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# Behaviour of Thermal Degradation of Some Poly (4-amino-2,6-pyrimidinodithiocarbonate) Metal Complexes

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## سلوك التحلل الحراري لبعض معقدات المعادن (4- امينو-6، 2-بريمدين ثنائي ثايوكاربامات)

**حسين مانع الميدمه، علي جمعان الشكيل وعاشور الكربولي**

**خلاصة:** تم تحري سلوك التحلل الحراري لمعقدات الحديد والكوبلت والنيكل لمتعدد[4-امينو-6،2-بريمدين ثنائي ثايوكاربامات] بالتحليل الحراري ألحجمي عند معدل تسخين 10 درجه مئوية لكل دقيقة في وجود النيتروجين. باستخدام طريقة كوتس-ريدفيرن التكاملية تم تقدير البيانات الحركية للخطوات المتعاقبة للتحلل المتتابع الملحوظ في منحنيات التحليل الحراري ألحجمي. عملية التحلل الحراري في هذه المعقدات الثلاث درست بالمقارنة لان منحنيات التحليل الحراري ألحجمي و منحنيات التحليل الحراري ألتفاضلي تبين الاختلاف في سلوك التحلل الحراري. تمت مناقشة الثبات الحراري لتحرر فتات الجسيمات عند الخطوات المتعاقبة للتحلل المتتابع لهذه المعقدات على أساس تأثير ا لسالبيه الكهربية والحجم الأيوني. وكما تم الأخذ في الاعتبار التباين في الثبات الحراري والاختلاف غير المنسجم في البيانات الحركية.

**ABSTRACT:** The thermal decomposition behaviour of the Fe(II), Co(II) and Ni(II) complexes of poly[4-amino-2,6-pyrimidinodithiocarbamate] has been investigated by thermogravimetric analysis (TGA) at a heating rate of 10°C $min^{-1}$ under nitrogen. The Coats-Redfern integral method is used to evaluate the kinetic parameters for the successive steps in the decomposition sequence observed in the TGA curves. The processes of thermal decomposition taking place in the three complexes are studied comparatively as the TGA and DTA curves indicate the difference in the thermal decomposition behaviour. The thermal stabilities for the release of the fragments at the successive steps in the sequential decomposition of these complexes are discussed in terms of electronegativity and ionic size effects. The difference in thermal stability and the inconsistent variation in the kinetic parameters of these complexes are considered.

KEYWORDS: Polydithiocarbamate complexes; Thermal behaviour; Kinetic parameters; Thermal stability.

## 1. Introduction

Over many decades, the thermal behaviour and properties of various types of materials and the thermal parameters of their degradation processes have been reliably widely studied by using the well-established thermal analysis methods (TG, DTG, DTA, DSC). As these methods allow determination of the chemical steps of the investigated degradation, the kinetic parameters for each step have been estimated by some methods (Brown *et al* 1980) and (Brown 2001). The evaluation of the kinetic parameters has been often performed by processing the data of a single thermogravimetric curve (TG curve) recorded at a certain heating rate and atmospheres (under nitrogen or air flow).

Some recent examples concerning the thermal and thermo-oxidative degradation of polymers or polymeric material, metal complexes, medicinal plant leaves and thermoplastic starch obtained by thermoanalytical methods (TG, DTG, DTA, DSC) have been reported (Martns *et al* 2003; Kim *et al* 2003; Giurginca and Zaharescu 2003; Gonzalez *et al* 2000; Chang *et al* 2000; El-Naggar *et al* 1997; Zidan 2001; Gad 2004; Al-Awadi *et al* 2008; Wang *et al* 2004; Bora 2000 and Mano *et al* 2003). The kinetic parameters evaluated for the successive steps in the decomposition sequence of these materials are based on considering a reaction order model for the kinetic analysis of a single TG curve data.

In our previous studies (El-Shekeil *et al* 1997; El-Shekeil *et al* 1998 and El-Shekeil *et al* 1999) a comparative study from the point of view of the DC electrical conductivity and its change with temperature variation (300-500 K) was illustrated for the polymer-metal complexes under investigation in the present work. As a result the activation energies worked out for different temperature segments were explained. The thermal analysis results (TGA and DTA) were invoked only to monitor the loss of adsorbed water in order to study its effect (i.e. the role of adsorbed water) on the DC electrical conductivity at 300 – 500 K range.

This adsorbed water effect study (El-Shekeil *et al* 1999) concludes that the water attaches itself to specific but nonequivalent points on the polymer chain. This attachment causes the localization of the N and/or S electron pairs and the creation of quantum quasi-particles; solitons and polarons. The release of this adsorbed water by temperature results in the release of quasi-particles. Hence, the increase of temperature excites the electrons from the soliton's level to the conduction band. These electrons either contribute to the number of the conductivity carriers or combine with the positive holes. The fast mechanism decrease the number of the conductivity carriers, which could be the reason for the exothermal phenomenon observed. The higher the released number of adsorbed water molecules, the higher the number of conductivity carriers, and as a result the higher the conductivity values.

