SYNTHESIS AND STRUCTURAL ASSESSMENT OF FLUORO, MIXED—FLUORO AND ACETYLACETONATO COMPOUNDS OF MANGANESE +(III) AND +(II)

AND

STUDIES OF REACTIVITY OF A NEW CHROMIUM(VI) REAGENT—PYRIDINIUM FLUOROCHROMATE (PFC)

Abstract

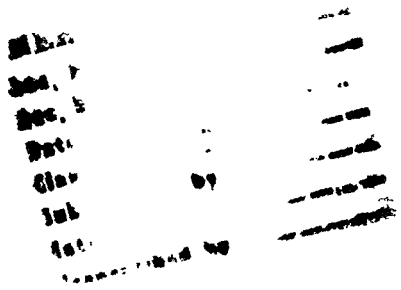
MANABENDRA NATH BHATTACHARJEE
DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL SCIENCES

A THESIS
SUBMITTED IN FULFILMENT OF
THE REQUIREMENT OF
THE DEGREE OF
DOCTOR OF PHILOSOPHY

To

THE NORTH-EASTERN HILL UNIVERSITY
SHILLONG 793001
INDIA

JANUARY, 1984



Synthesis and Structural Assessment of Fluoro, Mixed-Fluoro and Acetylacetonato Compounds of Manganese +(III) and +(II)

And

Studies of Reactivity of A New Chromium(VI) Reagent — PYRIDINIUM FLUOROCHROMATE(PFC)

Abstract

The thesis comprises of two parts and has altogether ten Chapters. While Chapters 1 to 8, based on the studies of synthesis and structural assessment of compounds of manganese +(III) and manganese +(II), constitute Part I of the thesis, Part II, consisting of two Chapters (chapters 9 and 10), contains the results of studies of reactivity of a new reagent 'Pyridinium Fluorochormate(VI) (PFC)'.

In Chapter 1, three new and general methods have been described for the synthesis of alkali-metal and ammonium pentafluoromanganates(III), A_2MnF_5 (A = Na, K, Cs or NH_4). The first method is based on the direct electron-transfer reaction between potassium permanganate, $KMnO_4$, and acetylacetone (Hacac) in the presence of alkali-metal or ammonium bifluoride, AHF_2, (A = Na, K, Cs or NH_4), leading to the synthesis of A_2MnF_5 compounds. This method does not

require anhydrous or aqueous HF. The basis of the second method is the reaction among MnO(OH), 40% HF and AHF_2 (A = Na, K, Cs or NH_4) giving A_2MnF_5 compounds. The third method involves the reaction of potassium permanganate, $KMnO_4$, with alkali-metal or ammonium bifluoride, AHF_2 (A = Na, K or NH_4), and 40% HF at ca 100 °C giving crystalline A_2MnF_5 compounds. This method does not require any extra reducing agent. The compounds have been characterised on the basis of the results of chemical analyses, chemical determination of the oxidation state of manganese, magnetic susceptibility measurements, infrared and electronic spectroscopic studies. The lower magnetic moments of A_2MnF_5 compounds (ca 3.2 BM) have been ascribed to antiferromagnetic exchange interaction between the contiguous manganese(III) ions through a —Mn—F—Mn— chain. The complex ion $[MnF_5]^{2-}$ has been shown, from i.r. and electronic spectral studies, to have a tetragonally elongated octahedral structure with a D_{4h} symmetry.

Chapter 2 describes the synthesis and structural assessment of $AMnF_4.H_2O$ compounds. Deep-brown crystalline compounds, alkali-metal tetrafluoromanganate(III) monohydrates, $AMnF_4.H_2O$ (A = Rb or Cs), have been synthesized directly from reactions of $KMnO_4$ with AHF_2 (A = Rb or Cs) and 40% HF at ca 100 °C without making use of any reducing

agent. Similar compounds were also obtained by the reaction of MnO(OH) with AHF_2 and 40% hydrofluoric acid at 100 ^{o}C. Characterization and assessment of molecular structure of the compounds were made from the results of elemental analyses, chemical determination of the oxidation state of manganese, magnetic susceptibility measurements, infrared and electronic spectroscopic studies. The i.r. and electronic spectra suggest a tetragonally elongated octahedral structure of the complex ion in the solid state, with a D_{4h} symmetry as a consequence of the Jahn-Teller effect on manganese(III). The complex ion, $[MnF_4]^-$, very likely, has a polymeric structure through trans-linked —F—Mn—F chains.

Chapter 3 of the thesis presents the synthesis and assessment of structure of alkali-metal and ammonium trifluoromonosulphatomanganates(III), $A_2[MnF_3(SO_4)]$ (A = Li, Na, K or NH_4). Pink-brown crystalline alkali-metal and ammonium trifluoromonosulphatomanganates(III), $A_2[MnF_3(SO_4)]$, have been synthesised in very high yields from the reaction of $KMnO_4$ (in the presence of formaldehyde solution) or MnO(OH) with 40% hydrofluoric acid and A_2SO_4 (A = Li, Na, K or NH_4). Also the reaction of MnO(OH) with 40% HF and $A_2S_2O_8$ (A = K or NH_4) affords $A_2[MnF_3(SO_4)]$. Persulphate, $S_2O_8^{2-}$, can not oxidise Mn^{3+} under the present

experimental conditions. While the chemically estimated oxidation states of manganese occur between 2.9 and 3.1, the room temperature magnetic moments lie in the range 4.0-4.2 BM. The observed magnetic moments suggest a lowering in the degree of antiferromagnetic exchange interaction in going from $[MnF_5]^{2-}$ to $[MnF_3(SO_4)]^{2-}$. The i.r. and electronic spectroscopic studies have been made. The i.r. spectra of the compounds suggest the lowering of symmetry of the SO_4^{2-} group from T_d to C_{2v} as a result of its coordination. It is not certain whether the SO_4^{2-} group is bonded in a chelated or a bridging bidentate manner. The complex ion, $[MnF_3(SO_4)]^{2-}$, may have a polymeric structure through a SO_4^{2-} bridging. However, the chances of fluoride bridging can not be totally ruled out. $(NH_4)_2[MnF_3(SO_4)]$ on being pyrolysed at 340 ^oC yields $MnSO_4$.

Synthesis and structural assessment of alkali-metal and ammonium trifluoromonooxalatomanganates(III), $A_2[MnF_3(C_2O_4)]$ (A = Na, K or NH_4) have been reported in <u>Chapter 4</u>. The $A_2[MnF_3(C_2O_4)]$ compounds have been synthesised from the reaction of MnO(OH), 40% HF and alkali-metal or ammonium oxalate, $A_2C_2O_4$ (A = Na, K or NH_4) at the molar ratio $MnO(OH):HF:A_2C_2O_4$ at 1:4-5:1. Characterization and assessment of molecular structure of

the compounds were made from the results of elemental analyses, chemical determination of the oxidation state of manganese, magnetic susceptibility measurements, infrared and electronic spectroscopic studies. The mixed-fluoro-oxalato-manganates(III) are deep pink in colour and are comparatively more stable than the corresponding trisoxalatomanganate(III) complex, $K_3[Mn(C_2O_4)_3].3H_2O$. While the chemically estimated oxidation state of manganese was found to be +3, the room temperature magnetic moments were found to lie between 4.2 and 4.3 BM. The relatively lower magnetic moment values owe their origin to a weak antiferromagnetic exchange interaction. Infrared spectra of the $A_2[MnF_3(C_2O_4)]$ compounds suggest the presence of bridging oxalato ($C_2O_4^{2-}$) group. The complex ion $[MnF_3(C_2O_4)]^{2-}$ may have a polymeric structure through a —Mn—O—C—C—O—Mn— chain and a weak —Mn—F—Mn— interaction.

The direct synthesis and electron-impact induced mass spectrometric studies of tris(acetylacetonato)manganese(III) constitute the basis of Chapter 5. It has been shown that a concentrated solution of $KMnO_4$ undergoes a ready electron-transfer reaction with acetylacetone (Hacac), in the absence of any buffer, giving a very high yield of tris-(acetylacetonato)manganese(III), $Mn(C_5H_7O_2)_3$. The pH of

the solution, recorded immediately after the formation of crystalline $Mn(acac)_3$ was found to be ca 5. Several advantages of the novel synthesis were discussed. The direct insertion technique has been found to be suitable for the mass spectrometric studies of $Mn(acac)_3$ compound. Electron-impact induced mass spectrometry showed the compound to be monomeric.

Chapter 6 of the thesis presents the synthesis of alkali-metal and ammonium trifluoroaquomanganates(II), $A[MnF_3(H_2O)]$ (A = Na, K, Rb, Cs or NH_4). The electron-transfer reaction between hydrazine hydrate and $KMnO_4$ in the presence of alkali-metal or ammonium bifluorides, AHF_2 (A = Na, K or NH_4), readily gives light pinkish-white alkali-metal or ammonium trifluoromonoaquomanganate(II), $A[MnF_3(H_2O)]$, in very high yields. The corresponding Rb^+ and Cs^+ salts have been obtained from the reactions of 20% hydrofluoric acid solution of $NH_4[MnF_3(H_2O)]$ with Rb_2CO_3 and Cs_2CO_3 respectively. The compounds have been characterised by elemental analyses, chemical determination of oxidation states of manganese in the compounds, room temperature magnetic susceptibility measurements, pyrolysis and infrared spectral studies. The i.r. spectra of the compounds showed the ν(Mn-F) to appear at ca 410 cm^{-1}. The results of i.r. spectral and pyrolysis studies suggest

the presence of coordinated water. The room temperature magnetic moments of the alkali-metal and ammonium trifluoromonoaquomanganates(II), $A[MnF_3(H_2O)]$, lie between 5.2 and 5.3 BM, well below the expected value for a high-spin d^5-system. Considerably lower moments presumably owe their origin to antiferromagnetic exchange interaction between contiguous Mn^{2+} ion through a —Mn—F—Mn— chain in the solid state. The complex species $[MnF_3(H_2O)]^-$ may have a polymeric structure through a weak —Mn—F—Mn— interaction.

In Chapter 7, the synthesis and assessment of structure of alkali-metal and ammonium fluoromonooxalatomanganates(II), $A[MnF(C_2O_4)]$ (A = Na, K or NH_4), have been described. The $A[MnF(C_2O_4)]$ compounds have been synthesized by the reactions of $KMnO_4$ or MnO(OH) with 40% hydrofluoric acid and alkali-metal or ammonium oxalate, $A_2C_2O_4$, at ca 100 °C. The compounds are white and stable for prolonged periods. $A[MnF(C_2O_4)]$ compounds have been characterized from the results of elemental analyses, magnetic susceptibility measurements, and infrared spectroscopic studies. The i.r. spectral studies of the compounds show that, unlike the trifluoromonooxalatomanganate(III) complexes described in Chapter 5, the fluoromonooxalatomanganate(II) complexes contain chelated oxalato groups.

The room temperature magnetic moments of alkali-metal and ammonium fluoromonooxalatomanganates(II), $A_2^{-}MnF(C_2O_4)_2$, have been found to be remarkably low. The values lie between 3.8 and 3.9 BM, showing that a strong antiferromagnetic exchange interaction is operative in the complexes. The complex species, very likely, has a polymeric structure through a strong —Mn—F—Mn— interaction.

Chapter 8 describes a new synthesis and mass spectrometric studies of bis(acetylacetonato)manganese(II) dihydrate, $Mn(C_5H_7O_2)_2.2H_2O$. The synthesis is based on the reaction of $Mn(OH)_2$ with acetylacetone (Hacac) in presence of a very small amount of formaldehyde. The method is direct and simple and does not require any buffer, unlike the method recommended in the literature for the synthesis of $Mn(C_5H_7O_2)_2.2H_2O$. The role of formaldehyde is to protect bis(acetylacetonato)manganese(II) from being oxidised. The method is rapid and gives the product in a very high yield. Electron-impact induced mass spectrum of the compound, recorded using the direct insertion technique, shows the compound to be monomeric in the vapour state. The spectrum also provides evidence for rearrangement to give $Mn-CH_3$ species.

The results of oxidations of organic substrates with a new and efficient oxidant pyridinium fluorochromate(VI),

$C_5H_5NHCrO_3F$ (PFC), have been described in Chapter 9. The synthetic potential of pyridinium fluorochromate(VI) reagent has been investigated, and it has been found that the new reagent (PFC) has certain advantages over similar oxidizing agents in terms of amounts of oxidant and solvent required, short reaction times, and high yields. Pyridinium fluorochromate(VI) in dichloromethane oxidizes primary and secondary alcohols to aldehydes or ketones in very high yields; the reagent has been successfully applied to the oxidation of benzoin to benzil, a tricyclic allylic alcohol, 4-oxotricyclo[5.2.1.$0^{2,6}$]-deca-3,8-diene, to the corresponding tricyclic enone respectively. PFC in dichloromethane also oxidizes anthracene and phenanthrene to anthraquinone and phenanthrene-9,10-quinone in 68% and 52% yields respectively. The yields may be raised to 98% and 72% by using acetic acid as the reaction medium. PFC does not react with acetonitrile which is a suitable medium for studying oxidation kinetics and mechanism. The results hitherto obtained with pyridinium fluorochromate(VI) (PFC) are very satisfactory and suggest the new reagent as a valuable addition to the existing oxidizing agents.

Chapter 10, indeed the last Chapter of the thesis, reports the kinetics and mechanism of the oxidation of alcohols by the new chromium(VI) reagent, pyridinium

fluorochromate (PFC). Pyridinium fluorochromate, $C_5H_5NHCrO_3F$, has been shown to oxidize benzyl alcohol, ethanol and cyclohexanol to benzaldehyde, acetaldehyde, and cyclohexanone respectively. While each of the oxidations, studied in acetonitrile-nitrobenzene (1:1, v/v) medium, has been found to be first order with respect to the oxidant, the rate is almost independent of the substrate concentration. The oxidation reactions are highly catalysed by acid. The acid-catalysed reactions being very fast, precluded determination of their order in acid media. The effects of temperature and solvent compositions were studied and activation parameters evaluated. The free energies of activation of the three reactions were found to lie between 91.82 and 92.65 kJ mol^{-1}. The near constancy of the $\Delta F^{\#}$ values suggest that a similar mechanism is operative in each of the three oxidations. From the results of these studies it appears that a hydride transfer mechanism is involved in the rate determining step of the PFC oxidations. Probable mechanisms have been discussed.

The results of studies described in Chapters 1, 2, 3, 5, 6, 9, and 10 have been either published or accepted for publication :

Chapter 1

(i) M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta and D. T. Khathing, J. Chem. Soc. Dalton Trans., 2587, 1981.

(ii) M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, A. Kathipri and D. T. Khathing, Synth. React. Inorg. Met.-Org. Chem., 485, 12, 1982.

(iii) M. N. Bhattacharjee and M. K. Chaudhuri, Ind. J. Chem., in press.

(iv) M. N. Bhattacharjee and M. K. Chaudhuri, Inorg. Syntheses, Approved by the Review Committee.

Chapter 2

M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta and A. Kathipri, Polyhedron, in press.

