



## Preparation of Chromium (III) Phthalate via Chromium (VI) Oxide using tertiary amyl alcohol as a solvent

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### ABSTRACT

Complexes  $[\text{CrO}_2(\text{C}_8\text{H}_5\text{O}_4)(\text{H}_2\text{O})_3]$  and  $[\text{CrO}_2(\text{C}_8\text{H}_5\text{O}_4)(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$  were prepared by reduction of  $\text{CrO}_3$  at room temperature by ethanol in the presence of phthalic acid ( $\text{H}_2\text{pht}$ ) yield solution that contains monomeric and dimeric Cr (III) complexes. A solution  $\text{H}_2\text{pht}/\text{Cr}$  molar ratio of 1:1 and 1:2 is indefinitely stable towards precipitation. Their analysis were done by using elemental (C and H), ICP-OES (for Cr %), UV-Vis, FTIR,  $^1\text{H}$ NMR and Fast Atomic Bombardment (FAB) Mass spectrometry, where as thermal behaviour was investigated by DSC.

**Keywords:** Chromium (III), tertiary amyl alcohol, thermal behaviour

### INTRODUCTION

Chromium is present everywhere and can be found in three forms; metal ore, trivalent chromium (III) and hexavalent Cr (VI). The trivalent forms occur naturally in many fresh vegetables and fruits, meat, grains and yeast. Recently insoluble, it is the prevalent form in surface soils where oxidation processes which covert chromium from the hexavalent to trivalent form are most common. Hexavalent chromium also occurs naturally, notably in water saturated (reducing) conditions and it is an indicator of human pollution. This form is relatively soluble and can move readily through soil to groundwater.<sup>1-3</sup>

Complexes which undergo ligand replacement within 1 minute at 25 °C and 0.1M reactant concentration are arbitrary termed labile; other less reactive complexes are referred to as inert and also suggested the inert/labile classification of metal complexes with respect to their kinetic stability. The lability of the complexes is dependent upon the activation energy while instability is decided by difference between the free energies of the reactants and the products<sup>4-5</sup>.

In the formation reaction involving replacement of aqua ligands bound to chromium (III) the lability of  $\text{Cr-OH}_2$  bond is also very susceptible to the nature of the ligands bound to chromium

(III) substrate, a behaviour typical of complexes with other metal ion as well. This is particularly true for ligand like biguide, aminopolycarboxylates, quadridentate Schiff bases porphyrine etc bound to chromium (III)<sup>6-7</sup>

#### Preparation of complexes

A solution of different molar concentration of CrO<sub>3</sub> (dissolved in tertiary amyl alcohol (TAA), mixed with ethanolic solution with different molar concentration of phthalic acid. The resulting solution was left standing in a closed flask at room temperature. After 24 h. precipitation began to separate from solution. The process continued for 5 days, after which time no further precipitation was observed. The stable suspension was filtered, and solid was washed with ethanol and TAA and dried in air.

#### Characterization 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.

##### 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<sup>-1</sup> 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 (<sup>1</sup>HNMR) spectrometry

The <sup>1</sup>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) and 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 University, Dhanbad, India. In each case the following methods was used:

Sample pan: Aluminium (perforated); Scan rate: 50 °C/Min; Start temperature: 50 °C

**Table 1: Details of samples and their identification**

Sample ID	CrO <sub>3</sub> :Organic acid: Solvent (Molar ratio)	CrO <sub>3</sub> :Organic acid (in gram)	Colour	Yield
PT1	CrO <sub>3</sub> :H <sub>2</sub> pht: TAA(1:1)	1:1.66	Blue- green	1.38g; 53%
PT2	CrO <sub>3</sub> :H <sub>2</sub> pht:TAA(1:2)	1:3.23	Bule-green	2.59g, 60%

**Table 2: Elemental (C&H) and ICP-OES analytical data of metal complexes**

Sample Id	Found (Calculated) (%)			Molecular formula
	C	H	Cr	
PT 1	32.88(31.68)	3.89(3.63)	16.95(17.16)	C <sub>8</sub> H <sub>11</sub> Cr O <sub>9</sub>
PT 2	31.21(29.91)	3.70(4.05)	15.08(16.20)	C <sub>8</sub> H <sub>13</sub> Cr O <sub>10</sub>

End temperature: 450°C; Purge gas: Nitrogen (at the rate of 20ml/min at the exist)

The following Perkin Elmer's DSC software was 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.