In this work, we present a comparative study of some polymer-metal complexes of a particular ligand with various metals. This study is based on the point of view of the thermogravimetric analysis (TGA) and its thermal parameters at a certain condition (i.e. heating rate of 10°C $\text{min}^{-1}$ under nitrogen). The chosen organic polymer, poly[4-amino-2,6-pyrimidinodithiocarbonate] (PPT),which is rich in electrons due to the existence of nitrogen and sulphur atoms, acts as a polymer ligand forming the desired complexes via coordination with the metal ion of the 3d-transition elements Fe(II), Co(II), Ni(II). The processes of thermal degradation taking place in these polymer-metal complexes have been investigated by thermal analysis methods (TG, DTG, and DTA). The Coats-Redfern integral method (Coats and Redfern. 1964) has been used to determine the associated kinetic parameters for the successive steps in the decomposition sequence. Although these three polymer-metal complexes are identical in terms of the ligand type around the metal ions of Fe(II), Co(II) and Ni(II), the difference in thermal decomposition behaviour and that in thermal stability are clearly observed.

Therefore, information concerning the thermal decomposition behaviour, thermal stability, mechanism and kinetics of the investigated degradation process obtained from the TG curves recorded for the three conducting polymer-metal complexes at a certain condition (i.e. heating rate of 10°C/min and nitrogen flow) has become of interest to be studied comparatively. Our first attempt similar to this pattern of study has recently been published (Al-Maydama *et al* 2006) for four conducting polymer-metal complexes of Fe(II), Co(II), Ni(II) and Zn(II) with polydithiooxamide ligand.

## 2. Experimental

### 2.1 Synthesis of polymer complexes and physical analysis

The details of the synthesis, physical measurements, characterization and identification as well as the DC electrical conductivity of the three conducting polymer complexes of interest (PPT-Fe, PPT-Co and PPT-Ni) and their structure, shown in structure 1, can be found in previous publications (El-Shekeil *et al* 1997; El-Shekeil *et al* 1998 and El-Shekeil *et al* 1999).

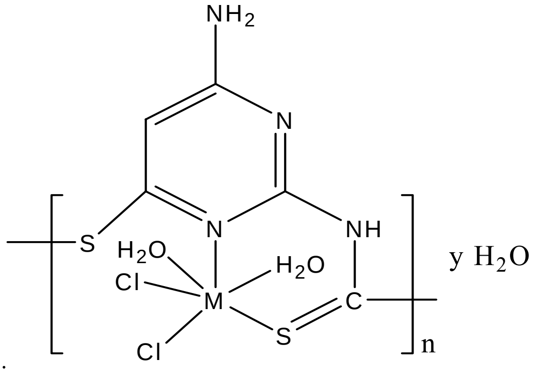
### 2.2 Thermal analysis

The TGA thermograms (TG and DTG) and DTA curves were obtained by using Shimadzu, thermogravimetric Analyzer, TGA-50, and DTA-50, respectively, at a heating rate of 10°C $min^{-1}$ under nitrogen flow and heating programme 20 – 1000°C.

### 2.3 Methods

From the TGA curves (TG, DTG) recorded for the successive steps in the decomposition process of these polymer complexes it was possible to determine the following characteristic thermal parameters for each reaction step:

Initial point temperature of decomposition ($T_i$) is the point at which DTG curve starts deviating from its base line. Final point temperature of decomposition ($T_f$) is the point at which DTG curve returns to its base line. Peak temperature, i.e. temperature of maximum rate of weight loss ($T_{DTG}$) is the point obtained from the intersection of tangents to the peak of DTG curve.



M = Fe, Co, Ni
Y = 2.5, 2, 1

Structure 1

Weight loss at the decomposition step (Δm) is the amount of mass that extends from the point $T_i$ up to the point $T_f$ on the TG curve. The material released at each step of the decomposition is identified by attributing the weight loss (Δm) at a given step to the component of similar weight calculated from the molecular formula of the investigated complexes and comparing that with literatures of relevant compounds considering their temperature. This may assist identifying the mechanism of reaction in the decomposition steps taking place in the polymer complexes under study.

Activation energy ($E_a$) of the decomposition step: the integral method used is the Coats-Redfern equation (Coats and Redfern. 1964) for reaction order $n \neq 1$, which when linearised for a correctly chosen curve yields the activation energy from the slope;

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]=\log\frac{ZR}{q\mathrm{E_a}}\left[1-\frac{2RT}{\mathrm{E_a}}\right]-\frac{\mathrm{E_a}}{2.303RT}$$

where: α = fraction of weight loss, $T$ = temperature ($K$), $n$ = order of reaction, $Z$ = pre-exponential factor, $R$ = molar gas constant, q = heating rate and $E_a$ = activation energy.