Chapter 3

M. N. Bhattacharjee and M. K. Chaudhuri, Polyhedron, in press.

Chapter 5

M. N. Bhattacharjee, M. K. Chaudhuri and D. T. Khathing, J. Chem. Soc. Dalton Trans., 669, 1982.

Chapter 6

M. N. Bhattacharjee and M. K. Chaudhuri

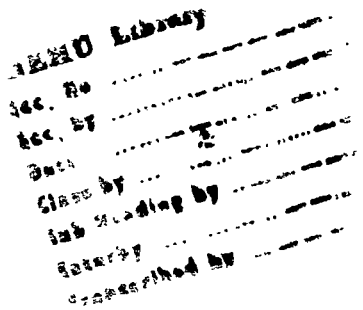
Ind. J. Chem., 977, 21A, 1982.

Chapter 9

M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, N. Roy and D. T. Khathing, Synthesis, 588, 1982

Chapter 10

M. N. Bhattacharjee, M. K. Chaudhuri and H. S. Dasgupta, Bull. Chem. Soc. Jpn., 0000, 57, 1984.



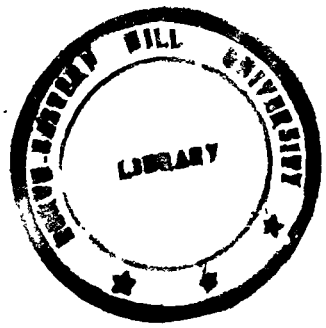
SYNTHESIS AND STRUCTURAL ASSESSMENT OF FLUORO, MIXED—FLUORO AND ACETYLACETONATO COMPOUNDS OF MANGANESE +(III) AND +(II)

AND

STUDIES OF REACTIVITY OF A NEW CHROMIUM(VI) REAGENT—PYRIDINIUM FLUOROCHROMATE (PFC)

MANABENDRA NATH BHATTACHARJEE
DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL SCIENCES

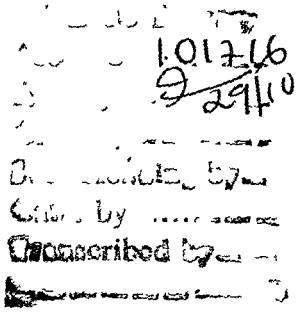
A THESIS
SUBMITTED IN FULFILMENT OF
THE REQUIREMENT OF
THE DEGREE OF
DOCTOR OF PHILOSOPHY



To

THE NORTH-EASTERN HILL UNIVERSITY
SHILLONG 793001
INDIA

JANUARY, 1984


1.01.16
9/29/10

To

MY MOTHER

North-Eastern Hill University

DEPARTMENT OF CHEMISTRY
Laitumkhrah. SHILLONG- 793003 (Meghalaya)

Phone : 26593
Grams : NEHU

Dr. M. K. Chaudhuri

I certify that the thesis entitled, "Synthesis and Structural Assessment of Fluoro, Mixed-fluoro and Acetylacetonato Compounds of Manganese +(III) and +(II) and Studies of Reactivity of A New Chromium(VI) Reagent - Pyridinium Fluorochromate (PFC)", submitted by Mr. Manabendra Nath Bhattacharjee 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.

Place : Shillong
Date : 23rd Jan, 1984

Kikir Kanti Chaudhuri
Signature of the Supervisor

North-Eastern Hill University

DEPARTMENT OF CHEMISTRY
Laitumkhrah, SHILLONG- 793003 (Meghalaya)

Phone : 26593
Grams : NEHU

December 12, 1983

This is to certify that Sri Manabendra Nath Bhattacharjee has satisfactorily completed the following Pre-Ph. D. courses, as prescribed by this university:

1. CHEM 640 - CHEMICAL KINETICS
2. CHEM 608 - BIO-INORGANIC CHEMISTRY

HEAD
DEPARTMENT OF CHEMISTRY
NORTH-EASTERN HILL UNIVERSITY
SHILLONG 793 003

Head
Department of Chemistry
North Eastern Hill University
Shillong-793003

C O N T E N T S

()()()()()()()

A C K N O W L E D G E M E N T

It is extremely exciting for me to realise that I have now reached the stage of writing the acknowledgement for my Ph. D. thesis. On the outset I would like to thank all those who helped me directly or indirectly for the research work.

My sincere and heartfelt thanks go to Dr. Mihir Kanti Chaudhuri, Reader in Chemistry, North-Eastern Hill University, Shillong, for suggesting the topics of research, inspiration, and constant supervision and guidance throughout the course of this work.

Thanks are also due to Dr. H. S. Dasgupta, Dr. D. T. Khathing and Dr. A. K. Sil for their interest in our work and their help. To Professors Alois Haas of Ruhr University, Bochum, West Germany, and A. J. Edwards of Birmingham University, U.K., I express my gratitude for allowing me to make use of some of the facilities available in their laboratories. It is my pleasure to place on record with thanks the help and cooperation which I received from the colleagues of our laboratory, Dr. N. Roy, Mr. S. K. Ghosh, Mr. A. Kathipri, Mr. Z.

Hiese, Mr. R. N. D. Purkayastha, Miss N. Islam and Mr. B. Das; from the colleagues of the department, Mr. K. P. Sarma, Mr. V. P. Shedbalkar, Miss. Bharati Bhattacharjee, Miss Mitra Bhattacharjee, Dr. A. K. Bhattacharjee, Mr. K. K. Bhattacharjee, Mr. S. N. Mazumdar, Mr. A. Debroy and Miss S. Islam, and my friends, Mr. S. Dasgupta, Dr. N. G. Goswami, Mr. S. Bhattacharjee and Mr. A. Choudhury.

I must thank the authorities of University (NEHU), the Dean of School of Physical Sciences, and the Head of the Department of Chemistry for allowing me to use all the available facilities required for my research work. It is my duty to acknowledge the help and good wishes of Dr. P. N. Pandey, Dr. R. K. Poddar and Dr. M. P. Mahajan and all the faculty members of the department of Chemistry, NEHU.

I wish to thank all the members of the non-teaching and technical staff of the Department of Chemistry for extending full cooperation to me over all these years, and to Kong Nancy Langstam especially for her affection and love.

I am grateful to the University for awarding me U.G.C. (New Delhi) fellowships (1980 onwards) which

enabled me to carry out research work for the Ph. D. degree.

I express my deep sense of gratitude to my beloved parents, brothers and sisters, and relatives for giving me inspiration, encouragement and enthusiasm to pursue with my research work.

Manabendra Nath Bhattacharjee

S U M M A R Y

The thesis comprises of two parts and has altogether ten Chapters. While Chapters 1 to 8, based on the studies of synthesis and structural assessment of compounds of manganese +(III) and manganese +(II), constitute Part I of the thesis, Part II, consisting of two Chapters (Chapters 9 and 10), contains the results of studies of reactivity of a new reagent 'Pyridinium Fluorochromate(VI) (PFC).

In Chapter 1, three new and general methods have been described for the synthesis of alkali-metal and ammonium pentafluoromanganates(III), A_2MnF_5 (A = Na, K, Cs or NH_4). The first method is based on the direct electron-transfer reaction between potassium permanganate, $KMnO_4$, and acetylacetone (Hacac) in the presence of alkali-metal or ammonium bifluoride, AHF_2, (A = Na, K, Cs or NH_4), leading to the synthesis of A_2MnF_5 compounds. This method does not require anhydrous or aqueous HF. The basis of the second

method is the reaction among MnO(OH), 40% HF and AHF_2 (A = Na, K, Cs or NH_4) giving A_2MnF_5 compounds. The third method involves the reaction of potassium permanganate, $KMnO_4$, with alkali-metal or ammonium bifluoride, AHF_2 (A = Na, K or NH_4), and 40% HF at ca 100 °C giving crystalline A_2MnF_5 compounds. This method does not require any extra reducing agent. The compounds have been characterised on the basis of the results of chemical analyses, chemical determination of the oxidation state of manganese, magnetic susceptibility measurements, infrared and electronic spectroscopic studies. The lower magnetic moments of A_2MnF_5 compounds (ca 3.2 BM) have been ascribed to antiferromagnetic exchange interaction between the contiguous manganese(III) ions through a —Mn—F—Mn— chain. The complex ion $[MnF_5]^{2-}$ has been shown, from i.r. and electronic spectral studies, to have a tetragonally elongated octahedral structure with a D_{4h} symmetry.

Chapter 2 describes the synthesis and structural assessment of $AMnF_4.H_2O$ compounds. Deep-brown crystalline compounds, alkali-metal tetrafluoromanganate(III) monohydrates, $AMnF_4.H_2O$ (A = Rb or Cs), have been synthesized directly from reactions of $KMnO_4$ with AHF_2 (A = Rb or Cs) and 40% HF at ca 100 °C without making use of any reducing

agent. Similar compounds were also obtained by the reaction of MnO(OH) with AHF_2 and 40% hydrofluoric acid at 100 °C. Characterization and assessment of molecular structure of the compounds were made from the results of elemental analyses, chemical determination of the oxidation state of manganese, magnetic susceptibility measurements, infrared and electronic spectroscopic studies. The i.r. and electronic spectra suggest a tetragonally elongated octahedral structure of the complex ion in the solid state, with a D_{4h} symmetry as a consequence of the Jahn-Teller effect on manganese(III). The complex ion, $[MnF_4]^-$, very likely, has a polymeric structure through trans-linked —F—Mn—F chains.

Chapter 3 of the thesis presents the synthesis and assessment of structure of alkali-metal and ammonium trifluoromonosulphatomanganates(III), $A_2[MnF_3(SO_4)]$ (A = Li, Na, K or NH_4). Pink-brown crystalline alkali-metal and ammonium trifluoromonosulphatomanganates(III), $A_2[MnF_3(SO_4)]$, have been synthesised in very high yields from the reaction of $KMnO_4$ (in the presence of formaldehyde solution) or MnO(OH) with 40% hydrofluoric acid and A_2SO_4 (A = Li, Na, K or NH_4). Also the reaction of MnO(OH) with 40% HF and $A_2S_2O_8$ (A = K or NH_4) affords $A_2[MnF_3(SO_4)]$. Persulphate, $S_2O_8^{2-}$, can not oxidise Mn^{3+} under the present

experimental conditions. While the chemically estimated oxidation states of manganese occur between 2.9 and 3.1, the room temperature magnetic moments lie in the range 4.0-4.2 BM. The observed magnetic moments suggest a lowering in the degree of antiferromagnetic exchange interaction in going from $[MnF_5]^{2-}$ to $[MnF_3(SO_4)]^{2-}$. The i.r. and electronic spectroscopic studies have been made. The i.r. spectra of the compounds suggest the lowering of symmetry of the SO_4^{2-} group from T_d to C_{2v} as a result of its coordination. It is not certain whether the SO_4^{2-} group is bonded in a chelated or a bridging bidentate manner. The complex ion, $[MnF_3(SO_4)]^{2-}$, may have a polymeric structure through a SO_4^{2-} bridging. However, the chances of fluoride bridging can not be totally ruled out. $(NH_4)_2[MnF_3(SO_4)]$ on being pyrolysed at 340 ^{o}C yields $MnSO_4$.

Synthesis and structural assessment of alkali-metal and ammonium trifluoromonooxalatomanganates(III), $A_2[MnF_3(C_2O_4)]$ (A = Na, K or NH_4) have been reported in Chapter 4. The $A_2[MnF_3(C_2O_4)]$ compounds have been synthesised from the reaction of MnO(OH), 40% HF and alkali-metal or ammonium oxalate, $A_2C_2O_4$ (A = Na, K or NH_4) at the molar ratio MnO(OH):HF:$A_2C_2O_4$ at 1:4-5:1. Characterization and assessment of molecular structure of

the compounds were made from the results of elemental analyses, chemical determination of the oxidation state of manganese, magnetic susceptibility measurements, infrared and electronic spectroscopic studies. The mixed-fluoro-oxalato-manganates(III) are deep pink in colour and are comparatively more stable than the corresponding trisoxalatomanganate(III) complex, $K_3[Mn(C_2O_4)_3].3H_2O$. While the chemically estimated oxidation state of manganese was found to be +3, the room temperature magnetic moments were found to lie between 4.2 and 4.3 BM. The relatively lower magnetic moment values owe their origin to a weak antiferromagnetic exchange interaction. Infrared spectra of the $A_2[MnF_3(C_2O_4)]$ compounds suggest the presence of bridging oxalato ($C_2O_4^{2-}$) group. The complex ion $[MnF_3(C_2O_4)]^{2-}$ may have a polymeric structure through a —Mn—O—C(=O)—C(=O)—O—Mn— chain and a weak —Mn—F—Mn— interaction.

The direct synthesis and electron-impact induced mass spectrometric studies of tris(acetylacetonato)manganese(III) constitute the basis of Chapter 5. It has been shown that a concentrated solution of $KMnO_4$ undergoes a ready electron-transfer reaction with acetylacetone (Hacac), in the absence of any buffer, giving a very high yield of tris-(acetylacetonato)manganese(III), $Mn(C_5H_7O_2)_3$. The pH of

the solution, recorded immediately after the formation of crystalline $Mn(acac)_3$ was found to be ca 5. Several advantages of the novel synthesis were discussed. The direct insertion technique has been found to be suitable for the mass spectrometric studies of $Mn(acac)_3$ compound. Electron-impact induced mass spectrometry showed the compound to be monomeric.

Chapter 6 of the thesis presents the synthesis of alkali-metal and ammonium trifluoroaquomanganates(II), $A[MnF_3(H_2O)]$ (A = Na, K, Rb, Cs or NH_4). The electron-transfer reaction between hydrazine hydrate and $KMnO_4$ in the presence of alkali-metal or ammonium bifluorides, AHF_2 (A = Na, K or NH_4), readily gives light pinkish-white alkali-metal or ammonium trifluoromonoaquomanganate(II), $A[MnF_3(H_2O)]$, in very high yields. The corresponding Rb^+ and Cs^+ salts have been obtained from the reactions of 20% hydrofluoric acid solution of $NH_4[MnF_3(H_2O)]$ with Rb_2CO_3 and Cs_2CO_3 respectively. The compounds have been characterised by elemental analyses, chemical determination of oxidation states of manganese in the compounds, room temperature magnetic susceptibility measurements, pyrolysis and infrared spectral studies. The i.r. spectra of the compounds showed the ν(Mn-F) to appear at ca 410 cm^{-1}. The results of i.r. spectral and pyrolysis studies suggest

the presence of coordinated water. The room temperature magnetic moments of the alkali-metal and ammonium trifluoromonoaquomanganates(II), $A[MnF_3(H_2O)]$, lie between 5.2 and 5.3 BM, well below the expected value for a high-spin d^5-system. Considerably lower moments presumably owe their origin to antiferromagnetic exchange interaction between contiguous Mn^{2+} ion through a —Mn—F—Mn— chain in the solid state. The complex species $[MnF_3(H_2O)]^-$ may have a polymeric structure through a weak —Mn—F—Mn— interaction.

