

Preparation, Spectral and Thermal Decomposition Characteristics of Chromium Complexes of Phthalic Acid

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Received 5 June 2015 / Accepted 26 June 2015

Abstract: Complexes $[\text{Cr}(\text{C}_8\text{H}_5\text{O}_4)(\text{OH})_2(\text{H}_2\text{O})_3]$ and $[\text{Cr}(\text{C}_8\text{H}_5\text{O}_4)(\text{OH})_2(\text{H}_2\text{O})_3]\text{H}_2\text{O}$ were prepared by using chromium trioxide (CrO_3) and phthalic acid. (Hereafter these phthalic acid complexes ($\text{Cr}/\text{H}_2\text{Pht}$) will be named as $\text{Cr}/\text{H}_2\text{Pht1}$ and $\text{Cr}/\text{H}_2\text{Pht2}$ respectively). Their spectral characterization was done by using elemental analysis (C and H), ICP-OES, UV-Vis spectroscopy, FTIR spectroscopy, ^1H NMR and Fast Atomic Bombardment (FAB) Mass spectrometry, whereas thermal decomposition was investigated by differential scanning calorimetric (DSC). Study includes thermal decomposition kinetics and lability nature of the complexes prepared.

Keywords: Chromium complexes, Lability nature, Thermal decomposition, Phthalic acid

Introduction

Hexavalent chromium is a powerful oxidant and finds a number of applications in organic synthesis. Reactions of chromium (VI) with oxygen-, nitrogen- and sulphur –containing reductants have been the subject of several investigators¹⁻³. In some instances the formation of oxygen-, nitrogen- and sulphur- chromium(VI) bonded intermediates have been proposed. The complexing agents (picolinic acid), organic acid (oxalic acid) and transition metal ions have some effect on reduction rate of chromium(VI) by different organic reductants. Chromium has several different oxides, amongst them Cr_2O_3 , CrO_2 and CrO_3 are of special significance. Chromium trioxide (CrO_3) dissolves in water, acetic anhydride, *t*-butyl alcohol, pyridine *etc.* and reacts vigorously with organic substances is widely used as an oxidant in synthetic organic chemistry. Chromium(III) is found to be an efficient catalyst (especially in alkaline medium) which catalyses the reaction with a measurable velocity⁴⁻⁷.

Complexes in which ligands can be replaced by other ligands in order to reach greater stability are divided into two groups. Complexes in which ligands are rapidly replaced by other are called labile complexes and those in which ligand substitution is slow are called inert complexes. Also, a complex is called inert, if the activation energies (E_a) of the formation

and decomposition reactions are large. It has been also reported that the covalent coordinate bond having energy 20-80 kcal/mol (83-334 kJ/mol) with first row metal-ligand bond show high stability with high lability, with the second row metal ligand bond show high stability and medium lability while with the third row metal-ligand bond show high stability and low lability⁸.

Thus it was thought of interesting to prepare and characterize complexes by using CrO_3 and phthalic acids. The spectral and thermal behavior of these complexes has also been investigated and the results are discussed in this paper.

Experimental

Phthalic acid from s.d. fine-chem, Chromic acid CrO_3 from Apex chemicals and ethyl alcohol from Merck were used as received.

Preparation of complexes

An aqueous solution of different molar concentration CrO_3 (dissolved in water) mixed with ethanolic solution with different molar concentration of phthalic acid. The resulting solution was 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 sample and their identification are summarized in Table 1.

Table 1. Details of samples and their identification

Sample ID	CrO_3 : phthalic acid : solvent (molar ratio)	Amount taken, g CrO_3 : phthalic acid.	Colour	Yield
Cr/ H_2Pht 1	CrO_3 : H_2Pht : H_2O (1:1)	1 : 1.66	Light green	0.73 g, 43%
Cr/ H_2Pht 2	CrO_3 : H_2Pht : H_2O (1:2)	1 : 3.23	Blue-green	2.38 g, 55%

Analysis of metal complexes

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. Elemental data of chromium complexes are given in Table 2.