A plot of log $\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$ versus $1/T$ gives the slope from which activation energy ($E_a$) was determined.

Order of reaction (n) is the one for which a plot of the Coats-Redfern expression gives the best straight line n among various trial values of n that are examined, i.e., by trial and error for various trial values of n, estimated by the Horovitz-Metzger method (Horovitz and Metzger 1963).

## 3. Results and discussion

The TGA (TG and DTG) and DTA curves recorded for the PPT-Fe, PPT-Co and PPT-Ni complexes (i.e., poly-4-amino-2,6-pyrimidinodithiocarbamate-Fe(II), Co(II) and Ni(II) complexes) are given in Figures 1 and 2. These curves, which characterize and compare the thermal decomposition behaviour of the complexes under study at the heating rate of 10°C $\text{min}^{-1}$ under nitrogen, generally show consecutive steps for almost uninterrupted weight losses in the sequential decomposition of these three polymer complexes (i.e. no clear plateau between the steps on TG curves) over the experimental temperature range (20–1000°C). Therefore, the maximum rate temperature of weight loss ($T_{DTG}$) is determined only for some steps in the decomposition sequence that their DTG plot shows a maximum rate of weight loss, and the peaks $T_{DTA}$ are observed only for some steps in the DTA curves.

In general, it is observed that the sequence of decomposition that takes place in these complexes starts with dehydration of adsorbed water followed by the release of coordination water, then bonded chlorine and then fragments of the backbone. This seems like a four-step decomposition process. However, close examination of the TG and DTG curves (Figure 1) reveals a three-step decomposition process for PPT-Fe(II) at the 20-564°C range and a six-step process of decomposition for PPT-Co(II) at the 25-897°C and PPT-Ni(II) at the 30-728°C range. The difference in the thermal decomposition behaviour of these three complexes can be seen more clearly in their TGA and DTA curves (Figures 1 and 2).

Table 1 compares the characteristic thermal and kinetic parameters determined or evaluated, from the TGA curves, for each step in the decomposition sequence of the complexes. It can be seen clearly (Table 1) that the weight losses obtained from the TGA curves and that calculated for the corresponding molecule or molecules are in good agreement as is the case for all of these complexes. As the composition of the final decomposition products (i.e. final residue) of these three complexes are not proved, thermal decomposition with ill-defined final states are considered for these complexes. The activation energies ($E_a$) are calculated from the slopes of the best fit straight lines, which regress satisfactorily ($0.9924 \leq r^2 \leq 0.9998$) for using the best values of reaction order (n) in the plots of the Coats-Redfern equation (Coats and Redfern. 1964).

The first-steps of decomposition in the TG curves at the 20-95°C, 25-96°C and 30-90°C range with temperatures of maximum rate of weight loss ($T_{DTG}$) in the DTG curves (Figure 1) at 43°C, 48°C and 55°C, and the associated exothermic peaks ($T_{DTA}$) in the DTA curves (Figure 2) at 52°C, 47°C and 54°C indicate the loss of two and half molecules, two molecules and one molecule of adsorbed water in the Fe, Co and Ni-polymer complexes , respectively. This corresponds well with weight losses data for Fe (Obs. 11.46%, Theor. 11.49%), Co (Obs. 9.20%, Theor. 9.33%) and Ni-polymer complex (Obs. 5.01%, Theor. 4.9%). The temperature ranges reported (Al-Maydama *et al* 2006; Donia *et al* 1990; Donia *et al* 1992 and Donia *et al* 1997) for releasing adsorbed water in some metal complexes are in good agreement with that mentioned above. The activation energies determined for these reactions in the polymer complexes of Fe, Co and Ni are 84.2 kJ $\text{mol}^{-1}$, 84.6 kJ mol$^{-1}$ and 84.1 kJ mol$^{-1}$, respectively. These three complexes show very close values of activation energy, temperature-range and reaction order for the dehydration reactions as summarized in Table 1.