In Chapter 7, the synthesis and assessment of structure of alkali-metal and ammonium fluoromonooxalatomanganates(II), $A[MnF(C_2O_4)]$ (A = Na, K or NH_4), have been described. The $A[MnF(C_2O_4)]$ compounds have been synthesized by the reactions of $KMnO_4$ or MnO(OH) with 40% hydrofluoric acid and alkali-metal or ammonium oxalate, $A_2C_2O_4$, at ca 100 °C. The compounds are white and stable for prolonged periods. $A[MnF(C_2O_4)]$ compounds have been characterized from the results of elemental analyses, magnetic susceptibility measurements, and infrared spectroscopic studies. The i.r. spectral studies of the compounds show that, unlike the trifluoromonooxalatomanganate(III) complexes described in Chapter 5, the fluoromonooxalatomanganate(II) complexes contain chelated oxalato groups.

The room temperature magnetic moments of alkali-metal and ammonium fluoromonooxalatomanganates(II), $A_2^{-}MnF(C_2O_4)_2^{-}$, have been found to be remarkably low. The values lie between 3.8 and 3.9 BM, showing that a strong antiferromagnetic exchange interaction is operative in the complexes. The complex species, very likely, has a polymeric structure through a strong —Mn—F—Mn— interaction.

Chapter 8 describes a new synthesis and mass spectrometric studies of bis(acetylacetonato)manganese(II) dihydrate, $Mn(C_5H_7O_2)_2.2H_2O$. The synthesis is based on the reaction of $Mn(OH)_2$ with acetylacetone (Hacac) in presence of a very small amount of formaldehyde. The method is direct and simple and does not require any buffer, unlike the method recommended in the literature for the synthesis of $Mn(C_5H_7O_2)_2.2H_2O$. The role of formaldehyde is to protect bis(acetylacetonato)manganese(II) from being oxidised. The method is rapid and gives the product in a very high yield. Electron-impact induced mass spectrum of the compound, recorded using the direct insertion technique, shows the compound to be monomeric in the vapour state. The spectrum also provides evidence for rearrangement to give $Mn-CH_3$ species.

The results of oxidations of organic substrates with a new and efficient oxidant pyridinium fluorochromate(VI),

$C_5H_5NHCrO_3F$ (PFC), have been described in Chapter 9. The synthetic potential of pyridinium fluorochromate(VI) reagent has been investigated, and it has been found that the new reagent (PFC) has certain advantages over similar oxidizing agents in terms of amounts of oxidant and solvent required, short reaction times, and high yields. Pyridinium fluorochromate(VI) in dichloromethane oxidizes primary and secondary alcohols to aldehydes or ketones in very high yields; the reagent has been successfully applied to the oxidation of benzoin to benzil, a tricyclic allylic alcohol, 4-oxotricyclo[5.2.1.$0^{2,6}$]-7-deca-3,8-diene, to the corresponding tricyclic enone respectively. PFC in dichloromethane also oxidizes anthracene and phenanthrene to anthraquinone and phenanthrene-9,10-quinone in 68% and 52% yields respectively. The yields may be raised to 98% and 72% by using acetic acid as the reaction medium. PFC does not react with acetonitrile which is a suitable medium for studying oxidation kinetics and mechanism. The results hitherto obtained with pyridinium fluorochromate(VI) (PFC) are very satisfactory and suggest the new reagent as a valuable addition to the existing oxidizing agents.

Chapter 10, indeed the last Chapter of the thesis, reports the kinetics and mechanism of the oxidation of alcohols by the new chromium(VI) reagent, pyridinium

fluorochromate (PFC). Pyridinium fluorochromate, $C_5H_5NHCrO_3F$, has been shown to oxidize benzyl alcohol, ethanol and cyclohexanol to benzaldehyde, acetaldehyde, and cyclohexanone respectively. While each of the oxidations, studied in acetonitrile-nitrobenzene (1:1, v/v) medium, has been found to be first order with respect to the oxidant, the rate is almost independent of the substrate concentration. The oxidation reactions are highly catalysed by acid. The acid-catalysed reactions being very fast, precluded determination of their order in acid media. The effects of temperature and solvent compositions were studied and activation parameters evaluated. The free energies of activation of the three reactions were found to lie between 91.82 and 92.65 kJ mol^{-1}. The near constancy of the $\Delta F^{\#}$ values suggest that a similar mechanism is operative in each of the three oxidations. From the results of these studies it appears that a hydride transfer mechanism is involved in the rate determining step of the PFC oxidations. Probable mechanisms have been discussed.

INTRODUCTION

Manganese is the first row Group VII B transition metal, twelfth most abundant element and constitutes about 0.085% of the earth's crust.[1] Apart from its various utilities in industrial as well as laboratory purposes, the importance of manganese or its compounds have also been detected in bio-systems. It has been implicated as a possible dioxygen evolving agent in photosynthesis.[2] In addition, it can activate enzymatic processes such as oxidative phosphorylation, synthesis of cholesterol, etc.[3] The recent advancement in understanding the chemical importance and behaviour of manganese and its compounds in inorganic as well as organic systems have considerably widened the scope of study and research relating to the chemistry of manganese.

The metal, twenty-fifth element in Periodic Table, has the ground state electronic configuration $[Ar]3d^5 4s^2$ and experiences the widest spectrum of oxidation states ranging from -3 to +7, of which +2 is the most stable one. While the lower oxidation states are usually found[4] in the carbonyl, nitrosyl and organometallic derivatives of manganese, different types of binary as well as complex compounds of the metal are available in its intermediate

oxidation states. The higher oxidation states of manganese, i.e. Mn^{5+} to Mn^{7+}, exist only in compounds containing oxide ligands and are susceptible to photochemical decomposition, depending upon pH.[5,6] Mn^{4+} shows a more extinsive ground state chemistry than the higher oxidation states, but, in general, their compounds are not very stable. The great stability of MnO_2, in fact, is due to its inherent insolubility; the other Mn^{4+} compounds are readily hydrolysed and reduced.[7] These higher valent manganese compounds are very strong oxidising agents and hence, they have got wide use in oxidation reactions in many organic and inorganic systems.

Manganese +(III) and Manganese +(II) are the two important and relatively more studied oxidation states of the metal. However, the simple ion of Mn^{3+} does not appear to exist, so that the stable salts of Mn^{3+} are mostly complex.[8] There are relatively few simple compounds of Mn^{3+} and only the acetate salt can be conveniently prepared. These compounds are strong oxidising agents, particularly for organic systems and in solution they are unstable with respect to disproportionation[8,9]:

$$2\ Mn^{3+} \longrightarrow Mn^{4+} + Mn^{2+}$$

$$Mn^{4+} + H_2O \longrightarrow MnO_2 + 4H^+ \quad : K \approx 10^9$$

The complexation of Mn^{3+} with anions, on the other hand, usually results in a lowering of the redox potential for the Mn(III)/Mn(II)

couple, and is dependent upon pH. Although the complex formation by the metal in its +3 state is of normally dissociative type[10] and that, the hydrolysis can occur at low acidities also,

$$Mn^{3+} + H_2O \longrightarrow Mn(OH)^{2+} + H^+ \quad K \approx 1$$

these can be minimised to a considerable extent at high acid concentration and with suitable complexing anions. Thus, Mn^{3+} can be stabilised in solution by sulphate, oxalate, pyrophosphate and some other complexing anions. This, however, does not give the complete picture, since even the most stable of the complex species, which is possibly a 7-coordinate complex anion $[Mn(EDTA)(H_2O)]^-$ undergoes slow decomposition due to oxidation of the ligand.[11] Suitable complexing agent for stabilising Mn^{3+} is thus always looked for. An extensive research in this regard has proved that fluoride ions (other halide ions in lesser degrees) can act most suitably in this regard. The study of fluoro-complexes of manganese(III) thus becomes a subject of considerable interest for chemists, which, as one among others, may pave the way for understanding the chemistry of trivalent manganese more clearly.

Manganese(III) has the $3d^4$ electronic configuration which is subject to Jahn-Teller distortion and the majority of the octahedral complexes of this d^4 ion are high-spin with magnetic moments of near spin-only value. Because of the odd number of electrons in e_g level, $[^5E_g\ (t_{2g}^3 e_g^1)$; $d^4\ (Mn^{III})]$, the

distrotion should be appreciable and it might be expected to resemble the distrotion in Cr^{2+} and Cu^{2+} compounds, namely, a considerable elongation of two trans-bonds with little difference in the lengths of the other four. Thus, whenever the subject of the Jahn-Teller effect arises, frequent references is made to high-spin manganese(III)[12-14] compounds. However, for the reasons mentioned earlier in this section, not many Mn^{3+} complexes have been well studied compared to that of the other tripositive first-row transition elements or other systems having a d^4 configuration. Hence, studies on various aspects, viz., synthesis, reactivity and structural assessment of different types of Mn^{3+} complexes was felt important and it was with this perspective that an attempt was made to study the fluoro complexes of manganese(III). In Chapter 1 of Part I of the thesis, a detail account of synthesis, characterisation and structural assessment of alkali-metal and ammonium pentafluoromanganates(III), A_2MnF_5 (A = Na, K, Cs or NH_4), has been presented. Chapter 2 embodies the synthesis and physico-chemical studies of heavier alkali-metal tetrafluoromanganates(III), $AMnF_4$ (A = Rb or Cs).

When a solution contains a metal ion and at least two different ligands there is always a finite possibility for the formation of mixed ligand complexes. Considering the potential donating ability of the counter anion and of the solvent molecule, there are very few cases indeed when this possibility is out of

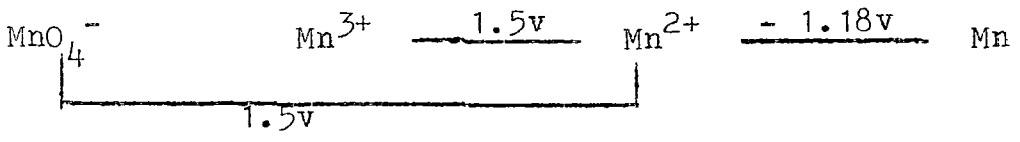
consideration.[15] Thus different types of mixed ligand complexes of various metals have been studied, methods to determine their stability constants have been elaborated, their importance in chemical[16,17] and biochemical[18,19] processes has been discussed, and the factors determining their stabilities have been theoretically treated. Three kinds of ternary complexes may be conveniently distinguished: (a) complexes containing two different unidentate ligands, (b) complexes containing one unidentate and one multidentate ligand; (c) complexes containing two different multidentate ligands; and these complexes may be formed either in substitution reaction or in addition reaction by the expansion of the coordination sphere. The earlier studies on manganese(III) mainly involved type (a)[20-22] and the type(c) complexes.[15,23-26] The type (b), however, is only sporadically reported,[27,28] and studies on this type of mixed ligand complexes are expected to generate new information. The relationship between the stabilities of a mixed ligand complex and its parent complexes has been long disputed and it was thought that the mixed ligand complexes are always more stable than could be expected on statistical grounds, but there are now many examples of the opposite behaviour.[15] Statistically, however, mixed ligand complex formation is always favoured,[29] which has been later supported[15] by elementary electrostatic consideration, steric effect and back-coordination.

It appears, therefore, that studies directed to mixed ligand complexes of manganese(III), particularly of the type (b) mentioned above, may generate some valuable information. Coming back to the case of manganese-fluorine system, one finds that there is a dearth of information regarding mixed fluoro complexes of manganese not only in its +3 but also in +2 states of the metal. There is only one reported[30] mixed fluoro-complex of manganese-(III), i.e., the potassium trifluoromonosulphatomanganate(III), $K_2[MnF_3(SO_4)]$, which was obtained only as a by-product of a reaction carried out for the synthesis of a fluoromanganate(III) complex. The situation thus demands for an extensive work on the mixed ligand complexes of manganese with fluoride being one of the coordinating ligands. It has been known[12,14,31] that most of the simple fluoro complexes of Mn^{3+} have magnetic moments lower than that expected for a normal manganese(III) case. This is ascribed to strong antiferromagnetic exchange interactions. The compounds of manganese(III) containing sulphato or oxalato ligands, on the other hand, exhibit normal magnetic behaviour.[32] It was therefore thought that a mixed ligand manganese(III) complex containing fluoride and sulphate or oxalate as ligands would present a different picture with regard to its magnetic properties. Further, the overall stabilities of such complexes are expected to be more than the corresponding binary complexes, and also they would constitute good examples of complexes of the type(b),

mentioned earlier in this section. In view of this, studies on mixed-fluoro complexes of manganese(III) were undertaken. The results of such studies are incorporated in Chapter 3 and 4. While Chapter 3 deals with alkali-metal and ammonium trifluoro-monosulphatomanganates(III), $A_2[MnF_3(SO_4)]$ (A = Li, Na, K or NH_4), Chapter 4 includes alkali-metal and ammonium trifluoromono-oxalatomanganates(III), $A_2[MnF_3(C_2O_4)]$ (A = Na, K or NH_4).

In a continuation of the studies of manganese(III) chemistry, and noting the importance of and interest on metal acetylaceto-nates,[33-42] it was thought important to develope a new and direct method for obtaining tris(acetylacetonato)manganese(III), $Mn(C_5H_7O_2)_3$. Accordingly, a simple and convenient method has been developed for the synthesis of $Mn(C_5H_7O_2)_3$. Chapter 5 of Part I of the thesis presents a detailed account of the new method of synthesis of $Mn(acac)_3$ (acac = acetylacetone) and results of mass spectrometric studies of the compound.

The most familiar oxidation state of manganese is its +2 state. Manganese(II) is stable towards thermal as well as photo-chemical reactions.[7] In neutral and acidic solutions the pink hexa-aquo ion is extremely resistant to oxidation as shown by the potentials:



In basic media, however, the hydroxide $Mn(OH)_2$ is formed and this is very prone to oxidation, even by air[43]:

$$MnO_2.yH_2O \xleftarrow{0.1v} Mn_2O_3.xH_2O \xleftarrow{-0.2v} Mn(OH)_2$$

The equilibrium constants for formation of the complexes of Mn^{2+} are low, compared to Mn^{2+} salts and those of the divalent cations of succeeding (Fe^{2+} —— Cu^{2+}) elements.[44,45] Moreover, owing to the large size of Mn^{2+} ion, it possesses no ligand field stabilisation energy either in tetrahedral or in octahedral field;[46] thus the manganese(II) ion forms complexes less easily than the manganese(III) ion. This general low ability of Mn^{2+} to form complexes in which electron pairing occurs, and the thermal stability of the sulphate, make the behaviour of the metal in its +2 state much more like that of a non-transition metal than like its neighbours Cr and Fe.[8] Further, the majority of Mn^{2+} compounds are high spin and in appropriate ligand environment it behaves most ideally. In octahedral fields, the d^5 configuration gives spin-forbidden as well as parity forbidden transitions imparting a weak colour of the compounds. But in tetrahedral field the compounds are somewhat more coloured (usually pale yellow/green) since the transitions here are though spin-forbidden but are no longer parity-forbidden.[43] All these factors, therefore, make the chemistry of the metal in +2 state an interesting one.

