–OCH_3$	C=O	C=N	C=C	M–O	M–N	M–Cl
	Ligand (I)	3480 (s)	3220– 3110(m)	2920 (m)	2820 (m)	–	1640 (vs)	1570 (s)	–	–	–
	Ligand (II)	3420 (br)	–	2920 (m)	2820 (m)	1665 (m)	1640 (m)	1555 (m)	–	–	–
	Ligand (III)	3420 (br)	–	2920 (m)	2820 (m)	1670 (s)	1640 (m)	1565 (m)	–	–	–
(1)	$[MnL^{I}Cl_2]_2·2C_2H_5OC_2H_5$	3400 (br)		2920 (m)	2820 (m)	1640 (m)	1610 (s)	1590 (s)	520 (m)	410 (m)	310 (m)
(2)	$[FeL^{I}Cl_2]·(2.5CH_3OH+0.5C_2H_5OC_2H_5+Cl)$	3400 (br)		2920 (m)	2820 (m)	1650 (m)	1610 (s)	1550 (m)	530 (m)	450 (m)	300 (m)
(3)	$[MnL^{II}_2CL_4]_n·(7CH_3OH+4H_2O+2Cl)_n$	3400 (br)		2915 (m)	2820 (m)	1650 (s)	1620 (s)	1570 (m)	520 (m)	410 (m)	320 (m)
(4)	$[Fe_2L^{II}_2Cl_4]_n·(2CH_3OH+10H_2O+2Cl)_n$	3400 (br)		2915 (m)	2820 (m)	1640 (m)	1620 (m)	1580 (m)	530 (m)	410 (m)	300 (m)

s=strong; br=broad; m=medium

L^{I}, *L*^{II}=Schiff bases derived from 6-formylkhellin and *o*-phenylenediamine were collected by filtration, washed subsequently by chloroform and methanol and then dried over $CaCl_2/P_4O_{10}$. The reactions can be represented as follows:

$$(2)\ \xleftarrow{FeCl_3\cdot 6H_2O\ (1:1:1)}\ \text{6-formylkhellin}+\textit{o}\text{-phenylenediamine}\ \xrightarrow{MnCl_2\cdot 4H_2O\ (1:1:1)}\ (1)$$

(ligand(I))

$$(4)\ \xleftarrow{FeCl_3\cdot 6H_2O\ (1:1:1)}\ \text{6-formylkhellin}+\textit{p}\text{-phenylenediamine}\ \xrightarrow{MnCl_2\cdot 4H_2O\ (1:1:1)}\ (3)$$

(ligand(II))

Elemental analysis (C, H) were carried out at Microanalytical centre of Cairo University, metal contents were estimated compleximetrically by back titration using EDTA and Eriochrome Black-T (EBT) indicator [13]. IR spectra were recorded using a Perkin Elmer 1430 spectrophotometer and KBr discs. Electronic spectra were measured in Nujol mulls using a Perkin Elmer Lambda-4B spectrophotometer. The magnetic susceptibility measurements were carried out at room temperature using a modified Goy-type magnetic balance Herts SG8 5HJ, England. Diamagnetic corrections were calculated from the values given by Selwood and Pascall's constants [14]. The molar conductivity measurements of the complexes were done in DMF (10^{-3} M) using Tacussel conductimeter type CD6N. The thermal analysis (DTA and TG) were carried out by using a Shimadzu DTA/TG-50 with a heating rate 10°C min^{-1} in nitrogen atmosphere. The flowing rate of N_2 is 30 $cm^3\ min^{-1}$. X-ray powder diffraction patterns were measured using a Shimadzu XD-3 diffractometer with CuK_α radiation.

Results and discussion

The ligands and their complexes are stable in air at room temperature. Complexes of ligand (I) have an appreciable solubility in hot dimethylformamide (DMF). Whilst those of ligand (II) are insoluble in most organic solvents. This behaviour may be attributed to their polymeric nature. The observed lower conductivity value of complex (1) in DMF (20 $cm^2\ \Omega^{-1}\ mol^{-1}$) reveals its non-electrolytic nature [15]. Complex (2) displays a higher value of molar conductance (129 $cm^2\ \Omega^{-1}\ mol^{-1}$) which is consistent with that of univalent electrolyte [16, 17]. The complexes are characterized by the presence of a large number of solvents of crystallization. This may be attributed to the presence of a high content of oxygen sites in the ligands, that are capable of formation of hydrogen bonding with the solvents.