Table 1. Characteristic parameters of thermal decomposition (10°C min$^{-1}$) for A; Fe(II), B; Co(II) and C; Ni(II) polymer complexes.

| Comp. | Step | TGA | | | | | n | $E_a$/ kJ mol$^{-1}$ | Heat/ J | Reaction |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Wt. loss % Obs. (Theor.) | $T_i$/°C | $T_f$/°C | Peak | | | | | |
| | | | | | $T_{DTG}$ | $T_{DTA}$ | | | | |
| A | 1 | 11.46 (11.49) | 20 | 95 | 43 | 52 | 2.5 | 84.20 | -0. 245 | - 2.5$H_2O$ (ads) |
| | 2 | 27.11 (27.28) | 190 | 442 | 378 | 306, 423 | 0.5 | 46.16 | -0.719, -1.05 | - [2$H_2O$ (coor) + 2Cl] |
| | 4 | 41.86 (41.87)<br>- | 442<br>- | 564<br>- | 480<br>- | 474,<br>546<br>598 | 2.1<br>- | 335.44<br>- | 0.285,<br>0.118<br>1.92 | - [89.1% of bb[a]]<br>Phase transfer |
| ***Final residual weight; (found 19.57%, cal. 19.36%)*** | | | | | | | | | | |
| B | 1 | 9.20 (9.33) | 25 | 96 | 48 | 47 | 2.5 | 84.6 | -0.0897 | - 2 $H_2O$ (ads) |
| | 2 | 2.31(2.33) | 99 | 146 | 119 | - | 2.2 | 124.72 | - | -25% of 2$H_2O$ (coor) |
| | 3 | 7.01 (7.0) | 148 | 255 | 199 | - | 0.8 | 51.65 | - | -75% of 2$H_2O$ (coor) |
| | 4 | 18.40 (18.36) | 258 | 471 | 301 | - | 3 | 96.29 | - | - 2Cl |
| | 5 | 31.13 (31.11)<br>- | 485<br>- | 586<br>- | 515<br>- | 515<br>597 | 3.5<br>- | 578.05<br>- | 7.07<br>1.20 | - [ 65.2% of bb]<br>Phase transfer |
| | 6 | 3.40 (3.34) | 826 | 897 | 868 | 833 | 2 | 1103.46 | 0.94 | - [7% of bb] |
| ***Final residual weight; (found 28.55%, cal. 28.53%)*** | | | | | | | | | | |
| C | 1 | 5.01 (4.9) | 30 | 90 | 55 | 54 | 2 | 84.10 | - 0.44 | - $H_2O$ (ads) |
| | 2 | 4.73 (4.9) | 90 | 150 | 113 | 111 | 2.2 | 112.8 | - 0.15 | - $H_2O$ (coor) |
| | 3 | 4.97 (4.9) | 155 | 227 | 210 | - | 0.6 | 68.99 | - | - $H_2O$ (coor) |
| | 4 | 19.28 (19.27) | 229 | 350 | 271 | 265 | 3 | 209.05 | - 0.69 | - 2Cl |
| | 5 | 14.81 (14.97) | 350 | 518 | - | 452 | 1.4 | 84.15 | - 0.66 | - [ 29.9% of bb] |
| | 6 | 35.19 (35.11) | 518 | 728 | 650 | 551<br>674 | 2.4 | 235.95 | 0.80<br>- 1.52 | - [ 70.1% of bb] |
| ***Final residual weight; (found 16.01%, cal. 15.95%)*** | | | | | | | | | | |

[a]bb; Backbone components (i.e. organic ligand around the metal)

In this dehydration process, the ease of adsorbed water desolvation (20°C ≤ T ≤ 96°C) in these complexes suggests the weak interaction of water, i.e. water plays little or no role in the lattice forces and occupies the crystal voids (Donia *et al* 1997 and Byran 1982). The small differences in the $T_{DTG}$ values (43, 48 and 55°C), the exothermic peaks with small differences in the $T_{DTA}$ values (52, 47 and 54°C) and the activation energies of almost similar values (84.2, 84.6 and 84.1 kJ mol$^{-1}$ for the Fe, Co and Ni complexes, respectively) suggest that the adsorbed water in these complexes may be identical. The shape and the strength of the dehydration DTG peaks indicate that the rate of dehydration in these complexes is almost similar.