It was observed that in aqueous solution the formation constants for halogeno complexes are very low,[47]

$$Mn^{++}_{aq} + Cl^{-} \rightleftharpoons MnCl^{+}_{aq} \qquad K \approx 3.85$$

and this varies with the nature of the halide ions used. Foster and Gill[48] have shown that for both the tetrahedral and octahedral arrangements of ligands about manganese(II), the relative values of the ligand field parameters are in the accepted order of the spectrochemical series, namely $I < Br < Cl < F \ll H_2O$ for structurally related compounds. Consequently, the halo complexes, particularly the fluoro-complexes, of the metal in its +2 oxidation state have found a remarkable importance.[47-52]

Tetrafluoromanganates(II) and trifluoromanganates(II) are the two most well studied fluoro-complex of the metal in its +2 oxidation state.[47,50-52] Report on the mixed fluoro complexes of manganese(II), however, appears to be very scanty. As a sequel of studies on fluoro and mixed fluoro complexes of manganese(III), it was felt worthwhile to extend such studies to manganese(II) also. Some success has been achieved in this direction and new complexes, viz., trifluoroaquomanganates(II) and fluoromonooxalatomanganates(II) have been synthesised. Chapter 6 describes the synthesis, characterisation and physico-chemical studies of alkali-metal and ammonium trifluoroaquomanganates(II), $A[MnF_3(H_2O)]$ (A = Na, K, Rb, Cs or NH_4), while the synthesis

and assessment of structure of alkali-metal and ammonium fluoromonooxalatomanganates(II) constitutes the subject matter of Chapter 7.

On realising the problems involved in the existing method of synthesis of bis(acetylacetonato)manganate(II) dihydrate, $Mn(C_5H_7O_2)_2.2H_2O$, a new method of synthesis of the compound has now been developed. The new method does not require any buffer which is considered to be a probable source of impurity. Chapter 8, indeed the last Chapter of Part I, contains the details regarding the new synthesis of $Mn(acac)_2.2H_2O$ and also the results of mass spectrometric studies of the compound.

Apart from manganese, the first row series of transition metals presents one more very important and versatile metal, viz., Chromium. Chromium, somewhat like manganese, exhibits a wide range of oxidation states, of which +6 and +3 represent the comparatively more familiar oxidation states of the metal. Chromium(VI) has the typically important property with regard to its oxidative potential for both organic and inorganic systems. Consequent upon this, there has been a good number of Chromium(VI) reagents developed for the oxidations of various types of organic substrates. It is generally observed, in such reactions that the initial chromium(VI) compound is reduced to its +3 state involving various intermediate stages.

The conversion of Cr^{6+} to Cr^{3+} or the reverse, involving a 3-electron change and having a low probability of being occured in a single step, implies the formation of chromium in intermediate oxidation states in such reactions. Evidences, obtained from kinetics and mechanistic studies, regarding the formation of transient intermediates support this view. Moreover, isolation of some Cr^{5+} and Cr^{4+} compounds, which are unstable in water, and the results of studies of induced oxidations[53,54] have produced some of the most convincing evidence for the formation of chromium in oxidation states +5 and +4 in electron-transfer reactions.

Chromium(VI) compounds are powerful oxidising agents and are extremely useful as oxidants in organic synthesis.[53] The chromium +(VI) reagents often used are chromic acid, dichromates, chromyl chloride, chromyl acetate, chromium trioxide-pyridine complex and t-butyl chromate. A wide range of oxidations which can be accomplished with these reagents also include the following: aryl alkanes and polycyclic aromatic hydrocarbons to aromatic acids with chromic acid and aqueous dichromate; oxidation of aryl alkanes to aldehydes and ketones by chromyl chloride and to acetates with chromyl acetate. One of the major uses of chromium(VI) in synthetic organic chemistry is oxidation of primary alcohols to aldehydes and secondary alcohols to ketones. The mechanisms of many systems have been investigated and

involvement of Cr^{5+} and Cr^{4+} intermediates in these organic oxidations have been established.

A new chromium(VI) reagent, pyridinium fluorochromate, $C_5H_5NHCrO_3F$ (PFC), was synthesised in this laboratory about two years ago, and it became necessary to study its reactivity with regard to oxidation of organic substances. Accordingly such studies have been made and the results are incorporated in Part II of this thesis. Chapter 9 describes the oxidation of organic substrates including polynuclear hydrocarbons involving pyridinium fluorochromate, $C_5H_5NHCrO_3F$ (PFC), while Chapter 10 presents an account of the kinetics and mechanism of oxidations of alcohols with PFC.

Each chapter of the thesis has been so designed as to make it a self-contained one. Thus, in every Chapter there is a brief introduction, and experimental, and results and discussion sections, followed by relevent bibliography. Some of the results have already been published, some are in the press and the rest are under communication.

REFERENCES

[1] R. D. W. Kemmitt, 'The Chemistry of Manganese, Technicium and Rhenium' in Pergamon Texts in Inorganic Chemistry, Oxford, Vol. 22, 1973, p.772.

[2] M. Calvin, Science, 375, 184, 1974.

[3] U. Weser, Structure and Bonding, 41, 5, 1968.

[4] Ref. 1, p. 782.

[5] J. H. Mathews and L. H. Dewey, J. Phys. Chem., 211, 17, 1913.

[6] G. Zimmerman, J. Chem. Phys., 825, 23, 1955.

[7] A. Harriman, Coord. Chem. Rev., 152, 28, 1979.

[8] C. W. Wood and A. K. Holliday, 'Inorganic Chemistry', 3rd ed., Butterworths, London, 1967, p. 336.

[9] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', 3rd ed., Wiley-Eastern, New Delhi, 1976, p. 849.

[10] H. Diebler, Z. Phys. Chem., 64, 68, 1969.

[11] R. E. Hainin and M. A. Suwyn, Inorg. Chem., 139, 142, 6, 1967.

[12] H. Aghabozorg, G. J. Palenik, R. C. Stoufer and J. Summers, Inorg. Chem., 3903, 21, 1982.

[13] D. Oelkrug, Angew Chem. Intern. Ed. Engl., 744, 5, 1966.

[14](a) F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', 4th ed., Wiley, 1980, p. 680.
(b) K. F. Purcell and J. C. Kotz, 'Inorganic Chemistry', Saunders, Philadelphia, 1977, p. 553.
(c) J. E. Huheey, 'Inorganic Chemistry', 2nd ed., Harper and Row, New York, 1978, p. 378.

[15]M. T. Beck, 'The Stability of Complexes in Solution' in MTP International Review of Science — Inorganic Chemistry : Series One, Vol. 9, (ed. M. L. Tobe), 1972, p. 19.

[16]Y. Marcus and I. Eliezer, Coord. Chem. Rev., 273, 41, 1969.

[17]Ya D. Fridman, Proc. 3rd Symp. Coord. Chem., Vol. 2 (Budapest: Akademiai Kiado), 1971.

[18]H. Siegel, Chimia, 489, 21, 1967.

[19]A. E. Martell, Proc. 3rd Symp. Coord. Chem., Vol. 2 (Budapest: Akademiai Kiado), 1971.

[20]M. Zangen, J. Inorg. Nucl. Chem., 867, 31, 1969.

[21]S. C. Srivastava and L. Newman, Inorg. Chem., 762, 6, 1967.

[22]F. Gaizer and M. T. Beck, J. Inorg. Nucl. Chem., 503, 28, 1966.

[23]Y. Kanemura and J. J. Waters, J. Inorg. Nucl. Chem., 1701, 29, 1967.

[24] W. D. Schaap and D. McMasters,
J. Am. Chem. Soc., 4699, 83, 1961.

[25] S. F. Condike and A. E. Martell,
J. Inorg. Nucl. Chem., 2455, 31, 1969.

[26] G. A. L'Heureux and A. E. Martell,
J. Inorg. Nucl. Chem., 481, 28, 1966.

[27] E. J. Bounsall and A. J. Poe, J. Chem. Soc. A, 286, 1966.

[28] K. Krishnan and P. A. Plane, Inorg. Chem., 85, 6, 1967.

[29] V. S. Sharma and J. Schubert, J. Chem. Educ., 506, 46, 1969.

[30] A. J. Edwards, J. Chem. Soc. A, 3074, 1971.

[31] S. Emori, M. Inoue, M. Kishita and M. Kubo,
Inorg. Chem., 1385, 8, 1969.

[32] B. N. Figgis and J. Lewis, Progr. Inorg. Chem., 37, 6, 1964.

[33] J. P. Fackler, Jr., Progr. Inorg. Chem., 361, 7, 1966.

[34] G. H. Cartledge, J. Am. Chem. Soc., 4416, 73, 1951.

[35] R. G. Charles and M. A. Powlikowski,
J. Phys. Chem., 440, 62, 1958.

[36] B. E. Bryant and W. C. Fernelius,
Inorg. Syntheses, 114, 5, 1957.

[37] W. C. Fernelius and B. E. Bryant, Inorg. Syntheses,
105, 5, 1957.

[38]M. Bartlett and G. J. Palenik, J. Chem. Soc., Chem. Commun., 416, 1970.

[39]D. N. Sen and N. Thankarajan, Ind. J. Chem., 94, 4, 1966.

[40]J. P. Fackler, Jr., M. J. Weeks and T. S. Davies, Inorg. Chem., 1994, 7, 1968.

[41]J. P. Fackler, Jr., and A. Avdeef, Inorg. Chem., 1864, 13, 1974.

[42]M. Mrakavova and L. Treindl, Chem. Zvasti, 785, 36, 1982.

[43]Ref. 9, p. 846.

[44]D. N. Haque and M. S. Zetter, Trans. Farad. Soc., 1176, 66, 1970.

[45]K. Kustin, R. F. Pasternaek and E. M. Weinstock, J. Am. Chem. Soc., 4610, 88, 1966.

[46]Ref. 7, p. 160.

[47](a) Ref. 9, p. 848.

(b) R. Colton and J. H. Canterford, 'Halide of the First Row Transition Metals', Wiley, 1969.

[48]J. J. Foster and N. S. Gill, J. Chem. Soc. A, 2625, 1968.

[49]T. A. Zordon and L. G. Hepler, Chem. Rev., 737, 68, 1968.

[50]K. Knox, Acta Cryst., 1115, 14, 1959.

[51]A. Zalkin, K. Lee and D. H. Templeton, J. Chem. Phys., 697, 37, 1962.

[52]R. D. Peacock and D. W. A. Sharp, J. Chem. Soc., 2762, 1959; and references therein.

[53]K. B. Wiberg, "Oxidation by Chromic Acid and Chromyl Compounds" in Oxidation in Organic Chemistry, Part 4, Academic Press, New York, 1965.

[54]J. O. Edwards, 'Inorganic Reaction Mechanisms', Benjamin, New York, 1964, p. 149.

PART I

Synthesis, Characterization and Assessment of Structure of Fluoro, Mixed-Fluoro and Acetylacetonato Compounds of Manganese +(III) and +(II)

CHAPTER 1

Alkali-Metal and Ammonium Pentafluoromanganates(III), $A_2[MnF_5]$ (A = Na, K, Cs or NH_4). New and Convenient Methods of Synthesis, Characterization and Structural Assessment *

Interest in the field of chemistry involving fluoro-containing transition metal compounds[1-9] seem to be never diminishing. Peculiarities of such compounds in respect of their magnetic and structural behaviours probably make them relatively more interesting than the compounds containing other halides, bonded to a metal centre. Some of the fundamental properties of fluorine, e.g., its high electronegativity and small ionic size render it suitable for stabilising higher oxidation states of metals. Although this is generally true, manganese presents a somewhat different story. Thus, the compounds like MnF_7 and

* Results of the work described in this Chapter have been published : J. Chem. Soc. Dalton Trans., 2587, 1981; Synth. React. Inorg. Met.-Org. Chem., 485, 12, 1982; Ind. J. Chem., In press.

$MnOF_5$ do not seem to be known, and indeed one finds that manganese, in its oxidation states +(IV), +(III) and +(II), responds more favourably to the formation of fluoro:complexes[10] under the appropriate conditions.

Coming to the case of manganese(III) and considering its enhanced basic character, it can be easily reconciled that an acidic ligand like fluoride must be able to stabilise[11,12] Mn^{3+} leading to the formation of stable fluoromanganate(III) complexes. Apart from the factors relating to stability of such complexes, coordination of a fluoride ligand to Mn^{3+} brings forth very notable magnetic and structural features. Consequent upon this there has been a continued interest[5,9,13-30] in the studies of various aspects of fluoromanganates(III) chemistry. Synthesis of fluoromanganate(III) complexes has, however, been a general problem. Most of the currently used methods are either based on dry reaction techniques involving anhydrous hydrogen fluoride, which is difficult to handle, or dependent on the use of such starting materials which are difficult to prepare and unstable under ordinary conditions. Alkali-metal pentafluoromanganates(III), $A_2[MnF_5]$ (A = Na, K, Cs or NH_4), for example, have been known for quite sometime, however, no convenient method has been available for their synthesis. It appears from literature that the reaction between a solution of MnF_3 in aqueous hydrofluoric acid and alkali-metal fluorides has been generally used for the synthe-

sis of $A_2[MnF_5]$ compounds.[21,27] The inherent problems of the method are the difficulties involved in the synthesis of MnF_3[31-33] and its stability under normal laboratory conditions. The other methods, viz., (i) the reaction between MnO_2 and KHF_2 in HF,[28] (ii) the electrolytic oxidations of MnF_2 in 40% hydrofluoric acid followed by the addition of a saturated solution of KHF_2 in hydrofluoric acid,[29] and (iii) the oxidation of manganese sulphate with $KMnO_4$ in hydrofluoric acid containing KHF_2,[30] have been used specifically for the synthesis of potassium pentafluoromanganate-(III) monohydrate, $K_2MnF_5.H_2O$. Further it was recently commented[34] that nothing more than the sparse synthesis has been reported for the cesium salt of pentafluoromanganate(III).

In view of this it was thought worthwhile to develope direct, simple and general methods for the synthesis of alkali-metal and ammonium pentafluoromanganates(III), $A_2[MnF_5]$ (A = Na, K, Cs or NH_4). Accordingly, three new methods have been developed for the synthesis of the title compounds. A detailed account of the three new methods of synthesis, characterisation of the compounds obtained thereof and assessment of structures of the compounds constitute the subject matter of this Chapter.

EXPERIMENTAL

The Chemicals used were all reagent grade products (B.D.H., E. Merck, Sarabhai M. Chemicals or Loba Chemie). Infrared spectra were recorded on a Perkin-Elmer model 125 spectrophotometer in nujol as well as in KBr media.

Magnetic susceptibility measurements were made by the Gouy method using $Hg[Co(NCS)_4]$ as the calibrant. The dimagnetic corrections were made using the data given in the literature.[35]

Reflectance spectra were recorded against MgO using Carl Zeiss Jena USU 2-P instrument.

Preparation of MnO(OH).[36] This compound was prepared by following the method described in literature.[36] In a typical preparation, a solution of 2.2 g (10 m mol) $MnSO_4.4H_2O$ in 350 ml of water was treated with 34 ml of a 3% H_2O_2 (30 m mol) solution. An amount of 50 ml of a 0.2 M ammonia solution (10 m mol) was added under constant stirring. The mixture was boiled for about 5 min and then filtered. The dark-brown compound was washed with about 1.5 lit of hot water on the filter and then dried over phosphorous pentoxide in vacuo.

