given in Table 2. The densities determined by the conventional method of liquid displacement, those calculated from lattice parameters[9] and the literature values[10,11] are also listed for comparison. The densities measured with the conventional liquid displacement method are found to give smaller values, as expected. Fairly good agreement is obtained in general between the values of the proposed method and those calculated from the lattice parameters[9]. Also, the values of this method agree very well with the literature values[10,11]. The proposed method is simple, intuitive, and yet gives quite an accurate result. This method will be especially of value when the sample is in powdery, porous form, or is reactive to displacing liquids.

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Thermochemical Behaviour of Some Salicyaldehyde G-P Complexes of Fe(III), Co(II), Cu(II) and Zn(II)

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Through two different techniques TGA and DSC the thermal decomposition processes of salicyaldehyde G-P complexes having the general formula: $[MCl_2(L)_2]^{2+}$ $2Cl^-$; where L = salicyaldehyde carbohydrazone pyridinum cation, and M = Fe (III), Co (II), Cu (II) and Zn (II), have been studied. From the obtained thermogravimetric curves the following parameters n, E_a, A, ΔS^*, $\Delta H'$ and ΔG^* were evaluated. The effect of the nature of the metal ions present in the complexes studied upon the calculated thermodynamic parameters was reported. A suitable mechanism for the thermal decomposition process was suggested.

Introduction

The thermal behaviour of the complexes plays a very important role for chemist to understand the mechanism of the thermal process. This thermal behaviour is based on the qualitative and quantitative analysis of the DTA and TG curves respectively[1-5]. The aim of the present work is to describe the thermochemical behaviour of some complexes, discuss the differences in their thermal stabilities and also to find a suitable mechanism for the thermal decomposition process.

Experimental

Syntheses of the complexes studied were carried out as

mentioned previously[6]. The stoichiometry of the solid compounds obtained was confirmed by the results of the elemental analysis, molar conductance of solution of the complex (see Table 1), and magnetic measurements.

The thermal decomposition has been studied in a Pt crucible by thermo-analyser [TGA-DTA (1600°C) GDTA 15, Setram Lyon-France and DSC 777 Lyon-France] using linear temperature programmer with a constant heating rate of 5 °C/min. Sample weight used was in the range of 20-37.2 mg.

Results and Discussion

Analysis of the DTA Curves. All the DTA curves obtained showed four different peaks. For example, in the case of the cobalt-complex the following peaks were observed:

1. A sharp endothermic peak at 254.3°C which corresponds to the dechlorination of the chloride ions. This was confir-

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Table 1. Results of the Elemental Analysis of the Solid Complexes

Complex	C% Found (Cal.)	H% (Cal.)	N%	Molar conductance, λ_m
$[Fe(L)]^{2+}2Cl^- \cdot 4H_2O$	34.1 (34.3)	3.9 (4.3)	8.2 (8.6)	200
$[Co(L)]^{2+}2Cl^- \cdot 3H_2O$	35.7 (35.3)	4.6 (4.2)	8.6 (8.8)	—
$[Cu(HL)]^{2+}2Cl^- \cdot 4H_2O$	32.6 (33.1)	3.6 (4.1)	7.8 (8.3)	200
$[Zn(HL)_2]^{4+}4Cl^-$	46.7 (46.6)	3.9 (4.1)	11.6 (11.0)	415

The general structure of these complexes can be represented as follow[6].
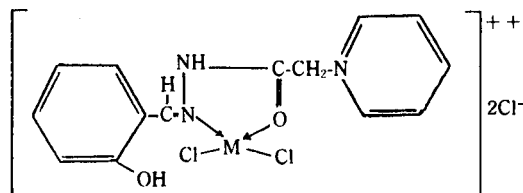
Table 2. Analysis of the TG Curve of the Cobalt Compound

Wt. loss, mg	t_1 min	t°C	dm	$-dm/dt$ $=v$	Log v (−)	$1/T\times10^3$
3.9	51.1	199.0	15.7	0.307	0.512	1.80
7.9	60.0	331.2	11.7	0.195	0.709	1.65
9.8	68.0	375.1	9.8	0.144	0.841	1.54
11.8	72.7	400.7	7.8	0.107	0.969	1.48
15.6	87.9	484.9	4.0	0.045	1.341	1.31
17.3	97.2	536.1	2.3	0.024	1.625	1.23
19.3	104.2	574.6	0.3	0.0028	2.540	1.17

med by the analysis of the first step of the corresponding TG curve.

