

MASS SPECTROMETRY OF SOME METAL COMPOUNDS  
AND  
STUDIES ON FLUORO AND ACETYLACETONATO  
COMPOUNDS OF CHROMIUM

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THE DEGREE OF DOCTOR OF PHILOSOPHY

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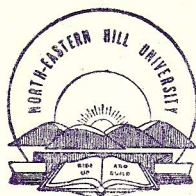


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I certify that the thesis entitled " Mass Spectrometry of Some Metal Compounds and Studies on Fluoro and Acetylacetonato Compounds of Chromium ", submitted by Mr. Nirmalendu Roy for the Degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong embodies the record of original investigation carried out by him under my supervision. He has been duly registered and the thesis presented is worthy of being considered for the Award of the Ph.D. Degree. This work has not been submitted for any Degree of any other University.

Date : 27 May, 1982

*Mihir Kanti Chaudhuri*  
Signature of the Supervisor

Place : Shillong.

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## CONTENTS

Inner cover page .....	i
Supervisor's Certificate .....	ii
Acknowledgements .....	iii
Introduction .....	1

### PART ONE

#### CHAPTER 1 :: Instrumentation, Processing and Presentation of Mass Spectra.

1.1. Introduction.....	4
1.2. Ion Source .....	5
1.3. Mass Analysers .....	8
1.4. Inlet Systems .....	13
1.5. Ion Detector and .....	14
recording of mass spectra	
1.6. Resolution .....	15
1.7. Processing and .....	16
presentation of mass spectra	
References .....	18

#### CHAPTER 2 :: Mass Spectrometry of Metal Compounds. Evidence of C-O cleavage in and Effect of Temperature on the Mass Spectra of Chloropentacarbonylmanganese.

2.1. Introduction .....	19
2.2. Experimental Section .....	21
2.3. Results and Discussion .....	24
References .....	27

CHAPTER 3 :: Mass Spectrometric Studies of  
 $\sqrt{\bar{C}F_3 E Mn(CO)_4} \sqrt{2}$ ,  $\sqrt{\bar{C}F_3 E Fe(CO)_3} \sqrt{2}$   
 (E= S, Se),  $CF_3 SeFe(CO)_2 C_5H_5$  and  
 $CF_3 S Cr(NO)_2 C_5H_5$ . Evidence of  
 Fluorine Shifts from Carbon to  
 Metal in and Effect of Temperature  
 on the Mass Spectra of  $SCF_3$  and  
 $SeCF_3$  Compounds of Manganese,  
 Iron and Chromium.

3.1. Introduction .....	28
3.2. Experimental Section .....	32
3.3. Results and Discussion .....	34
References .....	47

PART TWO

CHAPTER 4 :: The Direct Synthesis, Characterisation  
 and Structural Assessment of Alkali  
 Metal Hexafluorochromate(III),  $A_3 \sqrt{\bar{C}rF_6} \sqrt{7}$ .

4.1. Introduction .....	50
4.2. Experimental Section .....	52
4.3. Results and Discussion .....	57
References .....	61

CHAPTER 5 :: Synthesis and Spectroscopic Studies of  
 Alkali Metal Pentafluoroaquochromates(III),  
 $A_2 \sqrt{\bar{C}rF_5(H_2O)} \sqrt{7}$ .

5.1. Introduction .....	64
5.2. Experimental Section .....	65
5.3. Results and Discussion .....	70
References .....	75

CHAPTER 6 :: Synthesis and Physicochemical  
Studies of Alkali Metal  
Trioxyfluorochromates(VI),  
A  $\text{CrO}_3\text{F}$  and Pyridinium Trioxy-  
fluorochromate (VI),  $\text{C}_5\text{H}_5\text{NHCrO}_3\text{F}$ .

6.1. Introduction .....	77
6.2. Experimental Section .....	79
6.3. Results and Discussion .....	83
References .....	89

CHAPTER 7 :: A Novel Synthesis and Mass  
Spectrometric Investigation of  
Tris(acetylacetonato)chromium(III),  
 $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ .

7.1. Introduction .....	91
7.2. Experimental Section .....	93
7.3. Results and Discussion .....	96
References .....	99
Appendix : List of Publications .....	102

## FIGURES

1.1.	Electron impact ion source.....	6
1.2.	Double-focusing mass spectrometer..... of the Nier-Johnson type	11
1.3.	Double-focusing mass spectrometer..... of the Mattauch-Herzog type	12
4.1.	Infrared spectra of $(\text{NH}_4)_3\text{CrF}_6$ , $\text{K}_3\text{CrF}_6$ and $\text{Li}_3\text{CrF}_6 \cdot \text{H}_2\text{O}$ .....	59
5.1.	Infrared spectra of $(\text{NH}_4)_2\text{CrF}_5(\text{H}_2\text{O})$ , and $\text{K}_2\text{CrF}_5(\text{H}_2\text{O})$ .....	72
6.1.	Infrared spectra of $\text{NH}_4\text{CrO}_3\text{F}$ and $\text{KCrO}_3\text{F}$ .....	84
6.2.	Infrared spectrum of $(\text{C}_5\text{H}_5\text{NH})\text{CrO}_3\text{F}$ .....	87
7.1.	Infrared spectrum of $\text{Cr}(\text{acac})_3$ .....	98

