

NOT FOR ISSUE

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

ABSTRACT

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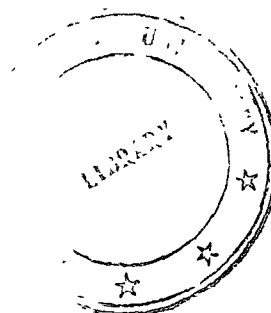
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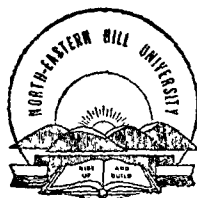


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I certify that the thesis entitled "Mass Spectrometry of Some Metal Compounds and Studies on Fluoro and Acetylacetonato Compounds of Chromium", submitted by Mr. Nirmalendu Roy for the Degree of Doctor of Philosophy of the North-Eastern Hill University, 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

Place : Shillong.

Mihir Kanti Chaudhuri
Signature of the Supervisor

ABSTRACT

The present thesis is based on work done on the studies of electron-impact induced mass spectrometry of some transition metal compounds, and the syntheses, characterisations and structural assessment of fluoro and fluoroaquo complexes of chromium (III), oxyfluoro complexes of chromium (VI) and tris (acetylacetonato)chromium (III). The work embodied in the thesis has been divided into two parts. Part One of the thesis deals with the mass spectrometric studies, while Part Two provides the synthesis, characterisation and structural assessment of the aforementioned types of chromium compounds. Chapters 1 - 3 constitute Part One of the thesis and Chapters 4 - 7 form Part Two.

Chapter 1 presents a brief review of the basic aspects on instrumentation of mass spectrometry with special reference to the type of instrument used in the present studies and some general aspects regarding processing and presentation of mass spectra.

In Chapter 2 the EI induced mass spectrometric studies on chloropentacarbonylmanganese have been described. The EI induced mass spectrometry of $\text{Mn}(\text{CO})_5\text{Cl}$ shows the evidence

of C - O cleavage in and the effect of temperature on the mass spectra of the compound. The mass spectra of the compound have been studied at 70 eV electron energy and at varying inlet temperatures of 20 - 250°C. Like the heavier metal carbonyl derivatives, $\text{Mn}(\text{CO})_5\text{Cl}$ exhibits signals due to carbido fragments. The spectrum run at 100°C shows the characteristic pattern of $\text{Mn}_2(\text{CO})_{10}$ which originates from the formation and recombination of $\text{Mn}(\text{CO})_5$ radicals. The spectral pattern changes further at an elevated temperature of 250°C showing the formation of $\text{Mn}_2(\text{CO})_8\text{Cl}_2$. The formation of $\text{Mn}_2(\text{CO})_8\text{Cl}_2$ in the present case may be either (i) through the dimerisation of $\text{Mn}(\text{CO})_5\text{Cl}$ with a simultaneous loss of two CO groups; or (ii) an ion/molecule interaction between $\text{Mn}(\text{CO})_5\text{Cl}$ and $[\text{Mn}(\text{CO})_3\text{Cl}]^+$ with the simultaneous transfer of one CO group from one Mn to the other leading to the formation of $[\text{Mn}_2(\text{CO})_8\text{Cl}_2]^+$. The mass spectrometric pyrolysis studies showed that very high temperature can change the EI induced fragmentation pattern.

Chapter 3 of the thesis discusses the electron-impact induced mass spectra of $[\text{CF}_3\text{SMn}(\text{CO})_4]_2$, $[\text{CF}_3\text{SeMn}(\text{CO})_4]_2$, $[\text{CF}_3\text{SFe}(\text{CO})_3]_2$, $[\text{CF}_3\text{SeFe}(\text{CO})_3]_2$, $\text{CF}_3\text{SeFe}(\text{CO})_2\text{C}_5\text{H}_5$ and $\text{CF}_3\text{SCr}(\text{NO})_2\text{C}_5\text{H}_5$. The compounds exhibit weak molecular ion peaks and undergo preferential and sequential loss of CO or NO groups. The CO or NO free fragments undergo typical loss of ECF_2 (E = S, Se) with the simultaneous shift of F atom from

carbon to metal, unlike the CH_3S derivatives of metal carbonyl which showed loss of CH_3 groups with cleavage of the S - C bonds from the CO free fragments. The ions $\left[\text{FFeC}_5\text{H}_5\right]^+$ and $\left[\text{FCrC}_5\text{H}_5\right]^+$ in the spectra of cyclopentadienyl compounds prefer expulsion of π - cyclopentadienyls. The pyrolysis effects on the spectra of the compounds have been studied. An increase in temperature eases the expulsion of ECF_2 groups from all the compounds and favours the formation of $\left[\text{Fe}(\text{C}_5\text{H}_5)_2\right]^+$ and $\left[\text{Cr}(\text{C}_5\text{H}_5)_2\right]^+$ in the cyclopentadienyl compounds.

Chapter 4, the first Chapter of Part Two, is based on the direct synthesis, characterisation and structural assessment of alkali metal hexafluorochromates(III), A_3CrF_6 . The reduction of an aqueous solution of CrO_3 with hydrazine hydrate in the presence of an excess of equimolar amounts of A^+OH and 40% HF yields green, crystalline alkali hexafluorochromates(III), A_3CrF_6 ($\text{A} = \text{NH}_4, \text{Na}, \text{K}$ or Rb) in very high yields. The lithium analogue has been prepared by using Li_2CO_3 instead of LiOH . The compounds have been characterised by chemical analyses, room temperature magnetic moments, infrared spectra and molar conductivity. Time - dependent molar conductivity studies of $(\text{NH}_4)_3\text{CrF}_6$ and K_3CrF_6 suggest that the compounds do not undergo decomposition in water at ambient temperatures. The observation of two characteristic bands in the infrared spectra of the compounds at ~ 535 and at $\sim 524 \text{ cm}^{-1}$, assigned to the ν_3 and ν_4 modes of Cr - F stretching.

vibrations suggest that A_3CrF_6 compounds presumably have octahedral structures.

Chapter 5 of the thesis deals with the synthesis and spectroscopic studies of alkali pentafluoroaquochromates (III), $A_2[CrF_5(H_2O)]$ ($A = NH_4, Na, K$ or Rb). It has been shown that chromium(VI) oxide undergoes a very facile reduction with formaldehyde solution in the presence of 40% hydrofluoric acid and AF ($A = NH_4, Na, K$ or Rb) giving green crystalline $A_2[CrF_5(H_2O)]$ in very high yields thereby providing a method for the direct synthesis of $A_2[CrF_5(H_2O)]$. Characterisation of the compounds was made from the results of chemical analyses, molar conductance measurements, pyrolysis, infrared and electronic spectroscopic studies. The structural assessment of the compounds was made from magnetic moments, i.r. and electronic spectroscopic data. The pyrolysis and infrared spectral studies confirmed the presence of coordinated water. The electronic spectra of $A_2[CrF_5(H_2O)]$ in the solid state and in solution suggest no apparent change in its structure.

Chapter 6 describes a novel synthesis of alkali metal trioxyfluorochromates(VI), $ACrO_3F$ ($A = NH_4, K, Rb$ or Cs). The synthesis is based on the reaction between alkali metal bifluorides AHF_2 , and CrO_3 in 1:1 molar ratio in a minimum amount of water. The compounds are highly crystalline and have been characterised by elemental analyses and infrared spectra

studies. The synthesis does involve the direct use of HF but utilises the concept of buffer action of AHF_2 . The concomitant presence of fluoride ions, H^+ and A^+ ion in solution arising from the dissociation of AHF_2 in water appears to be the driving force for the reaction. ACrO_3F compounds react with ammonia wherein Cr(VI) is reduced to Cr(III). Chapter 6 also embodies the synthesis of pyridinium fluorochromate, $\text{C}_5\text{H}_5\text{NHCrO}_3\text{F}$ (PFC). PFC has been synthesised by the addition of pyridine to a solution of CrO_3 in 40% hydrofluoric acid (molar ratio of pyridine : CrO_3 as 1:1) and warming the solution on a steam bath for a few minutes. The orange crystalline compound PFC, $\text{C}_5\text{H}_5\text{NHCrO}_3\text{F}$ melts at $106 - 108^\circ\text{C}$ and shows relatively less pronounced acidity than the corresponding chlorocompound $\text{C}_5\text{H}_5\text{NHCrO}_3\text{Cl}$ (PCC, 'Corey's Reagent'). PFC has been synthesised with a view to developing a new and efficient oxidant for organic substrates. The results of oxidations involving PFC, studied by some other workers of our laboratory, are very encouraging. However, the results of oxidation studies do not constitute any part of the present thesis.

Chapter 7, the last Chapter of the thesis, presents the direct synthesis of tris(acetylacetonato)chromium(III), $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$. In view of the growing interest on and versatile use of $\text{Cr}(\text{acac})_3$ a new and direct synthetic method of obtaining $\text{Cr}(\text{acac})_3$ has been developed. It is reported in this Chapter that the reaction between chromium(VI) oxide, CrO_3 and acetylacetone, in the absence of any buffer, readily give

nearly quantitative yield of tris(acetylacetonato)chromium(III) $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$. Characterisation of the compound has been made from chemical analysis, infrared and mass spectrometric studies. Advantages of the new synthetic method have been discussed. Electron - impact induced mass spectrometry of the compound, recorded using direct insertion technique, showed the compound to be monomeric in accord with the crystal structure of $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$.

The work described in Chapters 2, 3, 4, 6 and 7 of the present thesis have been published/accepted for publication while that of Chapter 5 is under communication.

Chapter 2

Org. mass Spectrom., 16 , 303 (1981).

Chapter 3

Org. mass Spectrom., 16 , 534 (1981).

Chapter 4

Synth. React. Inorg. Met - Org. Chem., 11 , 677 (1981)

Chapter 6

(a) On ACrO_3F

Ind. J. Chem., 20A , 1227 (1981).

(b) On $\text{C}_5\text{H}_5\text{NHCrO}_3\text{F}$ (PFC)

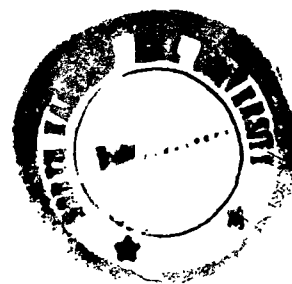
Synthesis (Stuttgart), in press (1982).

Chapter 7

Synth. React. Inorg. Met-Org. Chem., 12, 6th issue
 1015-1018 (1982)

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To



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Date : 27 May, 1982

Mihir Kanti Chaudhuri.
Signature of the Supervisor

Place : Shillong.

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Dated Shillong

27 May, 1982

Nirmalendu Roy.
(Nirmalendu Roy)

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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., $\text{Mn}(\text{CO})_5\text{Cl}$, $[\text{CF}_3\text{S Mn}(\text{CO})_4]_2$, $[\text{CF}_3\text{SeMn}(\text{CO})_4]_2$, $[\text{CF}_3\text{S Fe}(\text{CO})_3]_2$, $[\text{CF}_3\text{SeFe}(\text{CO})_3]_2$, $\text{CF}_3\text{SeFe}(\text{CO})_2\text{C}_5\text{H}_5$ 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 $[\text{CF}_3\text{S Mn}(\text{CO})_4]_2$, $[\text{CF}_3\text{SeMn}(\text{CO})_4]_2$, $[\text{CF}_3\text{S Fe}(\text{CO})_3]_2$, $[\text{CF}_3\text{SeFe}(\text{CO})_3]_2$, $\text{CF}_3\text{SeFe}(\text{CO})_2\text{C}_5\text{H}_5$ 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 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 ECP_2 ($\text{E}=\text{S}$ 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), $\text{A}_3[\text{CrF}_6]$ 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), $\text{A}_2[\text{CrF}_5(\text{H}_2\text{O})]$ 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), $A[CrO_3F]$, 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), $(C_5H_5NH)[CrO_3F]$. The pyridinium trioxyfluorochromate(VI), $(C_5H_5NH)[CrO_3F]$, (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), $Cr(C_5H_7O_2)_3$. In view of the extremely important nature of $Cr(C_5H_7O_2)_3$, 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 $Cr(C_5H_7O_2)_3$.

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 ^{elaborate} any 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.

PART ONE

Mass Spectrometric Studies Of Some Metal Compounds

Instrumentation, Processing and Presentation of Mass Spectra

1.1. Introduction

In general terms, a mass spectrometer is an instrument in which ions are produced from a vaporised molecule in a high vacuum. The ions thus produced are then separated according to their m/z (mass-to-charge ratio) values and finally recorded.

Regardless of their special design all mass spectrometers consist of three basic components. These are (i) the ion source where the gaseous ions are produced, (ii) the mass analyser in which the ions are separated, and (iii) the detector where the separated ions are detected and their intensity measured. All the three components are housed within a high-vacuum system associated with a variety of sophisticated sample introduction devices. In addition the output of the detector is connected to a recording system. Only a brief description of the type of instrument is given in this Chapter, however, for more detailed information references 1-5 form a suitable bibliography.

1.2. Ion Sources

Most mass spectrometric studies of metal compounds, including the ones described in the present thesis, have been carried out using the electron impact source (Figure 1.1). As evident from the name, ion production is based on an exchange of energy during collisions between molecules and a collimated beam of electrons. The same is introduced into the source at pressures of the order of 10^{-6} mm Hg ($1 \text{ mm Hg} = 133.32 \text{ Nm}^{-2}$). Electrons emitted from an electrically heated metal (tungsten or rhenium) filament, F, are collimated and accelerated as they pass through slits, S, and enter the ionisation chamber, C. The energy of the electron beam can be varied by changing the potential difference between the filament and the ionisation chamber. In the ionisation chamber a small fraction of the electrons interact with the gaseous molecules and produce ions, carrying both positive and negative charges, the remainder travel to and are collected by the anode trap, T. By maintaining the repeller plate, A, at a small potential positive with respect to B of the ionisation chamber, the positive ions are drawn out of the ionisation chamber through a slit in plate B, whilst negative ions are attracted to the repeller plate A and discharged. After passing through the slit in plate B the positive ions are accelerated by a large potential difference applied between slits and are projected into the analyser region.

Reversal of the polarity of the potentials applied to the repeller plate and the electrostatic accelerator results in acceleration of the negative ions and their entry into the mass analyser. Our mass spectrometric studies as well as of most others are concerned with positive ions and

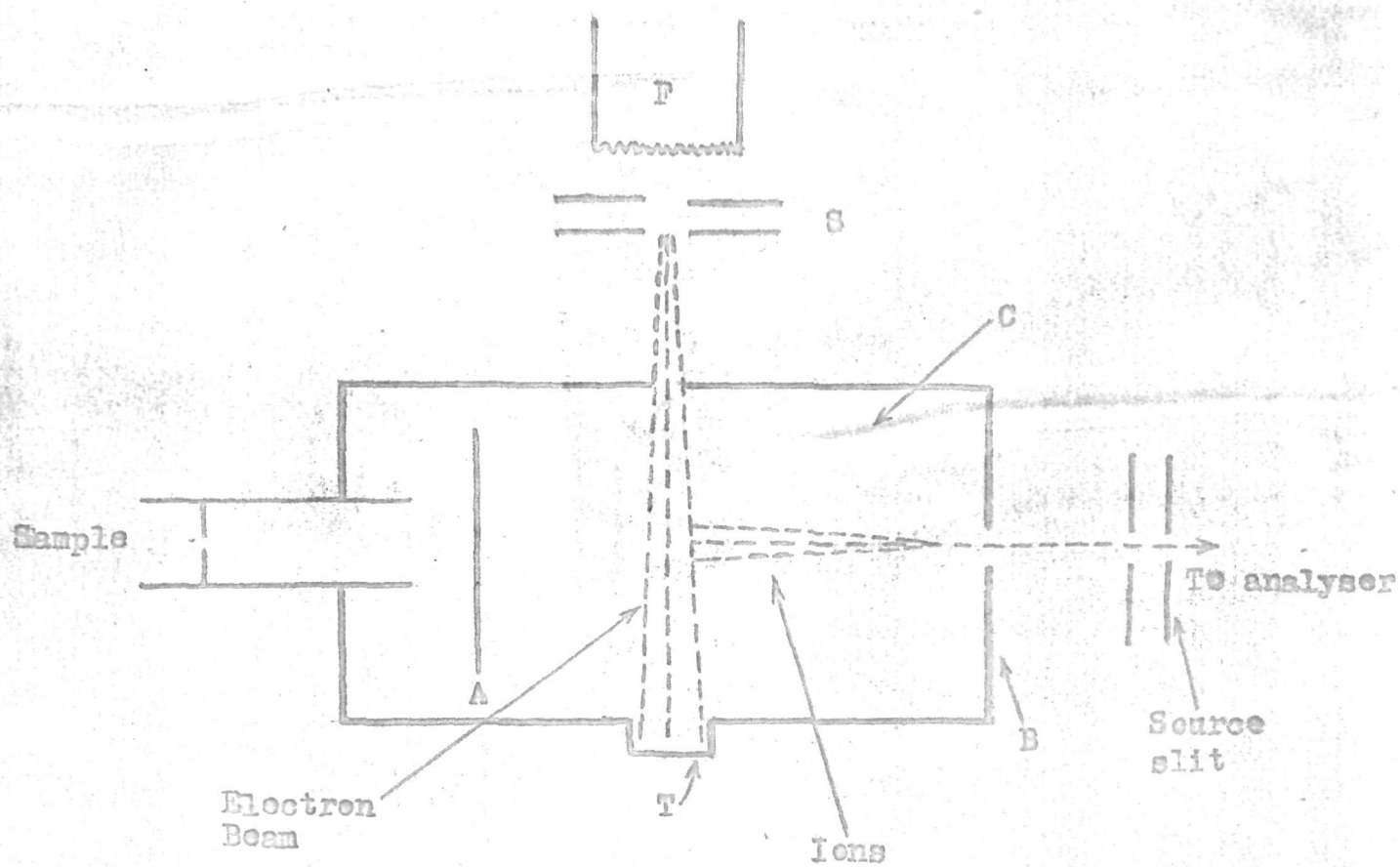


Fig. 1.1 Electron impact ion source

the subsequent discussions on mass spectrometry will deal only with these ions.

Since the ionisation potentials of most molecules(M) lie between 7 and 15 eV (1 eV = 96.48 kJ mol⁻¹ = 23.06 k cal mol⁻¹) and the energy of the electron beam generally used for mass spectrometric studies is 50 - 80 eV, not only does the ionisation process



occur, but also the molecular ion peak (M⁺) cracks down into a mixture of neutral and positively charged fragments. Thus this method of ionisation is extremely useful for structure determination. Furthermore, it is the only method by which appearance potentials of fragment ions can be directly measured. However, owing to the high emission temperature of the filament (ca. 2000⁰C for tungsten filaments) the temperature of the entire ionisation chamber rises to 100 - 150⁰C and this may cause pyrolysis of some compounds.

Three other types of ion sources have been used, to a very limited extent, in studies of metal compounds, namely (i) field ionisation, (ii) photoionisation, or (iii) chemical ionisation.

In the field ionisation source the ions are produced by passing the sample through a very strong electric field (ca. 10⁹ V m⁻¹). Such a field may be obtained by applying a high potential to a thin wire or sharp edge. In the photo-ionisation source the production of ions is accomplished by irradiation of the sample with ultraviolet light. These methods of ionisation produce mainly molecular ions and are thus suited to the determination of molecular weights of compounds.

1.3. Mass Analysers. Types of Mass Spectrometer

The majority of modern mass spectrometers use mass analysers which consists of some form of magnetic field. Of the two dozen or so other systems of mass analysis, only a few have been incorporated into commercial instruments. Mass spectrometers are usually classified according to the mass analyser employed. Only the instruments which have been used in the present studies and are generally in use in studies of metal compounds are considered briefly here.

1.3.1. Single-Focusing Instruments

An ion moving with uniform velocity in a magnetic field at right angles to the direction of its motion describes a circular path provided that the magnetic field is constant and uniform. This principle was exploited in an early design⁵ described by Dempster in 1918. The basis of the principle is as follows : the positive ions are accelerated in a potential gradient V and enter a uniform magnetic field H which is perpendicular to the direction of their motion. The ions of mass m and charge z acquire a velocity V and so have kinetic energy zV , which can be equated to the usual expression for kinetic energy,

$$zV = \frac{1}{2} mV^2 \quad (1.2)$$

The radius r of the circular path which the ions describe is given by the equation

$$HzV = mv^2/r \quad (1.3)$$

By combining equations (1.2) and (1.3) the field and potential gradient requirements for an ion with mass to charge ratio m/z travelling in an orbit of radius r are

given by
$$m/z = \frac{H^2 r^2}{2V} \quad (1.4)$$

The uniform magnetic field has a focusing action equivalent to that of a cylindrical lens so that the ions coming out from the source slit and having the same m/z value and the same velocity are brought to an approximate focus after suffering a deflection of 180° . Ions of other m/z values will come to a focus at other points. Thus this system is said to be single focusing for direction. It is evident from equation (1.4) that by scanning H at constant V , or by varying V at constant H , the ions of different m/z values can be brought successively to a focus at the detector (collector).

In the year 1940 it was shown that phenomenon of focusing of ion beams by causing deflection through 180° is infact a special case of the focusing action of any wedge-shaped magnetic field provided certain conditions are fulfilled. The ion beam should enter and leave the magnetic field at right angles to the field boundary, and inside the field the ion describes a path which is a sector of a circle. The angle subtended by this sector may be 60° , 90° or in the limiting case above, 180° . The separation of ions of different m/z values takes place in a manner exactly analogous to the 180° deflection, and beams of ions from the source situated at some distance from the field boundary are brought to a focus at a collector symmetrically placed on the other side of the sector magnetic field.

Sector instruments with a resolution in excess of 1000 are available. Large experimental instruments with $r=2500$ cm have achieved resolutions as high as 9000.

1.3.2. Double-Focusing Instruments

In practice, ions having the same m/z value have a

range of velocities on leaving the ion source. As a result, magnetic sector instruments cannot bring these ions to a focus at the same point and this limits their resolution. Improvements in resolution are possible by the introduction of velocity analysis prior to direction analysis. Velocity analysis is achieved by passing the ions through traverse electrostatic fields. Thus only ions with a narrow range of velocities are allowed to pass through. Instruments incorporating both direction and velocity analysis are described as double-focusing. Two types are commonly available, some of which even offer resolution in excess of 80000.

The first type was described in 1958 by Craig and Errock and was based upon the geometry suggested by Nier and Johnson (Figure 1.2). In this type of instrument the ions of any one m/z value are brought to a focus at the detector slit by varying the magnetic field and are recorded electrically.

The other type (Figure 1.3) is named after Mattauch and Herzog, who formulated the theory of double-focusing. In this design the deflections due to the electrostatic and magnetic fields respectively have opposite senses. The result is that all ions are brought to a focus in one plane and thus a complete mass spectrum may be recorded simultaneously by placing a photographic plate in this plane. The spectrum may also be scanned past a collector slit as in other instruments.

1.3.3. Double-Beam Instruments

The Nier-Johnson geometry has been modified by the introduction of an electrostatic deflection system so that

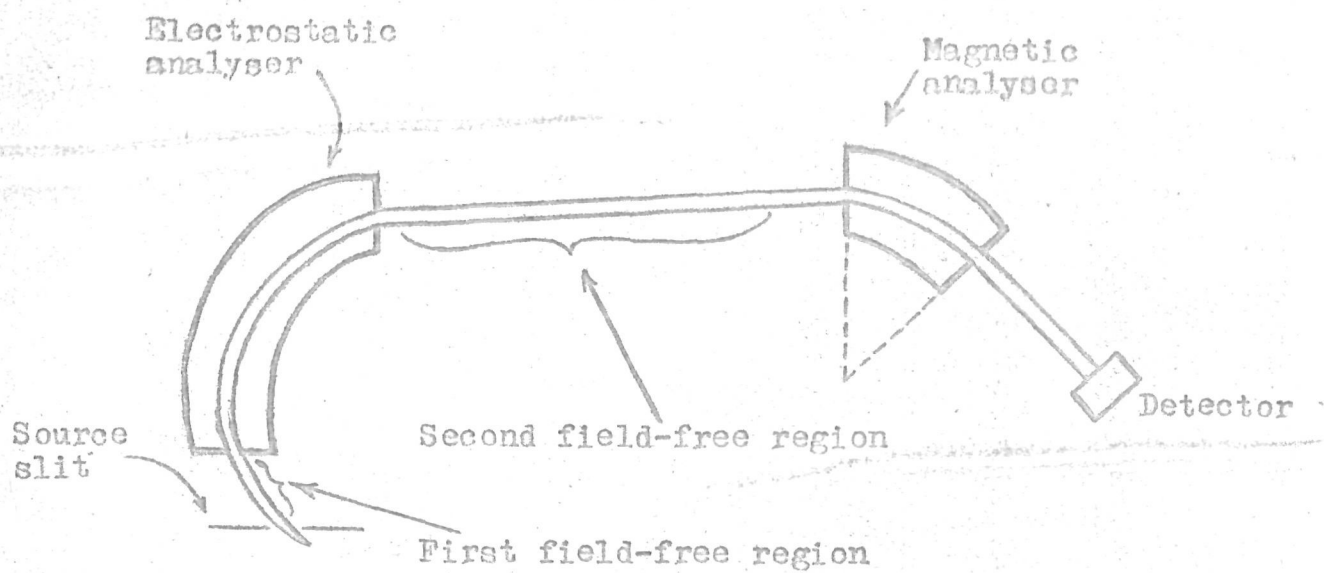


Fig.1.2 Double-focusing mass spectrometer of the Nier-Johnson type .

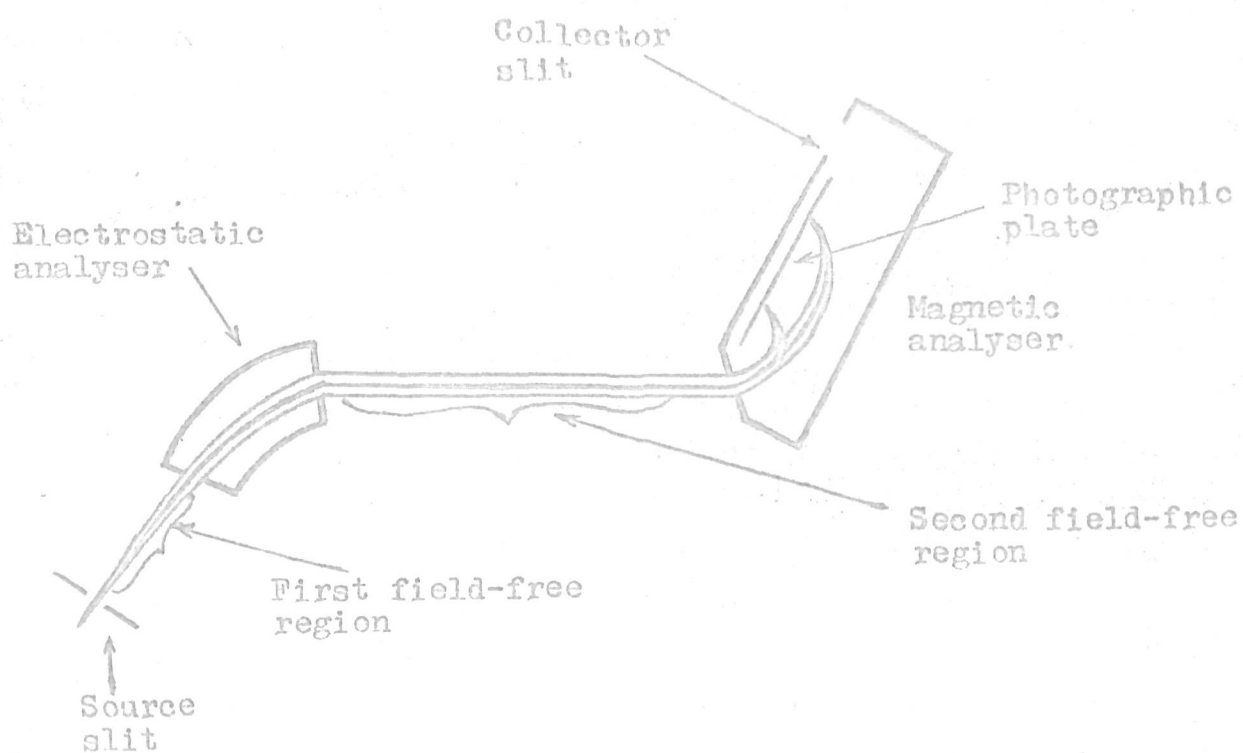


Fig. 1.3 Double-focusing mass spectrometer of the Mattauch-Herzog type

the beams from two separate ion sources may be directed to pass through same magnetic sector. After mass selection in the magnetic field the beams are again deflected apart, and fall on two separate collectors. Each ion source, collector and analyser system is pumped separately. The output of both are fed to a single recorder, the spectra appearing side by side upon the same chart. The advantage of this system is that scanning of the magnetic field has the same effect on both ion beams. This makes it possible to introduce into one source a standard compound whose mass spectrum is known and into the other a sample under investigation. As a result, chemical mass marking is obtained by simple comparison of the two spectra on the same chart.