Vibrational spectra

When 6-formylkhellin was treated with excess amines the corresponding 6-(aminomethylene)-7-amino derivatives with the general formula (IV) were obtained [10–12]. The reaction proceeds via the formation of anils which in turns undergoes a nucleophilic addition of one molecule of amine. The most characteristic (IR) bands of the ligands are given in Table 1.

Ligand (I)

Ligand (I) displays bands near 3480, 3220–3110 (split), 2920, 2820 and 1640 cm^{-1}. These bands are assigned to νOH, νNH, νCH–aliphatic, νOCH_3 and νC=N, respectively [16–21]. The appearance of νOH and νNH confirms the nucleophilic addition of one amine molecule via the conversion of (C=O) of the pyrone ring (appears at 1665 cm^{-1}) to a hydroxyl group. On the other hand, the disappearance of ν(C=O) of the aldehydic group, confirms its condensation with another molecule of amine to form the anil moiety (C=N), (vide the structure of ligand (I)).

Ligands (II) and (III)

Ligands (II) and (III) display bands near 3420, 2920, 2820, 1670–1665), 1640, and 1555 cm^{-1}. These bands are assigned to νOH of water, νCH-aliph. νOCH_3, νC=O, νC=N and νC=C, respectively [16–21]. The appearance of νC=O of pyrone ring (1670–1665 cm^{-1}), indicates that the condensation takes place via ($-NH_2$) group of amine and aldehydic (CHO) group of 6-formylkhellin. The disappearance of νNH_2 from the spectrum indicates that two molecule of 6-formylkhellin react with one molecule of amine to give the dianils. This was also confirmed by elemental analysis data. The TG mass losses correspond to one molecule of water of crystallization (2.8%) for ligand (II) and three molecules (8.2%) for ligand (III).

Complexes

The most characteristic infrared peaks of the investigated complexes are given in Table 1. The complexes display bands near 3400, 2920–2915, 2820 cm^{-1}. These bands were assigned to νOH of water and/or methanol molecules, νCH-aliph. and νOCH_3 moiety, respectively [16–18]. The observed peaks near 1650–1640 and 1620–1610 cm^{-1} were assigned to νC=O of pyrone ring and νC=N of azomethine group, respectively [19–21]. The observed shifts in these bands to lower frequency on comparison with those of the ligands and the parent 6-formylkhellin indicate the participation of both C=O and C=N moieties in the mode of coordination [21, 22]. This coordination behaviour indicates that, ligand (I) (template reaction between 6-formylkhellin, *o*-phenylenediamine and metal ion) behaves as a dianil rather than nucleophilic addition to give 6-(aminomethylene)-7-amino derivative (Scheme I). The spectra also show a band near 1590–1550 cm^{-1} which was assigned to νC=C of aromatic ring. The complexes also display bands in the regions 530–520 and 450–410 cm^{-1}. These bands are assigned to νM–O and νM–N, respectively [16, 21, 23–25]. The observed bands near 320–300 cm^{-1} was assigned to terminal νM–Cl [22, 26, 27].

