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Research Article

MASS SPECTROSCOPIC (FAB-MASS) STUDIES OF CHROMIUM TRIOXIDE-ORGANIC ACID COMPLEXES

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ABSTRACT

In the present study complexes of chromium were prepared using CrO_3, salicylic acid, benzoic acid and tertiary amyl alcohol as a solvent. Mass spectra (FAB-Mass) of solid samples were recorded. Mass spectra of Cr Complexes suggest that Complex of Cr/ben-TAA With molar ratio 1:1 (Cr/Hben/T/1) is probably monomeric and molar ratio 1:2 (Cr/Hben/T/2) is dimeric. Complexes of Cr/H_2sal-TAA with molar ratio 1:1 (Cr/H_2sal/T/1) and 1:2 (Cr/H_2sal/T/2) are probably dimeric OH^- bridged Cr (III) complexes.

Keywords: FAB-Mass, Cr-Complex, Monomeric, Dimeric.

1. INTRODUCTION

FAB Mass spectrometry is used to study thermally sensitive and large variety of compounds. The technique is useful for high resolution measurements as it employs a discharge beam of fast atoms of an inert gas travelling at 4-10kev to bombard the sample [1]. Ionic complexes and neutral complexes have been successfully examined using FAB Mass spectroscopy. This technique determines molecular weight structural data and provides characterisation of inorganic compounds, coordination complexes, organometallic complexes and metal clusters. Transition metal carbonyls were studied by mass spectrometry, principally in efforts to determine the isotopic abundance of the metal [2-5]. In the present investigation, we intended to prepare chromium complexes using Chromium trioxide, salicylic acid, benzoic acid and tertiary amyl alcohol as a solvent. The results obtained from FAB-Mass spectral have been investigated.

2. MATERIAL AND METHODS

2.1. Material Used: Details are presented in table 1

Chemical	Manufacturer	Formula	M.W.
Salicylic acid	S.d.fine-chem pvt. Ltd., Boisar, India	$C_7H_6O_3$	138
Chromic acid (CrO_3)	Apex Chemical, Mumbai, India	CrO_3	100
Tertiary amyl alcohol (2-methyl-2-butanol)	Merck-KGaA, Darmstadi, Germany	$C_5H_{12}O$	86
Ethyl alcohol	Merck-KGaA, Darmstadi, Germany	C_2H_5OH	46

2.2. Methods adopted:

Reduction of CrO_3 by ethanol in the presence of salicylic acid was done. Characterization of the chromium complexes prepared were carried out by Elemental analysis (C&H), Inductively coupled plasma optical emission spectroscopy (ICP-OES), Fast Atomic Bombardment (FAB) Mass spectroscopy.

2.3. Preparation of complexes

A solution of different molar concentration of CrO_3 (dissolved in tertiary amyl alcohol (TAA), mixed with ethanolic solution with different molar concentration of salicylic, benzoic acids. The resulting solution was left standing in a closed flask at room temperature. After 24 hrs, 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.

2.4. Characterization of samples by Elemental analysis (C&H)

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

2.5. Characterization of samples by 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

2.6. Characterization of samples by 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.

3. RESULTS AND DISCUSSION

3.1. 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 : 1 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.

Table 2: Details of samples and their identification

Sample ID	CrO_3:Organic acid: Solvent (Molar ratio)	Amount taken(g) CrO_3:Organic Acid	Colour	Yield
Cr/H_2sal/T/1	CrO_3: H_2sal: TAA (1:1)	1:1.38	Brown	1.33g, 56%
Cr/H_2sal/T/2	CrO_3: H_2sal: TAA (1:2)	1: 2.76	Dark-brown	2.82g, 75%
Cr/Hben/T/1	CrO_3: Hben: TAA (1:1)	1:1.22	Yellow-brown	1.00g, 45%
Cr/Hben/T/2	CrO_3: Hben: TAA (1:2)	1:2.44	Yellowish-green	1.72g, 50%

Table 3: Elemental(C&H) and ICP-OES analytical data of metal complexes

Sample Id	Found (Calculated) (%)			Molecular formula
	C	H	Cr	
Cr/H_2sal/T/1	26.72(25.35)	4.72(5.16)	23.00(24.41)	$C_9 H_{22} Cr_2 O_{12}$
Cr/H_2sal/T/2	34.61(35.16)	4.54(4.76)	18.7(19.05)	$C_{16} H_{26} Cr_2 O_{14}$
Cr/Hben/T/1	38.74(37.63)	4.96(5.23)	19.14(18.12)	$C_9 H_{15} Cr O_7$
Cr/Hben/T/2	39.45(37.35)	4.82(5.06)	19.37(20.23)	$C_{16} H_{26} Cr_2 O_{12}$

It was observed that as the molar ratio of Cr: acid increased the number of coordinating $Hsal^-$ and ben^- ligands in the complexes increased proportionally. In the reduction of Cr (VI) by ethanol when tertiary amyl alcohol solution of CrO_3 was mixed with alcoholic solution of salicylic and benzoic acid system chromium content also increased proportionally, which indicated the increases in the degree of polymerization of the metal complexes.

