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Research Paper

Preparation, Characterization and Thermodynamical Parameters of Some Picolinate Complexes

Chemistry

KEYWORDS : Metal picolinate; Thermal analysis; Thermodynamical parameters; Salting-in

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ABSTRACT

In this work, the complexes were synthesized by the interaction between the picolinic acid with some metal ions [Cr(III), Mn(II) and Ni(II)], then salted-in. The geometrical structures and the chemical formula of the complexes were characterized by several techniques; such as, elemental analysis, molar conductivity, thermal analysis, and thermodynamical parameters. The complexes after salting-in were fairly stable under normal atmospheric condition. Salting-in of chromium picolinate complex shows no change in the coordination sphere. The salting-in of bis-picolinato manganese (II) complex in different simple salts, KI, CaCl2 and Guanidinium hydrochloride, gives change in water of crystallization after several days; in all cases the complexes contains one extra water molecule. While in the case of Nickel picolinate it gives the same structure with Guanidinium hydrochloride and KI. For the two nickel complexes TGA were thermally decomposed in four successive steps, leaving NiO residue at >550C°, Thermodynamic parameters for the decomposition steps, by employing the CR and HM equations, the thermal stability of the complex reflected from the high values of the ΔE^* *the negative sign of the* ΔS^**.*

Introduction

Metals are essential for normal carbohydrate metabolism and they can facilitate the interaction of insulin with its receptor and play an essential role in supporting efficient insulin function and blood glucose control. Metal picolinates are more stable, better absorbed, and more bioavailable than other supplemental metals complexes. Patients take this picolinates for diabetes, weight loss, and to improve muscle mass [1-3]. Protein solubility is a complex function of the physiochemical nature of the proteins, pH, temperature and the concentration of the salt used. It also depends on whether the salt is Kosomtropic (stabilizes water structure) or Chaotropic (disrupts water structure). At low concentrations of salt, solubility of the proteins usually increases slightly (salting in). But at high concentrations of salt, the solubility of the proteins drop sharply (salting out) [4]. Salting-in effects are caused by changes in the tendency of dissociable R groups on the proteins to ionize [4]. Salting out is a common experimental procedure to precipitate proteins and separate them from a solution. Consequently, the solvation of ions in aqueous media is of prime importance in many areas including surface chemistry, environmental chemistry and geochemistry [5,6]. The hydration of multivalent metal ions is especially interesting because of the presence of well-defined solvation shells and the formation of specific complexes [7].

In the last decades there was a great interest in salting-in behavior of some complexes, thus the main object of this study is synthesis of Cr, Mn and Ni picolinate complexes, then salting-in with simple salts e.g. KI, $CaCl_2$ and guanidinhydrochloride to increase the solubility of these complex and the possibility of its absorption in the body if it used as drugs and investigation of the geometrical structure of these complexes. These complexes were prepared and characterized by elemental analysis, molar conductance measurements, thermogravimetric analysis and thermodynamic measurements.

Experimental

Materials

All chemicals used in this study were laboratory analytical grade; they include $CrCl_3.6H_2O$, $NiCl_2.6H_2O$, $MnCl_2.2H_2O$, 2-picolinic acid, KI, $CaCl_2$, and Guanidine hydrochloride, purchased from Aldrich and Merck Companies. Chromium, Manganese and Nickel picolinate complexes were prepared according to the methods described in the litreture [8,9]. In brief, nickel picolinate complexes (for example) were prepared as follow:

$[Ni(pic\text{-}O)_2].H_2O$: Bis-picolinatonickel (II) monohydrate was prepared by dissolving, $NiCl_2.6H_2O$ (2.38 g., 10 mmol) in 25 ml deionized water followed by dissolving picolinic acid (2.46g., 20 mmol) in 10 ml HC1 (1M) and slight excess of 3M potassium hydroxide the mixture was heated to reflux until solid appeared. On cooling, fine pale blue crystal are separated. The crystals were collected by filtration and dried in vacuum over silica gel.

$[Ni(pic)_2(H_2O)_2].2H_2O$/KI: 50 ml of an aqueous solution of KI (0.83 g., 5 mmol) as chaotropic agent was added to $Ni(pic\text{-}O)_2.H_2O$ (1.60 g., 5 mmol) the resultant blue color mixture was heated to boiling under reflux, the solid was partially dissolved (salting-in), its color unchanged. The insoluble part formed two different precipitate; one was light blue and the other was light violet. The dissolved part was evaporated until crystallization occurred and allowed to cool to room temperature; blue crystals were collected by filtration and dried in vacuum over silica gel.

