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SPECTRAL CHARACRISATION, THERMAL DECOMPOSITION AND KINETIC STUDY OF CHROMIUM (III) COMPLEXES WITH SALICYLIC ACID

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ABSTRACT

Two chromium complexes were prepared by using chromium trioxide (CrO_3) and salicylic acid. Complexes [Cr ($C_7H_5O_3$) $(OH)_2$ $(H_2O)_3$] $2H_2O$ and [Cr $(C_7H_5O_3)_2$ (OH) $(H_2O)_3$] H_2O were prepared with salicylic acid. Their spectral characterization was done by using Elemental analysis (C and H), Inductively coupled plasma optical emission spectroscopy (ICP – OES), Ultraviolet-visible (UV-VIS) Spectroscopy , Fourier Transform infrared (FTIR) spectroscopy, proton Nuclear Magnetic Resonance (^{1}HNMR) spectroscopy and Fast Atomic Bombardment (FAB) Mass spectrometry, whereas Thermal decomposition was investigated by Differential scanning calorimetric (DSC). Kinetic parameters were obtained from DSC and the low value of activation energy of the exothermic change indicated lability of the complexes. The study includes kinetics, lability and energetic nature of the complexes prepared.

Keywords: Chromium complexes, Thermal behavior, Elemental analysis, FTIR and DSC Studies

INTRODUCTION

Chromium (VI) is a common and important Oxidation state of the Chromium metal and the chemistry of Chromium (VI) is marked by strong covalent bond to Oxygen and halogens. These Compounds are strong Oxidants[1,2,3]. Chromium trioxide is a linear polymer, which is not very soluble in most of the known hydroxylic solvent but dissolves in water, acetic anhydrite, t-butyl alcohol, pyridine etc. with accompanying depolymerization. Chromium (VI) compounds irritate the skin and mucus membrane whereas chromium (III) is an essential trace metal ion in mammalian nutrition adding in the metabolism of glucose. There is no evidence for any toxic effect of Chromium (III)[4,5]. Chromium (III) is the cheapest transition metal ion which can be used for catalysis[6]. The kinetics of chromium(III)Schiff's base and nicotinic acid complexes1, aqua(EDTA) chromium(III) complexes[7], porphyrin and Cr(EDTA)(H_2O) complexes[8] and chromium (III) ethylenediamine-N,N'-diacetic acid complexes[9] were studied. Chromium (III) complexes are generally inert to the ligand substitution reactions[10] but reactions can be rapid under certain circumstances. Increased liability due to the presence of OH reported for Chromium (III)[11,12]. Lower enthalpy of activation for complexation reaction (92KJ mol^{-1}) and large negative value of ΔS(-175JK^{-1} mol^{-1}) suggest the more pronounced participation of incoming ligand in the transition state and confirm the transformation of the outer sphere complex into inner sphere complex[9]. Thus it was thought of interesting to prepare and characterize some complexes by using CrO_3 and salicylic acid. The spectral, Thermal behavior and Kinetics of these complexes have also been investigated and the results are discussed in this paper.

EXPERIMENTAL

Materials

Salicylic acid, Chromic acid CrO_3 and ethyl alcohol were used as received.

Preparation of Complexes

An aqueous solution of a different molar concentration of CrO_3 (dissolved in water) mixed with an ethanolic solution with a different molar concentration of salicylic acids. The resulting solution was

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refluxed for 30 min after which time a suspension had formed. It was filtered and solid was washed with ethanol and dried in air. Details of the sample and their identification are summarized in Table-1.

Table-1: Details of Samples and their Identification.

Sample ID	CrO_3: Salicylic Acid : Solvent (molar ratio)	Amount took (g) CrO_3:S.A.	Colour	Yield
Cr/H_2Sal 1	CrO_3: H_2Sal : H_2O (1:1)	1 : 1.38	Dark brown	0.95g, 40%
Cr/H_2Sal 2	CrO_3: H_2Sal : H_2O (1:2)	1 : 2.76	Brown-black	2.10g, 56%

Characterization of Samples

Elemental analysis (C&H): Elemental analysis(C&H) done at Sophisticated Analytical Instrument Facility (SAIF), Central Drug Research Institute, Lucknow, India

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

ICP-OES were recorded on Perkin Elmer 5300 DV (Dual view), diluted in acids, Plasma of Argon is the source, at Sophisticated Analytical Instrument Facility (SAIF), Indian Institute of Technology, Madras, India.