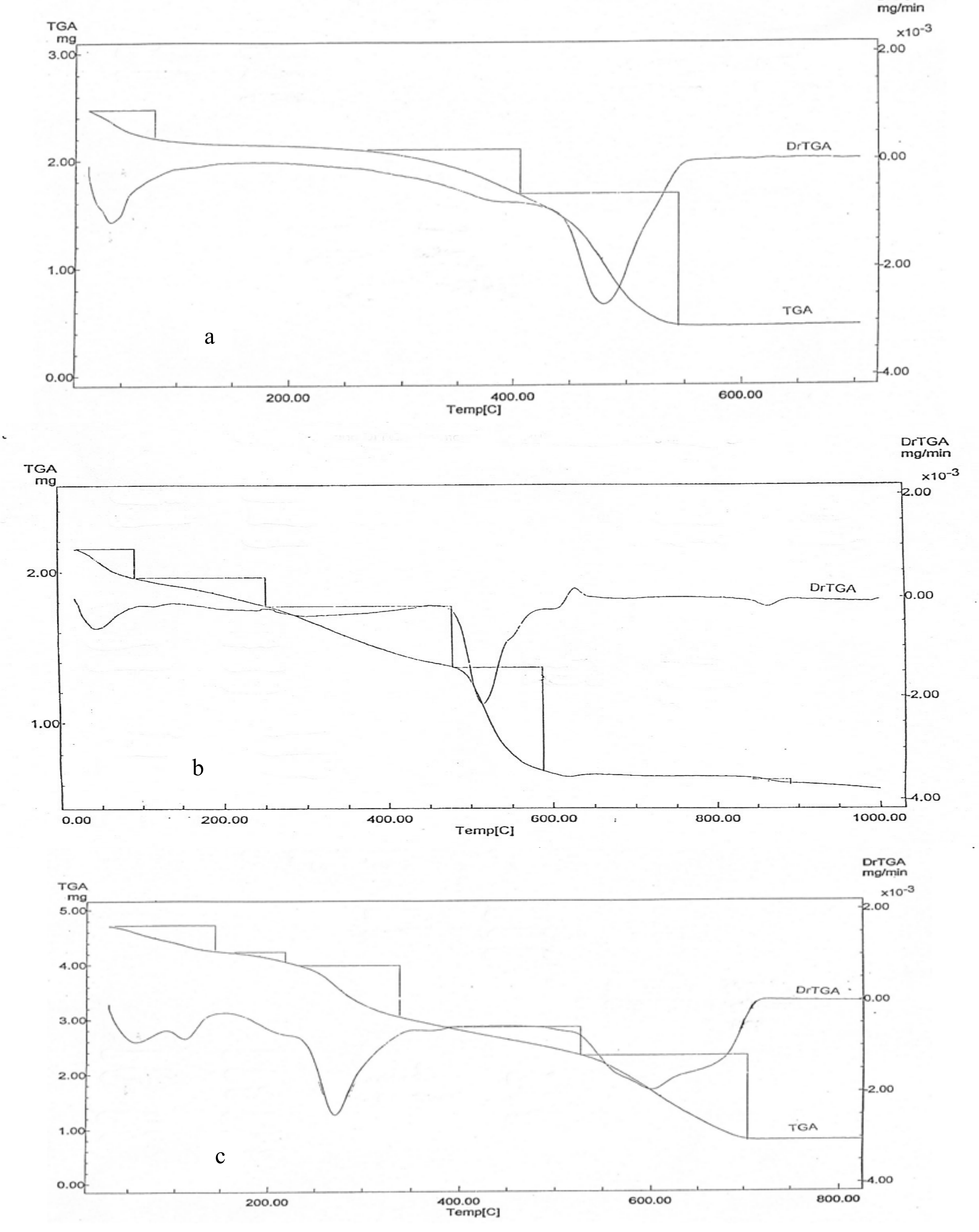


Figure 1. TGA and DTG thermograms of the PPT complexes of Fe (a), Co (b) and Ni (c) in nitrogen at the heating rate of 10°C °C $\mathrm{min}^{-1}$.

In the TG curves (Figure 1), continuous and slow bleed of weight losses are observed at the 190-442°C, 99-255°C and 90-227°C ranges for the polymer complexes of Fe, Co and Ni, respectively. These ranges are in good agreement with the temperature ranges reported (Al-Maydama *et al* 2006; Donia *et al* 1997; Donia and El-Boraey 1993) for the release of coordinated water molecules in some complexes of Fe, Co and Ni metals.

The second-step (190-442°C) of Fe-complex occurs with a broad and weak peak $T_{DTG}$ at 378°C and two broad exothermic peaks ($T_{DTA}$) at 306°C and 423°C. As a result, the weight loss of 27.11% indicates that the PPT-Fe complex continuously loses its two molecules of coordination water along with the two chlorine atoms (Theor. 27.28%) in one step. This step seems to be due to a complete overlapping of two consecutive steps, as the two consecutive DTA peaks (306°C and 423°C) indicate. At the 99-255°C range, the PPT-Co complex loses its two molecules of coordination water in two steps, i.e. second and third steps. The second-step (99-146°C) of a weak and broad $T_{DTG}$ (119°C) indicates the loss of 25% of the two water molecules (Obs. 2.31%, Theor. 2.33%), while the third-step (148-255°C) of a very weak and broad $T_{DTG}$ (199°C) indicates the loss of the remaining 75% of the two water molecules (Obs. 7.01%, Theor. 7.0%). The 90-227°C range in the PPT-Ni complex is for the second and third steps as the complex loses one molecule of its coordination water at each step. The second-step (90-150°C) of a broad $T_{DTG}$ (113°C) and a small exothermic peak $T_{DTA}$ (111°C) corresponds to the first molecule of coordination water (Obs. 4.73%, Theor. 4.90%), and the third-step (155-227°C) of a very weak and broad $T_{DTG}$ (210°C) is assigned to the second water molecule (Obs. 4.97%, Theor. 4.90%). Hence, The PPT-Ni complex shows more clearly the loss of two coordination water molecules in two steps; one molecule in each step.