Cr/H_2sal/T/1: [Cr_2O ($C_7H_5O_3$) (C_2H_5OH) $(OH)_3$ $(H_2O)_4$]

Anal: found C, 26.72; H, 4.72; Cr, 23.00 Calcd. For $C_9 H_{22} Cr_2 O_{12}$: C, 25.35; H, 5.16; Cr, 24.41

Calculated mol. wt. of the complex: 426; Observed Molecular Ion Peak (m/z): 422

The difference in molecular weight may correspond to the loss of $4H^+$ fragments.

Results from the FAB mass analysis were inferred on the basis as followed by Barnwal et al [6] on oxo-bridge multinuclear chromium assemblies, like trinuclear complex (m/z; 1329) [$Cr_3O(acac)_3$ $(OOCC_{15}H_{31})_3$].

Cr/H_2sal/T/2: [Cr_2O $(C_7H_5O_3)_2$ (C_2H_5OH) $(OH)_2(H_2O)_4$]

Anal: found C, 34.61; H, 4.54; Cr, 18.7 Calcd. For $C_{16} H_{26} Cr_2 O_{14}$: C, 35.16; H, 4.76; Cr, 19.05

Calculated mol. wt. of the complex: 546; Observed Molecular Ion Peak (m/z): 500

The difference in molecular weight may correspond to the loss of ethanol molecule fragment.

Cr/Hben/T/1: [$CrO_2(C_7H_5O_2)$ (C_2H_5OH) $(H_2O)_2$]

Anal.: found C, 38.74; H, 4.96; Cr, 19.14 Calcd. For $C_9H_{15}Cr O_7$: C, 37.63; H, 5.23; Cr, 18.12

Calculated mol. wt. of the complex: 287; Observed Molecular Ion Peak (m/z): 252

The difference in molecular weight may correspond to the loss of two molecules of water.

Cr/Hben/T/2: [Cr_2 $O(C_7H_5O_2)_2$ (C_2H_5OH) $(OH)_2$ $(H_2O)_4$]

Anal: found C, 39.45; H, 4.82; Cr, 19.37 Calcd. For $C_{16}H_{26}Cr_2 O_{12}$: C, 37.35; H, 5.06; Cr, 20.23

Calculated mol. wt. of the complex: 514; Observed Molecular Ion Peak (m/z): 516.