## INTRODUCTION

It is now self evident that, in recent years, inorganic chemistry has experienced an impressive renaissance. Academic and applied research in inorganic chemistry is flourishing, and the research outputs are growing exponentially. In last two decades or so mass spectrometry has undergone remarkable growth and has become an important technique of great utility in chemistry. Up to the mid 1960s, most of the applications of mass spectrometry were concerned with studies of organic compounds. However, since 1965 its impact has been extended into inorganic chemistry. The first studies were mainly concerned with volatile organometallic compounds, but later, with the advent of direct insertion inlet systems, studies of various types of metal compounds commenced. The usefulness of this technique in providing molecular weights and formulae, in helping with the elucidation of structure and bonding, and in deriving thermodynamic data, is now well established. PART ONE of the thesis aims to present an interpretative account of the electron impact induced mass spectrometric behaviour of some metal compounds viz.,  $\text{Mn}(\text{CO})_5\text{Cl}$ ,  $\text{CF}_3\text{S Mn}(\text{CO})_4$ ,  $\text{CF}_3\text{SeMn}(\text{CO})_4$ ,  $\text{CF}_3\text{S Fe}(\text{CO})_3$ ,  $\text{CF}_3\text{SeFe}(\text{CO})_3$ ,  $\text{CF}_3\text{SeFe}(\text{CO})_2\text{C}_5\text{H}_5$  and  $\text{CF}_3\text{S Cr}(\text{NO})_2\text{C}_5\text{H}_5$  and a semi-critical account of the applications of mass spectrometry in such compounds.

The first Chapter of PART ONE provides some basic aspects on instrumentation with special references to the type of instrument used for the present studies and a few general aspects of mass spectrometry. Chapter 2 gives an account of the EI induced fragmentation behaviour of  $\text{Mn}(\text{CO})_5\text{Cl}$  and attempts to show the evidence of C-O cleavage in and also studies the effect of temperature on the mass spectra of chloropentacarbonylmanganese. Chapter 3 describes the EI induced mass spectrometric behaviour of  $\text{CF}_3\text{S Mn}(\text{CO})_4$ ,  $\text{CF}_3\text{SeMn}(\text{CO})_4$ ,  $\text{CF}_3\text{S Fe}(\text{CO})_3$ ,  $\text{CF}_3\text{SeFe}(\text{CO})_3$ ,  $\text{CF}_3\text{SeFe}(\text{CO})_2\text{C}_5\text{H}_5$  and  $\text{CF}_3\text{S Cr}(\text{NO})_2\text{C}_5\text{H}_5$  compounds, studied under different inlet temperatures, and seeks to compare the behaviour of these compounds with those of the  $\text{SCH}_3$

substituted metal carbonyl derivatives and emphasises the usefulness of the technique because this type of compounds received rather scanty attention to date. Chapter 3 also attempts to provide with the evidences of fluorine shift from carbon to metal and relative ease of  $ECF_2$  (E=S or Se) expulsion with the raise in temperature. It is hoped that the mass spectrometric results described in the present thesis will be of use to researchers using mass spectrometry in studies of metal compounds and that it will provide something of interest to the synthetic chemists by illustrating some interrelationship between mass spectrometry and synthesis.

Among the various fields of current activity in inorganic chemistry recently there has been a considerable interest in the kinetic behaviour, photochemistry, single-crystal polarised electronic spectra, absolute configuration and synthesis and reactivity of various fluoro-containing complexes of chromium. In spite of this interest, however, there has been hardly any report on the direct, easy and general synthesis of fluoro-containing chromium complexes in its various oxidation states. This might be one of the reasons why not much of structural information available for such types of compounds. It is the principal aim of PART TWO of the present thesis, which is mainly based on the synthesis and structural assessment of some fluoro- and oxyfluoro-complexes of chromium(III) and chromium(VI), to fill, at least partly, this need.

The first Chapter of PART TWO provides the new general synthesis of alkali metal hexafluorochromates(III),  $A_3[CrF_6]^-$  and structural assessment of the compounds by various physical techniques. Chapter 5, the second Chapter of PART TWO, describes the direct general synthesis of alkali metal pentafluoroaquo-chromates(III),  $A_2[CrF_5(H_2O)]^-$  and it also attempts to make an assessment of the structure of the

complex species through magnetic susceptibility measurements, infrared and electronic spectral studies. Chapter 6, the third Chapter of PART TWO, gives the description of a novel method for the general synthesis of alkali metal trioxyfluorochromates(VI),  $A[\text{CrO}_3\text{F}]$ , without making use of hydrofluoric acid, and characterisation of the compounds. In addition, this Chapter also provides with the details of the synthesis and characterisation of pyridinium trioxyfluorochromate(VI),  $(\text{C}_5\text{H}_5\text{NH})[\text{CrO}_3\text{F}]$ . The pyridinium trioxyfluorochromate(VI),  $(\text{C}_5\text{H}_5\text{NH})[\text{CrO}_3\text{F}]$ , (PFC) has been synthesised with the specific intention of developing an efficient and new reagent for the oxidation of organic substrates. Oxidation of various organic substrates involving the new reagent PFC have also been studied in collaboration with other workers of our laboratory but the results of oxidations will not constitute any part of this thesis. Chapter 7, the fourth Chapter of PART TWO and indeed the last Chapter of the thesis, which deviates from the main stream of PART TWO, provides the description of a new direct synthesis and assessment of structure of tris(acetylacetonato)-chromium(III),  $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ . In view of the extremely important nature of  $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ , this work has been included in the thesis. The new synthetic method is based on the electron-transfer concept, does not require any buffer and gives very high yield of the compound in a relatively short time. Electron impact induced mass spectrometry has been used to establish the monomeric nature of  $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ .

Each Chapter of the thesis has been so designed as to make it self-contained more or less. Every Chapter contains its introduction and the relevant literature citations (references) thereby making an <sup>elaborate</sup> general introduction and a comprehensive list of reference for the whole thesis redundant. The work described in Chapters 2, 3, 4 and a part of Chapter 6 have been published, while those of Chapter 7 and another part of Chapter 6 have been accepted for publication. The work included in Chapter 5 has been communicated. Details regarding publications have been given in the opening pages of the corresponding Chapters.