1.4. Inlet Systems

There are several processes of introducing samples into a mass spectrometer. The selection of the method mainly depends on the volatility and thermal stability of the sample, the type of the ion source and the aim of the experiment.

Gases, highly volatile liquids and solids are often introduced by means of the gas inlet system. The system consists of a series of stopcocks and a reservoir into which sample is introduced. The sample is then admitted into the ion source via a leak. The sample can be introduced into the reservoir in several ways. In the freeze-out technique the sample is frozen and distilled into the reservoir. Introduction of samples may also be accomplished through a septum using a syringe or by using a sintered disc covered with mercury.

Heated inlet systems are necessary for less volatile

liquids and solids. Such systems are similar to that of gas inlet system but are enclosed in an oven which can be heated upto 250°C . Samples are introduced in heated inlets using the freeze-out technique or a sintered disc covered with molten gallium.

Samples can be introduced directly into the ion source using direct inlet system. Usually a direct insertion probe is used. The sample under investigation is loaded on the tip of the probe and inserted into the source which causes its vaporisation. Probes have also been developed which can be heated or cooled independently of the ion source. The temperature can be maintained between -50 to 350°C . Direct introduction systems are especially suitable for compounds of low thermal stability. Excellent spectra can be obtained using such systems from a few micrograms of samples.

1.5. Ion Detectors and Recording of Mass Spectra

The detection and measurement of the ions separated by the mass analyser can be carried out by electrical and photographic techniques.

The photographic technique has been used since many years, but is now superseded by electrical technique. Photographic detection is, however, still used for precise mass measurements and in conjunction with instruments with Mattauch-Herzog geometry.

The electrical detectors are principally of two types: (a) the Faraday cup, which is used in conjunction with a sensitive amplifier or an electrometer, and (b) the electron multiplier. The amplified output of the detector can be recorded using an ultraviolet (UV) galvanometer recorder, a

pen recorder, an oscilloscope or a magnetic tape. In the latter case the data are subsequently fed into a computer for processing. The output of the amplifier can also be fed into a computer so that the data acquisition occurs in real time. Galvanometers are the most widely used recorders. In this case a beam of UV light reflected on to a moving strip of UV - sensitive paper from the mirror galvanometer provides an instantly usable record.

When the electrical detection is used, the common practice is to scan the spectrum continuously and to bring ions of different m/z values successively to a focus at the detector. The signal produced for each series is known as the ion current, and its intensity is proportional to the number of ions reaching the detector.

1.6. Resolution

One of the very important parameter of mass spectrometers is the resolution or resolving power ($m/\Delta m$). This expresses the ability of the instrument to distinguish between ions of mass m and ions of closely similar mass $m + \Delta m$. Resolution is said to be achieved when there is a valley between adjacent peaks in the mass spectrum (see Fig. 1.1). The peaks should be of equal heights and the height of the valley is chosen arbitrarily a fraction, usually 0.1, of the peak height (10 percent valley definition), but other values, though less common, such as 0.05 and 0.01 have been used. There are alternative definitions for resolution and therefore it is important to be aware of the definition used while comparing the performance of commercial instruments.

Mass spectrometers are usually classified on the basis of their resolution capabilities into low, medium or high resolution instruments. Low resolution instruments

($m/\Delta m \sim 200$) and medium resolution instruments ($m/\Delta m \sim 500-5000$) are suitable for the determination of the unit m/z value. The determination of the precise mass of an ion requires a high resolution instrument ($m/\Delta m > 10000$).

1.7. Processing and Presentation of Mass Spectra

A mass spectrum is essentially a record of signals of varying intensity. These signals are measures of ion currents and have a distribution in time or space which can be related to the masses of the ions, their charges and velocities. Spectra are usually recorded electrically. A spectrum is essentially a plot of ion current intensity, versus m/z . The first step in processing this record is the assignment of m/z values to each peak. Relative ion current intensities are then obtained by comparing the areas of the peaks, or in the case of spectra, obtained by an exponentially decaying magnetic scan by comparison of the heights of the peaks.

The mass scale (x coordinate) of a spectrum depends on the type of mass spectrometer and on the mode of scanning used in recording it. When the scale is not linear, e.g. in spectra obtained with a magnetic deflection instrument by scanning the magnetic field, the counting may present problems. The counting can be facilitated in a variety of ways such as (i) making use of peaks due to the 'background' in the instrument, (ii) using a chemical mass marker, or (iii) employing an electronic mass marker.

In addition to sample peaks, a spectrum often shows peaks arising from small amounts of water and air introduced with the sample i.e. peaks at m/z 18 (H_2O^+), m/z 28 (N_2^+).

and m/z 32(O_2^+) and allow calibration of the low mass region of the spectrum. In the high mass region, calibration is achieved by using mass marker, usually a fluorine compound.

The most usual form of presentation of a spectrum is the line diagram also referred to as a bar graph or histogram. In such diagrams the m/z values are plotted horizontally and the intensity vertically. The intensity is usually expressed as relative abundance, which is conventionally expressed as the percentage intensity of a given peak or line relative to that of the base peak (most intense peak in the spectrum).

The advent of data processing systems has led to a new way of presenting mass spectra. The ion current may be digitised and the information stored. The data processor can then carry out a number of programmes. In the simplest case it may determine the integral mass by peak comparison and print out a list of mass numbers and ion current values which may be ultimately converted to cracking or fragmentation pattern. The precise mass of each ion may be determined by comparing the rate of arrival of known and unknown ions at the detector. If the instrument has sufficient resolution it is then possible for the data processor to carry out a programme for the determination of the atomic constitution of the ion from its precise mass.

The most sophisticated method of presenting mass spectra is to acquire a print out of the precise mass, atomic constitution and relative abundance of the ions, together with a simplified histogram, if required.

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Mass Spectrometry of Metal Compounds. Evidence of C - O Cleavage in and Effect of Temperature on the Mass Spectra of Chloropentacarbonylmanganese*

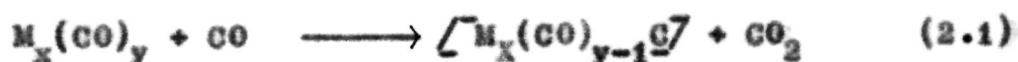
2.1. Introduction

Over the past fifteen years or so it has become increasingly apparent that mass spectrometry provides a simple, quick and reliable means of determining the precise molecular formulae and studying the structure and bonding of metal carbonyls and metal carbonyl derivatives. The convenience of this technique rests on the ease by which spectra may be obtained and also on the fact that very small amounts of compounds are required. This is an important consideration since the cost of metal carbonyl compounds is high. It is perhaps important to preface the discussion by outlining the type of information that we wish to derive from the present studies.

A number of carbonyl-carbido derivatives have been

* This work has been published in 'International Journal of Organic Mass Spectrometry' (London).
Ref. M.K. Chaudhuri, H.S. Dasgupta, N. Roy and D.T. Khathing, Org. Mass Spectrom., **16**, 303 (1981).

synthesised and characterised¹ since 1968. These molecules contain an isolated carbido-carbon atom and have been observed mainly in complexes of iron, ruthenium and osmium although an anionic rhodium species $[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$ has recently been reported. The source of the carbido-carbon is uncertain but is generally believed to arise from a process of the sort



Experimental evidence to support this supposition has been provided in the case of $\text{Ru}_6(\text{CO})_{17}\text{C}$ which is produced from $\text{Ru}_3(\text{CO})_{12}$.

The identification of such materials is very difficult. When $\text{Ru}_6(\text{CO})_{17}\text{C}$ was first reported it might have been reasonably predicted that species was the simple polynuclear carbonyl $\text{Ru}_6(\text{CO})_{18}$. Indeed the analytical data would reasonably support either formulation. However, the mass spectrum clearly showed that the peak of highest m/z value corresponded to $\text{Ru}_6\text{C}(\text{CO})_{17}^+$ and not $\text{Ru}_6(\text{CO})_{18}^+$. Other ions in the spectrum were due to the species $\text{Ru}_6\text{C}(\text{CO})_{17-n}^+$ with the stepwise loss of CO was occurring. Since in all other polynuclear carbonyls the ejection of O from the molecular ion had not been observed as a primary process it was quite reasonable to suppose that the correct formulation of the compound was $\text{Ru}_6(\text{CO})_{17}\text{C}$. This was later substantiated by X-ray analysis.

Ever since carbonyl-carbido compounds started becoming known or may be even slightly before that studies began on the mass spectrometric behaviour of metal carbonyl derivatives with special reference to the observation of metal carbonyl-carbido or metal-carbido fragments. Small abundances of a few fragment ion formed through cleavage of

a C-O bond, e.g., MC^+ , $MCOCO^+$ ($M=Co, Mn$) were also detected from two dimetallic carbonyls^{2,3}. Ions of these types, however, were observed in the spectra of the carbonyls of nickel and iron⁴ although chromium, molybdenum and tungsten hexacarbonyls seems to have produced small quantities of these ions⁵. Thus it becomes evident that carbido fragment ions $M_n(CO)_n C^+$ are commonly observed^{2,3} for the heavier metal ions but such carbido fragments are not very usual for lighter metal carbonyl derivatives.

Though some results of mass spectrometric investigations of $Mn(CO)_5Cl$ have been reported in the literature^{6,7} this compound was chosen in order to investigate the results of electron-impact studies. The present Chapter describes the results of EI studies of chloropentacarbonylmanganese, $Mn(CO)_5Cl$, at varying inlet temperatures, of special significance regarding both metal-carbon and carbon-oxygen bonding, and also the effect of temperature on the mode of EI induced fragmentation.

2.2. Experimental Section

Synthesis of Chloropentacarbonylmanganese, $Mn(CO)_5Cl$.— A mixture of 1.2 g (3.08 mmol) $Mn_2(CO)_{10}$ in a minimum volume of cyclohexane and 2.2 g (8.06 mmol) perchlorocyclopentadiene, C_5Cl_6 , was irradiated for 12 h in a sealed Pyrex tube kept at a distance of about 20 cm from the UV-lamp. The tube was then cooled in liquid nitrogen and opened, and the evolved CO was pumped off through a vacuum line. The tube was then warmed to 0°C and the mixture was filtered. The residue obtained from the reaction tube was washed with a small amount of dichloromethane. The product was sublimed at 40°C (0.1 mm Hg) which gave the pale-yellow crystalline

sublimate of $\text{Mn}(\text{CO})_5\text{Cl}$. The compound was recrystallised before use.

The mass spectra were run on a Varian MAT CH-5 mass spectrometer. The operating conditions were 70 eV electron energy, 20-250°C inlet temperature, resolution 1000 and acceleration voltage 8 kV.

The mass spectrum is given in Table 1 and the metastable ion data are given in Table 2. The observations were made with the field of the ionizing current strong enough to trap primary ions. The effect of temperature on the EI induced fragmentation pattern was studied at temperatures of 20°C, 50°C, 90°C, 100°C and 250°C respectively.

Metastable transition studies were made by taking help of the fact that the metastable peak corresponding to a particular transition will appear in a mass spectrum taken with a magnetic instrument at a mass m^* given by

$$m^* = (m_2)^2 / (m_1) \quad (2.2)$$

such that m_1 represents m/z value of the parent ion (or precursor ion) and m_2 represents the m/z value of the daughter ion.

Table 1. Mass Spectrum of $\text{Mn}(\text{CO})_5\text{Cl}$

Assignments	m/z	Intensity (%)
$\text{Mn}(\text{CO})_5\text{Cl}^+$	230	24.6
$\text{Mn}(\text{CO})_4\text{CCl}^+$	214	1.5
$\text{Mn}(\text{CO})_4\text{Cl}^+$	202	0
$\text{Mn}(\text{CO})_5^+$	195	11.2
$\text{Mn}(\text{CO})_3\text{Cl}^+$	174	14.8
$\text{Mn}(\text{CO})_4^+$	167	4.5
$\text{Mn}(\text{CO})_2\text{Cl}^+$	146	34.9
$\text{Mn}(\text{CO})_3^+$	139	6.1
$\text{Mn}(\text{CO})\text{Cl}^+$	118	27.6
$\text{Mn}(\text{CO})_2^+$	111	15.8
MnCCl^+	102	2.7

Table 1. contd.

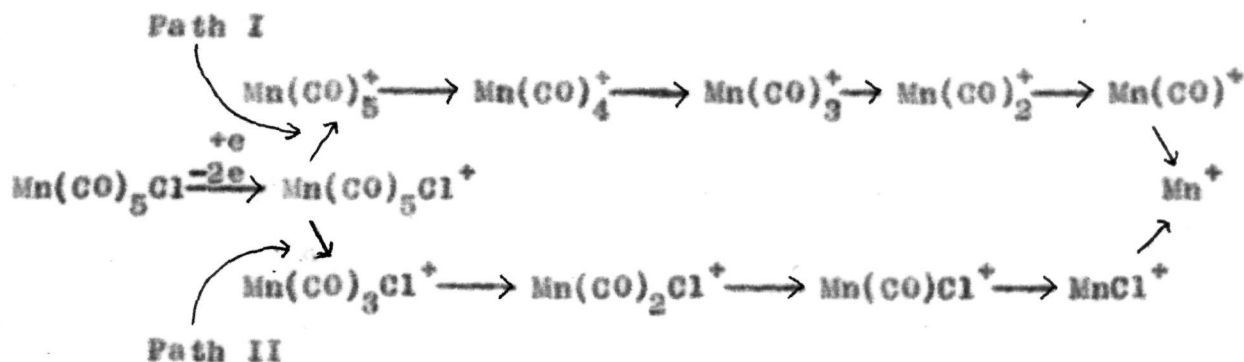
Mn(CO)_5^+	95	2.9
MnCl^+	90	47.1
MnCO^+	83	26.3
MnC_2^+	79	0.8
Mn C^+	67	12.6
Mn^+	55	88.7
CO^+	28	100

Table 2. Metastable Transitions in the Mass Spectrum of $\text{Mn(CO)}_5\text{Cl}$

m/z^*		Process	Neutral fragment lost
Observed	Calculated		
165.3	165.32	$230 \rightarrow 195$	Cl
143.1	143.02	$195 \rightarrow 167$	CO
115.6	115.69	$167 \rightarrow 139$	CO
88.7	88.64	$139 \rightarrow 111$	CO
62.1	62.06	$111 \rightarrow 83$	CO
54.1	54.08	$83 \rightarrow 67$	O
36.5	36.44	$83 \rightarrow 55$	CO
131.6	131.63	$230 \rightarrow 174$	2CO
122.5	122.50	$174 \rightarrow 146$	CO
95.5	95.36	$146 \rightarrow 118$	CO
88.1	88.16	$118 \rightarrow 102$	O
68.6	68.64	$118 \rightarrow 90$	CO
111.2	111.04	$174 \rightarrow 139$	Cl
84.5	84.39	$146 \rightarrow 111$	Cl
58.4	58.38	$118 \rightarrow 83$	Cl
33.6	33.61	$90 \rightarrow 55$	Cl

2.3. Results and Discussion

Table 1 and Table 2 present the essential features of the mass spectrum of chloropentacarbonylmanganese, $\text{Mn}(\text{CO})_5\text{Cl}$. It was observed in the present studies, in accord with the report of Edgar et al.⁷, that the spectrum measured at low temperature shows the molecular ion peak of moderate intensity (24.6%) at m/z 230. The molecular ion $[\text{Mn}(\text{CO})_5\text{Cl}]^+$ undergoes electron-impact induced fragmentation by two different pathways, as shown in Scheme 1. While one of the cracking path involves rupture of the Mn-Cl bond followed by stepwise losses of CO groups, the other involves the retention of the Mn-Cl bond with successive losses of CO groups.



Scheme 1

Metastable transition studies were made in order to see if any one of the two pathways is preferred over the other. Observed metastable peaks, however, support both the cracking patterns and suggest that both the pathways are equally probable and the fission of Mn-Cl and Mn-CO bonds compete with each other effectively. The most notable feature of the spectrum was the appearance of peaks at m/z 67, 79, 95, 102 and 214. These peaks have been attributed to the metal carbido fragments MnC^+ , MnC_2^+ , $\text{Mn}(\text{CO})\text{C}^+$, MnCCl^+ and $\text{Mn}(\text{CO})_4\text{CCl}^+$.

respectively. Such observations definitely suggest that, like heavier metal carbonyl derivatives,^{2,3} the lighter ones may also undergo appreciable C-O bond fission. It appears that there is hardly any definite report in literature on the loss of O from the lighter metal carbonyl derivatives. With a view to obtain further support for these assignments, metastable transitions relating to these particular peaks were also investigated. However, the weak nature of the peaks for these fragments precluded the observation of sufficient metastables, but the metastable peaks at 88.1 and 54.1 surely support the transitions $\text{Mn(CO)Cl}^+ \longrightarrow \text{MnCCl}^+ + \text{O}$ and $\text{Mn(CO)}^+ \longrightarrow \text{MnC}^+ + \text{O}$.

An assessment of the various chlorine containing fragments was made by checking the chlorine isotopic ratios. This is considered of extreme importance in the present case, because of the absence of any interference from manganese. Taking natural isotopic abundances of chlorine into consideration, the value of the ratio $[\text{M} + 2]/[\text{M}]$ for a given fragment containing one chlorine atom should be 0.32. The values of this ratio, for various chlorine containing fragments, in the present case appeared to be 0.30 or 0.31, lending additional support to the suggested fragmentation scheme.

In an attempt to study the effect of pyrolysis in the mass spectrum of $\text{Mn(CO)}_5\text{Cl}$, the spectrum of the compounds was studied at temperatures of 20°C, 50°C, 90°C, 100°C and 250°C respectively, maintaining 70 eV as the electron energy. It appeared from the above mentioned studies that the mass spectra run at 20°C, 50°C, and 90°C were essentially similar, but the spectral pattern changed at 100°C exhibiting a new peak at m/z 390. This peak has been assigned to $\text{Mn}_2(\text{CO})_{10}^+$ on the ground that the typical pattern conforms to that of $\text{Mn}_2(\text{CO})_{10}$. Somewhat identical observation was made by Svec and Junk¹⁰ a few years ago. It is believed that under high energy condition $\text{Mn(CO)}_5\text{Cl}$ forms Mn(CO)_5 radicals even at lower temperatures.

However, at 100°C the optimum concentration is reached such that the recombination through radical coupling gives rise to the formation of $\text{Mn}_2(\text{CO})_{10}$. Such formation and recombination of manganese pentacarbonyl radicals has also been observed previously carrying out the reactions under photochemical conditions⁹. Pyrolysis effect on some iron carbonyl derivatives under mass spectrometric conditions were reported by other workers about four years ago, from which some very useful conclusions were made by them. The observation of the peak in the spectrum of $\text{Mn}(\text{CO})_5\text{Cl}$ run at 100°C stimulated the interest to see the effect of further raise of temperature. Accordingly a spectrum of $\text{Mn}(\text{CO})_5\text{Cl}$ was run at 250°C. This spectrum reveals some very important differences. The most notable is the disappearance of the peak due to the ion $\text{Mn}(\text{CO})_5\text{Cl}^+$ (m/z 230) and most of the other peaks owing to $\text{Mn}(\text{CO})_x\text{Cl}^+ (x < 5)$ ions, and appearance of a peak at m/z 404. The ratio $[\text{M}+2] / [\text{M}]$ for m/z 404 was found to be 0.62, suggesting the presence of two Cl atoms in the fragment. Accordingly the peak was assigned the composition $\text{Mn}_2(\text{CO})_8\text{Cl}_2$. A compound of such composition has been known and its mass spectrum has also been reported⁷. It is believed that the formation of $\text{Mn}_2(\text{CO})_8\text{Cl}_2$ in the present case may be either (i) through the dimerization of $\text{Mn}(\text{CO})_5\text{Cl}$ with a simultaneous loss of two CO groups giving rise to $\text{Mn}_2(\text{CO})_8\text{Cl}_2$, which on ionization gives rise to the peak at m/z 404; or (ii) an ion/molecule interaction between $\text{Mn}(\text{CO})_5\text{Cl}^+$ and $\text{Mn}(\text{CO})_3\text{Cl}^+$ with simultaneous transfer of a CO group from one Mn to the other leading to the formation of $\text{Mn}_2(\text{CO})_8\text{Cl}_2^+$.

It has been observed that the intensity of various fragments increases with decreasing m/z values. This constitutes one of the very important observation and is presumably because of the increased metal to CO π -bonding between manganese having a low formal oxidation state and a smaller number of CO groups. Since the carbon valency

has to be maintained at four the increased π -back donation increases the Mn-C bond order with a simultaneous decrease in that of C-O, thus making the C-O bond more susceptible to increased temperature compared with the Mn-C bond.

It may concluded from the present studies that like heavier metal carbonyl derivatives, the lighter metal carbonyl derivatives may also exhibit carbon-oxygen bond fission, and very high temperature can change the EI induced fragmentation pattern.

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Mass Spectrometric Studies of $[\text{CF}_3\text{E Mn(CO)}_4]_2$,
 $[\text{CF}_3\text{E Fe(CO)}_3]_2$ (E = S, Se), $\text{CF}_3\text{SeFe(CO)}_2\text{C}_5\text{H}_5$ and
 $\text{CF}_3\text{SCr(NO)}_2\text{C}_5\text{H}_5$. 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

Mass Spectra of a large number of transition metal compounds have been reported in last fifteen years and a considerable amount of information concerning the behaviour of them under electron impact (EI) conditions has been accumulated. Attempts have been made to arrive at some generalisations with regard to the fragmentation pathways of many metal containing systems such as metal carbonyls, metal - π - cyclopentadienyls, metal- π - arenes and metal-fluorocarbon derivatives etc¹.

* The work discussed in this Chapter has been published in 'International Journal of Organic Mass Spectrometry' (London). Ref. M.K. Chaudhuri, H.S. Dasgupta, N. Roy and D.T. Khathing, Org. Mass Spectrom., **16**, 534 (1981).

The mass spectra of metal carbonyl compounds are characterised by the sequential loss of carbon monoxide from the parent molecular ion and only processes with very low energy requirements can compete with this decarbonylation. Although a large volume of information has been accumulated, many questions remain unanswered and many types of compounds are yet to be studied.

Since mid 1960s a spate of publications on mass spectrometric investigations of metal carbonyl compounds has appeared. Although Vilesov and Kurbatov² reported in 1961 the ionisation potentials of $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ determined by means of a photoionisation technique, the first comprehensive study of the nickel and iron compounds was made by Winters and Kiser³. They determined isotopic abundances of the metals, ion abundances and appearance potentials of various ions. The most prolific ions were the metal ion itself and the monocarbonylmetal ion but all possible ions of the type $\text{M}(\text{CO})_x^+$ were present together with some doubly charged species leading to the postulate that the respective ions were formed by successive losses of CO groups (reaction 3.1).



Conclusive evidence for the proposed fragmentation scheme was soon obtained⁴. Results of two independent studies^{5,6} appeared in 1965 which were in direct analogy with those of the nickel and iron carbonyls. Later on some more studies of the Group VI metal carbonyls have also been reported^{7,8}.

Studies on metal carbonyls and substituted metal carbonyls showed⁹ that thermal decompositions in the ion source were appreciable even at temperatures well below the expected thermal stability of the samples. Studies on pyrolysis effects are, however, not entirely in harmony. Pignaturo

and Lossing¹⁰ reported that the Group VI hexacarbonyls decomposed very little but Svec and Junk⁹ reported that decomposition of these hexacarbonyls began at lower temperatures.

Ionisation process of metal carbonyl molecules has been discussed in some detail. Vilesov and Kurbatov² postulated that the electron removed from the metal carbonyls during the ionisation process originated either from a p-orbital of the oxygen or else from the metal-carbon bond, thus indicating some metal-carbon double bond character. From their studies, Winters and Kiser⁵ suggested that the electron removed from the carbonyls on ionisation was one largely associated with the metal atom rather than with the carbonyl groups. Foffani et al.^{6,11} compared the ionisation potentials of Group VI metals and their hexacarbonyls, with trends in force constants of the M-C and C-O bonds and with the M-C bond lengths. They postulated that the degree of metal-ligand π -bonding is not a relevant factor in the ionisation potentials. Thus, they too argued that the electron removed by electron impact must belong to a molecular orbital very largely associated with the metal atom. This was further substantiated by Kiser¹² from the M.O. calculation on $\text{Ni}(\text{CO})_4$ showing that the highest occupied molecular orbital in $\text{Ni}(\text{CO})_4$ arises from the 3d nickel orbitals with relatively little contribution from the ligand orbitals. Calculations by Gray and Beach¹³ on Group VI hexacarbonyls also indicated that the highest occupied molecular orbitals should be the $t_{2g}(\pi)$. These arise from a combination of the d_e metal atomic orbitals with π and π^* orbitals of the CO ligand and are mainly localised on the metal.

Extensive studies have also been made on the binuclear¹⁴⁻¹⁶ and polynuclear^{15,18-21} metal carbonyls and several useful generalisations have been made thereof. The mass spectra of fluorocarbon derivatives of transition metals

display some unique features. While any carbonyl groups present appear to be eliminated in the usual stepwise fashion, fragmentation paths involving the fluorocarbon entities provide sharp contrasts with corresponding hydrocarbon derivatives. Decomposition of metal-containing ions include the elimination of (i) neutral metal fluorides, (ii) HF, (iii) neutral fluorocarbon species such as $\cdot\text{CF}_3$, CF_2 , $\cdot\text{CF}$ and (iv) F atoms¹. Loss of (i), (ii) and (iii) usually occurred after any carbonyl groups originally present had been expelled whereas loss of (iv) occurred both before and after. The rearrangement of one or more F atoms from ligand to the metals and subsequent elimination of the neutral metal fluoride species occurred in quite a few cases. This appears to be favoured with iron compounds¹. Similar decomposition steps were postulated in fragmentation mechanisms which were not metastable supported; these included extrusion of ReF_3 ²², $\text{C}_5\text{H}_5\text{FeF}^{22,23}$, $\text{C}_5\text{H}_5\text{RuF}^{22}$, $\text{CoF}^{22,23}$ and $\text{C}_5\text{H}_5\text{NiF}^{23}$. Fluorine migration from carbon to metal has also been reported to occur²⁴ during fragmentation of the compound $[\pi - \text{C}_5\text{H}_5\text{NiP}(\text{CF}_3)_2]_2$.

In the fragmentation of the compounds $\text{C}_2\text{F}_4\text{S}_2\text{Fe}_2(\text{CO})_6$ and $\text{C}_4\text{F}_6\text{S}_2\text{Fe}_2(\text{CO})_6$ an unusual mode of decomposition was noted, namely extrusion of FeF_2 after only three CO groups had been lost. These suggested that in each case the first three CO groups lost were all from the same iron atom; the remaining carbonyls in the resultant ions $\text{R}_f\text{S}_2\text{Fe}(\text{CO})_3^+$ were then lost in the familiar stepwise manner.

The mass spectra of the complexes $\text{C}_5\text{F}_6\text{ClM}(\text{CO})_5$ (M = Mn, Re) provided no evidence for elimination of metal fluoride entities in the fragmentation process but the losses of $\cdot\text{F}$, $\cdot\text{Cl}$ and Mn atoms and the neutral fragments $\cdot\text{CF}$, CF_2 and $\cdot\text{CF}_3$ from carbonyl free ions were metastable supported²⁵.

Although a number of fluorinated organosulfur and organoselenium derivatives of metal carbonyls and

cyclopentadienyl metal carbonyls or nitrosyls have been synthesised in recent years²⁶⁻³⁶ the mass spectral studies of such compounds have received less attention to date. It may be noted that the mass spectrometric studies of CH_3S derivatives of metal carbonyls³⁷ showed loss of CH_3 group with cleavage of the S-C bond from the CO free fragments.

The aim of this chapter is to discuss and to give the interpretative treatment of the most important types of fragmentation processes which occur during the mass spectrometric decomposition of some compounds of manganese, iron and chromium containing CF_3S and CF_3Se ligands in combination with several other ligands like CO, NO and C_5H_5 .

3.2. Experimental Section

Synthesis of the Compounds used for Mass Spectrometric Studies.

All manipulations were carried out under nitrogen or argon. Solvents were distilled before use.

Synthesis of $[\text{CF}_3\text{SMn}(\text{CO})_4]_2^{36}$ (1). ——— $\text{Mn}_2(\text{CO})_{10}$ and $\text{N}(\text{SCF}_3)_3$ in 1:2 mole proportions were irradiated in a Pyrex glass bomb for 12-15h at room temperature in presence of a minimum amount of CH_2Cl_2 -n-hexane (1:1) solution. The Pyrex tube was then cooled at -196°C and the generated CO was pumped off through a vacuum line. The tube was warmed to 0°C . The crystalline compound obtained was filtered and purified by recrystallisation from CH_2Cl_2 / n-hexane or by sublimation. The yield of the golden yellow $[\text{CF}_3\text{S Mn}(\text{CO})_4]_2$ (1) compound was 78%.