Preparation of Alkali-Metal and Ammonium Bifluorides, AHF_2 (A = Na, K, Rb, Cs or NH_4).[37] Alkali-metal and ammonium

bifluorides, AHF_2, were prepared by the method developed by Chaudhuri and Choudhury.[37]

In an example typical of the general procedure, powdered alkali-metal or ammonium 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 with constant stirring until precipitation was complete, and then allowed to settle. The white crystalline alkali-metal or ammonium bifluoride, AHF_2, was separated by decantation and washed several times with pyridine until the compound was free from hydrofluoric acid. The adhered pyridine was removed by washing with acetone and the compound was finally dried **in vacuo**.

Elemental Analyses.

(i) Estimation of Manganese.[38]

An accurately weighed amount of the compound was decomposed by boiling with 20-25 ml of 0.1 (N) sodium hydroxide solution. Hydrated manganese oxide thus formed was quantitatively separated by filtration, washed with water and then dissolved in a minimum amount of dil. HCl solution. About 0.5 g of hydroxylammonium chloride was added (to keep manganese in its +2 state) to the solution and then warmed after diluting to about 100 ml. The solution was neutralised by dropwise addition of dilute sodium hydroxide solution, and 2-3 ml of triethanolamine was added to

keep the manganese in solution before it was subsequently made alkaline. About 2 ml of the buffer solution (pH = 10) was then added to it followed by the addition of 4-5 drops of Erio T indicator. The solution was then titrated with a standard 0.05 M EDTA solution at about 40 ^{o}C, allowing sufficient time for complex formation, until the colour of the solution permanently changed from red to blue.

1 ml. of 0.05 M EDTA $\equiv$ 2.747 mg Mn.

(ii) Estimation of Fluoride.[39]

An exactly weighed amount of the complex was decomposed by boiling with 20-25 ml of 0.1 (N) sodium hydroxide solution. Hydrated manganese oxide was separated out by filtration and washed several times with water. The filtrate and washings were collected for fluoride estimation. To the combined filtrate and washings, 2 drops of bromo-phenol blue indicator and 3 ml of 10 percent sodium chloride solution were added, and the mixture was diluted to ca 250 ml. Dilute nitric acid was added to it until colour changed to just yellow, followed by the addition of dilute sodium hydroxide solution until the colour ultimately just changed to blue. The mixture was then treated with 1 ml of conc. hydrochloric acid and 5.0 g of lead nitrate, and then heated on a steam-bath. After all the lead nitrate had dissolved, 5.0 g of crystallised sodium acetate was added to the solution

and the whole was digested on a steam-bath for about half an hour with occassional stirring. The solution was then allowed to stand overnight.

For the gravimetric estimation,[39a] the precipated lead chloridefluoride was filtered through a weighed Gooch crucible (Grade 4) and weighed as PbClF after drying at 140-150 ^{o}C to constant weight.

In the volumetric analysis,[39b] the precipitated PbClF was quantitatively collected by filtration through a Whatman 542 paper and washed once with cold water, four times with a saturated solution of lead chloride fluoride, and finally once more with cold water. The precipitate was then dissolved in 100 ml of 5 per cent nitric acid by heating on a steam-bath for 4-5 min. A known excess of standard 0.1 (N) silver nitrate solution was then added to it, followed by digestion on a steam-bath for 30 minutes, and then cooled at room temperature in dark. The precipitated silver chloride was filtered through a sintered glass crucible, washed with cold water. The unreacted silver nitrate in the filtrate and washings was titrated with a standard 0.1 (N) potassium thiocyanate solution using 1 ml of ferric indicator solution untill one drop of thiocyanate produced a permanent faint brown colour.

The amount of silver nitrate in the filtrate, thus found, was subtracted from that originally added, and the fluoride

content of the sample was then calculated from the amount of silver nitrate consumed.

1 ml (N) $AgNO_3$ ≡ 0.0190 g F.

(iii) Estimations of Sodium, Potassium, Cesium and Nitrogen

(a) Determination of Sodium.[40] An accurately weighed amount of the compound was decomposed by treating with dilute ammonia solution. The precipitated hydrated manganese oxide was separated by filtration and washed with water. Sodium was then estimated, from the combined filtrate and washings, gravimetrically as Na_2SO_4 following the procedure described in literature.[40]

(b) Determination of Potassium or Cesium.[41] The manganese compound containing potassium or cesium was decomposed by treating with 0.1 (N) sodium hydroxide solution. The hydrated manganese oxide was separated by filtration and washed with water. From the combined filtrate and washings potassium or cesium was estimated gravimetrically as $KClO_4$ or $CsClO_4$ by the usual method.[41]

(c) Determination of Nitrogen. The estimation of nitrogen was accomplished by the micro analytical technique.

Chemical Determination of the Oxidation State of Manganese

The oxidation state of manganese in each of the compounds was determined chemically by the reduction of a known amount of the

compound with aqueous acidic iron(II) solution followed by estimation of unoxidised Fe^{2+} in the solution.

In an alternative method, the oxidation state of manganese was determined iodometrically by treating a freshly prepared potassium iodide solution acidified with dilute sulphuric acid, with a known amount of the compound followed by titration of the liberated iodine with a standard sodium thiosulphate solution.

Synthesis of Alkali-Metal and Ammonium Pentafluoromanganates(III), $A_2[MnF_5]$ (A = Li, Na, K, Cs or NH_4).

Three new methods have been developed for the synthesis of alkali-metal and ammonium pentafluoromanganates(III). Since the methods are general, in order to avoid repetation, only one representative procedure for each of the methods has been described. However, the details of the amounts of reagents used and the yields of the compounds are set out in the form of a Table after each method.

Method I

Synthesis of $A_2[MnF_5]$ (A = Na or NH_4) and $A_2[MnF_5].H_2O$ (A = K or Cs). An excess of alkali-metal or ammonium difluoride, AHF_2, was intimately mixed with solid potassium permanganate, $KMnO_4$, by powdering together in an agate mortar. The finely mixed powder was dissolved in a minimum volume of water

and filtered. The filtrate was collected in a polyethylene beaker and an excess of acetylacetone was added with constant stirring. An exothermic reaction set in and readily gave a rose-pink coloured microcrystalline product in almost quantitative yield.with the mother liquor becoming colourless. The compound was separated by centrifugation and purified by washing with heptane and finally dried in vacuo. In the case of the sodium salt, the powdered mixture $KMnO_4$-$NaHF_2$ was dissolved in water by slightly warming over a steam-bath in order to avoid using a large volume of water, otherwise necessary, owing to the lower solubility of $NaHF_2$. If properly planned, the whole process takes no more than 30-40 min. The specific gram amounts of the reagents used and the yields of the compounds are given in Table 1; however, the method can be scaled up to higher quantities as well.

Method II

Synthesis of $A_2[MnF_5]$ (A = Na or NH_4) and $A_2[MnF_5].H_2O$ (A = K or Cs). To a suspension of 1.0 g (11.4 m mol) MnO(OH) in a minimum volume of water, 0.5 ml of 40% hydrofluoric acid was added dropwise with constant stirring whereupon the MnO(OH) completely dissolved giving a dark brown solution (A). A concentrated solution of the respective bifluoride AHF_2 (A = Na, K, Cs or NH_4) in a small amount of 40% hydrofluoric acid was added

Table 1. Amounts of Reagents Used and Yields of Alkali-Metal and Ammonium Pentafluoromanganates(III)

Compound	Yield in g (%)	Amount of $KMnO_4$ in g (m mol)	Amount of AHF_2 in g (m mol)	Amount of Acetylacetone in g (m mol)
$(NH_4)_2[MnF_5]$	0.34 (97.1)	0.3 (1.9)	1.0 (17.5)	3.0 (30)
$Na_2[MnF_5]$	0.32 (86.5)	0.3 (1.9)	1.1 (17.7)	4.0 (40)
$K_2[MnF_5].H_2O$	0.44 (93.6)	0.3 (1.9)	1.0 (12.8)	3.0 (30)
$Cs_2[MnF_5].H_2O$	0.78 (95.1)	0.3 (1.9)	2.3 (13.4)	3.0 (30)

directly to the solution (A) with stirring whereby a rose-pink coloured, microcrystalline product appeared immediately. The product $A_2[MnF_5]$ or $A_2[MnF_5].H_2O$ was separated by centrifugation, washed with heptane until it was free from acid, and finally dried in vacuo. The details of amounts of the reagents used and yields of alkali-metal and ammonium pentafluoromanganates(III) are given in Table 2.

A slightly different method had to be adopted for the synthesis of $Li_2[MnF_5]$, for which a separate procedure is given.

To a suspension of 1.0 g (11.4 m mol) of MnO(OH) in a minimum volume of water, 6.0 ml (120 m mol) of 40% hydrofluoric acid was added with constant stirring and a dark brown solution was obtained. To this solution 1.7 g (23 m mol) of lithium carbonate was added in several portion with stirring. An amount of 2-3 ml ethanol was added to the solution, all at a time with vigorous stirring, and a rose-pink coloured product was obtained. The product, $Li_2[MnF_5]$, was immediately separated by centrifugation, washed several times with heptane to make it free from acid, and finally dried in vacuo. The yield of Li_2MnF_5 was 1.2 g (63.8%).

Method III

Synthesis of $(NH_4)_2[MnF_5]$ and $A_2[MnF_5].H_2O$ (A = Na or K).

Pure $KMnO_4$ and dry alkali-metal or ammonium bifluoride, AHF_2 (A = Na, K or NH_4), in the molar ratio 1:2, were separately

Table 2. Amounts of the Reaagnts Used and Yields of Alkali-Metal and Ammonium Pentafluoro-manganates(III)

Compound	Yield in g (%)	Amount of MnO(OH) in g (m mol)	Amount of 40% HF in ml (m mol)	Amount of AHF_2 in g (m mol)
$(NH_4)_2[MnF_5]$	1.9 (89.2)	1.0 (11.4)	2.0 (40)	1.5 (26.3)
$Na_2[MnF_5]$	1.8 (80.0)	1.0 (11.4)	2.5 (50.0)	1.6 (25.8)
$K_2[MnF_5].H_2O$	2.5 (88.7)	1.0 (11.4)	2.2 (44.0)	2.1 (26.9)
$Cs_2[MnF_5].H_2O$	2.2 (88.4)	0.5 (5.7)	1.2 (24.0)	2.3 (13.3)

dissolved in 40% hydrofluoric acid by slightly warming over a steam-bath. The two solutions were then mixed together and filtered to remove any undissolved impurity. The dark pink solution, thus obtained, was heated on a steam-bath with occassional stirring until the colour changed to deep brown (ca 20 min). Heating was continued until crystals began to appear, and the solution was then concentrated by heating in a similar manner for about 2 h. The reaction container was cooled to room temperature and the rose-pink crystallised $A_2[MnF_5].xH_2O$ (A = NH_4, x = 0; or A = Na or K, x = 1), was separated by decantation and finally dried on a filter paper. The compounds were recrystalised from 20% hydrofluoric acid. The specific gram amounts of the reagents used and yields of $(NH_4)_2[MnF_5]$, $Na_2[MnF_5].H_2O$ and $K_2[MnF_5].H_2O$ are set out in Table 3.

Analytical data, room-temperature magnetic moment values, structurally important i.r. bands and chemically estimated oxidation states of manganese are given in Table 4. The electronic spectral data and their assignments are reported in Table 5.

Table 3. Amounts of the Reagents Used and Yields of $(NH_4)_2[MnF_5]$, $Na_2[MnF_5].H_2O$ and $K_2[MnF_5].H_2O$

Compound	Yield in g (%)	Amount of $KMnO_4$ in g (m mol)	Amount of AHF_2 in g (m mol)	Amount of 40% HF in ml(m mol)
$(NH_4)_2[MnF_5]$	1.1 (93.0)	1.0 (6.3)	0.72 (12.6)	15 (300)
$Na_2[MnF_5].H_2O$	1.2 (88.0)	1.0 (6.3)	0.78 (12.6)	20 (400)
$K_2[MnF_5].H_2O$	1.4 (90.0)	1.0 (6.3)	0.98 (12.6)	15 (300)

RESULTS AND DISCUSSION

General Syntheses. —— The Method I described (vide Experimental Section) leads to the synthesis of pentafluoromanganates(III) of alkali-metals and ammonium, sufficient in number to leave little doubt that reductions with acetylacetone (acacH) could be developed for the synthesis of compounds of other transition metals. It has been shown subsequently that the acetylacetone is oxidised[42] in such reactions to give $\alpha,\alpha,\beta,\beta$-tetraacetylethane, $(CH_3CO)_2CH\text{-}CH(CH_3CO)_2$. The yields are almost quantitative and gram quantities of pentafluoromanganates(III) can be synthesised directly from $KMnO_4$ in about 30-40 min with very simple apparatus and without the use of hydrogen fluoride or even hydrofluoric acid. The alkali-metal and ammonium bifluorides AHF_2 (A = Na, K, Cs or NH_4), here act as fluorinating agents. The strategy for the present synthesis was that the reduction of Mn^{7+} by a relatively mild reducing agent like acetylacetone in the presence of F^- (stabilising species for Mn^{3+}) should enable the synthesis of pentafluoromanganates(III). In fact is appears that the success of the Method I largely depends on the presence of both H^+ and stabilising F^- ligands in the solution phase arising from AHF_2.

The Method II involves the reaction among MnO(OH), hydrofluoric acid and alkali-metal or ammonium bifluoride, AHF_2, and is also a general one. This method can be used for the synthesis of all but $Li_2[MnF_5]$ for which a slight modification is necessary owing to the extremely low solubility of LiF. The yields of alkali-metal and ammonium pentafluoromanganates(III), obtained by this method, are very high and the process can be scaled up. The overall reaction leading to the synthesis can be expressed as follows:

$$MnO(OH) + HF + 2\,AHF_2 \longrightarrow A_2[MnF_5] + 2\,H_2O$$

It is required to mention that since an acidic solution prevents pentafluoromanganates(III) from being hydrolysed, the reaction medium has to be maintained acidic by using a little excess of hydrofluoric acid and AHF_2. It is believed that, in the present case, freshly prepared MnO(OH) instantaneously reacts with hydrofluoric acid to form MnF_3 which then reacts with alkali metal or ammonium bifluoride to produce $A_2[MnF_5]$.