$[Ni(pic)_2(H_2O)_2]._2H_2O$/guan: 50 ml of an aqueous solution of guanidinehydrochloride (0.96 g., 10 mmol) as chaotropic agent was added to $Ni(pic\text{-}O)_2.H_2O$ (1.60 g., 5 mmol) the resultant blue color mixture was heated to boiling under reflux until all the solid $Ni(pic\text{-}O)_2.H_2O$ had dissolved to give blue solution. The solution was allowed to evaporate until crystallization occurred and allowed to cool to room temperature; blue crystals were collected by filtration and dried in vacuum over silica gel.

$[Ni(pic)_2(pic\text{-}H)H_2O].2H_2O$/KI: 50 ml of an aqueous solution of KI (2.49 g, 15 mmol) as chaotropic agent was added to $Ni(pic\text{-}O)_2.H_2O$ (1.60g, 5 mmol) the resultant blue color mixture was heated to boiling under reflux. The solid was partially dissolved (salting-in), the undissolved part was violet color, collected by filtration and allowed to cool to room temperature and dried in vacuum over silica gel.

Techniques

Elemental Analysis: All the prepared complexes have been subjected to C, H, and N elemental analyses using a CHN PerkinElmer M CHNS/O analyzer, model 2400. The analyses were made in triplicate, previously heating the material at 100 _C, under vacuum, for 60 min.

Conductivity Measurements: The molar conductance measurements of the complexes were calculated by measuring conductance of the investigated complexes (10-3M) in DMSO and acetonitrile: H2O solvents by using digital conductivity meter CMD 4320.

Thermal Analysis: Thermal analysis was performed using an automatically recording DT-3OH Shimadzu apparatus (Japan). Thermgravimeteric (*TG*) curves were recorded up to 1273 K at a heating rate 10 degree/min. in static air. Small portions (15-20 mg) of test sample were used in *TG* measurements at Micro Analytical Center, Faculty of Science, Cairo University.

Infrared Spectra: The infrared spectra were recorded as 1% KBr discs containing 2mg of compound dispersed in 200 mg KBr on the FT-IR 8201pc Shimadzu, spectrometer at room temperature in the range 200-4000 cm^{-1}, at the Faculty of Science, Cairo University

Results and Discussion

Elemental Analysis

The elemental analysis data of the all complexes are given in Table (1). It is worthy to mention that the measured values of different elements are in a good agreement with those calculated for proposed formula. The obtained data reveal that the complexes have the [M:L] ratios of 1:2 and 1:3. Complexes of the 1:3 ratio have the formula $[M(L)_3].H_2O$, here M is Cr(III) and L is picolinate ligand. The 1:2 [M:L] complexes have the chemical formula of the type $[M(L)_2xH_2O]nH_2O$, and $[M(L)_2(L\text{-}H)xH_2O]nH_2O$ where, L represents the picolinate anion, L-H represents picolinic form, M represents Mn(II) or Ni(II), while x and n represent the number of coordinated and hydrated water molecules, respectively.

Molar Conductivity Measurements of the Complexes

Conductivity measurements in non-aqueous solutions were carried out to help to find the coordination formula of the complexes under investigation. The measured conductivities of 10^{-3} M solutions in DMSO or acetonitrile:H_2O solvents for the prepared complexes are given in Table (1). The molar conductance (Λ_m) S cm^2 mol^{-1} is calculated by:

Λ_m = K\C

where: K = specific conductivity (S cm^{-1}).

C = the concentration of the complex solution (mol/l)

As shown in Table (1), the molar conductance of the prepared complexes was found to be 1-20 (Ω^{-1} cm^2 mol^{-1}**)**, which indicates the non-electrolytic nature of these complexes [9,10]. The non-conducting character of these complexes in DMSO and acetonitrile:H_2O solvent show that the coordination sphere is zero charged and the negative charged ligand ions compensate the positive charges on the metal ion.