Synthesis of $[\text{CF}_3\text{Se Mn}(\text{CO})_4]_2^{36}$ (2). ——— A mixture of $\text{Mn}_2(\text{CO})_{10}$ and $(\text{SeCF}_3)_2$ in 1:2 mole proportions were taken in a Pyrex glass bomb already containing a small

amount of CH_2Cl_2 -n-hexane (1:1) solution. The Pyrex bomb was irradiated for ca. 14h at room temperature. After the irradiation was over, the Pyrex tube was then cooled at -196°C and the generated CO was pumped off through a vacuum line. The tube was then warmed to 0°C and the golden-yellow crystalline compound was separated by filtration. The compound was purified by recrystallisation or by sublimation. Yield of $[\text{CF}_3\text{Se Mn(CO)}_4]_2$ (2) was 67%.

Synthesis of $[\text{CF}_3\text{S Fe(CO)}_3]_2^{36}$ (3).— Fe(CO)_5 and $\text{N(SCF}_3)_3$ in 1:2 mole proportions were irradiated in a Pyrex glass bomb for ca. 15h. at room temperature in presence of a minimum volume of CH_2Cl_2 -n-hexane (1:1) solution. After the irradiation was over the Pyrex tube was then cooled at -196°C and the generated CO was pumped off through a vacuum line. The tube was warmed to 0°C . The deep brown-red crystalline $[\text{CF}_3\text{S Fe(CO)}_3]_2$ (3) thus obtained was filtered and purified by recrystallisation from CH_2Cl_2 /n-hexane. Yield was 59%.

Synthesis of $[\text{CF}_3\text{Se Fe(CO)}_3]_2^{36}$ (4).— Fe(CO)_5 and $(\text{SeCF}_3)_2$ in 1:2 mole proportions were irradiated in a Pyrex glass bomb for 14h at room temperature in presence of a minimum amount of CH_2Cl_2 -n-hexane (1:1) solution. After the irradiation was over, the Pyrex tube was cooled at -196°C and the generated CO was pumped off through a vacuum line. The tube was warmed to 0°C . The deep brown-red crystalline compound $[\text{CF}_3\text{SeFe(CO)}_3]_2$ thus obtained was filtered and purified by recrystallisation from CH_2Cl_2 /n-hexane or by sublimation. Yield of $[\text{CF}_3\text{SeFe(CO)}_3]_2$ was 73%.

Synthesis of $\text{CF}_3\text{SeFe(CO)}_2\text{C}_5\text{H}_5^{34}$ (5).— A quantity of 0.5 g (1.4 mmol) of $[(\text{C}_5\text{H}_5)\text{Fe(CO)}_2]_2$ was dissolved

in 50 ml cyclohexane and the solution was heated to 45°C. To the hot solution 1.5 g (5.07 mmol) bistrifluoromethyl diselenide, $\text{CF}_3\text{Se-SeCF}_3$, with stirring. The reaction mixture was then kept at 45-50°C for a period of 72 h under continuous stirring. After the reaction was over, most of the solvent was removed from the cool mixture at 25/20 mm Hg. The compound was purified by recrystallisation from dichloromethane-pentane mixture at -78°C and brown malodorous crystals of $\text{CF}_3\text{SeFe(CO)}_2\text{C}_5\text{H}_5$ was obtained. The yield of the compound was 33%.

Synthesis of $\text{CF}_3\text{S Cr(NO)}_2\text{C}_5\text{H}_5^{32}$ (6).— A mixture of $\text{ClCr(NO)}_2\text{C}_5\text{H}_5$ and AgSCF_3 in 1:1 mole proportions were taken in acetone and was stirred for 6h at room temperature. The reaction mixture was filtered. Pentane was added to the filtrate and solvent was removed at ~25(40 mm Hg). The residue was purified by a soxhlet extraction with pentane for 1 day. From the extract a brown-yellow crystalline compound was obtained. Yield of $\text{CF}_3\text{SCr(NO)}_2\text{C}_5\text{H}_5$ was 70%.

The mass spectra were run on a Varian MAT CH-5 mass spectrometer. The operating conditions were 70 eV electron energy, resolution of 1000 and 8 kV accelerating voltage.

The mass spectra and the experimentally observed metastable transitions are presented in Tables 1-6. The observations were made with the field of the ionizing current strong enough to trap primary ions. The effect of temperature on the EI induced fragmentation was studied with allowance being made for pyrolysis reactions taking place in the ion source.

3.3. Results and Discussion



The mass spectra of the compounds 1 and 2 exhibit weak molecular ion peaks at m/z 536 and 632 (Table 1). The molecular ions do not undergo sequential loss of CO ligands, instead the molecular ions lose three CO groups in a single step leading to $(CF_3E)_2Mn_2(CO)_5^+$ ($E = S, Se$). The ion $(CF_3E)_2Mn_2(CO)_5^+$ subsequently loses one CO group followed by loss of an ECF_2 unit. It is interesting to note that the expulsion of ECF_2 group takes place with the simultaneous shift of F atom from carbon to metal giving $CF_3E Mn_2(CO)_4F^+$. This fragment loses four CO groups in steps, however, followed by the expulsion of the second ECF_2 unit to yield $Mn_2F_2^+$ ion. The fragment ion $Mn_2F_2^+$ undergoes successive losses of F atoms giving Mn_2^+ , which finally fragments to Mn^+ , the bare metal ion.

The signals at m/z 161 and 209 in the spectra of 1 and 2 were weak in nature. These signals have been assigned to Mn_2SF^+ and Mn_2SeF^+ ions. Appearance of these signals indicate the loss of CF_3 through the rupture of S-C or Se-C bonds. However, this could not be supported by the metastable transitions thus precluding any significance of such a process. The inference that may be drawn is that unlike the CH_3S derivatives of metal carbonyls which show preferential losses of CO groups followed by that of CH_3 through rupture of the S-C bond, the corresponding CF_3S or CF_3Se compounds exhibit loss of SCF_2 or $SeCF_2$ with the simultaneous shift of F from carbon to metal. The F atom shift is presumably favoured by the formation of a new bond between an electro-positive metal atom and F through the interaction of non-bonding p-orbitals of F with the vacant orbitals on the metal atom, enabling expulsion of an SCF_2 or $SeCF_2$ groups. Ionization of SCF_2 and $SeCF_2$ in the spectra of the compounds 1 and 2 gives strong signals at m/z 82 and 130 (Table 1) respectively.

In order to study the effect of pyrolysis on the expulsion of ECF_2 ($E = S, Se$) from $CF_3E Mn_2F^+$, the spectra

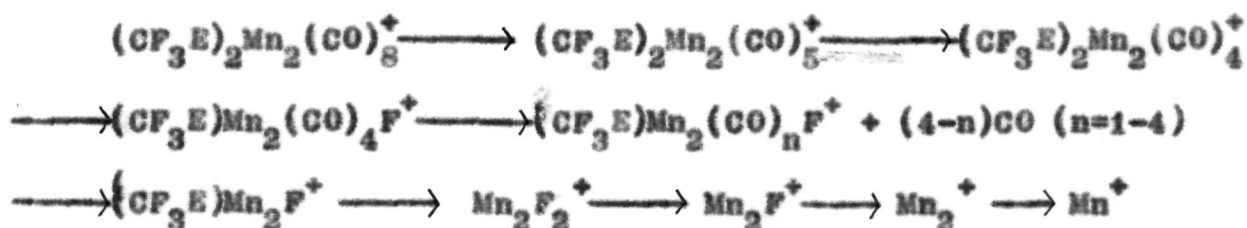
Table 1. Mass Spectra of $[\text{CF}_3\text{E Mn}(\text{CO})_4]_2^-$ (E = S, Se) Compounds

Assignments	E = S			E = Se		
	m/z	Intensity (%)	M+2/M	m/z	Intensity (%)	M+2/M
$(\text{CF}_3\text{E})_2\text{Mn}_2(\text{CO})_8^+$	536	4.5	0.089	638	5.1	0.97
$(\text{CF}_3\text{E})_2\text{Mn}_2(\text{CO})_5^+$	452	26.3	0.093	548	26.5	0.98
$(\text{CF}_3\text{E})_2\text{Mn}_2(\text{CO})_4^+$	424	31.5	0.091	520	33.8	0.95
$(\text{CF}_3\text{E})\text{Mn}_2\text{F}(\text{CO})_3^+$	314	44.9	0.046	362	48.6	0.49
$(\text{CF}_3\text{E})\text{Mn}_2\text{F}(\text{CO})_2^+$	286	35.6	0.047	334	33.2	0.48
$(\text{CF}_3\text{E})\text{Mn}_2\text{F}(\text{CO})^+$	258	29.8	0.045	306	28.7	0.47
$(\text{CF}_3\text{E})\text{Mn}_2\text{F}^+$	230	49.8	0.046	278	48.2	0.51
Mn_2F_2^+	148	58.7	-	148	59.1	-
Mn_2F^+	129	53.2	-	129	52.3	-
Mn_2^+	110	50.3	-	110	51.1	-
Mn^+	55	65.8	-	55	66.9	-
ECF_2^+	82	71.5	0.045	130	74.8	0.48
CO^+	28	100	-	28	100	-

Table 2. Metastable Transition in the Mass Spectra of $\text{[CF}_3\text{E Mn(CO)}_4\text{]}_2^-$ (E = S, Se)

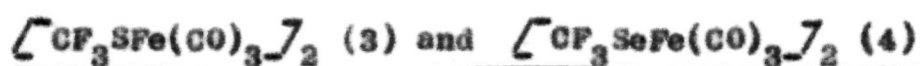
(S)	m/z*	(Se)	Process	Neutral fragment lost	
381.2	475.2	$(\text{CF}_3\text{E})_2\text{Mn}_2(\text{CO})_5^+$	$\longrightarrow$	$(\text{CF}_3\text{E})_2\text{Mn}_2(\text{CO})_5^+$	3CO
397.8	493.5	$(\text{CF}_3\text{E})_2\text{Mn}_2(\text{CO})_5^+$	$\longrightarrow$	$(\text{CF}_3\text{E})_2\text{Mn}_2(\text{CO})_4^+$	CO
275.9	292.5	$(\text{CF}_3\text{E})_2\text{Mn}_2(\text{CO})_4^+$	$\longrightarrow$	$(\text{CF}_3\text{E})\text{Mn}_2\text{F}(\text{CO})_4^+$	ECF_2
288.3	336.0	$(\text{CF}_3\text{E})\text{Mn}_2\text{F}(\text{CO})_4^+$	$\longrightarrow$	$(\text{CF}_3\text{E})\text{Mn}_2\text{F}(\text{CO})_3^+$	CO
260.5	308.2	$(\text{CF}_3\text{E})\text{Mn}_2\text{F}(\text{CO})_3^+$	$\longrightarrow$	$(\text{CF}_3\text{E})\text{Mn}_2\text{F}(\text{CO})_2^+$	CO
232.8	280.4	$(\text{CF}_3\text{E})\text{Mn}_2\text{F}(\text{CO})_2^+$	$\longrightarrow$	$(\text{CF}_3\text{E})\text{Mn}_2\text{F}(\text{CO})^+$	CO
205.0	252.6	$(\text{CF}_3\text{E})\text{Mn}_2\text{F}(\text{CO})^+$	$\longrightarrow$	$(\text{CF}_3\text{E})\text{Mn}_2\text{F}^+$	CO
95.2	78.8	$(\text{CF}_3\text{E})\text{Mn}_2\text{F}^+$	$\longrightarrow$	Mn_2F_2^+	ECF_2
112.5	112.5	Mn_2F_2^+	$\longrightarrow$	Mn_2F^+	F
93.8	93.8	Mn_2F^+	$\longrightarrow$	Mn_2^+	F
27.5	27.5	Mn_2^+	$\longrightarrow$	Mn^+	Mn

were run at 100°C. This showed that the intensity of the signal at m/z 148 due to $Mn_2F_2^+$ was increased from $\sim 59\%$ to $\sim 78\%$ and that those signals at m/z 230 owing to the fragment ion $CF_3Mn_2F^+$ in the spectrum of 1 and at m/z 278 owing to the ion $CF_3SeMn_2F^+$ in the spectrum of 2 decreased from $\sim 49\%$ to $\sim 23\%$, suggesting that pyrolysis plays an important role in the formation of ECF_2 . It may be relevant to mention at this point that the compound $SeCF_2$ has been prepared for the first time by Hass et al.³⁸ by pyrolysis of $B(SeCF_3)_3$. This constitutes a very good example to show the interrelationship between a synthetic study and a mass spectrometric study. The most probable fragmentation pattern of $(CF_3E)_2Mn_2(CO)_8$ ($E = S, Se$) may be given as shown in Scheme 1.



Scheme 1

Metastable transition studies were made with a view to gaining further information regarding the proposed fragmentation scheme. Enough metastables were observed which corresponded to all transitions from the molecular ion down to the bare Mn^+ ion. This gives strong support to the above mentioned scheme (Table 2). Assignments of various S and Se containing fragments have been verified by using the ratios $M+2/M$ and $M-2/M$ respectively³⁹, where $M+2$ represents the intensity of the peak two mass units more and $M-2$ is that of two mass units less than the most abundant ion of a given elemental composition M , and arise from the substitution of ^{34}S for ^{32}S and ^{78}Se for ^{80}Se . These tests give very strong credence to Scheme 1.



Essential features of the mass spectra of the compounds 3 and 4 have been presented in Tables 3 and 4. The compounds show weak signals due to molecular ions at m/z 482 and 578 respectively. An examination of the spectra of these two compounds reveals that unlike manganese compounds 1 and 2, the compounds 3 and 4 undergo preferential losses of six CO groups in steps. The loss of CO groups is followed by the successive losses of ECF_2 ($E = S, Se$) units with the simultaneous shift of F atoms from carbon to metal. The ions at m/z 150 in the spectra of 3 and 4 have been assigned to $Fe_2F_2^+$ the dipositive ion at m/z 75 owing to $Fe_2F_2^{2+}$ and a signal at m/z 112 due to Fe_2^+ occur. The formation of $Fe_2F_2^{2+}$ and Fe_2^+ indicates iron-iron bonding in 3 and 4. The general representation of the structure of the compounds 3 and 4 may be given as shown below (Figure 1)

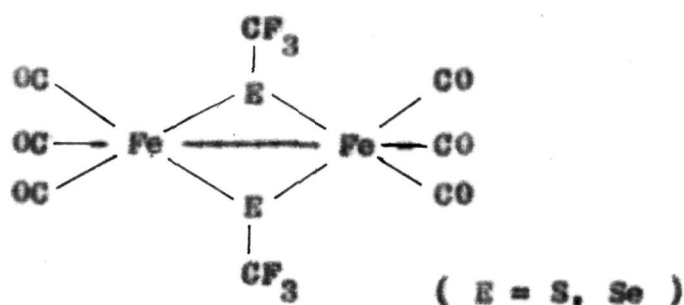


Figure 1

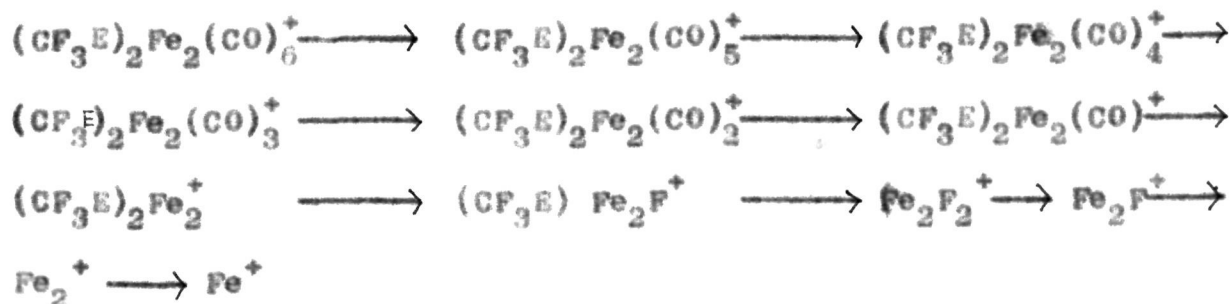
In order to obtain further information regarding fragmentation of the compounds 3 and 4, detailed metastable transition studies were made. The metastable transition studies reveal that the spectra of 3 and 4 exhibit not only the metastable peaks at m/z * 71.6 and 54.8, representing the degradation $(CF_3E)_2Fe_2^+ \longrightarrow Fe_2F_2^+$, but also enough metastables to permit elucidation of the fragmentation as depicted in Scheme 2.

Table 3. Mass Spectra of $[\text{CF}_3\text{E Fe(CO)}_3]_2$ (E = S, Se) Compounds

Assignments	E = S				E = Se			
	m/z	Intensity (%)	M-2/M	M+2/M	m/z	Intensity (%)		
$(\text{CF}_3\text{E})_2\text{Fe}_2(\text{CO})_6^+$	482	6.8	0.13	0.115	578	5.8		
$(\text{CF}_3\text{E})_2\text{Fe}_2(\text{CO})_5^+$	454	15.6	0.11	0.118	550	20.1		
$(\text{CF}_3\text{E})_2\text{Fe}_2(\text{CO})_4^+$	426	11.7 ^a	0.13	0.117	522	10.7		
$(\text{CF}_3\text{E})_2\text{Fe}_2(\text{CO})_3^+$	398	8.6	0.13	0.114	494	6.7		
$(\text{CF}_3\text{E})_2\text{Fe}_2(\text{CO})_2^+$	370	20.1	0.12	0.116	466	25.6		
$(\text{CF}_3\text{E})_2\text{Fe}_2(\text{CO})^+$	342	14.8	0.11	0.115	438	17.1		
$(\text{CF}_3\text{E})_2\text{Fe}_2^+$	314	60.6	0.12	0.114	410	12.6		
$(\text{CF}_3\text{E})\text{Fe}_2\text{F}^+$	232	12.7	0.12	0.046	280	5.6		
Fe_2F_2^+	150	72.5	0.12		150	73.3		
Fe_2^+	112	41.2	0.12		112	60.2		
Fe^+	56	58.7	0.06		56	52.6		
ECF_2^+	82	61.2		0.045	130	69.3		
$\text{Fe}_2\text{F}_2^{2+}$	75	12.8	0.12		75	11.2		

Table 4. Metastable Transition in the Mass Spectra of $[(CF_3E)Fe(CO)_3]^{7-2}$ (E = S, Se)

(S)	m/z^*		Process	Neutral fragment lost
		(Se)		
427.7		523.4	$(CF_3E)_2Fe_2(CO)_6^+ \rightarrow (CF_3E)_2Fe_2(CO)_5^+$	CO
399.7		495.4	$(CF_3E)_2Fe_2(CO)_5^+ \rightarrow (CF_3E)_2Fe_2(CO)_4^+$	CO
371.9		467.5	$(CF_3E)_2Fe_2(CO)_4^+ \rightarrow (CF_3E)_2Fe_2(CO)_3^+$	CO
343.9		439.6	$(CF_3E)_2Fe_2(CO)_3^+ \rightarrow (CF_3E)_2Fe_2(CO)_2^+$	CO
316.3		411.8	$(CF_3E)_2Fe_2(CO)_2^+ \rightarrow (CF_3E)_2Fe_2CO^+$	CO
288.2		383.7	$(CF_3E)_2Fe_2CO^+ \rightarrow (CF_3E)_2Fe_2^+$	CO
171.4		191.3	$(CF_3E)_2Fe_2^+ \rightarrow (CF_3E)Fe_2F^+$	ECF_2
96.9		80.3	$(CF_3E)Fe_2F^+ \rightarrow Fe_2F_2^+$	ECF_2
83.6		83.6	$Fe_2F_2^+ \rightarrow Fe_2^+$	F_2



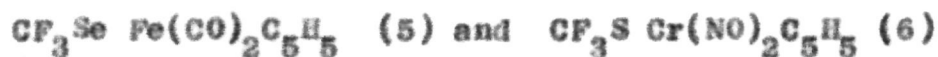
Scheme 2

Further support for Scheme 2 was obtained by making an assessment of the number of Fe and S atoms in a given fragment of $(\text{CF}_3\text{E})_2\text{Fe}_2(\text{CO})_6$ (3) from the ratios $M-2/M$ and $M+2/M$ respectively. Natural iron contains 5.90% ^{54}Fe in addition to 91.6% of the major isotope ^{56}Fe and 2.20 and 0.33%, respectively of the minor isotopes ^{57}Fe and ^{58}Fe . Natural sulfur contains 4.20% ^{34}S in addition to 95.0% of the major isotope ^{32}S and 0.75 and 0.017% respectively of the minor isotopes ^{33}S and ^{36}S . Natural carbon, oxygen and fluorine contain 98.9% ^{12}C , >99.7% ^{16}O , and 100% ^{19}F , respectively making other isotopes of these elements of minor significance in this mass spectrum. As a result of the relative abundances of the isotopes of these elements, the $_{\text{ion}}^{2m/z}$ units less than the most abundant ion of a given elemental composition arises mainly from the substitution of ^{54}Fe for ^{56}Fe . Therefore the ratio $M-2/M$ is often an indication of the number of iron atoms in a given fragment ion. Thus in ions with one or two iron atoms, the value of $M-2/M$ should be 0.0645 or 0.129, respectively on the basis of this treatment. For similar reasons the ratio $M+2/M$ may be an approximate indicator of the number of sulfur atoms in a given ion^{40,41}. For ions with one or two sulfur atoms, respectively, the value of $M+2/M$ is expected to be 0.0442 or 0.0884 on the basis of this treatment.

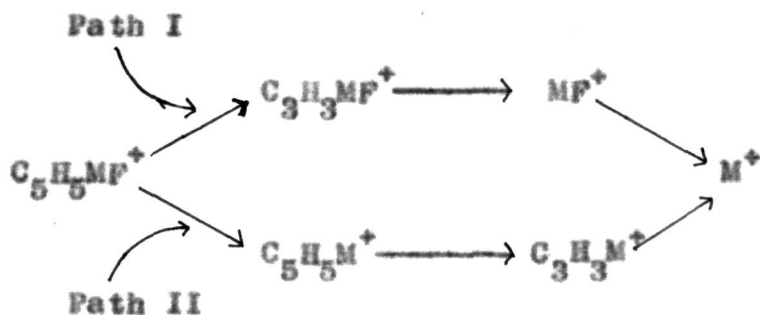
The values of the ratios $M-2/M$ and $M+2/M$ were

checked for the compound 3. The values agreed well with the proposed assignments. Similar checks could not be made in the case of 4, however, because of higher order interference between Fe and Se isotopes.

The significance of pyrolysis was studied by measuring the mass spectra of 3 and 4 at 100°C. The spectra run at 100°C show an increase in the intensity of the signal of the Fe_2F_2^+ ion from $\sim 73\%$ to $\sim 96\%$ and suggests that the high temperature facilitates the loss of ECF_2 (E = S, Se).



Tables 5 and 6 list the essential features of the mass spectra of the compounds 5 and 6. The salient aspects of these spectra are the weak molecule ion peaks at m/z 326 and 278. The molecular ions are followed by losses of two CO or NO groups in steps, giving $\text{CF}_3\text{EMC}_5\text{H}_5^+$ (E = Se, M=Fe and E=S, M=Cr). The fragment ion $\text{CF}_3\text{EMC}_5\text{H}_5^+$ subsequently loses an ECF_2 unit with the simultaneous transfer of F from carbon to Fe or Cr to yield $\text{C}_5\text{H}_5\text{MF}^+$ (M = Fe, Cr) as evidenced by metastable peaks at m/z^* 72.7 and 84.8 respectively. The further fragmentation of $\text{C}_5\text{H}_5\text{MF}^+$ seems to be very interesting because this appears to fragment in two different ways as shown in Scheme 3.



Scheme 3

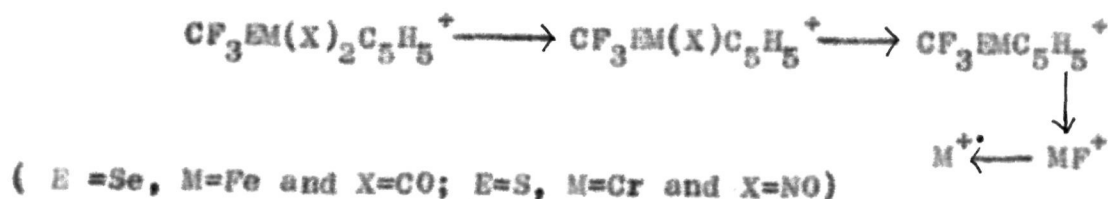
Table 5. Mass Spectra of $\text{CF}_3\text{SeFe}(\text{CO})_2\text{C}_5\text{H}_5$

Assignments	m/z	Intensity %	Metastable Transitions		Neutral fragment lost
			m/z	Process	
$\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SeCF}_3^+$	326	5.6			
$\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{SeCF}_3^+$	298	42.1	372.6	$\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SeCF}_3^+ \longrightarrow \text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{SeCF}_3^+$	CO
$\text{C}_5\text{H}_5\text{FeSeCF}_3^+$	270	29.1	244.6	$\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{SeCF}_3^+ \longrightarrow \text{C}_5\text{H}_5\text{FeSeCF}_3^+$	CO
$\text{C}_5\text{H}_5\text{FeF}^+$	140	92.7	72.7	$\text{C}_5\text{H}_5\text{FeSeCF}_3^+ \longrightarrow \text{C}_5\text{H}_5\text{FeF}^+$	SeCF_2
$\text{C}_5\text{H}_5\text{Fe}^+$	121	6.2	104.6	$\text{C}_5\text{H}_5\text{FeF}^+ \longrightarrow \text{C}_5\text{H}_5\text{Fe}^+$	F
$\text{C}_3\text{H}_3\text{Fe}^+$	95	20.3	74.6	$\text{C}_5\text{H}_5\text{Fe}^+ \longrightarrow \text{C}_3\text{H}_3\text{Fe}^+$	C_2H_2
Fe^+	56	23.8	33.0	$\text{C}_3\text{H}_3\text{Fe}^+ \longrightarrow \text{Fe}^+$	C_3H_3
CO^+	28	100			
$(\text{C}_5\text{H}_5)_2\text{Fe}^+$	186	7.9			
$\text{C}_5\text{H}_5\text{FeC}_3\text{H}_3^+$	160	38.7			
$\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2^+$	177	18.2	96.2	$\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SeCF}_3^+ \longrightarrow \text{C}_5\text{H}_5\text{Fe}(\text{CO})_2^+$	SeCF_3
$\text{C}_5\text{H}_5\text{Fe}(\text{CO})^+$	149	12.1			
SeCF_2^+	130	78.9			
$\text{FFeC}_5\text{H}_5^+$	114	63.2	92.8	$\text{FFeC}_5\text{H}_5^+ \longrightarrow \text{F FeC}_3\text{H}_3^+$	C_2H_2
F Fe^+	75	59.2	49.3	$\text{F FeC}_3\text{H}_3^+ \longrightarrow \text{F Fe}^+$	C_3H_3
Fe^+	56	23.8	41.9	$\text{F Fe}^+ \longrightarrow \text{Fe}^+$	F

Table 6. Mass Spectra of $\text{CF}_3\text{S Cr(NO)}_2\text{C}_5\text{H}_5$

Assignments	m/z	Intensity (%)	Metastable Transitions		Neutral fragment lost
			m/z	Process	
$\text{CF}_3\text{S Cr(NO)}_2\text{C}_5\text{H}_5^+$	276	7.2			
$\text{CF}_3\text{S Cr(NO)}\text{C}_5\text{H}_5^+$	248	52.5	221.2	$\text{CF}_3\text{S Cr(NO)}_2\text{C}_5\text{H}_5^+ \longrightarrow \text{CF}_3\text{S Cr(NO)}\text{C}_5\text{H}_5^+$	$\text{NO}^{(2)}$
$\text{CF}_3\text{S Cr C}_5\text{H}_5^+$	218	49.6	191.6	$\text{CF}_3\text{S Cr(NO)}\text{C}_5\text{H}_5^+ \longrightarrow \text{CF}_3\text{S CrC}_5\text{H}_5^+$	NO
$\text{FCrC}_5\text{H}_5^+$	136	35.8	84.8	$\text{CF}_3\text{S CrC}_5\text{H}_5^+ \longrightarrow \text{F CrC}_5\text{H}_5^+$	SCF_2
F Cr^+	71	66.3	37.1	$\text{F CrC}_5\text{H}_5^+ \longrightarrow \text{F Cr}^+$	C_5H_5
Cr^+	52	68.2	38.1	$\text{F Cr}^+ \longrightarrow \text{Cr}^+$	F
S CF_2^+	82	89.3			
NO^+	30	100			
CrC_5H_5^+	117	15.4	100.6	$\text{F CrC}_5\text{H}_5^+ \longrightarrow \text{CrC}_5\text{H}_5^+$	F
$\text{C}_5\text{H}_5\text{Cr(NO)}_2^+$	177	28.9	112.7	$\text{CF}_3\text{S Cr(NO)}_2\text{C}_5\text{H}_5^+ \longrightarrow \text{C}_5\text{H}_5\text{Cr(NO)}_2^+$	SCF_3
$\text{C}_5\text{H}_5\text{Cr(NO)}^+$	147	26.7	87.1	$\text{CF}_3\text{S Cr(NO)}\text{C}_5\text{H}_5^+ \longrightarrow \text{C}_5\text{H}_5\text{CrNO}^+$	SCF_3
$\text{Cr(C}_5\text{H}_5)_2^+$	182	35.8			

Metastable transition studies (Tables 5 and 6) suggest that both the pathways are probable. It may be noted that such F loss is very rare in organometallics^{1,42}. However, the loss of π - cyclopentadienyl appears to be more facile than that of the F atom, since the intensities due to MF^+ ($M=Fe, Cr$) ions are many times stronger than those of $C_5H_5M^+$. A similar observation was made by King and Welcman³² previously in the case of $C_5H_5TiF_2$. On the basis of the above observations, the fragmentation may be depicted as shown in Scheme 4.