2. A sharp exothermic peak at 279.3°C which may be due to the lattice rearrangement.

3. An exothermic shoulder peak at 345.3°C is consistent with the melting of the complex.

4. A strong broad endothermic one at 438.9°C may be attributable to a result of the decomposition to the chelate bonds, leading to the formation of the final stable product "metal oxide".

Analysis of the TG Curve. Table 2 shows the weight loss of the cobalt complex with the time (or temperature) as one example for such analysis. In order to evaluate the kinetic parameters n, E_a and A (they are order of the decomposition-process, the activation energy and the pre-exponential factor respectively), Chatterjee's method[7] was used. This method is based on the general equation for the rate of a heterogeneous kinetics, V

$$V = -\frac{dm}{dt} = km^n \qquad (1)$$

where k, m and t are the rate constant of the reaction, the

Table 3. The Evaluated Kinetic and Thermodynamic Parameters of the Investigated Compounds

Compound	n	E_a KJ/mol	log A	ΔH^* KJ/mol	ΔS^* KJ/mol/deg	ΔG^* KJ/mol
Fe-Complex	0.75	162.17	14.25	154.80	14.63	152.50
Co-Complex	0.87	240.73	12.21	231.90	15.17	215.60
Cu-Complex	0.80	193.60	13.81	179.76	14.92	168.13
Zn-Complex	0.92	154.55	12.93	138.45	17.86	129.27

active weight of the reacting material and the time elapsed from the start of the experiment respectively. Substituting k from the Arrhenius equation into the equation (1) gives:

$$\log V = \log A + n \log m - \frac{E_a}{2.303RT} \qquad (2)$$

Plotting log V versus $1/T$ gives a straight line. Its slope equals to $-E_a/2.30R$, and its intercept is log $A + n$ log m. From Table 3 it is clear that the order of the decomposition reaction (n) for all complexes is nearly unity. This means that the mechanism of the decomposition processes for all the complexes studied is the same. The activation energy of the complexes decreases in the following order:

Cu(II)<Co(II)>Fe(III)>Zn (II)-complex. This variation of the activation energy increases with the increase of the strength of the (O→M←N) bond, and increases with the increase in the cation radius. This leads to a stronger attraction between the central metal ion and the hetero atoms of the bidentate ligand. It is expected that the thermal stability and the activation energy also decrease as follows: Cu (II)>Co (II) >Fe (III)>Zn (II)-complex. The experimental lower thermal stability in the case of the Cu (II) compound than the Co (II) complex may be attributed to the special electronic configuration of the Cu (II) as $4s^1 3d^{10}$ which leads to shielding effect and hence decreases the attraction between the nucleous of the central metal ion and the hetero atoms of the ligand. This order of thermal stability of the complexes studied is in good agreement with the same arrangement for similar studies[8,9].

Analysis of the DSC Curves. The DSC curves of all the complexes studied showed two different peaks. The first one is an exothermic peak with small intensity at low temperature, and the second peak was a big endothermic one at high temperature (above 450°K). The thermodynamic parameters ΔH^*, ΔS^* and ΔG^*, [which are the activation enthalpy, activation entropy, and free energy change for the thermal decomposition process, respectively], were evaluated using the normal methods[10,11], and these values are given in Table 3. It is seemed from this table that all ΔH^* values for the different complexes have positive values which indicate that the decomposition reactions are endothermic processes. The positive values of ΔS^* for all complexes mean that the decomposition process is accompanied by the increase of the entropy change of the system due to the liberation of different fragments, and hence increases the disorder of the system. The positive values of ΔG^* as seen from Table 3 indicates that the decomposition reactions for all the investigated compounds are not spontaneously occurred, and the higher value corresponds to the higher thermal sta-

bility. From the above analysis data, it is clear that the decomposition process takes place through the following four steps:

1. The decomposition of the pyridinium rest, the formation of Cl_2 gas, and pyridine molecule are related to the first exothermic peak in DTA curves.

2. Decomposition of (-CH=N) and the formation of the volatile salicyaldehyde are related to the second exothermic peak.

3. The degradation of (N-C) bond, and the evolution of N_2 and CO are indicated by the first endothermic peak.

4. The last step which corresponds to the rupture of the bonds between the metal ion and the hetero atoms of the bindentate ligand gives the characteristic endothermic peak in DTA curves. As a result of this step, volatile metal oxide is formed. The breaking of the last bond is responsible for the difference in the activation energy of the various investigated complexes.

This suggested mechanism is similar to our first one given in the literature[12].

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