Table 2. Elemental data of complexes

Complexes	elemental analysis, % observed (calculated)		
	C	H	Cr
Cr/ H_2Pht 1	30.89 (31.48)	4.10 (4.26)	16.37(17.05)
Cr/ H_2Pht 2	30.28 (29.72)	4.84(4.64)	16.81(16.10)

UV-Vis spectrophotometry

UV-VIS spectra recorded on ECIL, Hyderabad, Double beam spectrophotometer UV5704SS, in the range 200-650 nm in the Department of Applied Chemistry, Indian School of Mines University, Dhanbad, India

The UV-Vis spectra of chromium complexes in DMSO are shown in Figure 1-2. Table 3 gives consolidated values of the peaks (along with absorbance) of these spectra.

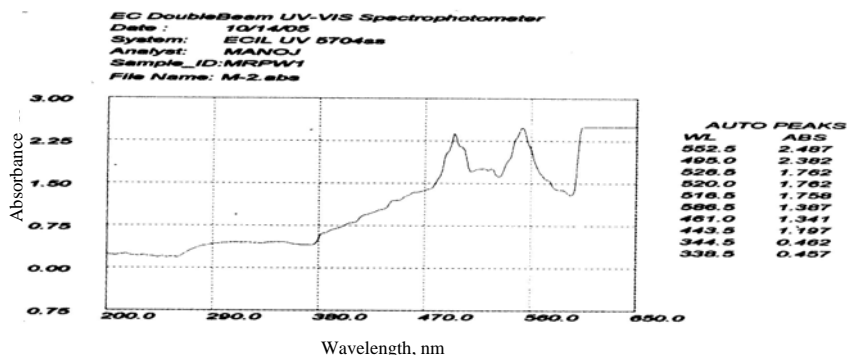
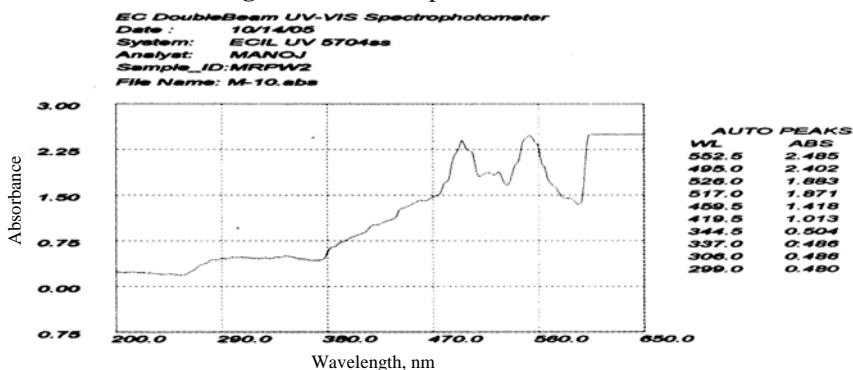
Figure 1. UV-Vis spectrum of Cr/H₂Pht 1Figure 2. UV-Vis spectrum of Cr/H₂Pht 2

Table 3. UV-Vis spectral data of chromium complexes in DMSO

Complexes	λ_{max} nm (log ϵ)
Cr/H ₂ Pht 1	552.5(2.487), 495(2.382), 526.5(1.762), 520.0(1.762), 516.5(1.758), 586.5(1.387), 461.0(1.341), 443.5(1.197), 344.5(0.462), 338.5(0.457)
Cr/H ₂ Pht 2	552.5(2.485), 495(2.402), 526.0(1.883), 517.0(1.871), 459.5(1.418), 419.5(1.013), 344.5(0.504), 337.0(0.486), 306.0(0.486), 299.0(0.480)

Fourier transform infrared spectrophotometry (FTIR)

The infrared spectra of solid samples were recorded in KBr pellets in the region 4000-400 cm⁻¹ on Perkin Elmer spectrum-2000, Fourier Transform Infrared (FTIR) spectrometer in auto mode in the Department of Applied Chemistry, Indian School of Mines University, Dhanbad, India.

The FTIR spectra were taken in auto mode and peak assignments are given in Table 4. The FTIR spectra of complexes Cr/H₂Pht 1 and Cr/H₂Pht 2 are shown in Figure 3-4 respectively.

