

Fourier Transform Infrared Spectrophotometry Studies of Chromium Trioxide-Phthalic Acid Complexes

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Abstract: In the present investigation Cr-metal complexes has been prepared using chromium tri-oxide and phthalic acid. FTIR spectra of solid samples were recorded. FTIR spectra of metal complexes suggest the coordination of the oxygen atoms to the metal ion and indicate that the product have been formed.

Keywords. Chromium tri-oxide, Cr-metal complex, Phthalic acid, FTIR

Introduction

Infrared spectroscopy is an essential and crucial characterization technique to elucidate the structure of matter at the molecular scale. The chemical composition and the bonding arrangement of constituents in a material in general can be obtained using Infrared spectroscopy. The FTIR technique can be used to analyze gases, liquids and solids with minimal preparation^{1,2}.

All organic compounds absorb IR radiation. The frequency absorbed varies with the functional groups present, Thus IR spectroscopy is a method of classifying unknown organic compounds by identifying the functional groups present in the compounds. The IR portion of the electromagnetic spectrum lies between visible light and microwaves. It is divided into three regions; the near IR (13000-4000 cm^{-1}), mid IR (4000-400 cm^{-1}) and far IR (400-10 cm^{-1}). Most organic functional group absorptions occur in the mid IR range, between 4000 and 400 cm^{-1} .

In general, more polar bonds absorb more intensely than less polar (and non-polar) bonds³. In the present investigation Cr-metal complexes has been prepared using chromium tri-oxide and phthalic acid and its characterization was done by FTIR.

Experimental

SET- I (S-1): 4.98 g of phthalic acid was dissolved in 100 mL $\text{C}_2\text{H}_5\text{OH}$ (Merck-KgaA) and 1 g of CrO_3 was dissolved in 40 mL of water. A solution of phthalic acid was

slowly added with stirring to solution of CrO_3 . The resulting solution was refluxed. The dark blue-green coloured compound formed was separated by filtration. It was washed with ethyl alcohol and dried in air. Yield 4.19g; 70%.

SET-II (S-2): 4.98 g of phthalic acid was dissolved in 100 mL $\text{C}_2\text{H}_5\text{OH}$ (Merck-KgaA) and 1 g of CrO_3 was dissolved in 40 mL of tertiary amyl alcohol (TAA). A solution of phthalic acid was slowly added with stirring to solution of CrO_3 . 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 no further precipitation was observed. The stable suspension was filtered, and solid was washed with ethanol and TAA and dried in air. Yield 4.01g; 67%.

Fourier transform infrared spectrophotometry

The FTIR spectra of solid samples were recorded on Perkin Elmer spectrum -2000, in the Department of Applied Chemistry, Indian School of Mines, Dhanbad, Jharkhand India. FTIR spectra of phthalic acid, chromium tri-oxide and their Cr/ H₂pht (Chromium phthalic acid complexes) are shown in Figure 1 to Figure 4 and their assignments are given in Table 1