The activation energies of the second-step reactions are calculated for the polymer complexes of Fe (46.16 kJ mol$^{-1}$), of Co (124.72 kJ mol$^{-1}$) and of Ni (112.8 kJ mol$^{-1}$), while for the third-step reactions the activation energies 51.65 kJ mol$^{-1}$ and 68.99 kJ mol$^{-1}$ are determined for the complexes of Co and Ni, respectively.

The weight loss (18.40%) at the fourth-step (258-471°C) of a very weak and broad $T_{DTG}$ (301°C), and the weight loss (19.28%) at the fourth-step (229-350°C ) of a large and strong $T_{DTG}$ (271°C) and a broad exothermic peak $T_{DTA}$ (265°C) are assigned to the release of two chlorine atoms in the PPT-Co (Theor. 18.36%) and PPT-Ni (Theor. 19.27%) complexes, respectively. The temperatures reported (Al-Maydama *et al* 2006; Donia *et al* 1992; Donia *et al* 1997; Donia and El-Boraey 1992 and Donia 1993) for the release of chlorine in some complexes of nickel (270°C, 315°C, 220-374°C, 217-291°C ) and in that of cobalt (300°C, 340°C, 300-400°C) are in accordance with that obtained. The activation energies calculated for the release of these two chlorine atoms in the complexes of Co and Ni are 96.29 kJ mol$^{-1}$, and 209.05 kJ mol$^{-1,}$ respectively.

As preceded, the complex of cobalt and that of nickel both lose their two coordination water in two overlapping or consecutive steps. The slow rate of releasing the water molecules, temperature range, order of reaction and activation energy observed for the two steps in complex of cobalt and in that of nickel are somewhat comparable (Table 1). This reflects similarity in the kinetic and nature of the activated molecule of these two complexes at the transition-state reaction. In the contrary, although the cobalt and nickel complexes lose their two chlorine atoms in one step at about nearly close temperature ranges with similar order of reaction, the activation energies associated with this reaction in the two complexes are vastly incomparable. This is because of various kinetic and nature of both complexes at the transition-state, i.e. their activated molecules are of different reaction nature. Hence, slow elimination of the chlorine atoms with a lower activation energy (96.29 kJ mol$^{-1}$), and the rapid one with a higher activation energy (209.05 kJ mol$^{-1}$) are observed for the cobalt and nickel complexes, respectively

On the other hand, if the initial temperatures ($T_i$) concerning the release of the coordination water and then the chlorine atoms (Table 1) are taken as a measure of the thermal stabilities of these complexes, the iron complex (190°C) show a higher thermal stability than those of cobalt and nickel, i.e. on the basis of $T_i$ values, the thermal stability of these complexes follows the order: Fe> Co> Ni. This can be discussed in terms of the repulsion among electron pairs in the valence shell of the central ion. Iron, cobalt and nickel ions in the investigated complexes have multiple bonding (six bonds) in their valence shells. But due to the higher electronegativity of nickel than that of cobalt and iron, the space occupied by a bonding pair in the valence shell of nickel is greater than that of cobalt and iron. This leads to a higher repulsion between the bonding pairs in the valence shell of nickel (smallest ionic size, i.e. Ni < Co < Fe), which in turns alter the bond angles from those of ideal octahedral, giving a lower stability (Moeller 1982 and Malik *et al* 1998 ). For this reason, the complex of Ni loses its coordinated water and bonded chlorine more rapidly than the others as indicated by the apparently strong peaks ($T_{DTG}$) at 113°C and 271°C, respectively.