Table 4. Peak assignments of FTIR of complexes

Complexes	ν (C=O)	ν (CO)	ν (-COO)	ν (CrO)	ν OH	δ (OC=O)+ ν (Cr-O)
Cr/H ₂ Pht 1	1619	1301	1419,1493, 1446	658, 533	3402	756
Cr/H ₂ Pht 2	1619	1298	1415,1492, 1546	657, 531	3403	754

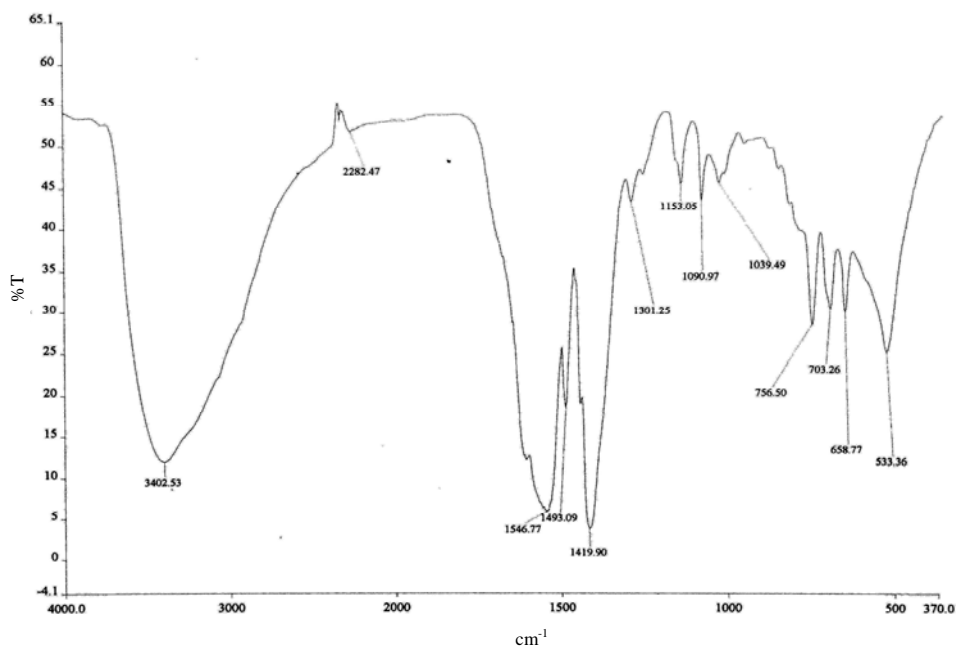


Figure 3. FTIR spectrum of Cr/H₂Pht 1

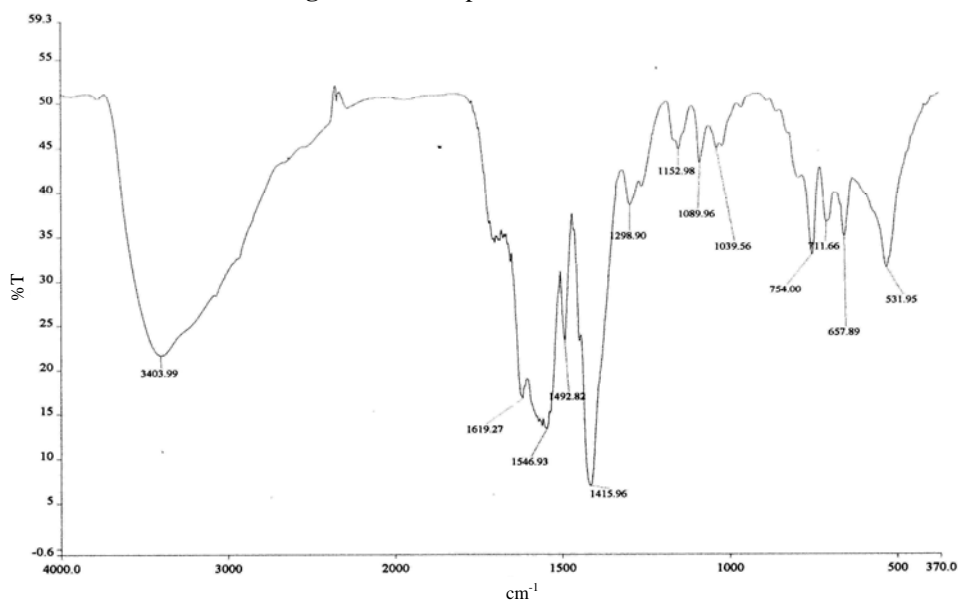


Figure 4. FTIR spectrum of Cr/H₂Pht 2

Proton nuclear magnetic resonance (¹H NMR) spectrometry

The ¹H NMR 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 and Lucknow, India.