UV-VIS Spectrophotometry

UV-VIS Spectra recorded on ECIL, Hyderabad, Double beam Spectrophotometer UV5704SS, in the range 200-650nm in the Department of Applied Chemistry, Indian School of Mines , Dhanbad, India.
Fourier Transform Infrared Spectrophotometry (FTIR): The infrared spectra of solid samples were recorded in KBr pellets in the region 4000-400cm^{-1} on Perkin Elmer spectrum-2000, Fourier Transform Infrared (FTIR) spectrometer in auto mode in the Department of Applied Chemistry, Indian School of Mines, Dhanbad, India.

Proton Nuclear Magnetic Resonance (^{1}HNMR) Spectrometry

The ^{1}HNMR spectra of complexes were recorded on Bruker DRX-300 instruments in DMSO using Tetramethylsilane (TMS) as an internal standard at Sophisticated Analytical Instrument Facility (SAIF), Central Drug Research Institute, Lucknow, India.

Fast Atomic Bombardment (FAB) Mass Spectroscopy

The FAB spectra were recorded on Jeol SX-102 (FAB) mass spectrometer instruments at Sophisticated Analytical Instrument Facility (SAIF), Central Drug Research Institute, Lucknow, India.

Differential Scanning Calorimetry (DSC)

DSC of chromium complexes was carried out on the Perkin Elmer's DSC-7 at Department of Applied Chemistry, Indian School of Mines , Dhanbad, India. In each case the following methods were used:
Sample pan: Aluminium (perforated); Scan rate: 50 ˚C/Min; Start temperature: 50˚C End temperature: 450 ˚C; Purge gas: Nitrogen (at the rate of 20ml/min at the exits)
The following Perkin Elmer's DSC software was used for the purpose: Standard (Version 2.1 and 3.1); Kinetics (3.1); Auto mode (3.1); The DSC was calibrated using indium and zinc as standard.

RESULTS AND DISCUSSION

The Physical and analytical parameters of Cr/H_2Sal complexes are summarized in Table-2 and are in agreement with the proposed molecular formula for the complexes.

Table-2: Elemental Data of Complexes

Complexes	Elemental Analysis (%), Observed (Calculated)		
	C	H	Cr
Cr/H_2Sal 1	27.08 (26.84)	5.60(5.43)	17.06(16.61)
Cr/H_2Sal 2	40.98 (40.48)	4.95(4.58)	13.24(12.53)

UV-VIS Spectrometry Studies

The UV-VIS spectra of chromium complexes in DMSO are shown in Table-3 gives consolidated values of the peaks (along with absorbance) of these spectra.

Table-3: UV-VIS Spectral Data of Chromium Complexes in DMSO

S. No.	Sample ID	λ_{max} nm (logε)
01.	Cr/H$_2$Sal 1	553.0(2.482), 442.5(2.400), 426.0(1.850), 447.5(1.846), 417.5(1.750), 383.5(1.481), 610.5(1.452), 434.5(0.494), 406.0(0.490), 457.5(0.480)
02.	Cr/H$_2$Sal 2	391.0(0.566), 442.5(0.562), 426.0(0.559), 447.5(0.559), 417.5(0.557), 383.5(0.557), 610.5(0.557), 434.5(0.550), 406.0(0.550), 457.5(0.548)

UV-visible spectra of complexes present two bands in the ranges of 400- 500 and 525-640nm which can be assigned respectively to $^4A_{2g} \rightarrow ^4T_{1g}$ and $^4A_{2g} \rightarrow ^4T_{2g}$ d-d transitions of octahedral chromium complexes[13]. In the complex Cr/ salicylic acid solutions (Cr/H$_2$sal) the bands observed at 442 and 553 nm of chromium in aqueous solution are characteristic of oligomeric species, probably the dimer complexes. The FTIR spectra of complexes Cr/H$_2$Sal 1 and Cr/H$_2$Sal 2 are shown in Figs.-1 and 2 respectively. The FTIR was taken in auto mode and peak assignments are given in Table 4.