Electronic spectra

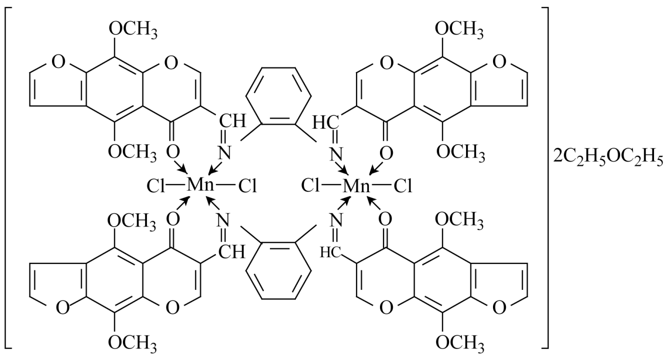
Electronic spectral data of the complexes in nujol mulls and their room temperature magnetic moments are given in Table 2. The spectrum of Mn(II) complex, (1) displays bands near 560–520 and 420 nm. These bands suggest an octahedral geometry around Mn(II) [28]. The lower magnetic moment value (3.0 BM) may be due to the presence of an equilibrium between high and low spin states [29] together with a metal–metal interaction. The spectrum of Mn(III) complex, (3) shows a broad band near 480 nm in both nujol mulls and DMF solution. This indicates that the complex doesn't alter its geometry in solution. The appearance of that band can be assigned to Jahn–Teller distorsion in an octahedral geometry around Mn(III) [28, 29]. The observed lowering in the magnetic moment value (4.3 BM) can be attributed to the presence of some extent of high–low spin equilibrium in the same solid [29]. The higher value of μ_{eff} (4.3 BM) of Mn(III) complex than that of Mn(II) complex (3.0 BM) is consistent with its structure, which shows no metal–metal interaction. The spectra of iron(III) complexes (2, 4) display absorption bands near 660–500 and 480 nm. These bands are assigned to octahedral geometry around Fe(III) [27, 30–32]. The magnetic moment value (5.5 BM) of complex (2) is consistent with high spin d^5 configuration in an octahedral field [27]. Whilst that of complex (4) is lower than that of high spin d^5 configuration, indicating the probability of an equilibrium between high and low spin states [33].

Table 2 Magnetic and electronic spectral data of the investigated complexes

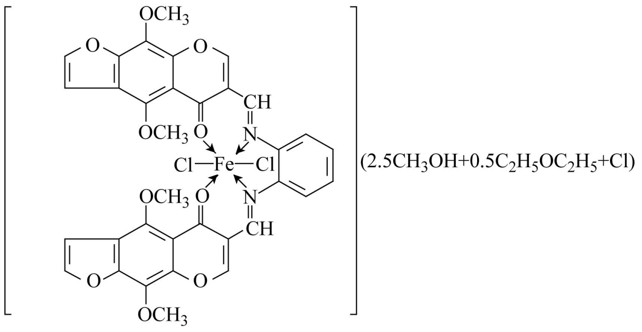
No.	Complex	μ_{eff}/BM	Electronic spectra in Nujol mulls/nm
(1)	$[MnL^{I}Cl_2]_2\cdot(2C_2H_5OC_3H_5)$	3.0	560–520 (w/br), 420 (m)
(2)	$[FeL^{I}Cl_2]\cdot(2.5CH_3OH+0.5C_2H_5OC_2H_5+Cl)$	5.5	600–500 (m/br), 450 (m)
(3)	$[Mn_2L^{II}_2Cl_4]_n\cdot(7CH_3OH+4H_2O+2Cl)_n$	4.3	480 (br)
(4)	$[Fe_2L^{II}_2Cl_4]_n\cdot(2CH_3OH+10H_2O+2Cl)_n$	4.0	600–520 (m/br), 480 (br)

br=broad; m=medium; w=weak

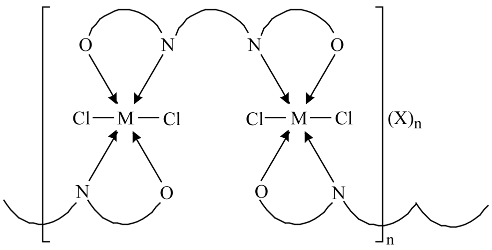
Based on the above arguments, together with the elemental analyses, and molar conductance (Table 1), the following formulae can be suggested.



(1)



(2)



(3) M=Mn, X=($7CH_3OH+4H_2O+2Cl$)

(4) M=Fe, X=($2CH_3OH+10H_2O+2Cl$)

Thermal studies

Ligands

DTA and TG curves of ligands (I), (II) and (III) are shown in Fig. 1. The thermal analysis data were also collected in Table 3. The DTA curve of ligand (I) shows a broad exothermic peak in the temperature range 33–252°C. TG curve shows no mass loss in that temperature range. This DTA peak can be assigned to lattice or chemical rearrangement of the compound. The observed DTA peak in the temperature range 252–310°C is assigned to material decomposition via the loss of one molecule of aniline. This assignment was confirmed by the TG mass losses (Table 3). DTA curve of ligand (II) shows a very weak endothermic peak in the temperature range 34–90°C. The TG mass loss (2.8%) in that temperature range confirms a loss of one molecule of water of crystallization. The lower temperature of dehydration as well as the very weak nature of DTA peak indicate that the water of crystallization doesn't participate in the lattice forces [34–37]. The curve displays also another endothermic peak in the temperature range 90–311°C which can be assigned to decomposition of the compound. TG data (Table 3) suggest that the decomposition takes place through the loss of two molecules of carbon monoxide as a result of the degradation of the pyrone ring. DTA curve of ligand (III) displays an endothermic peak in the temperature range 90–150°C. This peak is assigned to loss of three molecules (8.4%) of water of crystallization. It is seen that the loss of water of crystallization takes place in one definite step (strong DTA peak). This, in addition to the higher temperature