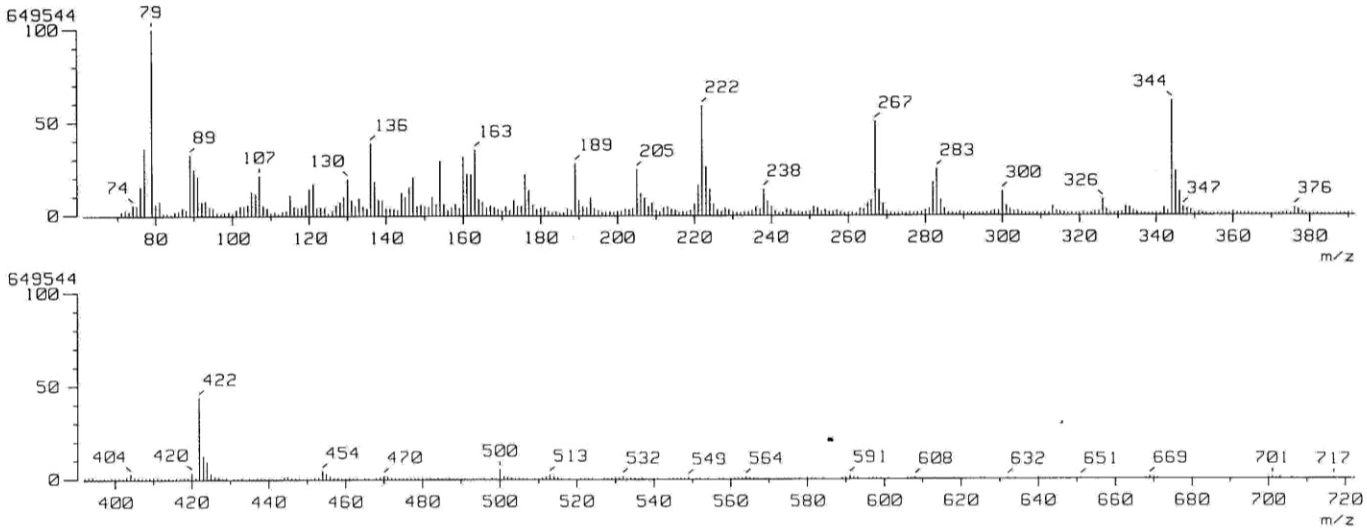

Fig. 1: FAB Mass Spectrum of Cr/H_2sal/T/1

Table 4: FAB mass data of complex Cr/H_2sal/T/1

Peak position	Expected fragmentation species	Calculated mass
422	$Cr_2O(C_7H_5O_3)(C_2H_5OH)(OH)_3(H_2O)_4$	426
404	$Cr_2O(C_7H_5O_3)(C_2H_5OH)(OH)_3(H_2O)_3$	408
300	$Cr\ O(C_7H_5O_3)(C_2H_5OH)(OH)_3$	302
283	$Cr\ O(C_7H_5O_3)(C_2H_5OH)(OH)_2$	285
267	$Cr\ O(C_7H_5O_3)(C_2H_5OH)(OH)$	268
222	$Cr\ O(C_7H_5O_3)(OH)$	222
205	$Cr\ O(C_7H_5O_3)$	205
189	$Cr\ (C_7H_5O_3)$	189
136	$(C_7H_5O_3)$	137
107	(C_7H_5O)	105
89	(C_7H_5)	89
77	(C_6H_5)	77