Table-4: Peak Assignments of FTIR of Complexes[14]

Complex	ν (C=O)	ν (CO)	ν (–COO)	ν (CrO)	νOH	δ(OC=O) +ν (Cr–O)
Cr/H$_2$Sal 1	1603	1243	1455, 1571	675, 531	3401	843, 764
Cr/H$_2$Sal 2	1603	1246	1467, 1535	674, 532	3239	844, 759

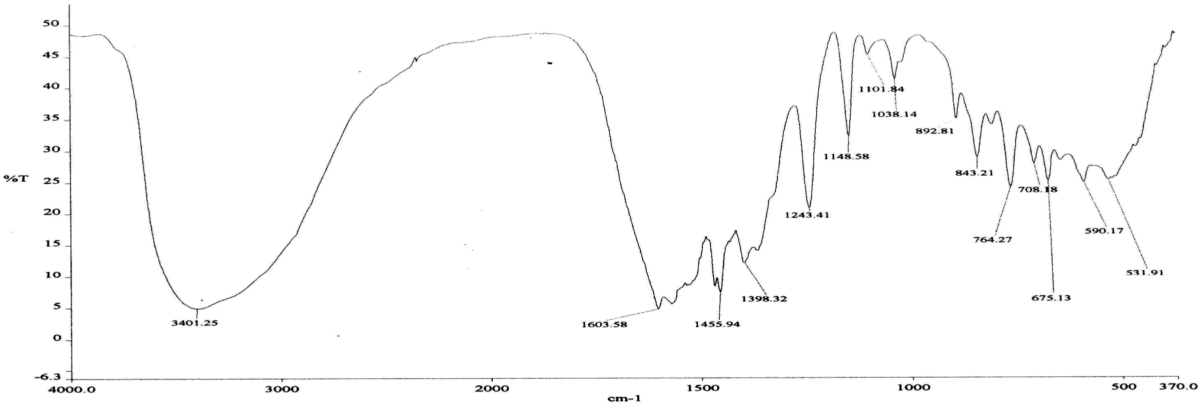

Fig.-1: FTIR Spectrum of Cr/H$_2$Sal (1)

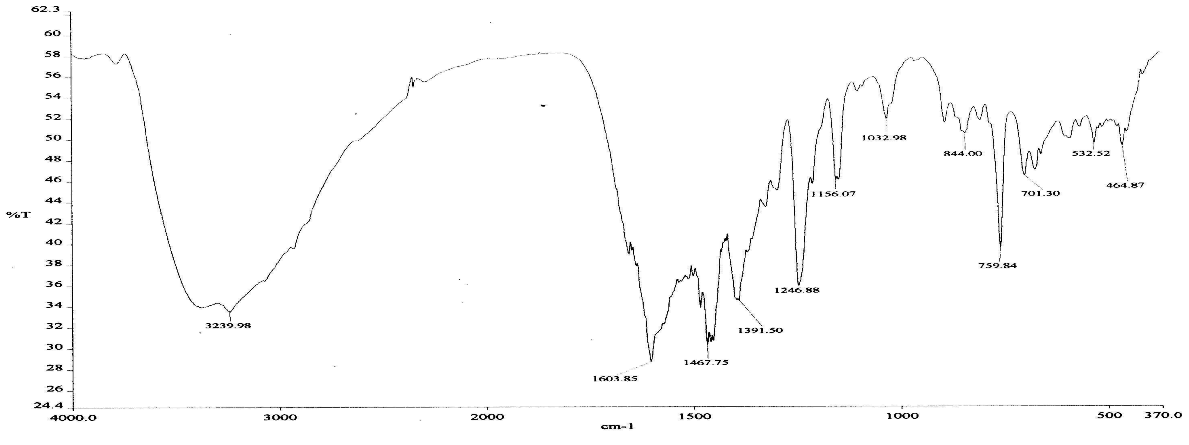

Fig.-2: FTIR Spectrum of Cr/H$_2$Sal (2)

FTIR spectra of complexes formed indicated the presence of coordinated water molecules and ortho-disubstitution in the complexes. The disappearance of the absorption bands of the salicylic acid due to O-H of the carboxyl group in the range 3240-2594 cm^{-1}, indicated deprotonation of the acidic group of the ligands and appearance of new bands in the region 600-700 cm^{-1} in the spectra of the complexes were attributed to ν (Cr-0). Thus FTIR results suggested coordination of oxygen atom to the metal ion and indicated the formation of new complex[15].

The ^{1}HNMR spectra of complexes were recorded on Bruker DRX-300 instruments in DMSO using TMS as an internal standard. The proton resonance spectral (^{1}HNMR) data of Cr/H_2Sal complexes are shown in Table-5.