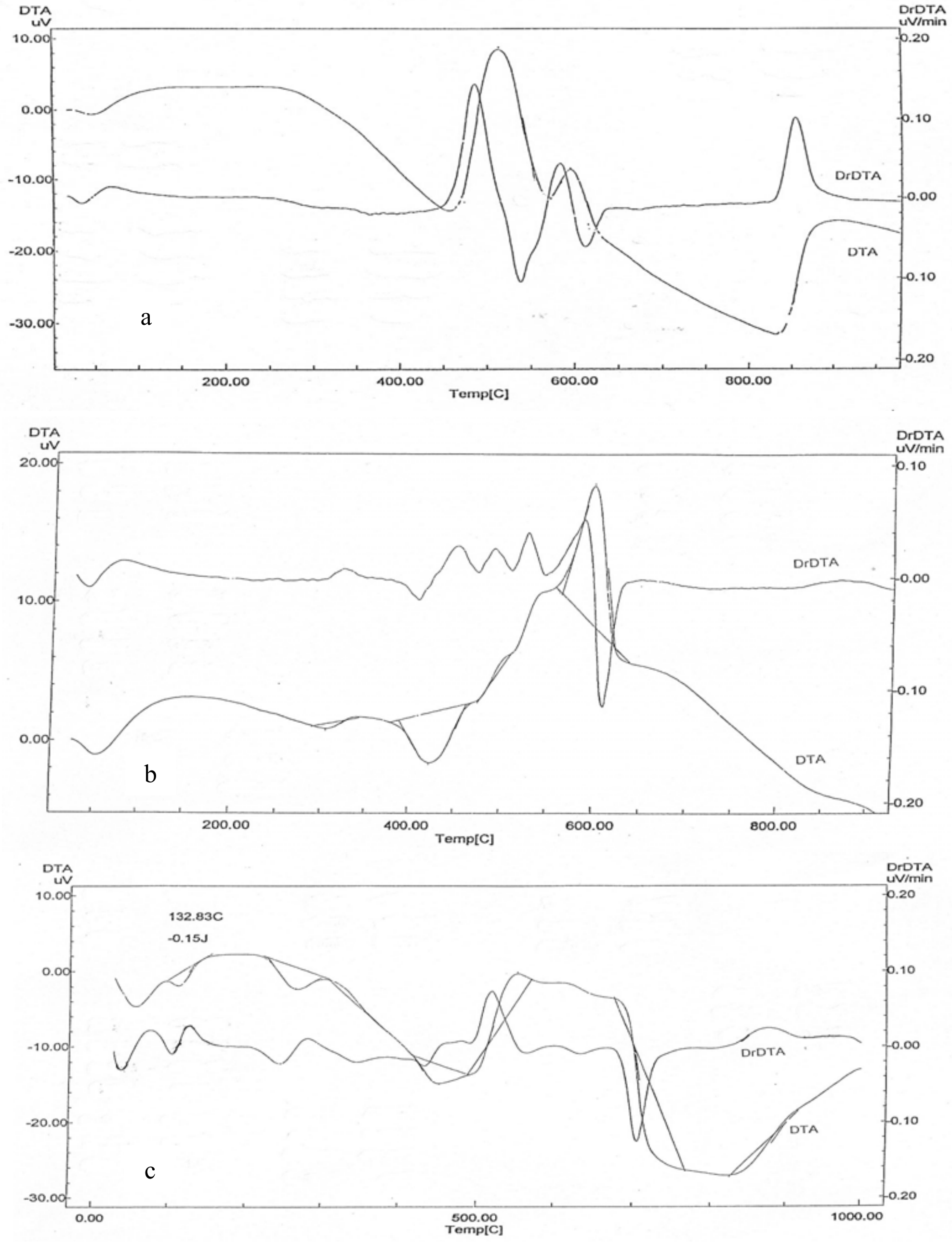


Figure 2. DTA and DrDTA thermograms of the PPT complexes of Fe (a), Co (b) and Ni (c) in nitrogen at the heating rate of 10°C °C min$^{-1}$.

The third-step (442-564°C) of a large and strong $T_{DTG}$ (480°C) and two very weak and broad successive endothermic peaks with a $T_{DTA}$ of 474°C and 546°C is due to a complete breakdown of the PPT-Fe backbone structure. The weight loss found (41.86%) is attributed to the elimination of 89.1% of the backbone components (Theor. 41.87%). The final residual weight found (19.57%) corresponds to an ill-defined final decomposition product (Theor. 19.36%). The activation energy calculated for this step is 335.44 kJ mol$^{-1}$. The large and strong endothermic peak ($T_{DTA}$) at 598°C which does not correspond to any weight loss in the TG curve may be due to some change in the crystalline structure of the final residue.

The complete decomposition of the PPT-Co backbone structure occurs at the fifth-step (485-586°C) of a large and strong $T_{DTG}$ (515°C) and a large and strong endothermic peak with a $T_{DTA}$ of 515°C. At this stage, the weight loss found (31.13%) in theTG curve indicate the elimination of 65.2% of the backbone (Theor. 31.11%). This leaves the deposition of a residue of an ill-defined compositom (Theor. 31.87%) that corresponds to the residual weight found (31.95%) in the TG curve at the end of this step. The small endothermic peak ($T_{DTA}$) at 597°C which does not correspond to any weight loss in the TG curve may be due to some change in the structure of the residual deposit. However, the weight loss (3.40%) at the small sixth-step (826-897°C) with a $T_{DTG}$ of 868°C and a large and broad endothermic peak ($T_{DTA}$) of 833°C is assigned to the decomposition of the residual deposit (i.e. residue) by losing 7% of the backbone components or 10.48% of the residue (Theor. 3.34%). The final decomposition product of an ill-defined composition found and calculated are 28.55% and 28.53%, respectively. The activation energies calculated for the fifth and sixth-step are 578.05 kJ mol$^{-1}$ and 1103.46 kJ mol$^{-1}$, respectively.