Scheme 4

The signals at m/z 177,149 and 186 in the spectrum of $CF_3SeFe(CO)_2C_5H_5$, 5, and at m/z 177,147 and 182 in that of $CF_3SCr(NO)_2C_5H_5$, 6, have been assigned to $C_5H_5M(X)^+$, $C_5H_5M(X)_2^+$ and $(C_5H_5)_2M^+$ ions. The occurrence of $(C_5H_5)_2M^+$ ions in the mass spectra appears to be a typical feature of the cyclopentadienyl carbonyl and nitrosyl derivatives of 3d transition metals⁴³. Another interesting feature of the spectra of the compounds 5 and 6 is the presence of $C_5H_5M(X)_n^+$ ($n=1,2$) ions. The presence of such ions suggests that the loss of ECF_3 ($E= S, Se$) competes with that of CO or NO.

In an attempt to study the significance of pyrolysis, the spectra of 5 and 6 were run at a temperature of 100°C instead of 20°C. The comparison of the spectra run at 20°C and at 100°C reveals that the two sets of spectra are essentially identical except that (i) the intensity of the signal due to $CF_3EMC_5H_5^+$ became weaker, suggesting that thermal decompositions of 5 and 6 are the likely origin of $(C_5H_5)_2M^+$ ions and that an elevated temperature facilitates the expulsion of ECF_2 units.

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PART TWO

Synthesis and Structural Assessment of Fluoro, Oxyfluoro and Acetylacetonato Compounds of Chromium

The Direct Synthesis, Characterization and Structural Assessment of Alkali Metal Hexafluorochromates (III),
 $A_3 [CrF_6]^*$

4.1. Introduction

Interest in the fluorine chemistry of elements has always existed for chemists and certainly does not appear to be diminishing ¹⁻⁷. Knowledge of the fluorine compounds of the transition metals has been increasing considerably, mainly because fluorine itself has ceased to be a laboratory curiosity as a result of simplification of its preparation and purification. New materials and improved techniques have made older synthetic methods very effective, but it is certainly true that a surprising amount of new work in this field has to be done.

*This work has been published.

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It is well established that fluorine is characterised by its extreme electronegativity and small ionic size and like oxygen it brings out high valencies of metals, e.g. Pt(VI) and Cu(III), though not necessarily always the highest. Lower valency fluorine compounds of transition metals are often unstable and difficult to synthesise.

There has been a considerable current interest in the studies of various aspects of fluorine-containing compounds of chromium(III).^{5,8-16} Syntheses of various fluorine-containing chromium(III) compounds seem to pose problems. Anhydrous conditions are necessary to obtain chromium(III) fluoride. It may be prepared by treatment of chromium(III) compounds with hydrogen fluoride at elevated temperature¹⁷⁻¹⁹ or by prolonged treatment of the metal with hydrogen fluoride. Even so the latter reaction does not go to completion²⁰. It appears that heating of $(\text{NH}_4)_3\text{CrF}_6$ in vacuo is a successful method of preparation of CrF_3 ¹⁸. One of the very important fluoride-containing complex of chromium(III) is hexafluorochromate(III) ion, $[\text{CrF}_6]^{3-}$. Although alkali metal hexafluorochromates(III), A_3CrF_6 (A = alkali metal), have been known for quite some time²¹, there has been no simple and straightforward method for the synthesis of this class of compounds reported to date. The methods recommended for their synthesis include (i) fluorination of the fused mixture of alkali metal halide and chromium(III) halide,^{21,22} (ii) preparation from a KHF_2 melt²³ and (iii) preparation of the complex from an aqueous acid solution of the chromium(III) halide.^{21,24} Method (i) has been recognised as a general method. While both methods (i) and (ii) suffer from difficult handling problems and require the use of uncommon reaction manipulations, method (iii) requires the use of chromium trifluoride as one of the starting reagents which involves an extra preparation. It has been reported, however, that the third method is especially suitable for large precipitating cations²¹. It is the aim of this Chapter to describe a novel and general method for the synthesis of

A_3CrF_6 ($A = NH_4, Li, Na, K$ or Rb) from aqueous medium, their characterization and structural assessment by some physico-chemical methods.

4.2. Experimental Section

All chemicals used for the synthesis were of reagent grade.

Molar conductivity measurements of solutions in double distilled conductivity water were carried out with a Toshniwal conductance bridge or a Philips conductivity bridge (No. PR 9500) using platinised platinum electrodes sealed in a PVC cell.

Magnetic susceptibility measurements were made at room temperature by the Guoy method using $Hg[Co(NCS)_4]$ as the calibrant. The diamagnetic corrections were made using the data given in the literature²⁵.

Infrared spectra of the A_3CrF_6 compounds were recorded on a Perkin-Elmer model 125 spectrophotometer.

4.2.1. Methods of Estimation of the Constituents

Estimation of Chromium^{26a}

The compounds were oxidised to give dichromates by boiling with excess of a persulphate solution in the presence of a very small amount of silver nitrate. After the oxidation was complete, excess of persulphate was destroyed by boiling the solution for about 40 min. The dichromate content of the resultant solution was then determined by the addition of a measured excess of a standard ferrous ammonium sulphate solution and titration of the excess of the latter with standard 0.1(N) potassium dichromate solution.

The standardisation of ferrous ammonium sulphate solution was accomplished by titrating with the standard 0.1 (N) potassium dichromate solution using diphenylamine sulphate^{na} as the indicator.

Estimation of Fluoride^{26b}

For the determination of fluoride content in the compounds, the compounds were first decomposed. Fluoride was precipitated quantitatively as lead chlorofluoride, PbClF . The chlorine in PbClF was then determined by Volhard's method from which the fluorine content was calculated. The volumetric procedure was carried out at p^{H} 3.6-5.6, so that the interference from chromates could be done away with.

Estimation of Alkali Metals

The alkali metals like Li, Na, K etc. were estimated gravimetrically as their sulphates. Chromium was separated from the compound and removed as hydroxide by treating with ammonium hydroxide solution before proceeding for the gravimetric estimation of alkali metals.

Estimation of Nitrogen

Nitrogen estimation was accomplished by either Kjeldahl's method or micro analytical technique.

4.2.2. Preparation of Alkali Metal Hexafluorochromates(III), A_3CrF_6

Ammonium hexafluorochromate (III), $(\text{NH}_4)_3\text{CrF}_6$

A quantity of 1.0 g (10 mmol) CrO_3 was dissolved in ca 8 ml water in a polythene conical flask, and 10.0 ml

25% ammonia solution was added to it. To the solution 5.0 ml (100 m mol) of 40% hydrofluoric acid was added, and the solution was stirred for about 2 min. Pure hydrazine hydrate (1.2 ml) was added very slowly along the side of the reaction vessel with constant stirring. After the addition was over, the content was heated on a boiling water bath for ca 1 h. A ca dark green coloured crystalline compound appeared and the supernatant liquid became almost colourless. The dark green crystalline $(\text{NH}_4)_3 \text{CrF}_6$ was separated by centrifugation and washed twice with a very small amount of water and then two to three times with acetone. The compound was finally dried in Vacuo. Yield 2.1 g (95.5%).

Analysis

Found: N, 19.36% ; Cr, 23.81% and F, 51.72%. The formula $(\text{NH}_4)_3 \text{CrF}_6$ requires : N, 19.09% ; Cr, 23.62% and F, 51.78%.

Molar conductance (Δ_M), $368 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Magnetic moment (μ_{eff}), 3.82 BM at 303°K .

IR bands (cm^{-1}) and assignments

536m	ν_3 ($\nu_{\text{Cr-F}}$)
524s	ν_4 ($\nu_{\text{Cr-F}}$)
3042s	ν_1 ($\nu_{\text{N-H}}$)
3157m	ν_3 ($\nu_{\text{N-H}}$)
1402s	ν_4 ($\nu_{\text{N-H}}$)

Sodium hexafluorochromate (III), $\text{Na}_3 \text{CrF}_6$

A quantity of 1.0 g (10m mol) CrO_3 was dissolved in ca 10 ml water in a polythene beaker, and 4.0g (100 m mol) sodium hydroxide was added to it. To the solution 5.0 ml (100 m mol) of 40% hydrofluoric acid was added, and the solution was stirred for about 5 min. Pure hydrazine

hydrate (1.2 ml) was then added very slowly along the wall of the beaker with constant stirring. The solution was then heated on a boiling water bath for ca 45 min whereupon the mother liquor became colourless and a green crystalline compound precipitated. The green Na_3CrF_6 was separated by centrifugation and purified by washing with a small amount of water at least twice followed by washing with acetone. The compound was finally dried in vacuo. Yield: 2.2 g (93.6%).

Analysis

Found: Na, 29.48% ; Cr, 22.23% and F, 48.57% . The formula Na_3CrF_6 requires : Na, 29.36% ; Cr, 22.13% and F, 48.51% .

Molar conductance (Δ_M), $365 \text{ ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$.

Magnetic moment (μ_{eff}), 3.81 BM at 302°K .

IR bands (cm^{-1}) and assignments

535m ν_3 ($\nu_{\text{Cr-F}}$)

523s ν_4 ($\nu_{\text{Cr-F}}$)

Potassium hexafluorochromate (III), K_3CrF_6

The compound K_3CrF_6 was prepared in a manner analogous to that described for Na_3CrF_6 . The synthesis was carried out using the molar ratio of CrO_3 : KOH : HF as 10: 100: 100 and 1.2 ml hydrazine hydrate per 1.0 g CrO_3 for the reduction. Yield of K_3CrF_6 from 1.0 g CrO_3 was 2.1 g (74.2%).

Analysis

Found : K, 44.48% ; Cr, 18.40% and F, 40.32%. The formula K_3CrF_6 requires : K, 44.41% ; Cr, 18.36% and F, 40.24%.

Molar conductance (Δ_M), 368 ohm⁻¹cm² mol⁻¹.

Magnetic moment (μ_{eff}), 3.82 BM at 302°K.

IR bands (cm⁻¹) and assignments

536w ν_3 ($\nu_{\text{Cr-F}}$)

525s ν_4 ($\nu_{\text{Cr-F}}$)

Rubidium hexafluorochromate (III), Rb₃CrF₆

Rb₃CrF₆ was synthesised by following the procedure analogous to that of Na₃CrF₆. The molar ratio of CrO₃ : RbOH : HF was maintained at 10 : 100 : 100. Reduction of CrO₃ was done with hydrazine hydrate using 1.2 ml of hydrazine hydrate per 1.0 g CrO₃. The yield of Rb₃CrF₆, starting from 1.0 g CrO₃, was 3.4 g (80.5%).

Analysis

Found : Rb, 60.87% ; Cr, 12.38% and F, 27.17% . The formula Rb₃CrF₆ requires: Rb, 60.70%; Cr, 12.31% and F, 26.99%.

Molar conductance (Δ_M), 369 ohm⁻¹ cm²mol⁻¹.

Magnetic moment (μ_{eff}), 3.84 BM at 302°K.

IR bands (cm⁻¹) and assignments

534m ν_3 ($\nu_{\text{Cr-F}}$)

524s ν_4 ($\nu_{\text{Cr-F}}$)

Lithium hexafluorochromate (III) monohydrate, Li₃CrF₆ . H₂O

A quantity of 1.0 g (10m mol) CrO₃ was dissolved in 15 ml water in a polythene beaker, and a filter paper bag

containing 3.7 g (100 μ mol) lithium carbonate was kept soaking in the solution. A 5ml portion of 40% hydrofluoric acid was added to the solution followed by the slow addition of 1.2 ml of pure hydrazine hydrate with constant stirring. After the addition was over, the content was heated on a boiling water-bath for ca 2 h and a green crystalline compound was obtained. The crystalline product was separated by centrifugation and purified by washing with water and finally with acetone. The compound was dried in vacuo. Yield : 1.45 g (71%).

Analysis

Found : Li, 10.24%; Cr, 25.52% and F, 55.78%. The formula $\text{Li}_3\text{CrF}_6 \cdot \text{H}_2\text{O}$ requires: Li, 10.16 % ; Cr, 25.39 % and F, 55.65% .

Molar conductance (Δ_M), 374 $\text{ohm}^{-1}\text{cm}^2 \text{mol}^{-1}$.

Magnetic moment (μ_{eff}), 3.80 BM at 302^oK.

IR bands (cm^{-1}) and assignments

533 m	ν_3 ($\nu_{\text{Cr-F}}$)
525s	ν_4 ($\nu_{\text{Cr-F}}$)
1635m	δ_{HOH}
3450m, br	$\nu_{\text{O-H}}$

4.3. Results and Discussion

It has been reported ²⁷ that the principal characteristic of chromium(III) complexes is their relative kinetic inertness in aqueous solution and it is owing to this that they persist for long periods of time in solution and that so many complex species can be isolated as solids. With this

in view it was thought that the reduction of CrO_3 in the presence of F^- ions in an aqueous medium might be one of the feasible route to the synthesis of CrF_6^{3-} . Thus, a concentrated solution of CrO_3 was reduced with hydrazine hydrate at ambient temperature in the presence of A^+ (A = alkali metal) and F^- ions. The strategy of the reaction was that chromium (VI) being a strong oxidising agent on being reduced would lose oxygen, and coordinatively unsaturated $\text{Cr}^{+n}(n < 6)$ would be formed. The coordinatively unsaturated Cr^{+n} species would in turn react with F^- ions to give rise to $[\text{CrF}_6]^{3-}$. The possibility of formation of the hexaquo ion $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ generally exists with chromium (III) in aqueous solution but such a possibility was precluded in the present case owing to the presence of an excess of F^- ions in the solution.

Room temperature reduction of a concentrated solution of CrO_3 with hydrazine hydrate in the presence of excess of AOH (alkali hydroxide) and 40% HF , maintaining the ratio of $\text{Cr} : \text{F} : \text{A}$ at $1 : 10 : 10$, readily gave a green crystalline compound. For the synthesis of the lithium analogue, Li_2CO_3 was used in lieu of LiOH . Elemental analyses suggested the ratio of $\text{A} : \text{Cr} : \text{F}$ as $3 : 1 : 6$. In view of the analytical data the empirical formula appeared to be A_3CrF_6 .

The alkali metal hexafluorochromates (III), A_3CrF_6 , thus synthesised are quite stable and can be stored for any length of time. The stability can be ascertained by periodic estimation of chromium and fluorine contents in the compounds. The compounds appear to be soluble in water and insoluble in common organic solvents. The molar conductivities of the A_3CrF_6 ($\text{A} = \text{NH}_4, \text{Li}, \text{Na}, \text{K}$ or Rb) compounds in water at 27°C were found to lie between 365 and $374 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ (vide Experimental section). These values suggest a 1:3 type of electrolytic nature of

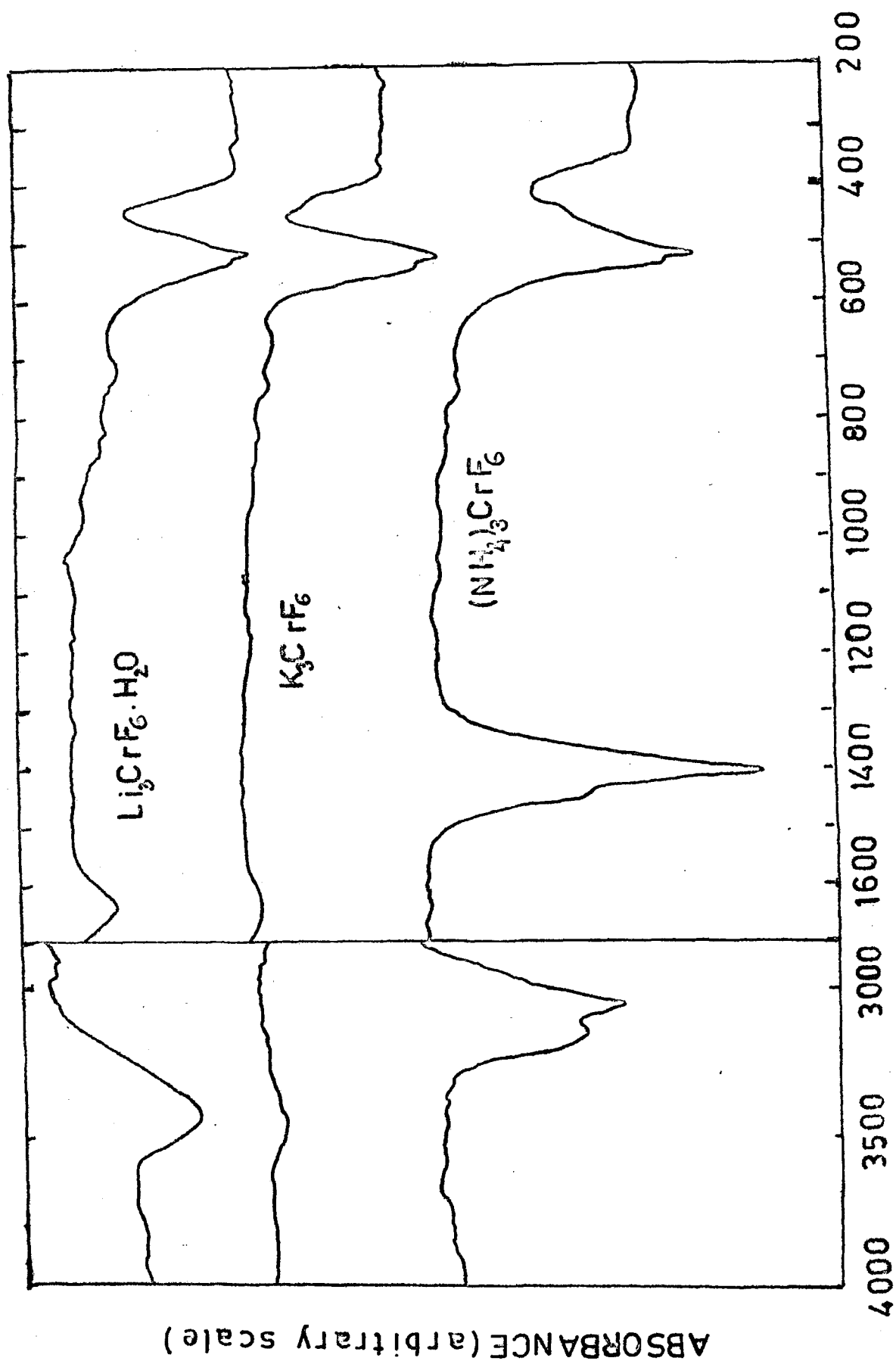


Fig : 4.1. IR spectra

the compounds in accord with the suggested formula A_3CrF_6 . In order to study the stability of the compounds in water, time-dependant molar conductivities were made. Studies of molar conductivities of the solutions of $(NH_4)_3CrF_6$ and K_3CrF_6 , chosen as representatives, at an interval of 7, 15, 30, 45 and 60 days showed no apparent change in the Δ_M values. This suggests the stability of the compounds in water and supports the contention that the compounds neither undergo hydrolysis nor decompose to any appreciable extent.

The room temperature magnetic susceptibility measurements gave effective magnetic moment values of A_3CrF_6 occurring between 3.80 and 3.84 BM. These are in conformity with the magnetic moments of the octahedral chromium (III) (t_{2g}^3) complexes²⁸⁻³⁰. The magnetic moment values obtained in the present case and the electronic absorption spectra of CrX_6^{3-} reported previously³¹ are consistent with a spin-free d^3 -configuration of chromium in an octahedral field. It is expected, in such cases, that the values for the magnetic moments must be very near to the spin-only values since $^4A_{2g}$ ground state derived from the $4F$ free ion term has no angular momentum. Further there are no high energy states of the proper symmetry to mix with the $^4A_{2g}$ and introduce orbital angular momentum into the ground state.

The infrared spectra of the series of five compounds synthesised by a general method resemble each other very closely suggesting that the compounds are isostructural. The spectra generally exhibit two characteristic bands (Experimental Section), one at ~ 535 and the other at $\sim 524\text{ cm}^{-1}$. By analogy these bands have been assigned to the ν_3 and ν_4 modes of the Cr-F stretching vibrations. These observations suggest that the hexafluorochromates (III), A_3CrF_6 have octahedral structures because it has been established by Peacock and Sharp³² that an octahedral ion of the MF_6^{n-}

should have two (ν_3 and ν_4) infrared active M-F vibrations. Three additional bands at 3042s, 3157m and 1402s cm^{-1} respectively in the case of $(\text{NH}_4)_3\text{CrF}_6$ compound have been attributed to the N-H vibrations and have been assigned as the ν_1 , ν_3 and ν_4 modes of NH_4^+ . Two extra bands at 1635m and 3450 m, br cm^{-1} , observed in the case of the lithium compound, have been assigned to the δ_{HOH} and $\nu_{\text{O-H}}$ modes of water present in the compound as water of crystallisation. The lowering of the $\nu_{\text{O-H}}$ relative to that in the free water molecule and broadening of the band have been attributed to intramolecular hydrogen bonding in $\text{Li}_3\text{CrF}_6 \cdot \text{H}_2\text{O}$.

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**Synthesis and Spectroscopic Studies of Alkali Metal
Pentafluoroaquochromates (III), $A_2[CrF_5(H_2O)]^{2-}$**

5.1. Introduction

Chromium (III) has been known to form two mononuclear fluoro complexes¹ $[CrF_6]^{3-}$ and $[CrF_5(H_2O)]^{2-}$. The methods currently used for the synthesis of these complexes involve (i) fusing of the alkali metal fluorides and chromium (III) fluoride and (ii) precipitation from an aqueous solution of chromium (III) fluoride^{1,2}. Both the methods require chromium(III) fluoride as one of the starting materials, which needs an extra preparation, and the methods also suffer from some additional disadvantages mentioned in Chapter 4. Moreover, it has been stated³ that hardly any structural data are available on these mononuclear species.

* The work described in this Chapter has been communicated.
Ref: M.K. Chaudhuri and N. Roy, Synth. React. Inorg. Metal-Org. Chem., 1982 (communicated).

With this in view, it was thought important to improvise a direct general synthesis of $A_2[CrF_5(H_2O)]$ (A = alkali metal) and make an assessment of the structure by spectroscopic methods. The present Chapter describes the direct general synthesis of $A_2[CrF_5(H_2O)]$ and the structural assessment made by various physico-chemical methods.

5.2. Experimental Section

All chemicals used for the synthesis were reagent grade products (B.D.H. , E.Merck, Sarabhai M.).

Molar conductances were measured using a Philips PR 9500 conductivity bridge . Conductivity grade water was used for making solutions of the compounds.

Magnetic susceptibility measurements were accomplished by the Guoy method using $Hg[Co(NCS)_4]$ as the calibrant. The diamagnetic corrections were made using the data given in the literature³. The susceptibility measurements were made at room temperature.

Infrared spectra of the $A_2[CrF_5(H_2O)]$ compounds were recorded on a Perkin-Elmer model 125 spectrophotometer.

Electronic spectra in aqueous media were recorded on a Beckman model UV-26 spectrophotometer.

Reflectance spectra were recorded against MgO using Carlzeiss Jena VSU 2-P instrument.

5.2.1. Methods of Estimation of the Constituents

Since the methods of estimation of the constituents were the same as those described in Chapter 4, they are not described in this Chapter.

5.2.2. Synthesis of Alkali Metal Pentafluoroaquochromates(III), $\Lambda_2 [\text{CrF}_5(\text{H}_2\text{O})]$

Ammonium Pentafluoroaquochromate (III), $(\text{NH}_4)_2 [\text{CrF}_5(\text{H}_2\text{O})]$

Solid CrO_3 (1.0 g, 10.0 mmol) and NH_4F (0.74 g, 20.0 mmol) were mixed by powdering together in an agate mortar. The mixture was dissolved in 20.0 ml (400 mmol) of 40% hydrofluoric acid in a covered polythene beaker by slightly warming over a boiling water bath. To the warm solution, 10.0 ml of 37-40% formaldehyde solution was added dropwise with constant stirring. The orange colour of the solution was changed to intense green with the simultaneous appearance of a small amount of green precipitate. The solution was filtered warm and the dark green coloured filtrate was concentrated to nearly one-fourth of the original volume by heating over a boiling water bath. The reaction container was allowed to cool at room temperature for ca 2 h. The green crystalline $(\text{NH}_4)_2 [\text{CrF}_5(\text{H}_2\text{O})]$ thus obtained was separated by centrifugation and washed four times with cold water and finally twice with alcohol and then dried in vacuo. Yield of $(\text{NH}_4)_2 [\text{CrF}_5(\text{H}_2\text{O})]$ was 1.95 g (97.0%).

Analysis

Found: N, 13.98%, Cr, 25.91%, F, 47.35% and H, 5.11%. The formula $(\text{NH}_4)_2 [\text{CrF}_5(\text{H}_2\text{O})]$ requires: N, 13.91%, Cr, 25.86%;

F, 47.24% and H, 5.02%.

Molar conductance (Δ_m), $264 \text{ ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$.

Magnetic moment (μ_{eff}), 3.84 B M at 299°K.

IR bands (cm^{-1}) and assignments

535 m	↘	Cr-F
516 s	↘	Cr-F
3105 m, br	↘	O -H
1620 m, br	δ	H-O-H
3041 s	↘	N-H
1400 s	↘	N-H

Electronic spectral data

$^{15772} \text{ cm}^{-1}$ $^4\text{A}_{2g} \longrightarrow ^4\text{T}_{2g}$ $10Dq = 15772 \text{ cm}^{-1}$ $B' = 772 \text{ cm}^{-1}$
 (15625) (15625) (765)

$^{23809} \text{ cm}^{-1}$ $^4\text{A}_{2g} \longrightarrow ^4\text{T}_{1g} \text{ (P)}$

(23255)

35089 $^4\text{A}_{2g} \longrightarrow ^4\text{T}_{1g} \text{ (P)}$
 (35087)

values in parentheses are reflectance spectral values.

Sodium Pentafluoroaquochromate III), $\text{Na}_2[\text{CrF}_5(\text{H}_2\text{O})]$

Sodium pentafluoroaquochromate(III), $\text{Na}_2[\text{CrF}_5(\text{H}_2\text{O})]$ was synthesised in a manner analogous to that described for the synthesis of the corresponding ammonium salt. The synthesis was carried out with 1.0 g (10.0 mmol) CrO_3 , 0.84g (20.0 mmol) NaF , 20.0 ml (400 mmol) 40% hydrofluoric acid and 10.0 ml 37-40% formaldehyde. Yield of $\text{Na}_2[\text{CrF}_5(\text{H}_2\text{O})]$ was 1.7 g (81.5%).

Analysis

Found: Na, 21.83% ; Cr, 24.72% and F, 45.22% . The formula $\text{Na}_2[\text{CrF}_5(\text{H}_2\text{O})]$ requires: Na, 21.79%, Cr, 24.65% and F, 45.02% .

Molar conductance (Δ_M), $265 \text{ ohm}^{-1}\text{cm}^2 \text{ mol}^{-1}$.

Magnetic moment (μ_{eff}), 3.83 B M at 299°K .

IR bands (cm^{-1}) and assignments

536 m	$\curvearrowright$ Cr-F
516 s	$\curvearrowright$ Cr-F
3115 m, br	$\curvearrowright$ O-H
1635 w, br	δ H-O-H

Potassium Pentafluoroaquochromate (III), $\text{K}_2[\text{CrF}_5(\text{H}_2\text{O})]$

The method of synthesis of the potassium salt, $\text{K}_2[\text{CrF}_5(\text{H}_2\text{O})]$ was similar to those of the analogous ammonium and sodium salt of pentafluoroaquochromate (III). Starting with 1.0 g (10.0 m mol) CrO_3 , 1.16 g (20.0 m mol) KF and 20.0 ml (400 m mol) 40% hydrofluoric acid and performing the reduction using 10.0 ml 37-40% formaldehyde, the green crystalline potassium pentafluoroaquochromate(III), $\text{K}_2[\text{CrF}_5(\text{H}_2\text{O})]$ was obtained. Yield: 1.64 g (67.5%).

Analysis

Found: K, 32.23% ; Cr, 21.49% , and F, 39.33 % . The formula $\text{K}_2[\text{CrF}_5(\text{H}_2\text{O})]$ requires: K, 32.15% ; Cr, 21.49% and F, 39.33%.

Molar conductance (Δ_M), $263 \text{ ohm}^{-1}\text{cm}^2 \text{ mol}^{-1}$.

Magnetic moment (μ_{eff}), 3.82 B M at 299°K .