The proton resonance spectral (^1H NMR) data of complexes $\text{Cr}/\text{H}_2\text{Pht1}$ and $\text{Cr}/\text{H}_2\text{Pht2}$ are shown in Figure 5-6 respectively. ^1H NMR spectral data of complexes and their assignments are given in Table 5.

Table 5. ^1H NMR spectral data of complexes and their assignments

Complexes	Assignments, δ
$\text{Cr}/\text{H}_2\text{Pht1}$	7.88 – 7.53 (4H, ArH), 3.33 (–OH), (2.05 – 2.50) Protio solvent component
$\text{Cr}/\text{H}_2\text{Pht2}$	7.88 – 7.54 (4H, ArH), 3.65(–OH), 2.72 – 2.27 (Protio solvent component)

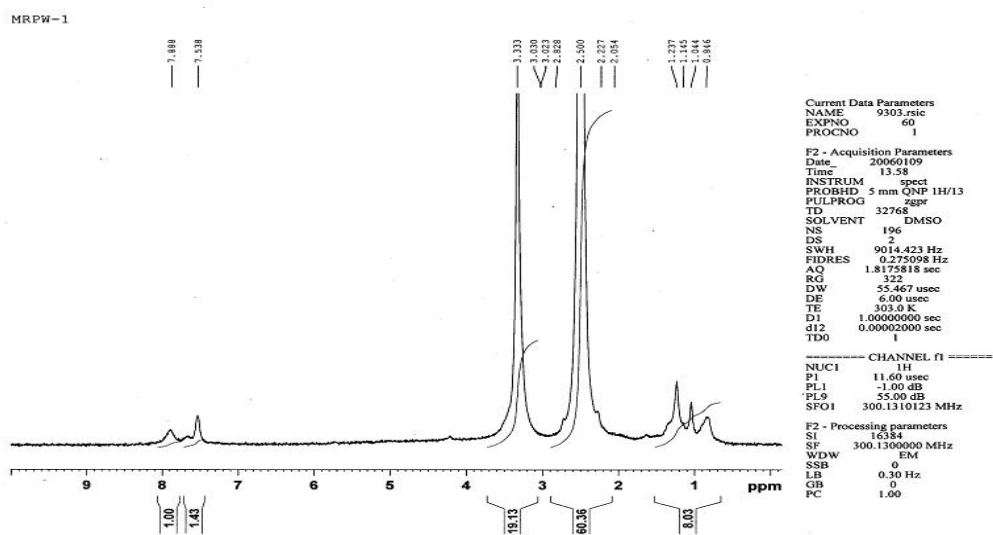


Figure 5. ^1H NMR spectrum of $\text{Cr}/\text{H}_2\text{Pht1}$

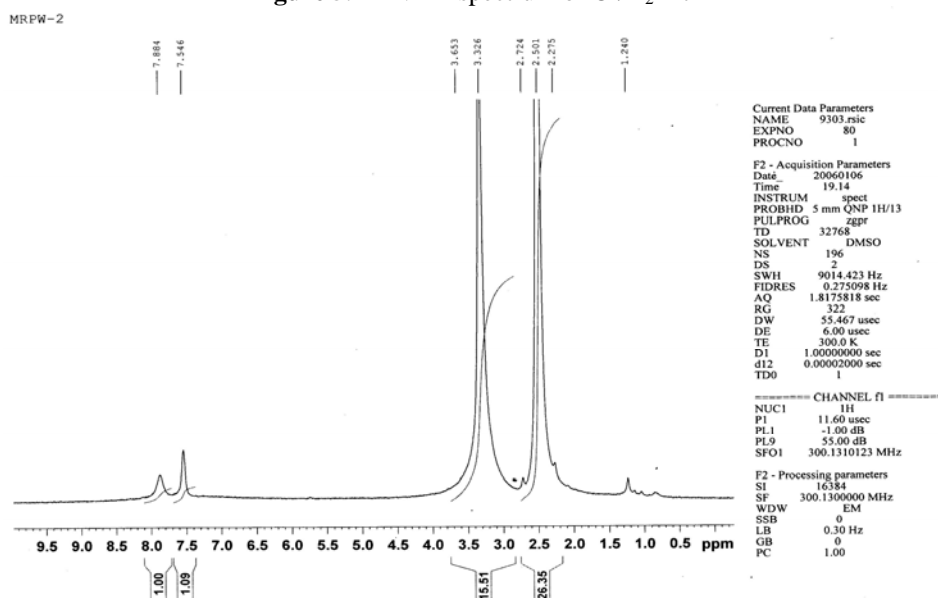


Figure 6. ^1H NMR spectrum of $\text{Cr}/\text{H}_2\text{Pht2}$

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 and Lucknow, India

The FAB Mass spectra, of complexes Cr/H₂Pht1 and Cr/H₂Pht2 are shown in Figure 7-8 respectively and their expected fragmentation species are given in Table 6-7 respectively. The results from FAB Mass spectra were inferred on the basis as followed by Barnwal *et al.*,⁹ on oxo-bridge multinuclear chromium assemblies like trinuclear complex [Cr₃O(acac)₃(OCCC₁₅H₃₁)₃].