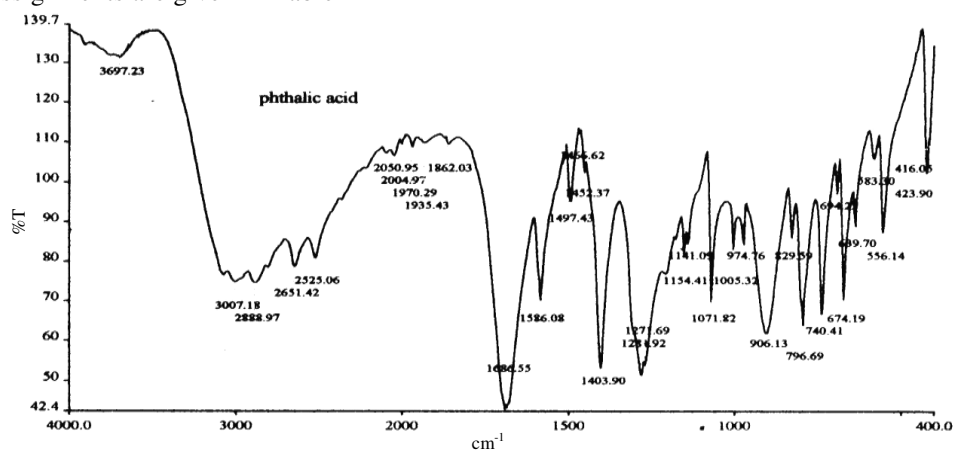


Figure 1. FTIR spectrum of phthalic acid

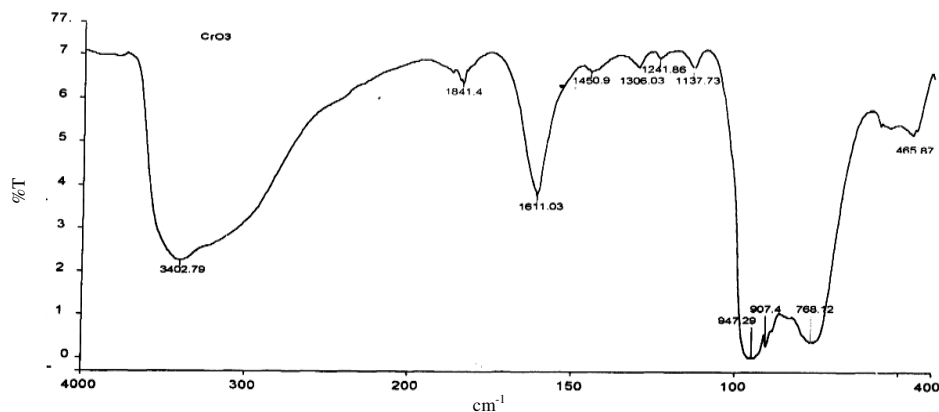


Figure 2. FTIR spectrum of chromium trioxide

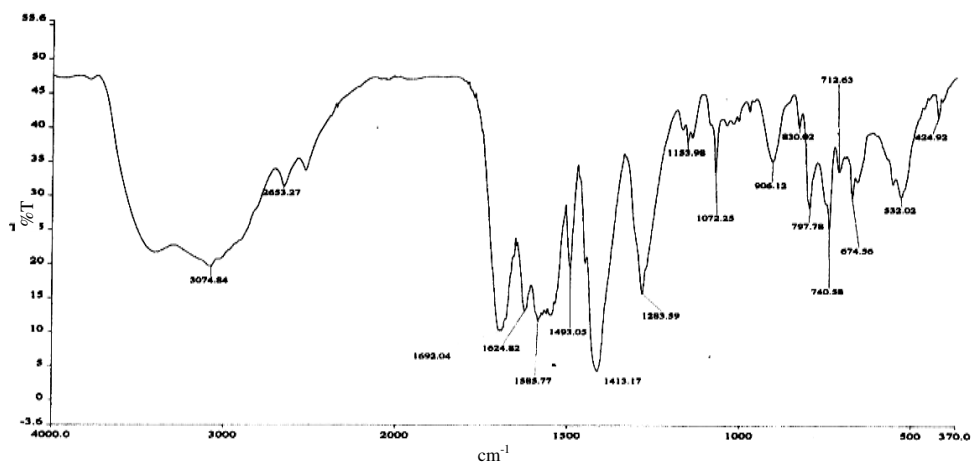


Figure 3. FTIR Spectrum of S-1

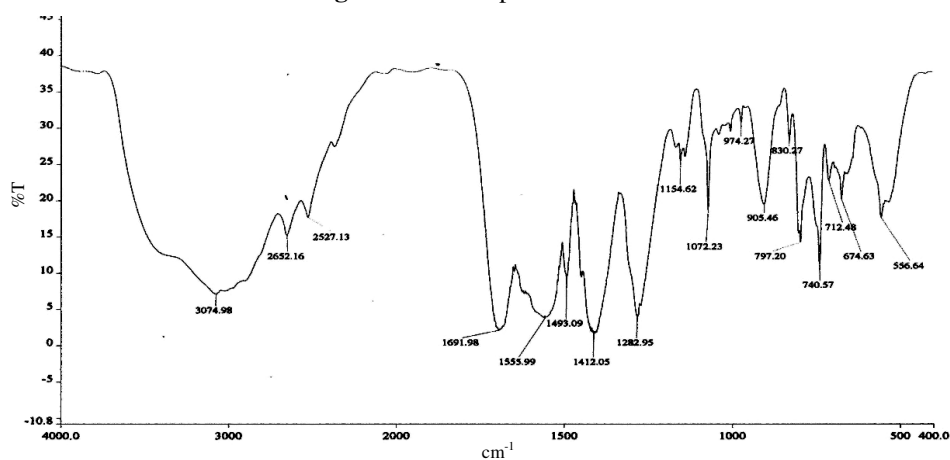


Figure 4. FTIR spectrum of S-2

Table 1. Details of samples and their identification

Sample ID	CrO ₃ :phthalic acid: Solvent (Molar ratio)	CrO ₃ :phthalic acid (g)	Colour	Yield
S-1	CrO ₃ : H ₂ pht: H ₂ O(1:3)	1:4.98	Dark blue-green	4.19 g, 70%
S-2	CrO ₃ : H ₂ pht: TAA(1:3)	1:4.98	Blue-grey	4.01 g, 67%

Phthalic acid: Infrared (cm⁻¹) 3697, 3007, 2888, 2651, 2525, 2050, 2004, 1970, 1935, 1862, 1686, 1586, 1497, 1466, 1452, 1403, 1281, 1271, 1154, 1141, 1071, 1005, 974, 906, 829, 796, 740, 694, 674, 639, 583, 556, 423, 416, Chromium-trioxide: Infrared (cm⁻¹) 3402, 1841, 1611, 1450, 1306, 1241, 1137, 947, 907, 768, 465, **S-1**: Infrared (cm⁻¹): 3074, 2653, 1692, 1624, 1585, 1493, 1413, 1283, 1153, 1072, 906, 830, 797, 740, 712, 674, 532, 424, **S-2**: Infrared (cm⁻¹): 3074, 2652, 2527, 1691, 1555, 1493, 1412, 1282, 1154, 1072, 974, 905, 830, 797, 740, 712, 674, 556.