IR bands (cm^{-1}) and assignments

535 m	$\curvearrowright$ Cr-F
512 s	$\curvearrowright$ Cr-F
3110 m, br	$\curvearrowright$ O-H
1635 w, br	δ H-O-H

Electronic spectral data

15902 cm^{-1}	${}^4\text{A}_{2g} \longrightarrow {}^4\text{T}_{2g}$	$10\text{Dq} = 15902 \text{ cm}^{-1}$ $\text{B}^1 = 734 \text{ cm}^{-1}$
23705 cm^{-1}	${}^4\text{A}_{2g} \longrightarrow {}^4\text{T}_{1g} (\text{F})$	
35010 cm^{-1}	${}^4\text{A}_{2g} \longrightarrow {}^4\text{T}_{1g} (\text{P})$	

Rubidium Pentafluoroaquochromate (III), $\text{Rb}_2 [\text{CrF}_5(\text{H}_2\text{O})]$

Synthetic procedure for $\text{Rb}_2 [\text{CrF}_5(\text{H}_2\text{O})]$ was the same as those of the other salts of pentafluoroaquochromate (III) described above. A quantity of 1.0 g (10.0 m mol) CrO_3 was mixed with 2.09 g (20.0 m mol) RbF and 20.0 ml (400 m mol) 40% HF and the reduction was carried out with 10.0 ml formaldehyde (37-40% solution). Yield of the green rubidium pentafluoroaquochromate(III), $\text{Rb}_2 [\text{CrF}_5(\text{H}_2\text{O})]$ was 2.82 g (83.9%).

Analysis

Found: Rb , 50.95% ; Cr , 15.57% and F , 28.38%. The formula $\text{Rb}_2 [\text{CrF}_5(\text{H}_2\text{O})]$ requires : Rb , 50.89% ; Cr , 15.48 % and F , 28.27% .

Molar conductance (Δ_M), $253 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

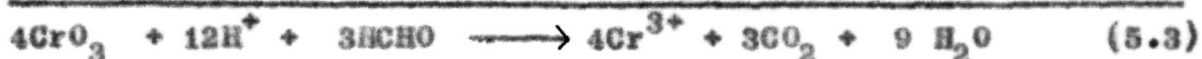
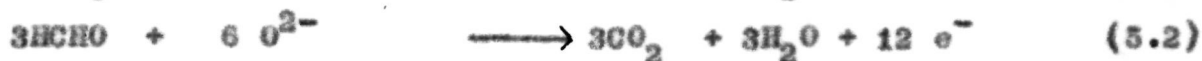
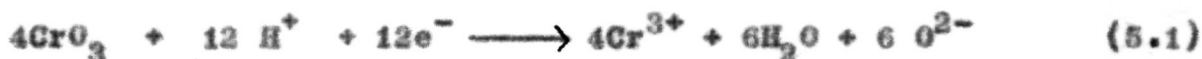
Magnetic moment (μ_{eff}), 3.81 B M at 299°K .

IR Bands (cm^{-1}) and assignments

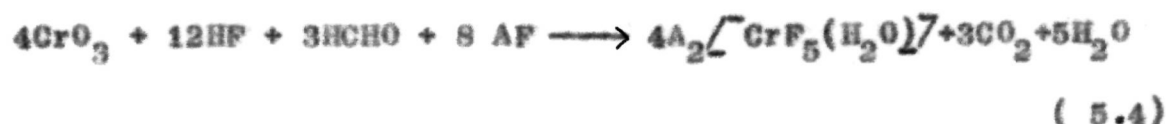
535 m	$\curvearrowright$ Cr-F
515 s	$\curvearrowright$ Cr-F
3120 m, br	$\curvearrowright$ O-H
1620 w, br	δ H-O-H

5.3. Results and Discussion

Direct synthesis ————— The reduction of CrO_3 with formaldehyde solution in the presence of 40% hydrofluoric acid and alkali fluorides AF leads to the synthesis of pentafluoroaquochromates(III) of alkali metals, $\text{A}_2[\text{CrF}_5(\text{H}_2\text{O})]$ sufficient in number and in very high yields leaving little doubt that such methods can be developed for the syntheses of similar types of compounds of other transition metals. Very recently the role of hydrazine hydrate in the synthesis of $[\text{CrF}_6]^{3-}$ from chromium(VI)⁵ and that of acetalacetone in the synthesis of $[\text{MnF}_5]^{2-}$ from manganese (VII)⁶ and also some other Mn^{3+} compounds⁷ from Mn^{7+} have been emphasised. The advent of this concept has definitely simplified the synthesis of fluoro compounds of transition metals. This concept has now been extended for the synthesis of $\text{A}_2[\text{CrF}_5(\text{H}_2\text{O})]$. The basis of the present selection is that formaldehyde can act as a reducing agent giving CO_2 and H_2O and that chromium(VI) is a very well established oxidising agent for organic substrates.⁸⁻¹² Thus, it was thought that the electron transfer reaction between formaldehyde and CrO_3 in the presence of F^- ligands would give rise to the formation of fluoro compounds of chromium (III). The most probable course of the reaction may be expressed by the following sequence of chain processes so that the formation and very high yields of alkali metal pentafluoro-aquochromates (III) are easily understood.



The success of the present synthesis depends on the key roles played by formaldehyde, hydrofluoric acid and alkali metal fluoride AF (A=NH₄, Na, K or Rb) and the net reaction can be written as (5.4).



Characterisation and Assessment of Structure— The alkali pentafluoroaquochromates (III), $\text{A}_2[\text{CrF}_5(\text{H}_2\text{O})]$, obtained by the present method are all green and well crystalline compounds. They are stable for long periods without any decomposition which can be ascertained from their unaltered appearance and periodic estimation of chromium. The compounds are not very highly soluble in water and insoluble in common organic solvents. The elemental analyses suggest the stoichiometry of A: Cr: F: H as 2:1:5:2. The molecular weights calculated on the basis of elemental analyses were made use of for the molar conductance studies. The molar conductances of the $1 \times 10^{-3}(\text{M})$ solutions of the newly synthesised compounds were found to lie between 250 and 265 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ at 27°C (Experimental Section) indicating 1:2 type of electrolytic nature of the compounds. These results lead to the formulation of the compounds as $\text{A}_2[\text{CrF}_5(\text{H}_2\text{O})]$. The molar conductance measurements as a function of time did not show any apparent change in the Δ_{M} values and confirms the stability of the compounds in water.

The room temperature magnetic moments of the compounds are quite straightforward and occur between 3.81 and 3.84 B M. The values are highly comparable to each other and are very close to the spin-only value of 3.88 B M for an octahedral chromium(III) species and are in accord with the crystal field energy studies of Hatfield et al.¹³ The results

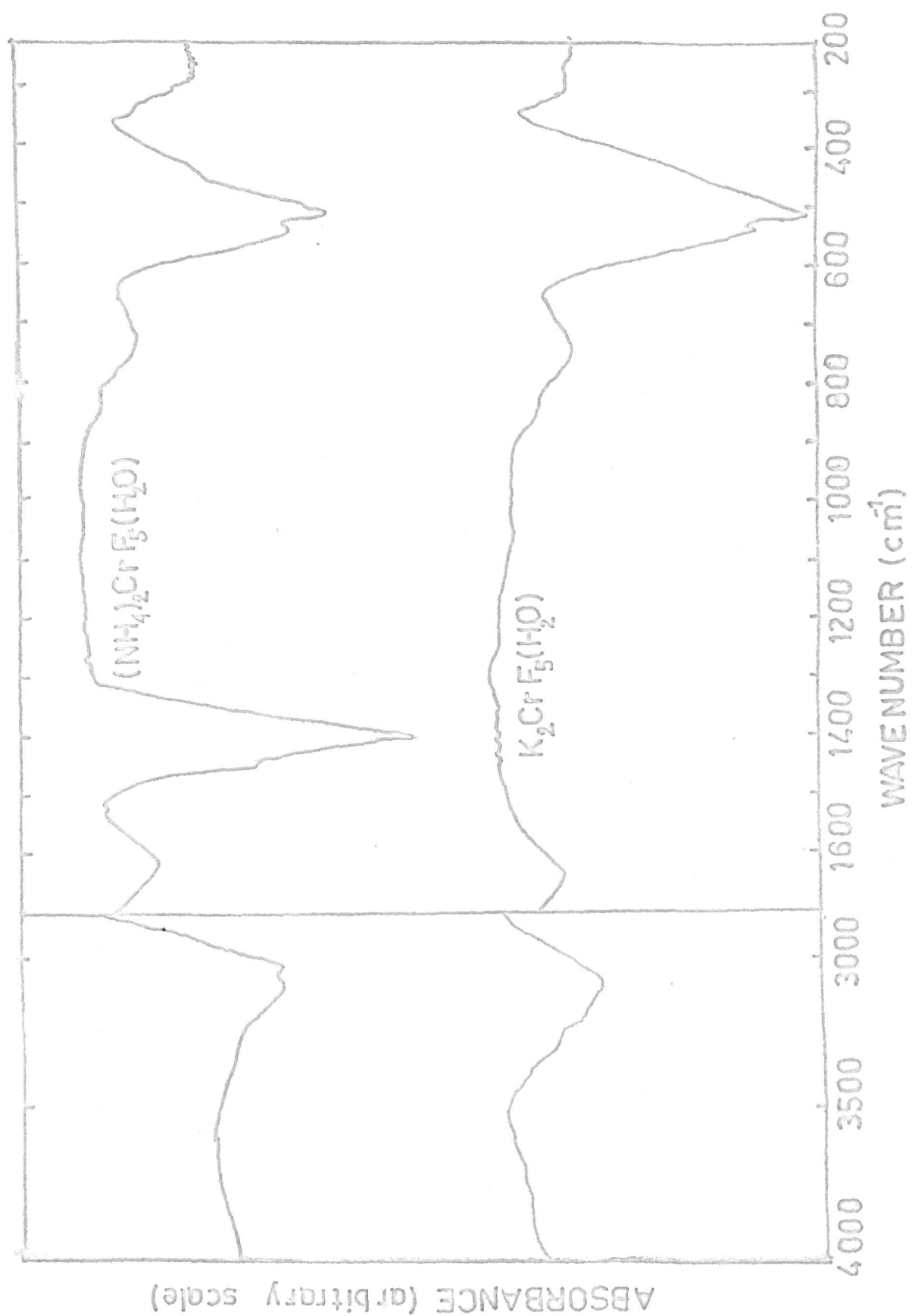


Fig: 5.1. IR spectra

also agree well with the one predicted from theory. Since the $^4A_{2g}$ ground state derived from 4P free ion has no angular momentum and also there is no high energy states of proper symmetry to mix with the $^4A_{2g}$ state, the magnetic moments must be very near to the spin-only values. That is precisely observed in the present cases.

The infrared spectra of the compounds taken in both mull and KBr media exhibit two characteristic bands (vide Experimental Section) at ~ 535 and at $\sim 515 \text{ cm}^{-1}$ which have been assigned to $\nu_{\text{Cr-F}}$ modes. These values agree very well with the $\nu_{\text{Cr-F}}$ modes observed in some similar cases.^{5,14} An important feature of all the spectra is the absorptions at ca $3110 (\text{m, br})$ and at ca $1630 (\text{w, br}) \text{ cm}^{-1}$ which have been assigned to the $\nu_{\text{O-H}}$ and $\delta_{\text{H-O-H}}$ modes of coordinated water. The shifting of $\nu_{\text{O-H}}$ towards lower frequency and broadening of the band as well as weakening and broadening of $\delta_{\text{H-O-H}}$ bands relative to those of free water are ascribed to intramolecular hydrogen bonding.¹⁵⁻¹⁷ The two additional bands at 3041 and 1400 cm^{-1} in the spectrum of $(\text{NH}_4)_2 [\text{CrF}_5(\text{H}_2\text{O})]$ have been assigned to the ν_1 and ν_4 modes of NH_4^+ . The ν_3 mode of NH_4^+ could not, however, be identified owing to its overlap with the broad $\nu_{\text{O-H}}$ band at ca 3110 cm^{-1} .

Evidence with regard to the presence of coordinated water was also obtained from the pyrolytic studies of $(\text{NH}_4)_2 [\text{CrF}_5(\text{H}_2\text{O})]$. The facts, that the compound does not lose any weight even when it is pyrolysed at $170-185^\circ \text{C}$, shows no alteration in the elemental analyses and infrared spectra before and after heating, lend credence to the contention that the water molecule is coordinated to chromium.

In order to get further information and compare the structural behaviour in the solid state and in solution,

the electronic spectra of $(\text{NH}_4)_2[\text{CrF}_5(\text{H}_2\text{O})]$ and $\text{K}_2[\text{CrF}_5(\text{H}_2\text{O})]$ in solutions and the reflectance spectrum of $(\text{NH}_4)_2[\text{CrF}_5(\text{H}_2\text{O})]$ were recorded at ambient temperatures. The spectra show three bands at ca 15750, at ca 23500 and at ca 35050 cm^{-1} . It is expected that the electronic spectra of octahedral chromium(III) complexes should exhibit three bands owing to the transitions ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$, ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{P})$. Since that too is observed in the present cases irrespective of whether the spectrum is recorded on a solid state or in a solution, it is presumed that the pentafluoroaquochromate(III) ion, $[\text{CrF}_5(\text{H}_2\text{O})]^{2-}$ possesses an octahedral geometry and that there is no stereochemical non-rigidity of the complex species in the solid state and in solution.

The $\Delta_o(10Dq)$ values were found to occur between 15600 and 15900 cm^{-1} (vide Experimental Section) and agree with the discussion of energy levels by Fenske et al.¹⁸ The values obtained in the present case are essentially the same as that experimentally found for CrF_6^{3-} ¹⁹ suggesting that the coordination environments in both the cases are more or less similar. As the transitions are between states of the same spin multiplicity, the only Racah parameter B' has been considered of significance in the present cases. The values of B' calculated on the basis of the experimental data were found to lie between 730 and 770 cm^{-1} well below 918 cm^{-1} , the value typical for that of free Cr^{3+} ion. A reduction of B' parameter from 918 to 770-730 cm^{-1} is attributed to delocalization of the chromium electrons over molecular orbitals that encompass both chromium and fluorine orbitals indicating the covalent nature of Cr-F bonds in the compounds.

It may be concluded that the alkali metal pentafluoroaquochromates(III), $\text{A}_2[\text{CrF}_5(\text{H}_2\text{O})]$ can be synthesised directly by the reduction of CrO_3 in the presence of AF and 40% HF and that Cr^{3+} finds itself in this complex in an octahedral environment.

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Synthesis and Physicochemical Studies of Alkali Metal
Trioxyluorochromates (VI), ACrO_3F^* and Pyridinium
Trioxyluorochromate (VI), $\text{C}_5\text{H}_5\text{NH CrO}_3\text{F}^{**}$

6.1. Introduction

Chromium (VI) chemistry has been one of the areas of interest to chemists for quite a long time. One common property of chromium (VI) compounds is that they are potent oxidising agents, although kinetically they cover a very wide range¹. The halogen containing chromium (VI) compounds can be divided into two principal classes viz., (i) chromyl halides^{2,3}

* Synthesis of alkali metal trioxyluorochromates (VI), ACrO_3F has been published .

Ref: M.K.Chaudhuri, H.S.Dasgupta and N.Roy, Ind.J.Chem., **20A**, 1227 (1981).

** Synthesis of pyridinium trioxyluorochromate (VI), $\text{C}_5\text{H}_5\text{NH CrO}_3\text{F}$ constitutes a part of a paper accepted for publication in Synthesis (Stuttgart).

Ref: M.N.Bhattacharjee, M.K.Chaudhuri, H.S.Dasgupta, N.Roy and D.T. Khathing, Synthesis, in press.

and halochromates.^{2,4,5} Four chromyl halides e.g., CrO_2F_2 , CrO_2FCl , CrO_2Cl_2 and CrO_2Br_2 have been known. The main halochromate (VI) is CrO_3X^- (X = F or Cl). In the case of fluorine two more oxyfluorochromates(VI) namely, $\text{CrO}_4\text{F}^{3-}$ and $\text{CrO}_2\text{F}_4^{2-}$ are also reported.^{6,7}

The methods, currently in use, for the synthesis of alkali metal trioxyfluorochromates (VI), ACrO_3F involve either the reaction between alkali metal dichromates and hydrofluoric acid or the reaction among CrO_3 , alkali metal fluorides and hydrofluoric acid. Since an easy general and fast method is now available for the synthesis of alkali metal bifluorides, AHF_2 ⁸, it appears interesting to see whether alkali metal trioxyfluorochromates(VI), ACrO_3F could be prepared from CrO_3 and AHF_2 without the use of any hydrofluoric acid.

Very recently a lot of work has been done on the oxidation of various types of organic substrates involving the oxidising agents based on trioxychlorochromate (VI), CrO_3Cl^- .⁹⁻¹¹ It appears certain that there has been a continued and growing current interest in the development of new chromium(VI) reagents⁹⁻¹³ for the oxidation of organic substrates, particularly alcohols. Mildness of conditions of oxidations, specificity and effectiveness of a reagent appear to be the prerequisites for success. Although a large number of 'mild' oxidants have been available, many of them prove impractical, when scaling up above submolar level is desired. In view of this it was thought important to develop a new reagent which would be an efficient oxidant for organic substrates. The effectiveness of a chromium(VI) reagent can be enhanced if such a reagent contains F bonded to chromium(VI).

The aim of the present Chapter is to describe a novel method for the synthesis of alkali metal trioxyfluorochromates(VI), ACrO_3F and the synthesis of a new and

efficient oxidant, pyridinium trioxo-fluorochromate(VI), $C_5H_5NH CrO_3F$, along with their characterisation by chemical and physico-chemical methods.

6.2. Experimental Section

All chemicals used were reagent grade products. Alkali metal bifluorides were synthesised by the method developed by Chaudhuri and Chaudhury.⁸

Preparation of alkali metal bifluorides, AMF_2

In an example typical of the general procedure, powdered alkali metal carbonate, hydroxide or fluoride was dissolved in 40% hydrofluoric acid maintaining the ratio of A : HF at 1:4. To the clear solution pyridine was added slowly with constant stirring until the precipitation was complete and then allowed to settle. The white crystalline AMF_2 thus obtained was separated by decantation and washed free from hydrofluoric acid by pyridine and then the adhered pyridine was removed by washing with acetone and finally dried in vacuo.

Molar conductances were measured using a Philips PR 9500 conductivity bridge.

Infrared spectra of the compounds were recorded on a Perkin-Elmer model 125 spectrophotometer.

6.2.1. Methods of Estimation of the Constituents

Methods of estimation of chromium and fluoride were the same as those described in Chapter 4. C, H and N estimations

were made by Micro-Analytical technique (analysis were done in the Analytical laboratory of Anorganische Chemie II, Ruhr Universitaet Bochum, Postfach 102148, West Germany).

6.2.2. Synthesis of Alkali Metal Trioxyfluorochromates (VI), $ACrO_3F$

Since the methods of synthesis of alkali metal trioxyfluorochromates (VI), $ACrO_3F$, are similar only a typical method is described.

In a representative method, respective alkali metal bifluoride was dissolved in a minimum volume of water and the solution was heated on a boiling water bath for about 10 min. To the hot solution powdered CrO_3 was added with stirring, maintaining the molar ratio of $CrO_3 : AHF_2$ as 1:1. The solution was maintained hot for another 15-20 min. and then allowed to cool in a freezer. On cooling orange-yellow coloured $ACrO_3F$ ($A = NH_4, K, Rb$ or Cs) was obtained in very high yield. The compound was separated by filtration and dried in vacuo.

Ammonium Trioxyfluorochromate (VI), $(NH_4)CrO_3F$

Starting from 1.0g (10.0 mmol) CrO_3 and 0.57g (10.0 mmol) NH_4HF_2 , 0.95g (69%) ammonium trioxyfluorochromate (VI) NH_4CrO_3F was obtained.

Analysis

Found : N, 10.53% ; Cr, 38.11% and F, 13.62%. The formula NH_4CrO_3F requires : N, 10.22% ; Cr, 37.94% and F, 13.86%.

Significant infrared bands (cm^{-1}) and their assignments.

904 cm^{-1}

ν_s Cr-O

954 s	↷ as Cr-O
634 s	↷ Cr-F

Potassium Trioxyfluorochromate (VI), KCrO_3F

Synthesis of KCrO_3F was performed with 1.0g (10.0 m mol) CrO_3 and 0.78g (10.0 m mol) KHF_2 . Yield of KCrO_3F was 1.5g (92%).

Analysis

Found : K, 24.94% ; Cr, 32.88% and F, 12.32% . The formula KCrO_3F requires: K, 24.73% ; Cr, 32.89% and F, 12.02%.

Significant infrared bands (cm^{-1}) and their assignments.

905 m	↷ s Cr-O
954 s	↷ as Cr-O
634 s	↷ Cr-F

Rubidium Trioxyfluorochromate (VI), RbCrO_3F

An amount of 1.0g (10.0 m mol) CrO_3 and 1.25g (10.0 m mol) RbHF_2 gave the yield of RbCrO_3F as 1.43g (70%).

Analysis

Found: Rb, 42.08% ; Cr, 25.51% and F, 9.48% . The formula RbCrO_3F requires : Rb; 41.80%, Cr, 25.43% and F, 9.29% .

Significant infrared bands (cm^{-1}) and their assignments

905 m	↷ s Cr-O
955 s	↷ as Cr-O
634 s	↷ Cr-F

Cesium Trioxyfluorochromate (VI) CsCrO_3F

In a typical reaction 1.0g (10.0 m mol) CrO_3 was reacted with 1.72 g (10.0 m mol) CsHF_2 . The yield of cesium trioxyfluorochromate (VI) CsCrO_3F , was 1.95g(77%).

Analysis

Found : Cs, 52.91% ; Cr, 20.72% and F, 7.83%. The formula CsCrO_3F requires: Cs, 52.76% ; Cr,20.64% and F,7.54%.

Significant infrared bands (cm^{-1}) and their assignments

904 m	$\curvearrowright$ s Cr-O
953 s	$\curvearrowright$ as Cr-O
635 s	$\curvearrowright$ Cr-F

6.2.3. Synthesis of Pyridinium Trioxyfluorochromate (VI), $\text{C}_5\text{H}_5\text{NHCrO}_3\text{F}$

A quantity of 15.0 g (150 m mol) of CrO_3 was dissolved in 25 ml of water followed by the addition of 11.25 ml (225 m mol) of 40% hydrofluoric acid in a polythene beaker at room temperature with constant stirring. In about 5 min a clear orange coloured solution was obtained. A quantity of 12.3 ml (150 m mol) of pyridine was slowly added to this solution with constant stirring. The mixture was heated on a steam bath for about 15 min and then allowed to cool at room temperature for about 30-35 min and bright orange coloured crystalline pyridinium trioxyfluorochromate (VI), $\text{C}_5\text{H}_5\text{NHCrO}_3\text{F}$ was obtained. The compound was separated by filtration and pressed between the folds

of filter paper and finally dried in vacuo for about 1 h. The yield of pyridinium trioxyfluorochromate (VI), $C_5H_5NHCrO_3F$ was 27.9 g (93.5%). Pyridinium trioxyfluorochromate (VI), $C_5H_5NHCrO_3F$ (PFC) melts at 106-108°C.

Analysis

Found: Cr, 26.17% ; F, 9.58% ; C, 30.12% ; N, 6.96% and H, 3.07%. The formula $C_5H_5NHCrO_3F$ requires: Cr, 26.12% ; F, 9.54% ; C, 30.16% ; N, 7.04% and H, 3.04% .

Molar conductance (Δ_M), 128 $ohm^{-1}cm^2mol^{-1}$.

Characteristic infrared bands(cm^{-1}) and assignments

908	↘ ₁
640	↘ ₂
340	↘ ₃
952	↘ ₄
373	↘ ₅
262	↘ ₆

6.3. Results and Discussion

Alkali Metal Trioxyfluorochromates(VI), $ACrO_3F$ — The alkali metal trioxyfluorochromates(VI) are highly crystalline, orange-yellow coloured compounds. They are not very stable in moist air, but can be stored in sealed polythene bags. They are soluble in water but the dissolution is always associated with decomposition. The compounds are not soluble in common organic solvents. $ACrO_3F$ compounds attack glass in the presence of moist air.

The oxidation state of chromium in the compounds was determined iodometrically by reduction of a known amount of the compound with acidified potassium iodide

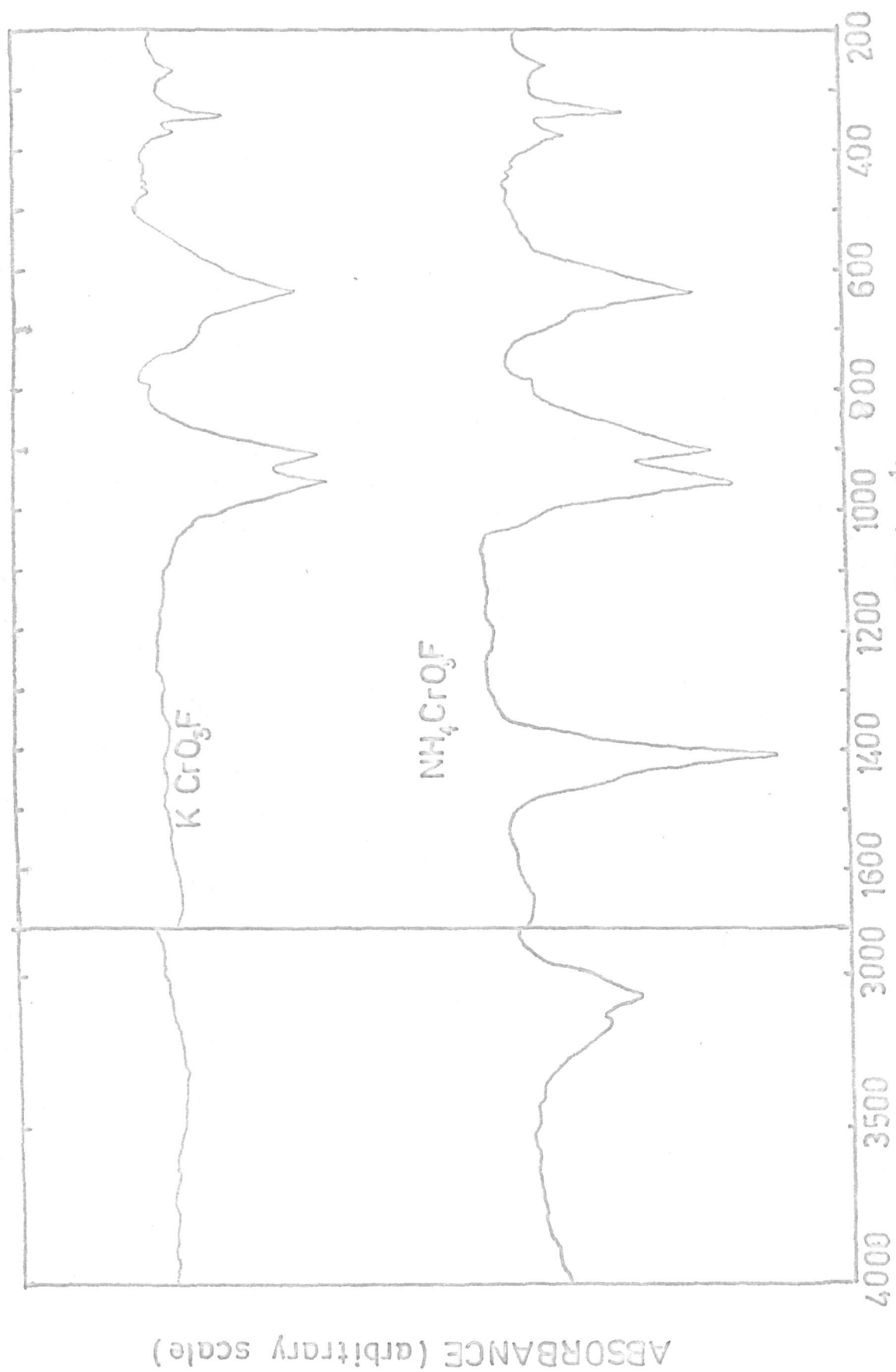


Fig: 6.1. IR spectra

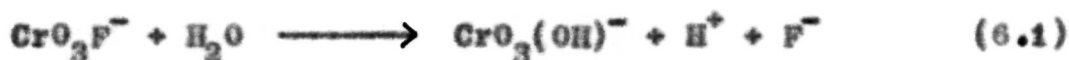
solution followed by titration of the liberated iodine with standard sodium thiosulphate solution. Chemical determination of the oxidation state of chromium in the compounds gave +6 in accord with the formula. The +6 oxidation state of chromium was further supported by the room temperature magnetic susceptibility measurements. The diamagnetic nature of the compounds conform to the +6 oxidation state of chromium in each of the compounds.

The attempts to study the molar conductances of alkali metal trioxyfluorochromates(VI), ACrO_3F were unsuccessful. The values obtained were always higher than those expected for 1:1 types of electrolytes. This shows the unstable nature of the compounds in aqueous solution.

The infrared spectra of the newly synthesised ACrO_3F compounds compare very well with each other, showing that they are identical both structurally and stoichiometrically. The spectra also resemble the spectrum of KCrO_3F reported in the literature.¹⁴ The three absorptions at ca 904 cm^{-1} , at ca 635 cm^{-1} and at ca 954 cm^{-1} respectively, may be quoted as representative of the typical spectrum of the complex ion CrO_3F^- . These absorptions have been assigned to the $\nu_{\text{as}} \text{Cr-O}$, $\nu_{\text{as}} \text{Cr-F}$ and $\nu_{\text{as}} \text{Cr-O}$ modes respectively.