Table (1): Elemental analysis and molar conductance of the complexes

Complex	M. Wt	C% Calc (Found)	H% Calc (Found)	N% Calc (Found)	Conductance Ω^{-1} cm^2 mol^{-1}
mer-$[Cr(pic\text{-}O)_3].H_2O$	436.32	49.55 (**49.44**)	3.23 (**2.53**)	9.63 (**9.58**)	13.61
fac-$[Cr(pic)_3].H_2O$	436.32	49.55 (**49.44**)	3.23 (**3.60**)	9.63 (**9.92**)	14.73
$[Mn(pic)_2(H_2O)_2]$	335.17	43.00 (**42.76**)	3.60 (**2.50**)	8.36 (**8.28**)	20.95
$[Mn(pic)_2(H_2O)_2]H_2O$	353.18	40.81 (**41.06**)	3.99 (**3.91**)	7.93 (**7.94**)	1.971
$[Ni(pic\text{-}O)_2]H_2O$	320.93	44.91 (**45.56**)	3.14 (**3.64**)	8.73 (**8.94**)	3.09
$[Ni(pic)_2(H_2O)_2].2H_2O$	374.97	38.44 (**39.21**)	4.3 (**4.61**)	7.47 (**7.69**)	1.19
$[Ni(pic)_2(pic\text{-}H)H_2O]_2H_2O$	480.07	45.03 (**44.60**)	3.99 (**3.19**)	8.75 (**9.17**)	4.16

Thermal Analysis and Thermodynamic data

This work includes measurements for the thermal stability of the obtained complexes after salted-in. Since it is usually difficult to distinguish between the hydrated and coordinated water molecules, thermo analytical techniques have been employed to study the thermal dissociation of coordination compounds. The thermal decomposition behaviour of pyridine-carboxylate with many metals such as Cu^{+2} , Ni^{+2}, Zn^{+2}, Cd^{+2}, Co^{+2} , Mn^{+2} and Fe^{+3} with picolinic, nicotinic, isonicotinic, pyridinedicarboxylic, benzoic acids have been investigated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) techniques [11,12]. Two methods are mentioned in the literature related to decomposition thermodynamic studies, Coats-Redfernand (CR) and Horowitz-Metzger(HM), and both two methods were applied in this study.

TGA of $[Cr(pic)_3].H_2O$ Complex The TGA curves of the $[Cr(pic)_3].H_2O$ complex, are shown in Fig. (1). The complex shows three-stages of the mass loss. The first mass loss in the range of 55-150 °C attributed to the loss of hydrated water molecule and formation of $[Cr(pic)_3]$; with a total weight loss of about 3.45% (found) 3.13% (calc.). The second decomposition step occurs in the temperature range 340-430 °C leads to formation of $CrC_7H_4NO_4$; with a total weight loss of about 44.83% (found) 45.84% (calc.). The last decomposition step occurs in the temperature range 440-470 °C at which the compound with the formula $CrC_7H_4NO_4$ with a total weight loss of about 34.48% (found) 34.38% (calc.); was completely decomposed leaving Cr_2O_3 residue; with a total weight loss of about 17.24% (found) 17.42% (calc.).

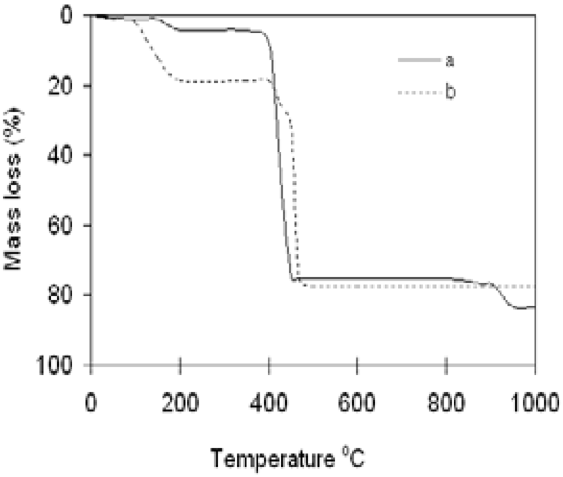

Fig. (1): TGA Profiles of the complexes: (a) $[Cr(pic)_3]H_2O$ and (b) $[Mn(pic)_2(H_2O)]H_2O$.

The thermodynamic parameters of decomposition processes of dehydrated complex namely activation energy (ΔE*), Arrhenius factor (A), enthalpy (ΔH*), entropy (ΔS*) and Gibbs free energy change of the decomposition (ΔG*) have been calculated graphically by employing the CR and HM relations [11] and cited in Table (2). The most significant result is the considerable thermal stability of the complex reflected from the high values of the activation energy of the decomposition which are in second and third steps. The second essential result from Table (2) is the entropy change ΔS* for the formation of the activated complex from the starting reactant is in the first step of the negative values. The negative sign of the ΔS* suggests that activated complex have more ordered systems than reactants [13,14].