#### Elemental(C&H %) and ICP-OES (Cr %) Analysis of complexes

Elemental (C&H) and ICP-OES (Cr) analytical data of metal complexes are shown in Table 2. The complexes formed were brightly colored and were insoluble in water and in common organic solvents, but was found to be soluble in DMSO at room temperature. It was observed that as the molar ratio of Cr: acid increased the number of coordinating Hpht ligands in the complexes increased proportionally.

#### UV-VIS spectrometry studies

The UV-VIS studies of chromium complexes and their consolidated values of the peaks (along with absorbance) of these spectra are given in Table 3.

It was reported<sup>8</sup> that the electronic spectrum for solution prepared by dissolving active Cr (III)-hydroxide in ethanolic solution of H<sub>2</sub>pht has absorption maxima at 587 and 436nm. The two maxima lie in the region of the  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  and  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  d-d transitions of octahedral chromium complexes. It was also suggested that these solutions

contain a mixture of low oligomeric Cr (III) complexes in the form of ions and ionic associates.

UV-visible spectra of both the complexes present two bands in the ranges of 467- 500 and 525nm which can be assigned respectively to  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  and  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  d-d transitions of octahedral chromium complexes.

In the case of Cr/ phthalic acid solutions (Cr/H<sub>2</sub>pht) the bands observed at 495 and 553 nm of chromium in aqueous solution are characteristic of oligomeric species, probably the monomeric complexes.

#### FTIR studies of Cr/ H<sub>2</sub>pht complexes

The FTIR of Cr/ H<sub>2</sub>pht complexes and their assignments are given in Table 4.

**PT1:** Infrared (Cm<sup>-1</sup>): 3399, 1695, 1551, 1415, 1152, 1039, 755, 703, 656, 538, 376

**PT2:** Infrared (Cm<sup>-1</sup>): 3071, 1697, 1554, 1492, 1412, 1283, 1154, 1072, 797, 750, 712, 536

The characteristic absorption peak at 1686 cm<sup>-1</sup> and 1281 cm<sup>-1</sup> may be attributed to C=O of and C-O stretching frequency of carboxyl group of phthalic acid respectively. The absorption peaks at 1403, 1452, 1466, 1497 and 1586 cm<sup>-1</sup> are probably due to the  $\nu$  (-COO) stretching frequency of carboxyl group of phthalic acid. The absorption of O-H stretching of one carboxyl group appeared

**Table 3: UV-VIS spectral data of chromium complexes in DMSO**

Sample ID	$\lambda_{max}$ nm (log $\epsilon$ )
PT1	552.5(2.485), 495(2.395), 503.0(2.090), 520.5(1.801), 525.5(1.795), 512.0(1.787), 467.5(1.408), 587.5(1.405), 459.0(1.382), 420.5(0.994)
PT2	615.5(1.734), 603.5(1.687), 625.5(1.665), 633.0(1.653), 640.5(1.651), 646.0(1.624), 553.5(1.622), 495.0(1.496), 519.5(1.305), 509.5(1.264)

**Table 4: FTIR spectral data of Cr/ H<sub>2</sub>pht complexes and their assignment in cm<sup>-1</sup>**

Sample Id	$\nu$ (C=O)	$\nu$ (CO)	$\nu$ (-COO)	$\nu$ (Cr-O)	$\nu$ (O-H)of -COOH	$\delta$ (OC=O) + $\nu$ (Cr-O)
PT1	1695	1283	1415,1551	656,538	3399	755
PT2	1697	1283	1412,1492,1554	650,536	3071	797

as a sharp band at  $3697\text{cm}^{-1}$ . The absorption of O-H stretching of second carboxyl group appeared as a broad band near  $3007\text{cm}^{-1}$ - $2525\text{cm}^{-1}$ . The absorption peak at  $2888\text{cm}^{-1}$  and  $2651\text{cm}^{-1}$  was due to the C-H stretching (superimposed upon O-H stretching). The sharp absorption peak at  $740\text{cm}^{-1}$  indicates the ortho-disubstitution in the phthalic acid, other vibrational frequency at  $3007\text{cm}^{-1}$  and  $1686\text{cm}^{-1}$  are assigned to  $\nu$  (C-H) &  $\nu$  (C=C) of aromatic ring respectively.