The novel method, described in the present Chapter, for the synthesis of alkali metal trioxyfluorochromates (VI), ACrO_3F has an advantage that it does not require the use of hydrofluoric acid and provides a very good example of alkali metal bifluorides AHF_2 , acting as fluorinating agent. The synthesis was planned based on the concept of buffer action of alkali metal bifluorides, AHF_2 , and the concomitant presence of F^- , H^+ and A^+ ions in a solution

owing to the dissociation of AHP_2 in water. Under such a condition the solution definitely reacts acidic^{8,15,16} making the situation conducive to achieve the goal. The direct reaction between CrO_3 and alkali fluorides, AF did not appear very feasible, because of the tendency of CrO_3F^- to undergo hydrolysis giving $\text{CrO}_3(\text{OH})^-$ according to the equation:

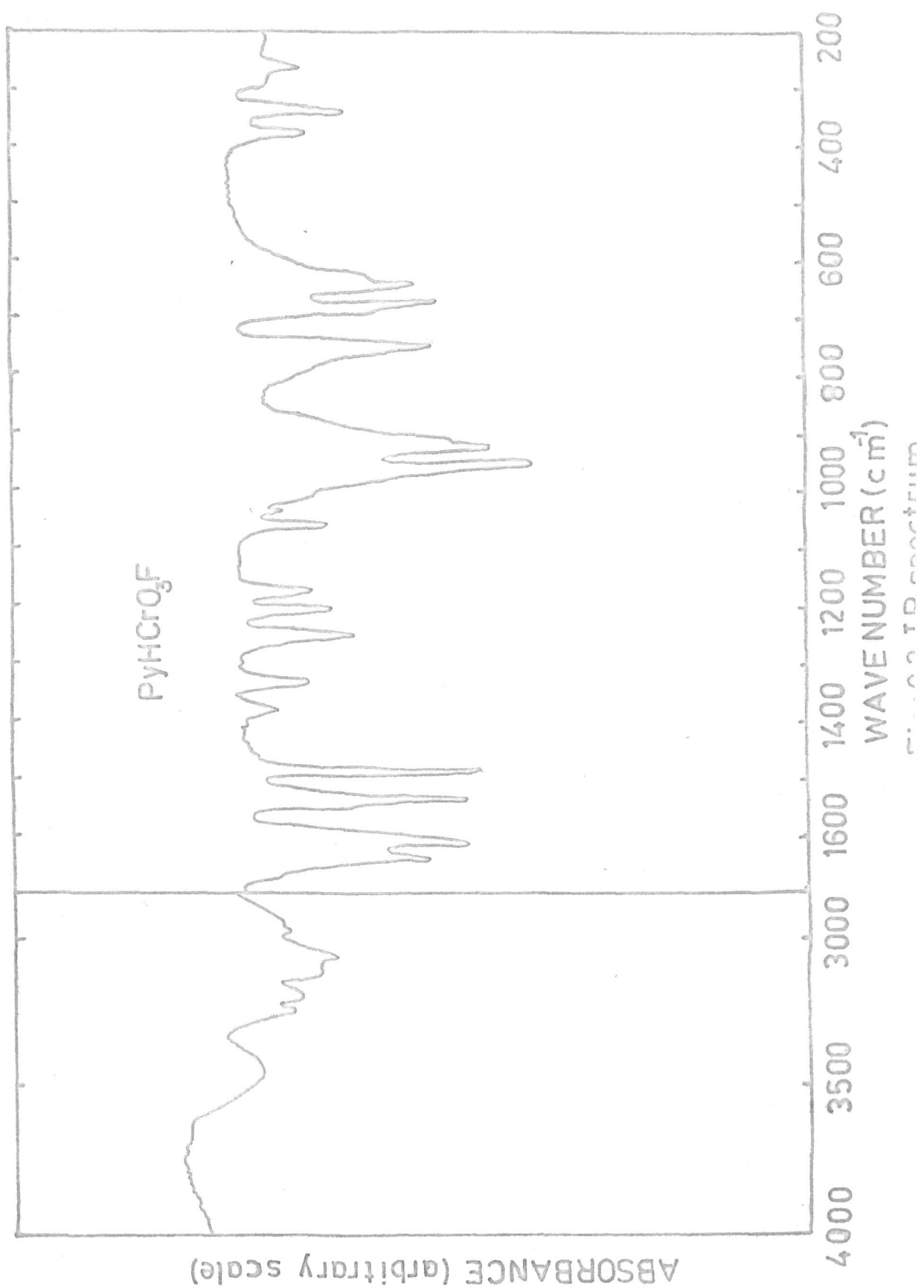


The alkali metal trioxyfluorochromates (VI), ACrO_3F decompose when heated. They react with ammonium wherein chromium (VI) is reduced to chromium (III).

Pyridinium Trioxyfluorochromate (VI), $\text{C}_5\text{H}_5\text{NHCrO}_3\text{F}$ (PFC)—

The compound pyridinium trioxyfluorochromate (VI) needs a special mention, because this was synthesised with a specific intention. It may be emphatically mentioned that PFC is easily and cheaply synthesised in very high yield (93-94%) by adding pyridine to a stirred aqueous solution of CrO_3 in 40% hydrofluoric acid maintaining the molar ratio of CrO_3 : HF : pyridine at 1:1.5 :1. The compound is orange in colour and very highly crystalline in nature. PFC can be stored in sealed polythene bag for prolonged periods and the stability and purity of the compound can be checked by periodic estimation of chromium(VI) content simply by iodometry. Pyridinium trioxyfluorochromate (VI) melts at 106-108°C.

$\text{C}_5\text{H}_5\text{NHCrO}_3\text{F}$ (PFC) is soluble in water, dimethylformamide, acetone and sparingly soluble in benzene, carbon tetrachloride, chloroform and hexane and slightly more in methylene chloride. The molar conductance, Δ_M (25°C) of a 10^{-3}M solution of PFC in water was found to be





$128 \text{ ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ suggesting the uni-uni valent electrolytic nature of the compound in accord with the formula. The observed molar conductance value also suggests the stability of the compound.

The infrared spectrum of the compound exhibits bands of $908(\nu_1)$, $640(\nu_2)$, $340(\nu_3)$, $952(\nu_4)$, $373(\nu_5)$, and $262(\nu_6) \text{ cm}^{-1}$. These bands are regarded as characteristics for the CrO_3F^- ion¹⁴. The infrared spectral studies adduce further support to the identity of the compound.

Two important properties which need mention are that (i) PFC does not react with acetonitrile, a suitable medium for studying kinetics and mechanisms of oxidation and that (ii) it has relatively less pronounced acidity. The pH of a $1 \times 10^{-2} \text{ (M)}$ solution of PFC has been found to be 2.45 whilst that of $1 \times 10^{-2} \text{ (M)}$ solution of pyridinium trioxychlorochromate(VI), $\text{C}_5\text{H}_5\text{NHCrO}_3\text{Cl}$ (PCC) has been observed to be 1.75. It appears that a less pronounced acidity of an oxidising agent is sometime preferred for certain specific type of work in organic chemistry.^{9,10}

The oxidation reactions involving the new reagent PFC, does not constitute any part of the present thesis. However, such studies have been done in collaboration with other workers and the details of the results of oxidations will be described elsewhere. The results of oxidations, thus far, appear to be extremely satisfactory and lend credence to the contention that PFC most probably will qualify as a valuable addition to the efficient oxidants available to the synthetic organic chemists and also to the present methodology.

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**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

The growing interest and extensive use of tris(acetylacetonato)chromium(III) have rendered it as an extremely important synthetic compound of chromium. The compound $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ has been used as a catalyst for polymerisation,^{1,2} oxidation,³ as a semiconductor,⁴ as an additive⁵ in rubber, plastic and paints and for chromium plating from organic solvents,⁵ and also for extraction separation of chromium from other metals.⁶⁻⁸ Nuclear magnetic resonance spectroscopy is another area where $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ finds an

* The work described in this Chapter has been accepted for publication.

Ref: M.K. Chaudhuri, N. Roy and D.T. Khathing,

Synth. React. Inorg. Met.-Org. Chem., 12, 6th Issue (1982)

extensive use as a C-13 N.m.r. chemical shift reagent for nitrogen containing aromatic compounds⁹, shift reagent for amines,¹⁰ shiftless relaxation reagent for C-13 N.m.r. of iron complexes¹¹, line shape analysis studies in N.m.r. spectroscopy¹² and also as a paramagnetic relaxation reagent in structural studies.¹³

Tris(acetylacetonato)chromium(III) has been known for more than fifty years and a number of methods of its synthesis have been reported. Some of the very early methods are cumbersome and give low yields of the product.^{14,15} The method developed to circumvent these difficulties by the homogeneous control of pH¹⁶ has the following disadvantages: (i) it is quite time consuming, (ii) the end-product obtained by the method may be contaminated by urea and its decomposition products, owing to the use of a very large excess of urea in order to control the pH, and (iii) the yield of $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ obtained by this method is lowered if the initial pH range is not maintained properly, perhaps because of the formation of hydroxoaminechromium (III) species.¹⁷⁻²⁰ Recently, in 1977 the formation of tris(acetylacetonato)-chromium (III), $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$, has been reported²¹ on the basis of a study made on a submolar level. It also appears that a small increase in acidity may contaminate the product, as implied by the isolation of the intermediate product bis(acetylacetonato)trichloroethanoatoaqueochromium-(III).²² Also the contamination of the product by trichloroethanoate which is used²¹ to control the pH, can not be ruled out. It may also be mentioned that the methods currently employed for the synthesis of $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ ^{5,16} require chromium(III) species as a starting material which needs an extra preparation and purification.

In this Chapter a novel and rapid method has been described of the synthesis of $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$. The method is

based on the concept of electron transfer reaction and does not require any buffer.

7.2. Experimental Section

All chemicals were reagent grade products.

Infrared spectrum of the compound was recorded on a Perkin-Elmer model 125 spectrophotometer.

The mass spectra of the compound were recorded on a Varian MAT CH-5 mass spectrometer. The sample was introduced into the ionisation chamber using a direct insertion probe. The operation conditions were electron energy, 70 eV ; source temperature, 50⁰C; resolution 1000; and accelerating voltage 8 kV. The mass spectrometric observations were made with the field of ionizing current sufficiently strong to trap primary ions.

7.2.1. Methods of Estimation of the Constituents

For the estimation of chromium in $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$, the compound was decomposed by treating with a small amount of very concentrated sulphuric acid. The operation was repeated several times in order to ensure complete removal of organic residue. The chromium was converted to chromium sulphate. The rest of the procedure was the same as that described in Chapter 4.

C,H estimations were accomplished by micro analytical methods.

7.2.2. Synthesis of Tris(acetylacetonato)chromium (III),
 $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$

A quantity of 2.6 g (20.0 m mol) of powdered CrO_3 was added to 20.0g (200 m mol) distilled acetylacetone with constant stirring when an exothermic reaction set in and the colour of the solution became dark violet. Stirring was continued for another 10 min after the addition was complete. The solution was then concentrated by heating over a steam-bath for about 4 h in an open beaker and subsequently cooled for about 1h in a freezer. The dark pink-violet shiny crystals of $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ was filtered off and washed several times with water and finally dried in vacuo. The yield of $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ was 6.5g (93%). The compound thus obtained was very pure and gave extremely satisfactory analysis. The compound can be recrystallised, if desired, by dissolving it in minimum volume of hot benzene followed by the addition of hot light-petroleum (b.p. 40-60°C) and then cooling at about 0°C. The yield of recrystallised tris(acetylacetonato)chromium (III), $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ was 5.8g (83%). The compound melts sharply at 216 °C. The method may be scaled up to higher quantities.

Analysis

Found: C, 51.52% ; H, 6.11% and Cr, 14.87% . The formula $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ requires: C, 51.57% ; H, 6.07% and Cr, 14.88%.

The molecular weight was found to be 349 (mass spectrometrically).

Infrared bands (cm^{-1}) and their assignments.

3060 m	$\curvearrowright$ CH
2998 m)	
2966 m)	$\curvearrowright$ CH ₃
2924 m)	

1572 w	$\nu_{\text{C}=\text{C}} + \nu_{\text{C}=\text{O}}$
1520 s	$\nu_{\text{C}=\text{O}} + \nu_{\text{C}=\text{C}}$
1447 w	$\delta_{\text{CH}} + \nu_{\text{C}=\text{C}}$
1274 m	$\nu_{\text{C}-\text{CH}_3} + \nu_{\text{C}=\text{C}}$
1166m, br	$\delta_{\text{CH}} + \nu_{\text{C}-\text{CH}_3}$
932 m	$\nu_{\text{C}=\text{C}} + \nu_{\text{C}=\text{O}}$
793 s) 774 s) 771 w)	π_{CH}
681 s	Ring mode + ν_{CrO}
660 w	π ring
599 m	Ring + ν_{CrO}
462 s	$\nu_{\text{CrO}} + \delta_{\text{C}-\text{CH}_3}$
418 w	Ring mode
360	$\nu_{\text{Cr-O}}$

Mass Spectral Data for $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$

(a) Major peaks

Assignment	m/z	Intensity (%)
$\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3^+$	349	20
$\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_2^+$	250	100
$\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_4\text{H}_4\text{O}_2)^+$	235	7
$\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)^+$	151	42
$\text{Cr}(\text{C}_4\text{H}_4\text{O}_2)^+$	136	3
Cr^+	52	4

(b) Metastable Transitions

* m/z			
Observed	Calculated	Process	Fragment lost
179.2	179.08	349 → 250	$C_5H_7O_2$
220.9	220.90	250 → 235	CH_3
97.1	97.03	235 → 151	$C_4H_4O_2$
122.5	122.49	151 → 136	CH_3

7.3. Results and Discussion

Chelating ability of acetylacetone (acacH) has long been recognised and on the basis of some very recent studies²³ on the synthesis of Mn^{+3} compounds from Mn^{+7} , its ability to act as a suitable reducing agent has also been demonstrated beyond doubt. In view of this it was thought that it might be feasible to synthesise $Cr(C_5H_7O_2)_3$ directly from CrO_3 by the action of acetylacetone. Naturally an excess of acetylacetone (acacH) has to be used such that after the red-ox reaction an appreciable amount of it must be available in the medium to act as ligands. In fact the reaction between CrO_3 and $(CH_3CO)_2CH_2(acacH)$ readily gives tris(acetylacetonato)chromium(III), $Cr(C_5H_7O_2)_3$, in extremely high yield. The method does not require any buffer but the course of the reaction is probably such that it maintains the required pH giving rise to the successful formation of the desired product. The pH of the solution, recorded immediately after the formation of $Cr(C_5H_7O_2)_3$ was found to be ~5. It is difficult to put forward the mechanism of the reaction in the absence of complete information about the oxidised products of acetylacetone.

The yield of $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$, obtained by this method is very high and the time of reaction is comparatively less than those currently used for the synthesis of tris(acetylacetonato)chromium(III). The compound melts at 216°C and is highly soluble in many organic solvents giving dark pink-violet coloured solutions. The compound has been characterised by analysing for C, H and Cr, determination of melting point and by studying its infrared and mass spectra.

The infrared spectrum of the compound (vide Experimental Section) shows the characteristics of chelated acetylacetonates (acac^-). The M-O stretching vibrations of acetylacetonato complexes of transition metals are most important since they provide direct information about the strength of the M-O bonds.²⁴⁻²⁶ The Cr-O stretching frequency was observed at 360 cm^{-1} in the present case which is in conformity with the earlier observations made by others²⁴⁻²⁶ in their infrared spectroscopic studies of such compounds. The spectrum is in full accord with those of $\text{Cr}(\text{acac})_3$ and other $\text{M}(\text{acac})_3$ reported in the literature.²⁶ This gives support to the identity of the compound.

The mass spectrum of the compound was recorded using a direct insertion probe for introducing the sample directly into the ion-chamber without any prior heating. The essential features of the mass spectra have been given in Experimental section. The spectrum recorded at 50°C shows a peak of 20% intensity at m/z 349, and has been assigned to $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3^+$ ion which is, in fact, the molecular ion peak. The fragment $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3^+$ loses one $\text{C}_5\text{H}_7\text{O}_2$ group to give $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_2^+$ ion as evidenced by the peak at m/z 250.

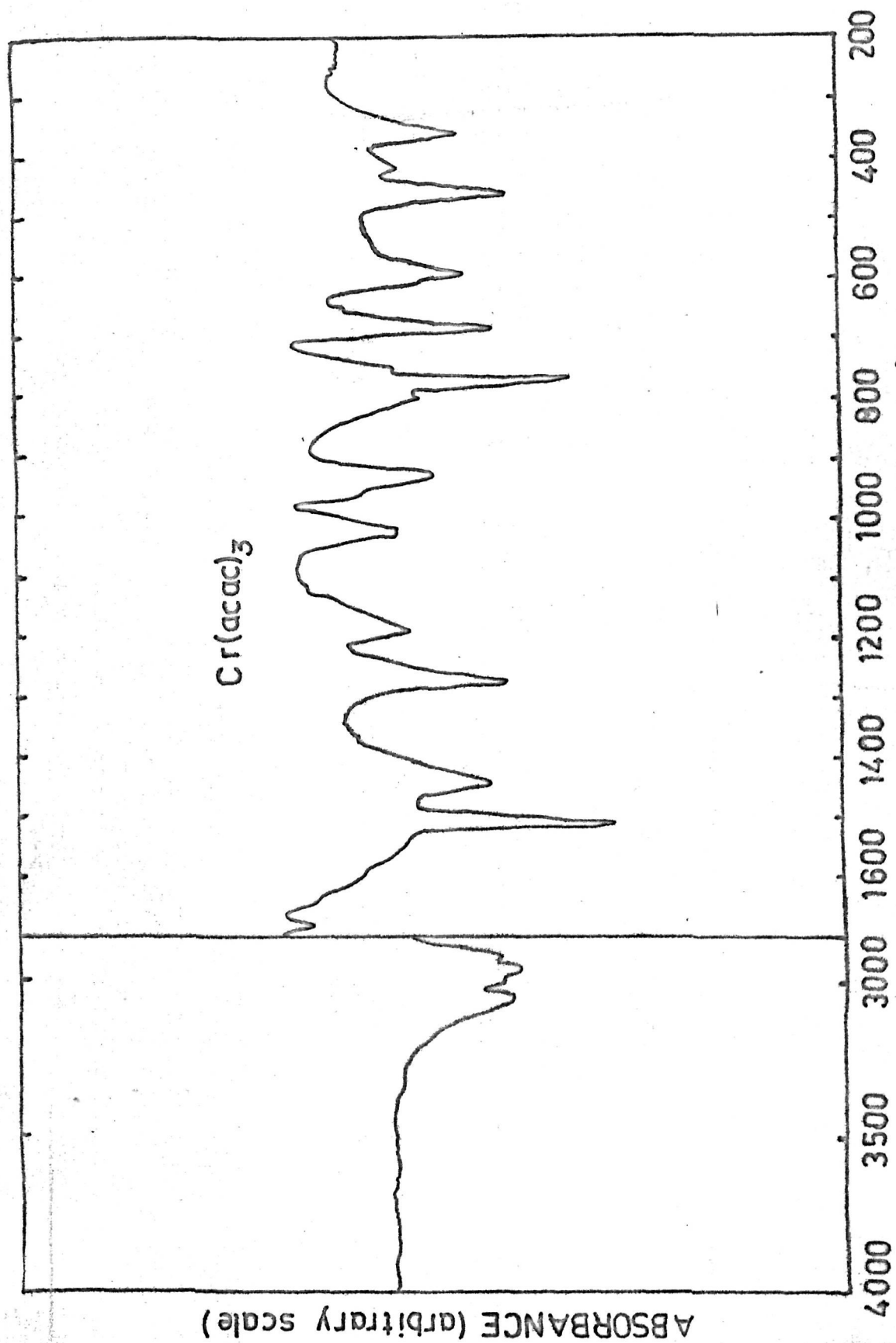
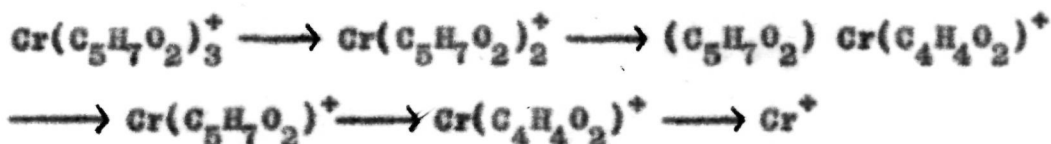


Fig: 7.1. IR spectrum

The peak at m/z 250 is the dominant peak (100%) in the spectrum of the compound. The ion $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_2^+$, however, does not undergo loss of a further $\text{C}_5\text{H}_7\text{O}_2$ group as such, instead it loses a CH_3 unit followed by the loss of $\text{C}_4\text{H}_4\text{O}_2$ to yield the fragment ion $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)^+$ at m/z 151. The ion $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)^+$ loses CH_3 unit first and then $\text{C}_4\text{H}_4\text{O}_2$ ultimately giving the bare metal ion Cr^+ . Enough metastable peaks were observed to support the transitions. In view of this, the most probable fragmentation pathway may be given as in Scheme 1.



Scheme 1

The mass spectrometric results adduce further support to the identity and purity of the compound, conform to the monomeric nature of $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ and compare very well with the reported data²⁷⁻²⁹.

It may, therefore, be concluded that tris(acetylacetonato)chromium(III), $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$, can be synthesised directly from CrO_3 without the use of any buffer. It is hoped that similar methods can be used for the synthesis of acetylacetonato compounds of other transition metals as well.

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APPENDIX

List of Publications :

1. Mass Spectrometry of Metal Compounds. Evidence of C - O Cleavage in and Effect of Temperature on the Mass Spectra of Chloropentacarbonylmanganese
- M.K. Chaudhuri , H.S. Dasgupta, N. Roy & D.T. Khathing.

Org. Mass Spectrom., 16, 303 (1981).
2. Mass Spectrometry of Metal Compounds
II - Mass Spectrometric Studies of $\left[\text{CF}_3\text{EMn}(\text{CO})_4 \right]_2$,
 $\left[\text{CF}_3\text{EFe}(\text{CO})_3 \right]_2$ (E = S, Se), $\text{CF}_3\text{SeFe}(\text{CO})_2\text{C}_5\text{H}_5$ and
 $\text{CF}_3\text{SCr}(\text{NO})_2\text{C}_5\text{H}_5$ --- M.K. Chaudhuri, H.S. Dasgupta,
N. Roy and D.T. Khathing.

Org. Mass Spectrom., 16, 534 (1981).
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Mass Spectrometry of Metal Compounds. Evidence of C—O Cleavage in and Effect of Temperature on the Mass Spectra of Chloropentacarbonylmanganese

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The mass spectrum of $\text{Mn}(\text{CO})_5\text{Cl}$ has been studied at 70 eV and at varying inlet temperatures of 20–250 °C. Like the heavier metal carbonyl derivatives, $\text{Mn}(\text{CO})_5\text{Cl}$ exhibits peaks due to carbido fragments. The spectrum run at 100 °C shows the characteristic pattern of $\text{Mn}_2(\text{CO})_{10}$ which originates from the formation and recombination of the $\text{Mn}(\text{CO})_5$ radical. The spectral pattern changes further at an elevated temperature (250 °C) showing the formation of $\text{Mn}_2(\text{CO})_8\text{Cl}_2$. The effect of pyrolysis has been discussed.

INTRODUCTION

Mass spectrometry has been well accepted as an important physical tool in the field of transition metal carbonyl and organometallic chemistry. In the course of an extended investigation into the behaviour of various substituted metal carbonyl derivatives under electron impact (EI),^{1,2} we studied the mass spectra of $\text{Mn}(\text{CO})_5\text{Cl}$. Some results of mass spectral investigations of this compound have been reported in the literature;^{3–5} two simultaneous and parallel fragmentation patterns, one involving rupture of the Mn—Cl bond followed by stepwise losses of CO groups and the other involving retention of the Mn—Cl bond with stepwise losses of CO groups were observed. The present work reports the results of EI studies on chloropentacarbonylmanganese, $\text{Mn}(\text{CO})_5\text{Cl}$, at varying inlet temperatures, of special significance regarding both metal–carbon and carbon–oxygen bonding, and also the effect of temperature on the mode of EI induced fragmentation.

EXPERIMENTAL

Chloropentacarbonylmanganese, $\text{Mn}(\text{CO})_5\text{Cl}$, was prepared by the method described by Chaudhuri⁶ and recrystallized before use. The mass spectra were run on a Varian MAT CH-5 mass spectrometer. The operating conditions were 70 eV electron energy, 20–250 °C inlet temperature, resolution of 1000 and 8 kV accelerating voltage.

The mass spectrum is given in Table 1 together with metastable ion data. The observations were made with

Table 1. Mass spectra of $\text{Mn}(\text{CO})_5\text{Cl}$

Assignments	m/z	Intensity (%)
$[\text{Mn}(\text{CO})_5\text{Cl}]^+$	230	24.6
$[\text{Mn}(\text{CO})_4\text{CCl}]^+$	214	1.5
$[\text{Mn}(\text{CO})_4\text{Cl}]^+$	202	0
$[\text{Mn}(\text{CO})_5]^+$	195	11.2
$[\text{Mn}(\text{CO})_3\text{Cl}]^+$	174	14.8
$[\text{Mn}(\text{CO})_4]^+$	167	4.5
$[\text{Mn}(\text{CO})_2\text{Cl}]^+$	146	34.9
$[\text{Mn}(\text{CO})_3]^+$	139	6.1
$[\text{Mn}(\text{CO})\text{Cl}]^+$	118	27.6
$[\text{Mn}(\text{CO})_2]^+$	111	15.8
$[\text{MnCCl}]^+$	102	2.7
$[\text{Mn}(\text{CO})\text{C}]^+$	95	2.9
$[\text{MnCl}]^+$	90	47.1
$[\text{Mn}(\text{CO})]^+$	83	26.3
$[\text{MnC}_2]^+$	79	0.8
$[\text{MnC}]^+$	67	12.6
$[\text{Mn}]^+$	55	88.7
$[\text{CO}]^+$	28	100

Metastable transitions in the mass spectrum of $\text{Mn}(\text{CO})_5\text{Cl}$

m/z*		Process	Neutral fragment lost
Observed	Calculated		
165.3	165.32	230 → 195	Cl
143.1	143.02	195 → 167	CO
115.6	115.69	167 → 139	CO
88.7	88.64	139 → 111	CO
62.1	62.06	111 → 83	CO
54.1	54.08	83 → 67	O
36.5	36.44	83 → 55	CO
131.6	131.63	230 → 174	2 CO
122.5	122.50	174 → 146	CO
95.5	95.36	146 → 118	CO
88.1	88.16	118 → 102	O
68.6	68.64	118 → 90	CO
111.2	111.04	174 → 139	Cl
84.5	84.39	146 → 111	Cl
58.4	58.38	118 → 83	Cl
33.6	33.61	90 → 55	Cl

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the field of the ionizing electron current strong enough to trap primary ions. The effect of temperature on the EI induced fragmentation pattern was studied.

RESULTS AND DISCUSSION

Table 1 presents the essential features of the mass spectrum of $\text{Mn}(\text{CO})_5\text{Cl}$. It was observed in the present studies, in accord with the report of Edgar *et al.*,⁴ that the spectrum measured at low temperature shows the molecular ion peak at m/z 230. The molecular ion undergoes EI induced fragmentation by two different pathways as shown in Scheme 1.

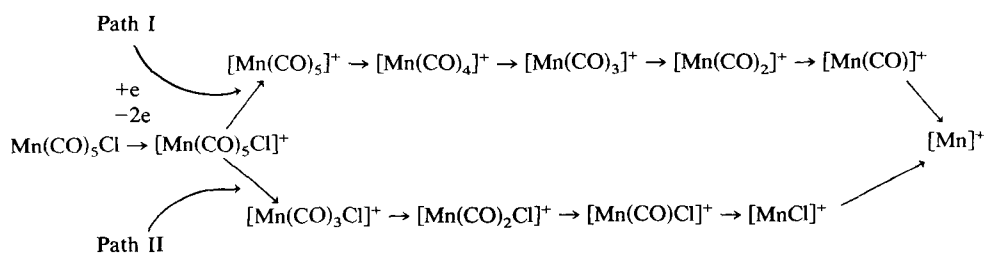
Metastable peaks supporting both the pathways from the molecular ion down to the bare metal ion $[\text{Mn}]^+$ were observed in the spectrum of $\text{Mn}(\text{CO})_5\text{Cl}$, suggesting that the fission of the Mn—Cl and Mn—CO bonds compete effectively, making both paths equally probable. A notable feature of the spectrum was the appearance of peaks at m/z 67, 79, 95, 102 and 214. These peaks have been attributed to the carbido fragments $[\text{MnC}]^+$, $[\text{MnC}_2]^+$, $[\text{Mn}(\text{CO})\text{C}]^+$, $[\text{MnCCl}]^+$ and $[\text{Mn}(\text{CO})_4\text{CCl}]^+$, respectively. Such observations definitely suggest that, like heavier metal carbonyl derivatives,^{7,8} the lighter ones may also undergo appreciable C—O bond fission. So far as we are aware, there is no definite report in literature on the loss of O from the lighter metal carbonyl derivatives. To obtain further support for these assignments, metastable transitions relating to these particular peaks were also investigated. However, the weak nature of the peaks for these fragments precluded the observation of sufficient metastables, but the metastable peaks at m/z 88.1 and 54.1 support the transitions $[\text{Mn}(\text{CO})\text{Cl}]^+ \rightarrow [\text{MnCCl}]^+ + \text{O}$ and $[\text{Mn}(\text{CO})]^+ \rightarrow [\text{MnC}]^+ + \text{O}$.

