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 fluoroaque 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 Mn(CO)₅Cl 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, Mn(CO)$_5$Cl exhibits signals due to carbido fragments. The spectrum run at 100°C shows the characteristic pattern of Mn$_2$(CO)$_{10}$ which originates from the formation and recombination of Mn(CO)$_5$ radicals. The spectral pattern changes further at an elevated temperature of 250°C showing the formation of Mn$_2$(CO)$_8$Cl$_2$. The formation of Mn$_2$(CO)$_8$Cl$_2$ in the present case may be either (i) through the dimerisation of Mn(CO)$_5$Cl with a simultaneous loss of two CO groups; or (ii) an ion/molecule interaction between Mn(CO)$_5$Cl and Mn(CO)$_5$Cl$^+$ with the simultaneous transfer of one CO group from one Mn to the other leading to the formation of Mn$_2$(CO)$_8$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 CF$_3$S(Mn(CO))$_4$, CF$_3$SeMn(CO)$_4$, CF$_3$SeFe(CO)$_3$, CF$_3$SeFe(CO)$_2$C$_5$H$_5$, and CF$_3$Sc(NO)$_2$C$_5$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$_3$S 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 $\text{FeC}_5\text{H}_5^-$ and $\text{FeC}_5\text{H}_5^-$ in the spectra of cyclopentadienyl compounds prefer expulsion of $\pi$-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 $\text{FeC}_5\text{H}_5^+$ and $\text{CrC}_5\text{H}_7^+$ 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), $A_3\text{CrF}_6$. The reduction of an aqueous solution of $\text{CrO}_3$ with hydrazine hydrate in the presence of an excess of equimolar amounts of $A\text{OH}$ and 40% HF yields green, crystalline alkali hexafluorochromates(III), $A_3\text{CrF}_6$ ($A=\text{NH}_4, \text{Na}, \text{K}$ or Rb) in very high yields. The lithium analogue has been prepared by using Li$_2$CO$_3$ 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 $K_3\text{CrF}_6$ 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 $\sim$535 and at $\sim$52 cm$^{-1}$, assigned to the $\nu_3$ and $\nu_4$ modes of Cr-F stretchi...
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), $A_2[CrF_5(H_2O)]^7$ ($A = NH_4$, 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 $A\text{F}(A = NH_4, Na, K \text{ or Rb}$) giving green crystalline $A_2[CrF_5(H_2O)]^7$ in very high yields thereby providing a method for the direct synthesis of $A_2[CrF_5(H_2O)]^7$. 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 $A_2[CrF_5(H_2O)]^7$ 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 AHF₂. The concomitant presence of fluoride ions, H⁺ and A⁺ ion in solution arising from the dissociation of AHF₂ in water appears to be the driving force for the reaction. ACrO₃F compounds react with ammonia wherein Cr(VI) is reduced to Cr(III). Chapter 6 also embodies the synthesis of pyridinium fluorochromate, C₅H₅NHCrO₃F (PFC). PFC has been synthesised by the addition of pyridine to a solution of CrO₃ in 40% hydrofluoric acid (molar ratio of pyridine : CrO₃ as 1:1) and warming the solution on a steam bath for a few minutes. The orange crystalline compound PFC, C₅H₅NHCrO₃F melts at 106 - 108°C and shows relatively less pronounced acidity than the corresponding chlorocompound C₅H₅NHCrO₃Cl (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), Cr(C₅H₇O₂)₃. In view of the growing interest on and versatile use of Cr(acac)₃ a new and direct synthetic method of obtaining Cr(acac)₃ has been developed. It is reported in this Chapter that the reaction between chromium(VI) oxide, CrO₃ and acetylacetone, in the absence of any buffer, readily give
nearly quantitative yield of tris(acetylacetonato)chromium(III) \( \text{Cr(C}_5\text{H}_7\text{O}_2)_3 \). 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 \( \text{Cr(C}_5\text{H}_7\text{O}_2)_3 \).

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**


**Chapter 3**


**Chapter 4**


**Chapter 6**

(a) On \( \text{ACrO}_3\text{F} \)


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


**Chapter 7**