Table-5:^{1}HNMR Spectral Data of Complexes and their Assignments[16].

Complexes	Assignments (δ)
Cr/H_2Sal 1	8 – 9 (4H, ArH), 3.46 – 3.26 (–OH, Ar), 2.56-2.44 (Protio solvent Component), 1.23 (–OH)
Cr/H_2Sal 2	7.76 – 7.48 (4H, ArH), 6.91 (4H, ArH), 3.55 (–OH, Ar) 2.72 – 2.27 (Protio solvent component) 1.23 (–OH).)

The FAB Mass spectra, recorded on Jeol SX – 102 (FAB) Mass spectrometer instruments, of complexes Cr/H_2Sal and their expected fragmentation species, are given in Table 6-7. The results from FAB Mass spectra were inferred on the basis as followed by Barnwal et al[17] on oxo-bridge multinuclear chromium assemblies like trinuclear complex $[Cr_3O\ (acac)_3\ (OCCC_{15}H_{31})_3]$.

Cr/H_2Sal 1 $[Cr\ (C_7H_5O_3)\ (OH)_2\ (H_2O)_3]\ 2H_2O$ Anal: found C, 27.08; H, 5.60; Cr, 17.06 Calcd. For $C_7H_{17}CrO_{10}$: C, 26.84; H, 5.43; Cr, 16.61 Calculated molecular wt. of the complex : 313; Observed molecular ion peak : 307. The difference in molecular weight may correspond to the loss of half-molecule of water.

Table-6: FAB Mass Data of Complex Cr/H_2Sal (**1**)

Peak Position	Expected Fragmentation Species	Calculated Mass
307	$Cr\ (C_7H_5O_3)\ (OH)_2\ (H_2O)_3\ 2H_2O$	313
289	$Cr\ (C_7H_\sigma O_3)\ (OH)_2\ (H_2O)_3\ H_2O$	295
273	$Cr\ (C_7H_5O_3)\ (OH)_2\ (H_2O)_3$	277
258	$Cr\ (C_7H_5O_3)\ (OH)_2\ (H_2O)_2$	259
226	$Cr\ (C_7H_5O_3)\ (OH)_2$	223
209	$Cr\ (C_7H_5O_3)\ (OH)$	206
154	$(C_7H_5O_3)\ (OH)$	154
137	$C_7H_5O_3$	137

Cr/H_2Sal 2 $[Cr\ (C_7H_5O_3)_2\ (OH)\ (H_2O)_3\ ]\ H_2O$ Anal: found C, 40.98; H, 4.95; Cr, 13.24 Calcd. For $C_{14}H_{19}CrO_{11}$: C, 40.48; H, 4.58; Cr, 12.53. Calculated mol. wt. of the complex: 415; Observed molecular ion peak (m/z): 422 The difference in molecular weight may correspond to the associated half-molecule of water.

Table-7: FAB Mass Data of Complex Cr/H_2 Sal (**2**)

Peak Position	Expected Fragmentation Species	Calculated Mass
422	$Cr\ (C_7H_5O_3)\ (OH)\ (H_2O)_3\ H_2O$	415
403	$Cr\ (C_7H_5O_3)\ (OH)\ (H_2O)_3$	397
377	$Cr\ (C_7H_5O_3)\ (OH)\ (H_2O)_2$	379
360	$Cr\ (C_7H_5O_3)\ (OH)\ (H_2O)$	361
344	$Cr\ (C_7H_5O_3)\ (OH)$	343
326	$Cr\ (C_7H_5O_3)_2$	326
189	$Cr\ (C_7H_5O_3)$	189
137	$C_7H_5O_3$	137

Thermal Decomposition Studies on Cr/H_2Sal Complexes

DSC of Cr/H_2Sal complexes was carried out on the Perkin Elmer's DSC – 7 and thermograms are shown in Figs.-3 to 6 respectively. Their kinetic parameters are given in Table-8.

Table-8: Kinetic Parameters of Complexes Obtained From DSC Thermogram.