It may be noted that while the Method I requires acetylacetone (acacH) as the reducing agent for the synthesis of pentafluoromanganates(III), the Method II requires MnO(OH), as one of the starting materials, which needs an extra preparation. The Method III, however, does not require any of the above-mentioned reagents. This method is based on the reaction of $KMnO_4$, in 40% hydrofluoric acid, with alkali-metal or ammonium bifluoride,

AHF_2, (A = Na, K or NH_4) at steam-bath temperatures. The reaction of $KMnO_4$, in 40% HF, with AHF_2, at ca 100 °C leads to the synthesis of rose-pink coloured, crystalline alkali-metal and ammonium pentafluoromanganates(III), $A_2[MnF_5]$ (A = Na, K or NH_4), in very high yields. The procedure involved is very simple, and the method can be scaled up to higher quantities. The reaction is best monitored by noting the change of colour of the reaction mixture from dark pink to deep brown indicating the reduction of Mn^{7+} to Mn^{3+}, which is generally complete in about 20-25 min. It is difficult to propose the actual mechanism of the electron-transfer reaction taking place in the present case. However, it could be possible that the red-ox reaction between $KMnO_4$ and water might have taken place since oxidation of fluoride to fluorine should not be possible under such conditions. The Method III appears to be the most direct method, but it has the obvious limitation that it can not be applied to the synthesis of pentafluoromanganate(III) of a heavier alkali-metal, namely cesium.

Characterisation and Structural Evaluation. —— The alkali-metal and ammonium pentafluoromanganates(III), A_2MnF_5 (A = Li, Na, K, Cs or NH_4) are all rose-pink coloured crystalline products, unstable in water. They attack glass in the presence of moist air, but can be stored in sealed polythene envelopes for prolonged periods. The stability of the compounds

can be ascertained by periodic estimation of manganese content and determination of oxidation state of the metal.

The chemical determination of oxidation state of manganese is particularly emphasised because the fluoromanganates(III), even at room temperature, might exhibit antiferromagnetic behaviour[13,14,19,21] leading to confusion with regard to the actual oxidation state of the metal. The chemically estimated oxidation states of manganese lie between 2.9 and 3.1 (Table 4) lending strong credence to the contention that manganese in each of the compounds has an oxidation number of +3. It is interesting to note that the NH_4^+, Li^+ and Na^+ salts are generally anhydrous, of the type $A_2[MnF_5]$, whilst the K^+ and Cs^+ salts are monohydrates, $A_2[MnF_5].H_2O$, even though their methods of synthesis are the same.

The structure and composition of the ammonium salt has been the subject matter of some debate;[23,43] although the species consisting of tetragonally elongated octahedra linked through bridging fluoride ions is generally favoured. Based on the results of replicate chemical analyses and infrared spectral studies, the present work also confirms that the ammonium salt is $(NH_4)_2[MnF_5]$ and not $(NH_4)_2[MnF_4(OH)]$. Repeated chemical analyses always conform to the atomic ratio of Mn:F as 1:5, and the infrared spectrum of the compound neither showed any absorption in the δ_{M-O-H} region (1200-900 cm^{-1}) nor absorbed at

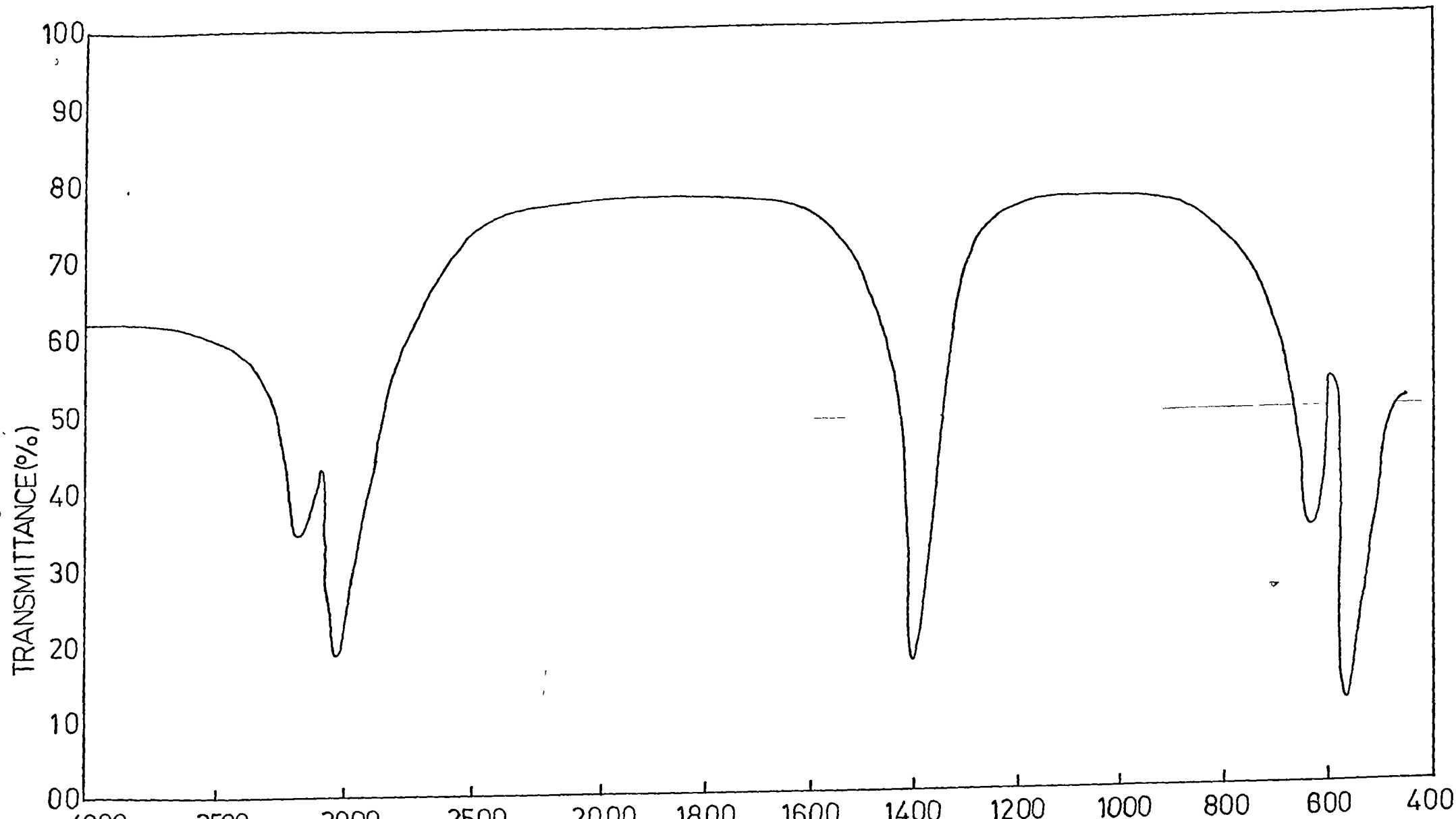
Table 4. Analytical Data, Magnetic Moments, Estimated Oxidation States, and Structurally Significant IR Bands of Alkali-Metal and Ammonium Pentafluoromanganates(III).

Compound	μ_{eff}/BM at 302 K	Estimated Oxidation states of Mn	% found (% calcd)			IR Band cm^{-1}	Assignments	
			A/N	Mn	F			
$(NH_4)_2[MnF_5]$	3.19	3.0	15.15	29.65	51.32	614m ..	$\nu_{(Mn-F)}$	ν_3
			(15.05)	(29.55)	(51.05)	564s ..	$\nu_{(Mn-F)}$	ν_4
						3040s ..	$\nu_{(N-H)}$	ν_1
						3157m ..	$\nu_{(N-H)}$	ν_3
						1400s ..	$\nu_{(N-H)}$	ν_4
$Li_2[MnF_5]$	3.27	3.1	8.82	33.77	58.13	615m ..	$\nu_{(Mn-F)}$	ν_3
			(8.47)	(33.54)	(57.99)	565s ..	$\nu_{(Mn-F)}$	ν_4
$Na_2[MnF_5]$	3.21	3.0	23.4	28.24	48.6	615m ..	$\nu_{(Mn-F)}$	ν_3
			(23.5)	(28.05)	(48.5)	565s ..	$\nu_{(Mn-F)}$	ν_4

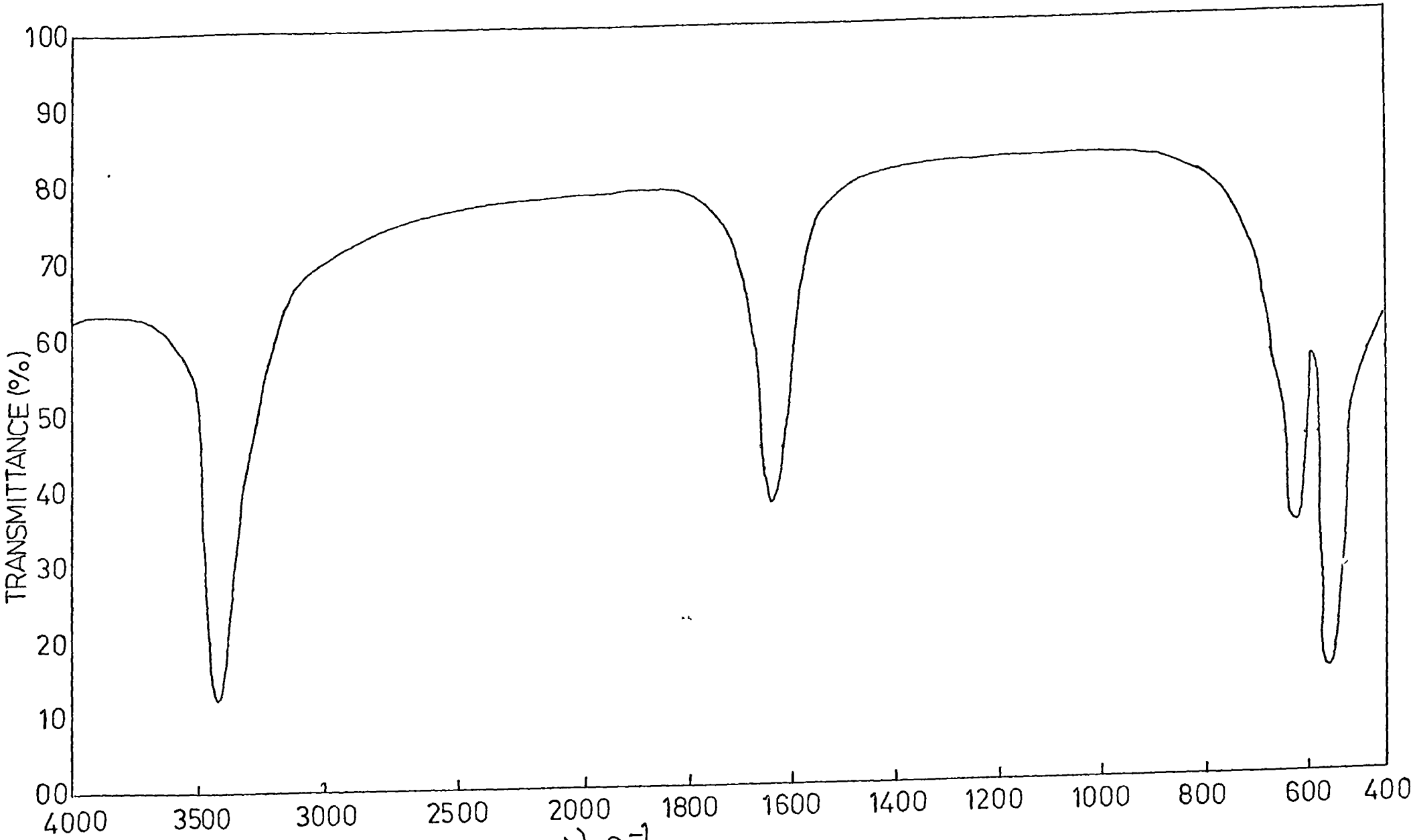
Table 4. contd..... /-

Table 4. (contd.)

Compound	μ_{eff}		A/N %	Mn%	F %	IR	Assignments	
$K_2[MnF_5].H_2O$	3.3	2.9	31.8	22.4	38.7	616m ..	$\nu_{(Mn-F)}$	ν_3
			(31.75)	(22.3)	(38.6)	565s ..	$\nu_{(Mn-F)}$	ν_4
						3460s ..	$\nu_{(O-H)}$	
						1635m ..	$\delta_{(H-O-H)}$	
$Cs_2[MnF_5].H_2O$	3.2	3.1	61.2	12.7	21.85	614m ..	$\nu_{(Mn-F)}$	ν_3
			(61.3)	(12.65)	(21.9)	564s ..	$\nu_{(Mn-F)}$	ν_4
						3455s ..	$\nu_{(O-H)}$	
						1640m ..	$\delta_{(H-O-H)}$	



IR Spectra of $(NH_4)_2[MnF_5]$ (4000-400 cm^{-1})



IR Spectra of $K_2[MnF_5].H_2O$ (4000-400 cm^{-1})

$\sim$3600 cm^{-1} which is typical for ν_{O-H}.[44] The absorption at 3040s, 3157m and 1400s cm^{-1} have been assigned as ν_1, ν_3 and ν_4 modes, respectively, of NH_4^+ and correlate very well with those of the analogous ammonium pentachloromanganate(III).[45] The bands at 614m and 565s cm^{-1} have assigned to ν_3 and ν_4 vibrational modes[46] of Mn-F.

The infrared spectra of alkali-metal and ammonium pentafluoromanganates(III), $A_2[MnF_5]$ (A = Li, Na, K, Cs or NH_4), resemble each other very closely, suggesting thereby that they are all identical structurally and stoichiometrically. Typical of all spectra are the two absorptions at $\sim$615 and $\sim$565 cm^{-1}. The occurrence of vibrations at a relatively low wavenumber in the i.r. spectra implies the presence of octahedral or distorted octahedral MF_6^{n-}, and in keeping with this there are two readily identifiable ν_{Mn-F} bands at ca 615 and ca 565 cm^{-1} [cf. the analysis of ν_{M-F} in MF_6^{n-} complexes][46] Thus, it is evident that Mn^{3+} in $[MnF_5]^{2-}$ displays the Jahn-Teller effect, assumes a distorted octahedral structure with each octahedron being linked to its nearest neighbour through a bridging fluoride ion, and conforms to the crystal structure of $K_2[MnF_5].H_2O$ reported by Edwards.[15] The K^+ and Cs^+ salts show two extra bands at ca 1640 and ca 3460 cm^{-1}, which have been assigned to the δ_{H-O-H} and ν_{O-H} vibrational modes of uncoordinated water, and are in accord with the earlier observations[15,21] and also agree well

with the crystal structure[15] of $K_2[MnF_5].H_2O$. The X-ray data collected from the crystals of the ammonium salt[47] synthesised by the new methods gave the following cell dimensions: a = 6.218(2), b = 7.955(5) and c = 10.716(3) ^oA, and are in excellent agreement with those obtained earlier by Sears and Hoard[14] from $(NH_4)_2[MnF_5]$. This adduces support to the contention that the structures of the compounds obtained by the new methods are the same as those evaluated earlier.[14,15]

The electronic spectra of $(NH_4)_2[MnF_5]$ and $K_2[MnF_5].H_2O$ were recorded and the band positions are summarised in Table 5. The spectra of the two compounds are generally similar, and exhibit three bands at ca 12,000, ca 18,500 and ca 21,000 cm^{-1} designated as band I, II and III respectively. While the band I in each case is broad and stronger than the visible bands II and III, the band III appears as a shoulder. The bands have been assigned, in line with the argument of Davis, Fackler and Weeks,[48] to the transitions $^5B_{1g} \longrightarrow {}^5A_{1g}$, $^5B_{1g} \longrightarrow {}^5B_{2g}$ and $^5B_{1g} \longrightarrow {}^5E_g$ respectively, arising from the appreciably large splitting of ^5E_g ground state of manganese(III) in the complex ion MnF_5^{2-} as a consequence of Jahn-Teller effect. The result of electronic spectral studies suggest that the effective field around manganese(III) in the complex ion is D_{4h}, and conforms well with the reported structure of $(NH_4)_2[MnF_5]$[14] and $K_2[MnF_5].H_2O$.[15]

Table 5. Electronic Spectral Data of $(NH_4)_2[MnF_5]$ and $K_2[MnF_5].H_2O$

Compound	Band I $^5B_{1g} \rightarrow {}^5A_{1g}$ cm^{-1}	Band II $^5B_{1g} \rightarrow {}^5B_{2g}$ cm^{-1}	Band III $^5B_{1g} \rightarrow {}^5E_g$ cm^{-1}
$(NH_4)_2[MnF_5]$	12,100	18,100	21,000
$K_2[MnF_5].H_2O$	12,000	18,700	21,300

The room-temperature (302 K) magnetic moments of $A_2[MnF_5]$ (A = Li, Na, K, Cs or NH_4) lie between 3.19 and 3.3 BM (1 BM = 0.927×10^{-23} A m^2). The values agree well with those reported previously,[13,19] and correlate very well with the proposed structure mentioned above. The lowering of magnetic moments is not to be attributed to spin-pairing, but presumably owes its origin to antiferromagnetic exchange interaction between contiguous manganese(III) ions through a —Mn— F —Mn— chain, in keeping with the reported structure of $(NH_4)_2[MnF_5]$[14] and $K_2[MnF_5].H_2O$.[15]

Thus it is evident, from the results of studies, described in this Chapter, that alkali-metal and ammonium pentafluoromanganates(III), $A_2[MnF_5]$ (A = Li, Na, K, Cs or NH_4), can be synthesised by more direct and convenient methods than those described in the literature. The structures of the compounds synthesised by the new methods are similar to those synthesised by the literature methods.