An assessment of the various chlorine-containing fragments was made by checking the chlorine isotopic ratios in the absence of any interference from manganese. The ratio $[M+2]/[M]$ for a given fragment containing one chlorine atom should be 0.32. The values of this ratio in the present case appeared to be 0.30 or 0.31, lending additional support to the suggested fragmentation scheme.

In an attempt to assess the significance of pyrolysis in the mass spectrum of $\text{Mn}(\text{CO})_5\text{Cl}$, the spectrum of the compound was studied at temperatures of 20 °C,

50 °C, 90 °C, 100 °C and 250 °C respectively, maintaining 70 eV as the electron energy. The mass spectra run at 20 °C, 50 °C and 90 °C were essentially similar, but the spectral pattern changed at 100 °C exhibiting a new peak at m/z 390 due to $\text{Mn}_2(\text{CO})_{10}$. The typical spectral pattern conforms to that of $\text{Mn}_2(\text{CO})_{10}$. An identical observation was also made by Svec and Junk.⁹ It is generally believed that $\text{Mn}(\text{CO})_5\text{Cl}$ forms $\text{Mn}(\text{CO})_5$ radicals even at lower temperatures. However, at 100 °C the optimum concentration is reached such that the recombination through radical coupling gives rise to $\text{Mn}_2(\text{CO})_{10}$. Such formation and recombination of manganese pentacarbonyl radical has also been observed previously by us in a photoinduced reaction.⁶ At 250 °C the spectrum revealed some very important differences. The most notable was the disappearance of the ion $[\text{Mn}(\text{CO})_5\text{Cl}]^+$ (m/z 230) and most of the other $[\text{Mn}(\text{CO})_x\text{Cl}]^+$ ($x < 5$) ions, and appearance of a peak at m/z 404. The ratio $[M+2]/[M]$ for m/z 404 was 0.62, suggesting the presence of two Cl atoms in the fragment. Accordingly the peak was assigned the elemental composition $\text{Mn}_2(\text{CO})_8\text{Cl}_2$. A compound of such composition is known and its mass spectrum has also been reported.⁴ It is believed that the formation of $\text{Mn}_2(\text{CO})_8\text{Cl}_2$ in the present case may be either (i) through the dimerization of $\text{Mn}(\text{CO})_5\text{Cl}$ with a simultaneous loss of two CO molecules giving rise to $\text{Mn}_2(\text{CO})_8\text{Cl}_2$, which on ionization gives rise to peak at m/z 404; or (ii) an ion/molecule interaction between $\text{Mn}(\text{CO})_5\text{Cl}$ and $[\text{Mn}(\text{CO})_3\text{Cl}]^+$ with simultaneous transfer of a CO group from one Mn to the other leading to the formation of $[\text{Mn}_2(\text{CO})_8\text{Cl}_2]^+$.

It has been observed that the intensity of various carbido fragments increases with decreasing m/z values. This is presumably because of the increased metal to CO π -bonding between a particular metal having a low formal oxidation state and a smaller number of CO groups. Since the carbon valency has to be maintained at four the increased π back donation increases the M—C bond order with a simultaneous decrease in that of C—O, making the C—O bond relatively more susceptible to increased temperature compared with the M—C bond. Finally, it may be stated that like heavier metal carbonyl derivatives, the lighter metal carbonyl derivatives may also exhibit carbon-oxygen bond fission, and very high temperature can change the EI induced fragmentation pattern.



Scheme 1

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Mass Spectrometry of Metal Compounds

II—Mass Spectrometric Studies of $[\text{CF}_3\text{EMn}(\text{CO})_4]_2$, $[\text{CF}_3\text{EFe}(\text{CO})_3]_2$ ($\text{E} = \text{S}, \text{Se}$), $\text{CF}_3\text{SeFe}(\text{CO})_2\text{C}_5\text{H}_5$ and $\text{CF}_3\text{SCr}(\text{NO})_2\text{C}_5\text{H}_5$

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The electron impact induced mass spectra of $[\text{CF}_3\text{SMn}(\text{CO})_4]_2$, $[\text{CF}_3\text{SeMn}(\text{CO})_4]_2$, $[\text{CF}_3\text{SFe}(\text{CO})_3]_2$, $[\text{CF}_3\text{SeFe}(\text{CO})_3]_2$, $\text{CF}_3\text{SeFe}(\text{CO})_2\text{C}_5\text{H}_5$ and $\text{CF}_3\text{SCr}(\text{NO})_2\text{C}_5\text{H}_5$ are reported. These compounds exhibit weak molecular ion peaks and undergo preferential loss of CO or NO groups. The CO or NO free fragments suffer typical loss of ECF_2 ($\text{E} = \text{S}, \text{Se}$) with the simultaneous shift of F from carbon to metal. The ions $[\text{FFeC}_5\text{H}_5]^+$ and $[\text{FCrC}_5\text{H}_5]^+$ in the spectra of the cyclopentadienyl compounds prefer expulsion of π -cyclopentadienyls. The pyrolysis effects on the spectra of the compounds have been studied. An increase in temperature eases the expulsion of ECF_2 groups from all the compounds and favors the formation of $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+$ and $[\text{Cr}(\text{C}_5\text{H}_5)_2]^+$ in the cyclopentadienyl compounds.

INTRODUCTION

Although a number of fluorinated organosulfur and organoselenium derivatives of metal carbonyls and cyclopentadienyl metal carbonyls or nitrosyls have been synthesized in recent years,¹⁻¹¹ the mass spectral studies of such compounds have received less attention to date. It may be noted that the mass spectra of CH_3S derivatives of metal carbonyls¹² showed loss of the CH_3 group with cleavage of the S—C bond from the CO free fragments. In continuation of our studies on electron impact (EI) induced mass spectra of inorganic compounds^{13,14} it was thought important to investigate the mass spectra of CF_3S and CF_3Se derivatives of metal carbonyls and substituted metal carbonyls or nitrosyls. This paper describes the mass spectra of a series of CF_3S and CF_3Se compounds of manganese, iron and chromium.

EXPERIMENTAL

Compounds $[\text{CF}_3\text{SMn}(\text{CO})_4]_2$ (1), $[\text{CF}_3\text{SeMn}(\text{CO})_4]_2$ (2), $[\text{CF}_3\text{SFe}(\text{CO})_3]_2$ (3), $[\text{CF}_3\text{SeFe}(\text{CO})_3]_2$ (4), $\text{CF}_3\text{SeFe}(\text{CO})_2\text{C}_5\text{H}_5$ (5) and $\text{CF}_3\text{SCr}(\text{NO})_2\text{C}_5\text{H}_5$ (6) were prepared by literature methods^{11,9,7} and purified by recrystallization before use. The mass spectra were run on a Varian MAT CH-5 mass spectrometer. The experimental conditions were the same as described previously.¹⁴

The mass spectra and the experimentally observed metastable transitions are presented in Tables I-4.

The observations were made with the field of the ionizing current strong enough to trap primary ions. The effect of temperature on the EI induced fragmentation was studied with allowance being made for pyrolysis reactions taking place in the ion source.

RESULTS AND DISCUSSION

$[\text{CF}_3\text{SMn}(\text{CO})_4]_2$ (1) and $[\text{CF}_3\text{SeMn}(\text{CO})_4]_2$ (2)

The mass spectra of 1 and 2 exhibit weak molecular ion peaks at m/z 536 and 632 (Table 1). Each of the molecular ions loses three CO groups in a single step leading to $[(\text{CF}_3\text{E})_2\text{Mn}_2(\text{CO})_5]^+$ ($\text{E} = \text{S}, \text{Se}$), which subsequently loses one CO group followed by loss of an ECF_2 unit with the simultaneous shift of F from carbon to metal giving $[\text{CF}_3\text{EMn}_2(\text{CO})_4\text{F}]^+$. This fragment loses four CO groups in steps, however, followed by the expulsion of the second ECF_2 unit to yield $[\text{Mn}_2\text{F}_2]^+$ ion which undergoes successive losses of F atoms giving $[\text{Mn}_2]^+$, which finally fragments to $[\text{Mn}]^+$.

The signals at m/z 161 and 209 in the spectra of 1 and 2 due to $[\text{Mn}_2\text{SF}]^+$ and $[\text{Mn}_2\text{SeF}]^+$ indicate the loss of CF_3 through the rupture of S—C or Se—C bonds. However, this could not be supported by the metastable transitions, precluding any significance of such a process. Thus, unlike the CH_3S derivatives of metal carbonyls which show preferential losses of CO groups followed by that of CH_3 through rupture of the S—C bond, the corresponding CF_3S or CF_3Se compounds exhibit loss of SCF_3 or SeCF_3 with the simultaneous shift of F from carbon to metal. This is presumably favoured by the formation of a new bond

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Table 1. Mass spectra of $[(CF_3E)Mn(CO)_4]_2$ (E = S, Se) complexes

Assignments	E = S			E = Se		
	m/z	Intensity (%)	M + 2/M	m/z	Intensity (%)	M + 2/M
$[(CF_3E)_2Mn_2(CO)_8]^+$	536	4.5	0.089	632	5.1	0.97
$[(CF_3E)_2Mn_2(CO)_5]^+$	452	28.3	0.093	548	26.5	0.98
$[(CF_3E)_2Mn_2(CO)_4]^+$	424	31.5	0.091	520	33.8	0.95
$[(CF_3E)Mn_2F(CO)_3]^+$	314	44.9	0.046	362	48.6	0.49
$[(CF_3E)Mn_2F(CO)_2]^+$	286	35.6	0.047	334	33.2	0.48
$[(CF_3E)Mn_2F(CO)]^+$	258	29.8	0.045	306	28.7	0.47
$[(CF_3E)Mn_2F]^+$	230	49.8	0.046	278	48.2	0.51
$[Mn_2F_2]^+$	148	58.7	—	148	59.1	—
$[Mn_2F]^+$	129	53.2	—	129	52.3	—
$[Mn_2]^+$	110	50.3	—	110	51.1	—
$[Mn]^+$	55	65.8	—	55	66.9	—
$[ECF_2]^+$	82	71.5	0.045	130	74.8	0.48
$[CO]^+$	28	100	—	28	100	—

Metastable transitions in the mass spectra of $[(CF_3E)Mn(CO)_4]_2$

m/z*		Process	Neutral fragment lost
(S)	(Se)		
381.2	475.2	$[(CF_3E)_2Mn_2(CO)_8]^+ \rightarrow [(CF_3E)_2Mn_2(CO)_5]^+$	3CO
397.8	493.5	$[(CF_3E)_2Mn_2(CO)_5]^+ \rightarrow [(CF_3E)_2Mn_2(CO)_4]^+$	CO
275.9	292.5	$[(CF_3E)_2Mn_2(CO)_4]^+ \rightarrow [(CF_3E)Mn_2F(CO)_4]^+$	ECF ₂
288.3	336.0	$[(CF_3E)Mn_2F(CO)_4]^+ \rightarrow [(CF_3E)Mn_2F(CO)_3]^+$	CO
260.5	308.2	$[(CF_3E)Mn_2F(CO)_3]^+ \rightarrow [(CF_3E)Mn_2F(CO)_2]^+$	CO
232.8	280.4	$[(CF_3E)Mn_2F(CO)_2]^+ \rightarrow [(CF_3E)Mn_2F(CO)]^+$	CO
205.0	252.6	$[(CF_3E)Mn_2F(CO)]^+ \rightarrow [(CF_3E)Mn_2F]^+$	CO
95.2	78.8	$[(CF_3E)Mn_2F]^+ \rightarrow [Mn_2F_2]^+$	ECF ₂
112.5	112.5	$[Mn_2F_2]^+ \rightarrow [Mn_2F]^+$	F
93.8	93.8	$[Mn_2F]^+ \rightarrow [Mn_2]^+$	F
27.5	27.5	$[Mn_2]^+ \rightarrow [Mn]^+$	Mn

Table 2. Mass spectra of $[(CF_3E)Fe(CO)_5]_2$ (E = S, Se) complexes

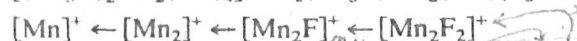
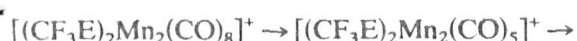
Assignments	E = S				E = Se	
	m/z	Intensity (%)	M + 2/M	M + 2/M	m/z	Intensity (%)
$[(CF_3E)_2Fe_2(CO)_6]^+$	482	6.8	0.13	0.115	578	5.8
$[(CF_3E)_2Fe_2(CO)_5]^+$	454	15.6	0.11	0.118	550	20.1
$[(CF_3E)_2Fe_2(CO)_4]^+$	426	11.7	0.13	0.117	522	10.7
$[(CF_3E)_2Fe_2(CO)_3]^+$	398	8.6	0.13	0.114	494	6.7
$[(CF_3E)_2Fe_2(CO)_2]^+$	370	20.1	0.12	0.116	466	25.6
$[(CF_3E)_2Fe_2(CO)]^+$	342	14.8	0.11	0.115	438	17.1
$[(CF_3E)_2Fe_2]^+$	314	60.6	0.12	0.114	410	12.6
$[(CF_3E)Fe_2F]^+$	232	12.7	0.12	0.046	280	5.6
$[Fe_2F_2]^+$	150	72.5	0.12		150	73.3
$[Fe_2]^+$	112	41.2	0.12		112	60.2
$[Fe]^+$	56	58.7	0.06		56	52.6
$[ECF_2]^+$	82	61.2		0.045	130	69.3
$[Fe_2F_2]^{2+}$	75	12.8	0.12		75	11.2

Metastable transitions in the mass spectra of $[(CF_3E)Fe(CO)_5]_2$

m/z*		Process	Neutral fragment lost
(S)	(Se)		
427.7	523.4	$[(CF_3E)_2Fe_2(CO)_6]^+ \rightarrow [(CF_3E)_2Fe_2(CO)_5]^+$	CO
399.7	495.4	$[(CF_3E)_2Fe_2(CO)_5]^+ \rightarrow [(CF_3E)_2Fe_2(CO)_4]^+$	CO
371.9	467.5	$[(CF_3E)_2Fe_2(CO)_4]^+ \rightarrow [(CF_3E)_2Fe_2(CO)_3]^+$	CO
343.9	439.6	$[(CF_3E)_2Fe_2(CO)_3]^+ \rightarrow [(CF_3E)_2Fe_2(CO)_2]^+$	CO
316.3	411.8	$[(CF_3E)_2Fe_2(CO)_2]^+ \rightarrow [(CF_3E)_2Fe_2(CO)]^+$	CO
288.2	383.7	$[(CF_3E)_2Fe_2(CO)]^+ \rightarrow [(CF_3E)_2Fe_2]^+$	CO
171.4	191.3	$[(CF_3E)_2Fe_2]^+ \rightarrow [(CF_3E)Fe_2F]^+$	ECF ₂
96.9	80.3	$[(CF_3E)Fe_2F]^+ \rightarrow [Fe_2F_2]^+$	ECF ₂
83.6	83.6	$[Fe_2F_2]^+ \rightarrow [Fe_2]^+$	F ₂

between an electropositive metal atom and F through the interaction of non-bonding p-orbitals of F with the vacant orbitals on the metal atom, expelling an SCF_2 or SeCF_2 group, ionization of which gives strong signals at m/z 82 or 130 (Table 1) respectively.

In order to study the effect of pyrolysis on the expulsion of ECF_2 ($\text{E} = \text{S, Se}$) from $[(\text{CF}_3\text{E})\text{Mn}_2\text{F}]^+$, the spectra were run at 100°C . This showed that the intensity of the signal at m/z 148, due to $[\text{Mn}_2\text{F}_2]^+$ was increased from $\sim 59\%$ to $\sim 78\%$ and that those signals at m/z 230 in the spectrum of **1** and at m/z 278 in the spectrum of **2** decreased from $\sim 49\%$ to $\sim 23\%$, suggesting that pyrolysis plays an important role in the formation of ECF_2 . It may be mentioned that SeCF_2 has been prepared for the first time by Haas *et al.*¹⁵ by pyrolysing $\text{B}(\text{SeCF}_3)_3$. The most probable fragmentation pattern of $(\text{CF}_3\text{E})_2\text{Mn}_2(\text{CO})_8$ may be as shown in Scheme 1.



Scheme 1

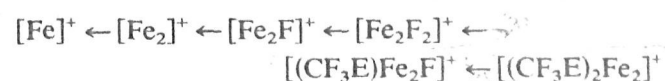
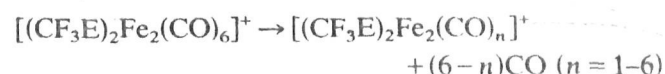
All transitions from the molecular ion down to the basic $[\text{Mn}]^+$ ion have been supported by the appropriate metastables (Table 1). Assignments of various S and Se containing fragments have been verified using the ratios $M+2/M$ and $M-2/M$ respectively, where $M+2$ is the intensity of the peak two mass units more and $M-2$ is that of two mass units less than the most abundant ion of a given elemental composition M , and arise from the substitution of ^{34}S for ^{32}S and ^{78}Se for ^{80}Se . These tests give strong credence to Scheme 1.

$[\text{CF}_3\text{SFe}(\text{CO})_3]_2$ (**3**) and $[\text{CF}_3\text{SeFe}(\text{CO})_3]_2$ (**4**)

Table 2 presents the mass spectra of **3** and **4**. The compounds show weak signals due to molecular ions

at m/z 482 and 578 respectively. Unlike **1** and **2**, compounds **3** and **4** undergo preferential losses of six CO groups in steps, followed by the successive losses of ECF_2 units with the simultaneous shift of F atoms from carbon to metal. The ions at m/z at 150 in the spectra of **3** and **4** have been assigned to $[\text{Fe}_2\text{F}_2]^+$ since the dipositive ion at m/z 75 due to $[\text{Fe}_2\text{F}_2]^{2+}$ and a signal at m/z 112 due to $[\text{Fe}_2]^+$ occur. The formation of $[\text{Fe}_2\text{F}_2]^{2+}$ and $[\text{Fe}_2]^+$ indicates iron-iron bonding in **3** and **4**.

The spectra of **3** and **4** exhibit not only the metastable peaks at m/z 71.6 and 54.8, representing the degradation $[(\text{CF}_3\text{E})_2\text{Fe}_2]^+ \rightarrow [\text{Fe}_2\text{F}_2]^+$, but also enough metastables to permit elucidation of the fragmentation as depicted in Scheme 2.



Scheme 2

Further support for Scheme 2 was obtained by making an assessment of the number of Fe and S atoms in a given fragment of $(\text{CF}_3\text{S})_2\text{Fe}_2(\text{CO})_6$ (**3**) from the ratios $M-2/M$ and $M+2/M$ respectively, in a manner analogous to those discussed above. Similar checks could not be made in the case of **4**, however, because of higher order interference between Fe and Se isotopes.

The fact that the spectra of the compounds **3** and **4** run at 100°C show an increase in the intensity of the signal of the $[\text{Fe}_2\text{F}_2]^+$ ion from $\sim 73\%$ to $\sim 96\%$, suggests that the high temperature facilitates the loss of ECF_2 ($\text{E} = \text{S, Se}$).

$\text{CF}_3\text{SeFe}(\text{CO})_2\text{C}_5\text{H}_5$ (**5**) and $\text{CF}_3\text{SCr}(\text{NO})_2\text{C}_5\text{H}_5$ (**6**)

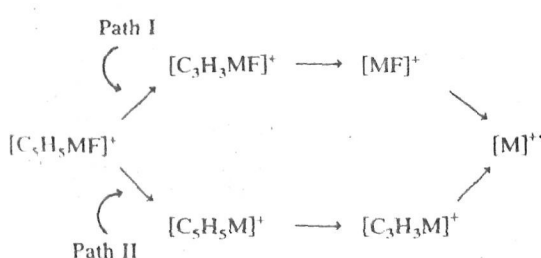
Tables 3 and 4 list the essential features of the mass spectra of **5** and **6**. The salient aspects of these spectra

Table 3. Mass spectra of $\text{CF}_3\text{SeFe}(\text{CO})_2\text{C}_5\text{H}_5$

Assignments	m/z	Intensity (%)	Metastable transitions		Neutral fragment lost
			m/z^*	Process	
$[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SeCF}_3]^+$	326	5.6			
$[\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{SeCF}_3]^+$	298	42.1	372.6	$[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SeCF}_3]^+ \rightarrow [\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{SeCF}_3]^+$	CO
$[\text{C}_5\text{H}_5\text{FeSeCF}_3]^+$	270	28.1	244.6	$[\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{SeCF}_3]^+ \rightarrow [\text{C}_5\text{H}_5\text{FeSeCF}_3]^+$	CO
$[\text{C}_5\text{H}_5\text{FeF}]^+$	140	92.7	72.7	$[\text{C}_5\text{H}_5\text{FeSeCF}_3]^+ \rightarrow [\text{C}_5\text{H}_5\text{FeF}]^+$	SeCF_2
$[\text{C}_5\text{H}_5\text{Fe}]^+$	121	6.2	104.6	$[\text{C}_5\text{H}_5\text{FeF}]^+ \rightarrow [\text{C}_5\text{H}_5\text{Fe}]^+$	F
$[\text{C}_3\text{H}_3\text{Fe}]^+$	95	20.3	74.6	$[\text{C}_5\text{H}_5\text{Fe}]^+ \rightarrow [\text{C}_3\text{H}_3\text{Fe}]^+$	C_2H_2
$[\text{Fe}]^+$	56	23.8	33.0	$[\text{C}_3\text{H}_3\text{Fe}]^+ \rightarrow [\text{Fe}]^+$	C_3H_3
$[\text{CO}]^+$	28	100			
$[(\text{C}_5\text{H}_5)_2\text{Fe}]^+$	186	7.9			
$[\text{C}_5\text{H}_5\text{FeC}_3\text{H}_3]^+$	160	38.7			
$[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]^+$	177	18.2	90.2	$[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SeCF}_3]^+ \rightarrow [\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]^+$	SeCF_3
$[\text{C}_5\text{H}_5\text{Fe}(\text{CO})]^+$	149	12.1			
$[\text{SeCF}_2]^+$	130	78.9			
$[\text{FFeC}_3\text{H}_3]^+$	114	63.2	92.8	$[\text{FFeC}_5\text{H}_5]^+ \rightarrow [\text{FFeC}_3\text{H}_3]^+$	C_2H_2
$[\text{FFe}]^+$	75	59.2	49.3	$[\text{FFeC}_3\text{H}_3]^+ \rightarrow [\text{FFe}]^+$	C_3H_3
$[\text{Fe}]^+$	56	23.8	41.9	$[\text{FFe}]^+ \rightarrow [\text{Fe}]^+$	F

Table 4. Mass spectra of $\text{CF}_3\text{SCr}(\text{NO})_2\text{C}_5\text{H}_5$

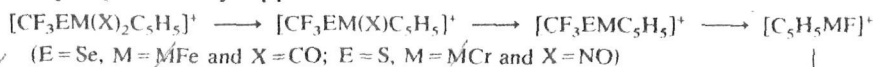
Assignments	m/z	Intensity (%)	Metastable transitions		Neutral fragment lost
			m/z	Process	
$[\text{CF}_3\text{SCr}(\text{NO})_2\text{C}_5\text{H}_5]^+$	278	7.2			
$[\text{CF}_3\text{SCr}(\text{NO})\text{C}_5\text{H}_5]^+$	248	52.5	221.2	$[\text{CF}_3\text{SCr}(\text{NO})_2\text{C}_5\text{H}_5]^+ \rightarrow [\text{CF}_3\text{SCr}(\text{NO})\text{C}_5\text{H}_5]^+$	NO
$[\text{CF}_3\text{SCrC}_5\text{H}_5]^+$	218	49.6	191.6	$[\text{CF}_3\text{SCr}(\text{NO})\text{C}_5\text{H}_5]^+ \rightarrow [\text{CF}_3\text{SCrC}_5\text{H}_5]^+$	NO
$[\text{FCrC}_5\text{H}_5]^+$	136	35.8	84.8	$[\text{CF}_3\text{SCrC}_5\text{H}_5]^+ \rightarrow [\text{FCrC}_5\text{H}_5]^+$	SCF_2
$[\text{FCr}]^+$	71	66.3	37.1	$[\text{FCrC}_5\text{H}_5]^+ \rightarrow [\text{FCr}]^+$	C_5H_5
$[\text{Cr}]^+$	52	68.2	38.1	$[\text{FCr}]^+ \rightarrow [\text{Cr}]^+$	F
$[\text{SCF}_2]^+$	82	89.3			
$[\text{NO}]^+$	30	100			
$[\text{CrC}_5\text{H}_5]^+$	117	15.4	100.6	$[\text{FCrC}_5\text{H}_5]^+ \rightarrow [\text{CrC}_5\text{H}_5]^+$	F
$[\text{C}_5\text{H}_5\text{Cr}(\text{NO})_2]^+$	177	28.9	112.7	$[\text{CF}_3\text{SCr}(\text{NO})_2\text{C}_5\text{H}_5]^+ \rightarrow [\text{C}_5\text{H}_5\text{Cr}(\text{NO})_2]^+$	SCF_3
$[\text{C}_5\text{H}_5\text{Cr}(\text{NO})]^+$	147	26.7	87.1	$[\text{CF}_3\text{SCr}(\text{NO})\text{C}_5\text{H}_5]^+ \rightarrow [\text{C}_5\text{H}_5\text{Cr}(\text{NO})]^+$	SCF_3
$[\text{Cr}(\text{C}_5\text{H}_5)_2]^+$	182	35.8			



Scheme 3

are the weak molecular ion peaks at m/z 326 and 278, followed by losses of two CO or NO groups in steps, giving $[\text{CF}_3\text{EMC}_5\text{H}_5]^+$ ($\text{E} = \text{Se}$, $\text{M} = \text{Fe}$ and $\text{E} = \text{S}$, $\text{M} = \text{Cr}$) which subsequently loses an ECF_2 unit with the simultaneous transfer of F from C to Fe or Cr to yield $[\text{C}_5\text{H}_5\text{MF}]^+$ ($\text{M} = \text{Fe}$, Cr) as evidenced by metastable peaks at m/z 72.7 and 84.8 respectively. The fragmentation of $[\text{C}_5\text{H}_5\text{MF}]^+$ is interesting because this seems to fragment in two different ways as shown in Scheme 3.

Metastable transition studies (Tables 3 and 4) suggest that both the pathways are probable. It may be noted that such F loss is very rare in organometallics.^{16,17} However, the loss of π -cyclopentadienyl appears to be



Scheme 4



more facile than that of the F atom, since the intensities of the signals due to $[\text{MF}]^+$ ($\text{M} = \text{Fe}$, Cr) ions are many times stronger than those of $[\text{C}_5\text{H}_5\text{M}]^+$. A similar observation was made previously⁷ in the case of $\text{C}_5\text{H}_5\text{TiF}_2$. On the basis of the above observations, the fragmentation may be depicted as shown in Scheme 4.

The signals at m/z 177, 149 and 186 in the spectrum of **5** and at m/z 177, 147 and 182 in that of **6** have been assigned to $[\text{C}_5\text{H}_5\text{M}(\text{X})_2]^+$, $[\text{C}_5\text{H}_5\text{M}(\text{X})]^+$ and $[(\text{C}_5\text{H}_5)_2\text{M}]^+$ ions. The occurrence of $[(\text{C}_5\text{H}_5)_2\text{M}]^+$ ions in the mass spectra appears to be a typical feature of the cyclopentadienyl carbonyl and nitrosyl derivatives of 3d transition metals.¹⁸ The presence of $[\text{C}_5\text{H}_5\text{M}(\text{X})_n]^+$ ($n = 1, 2$) ions suggests that the loss of ECF_3 competes with that of CO or NO.

In an attempt to study the significance of pyrolysis, the spectra of **5** and **6** were run at a temperature of 100°C instead of 20°C . The two sets of spectra were essentially identical except that (i) the intensity of the signal of $[(\text{C}_5\text{H}_5)_2\text{M}]^+$ became stronger and that (ii) the signal due to $[\text{CF}_3\text{EMC}_5\text{H}_5]^+$ became weaker, suggesting that thermal decompositions of **5** and **6** are the likely origin of $[(\text{C}_5\text{H}_5)_2\text{M}]^+$ ions and that an elevated temperature facilitates the expulsion of ECF_2 units.