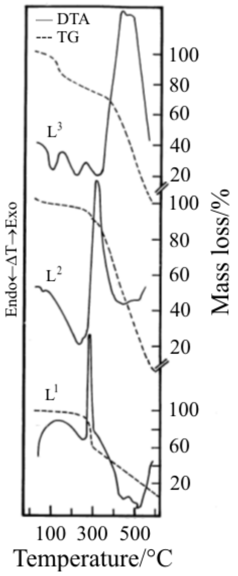


Fig. 1 DTA and TG curves of ligands (L^1, L^2, L^3)

of dehydration relative to that of ligand (II), indicates the participation of water molecules in the lattice forces. The dehydration peak was followed by two endothermic peaks with maxima at 244 and 343°C, respectively. These peaks are assigned to melting (244°C) together with the loss of two molecules of carbon monoxide in two individual steps as shown in TG curve. Again, the decomposition takes place via the decomposition of the pyrone ring. The great similarity between the thermal behaviour of both ligands (II) and (III) reflects their similarity in room temperature structures. The observed differences in their thermal stability may be related to the different number and the nature of interaction of water of crystallization. On the other hand, the higher thermal stability and different thermal behaviour of ligand (I) relative to that of (II) and (III) can be attributed to their different structures.

Complexes

DTA and TG curves of the complexes are shown in Fig. 2. The thermal analysis data are also given in Table 3. DTA and TG curves indicate that the complexes loss their solvent of crystallization in one or more steps. The desolvation process is generally extended over a broad temperature range (24–245°C) and mainly starts from room temperature. This process sometimes overlap with the decomposition process (complexes 2 and 4). The appearance of different endothermic DTA peaks at different temperature ranges indicates the different nature of interaction of the solvents of crystallization in the lattice. The lower onset temperature of desolvation process and its extended range of temperature indicate that the solvents of crystallization are present in the crystal voides and therefore play no significant role in the lattice forces [34–38]. The desolvation peaks are fol-

Table 3 DTA and TG data of the investigated ligands and their complexes

No.	Compound	Temperature/°C		Mass loss/%		Reaction	Assignment
		DTA	TG	calc.	found		
	Ligand (I)	33–252 (max. 136)				c	
		252–310° (max. 292)	252–310	18.6	18.7	d	$-RNH_2$
	Ligand (II)	34–90	34–90	2.8	2.8	a	$-H_2O$
		90–311	90–311	9.0	8.8	d	–2CO
	Ligand (III)	90–150 (max. 126)	90–150	8.0	8.3	a	$-3H_2O$
		150–180 (max. 244)	–			–	meltimg
		280–385 (max. 343)	150–385	8.2	8.3	d	–2CO
(1)	$[MnL^ICl_2]_2 \cdot 2C_2H_5OC_2H_5$	24–70	24–70	6.7	6.7	b	$-1.5C_2H_5OC_2H_5$
		70–140	70–140	1.1	1.0	b	$-0.25C_2H_5OC_2H_5$
		140–190	140–190	1.1	1.0	b	$-0.25C_2H_5OC_2H_5$
		190–313°	190–313		17.26	d	
		313–582	313–582		67.5	d	
			at 582	6.6	6.5*		≡2Mn
(2)	$[FeL^ICl_2] \cdot (2.5CH_3OH+0.5C_2H_5OC_2H_5+Cl)$	34–105	34–105	4.1	4.0	b	$-0.5C_2H_5OC_2H_5$
		105–170	105–170	1.7	1.7	b	–0.5CHOH
		170–245	170–245	7.1	7.1	b	–2CHOH
		245–710●				d	
(3)	$[MnL^{II}_2Cl_4]_n \cdot (7CH_3OH+4H_2O+2Cl)_n$	24–130	24–130	15.9	16.0	a+b	$-(7CHOH+4H_2O)$
		200–670°	130–670		73.9	d	–
			at 670	10.1	10.1*		$\equiv 2MnO_{2.5}$
(4)	$[Fe_2L^{II}_2Cl_4]_n \cdot (2CH_3OH+10H_2O+2Cl)_n$	26–170	26–170	13.5	13.5	a	$-(10H_2O+2CH_3OH)$
		170–470°	170–470	76.5		d	–
		470–775	at 470	9.7	9.9*		$\equiv 2FeO_2$