Table (2): Thermodynamic parameters of the indicated complexes

Steps	E* KJmol^{-1}	ΔS* Jmol^{-1}K^{-1}	ΔH* KJ-mol^{-1}	ΔG* KJ-mol^{-1}	A (S^{-1})
$[Cr(pic)_3].H_2O$					
Step 1: 55-150 °C	81 **(68)**	-50 **(-114)**	88 **(65)**	97 **(108)**	$1.9*10^{10}$ **($8.8*10^{6}$)**
Step 2: 340-430 °C	294 **(270)**	160 **(131)**	289 **(264)**	181 **(176)**	$3.2*10^{21}$ **($9.3*10^{19}$)**
Step 3: 440-470 °C	487 **(472)**	386 **(387)**	481 **(465)**	199 **(183)**	$2.2*10^{33}$ **($2.5*10^{33}$)**
$[Mn(pic)_2(H_2O)_2].H_2O$					
Step 1: 40-120 °C	59 **(88)**	-72 **(-68)**	57 **(85)**	80 **(107)**	$1.2*10^{9}$ **($1.8*10^{9}$)**
Step 2: 140-300 °C	144 **(136)**	72 **(37)**	140 **(132)**	109 **(116)**	$5.4*10^{16}$ **($8*10^{14}$)**
Step 3: 350-550 °C	347 **(305)**	198 **(158)**	341 **(299)**	198 **(185)**	$3.2*10^{23}$ **($2.7*10^{21}$)**
$[Ni(pic)_2(H_2O)_2]2H_2O$					
Step 1: 50-140 °C	50 **(44)**	-124 **(-151)**	47 **(41)**	91 **(95)**	$2.3*10^{6}$ **($9.1*10^{4}$)**
Step 2: 150-250 °C	171 **(136)**	77 **(27)**	167 **(132)**	130 **(118)**	$1.1*10^{17}$ **($2.8*10^{14}$)**
Step 3: 350-450 °C	59 **(142)**	-19 **(-64)**	154 **(137)**	166 **(178)**	$1.2*10^{12}$ **($5.7*10^{9}$)**
Step 4: 500-550 °C	46 **(34)**	-232 **(-92)**	40 **(28)**	209 **(95)**	$1.1*10^{6}$ **($2.4*10^{8}$)**
$[Ni(pic)_2(pi\text{-}H)H_2O].2H_2O$					
Step 1: 200-320 °C	78 **(77)**	-123 **(-153)**	74 **(72)**	139 **(154)**	$3.8*10^{6}$ **($10.5*10^{4}$)**
Step 2: 325-360 °C	401 **(369)**	381 **(338)**	396 **(364)**	161 **(156)**	$1.1*10^{33}$ **($6.2*10^{30}$)**
Step 3: 380-450 °C	151 **(125)**	-59 **(-91)**	145 **(120)**	186 **(182)**	$1.1*10^{10}$ **($2.3*10^{8}$)**
Step 4: 455-550 °C	479 **(432)**	373 **(324)**	473 **(426)**	198 **(187)**	$4.9*10^{32}$ **($1.4*10^{30}$)**

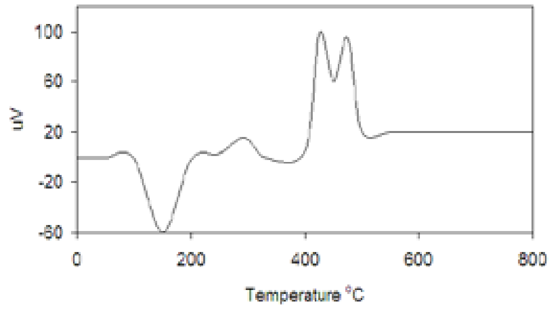

Fig. (2): DTA profile of $[Mn(pic)_2(H_2O)]H_2O$.

TGA and DTA of $[Mn(pic)_2(H_2O)_2].H_2O$ Complex TGA and DTA curves of the manganese complex are shown in Figs. (1,2). The correlations between the different decomposition steps of the complex with the corresponding weight losses are discussed in terms of the proposed formulae of the complex as follows:

Mn(II) complex with a general formula $[Mn(pic)_2(H_2O)_2].H_2O$ was thermally decomposed in three successive steps. The first step (40-120 °C) with an estimated mass loss of 5.15% (calculated mass loss 5.09%) could be assigned to the loss of the hydrated water molecule in the outer sphere. The second decomposition step (140-300 °C) with an estimated mass loss of 10.38% (calculated mass loss 10.19%) could be assigned to the successive loss of two coordinated water molecules. The DTA curve (Fig. 2) shows lose of the two water molecule in two steps, an endothermic peak at 155°C and an exothermic peak at 304°C. The third step (350-550 C°) with an estimated mass loss of 65.28% (calculated mass loss 64.55%) attributed to the successive loss of two ligand molecules in two exothermic steps with peaks at 438 and 472 °C in the DTA curve, due to rearrangement or phase transformation leaving MnO residue (estimated residual mass 19.19% and calculated mass 20.10%). Thermodynamic parameters for the decomposition steps, by employing the Coats-Redfern and Horowitz-Metzger equations, to calculated values of ΔE*, A, ΔS*, ΔH* and ΔG* are summarized in Table (2). The thermal stability of the complex reflected from the high values of the activation energy of the decomposition for the 2nd and 3rd steps. While in the first step the thermal stability is reflected from the negative sign of the ΔS* that indicates that the decomposition reactions proceed with a lower rate than the normal ones [10].

TGA of $[Ni(pic)_2(H_2O)_2].2H_2O$ Complex TGA curves of the nickel complexes are shown in Fig (3). The correlation between the different decomposition steps and corresponding weight losses are discussed in terms of the proposed formula of the complex as follows: Ni(II) complex with a general formula $[Ni(pic)_2(H_2O)_2].2H_2O$ was thermally decomposed in four successive steps. The first decomposition step 50-140 °C with an estimated mass loss of 9.81% (calculated mass loss 9.60%) assigned to the successive loss of two hydration water molecules. The second step occurred at 150-250 °C with an estimated mass loss of 8.72% (calculated mass loss 9.60%) attributed to the successive loss of two coordinated water molecules. The third step appeared at 350-450 °C, represents the loss of a large amount of the organic moiety, around 39.25% mass loss. From the residual formula one can estimate a loss of two pyridine molecules (calc. 39.47%), leaving a stable nickel oxalate which successively decomposes between 500-550°C correspond to with a mass loss of about 23.83% (calc. 23.47%) leaving NiO residue. Total found residual mass 18.39% (total calculated residual mass 19.92%).

Thermodynamic parameters for the decomposition steps were evaluated graphically and given in Table (2). The most significant result is the considerable thermal stability of the complex reflected from entropy change ΔS* for the formation of the activated complex from the starting reactants is in most cases of negative values, negative sign of the ΔS* indicates to the same reason mentioned in previous complexes. But in the second step the thermal stability is reflected from the high values of the activation energy of the decomposition.

TGA of $[Ni(pic)_2(pi\text{-}H)H_2O].2H_2O$ Complex Fig. (3) shows the TGA data of the nickel complex $[Ni(pic)_2(pi\text{-}H)H_2O]2H_2O$. It was thermally decomposed in four successive decomposition steps. The first decomposition step was found within the temperature range 200-320 °C with an estimated mass loss 10.71% (calculated mass loss 11.25%) could be assigned to the successive loss of hydrated water and coordinated water molecules. The second step occurred at 325-360 °C with an estimated mass loss of 25.71% (calculated mass loss 25.6%) could be assigned to the successive loss of picolinate form molecule. The third and fourth steps occurred at 380-450 and 455-550 °C with an estimated mass loss 25.71, 25.71% (calculated mass loss 25.41, 25.41%) respectively; was attributed to the loss of picolinato anion ligand molecules, leaving NiO residue. Total found residue 12.16% (total calculated residue 15.56%). The thermodynamic parameters for the decomposition steps were evaluated and given in Table (2). The thermal stability of the complex reflected from the high values of the activation energy of the decomposition which are in second and fourth step, while the thermal stability in the first and third steps are reflected from the negative sign of the ΔS* that indicates to the same reason mentioned in previous complexes.

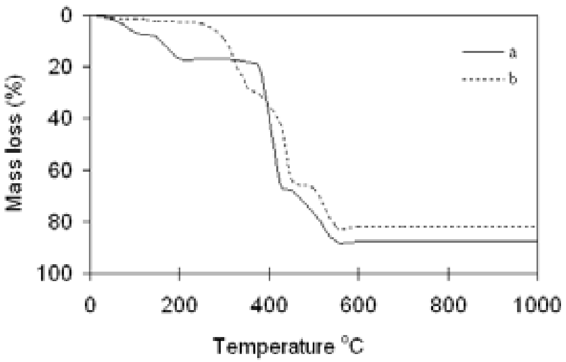

Fig. (3): TGA Profiles of the complexes (a) $[Ni(pic)_2(H_2O)_2]2H_2O$ (b) $[Ni(pic)_2(pi\text{-}H)H_2O]2H_2O$.