REFERENCES

[1] J. W. Vaughn, Synth. React. Inorg. Met.-Org. Chem., 585, 9, 1979.

[2] R. G. Limck, Inorg. Chem., 3143, 12, 1977.

[3] J. W. Vaughn, Inorg. Chem., 2397, 20, 1981.

[4] J. W. Vaughn, Inorg. Chem, 844, 22, 1983.

[5] W. Massa, Inorg. Nucl. Chem. Lett., 253, 13, 1977.

[6] J. E. Fergusson, 'Halogen Chemistry of Chromium, Molybdenum and Tungsten', in Halogen Chemistry (ed. V. Gutman), Vol. 3, Academic Press, New York, 1967.

[7] R. D. Peacock, Progr. Inorg. Chem., 41, 2, 1966.

[8] M. K. Chaudhuri and S. K. Ghosh, Inorg. Chem, 4020, 21, 1982.

[9] M. K. Chaudhuri, J. C. Das and H. S. Dasgupta, J. Inorg. Nucl. Chem., 85, 43, 1981.

[10] A. Angelbrecht and A. V. Grosse, J. Am. Chem. Soc., 2042, 76, 1954.

[11] H. J. Emeleus and A. G. Sharpe, 'Modern Aspects of Inorganic Chemistry', ELBS and Routledge and Kegan Paul, 4th ed, 1973, p. 124.

[12] R. G. Pearson, J. Am. Chem. Soc., 3533, 85, 1963.

[13]S. Emori, M. Inoue, M. Kishita and M. Kubo,
Inorg. Chem., 1385, 8, 1969.

[14]D. R. Sears and H. L. Hoard, J. Chem. Phys., 1066, 50, 1969.

[15]A. J. Edwards, J. Chem. Soc. A., 2653, 1971.

[16]P. Bukovec and V. Kaucic, Acta Cryst., 3339, B34, 1978.

[17]W. Massa, Z. anorg. Chem., 254, 415, 1975.

[18]P. Bukovec, B. Orel and J. Siftar, Monatsch, 1299, 105, 1974.

[19]R. D. Peack, J. Chem. Soc., 4684, 1952.

[20]Bode and Voss, Z. anorg. Chem., 190, 1, 1957.

[21]E. Mueller and P. Koppe, Z. anorg. Chem., 160, 68, 1910.

[22]W. E. Hatfield and W. E. Parker,
Inorg. Ncul. Chem. Lett., 7, 1, 1965.

[23]R. Dingle, Inorg. Chem, 1287, 4, 1965.

[24]R. Dingle, J. Mol. Spectry, 426, 9, 1962.

[25]R. Dingle, Acta Chem. Scand., 33, 20, 1966.

[26]N. S. Hush and R. J. M. Hobbs,
Progr. Inorg. Chem., 317, 10, 1970.

[27]I. G. Ryss and B. S. Vitukhnovskoya,
Zh. Neorg. Khim., 1185, 3, 1958.

[28]W. G. Palmer, 'Experimental Inorganic Chemistry', Cambridge,
London, 1954.

[29]B. Cox and A. G. Sharpe, J. Chem. Soc., 1798, 1954.

[30]J. T. Grey, J. Am. Chem. Soc., 605, 68, 1946.

[31]H. J. Emeleus and G. L. Hurst, J. Chem. Soc., 396, 1964.

[32]E. E. Aynsley, R. D. Peacock and P. L. Robinson, J. Chem. Soc., 1622, 1950.

[33]A. G. Sharpe and A. A. Woolf, J. Chem. Soc., 798, 1951.

[34]P. Bukovec and V. Kaucic, J. Chem. Soc., 945, 1977.

[35]B. N. Figgis and J. Lewis, 'Modern Coordination Chemistry', J. Lesis and R. G. Wilkins (Ed.), Chapter 6, Interscience, New York, 1960.

[36]G. Brauer, (ed.), 'Handbook of Preparative Inorganic Chemistry', Vol. 2, Academic Press, London, 1965, p. 1457.

[37]M. K. Chaudhuri and P. K. Choudhury, Chem. Ind. (London),88,1979.

[38]A. I. Vogel, 'A Text Book of Quantitative Inorganic Analysis', 3rd ed., Longman-Green & Co., London, 1962, p. 434.

[39]Ref. 38, (a) p. 569; (b) p. 269.

[40]Ref. 38, p. 557.

[41]Ref. 38, p. 562.

[42]M. N. Bhattacharjee, M. K. Chaudhuri, S. K. Ghosh, Z. Hiese and N. Roy, J. Chem. Soc. Dalton Trans., 0000, 1983.

[43]N. S. Hush and R. J. M. Hobbs, Progr. Inorg. Chem., 259, 10, 1968.

[44]K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', 2nd ed., Wiley-Interscience, 1970, p. 168.

[45]C. F. Bell and D. N. Waters, J. Inorg. Nucl. Chem., 773, 39, 1977.

[46]R. D. Peacock and D. W. A. Sharp, J. Chem. Soc., 2762, 1959.

[47]A. J. Edwards, personal communication.

[48]T. S. Davis, J. P. Fackler, Jr., and M. J. Weeks, Inorg. Chem., 1994, 7, 1968.

CHAPTER 2

Alkali-Metal Tetrafluoromanganate(III) Monohydrates, $AMnF_4 \cdot H_2O$ (A = Rb or Cs). First Synthesis From Aqueous Media, Characterization and Structural Assessment*

It has been known that manganese(III) forms three different types of complex fluorides,[1,2] viz., hexafluoromanganates(III), pentafluoromanganates(III) and tetrafluoromanganates(III). Hexafluoromanganates(III) were studied[3,4] previously by many workers. The case of pentafluoromanganates(III) has been discussed in Chapter 1 of this thesis. The anhydrous salts of the alleged complex ion tetrafluoromanganate(III), MnF_4^-, were described by Hoppe[5] in 1956, and, it appears that, since then there has been a continued interest on studies[6-14] of various aspects involving the complex species MnF_4^-, and some related ones. Although the alleged complex species, MnF_4^-, has been known for some time, there has not been any report on the

* This work has been accepted for publication : Polyhedron, Paper No. 902 (1983).

synthesis of salts of tetrafluoromanganate(III) ion from aqueous solutions. The literature methods[6,7] for the synthesis of such compounds involve dry reaction techniques, complicated conditions and make use of starting materials, which need extra preparations. Thus, for example, the method described by Hoppe[6,7] was based on the reduction of alkali-metal pentafluoromanganates(IV), $AMnF_5$, at high temperatures:

$$AMnF_5 \xrightarrow{350\text{-}400\ ^{o}C} AMnF_4 + HF$$

and the one described by Massa[8] was based on a "symproportion" reaction between manganese(II) and manganese(IV) fluoro compounds:

$$A_2MnF_6 + MnF_2 \longrightarrow 2\ AMnF_4$$

In view of the above it was thought that newer methods of synthesis of tetrafluoromanganates(III), particularly from aqueous media, must be looked for. Accordingly, two methods of synthesis of heavier alkali-metal tetrafluoromanganates(III), $AMnF_4$ (A = Rb or Cs), have been developed. Chapter 2 of the thesis presents a detailed account of the new methods of syntheses, characterization and structural evaluation of two heavier alkali-metal tetrafluoromanganate(III) monohydrates, namely, $RbMnF_4.H_2O$ and $CsMnF_4.H_2O$.

EXPERIMENTAL

All chemicals were of reagent grade (E. Merck, B.D.H., Sarabhai M. Chemicals).

Infrared spectra of KBr pellets and nujol mulls of the compounds were recorded on a Perkin-Elmer model 125 spectrophotometer.

Reflectance spectra were recorded against MgO using a Carl Zeiss Jena VSU 2-P instrument.

Magnetic susceptibility measurements were made, at room temperature, by the Gouy method. $Hg[Co(NCS)_4]$ was the calibrant.

MnO(OH) and rubidium and cesium bifluorides were prepared by the methods already described in Chapter 1.

Elemental Analyses. Estimations of manganese, fluoride and alkali-metals were made quantitatively by adopting the methods mentioned earlier (Chapter 1).

Chemical Determination of the Oxidation State of Manganese. The oxidation state of manganese in each of the compounds was determined by the methods mentioned in Chapter 1.

Synthesis of Alkali-Metal Tetrafluoromanganate(III) Monohydrates, $AMnF_4 \cdot H_2O$ (A = Rb or Cs). Since the two methods developed for the synthesis of the title compounds are general, only two representative procedures are described.

Method I

Pure $KMnO_4$ and dry AHF_2 (A = Rb or Cs) in the molar ratio 1:2, were separately dissolved in 40% hydrofluoric acid by slightly warming over a steam-bath. The two solutions were mixed together and filtered to remove any undissolved impurity. The dark pink filtrate, thus obtained, was heated on a steam-bath (ca 100 °C) with occassional stirring, while the colour changed to deep brown in about 20 min. Heating was continued until crystals began to appear. The reaction mixture was further concentrated by heating in a similar manner for about 2 h, and then allowed to cool in a freezerfor about 5 h. The deep brown crystallized $AMnF_4 \cdot H_2O$ compound was separated by decantation and dried by placing between folds of filter papers, and then stored in a polyethelene capsule. The specific gram amounts of the reagents used and the yields of $AMnF_4 \cdot H_2O$ (A = Rb or Cs) are reported in Table 1.

Method II

Freshly prepared MnO(OH) and dry AHF_2 (A = Rb or Cs), maintaining the molar ratio 1:2, were separately dissolved in

Table 1. Amounts of the Reagents Used and the Yields of $AMnF_4.H_2O$ (A = Rb or Cs)

Compound	Yield in g (%)	Amount of $KMnO_4$ in g (m mol)	Amount of AHF_2 in g (m mol)	Amount of 40% HF in ml (m mol)
$RbMnF_4.H_2O$	1.3 (88)	1.0 (6.3)	1.6 (12.6)	20 (400)
$CsMnF_4.H_2O$	0.7 (79)	0.5 (3.2)	1.1 (6.4)	12 (240)

excess of 40% hydrofluoric acid. Both the solutions were warmed over a steam-bath for ca 5 min and then mixed together under magnetic stirring. The deep brown solution thus obtained was filtered, and the filtrate was concentrated by heating over a steam-bath (ca 100 °C) until deep brown crystals just started appearing. Heating was continued for a further period of about 2 h. The reaction container was then cooled, for 5-7 h, in a freezer, and the crystalline $AMnF_5.H_2O$ was obtained in a very high yield with the mother liquor becoming practically colourless. The crystals were separated in a manner analogous to that

described under Method I. The amounts of the reagents used and the yields of $AMnF_4.H_2O$ (A = Rb or Cs) obtained by Method II are summarised in Table 2.

Table 2. Amounts of the Reagents Used and the Yields of $AMnF_4.H_2O$ (A = Rb or Cs)

Compound	Yield in g (%)	Amount of MnO(OH) in g (m mol)	Amount of AHF_2 in g (m mol)	Amount of 40% HF in ml (m mol)
$RbMnF_4.H_2O$	2.2 (82)	1.0 (11.4)	2.84 (22.8)	20 (400)
$CsMnF_4.H_2O$	1.3 (81)	0.5 (5.7)	1.96 (11.4)	15 (300)

The analytical data, chemically determined oxidation state of manganese, magnetic moment values and the infrared band positions are set out in the Table 3, while the electronic spectral data and their assignments are given in Table 4.