Cr/H₂Pht 1 [Cr (C₈H₅O₄) (OH)₂ (H₂O)₃] Anal: found C, 30.89; H, 4.10; Cr, 16.37 Calcd. For C₈ H₁₃ Cr O₉: C, 31.48; H, 4.26; Cr, 17.05

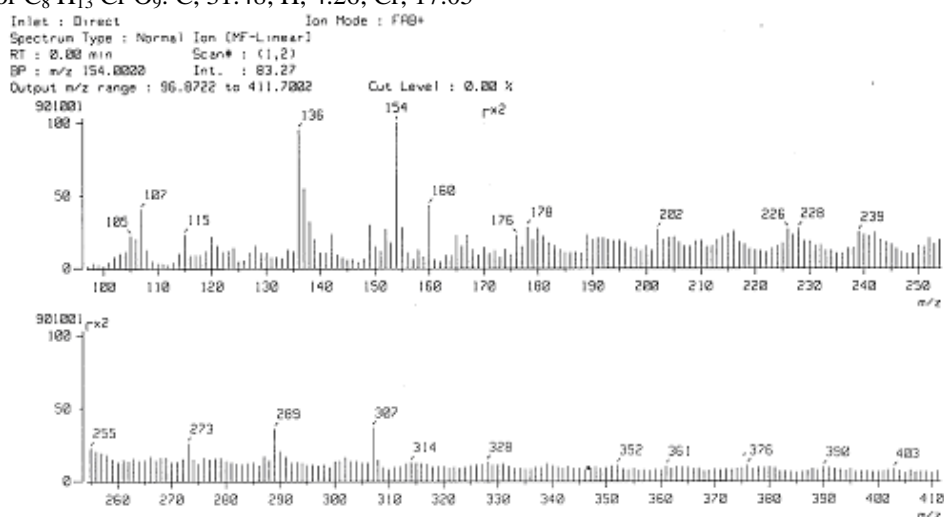


Figure 7. FAB Mass Spectrum of Cr/H₂Pht 1

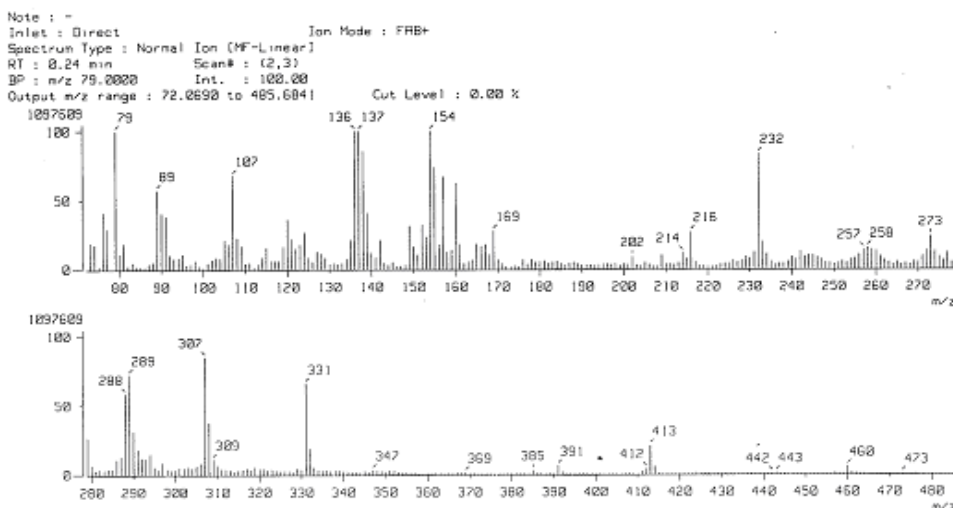


Figure 8. FAB Mass Spectrum of Cr/H₂Pht 2

Table 6. FAB Mass data of complex Cr/H₂Pht 1

Peak position	Expected fragmentation species	Calculated Mass
307	Cr (C ₈ H ₅ O ₄) (OH) ₂ (H ₂ O) ₃	305
289	Cr (C ₈ H ₅ O ₄) (OH) ₂ (H ₂ O) ₂	287
273	Cr (C ₈ H ₅ O ₄) (OH) ₂ (H ₂ O)	269
202	Cr (C ₈ H ₅ O ₃)	201
154	Cr (COC ₆ H ₅)	157
105	CoC ₆ H ₅	105