In the TGA curve (Figure 1c), it can be seen clearly that a complete breakdown of the PPT-Ni backbone structure takes place in two consecutive steps, i.e. fifth and sixth-step. At the fifth-step (350-518°C) of a broad exothermic peak ($T_{DTA}$) at 452°C, the PPT-Ni complex loses 29.9% of its backbone components (Theor. 14.97%) at slow rate corresponding to the weight loss found (14.81%). The weight loss found (35.19%) at the sixth-step (518-728°C) of a very large and broad $T_{DTG}$ (650°C) with a very broad exothermic peak $T_{DTA}$ (674°C) indicates the rapid loss of the remaining 70.1% of the backbone components (Theor. 35.11%). The final decomposition product of an ill-defined composition (Theor. 15.95%) corresponds to the residual weight found (16.01%) in the TG curve at the end of this step. The irregular shape of the DTG curve in the (518-728°C) range and the endothermic peak ($T_{DTA}$) at 551°C indicate more than one reaction took place in the sixth-step. The activation energy determined for the fifth and sixth-step are 84.15 kJ mol$^{-1}$ and 235.95 kJ mol$^{-1}$, respectively.

At the stage after the release of coordination water and chlorine the iron, cobalt and nickel ion in the complexes are converted from multiple bonding (six bonds) to lower bonding (two bonds) in their valence shells. In consequence, it is noteworthy that the situation here may be inverted with lower coordination numbers, where the repulsion between electron pairs is decreased. Therefore, the electronegativity of the central metal ion becomes the predominant factor in the stability (Donia *et al* 1992). This is evident in the complete decomposition of the backbone structure of the iron, cobalt and nickel complexes, if the initial temperature ($T_i$) of the complete backbone decomposition is used as a measure of the thermal stability. This can be discussed as follows:

1) In the case of iron and cobalt complexes, the complete decomposition of their backbone structure that takes place rapidly in one single step suggests a higher thermal stability (485°C) for cobalt than that for iron (437°C). This is also confirmed by the values of the maximum rate temperature of weight loss ($T_{DTG}$) at 515°C and 480°C determined for the backbone decomposition in the cobalt and iron complexes, respectively. The small thermal stability difference (48°C) between the backbone decomposition in cobalt and that in iron, and also the small difference (35°C) between the values of their $T_{DTG}$ may be attributed mainly to the higher electronegativity of cobalt than that of iron.

2) Unlike the iron and cobalt complexes, the nickel complex shows two initial temperatures (350°C and 518°C) indicating two thermal stabilities for the two successive steps in the decomposition of the backbone.The lower thermal stability (350°C) may be related to the strain that the backbone structure of nickel experiences more due to the smaller ionic size of nickel relative to that of cobalt and iron. This interpretation is confirmed by the TG weight loss (14.81%), which relieves the strain in the backbone by the decomposition of about 30% of the

backbone components (14.97%), and consequently one more step of a higher temperature range (518-728°C) is required for the completion of the backbone decomposition.

The higher thermal stability (518°C) due to the completion of the backbone decomposition with a higher $T_{DTG}$ of 650°C can be attributed to the higher electronegativity of nickel than that of iron and cobalt, proving the predominant roll of the electronegativity in the stability. The higher thermal stability difference (135°C) between the complete and the partial decomposition of the backbone in both complexes of cobalt and nickel, respectively, reflects the strain in the backbone angles may be due to mainly the smaller ionic size and partially the higher elecronegativity of nickel than those of cobalt. However, the small thermal stability difference (33°C) between the completion of the backbone decomposition in the complex of nickel and the complete backbone decomposition of cobalt may be attributed to the higher electronegativity of nickel than that of cobalt.

## 4. Conclusion

The thermal properties of these three metal-complexes were investigated and the activation energy of each step in the decomposition sequences was determined by using Costs-Redfern expression. The almost similar kinetic parameters and the $T_{DTA}$ values of the dehydration suggest that adsorbed water molecules in these complexes are identical.

The activation energies of the two coordinated water in the cobalt and nickel complexes are of close values, indicating similar kinetic and decomposition reactions nature of the activated complexes at the transition-state. However, the differences in the activation energies values for the release of the two chlorine atoms and that for the backbone structure distraction are due to different kinetic and nature of the activated complexes decomposition reactions at the transition-state.

Although the three complexes are of a particular ligand with a variety of metals, their TGA curves exhibit various and not identical decomposition reactions. This may be attributed to the various metals and not to the particular ligand.

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