a=dehydration; b=desolvation; c=lattice or chemical rearrangement; d=decomposition; ●=splitted; *=final product percent; °=exo

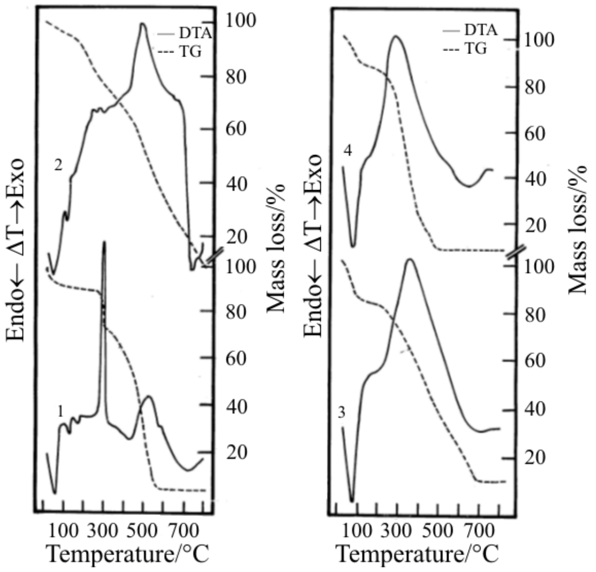


Fig. 2 DTA and TG curves of complexes (1–4)

lowed by a number of exothermic peaks in the temperature range (170–670°C). These peaks are assigned to material decomposition. Manganese(II) complex, (1) starts its decomposition at 190°C to give manganese metal as a final product at 582°C. The formation of manganese metal confirms the reducing behavior of the ligand (I) during its thermal decomposition [39]. Manganese(III) complex, (3) starts its decomposition at 200°C to give $MnO_{2.5}$ as a final product (Table 3). The formation of a high oxidation state of manganese in spite of the reducing properties of the ligand during its decomposition can be explained on the basis of the very low reducibility of Mn(III) in comparison with that of Mn(II) [40] and/or the lower reducing properties of ligand (II) during its decomposition. Iron(III) complex, (2) starts its decomposition at 245°C. The complex doesn't complete its decomposition up to 800°C, indicating its higher thermal stability. This higher thermal stability may be attributed to the presence of three fused chelate rings with higher degree of conjugation around the metal ion. Iron(III) complex, (4) starts its decomposition at 170°C to give finally FeO_2 as a final product. The formation of this type of oxide (FeO_2) confirms the lower reducing properties of ligand (II) *vs*. oxidation state(III) of iron and manganese. The final product of the thermal decomposition of complexes (1, 3 and 4) were investigated by means of X-ray and IR spectra. X-ray spectra show that the oxides obtained are characterized by a lower degree of crystallinity. IR spectra show no characteristic peaks of the ligand, indicating the complete decomposition of the complexes at the corresponding temperature (Table 3).

On the basis of the above studies, the following points can be outlined:

1] Ligand (I) gives monomeric or dimeric complexes whereas ligand (II) gives polymeric complexes.

2] The complexes obtained are characterized by the presence of different solvents of crystallization with different nature of interaction.

3] Ligand (I) displays a different thermal behaviour from that of ligands (II) and (III). This may be attributed to their different structures.

4] *o*-phenylenediamine derivative (ligand (I)) displays reducing properties during the thermal decomposition of its metal complexes to give finally the metal. Whilst *p*-phenylenediamine derivative (ligand (II)) displays oxidation effect to give abnormal oxides ($MnO_{2.5}$ and FeO_2).

5] Ligand (II) stabilized the oxidation state (III) for manganese in the solid complex.

6] The thermal behaviour of the ligands and their metal complexes is consistent with their room temperature structures.

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