In the IR spectrum of the complexes the band at  $1695$ - $1697\text{cm}^{-1}$  are attributed to C=O stretching of complexes<sup>9</sup>. The absorption bands in the range  $1283\text{cm}^{-1}$  is attributed to C-O of carboxyl group. The symmetric and asymmetric stretching vibrations of COO<sup>-</sup> group are observed at  $1551$ - $1554\text{cm}^{-1}$  as a shoulder and  $1412$ - $1492\text{cm}^{-1}$  as a strong peak respectively, The sharp absorption band of the phthalic acid due to O-H of the one carboxyl group in the range  $3697\text{cm}^{-1}$  disappears in the complexes and new bands appears in the range  $3071$ - $3399\text{cm}^{-1}$  due to the intermolecular hydrogen bonded  $\nu$  (O-H) of the carboxyl group. Disappearance of the absorption bands of the phthalic acid due to O-H of the second carboxyl

group in the range  $3007$ - $2525\text{cm}^{-1}$  in the complexes indicates the deprotonation of the one acidic group of the ligand and appearance of new bands in the region  $536$ - $650\text{cm}^{-1}$  in the spectra of complexes are attributed to  $\nu$  (Cr-O) as seen in the spectra of metal complexes suggest the coordination of the oxygen atoms to the metal ion and indicate that the product has been formed<sup>10</sup>. Cr/phthalic acid-TAA (Cr/H<sub>2</sub>pht-TAA) complexes PT1 and PT2 show bands in the  $1039$ - $1072\text{cm}^{-1}$  region that can be assigned to Cr-O vibrations<sup>11-12</sup>. Strong and medium bands appear in this region of the spectrum of the Cr/phthalic acid-TAA (Cr/H<sub>2</sub>pht-TAA) complexes.

### <sup>1</sup>H NMR studies of Cr/ H<sub>2</sub>pht complexes

Proton resonance spectral data of Cr/ H<sub>2</sub>pht complexes and their assignments are given in Table 5.

Experimental results for the complexes show that the peaks of protons belonging to different groups were very broad and could not be distinguished. The <sup>1</sup>H NMR spectra of complexes slightly changed compared to those of the corresponding ligand. The aromatic ring protons show peak at 6.64-7.88 ppm and a comparison of this spectrum with the spectrum

**Table 5: <sup>1</sup>H NMR spectral data of Cr/ H<sub>2</sub>pht complexes and their assignment in  $\delta$**

Complexes	Chemical Shift	Assignment
PT1	3.32, 2.50, 1.23, 1.15, 1.04, 0.86, 0.82	3.32 (-OH), 2.50 (Protio-solvent component)
PT2	7.84, 7.56, 6.64, 3.47, 2.50, 1.74, 1.35, 1.24, 1.04, 0.82	6.64-7.84(4H, ArH), 3.47 (-OH), 2.50 (Protio-solvent component), 0.82-1.24 (may be due to the -CH <sub>2</sub> group of amyl group)

**Table 6: FAB mass data of complex PT1**

Peak position	Expected fragmentation species	Calculated mass
307	CrO <sub>2</sub> (C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> ) (H <sub>2</sub> O) <sub>3</sub>	303
289	CrO(C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> ) (H <sub>2</sub> O) <sub>3</sub>	287
273	Cr(C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> ) (H <sub>2</sub> O) <sub>3</sub>	271
216	Cr(C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> )	217
165	(C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> )	165
137	(C <sub>7</sub> H <sub>5</sub> O <sub>3</sub> )	137

of the free ligand confirmed a downfield shift due to coordination. The <sup>1</sup>H NMR spectrum of the complex MRPT1 showed resonance at 3.32 ppm, which may be for the presence of -OH of the complex. Similarly the <sup>1</sup>H NMR spectrum of the complex MRPT2 showed resonances at 3.47 ppm and 0.82-1.24 ppm, which may be for the presence of proton of -OH of the complex and methylene protons of -CH<sub>2</sub> of the amyl group respectively. The complexes show resonances at 2.50 ppm, which may be for the presence of protio-solvent component<sup>13</sup>.

**Table7: FAB mass data of complex PT2**

Peak position	Expected fragmentation species	Calculated mass
320	CrO <sub>2</sub> (C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> ) (H <sub>2</sub> O) <sub>4</sub>	321
307	CrO(C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> ) (H <sub>2</sub> O) <sub>4</sub>	305
289	CrO(C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> ) (H <sub>2</sub> O) <sub>3</sub>	287
273	Cr (C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> ) (H <sub>2</sub> O) <sub>3</sub>	271
216	Cr (C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> )	217
167	(C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> )	165
136	(C <sub>7</sub> H <sub>5</sub> O <sub>3</sub> )	137
107	(C <sub>7</sub> H <sub>5</sub> O)	105
89	(C <sub>7</sub> H <sub>5</sub> )	89
79	(C <sub>6</sub> H <sub>5</sub> )	77

Calculated mol. Wt. of the complex: 321;  
Observed molecular Ion Peak (m/z): 320

**DSC studies of Cr/ H<sub>2</sub>pht complexes:**

DSC thermogram of Cr/ H<sub>2</sub>pht complexes and their kinetic parameter are given in table 8.