Table 7. FAB Mass data of complex Cr/H₂Pht 2

Peak Position	Expected fragmentation species	Calculated mass
331	Cr (C ₈ H ₅ O ₄) (OH) ₂ (H ₂ O) ₃ H ₂ O	323
307	Cr (C ₈ H ₅ O ₄) (OH) ₂ (H ₂ O) ₃	305
288	Cr (C ₈ H ₅ O ₄) (OH) ₂ (H ₂ O) ₂	287
273	Cr (C ₈ H ₅ O ₄) (OH) ₂ (H ₂ O)	269
232	Cr (C ₈ H ₅ O ₄) (OH)	234
216	Cr (C ₈ H ₅ O ₄)	217
154	Cr (OCC ₆ H ₅)	157
107	COC ₆ H ₅	105
79	C ₆ H ₅	77

Calculated mol wt of complex: 305 observed molecular ion peak (*m/z*): 307. The difference in molecular weight may correspond to the associated 2H⁺ fragments

Cr/H₂Pht 2 [Cr (C₈H₅O₄) (OH)₂ (H₂O)₃] H₂O Anal: found C, 30.28; H, 4.84; Cr, 16.81 Calcd. For C₈ H₁₅ Cr O₁₀: C, 29.72; H, 4.64; Cr, 16.10

Calculated mol. wt of complex: 323 Observed molecular ion peak (*m/z*): 331. The difference in molecular weight may correspond to the associated half molecule of water.

Differential scanning calorimetry (DSC)

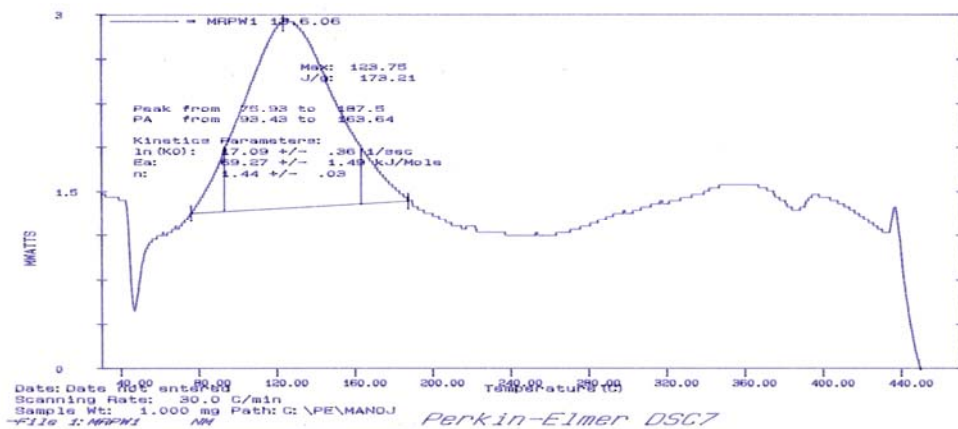
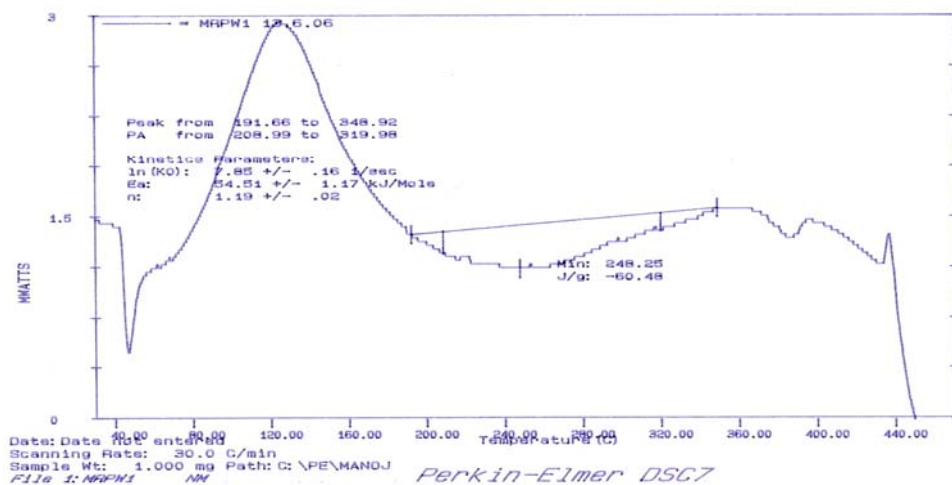
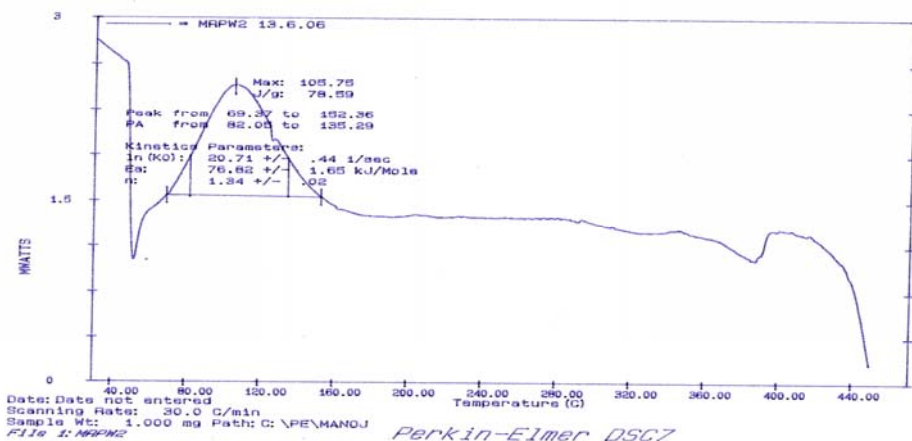
DSC of chromium complexes, was carried out on the Perkin Elmer's DSC-7 at Department of Applied Chemistry, Indian School of Mines University, Dhanbad, India In each case the following methods was used:

Sample pan: Aluminium (perforated); Scan rate: 50 °C/Min; Start temperature: 50°C End temperature: 450 °C; Purge gas: Nitrogen (at the rate of 20 mL/min at the exist). The following Perkin Elmer's DSC software were used for the purpose: Standard (Version 2.1 & 3.1); Kinetics (3.1); Auto mode (3.1); The DSC was calibrated using indium and zinc as standard.

DSC thermograms of complexes Cr/H₂Pht1 and Cr/H₂Pht2 are shown in Figure 9-12 respectively. Their kinetic parameters are given in Table 8.

Table 8. Kinetic parameters of complexes obtained from DSC thermogram.

Complexes	Temp. range °C	Peak Temp. °C	lnKo	Change in enthalpy ΔH (J/g)	Activation energy, kJ/mol	Order of reaction
Cr/H ₂ Pht 1 A	75.93-187.50	123.75	17.05±0.36	173.21	69.27±1.49	1.44±0.03
Cr/H ₂ Pht1B	191.66-348.92	248.25	7.85 ± 0.16	-60.48	54.51±1.17	1.19±0.2
Cr/H ₂ Pht2 A	69.37-152.36	105.75	20.71±0.44	78.59	76.82±1.65	1.34±0.02
Cr/H ₂ Pht2 B	350.54-400.1	387.15	55.96±1.2	-10.27	323.69±6.99	0.54±0.01

Figure 9. DSC thermogram of Cr/H₂Pht 1 AFigure 10. DSC thermogram of Cr/H₂Pht1BFigure 11. DSC thermogram of Cr/H₂Pht2 A