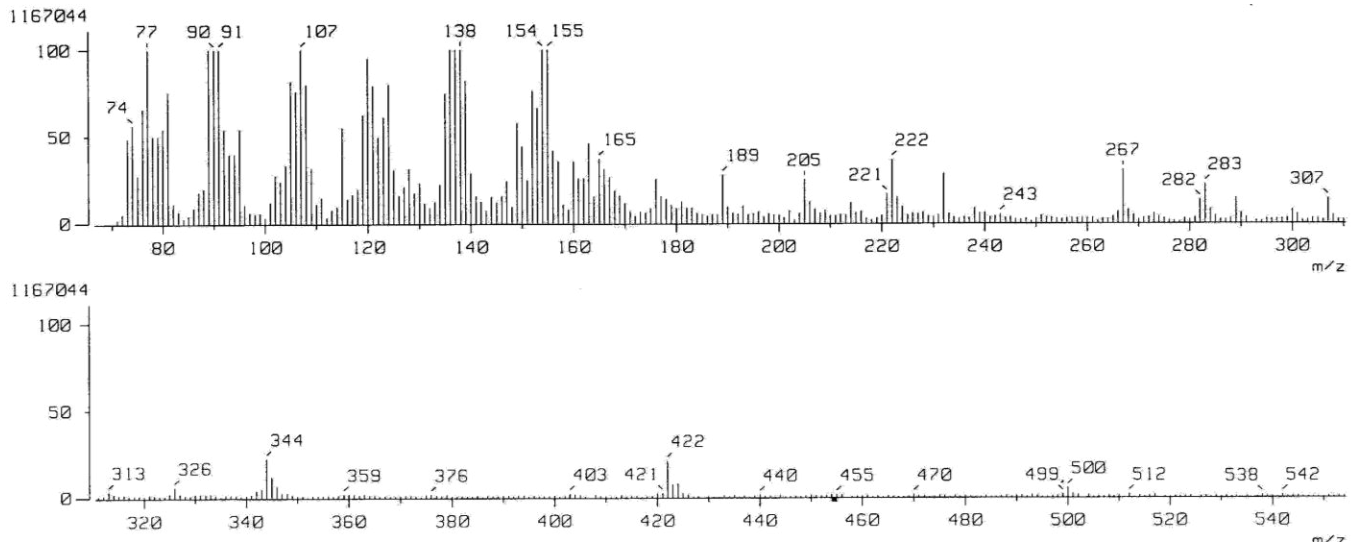

Fig. 2: FAB Mass Spectrum of Cr/H_2sal/T/2

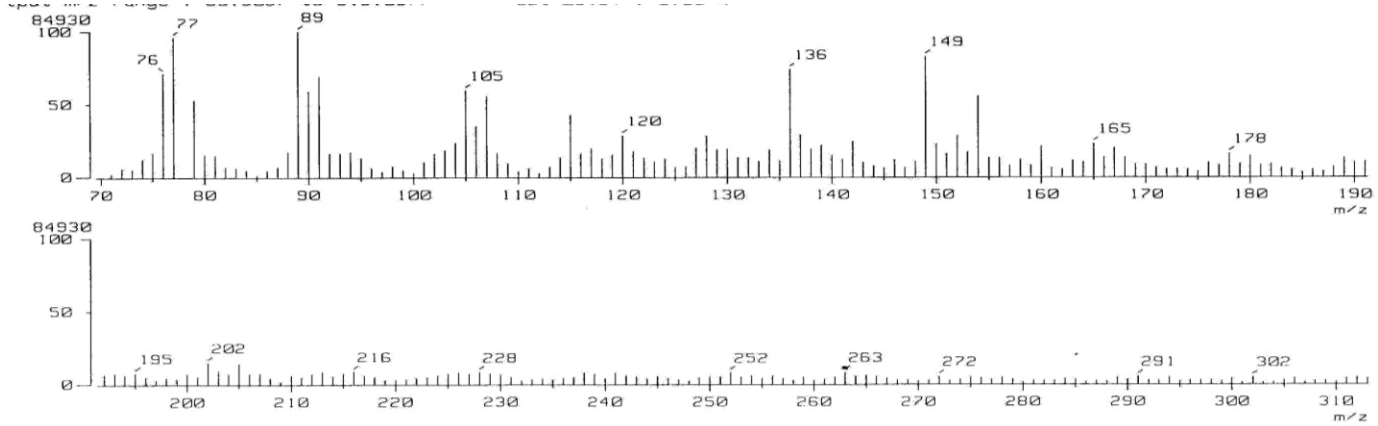

Fig. 3: FAB Mass Spectrum of Cr/Hben/T/1

Table 5: FAB mass data of complex Cr/H_2sal/T/2

Peak position	Expected fragmentation species	Calculated mass
500	$Cr_2O(C_7H_5O_3)_2(OH)_2(H_2O)_4$	500
344	$Cr_2O(C_7H_5O_3)(OH)_2(H_2O)_3$	345
326	$Cr_2O(C_7H_5O_3)(OH)_2(H_2O)_2$	327
307	$Cr_2O(C_7H_5O_3)(OH)_2(H_2O)$	309
243	$Cr(C_7H_5O_3)(OH)_2(H_2O)$	241
222	$Cr(C_7H_5O_3)(OH)_2$	223
205	$Cr(C_7H_5O_3)(OH)$	206
189	$Cr(C_7H_5O_3)$	189
138	$(C_7H_5O_3)$	137
107	(C_7H_5O)	105
90	(C_7H_5)	89
77	(C_6H_5)	77

Table 6: FAB mass data of complex Cr/Hben/T/1

Peak position	Expected fragmentation species	Calculated mass
252	$CrO_2(C_7H_5O_2)(C_2H_5OH)$	251
216	$Cr(C_7H_5O_2)(C_2H_5OH)$	219
202	$Cr(C_7H_5O_2)(C_2H_5-)$	202
178	$Cr(C_7H_5O_2)$	173
120	$(C_7H_5O_2)$	121
105	(COC_6H_5)	105
89	(CC_6H_5)	89
77	(C_6H_5)	77

The difference in molecular weight may correspond to the loss of $2H^+$ fragments

Reduction of Cr (VI) by ethanol takes place in the presence of salicylic acid, when the ethanolic solution of salicylic acid and the solution of CrO_3 in tertiary amyl alcohol were mixed; no precipitate appeared at room temperature. Leaving the reaction mixture for 24 hrs resulted in formation of precipitate. Oxide and the acid taken in different molar ratio 1:1 and 1:2resulted in low oligomeric complexes of Cr (III). Complexes of Cr/H_2sal-TAA with molar ratio 1:1 (Cr/H_2sal/T/1) and 1:2 (Cr/H_2sal/T/2) are probably dimeric OH^- bridged Cr (III) complexes.