Infrared Spectroscopic Investigation

The infrared spectra (IR) of the complexes under investigation are compared with that of the free picolinic acid and sodium picolinate to determine the change that might have taken place during the complexation. Salting-in of nickel picolinate complexe $[Ni(pic)_2].H_2O$, with simple salts afforded a complexes of the formula $[Ni(pic)_2(pic\text{-}H)H_2O].2H_2O$, and $[Ni(pic)_2(H_2O)_2].2H_20$.

The room temperature IR of the crystalline picolinic acid, the sodium salt of the picolinic acid, $[Ni(pic)_2].H_2O$, $[Ni(pic)_2(pic\text{-}H)H_2O].2H_2O$, and $[Ni(pic)_2(H_2O)_2].2H_2O$ complexes are given together with tentative assignments of the bands in Fig (1). In the high frequency region hydrogen bonding involving the carboxylic acid group is considerable and causes very broad bands of the type (O-H...O) centered at 3435 cm^{-1}, which is observed in the free acid, indicating the presence of the picolinic acid form. This is a splitted sharp band representing two different modes of hydrogen bonding at 3505 and 3433 cm^{-1} in the complex indicating that the hydrogen bonding are caused by both the picolinic acid form and water molecule with Picolinate ligand [17].

The complex $[Ni(pic)_2(H_2O)_2].2H_2O$ have strong and broad bands at 3370 and 3164 cm^{-1} respectively; due to hydrogen bonding of water molecules. This indicates that water molecules are inside and outside the coordination sphere. Bands near 2560, 2150 and 2050 cm^{-1} which appears in the free acid spectrum are completely absent in the complex, as well as in the corresponding salt spectra, showing that nitrogen atoms do not have hydrogen bonding but are involved in the coordination of nickel [15.16]. The ν_{as}(-COOH) vibration frequencies of the free picolinic acid at 1719 cm^{-1} are shifted to lower frequencies at 1625 cm^{-1} for the sodium salt of picolinic acid, compared to the free ligand, the solid complex shows a broad to strong bands at 1725 cm^{-1}, and weak one at 1662 cm^{-1}. This result suggests that the complex contains both coordinated neutral picolinic acid as well as the picolinate anion, the weak band at 1662 cm-1 is not clear from νas(-COOH), this prove the presence of hydrogen bonding between water molecule and picolinato anion as shown in the $[Mn(pic)_2(pic\text{-}H)]OH$ complex [16,17]. The other complex $[Ni(pic)_2(H_2O)_2].2H_2O$ is in agreement with sodium salt, and shows a slight increase of $v_{as}(-COO^-)$ 1626 cm^{-1}, and a decrease of $v_s(-COO^-)$ to strong band at 1378 cm^{-1}, which is indicative of bidentate coordination mode as was found for other picolinato complexes [15,18].

In the far-IR region we tentatively assigned the medium strong bands at 436 and cm^{-1} cm"¹ as [ν Ni-N(pic)] and 291 and 298 cm^{-1} as [ν Ni-O(pic)] for $[Ni(pic)_2(pic\text{-}H)H_2O]2H_2O$ and $[Ni(Pic)_2(H_2O)_2]2H_2O$ respectively [18,19].

Conclusions

The solubility of the complexes under testing changing from partially soluble (like $[Cr(pic\text{-}O)H_2O)$ and $[Ni(pic)_2]H_2O$ in KI) to completely soluble (like $[Mn(pic\text{-}O)_2(H_2O)_2]$ and $[Ni(pic)_2]H_2O$ in Gaun). Results obtaind from elemental analysis show that the complexes have the ratio between metal and ligand in the form 1:2 (for manganese and nickel picolinate) and 1:3 (for chromium and picolinate). Molar conductance measurements show that all these complexes are non electrolytes. TGA analysis reveal that both chromium and manganese complexes decomposed through three steps leaving the metal oxide residue (Cr_2O_3 and MnO) at >550 °C, but nickel complex was decomposed through four steps leaving the NiO residue at >550 °C. The thermodynamic activation parameters of decomposition processes by employing the CR and HM relations reveal that the most significant result is the considerable thermal stability of the complex reflected from the high values of the ΔE* and the negative sign of the ΔS*.

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