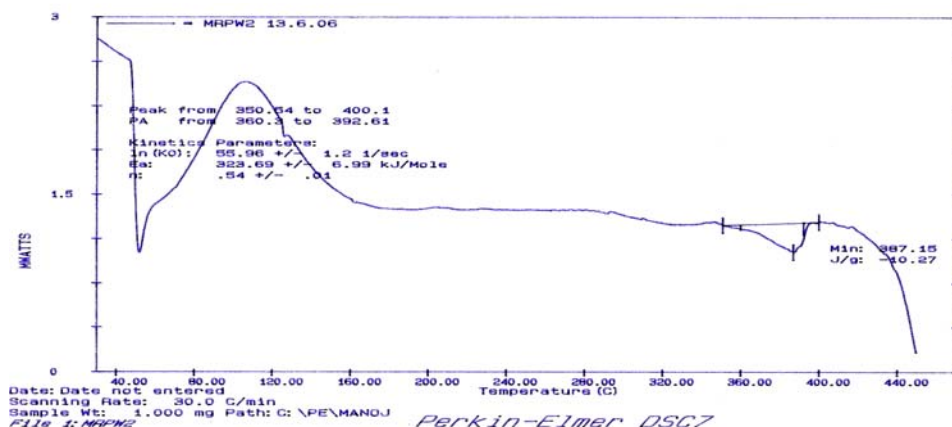


Figure 12. DSC thermogram of Cr/H₂Pht 2 B

Results and Discussion

The physical and analytical parameters of Cr/H₂Pht complexes are summarized in Table 2 and are in agreement with the proposed molecular formula for the complexes. In the UV – Vis spectra of both complexes, the bands observed at 495 and 553 nm lie in the region of the ⁴A₂g → ⁴T₁g and ⁴A₂g → ⁴T₂g d-d transitions of octahedral chromium complexes^{10,11}.

FTIR spectroscopic analysis also confirms the structure of the complexes. FTIR bands of phthalic acid with that of Cr/H₂Pht complexes shows a slight shifting of bands, due to the strong electropositivity of metal ion compared to that of portion in acid. The band at 1619 cm⁻¹ are attributed to C=O stretching of complexes¹².

FTIR spectra of complexes formed indicated the presence of coordinated water molecules in the complexes and ortho-disubstitution in both the complexes. Disappearance of the absorption bands of the phthalic acid due to O-H of the carboxyl group in the range 3007-2525 cm⁻¹ and 3240-2594 cm⁻¹ respectively, 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 both the complexes were attributed to ν (Cr-O). Thus FTIR results suggested coordination of oxygen atom to the metal ion and indicated formation of new complex¹³.

¹H NMR of Cr/H₂Pht complexes showed that deprotonation of only one –COOH group of the phthalic acid took place and the complex formed was not through the –OH of the acid. Both the complexes show resonance at 2.05-2.72 ppm, which may be for the presence of protio- solvent component¹⁴.

DSC thermogram of Cr/H₂Pht complexes showed the values of kinetic parameters – enthalpy (ΔH), activation energy (E_a), lnK₀ and order of reaction (n) for the dehydration and decomposition of the dehydrated complexes. The values of activation energy are useful for the comparison of the thermal stability of these compounds.

The activation energy of Cr/H₂pht1 and Cr/H₂pht 2 complexes were found to be 54.51-69.27 kJ/mol and 76.82-323.69 kJ/mol respectively. The first step decomposition of the complex Cr/H₂pht1 showed 69.27 kJ/mol, activation energy in the temperature 64.78 °C to 177 °C while in the second step decomposition showed 54.51 kJ/mol, activation energy in the temperature range 191.66-348.92 °C. The first step decomposition of the complex Cr/H₂pht2 showed 76.82 kJ/mol, activation energy in the temperature 69.37-152.36 °C.

In Cr/H₂Pht complexes, low value of activation energy⁸ of the first and second step decomposition indicated lability of the complex. DSC studies indicated that the Cr/H₂Pht complexes may be stable at ambient temperature may be labile at higher temperature.

Conclusion

Complexes [Cr(C₈H₅O₄)(OH)₂(H₂O)₃] and [Cr(C₈H₅O₄)(OH)₂(H₂O)₃]H₂O were prepared by using chromium trioxide (CrO₃) and phthalic acid. FTIR spectra of complexes formed indicated the presence of coordinated water molecules and ortho-disubstitution in both the complexes. ¹H NMR of Cr/H₂Pht complexes showed that deprotonation of only one –COOH group of the phthalic acid took place and the complex formed was not through the –OH of the acid. FAB-Mass results showed the complexes Cr/H₂Pht 1 and Cr/H₂Pht 2 featured monodentate HPh[–] and OH[–] ligands and both the complexes are probably monomeric. DSC thermogram of Cr/H₂Pht complexes showed, low value of activation energy of the first and second step decomposition, indicated lability of the complexes.

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