Sample Code	Temp. Range (^{0}C)	Peak Temp. (^{0}C)	Inko	Change in Enthalpy, ΔH (J/g)	Activation Energy (KJ/mol)	Order of Reaction
Cr/H_2Sal 1 A Cr/H_2Sal1 B	70.68-169.11 240.16-359.29	120.03 309.71	20.93±0.45 8.56±0.18	203.32 –42.76	80.57±1.74 62.89±1.35	1.37±0.02 0.71±0.01
Cr/H_2Sal 2 A Cr/H_2Sal2 B	64.77-177 235.25-423.48	162.55 307.25	4.01±0.08 3.7±0.8	152.51 –229.25	28.24±0.61 42.41±0.91	0.63±0.01 0.89±0.01

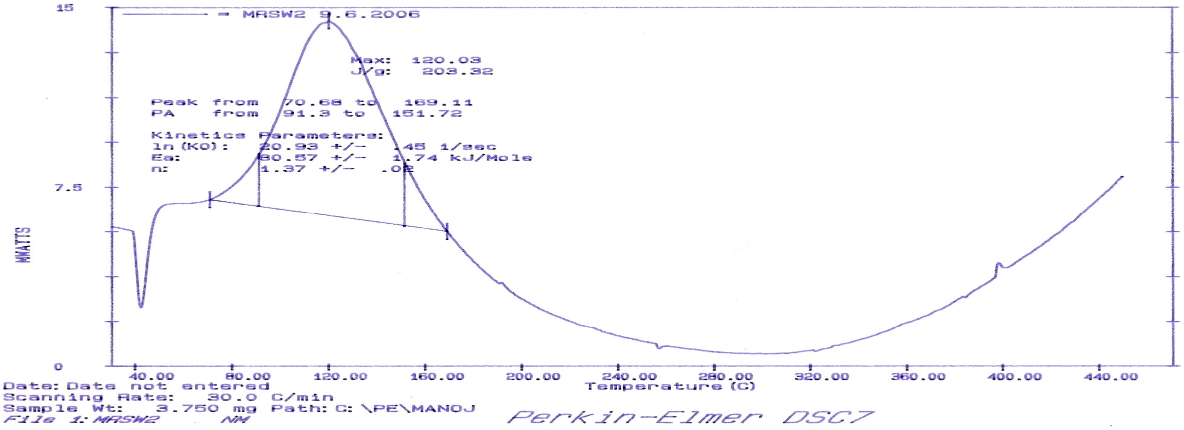

Fig.-3: DSC Thermogram of Cr/H_2Sal 1 A

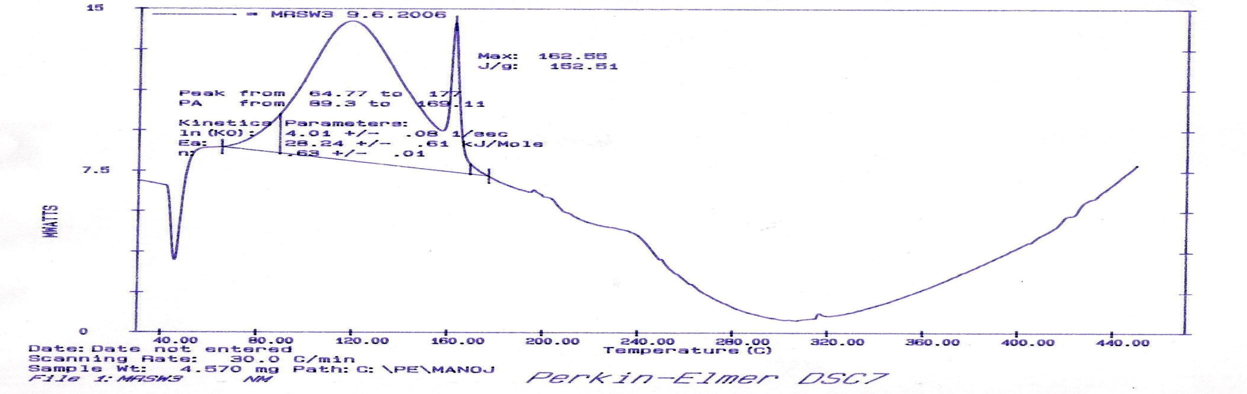

Fig.-4: DSC Thermogram of Cr/H_2Sal 1 B

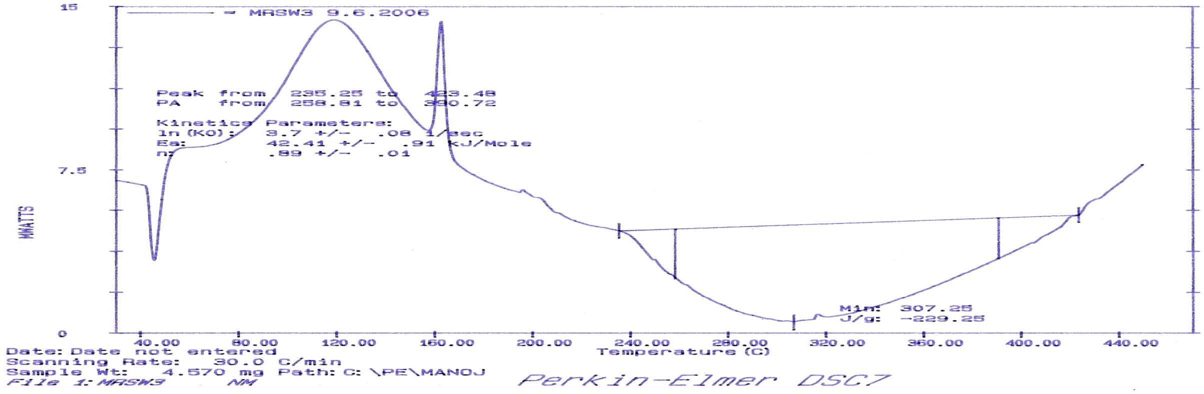

Fig.-5: DSC Thermogram of Cr/H_2Sal 2 A

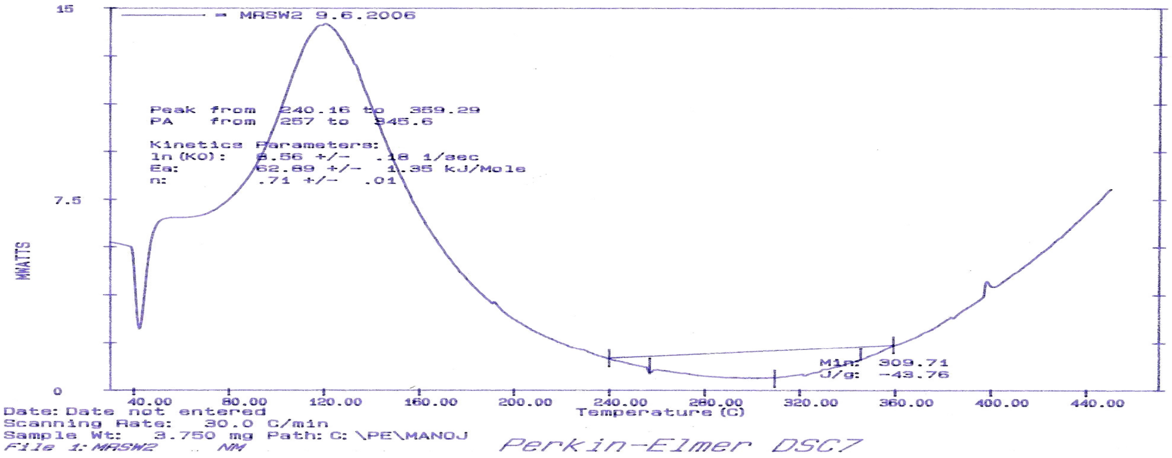

Fig.-6: DSC Thermogram of Cr/H_2Sal 2 B

The kinetic parameters: enthalpy (ΔH), activation energy (Ea), $\ln K_0$, the order of reaction (n) and a peak temperature of the Cr/ Salicylic acid complexes were determined from DSC thermogram. Generally, second step decomposition was noticed to be an exothermic process and heat flow takes place at 167.36, 309.71, 307.25, 274.8, 295.75, 291.05 and 303.45ºC and showed a low value of activation energy, indicating lability of the complexes. The decomposition follows the first order of reaction. The complexes showed an endothermic peak between 84.9 to 162.55ºC for dehydration process[18]. The final step change of Cr/H_2sal complexes (monomeric, dimeric in nature) could not be recorded as scanning was done up to 450 ºC.

CONCLUSION

Two chromium complexes were prepared by using chromium trioxide (CrO_3) and salicylic acid. Complexes [Cr ($C_7H_5O_3$) $(OH)_2$ $(H_2O)_3$] $2H_2O$ and [Cr $(C_7H_5O_3)_2$ (OH) $(H_2O)_3$] H_2O were prepared with salicylic acid. The low value of activation energy of the exothermic change indicated the lability of the complexes. Thus the kinetics and lability of the complexes could be predicted from the DSC.

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