Table 2. FTIR spectral data of Cr/ H₂pht (Chromium-phthalic acid) complexes and their assignment in cm⁻¹

Sample ID	$\nu(\text{C}=\text{O})$	$\nu(\text{CO})$	$\nu(-\text{COO})$	$\nu(\text{Cr}-\text{O})$	$\nu(\text{O}-\text{H})$ of $-\text{COOH}$	$\delta(\text{OC}=\text{O})+\nu$ (Cr-O)
S-1	1624	1283	1413,1493,1585	674,532	3074	797,830
S-2	1691	1282	1412,1493,1555	674,556	3074	797,830

The characteristic absorption peak at 1686 cm⁻¹ and 1281 cm⁻¹ 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⁻¹ are probably due to the $\nu(-\text{COO})$ stretching frequency of carboxyl group of phthalic acid. The absorption of O-H stretching of one carboxyl group appeared as a sharp band at 3697 cm⁻¹. The absorption of O-H stretching of second carboxyl group appeared as a broad band near 3007 cm⁻¹-2525 cm⁻¹. The absorption peak at 2888 cm⁻¹ and 2651 cm⁻¹ was due to the C-H stretching (superimposed upon O-H stretching). The sharp absorption peak at 740 cm⁻¹ indicates the ortho-disubstitution in the phthalic acid, other vibrational frequency at 3007 cm⁻¹ and 1686 cm⁻¹ are assigned to $\nu(\text{C}-\text{H})$ & $\nu(\text{C}=\text{C})$ of aromatic ring respectively.

In the IR spectrum of the complexes the band at 1624-1692 cm⁻¹ are attributed to C=O stretching of complexes⁴. The absorption bands in the range 1282-1283 cm⁻¹ are attributed to C-O of carboxyl group. The symmetric and asymmetric stretching vibrations of COO⁻ group are observed at 1555-1585 cm⁻¹ as a shoulder and 1412-1493 cm⁻¹ as a strong peak respectively, together with a strong 1650 cm⁻¹ peak due to the $\nu(\text{O}-\text{H})$ of water. The sharp absorption band of the phthalic acid due to O-H of the one carboxyl group in the range 3697 cm⁻¹ disappears in the complexes and new bands appears in the range 3074 cm⁻¹ due to the intermolecular hydrogen bonded $\nu(\text{O}-\text{H})$ 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 2527-2653 cm⁻¹ in the complexes indicates the deprotonation of the one acidic group of the ligand and appearance of new bands at 674, 556, 532 cm⁻¹ in the spectra of complexes are attributed to $\nu(\text{Cr}-\text{O})$ 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 formed⁵. The complexes show bands in the 1072 and 712-740 cm⁻¹ region that can be assigned to phenyl ring vibrations. Medium intensity bands appearing in the 3074 cm⁻¹ region correspond to aromatic $\nu(\text{C}-\text{H})$.

Cr/phthalic acid-TAA (Cr/H₂pht-TAA) complex (S-2) show bands in the 974 and 1072 cm⁻¹ region that can be assigned to Cr-O vibrations. The difference between the spectra of Cr/phthalic acid-water (Cr/H₂pht-water) complex (S-1) and Cr/phthalic acid-TAA (Cr/H₂pht-TAA) complex may be found in the 974-1072 cm⁻¹ where the stretching bands of the Cr-O group are expected to appear⁶⁻⁷. Strong and medium bands appear in this region of the spectrum of the Cr/phthalic acid-TAA (Cr/H₂pht-TAA) complex, whereas only weak bands are present in the same region of the spectrum of the Cr/phthalic acid-water (Cr/H₂pht-water) complex. Some weak bending modes are also observed at 1072 cm⁻¹ and 740 cm⁻¹ due to (OCO). IR spectra of complexes, a broad shoulder absorption in the range 3074 cm⁻¹ is observed indicating the presence of coordinated water molecule in the complexes. The sharp absorption peak at 797 cm⁻¹ indicates the ortho-disubstitution in the chromium- phthalic acid complex. The peaks observed in the region below 700 cm⁻¹ are due to the metal ligand vibrations.

Conclusion

The sharp absorption band of the phthalic acid due to O-H of the one carboxyl group disappears in the complexes and new bands appear due to the intermolecular hydrogen bonded $\nu(\text{O-H})$ of the carboxyl group. Disappearance of the absorption bands of the phthalic acid due to O-H of the second carboxyl group in the complexes indicates the deprotonation of the one acidic group of the ligand and appearance of new bands in the spectra of complexes are attributed to $\nu(\text{Cr-O})$ as seen in the spectra of metal complexes suggest the coordination of the oxygen atoms to the metal ion and indicate that the product/complexes have been formed.

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