**Cr/H<sub>2</sub>pht complexes**

Changes in the kinetic parameters-enthalpy ( $\Delta H$ ), activation energy (Ea),  $\ln K_0$ , order of reaction (n) and peak temperature of the Cr/ acid complexes are observed from DSC thermogram. In both the cases reaction with an exothermic heat flow took place at 226.98 and 403.98°C. The second step decomposition was found to be an exothermic process, having high value of activation energy. The

**Table 8: Kinetic parameters of Cr/H<sub>2</sub>pht complexes obtained from DSC thermogram**

Sample code	Temperature range(°C)	Peak temp. (°C)	$\ln k_0$	Change in enthalpy (DH)(J/g)	Activation energy(Ea) (KJ/mol)	order of reaction
PT1A	70.68-175.67	118.05	17.53±0.37	175.21	69.4±1.49	1.41±0.03
PT1B	180.88-330.85	226.98	1.33±0.02	- 66.82	26.77±0.57	0.7±0.01
PT2A	67.4-183.55	114.75	15.87±0.34	105.44	63.85±1.37	1.5±0.03
PT2B	345.44-428.07	403.38	34.17±0.73	- 18.69	210.38±4.54	1±0.02

**FAB Mass of Cr/ H<sub>2</sub>pht complexes**

Results from the FAB mass analysis were inferred on the basis as followed by Barnwal *et al.*, [14]. The FAB Mass of Cr/ H<sub>2</sub>pht complexes and their expected fragmentation species are given in Table6-7.

**PT 1: [CrO<sub>2</sub>(C<sub>8</sub>H<sub>5</sub>O<sub>4</sub>) (H<sub>2</sub>O)<sub>3</sub>]**

Anal.: found C, 32.88; H, 3.89; Cr, 16.95 Calcd. For C<sub>8</sub>H<sub>11</sub>CrO<sub>9</sub>: C, 31.68; H, 3.63; Cr, 17.16

Calculated mol. wt. of the complex: 303;  
Observed molecular Ion Peak (m/z): 307

The difference in molecular weight may correspond to the association of 4H<sup>+</sup> fragmentation

**PT 2: [CrO<sub>2</sub>(C<sub>8</sub>H<sub>5</sub>O<sub>4</sub>) (H<sub>2</sub>O)<sub>3</sub>] .H<sub>2</sub>O**

Anal.: found C, 31.21; H, 3.70; Cr, 15.08 Calcd. For C<sub>8</sub>H<sub>13</sub>Cr O<sub>10</sub>: C, 29.91; H, 4.05; Cr, 16.20

decomposition followed first and second order of reaction. The complexes showed an endothermic peak between 70.68 to 183.55°C for dehydration process<sup>15</sup>. First step decomposition is associated with endothermic process while generally second is associated with exothermic process. The final step change of Cr/H<sub>2</sub>pht complexes (oligomeric in nature) could not be recorded as scanning was done upto 450 °C.

**CONCLUSION**

When CrO<sub>3</sub> dissolved in tertiary amyl alcohol (TAA) is mixed at room temperature with an ethanolic solution of phthalic acid, reduction of chromium (VI) by ethanol takes place yielding solutions of chromium (III). Results showed that the complexes formed were probably monomeric. It was noted that changing the reaction condition, only slowed down the reaction, rate of formation of complexes, not the nature of products. The UV-Vis spectral analysis of complexes indicated formation

of octahedral chromium complexes. FTIR spectra of the complexes formed indicated presence of Co-ordinated water molecules in the complexes. Deprotonation of one acidic group of the ligand is shown by FTIR as well as NMR spectrometry while appearance of new bands in the FTIR spectra of complexes suggested co-ordination of oxygen atoms to the metal ions and indicated formation of

new compound. From the FAB mass spectrometry molecular formula of the complexes formed could be predicted. The kinetics and the lability of complexes could be predicted from the DSC. DSC studies indicated that the Cr/H<sub>2</sub>pht complexes may be stable at the ambient temperature, may be labile at higher temperature.

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