CrO_3 dissolved in solvent tertiary amyl alcohol (TAA), upon mixing with an ethanolic solution of benzoic acid at room temperature, reduction of Cr (VI) occurrs. No precipitation was observed at room temperature until the reaction mixture was left for 24 hrs. With CrO_3 (in TAA) and benzoic acid, Cr/Hben-TAA, taken in different molar ratio 1:1 (Cr/Hben/T/1) and 1:2 (Cr/Hben/T/2) resulted in monomeric complex in the first case and dimeric products in the second cases, probably dimeric OH^- bridged Cr (III) complexes.

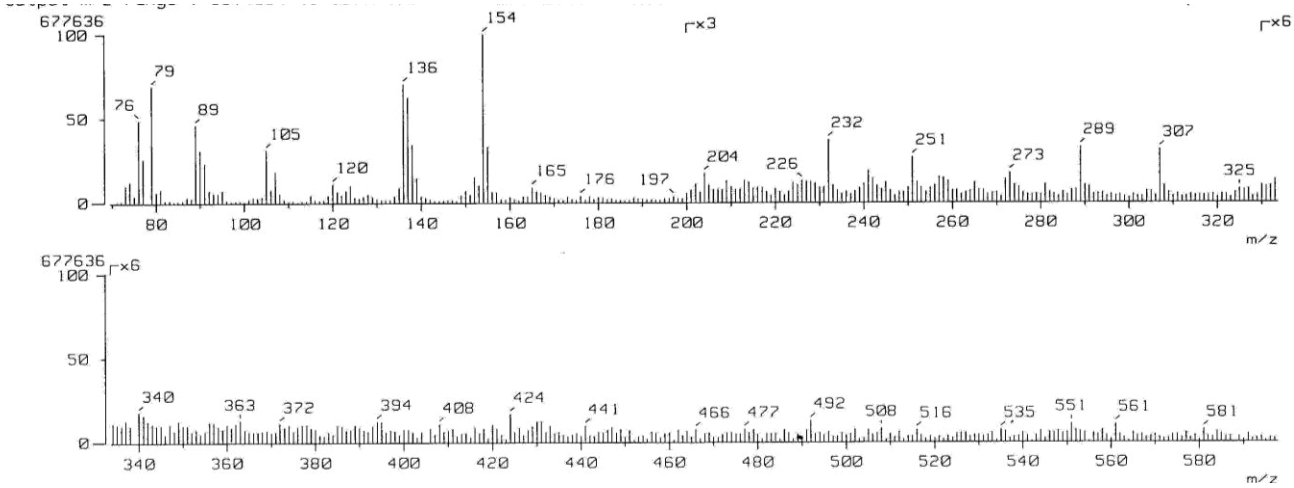

Fig. 4: FAB Mass Spectrum of Cr/Hben/T/2

Table 7: FAB mass data of complex Cr/Hben/T/2

Peak position	Expected fragmentation species	Calculated mass
516	$Cr_2O(C_7H_5O_2)_2(C_2H_5OH)(OH)_2(H_2O)_4$	514
492	$Cr_2O(C_7H_5O_2)_2(C_2H_5OH)(OH)_2(H_2O)_3$	496
477	$Cr_2O(C_7H_5O_2)_2(C_2H_5OH)(OH)_2(H_2O)_2$	478
441	$Cr_2O(C_7H_5O_2)_2(C_2H_5OH)(OH)_2$	442
424	$Cr_2O(C_7H_5O_2)_2(C_2H_5OH)(OH)$	425
408	$Cr_2O(C_7H_5O_2)_2(C_2H_5OH)$	408
363	$Cr_2O(C_7H_5O_2)_2$	362
307	$CrO(C_7H_5O_2)_2$	310
273	$CrO(C_7H_5O_2)(CC_6H_5)$	278
251	$Cr(C_7H_5O_2)(C_6H_5)$	250
176	$Cr(C_7H_5O_2)$	173
154	$Cr(COC_6H_5)$	157
105	(COC_6H_5)	105
89	(CC_6H_5)	89
77	(C_6H_5)	77

4. CONCLUSION

Mass spectra of Cr complexes confirm the proposed formula by showing peaks corresponding to the calculated atomic mass. It also shows a series of peaks corresponding to the various fragments of complex. Their intensity gives an idea of stability of fragments. Complex of Cr/ben-TAA With molar ratio 1:1 (Cr/Hben/T/1) is probably monomeric and molar ratio 1:2 (Cr/Hben/T/2) is dimeric. Complexes of Cr/H_2sal-TAA with molar ratio 1:1 (Cr/H_2sal/T/1) and 1:2 (Cr/H_2sal/T/2) are probably dimeric OH^- bridged Cr (III) complexes.

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