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THE DIRECT SYNTHESIS AND CHARACTERIZATION OF ALKALI
METAL HEXAFLUOROCHROMATES(III), $M^I_3CrF_6$

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ABSTRACT

The reduction of an aqueous solution of CrO_3 with hydrazine hydrate in the presence of an excess of equimolar amounts of $M^I OH$ and 40% HF yields green, crystalline alkali hexafluorochromates(III), $M^I_3CrF_6$ ($M^I = NH_4, Na, K$ or Rb), in very high yield. The lithium analogue has been prepared by using Li_2CO_3 instead of lithium hydroxide. The compounds have been characterized by elemental analyses, room temperature magnetic moments, infrared spectra and molar conductivity. Time dependent molar conductivity studies of $(NH_4)_3CrF_6$ and K_3CrF_6 suggest that the compounds do not undergo decomposition in water at ambient temperatures.

INTRODUCTION

Albeit alkali metal hexafluorochromates(III), $M^I_3CrF_6$, have been known for quite some time¹; there has

been no simple and straight forward method for the synthesis of this class of compounds reported to date. The recommended methods include (i) fluorination of the fused mixture of alkali metal halide and chromium(III) halide,^{1,2} (ii) preparation from a KHF_2 melt³ and (iii) precipitation of the complex from an aqueous acid solution of the chromium(III) halide.^{1,4} Method (i) has been recognised as a general method. While both methods (i) and (ii) suffer from difficult handling problems and require the use of uncommon reaction manipulations, method (iii) requires the use of chromium trifluoride as one of the starting reagents which involves an extra preparation; however, it has been reported that the third method is especially suitable for large precipitating cations.¹ In a continuation of our studies of fluoro and oxyfluoro compounds of various transition metals^{5,6} we now report a novel and general method for the synthesis of $\text{M}^{\text{I}}_3\text{CrF}_6$ ($\text{M}^{\text{I}} = \text{NH}_4, \text{Li}, \text{Na}, \text{K}$ or Rb) from aqueous medium.

RESULTS AND DISCUSSION

It has been reported⁷ that the principal characteristic of Cr(III) complexes is their relative kinetic inertness in aqueous solution and it is owing to this that they persist for long periods of time in solution and that so many complex species can be isolated as solids. With this in view, a concentrated solution of CrO_3 was reduced with hydrazine hydrate at ambient temperature in the presence of an excess of M^{I} and F^- ions. The strategy of the reaction was that Cr(VI) being a strong oxidizing agent on being reduced would lose oxygen, and coordinatively unsaturated $\text{Cr}^{+\text{n}}$ ($\text{n} < 6$) would be formed

which would in turn react with F^- ions to give rise to $[CrF_6]^{3-}$. The possibility of formation of the hexaquo ion $[Cr(H_2O)_6]^{3+}$ was precluded owing to the presence of an excess of F^- ions in the solution.

Room temperature reduction of a concentrated solution of CrO_3 with hydrazine hydrate in the presence of excess of $M^I OH$ and 40% HF, maintaining the ratio of $Cr:F:M^I$ at 1:10:10, readily gave a green crystalline compound. For the lithium analogue, Li_2CO_3 was used in lieu of $LiOH$. Elemental analyses suggested the ratio of $M^I:Cr:F$ as 3:1:6. In view of the analytical data the empirical formula appeared to be $M_3^I CrF_6$.

The compounds are quite stable and can be stored for any length of time. They appear to be soluble in water and insoluble in common organic solvents. The molar conductivities of the compounds in water at 27° lie between 365 and $374 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ suggesting a 1:3 type of electrolytic nature of the compounds in accord with the suggested formula $M_3^I CrF_6$. Further studies of molar conductivities of the solutions of $(NH_4)_3CrF_6$ and K_3CrF_6 , chosen as representatives, at an interval of 7, 15, 30, 45 and 60 days indicated no apparent change in the Δ_M values. This shows the stability of the compounds in water and supports the contention that the compounds neither undergo hydrolysis nor decompose to any appreciable extent.

The room temperature magnetic susceptibility measurements gave effective magnetic moment values occurring between 3.80 and 3.84 BM (see TABLE I) which are in conformity with the magnetic moments of the octahedral $Cr(III) (t_{2g}^3)$ complexes.⁸⁻¹⁰

The IR spectra of the compounds are rather straightforward and generally exhibit two bands (TABLE I), one

at ~ 535 and the other at ~ 524 cm^{-1} . By analogy¹¹ these bands have been assigned to the ν_3 and ν_4 modes of the Cr-F stretching vibrations. These observations suggest that the hexafluorochromates(III), $\text{M}^{\text{I}}_3\text{CrF}_6$ presumably have octahedral structures because it has been established by Peacock and Sharp¹¹ that an octahedral ion MF_6^{n-} should have two (ν_3 and ν_4) IR active M-F vibrations. Two additional bands at $1635(\text{m})$ and $3450(\text{s,br})\text{cm}^{-1}$, observed in the case of the lithium compound, have been assigned to the δ_{HOH} and ν_{OH} modes of water present as water of crystallization in the compound. The lowering of the ν_{OH} relative to that in the free water molecule and broadening of the band have been attributed to intramolecular hydrogen bonding in $\text{Li}_3\text{CrF}_6 \cdot \text{H}_2\text{O}$.

EXPERIMENTAL

All chemicals used were of reagent grade. Infrared spectra were recorded on a Perkin-Elmer model 125 Spectrometer. Molar conductivities were measured at room temperature using a Toshniwal conductance bridge. Magnetic susceptibility measurements were made at room temperature by the Guoy method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant.

All experimental data are set out in the TABLE I.

Preparation of Alkali Metal Hexafluorochromates(III),



Ammonium hexafluorochromate(III), $(\text{NH}_4)_3\text{CrF}_6$ —

A quantity of 1.0g (10 mmol) CrO_3 was dissolved in ca 8 ml water in a polythene conical flask, and 10.0 ml 25% ammonia solution was added to it. To the solution 5.0 ml (100 mmol) of 40% hydrofluoric acid was added, and

the solution was stirred for ca 2 min. Pure hydrazine hydrate (1.2 ml) was added very slowly along the side of the reaction vessel with constant stirring. After the addition was over, the content was heated on a boiling water bath for ca 1h. A dark green coloured crystalline compound appeared and the supernatant liquid became almost colourless. The dark green crystalline $(\text{NH}_4)_3\text{CrF}_6$ was separated by centrifugation and washed twice with a very small amount of water and then two or three times with acetone. The compound was finally dried in vacuo. Yield : 2.1g (95.5%).

Sodium hexafluorochromate(III), Na_3CrF_6

A quantity of 1.0g (10 mmol) CrO_3 was dissolved in ca 10 ml water in a polythene beaker, and 4.0g (100 mmol) sodium hydroxide was added to it. To the solution 5.0 ml (100 mmol) of 40% hydrofluoric acid was added, and the solution was stirred for ca 5 min. Pure hydrazine hydrate (1.2 ml) was then added very slowly along the wall of the beaker with constant stirring. The solution was then heated on a boiling water bath for ca 45 min whereby the mother liquor became colourless and a green crystalline compound precipitated. The green Na_3CrF_6 was separated by centrifugation and purified by washing with a small amount of water at least twice followed by washing with acetone. The compound was finally dried in vacuo. Yield : 2.2g (93.6%).

Potassium hexafluorochromate(III), K_3CrF_6 , and rubidium hexafluorochromate(III), Rb_3CrF_6

K_3CrF_6 and Rb_3CrF_6 have been prepared in a manner analogous to that described for Na_3CrF_6 . In each case the molar ratio of CrO_3 : M^+OH :HF was maintained at

10:100:100, and 1.2 ml hydrazine hydrate was used per 1.0g of CrO_3 for the reduction. Yield of K_3CrF_6 from 1.0g CrO_3 was 2.1g (74.2%) and that of Rb_3CrF_6 from 1.0g CrO_3 was 3.4g (80.5%).

Lithium hexafluorochromate(III) monohydrate, $\text{Li}_3\text{CrF}_6 \cdot \text{H}_2\text{O}$

A quantity of 1.0g (10 mmol) CrO_3 was dissolved in 15 ml water in a polythene beaker, and a filter paper bag containing 3.7g (100 mmol) lithium carbonate was kept soaking in the solution. A 5 ml (100 mmol) portion of 40% hydrofluoric acid was added to the solution followed by the slow addition of 1.2 ml of pure hydrazine hydrate with constant stirring. After the addition was over, the content was heated on a boiling water bath for ca 2h and a green crystalline compound was obtained. The crystalline product was separated by centrifugation and purified by washing with water and finally with acetone. The compound was dried in vacuo. Yield : 1.45g (71%).

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TABLE I

Analytical Data, Magnetic Moment and Molar Conductance Values and Structurally Important IR Bands of Alkali Metal Hexafluorochromates(III), $M^I_3CrF_6$

Compound	μ_{eff} BM at 302°K	Molar Conduc- tance ($\Delta M \text{ ohm}^{-1} \text{ cm}^2$ mol^{-1})	Found % (Calcd.%)		IR bands (cm^{-1})	Assignments
			M^I or N	Cr		
$(NH_4)_3CrF_6$	3.82	368	19.36 (19.09)	23.81 (23.62)	536 m	ν_3
					524 s	ν_4
$Li_3CrF_6 \cdot H_2O$	3.80	374	10.24 (10.16)	25.52 (25.39)	533 m	ν_3
					525 s	ν_4
					1635 m	δ_{HOH}
					3450 s, br	ν_{OH}
Na_3CrF_6	3.81	365	29.48 (29.36)	22.23 (22.13)	535 m	ν_3
					523 s	ν_4
K_3CrF_6	3.82	368	44.48 (44.41)	18.40 (18.36)	536 w	ν_3
					525 s	ν_4
Rb_3CrF_6	3.84	369	60.87 (60.70)	12.38 (12.31)	534 m	ν_3
					524 s	ν_4

TABLE 1 — CHARACTERISATION DATA OF ALKALI METAL TRIOXYFLUOROCHROMATES (VI)

Compound	Yield %	Found (%) (calc)		
		M ^I or N	Cr	F
NH ₄ CrO ₃ F	67-70	10.53 (10.22)	38.11 (37.94)	13.62 (13.86)
KCrO ₃ F	89-92	24.94 (24.73)	32.88 (32.89)	12.32 (12.02)
RbCrO ₃ F	68-70	42.08 (41.80)	25.51 (25.41)	9.48 (9.29)
CsCrO ₃ F	75-78	52.91 (52.76)	20.72 (20.64)	7.81 (7.54)

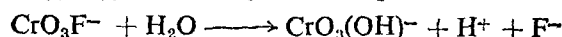
necessary to synthesise various M^ICrO₃F (M^I = NH₄, K, Rb or Cs). Such trioxo-fluorochromates (VI) have been known for quite some time^{6,7}. The reported methods for their preparation involve either difficult reaction manipulation or are slow and require the direct use of hydrofluoric acid^{6,7}. In this note a novel and fast method is described for the preparation of the title compounds in very high yields.

Reagent grade CrO₃ was used. Alkali metal bifluorides, M^IHF₂, were prepared by the method developed in this laboratory⁸.

In a typical preparation, respective alkali metal bifluoride was dissolved in a minimum volume of water and the solution heated on a boiling water bath for 10 min. To the hot solution stoichiometric amount of powdered CrO₃ was added with stirring, maintaining the ratio of CrO₃ : M^IHF₂ as 1:1. The solution was maintained hot for another 15-20 min and then allowed to cool in a freezer whereby orange-yellow coloured M^ICrO₃F (M^I = NH₄, K, Rb and Cs) was obtained in very high yield. The compound was separated by filtration and dried *in vacuo*.

The alkali metal trioxo-fluorochromates (VI) obtained are highly crystalline, orange-yellow coloured compounds (Table 1). The compounds are not very stable in moist air. They attack glass in the presence of moist air but can be stored in sealed polythene bags. The IR spectra of the newly synthesised M^ICrO₃F recorded on a Perkin-Elmer model 125 have been compared with the corresponding reported data⁹. The typical absorption at ~904(m), ~635(s) and ~954(s) cm⁻¹ have been attributed to ν_{as} Cr-O, $\nu_{\text{Cr-F}}$ and ν_{as} Cr-O respectively.

The method used for the synthesis does not involve the direct use of HF and is based on the concept of buffer action of alkali metal bifluorides M^IHF₂ and the concomitant presence of fluoride ions, H⁺ and M^{I+} ions in a solution obtained by the dissociation of alkali metal bifluorides M^IHF₂ in water. Under such a condition the solution definitely reacts acidic^{9,10,11}. The direct reaction between CrO₃ and M^IF did not appear feasible, because of the tendency of [CrO₃F]⁻ to undergo hydrolysis giving [CrO₃(OH)]⁻ according to the equation:



The alkali metal trioxo-fluorochromates (VI) are almost insoluble in common organic solvents and are

A Novel Synthesis of Alkali Metal Trioxo-fluorochromates (VI)

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Reaction between alkali metal bifluorides M^IHF₂ (M^I = NH₄, K, Rb or Cs) and CrO₃ in 1:1 molar ratio in a minimum amount of water gives alkali metal trioxo-fluorochromates (VI), M^ICrO₃F in very high yields. The compounds have been characterised by elemental analyses and IR spectral studies. The advantages of the new method are discussed.

In the course of our investigation on the fluoro and oxyfluoro compounds of transition metals¹⁻⁴ and in continuation of our studies on the use of alkali metal bifluorides M^IHF₂ (M^I = NH₄, Na, K, Rb or Cs) as fluorinating agents^{3,4} it became

easily hydrolysed in water. They decompose when heated. $\text{M}^+\text{CrO}_3\text{F}$ reacts with ammonia wherein Cr(VI) is reduced to Cr(III) .

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**Pyridinium Fluorochromate; A New and Efficient
Oxidant for Organic Substrates**

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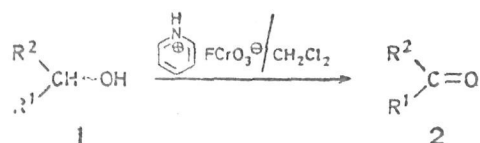
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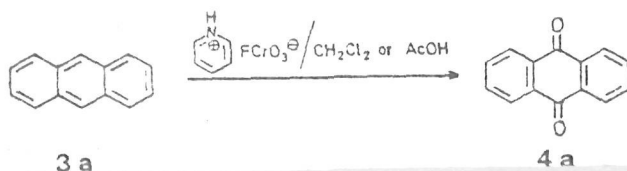
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There is continued interest in the development of new chromium(VI) reagents¹⁻⁵ for the effective and selective oxidation of organic substrates, in particular alcohols, under mild conditions. Of the large number of "mild" oxidizing agents available many prove impractical when the reactions are performed on a larger (mol) scale. In recent years, significant improvements were achieved by the use of new oxidizing agents such as pyridinium chlorochromate^{2,3}, pyridinium dichromate⁴, and 2,2'-bipyridinium chlorochromate⁵. We have now investigated the synthetic potential of pyridinium fluorochromate, C₅H₅NHCrO₃F, and we have found that this reagent has certain advantages over similar oxidizing agents in terms of amounts of oxidant and solvent required, short reaction times, and high yields. Further, pyridinium fluorochromate does not react with acetonitrile which is a suitable medium for studying oxidation kinetics and mechanism. The acidity of pyridinium fluorochromate (pH of a 0.01 molar solution: 2.45) is less pronounced than that of pyridinium chlorochromate (pH of a 0.01 molar solution: 1.75). The results hitherto obtained with pyridinium fluorochromate are very satisfactory and suggest the new reagent as a valuable addition to the existing oxidizing agents.

Pyridinium fluorochromate in dichloromethane oxidizes primary (1a-d) and secondary alcohols (1e) to the corresponding aldehydes or ketones (2) in high yields; the reagent has also been successfully applied to the oxidation of benzoin (1g) and a tricyclic allylic alcohol (1f) to benzil (2g) and a tricyclic enone (2f), respectively.



Pyridinium fluorochromate in dichloromethane also oxidizes anthracene (3a) and phenanthrene (3b) to anthraquinone (4a) and phenanthrene-9,10-quinone (4b) in 68% and 52% yields, respectively. To our knowledge, these yields are higher than those obtained by other oxidizing agents under mild conditions and they may even be raised to 98% and 72% by using acetic acid as reaction medium.



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The attempted analogous oxidation of naphthalene so far led only to ~25% of oxidation product.

Pyridinium fluorochromate is easily prepared in 93–94% yield from pyridine, aqueous 40% hydrofluoric acid, and chromium(VI) oxide in a molar ratio of 1:1.5:1. The orange crystalline reagent can be stored in sealed polythene bags for long periods without decomposition. The chromium(VI) content may be easily determined iodometrically. The molar conductance of the reagent in water (see procedure) suggests an univalent electrolytic nature in accordance with the formula shown; this fact may account for the stability of the compound. The I.R. spectrum is similar to that of potassium fluorochromate⁶. Pyridinium fluorochromate is soluble in water, dimethylformamide, and acetone; it is less soluble in dichloromethane and only sparingly soluble in benzene, carbon tetrachloride, chloroform, and hexane.

Pyridinium Fluorochromate(VI), $C_5H_5NHCrO_3F$:

Chromium(VI) oxide (CrO_3 ; 15.0 g, 0.15 mol) is dissolved in water (25 ml) in a polythene beaker and 40% hydrofluoric acid (11.25 ml, 0.225 mol) is added with stirring at room temperature. Within 5 min, a clear orange solution results. To this solution, pyridine (12.3 ml, 0.15 mol) is added slowly with stirring. The mixture is heated on a steam bath for ~15 min, then cooled to room temperature, and allowed to stand for 30–35 min. The bright orange, crystalline pyridinium fluorochromate is isolated by filtration, pressed between the folds of filter paper, and dried in vacuo for ~1 h; yield: 27.9 g (93.5%); m.p. 106–108 °C.

$C_5H_5NHCrFNO_3$ calc. C 30.16 H 3.04 Cr 26.12 F 9.54 N 7.04 (199.1) found 30.12 3.07 26.17 9.58 6.96
I.R. (KBr): $\nu = 908$ (ν_1), 640 (ν_2), 340 (ν_3), 952 (ν_4), 373 (ν_5), 262 (ν_6) cm^{-1} .

Molar conductance of a 0.001 molar solution of pyridinium fluorochromate in water: $\Lambda_m(25^\circ C) = 128 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

The above procedure can be performed on a 200 g scale without any difficulty.

Oxidation of Organic Substrates (1, 3) with Pyridinium Fluorochromate; General Procedure:

The reaction is carried out in a dry round-bottom flask fitted with reflux-condenser and efficient stirrer. To a vigorously stirred suspension of pyridinium fluorochromate (generally 10 g) in dichloromethane (generally 18 ml), a solution of the substrate in a small amount of dichloromethane is added all at once, the molar ratio of substrate to oxidant being 1:1.25–1.5 in the case of alcohols (1) and 1:2.5 in the case of polycyclic arenes (3) (see Table). The mixture is stirred for the time indicated in the Table [The progress of the reaction may be followed by T.L.C. on SiO_2 using benzene/ethyl acetate (90/10) as eluent]. The mixture is diluted with ether (1/1 vol/vol) and filtered through a short column of silica gel to give a clear solution. This solution is evaporated and the residual product purified by distillation, recrystallization, or column chromatography.

The above procedure may be carried out on 1–100 g scales without any problem.

4-Oxotricyclo[5.2.1.0^{2,6}]deca-3,8-diene (2f); Typical Procedure:

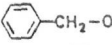
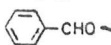
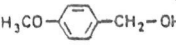
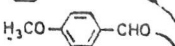
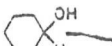
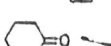
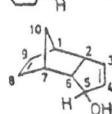
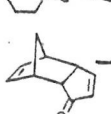
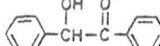
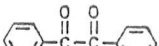
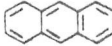
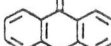
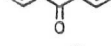
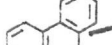
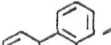
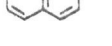
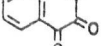
In a 250 ml round-bottom flask fitted with reflux condenser and stirrer is placed a suspension of pyridinium fluorochromate (16.15 g, 81.2 mmol) in dichloromethane (30 ml). To this, a solution of 4-hydroxytricyclo[5.2.1.0^{2,6}]deca-3,8-diene¹⁷ (1f; 8.0 g, 54.05 mmol) in dichloromethane (40 ml) is added with vigorous stirring which is continued for 90 min. The reaction is monitored by T.L.C. on silica gel using benzene/ethyl acetate (90/10) as eluent. To the resultant mixture, dry ether (100 ml) is added and the mixture is filtered through a short silica gel column (1 cm $\times$ 1 cm). The contents of the column are thoroughly washed with ether (3 $\times$ 40 ml) and filtered. The combined filtrates are evaporated on a steam bath and the oily residue, which solidifies on standing, is recrystallized from pentane; yield of colorless crystalline 2f: 7.3 g (92%); m.p. 79–80 °C (Ref.¹⁴, m.p. 11–11 °C).

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Table. Oxidation of Alcohols (1) and Polycyclic Arenes (3) with Pyridinium Fluorochromate

Substrate	Substrate/ Oxidant [mol/mol]	Solvent	Reaction time	Product ^a	Yield [%]	m.p. or b.p./torr [°C] found	m.p. or b.p./torr [°C] reported
1a $n\text{-C}_4\text{H}_9\text{-OH}$	1/1.5	CH_2Cl_2	2 h	2a $n\text{-C}_3\text{H}_7\text{-CHO}$	94	b.p. 74°/760	b.p. 75°/760 ¹⁰
1b $n\text{-C}_7\text{H}_{15}\text{-OH}$				2b $n\text{-C}_6\text{H}_{13}\text{-CHO}$			
1c 				2c 			
1d 				2d 			
1e 				2e 			
1f 				2f 			
1g 	1/1.5	CH_2Cl_2	2.5 h	2g 	98	m.p. 95°	m.p. 95° ¹³
3a 	1/2.5	CH_2Cl_2	4 h	4a 	68	m.p. 274°	m.p. 275° ¹⁵
3a 	1/2.5	AcOH	1.5 h	4a 	98	m.p. 205°	m.p. 206.5-207.5° ¹⁶
3b 	1/2.5	CH_2Cl_2	5 h	4a 	52		
3b 	1/2.5	AcOH	2 h	4b 	72		

^a The purity of the liquid products was found to be > 99% by ^{13}C NMR analysis.

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A NOVEL SYNTHESIS OF

TRIS(ACETYLACETONATO)CHROMIUM(III), $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$

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ABSTRACT

Chromium(VI) oxide, CrO_3 , reacts with acetylacetone, in the absence of any buffer, readily giving a nearly quantitative yield of tris(acetylacetonato)chromium(III), $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$. The compound has been characterised by chemical analysis, infrared and mass spectrometric studies. EI induced mass spectrometry showed the compound to be monomeric.

INTRODUCTION

In the course of our extended investigations of chromium chemistry^{1,2}, it became necessary for us to synthesise tris(acetylacetonato)chromium(III), $\text{Cr}(\text{acac})_3$. The growing interest on and versatile use of $\text{Cr}(\text{acac})_3$ ³⁻⁵ have made it an extremely important synthetic compound. $\text{Cr}(\text{acac})_3$ has been known for quite some time and a number of methods of its synthesis have been reported. Some of the very early methods are cumbersome and give

very low yields¹⁰. The method developed in order to circumvent these difficulties by the homogeneous control of pH¹¹ has the following disadvantages: (i) it is slow, (ii) the end-product may be contaminated by the buffer which is used in a very large excess, and (iii) the yield of $\text{Cr}(\text{acac})_3$ is lowered if the initial pH range is not maintained properly, presumably owing to the formation of hydroxoacetylchromium(III) species¹². It may be mentioned that the methods currently employed for the synthesis of $\text{Cr}(\text{acac})_3$ ^{5,11} require chromium(III) species as a starting material which needs a separate preparation and purification. In this communication a novel and fast method has been described, for the synthesis of the title compound, which neither uses any $\text{Cr}(\text{III})$ species as a starting material nor requires any buffer.

RESULTS AND DISCUSSION

The chelating ability of acetylacetone has long been recognised and, based on some very recent studies^{13,14} on the synthesis of Mn^{+3} compounds from Mn^{+2} , its potential as a suitable reducing agent has also been proved beyond doubt. In view of this it was thought feasible to synthesise the title compound directly from CrO_3 by the action of acetylacetone. An excess of acetylacetone (acacH) should be used such that after the red-ox reaction an appreciable amount of acacH will be available in the medium to act as ligands. In fact the reaction between CrO_3 and $(\text{CH}_3\text{CO})_2\text{CH}_2$ readily gives tris(acetylacetonato)chromium(III) in extremely high yield. The method does not require any buffer but the course of the reaction is probably such that it maintains the required pH by itself giving rise to the successful formation of the desired product. The pH of the solution, recorded immediately after the formation of $\text{Cr}(\text{acac})_3$ was found to be ~ 9 . It is difficult for us to put forward the

mechanism of the reaction in the absence of complete information about the oxidised products of acetylacetone. Analogous procedures have been used, with success in our laboratory, for the syntheses of $\text{Ln}(\text{acac})_3$ from $\text{Ln}(\text{VII})^{14}$ and $\text{Ln}(\text{acac})_2(\text{H}_2\text{O})_2$ from $\text{Ln}(\text{III})$ and it is hoped that this concept may be extended to the synthesis of acetylacetonates of other transition metals as well.

The yield of $\text{Cr}(\text{acac})_3$ obtained by this method is very high and the time of reaction is comparatively less. The compound melts at 216°C and is highly soluble in many organic solvents giving dark pink-violet coloured solutions. The compound has been characterised by analysing for C, H and Cr, determination of melting point and studying its infrared and mass spectra. The infrared spectrum of the compound is rather straight forward and show the characteristics of chelated acetylacetonates (acac^-). The spectrum is in full accord with those of $\text{Cr}(\text{acac})_3$ and other $\text{M}(\text{acac})_3$ reported in the literature¹⁵. The mass spectrum of the compound was recorded using a direct insertion probe for introducing the sample directly to the ion-chamber without any prior heating. The spectrum of the compound shows a peak of 20% intensity at m/z 349 and has been assigned to $[\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_2]^{7+}$ ion which in fact is the molecular ion peak. The dominant peak (100%) in the spectrum of the compound was at m/z 250 due to $[\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_2]^{7+}$ ion with the main fragmentation pathway being $[\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3]^{7+}$ (m/z 349, 20%) $\longrightarrow$ $[\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_2]^{7+}$ (m/z 250, 100%) $\longrightarrow$ $[\text{C}_5\text{H}_7\text{O}_2]\text{Cr}(\text{C}_4\text{H}_4\text{O}_2)^{7+}$ (m/z 235, 7%) $\longrightarrow$ $[\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)]^{7+}$ (m/z 151, 42%) $\longrightarrow$ $[\text{Cr}(\text{C}_4\text{H}_4\text{O}_2)]^{7+}$ (m/z 135, 5%) $\longrightarrow$ $[\text{Cr}]^{7+}$ (m/z 52, 4%). The mass spectrometric results adduce further support to the identity and purity of the compound, conform to the monomeric nature of $\text{Cr}(\text{acac})_3$ and compare very well with the reported data¹⁶⁻¹⁸.

EXPERIMENTAL

The chemicals used were reagent grade products. Infrared spectral measurements were made on a Perkin-Elmer model 125 spectrophotometer. The mass spectrum was recorded on a Varian MAT CM-5 mass spectrometer. The operating conditions were 70 eV electron energies, 30° source temperature, resolution 1000 and 8 kV accelerating voltage.

Synthesis of Tris(acetylacetonato)chromium(III), $[\text{Cr}(\text{acac})_3] \cdot 7\text{H}_2\text{O}$. — A quantity of 2.0g (20.0 mmol) of powdered CrO_3 was added to 20.0g (200.0 mmol) distilled acetylacetone with constant stirring whereupon an exothermic reaction set in and the colour of the solution became dark violet. Stirring was continued for another 5-10 min after the addition was complete. The solution was heated over a steam-bath for ca. 4h in an open beaker and then allowed to cool for ca. 1h in a freezer. The dark pink-violet shiny crystals of $[\text{Cr}(\text{acac})_3] \cdot 7\text{H}_2\text{O}$ were filtered off and washed several times with water and finally dried in vacuo. The yields of $[\text{Cr}(\text{acac})_3] \cdot 7\text{H}_2\text{O}$ was 6.5g (93%). The compound thus obtained was very pure and gave extremely satisfactory analysis. If desired, the compound can be recrystallised by dissolving it in the minimum volume of hot benzene followed by the addition of hot light petroleum (bp. $40-60^\circ\text{C}$) and then cooling at ca. 0°C . The yield of the recrystallised $[\text{Cr}(\text{acac})_3] \cdot 7\text{H}_2\text{O}$ was 5.8g (83%). The compound melts sharply at 216°C . The method may be scaled up to higher quantities (Found (%): C, 51.52; H, 6.11; Cr, 14.87. Calc. (%) for $\text{C}_{15}\text{H}_{21}\text{CrO}_6$: C, 51.57; H, 6.07; Cr, 14.88). The molecular weight was found to be 349 mass spectrometrically.

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