RESULTS AND DISCUSSION

It has been known for quite some time that alkali-metal and ammonium salts of the anion MnF_5^{2-} can be synthesised from aqueous media,[15-17] but the synthesis of salts of MnF_4^- ion under such conditions has not previously been reported. The brown coloured salts of the alleged MnF_4^- ion were prepared always by dry methods.[6-8] In the course of studies on fluoromanganates(III) chemistry (vide Chapter 1), it was observed that the solutions of $A_2[MnF_5]$ (A = NH_4 or Na, K, Cs) in 40% hydrofluoric acid on concentration, by heating at ca 100 °C, reproduced $A_2[MnF_5]$ only when the counter cation, A^+, was Na^+, K^+ or NH_4^+, but not, however, with $A^+ = Cs^+$, instead in the case of the cesium salt a deep brown crystalline compound with the atomic ratio. Mn:F as 1:4, was obtained. Subsequently it was noticed that reaction of $KMnO_4$ with AHF_2 (A = Na, K, Cs or NH_4) in 40% hydrofluoric acid at ca 100 °C gave similar results. Further it was observed that reactions of MnO(OH) in AHF_2 and 40% hydrofluoric at ca 100 °C led to rose-pink crystalline compounds with A being Na, K or NH_4, and a dark brown compound with A being Cs, and thought that the brown crystals could be the corresponding salts of MnF_4^- ion. Accordingly, in line with our contention, two series of reactions were carried out at ca 100 °C (steam-bath)

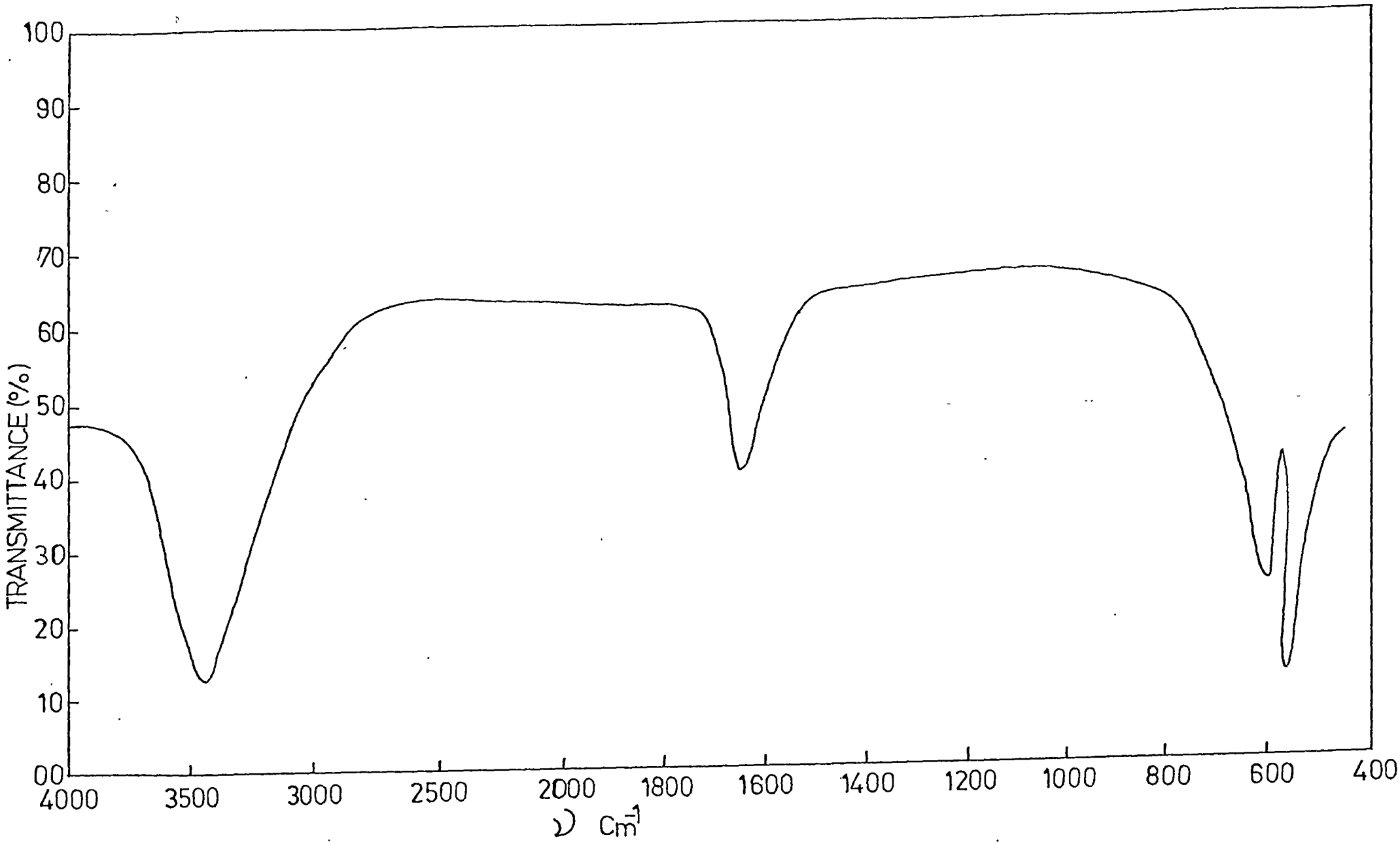
with one series involving $KMnO_4$, AHF_2 (A = Rb or Cs) and 40% hydrofluoric acid, and the other series involving MnO(OH), AHF_2 (A = Rb or Cs) and 40% HF (vide Experimental section). Each of the reactions ultimately afforded deep brown crystalline compound of the type $AMnF_4.H_2O$ (A = Rb or Cs). It is necessary to mention that these methods yield $AMnF_4.H_2O$ compounds only with heavier counter cations like Rb^+ and Cs^+, and the temperature at which such reactions should be carried out is ca 100 °C.

The newly synthesised compounds are insoluble in common organic solvents, and in water they decompose, thereby precluding their molar conductance measurements. They attack glass in the presence of moisture, however, they are capable of being stored undecomposed in sealed polythene capsules. The stability of the compounds can be ascertained by periodic estimation of the manganese content, and determination of oxidation state of the metal by chemical methods.

The importance of chemical determination of oxidation state of manganese, in such compounds, has been explained in Chapter 1. The chemically estimated oxidation state of manganese in the compounds, has been found to lie between 2.9 and 3.1. This supports the contention that manganese, in each of the two compounds, occurs in its +3 state. Magnetic susceptibility measurements show that the room temperature magnetic moments of $RbMnF_4.H_2O$ and $CsMnF_4.H_2O$ are 4.9 and 5.1 BM (1 BM = 0.927×10^{-23}

Table 3. Analytical Data, Magnetic Moment Values, Estimated Oxidation States of Manganese, Structurally Significant Infrared Bands of $AMnF_4 \cdot H_2O$ (A = Rb or Cs)

Compound	μ_{eff}/BM at 299 K	Estimated Oxidation states of Mn	% found (% Calc.)			IR Bands cm^{-1}	Assignments
			A	Mn	F		
$RbMnF_4 \cdot H_2O$	4.9	2.9	36.5 (36.46)	23.57 (23.44)	32.5 (32.42)	600m ...	$\nu_{(Mn-F)}$
						530s ...	$\nu_{(Mn-F)}$
						3465s ...	$\nu_{(O-H)}$
						1640m ...	$\delta_{(H-O-H)}$
$CsMnF_4 \cdot H_2O$	5.1	3.1	47.3 (47.15)	19.54 (19.49)	26.85 (26.96)	600m ...	$\nu_{(Mn-F)}$
						535s ...	$\nu_{(Mn-F)}$
						3460s ...	$\nu_{(O-H)}$
						1642m ...	$\delta_{(H-O-H)}$



IR Spectra of $Cs[MnF_4].H_2O$ (4000-400 cm^{-1})

A m^2) respectively. The values correspond to the spin-only value for four unpaired electron, 4.9 B.M., and are in conformity with those found for the salts of the alleged MnF_4^- species previously synthesised by dry methods.[6-8]

The infrared spectra, in the region of 4000-200 cm^{-1}, of $RbMnF_4.H_2O$ and $CsMnF_4.H_2O$ resemble each other very closely suggesting that the compounds are similar both structurally and stoichiometrically. The most prominent feature of the spectra is the absorptions in the relatively low wave number. It is quite reasonable to assign these bands to manganese-fluorine vibrations.[3] The spectral pattern implies the presence of octahedral or distorted octahedral MF_6^{n-}, and in keeping with this there are two readily identifiable ν_{Mn-F} bands at 600 and $\sim$530 cm^{-1} (cf. the analysis of ν_{M-F} in MF_6^{n-} complexes).[3,16,17] This therefore leads us to believe that the alleged MnF_4^- species assumes a distorted octahedral structure probably with axial elongation through trans-linked —Mn—F—Mn—F—Mn— chains. In addition to the halide dependent bands, the compounds exhibit two vibrations at ca 1640 and ca 3460 cm^{-1}. These bands resemble in their shapes and positions, those observed for the $K_2MnF_5.H_2O$ in which it has been proved that it contains one molecule of uncoordinated water.[18] This therefore enables one to infer that the compounds described in this Chapter probably contain one molecule of unccordinated water in each of them.

The reflectance spectra of $RbMnF_4 \cdot H_2O$ and $CsMnF_4 \cdot H_2O$ are similar and each of them exhibits three bands at $\sim$12,000, $\sim$18,500 and $\sim$22,000 cm^{-1}, designated as bands I, II and III respectively. The band I in each case is broad and stronger than the visible bands II and III. The three bands have been assigned[19] to the transitions $^5B_{1g} \longrightarrow {}^5A_{1g}$, $^5B_{1g} \longrightarrow {}^5B_{2g}$ and $^5B_{1g} \longrightarrow {}^5E_g$ respectively, arising from the appreciably large splitting of ^5E_g ground state of manganese(III) in the complex, as a consequence of Jahn-Teller effect. The result is in agreement with our contention that the effective field around manganese(III) in the complex species is most probably D_{4h}, and accordingly the electronic d-d states for the manganese(III) in the tetragonally elongated configuration can be arranged energetically as $^5B_{1g} < {}^5A_{1g} < {}^5B_{2g} < {}^5E_g$. A comparison of the low-energy band (band I), assigned to $^5B_{1g} \longrightarrow {}^5A_{1g}$ transition in the reflectance spectra of MnF_6^{3-} ($\sim$9,000 cm^{-1})[20,21] and in those present complexes ($\sim$12,000 cm^{-1}), show a very appreciable shift in position. This shift is a clear reflection of the Jahn-Teller effect leading to a tetragonally elongated octahedral structure[19] of complex ion through trans-linked —Mn—F—Mn—F— chains.

It appears, therefore, that the heavier alkali-metal (Rb or Cs) salts of the alleged MnF_4^- ion can be synthesised from aqueous media under the appropriate conditions. The complex ion most probably has a polymeric structure through translinked -Mn-F-Mn- chains.

Table 4. Electronic Spectral Data of $AMnF_4 \cdot H_2O$ (A = Rb or Cs)

Compound	Band I $^5B_{1g} \rightarrow {}^5A_{1g}$ cm^{-1}	Band II $^5B_{1g} \rightarrow {}^5B_{2g}$ cm^{-1}	Band III $^5B_{1g} \rightarrow {}^5E_g$ cm^{-1}
$RbMnF_4 \cdot H_2O$	12,100	18,400	21,700
$CsMnF_4 \cdot H_2O$	12,000	18,800	22,800

REFERENCES

[1] W. Levason and C. A. McAuliffe, Coord. Chem. Rev., 353, 7, 1972.

[2] G. Siebert and R. Hoppe, Z. anorg. Chem., 117, 391, 1972.

[3] R. D. Peacock and D. W. A. Sharp, J. Chem. Soc., 2762, 1959.

[4] (a) B. Cox and A. G. Sharpe, J. Chem. Soc., 1798, 1954.

(b) B. Cox, J. Chem. Soc., 3251, 1954.

(c) H. Bode, H. Jenssen and V. Bandte,
Angew. Chem., 304, 65, 1953.

(d) A. G. Sharpe and A. A. Woolf, J. Chem. Soc., 798, 1951.

[5] R. Hoppe, K. Blinne and W. Liebe, International Conference on Coordination Chemistry, London, 1959; Chem. Soc. (London), Special Publication, 1956, 83.

[6] R. Hoppe, W. Dahne and W. Klemm,
Ann. Chim. (Paris), 658, 1, 1962.

[7] R. Hoppe, W. Liebe and W. Dahne,
Z. Anorg. Allgem. Chem., 276, 307, 1961.

[8] W. Massa, Inorg. Nucl. Chem. Lett., 253, 13, 1977.

[9] P. Bukovec and J. Sifter, Thermochim. Acta, 117, 21, 1977

[10] P. Bukovec and J. Sifter, Monatsch Chem., 387, 108, 1977.

[11] P. Bukovec and V. Kaucic,
J. Chem. Soc. Dalton Trans., 945, 1977.

[12] V. Kaucic and P. Bukovec,
J. Chem. Soc. Dalton Trans., 1512, 1979.

[13] W. Massa and M. Steiner, J. Solid State Chem., 137, 32, 1980.

[14] B. R. Stults, R. S. Marianelli and V. W. Day,
Inorg. Chem., 722, 14, 1975.

[15] E. Mueller and P. Koppe, Z. anorg. Chem., 160, 68, 1910.

[16] M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta and
D. T. Khathing, J. Chem. Soc. Dalton Trans., 2587, 1981.

[17] M. N. Bhattacharjee, M. K. Chaudhuri, A. Kathipri, H. S.
Dasgupta and D. T. Khathing, Synth. React. Inorg. Met.-Org.
Chem., 485, 12, 1982.

[18] A. J. Edwards, J. Chem. Soc. A, 2653, 1971.

[19] T. S. Davis, J. P. Fackler, Jr., and T. J. Weeks,
Inorg. Chem., 1994, 7, 1968.

[20] W. E. Hatfield and W. E. Parker,
Inorg. Nucl. Chem. Lett., 7, 1, 1965.

[21] D. Oelkrug, Angew. Chem. Intern. Ed. Engl., 744, 5, 1966.

CHAPTER 3

First Reported Synthesis and Physico-Chemical Studies of Alkali-Metal and Ammonium Trifluoromonosulphatomanganates(III), $A_2[MnF_3(SO_4)]$ (A = Li, Na, K, or NH_4)*

Although the tripositive oxidation state is quite common for many first-row transition metals, manganese(III) presents a different story probably because of its strong oxidising power and photolytic instability.[1] It has been shown in Chapters 1 and 2 that fluoride is one of the very important ligand for stabilising manganese(III). In addition to fluoride, the anions like sulphate, oxalate, pyrophosphate, etc. are also expected to form stable compounds of manganese(III).[2] Sulphato complexes of manganese(III) seem to have been rather less exhaustively studied, probably because of the lack of many well-defined sulphato compounds of manganese(III).[3] The most

* The work described in this Chapter has been accepted for publication:
Polyhedron, Ms. No. 902 (1983), in press.

studied sulphato compound of manganese(III) is the $CsMn(SO_4)_2 \cdot 12H_2O$ compound. It has been shown that this compound is an alum of Mn^{3+}, and in which the Mn^{3+} ion is surrounded by a nearly regular octahedron of water molecules.[4-7] The magnetic moment of the compound was observed to be normal (μ = 4.81 BM at 290 K)[5], unlike the binary fluoro-complexes of manganese(III) described in Chapter 1. Survey of literature further shows that a mixed-ligand fluoro complex of manganese(III), $K_2[MnF_3(SO_4)]$, is probably the only known mixed-fluoro complex of manganese(III), was obtained as a by-product in the preparation of $K_2MnF_5 \cdot H_2O$ by Palmer's method.[8] Subsequently crystal structure of the compound was determined.[8] It appears that the complex ion, $[MnF_3(SO_4)]^{2-}$, represents a very interesting example in which opposite type of Jahn-Teller effect, that axial contraction and equatorial elongation, is observed.[8] However, there appears to be no report in the literature concerning directly the synthesis of various salts of the complex ion, $[MnF_3(SO_4)]^{2-}$, characterisation and physico-chemical studies. Thus, it was thought worthwhile to undertake such studies.

Chapter 3 of the thesis reports three general methods of synthesis of alkali-metal and ammonium trifluoromonosulphatomanganates(III), $A_2[MnF_3(SO_4)]$; also, characterisation, and the results of physico-chemical studies of $A_2[MnF_3(SO_4)]$ compounds. Also presented in this Chapter is a set of internally

consistend data concerning the effect of sulphate ligand on the magnetic properties of fluoro-manganates(III).

EXPERIMENTAL

The chemicals used were all reagent grade products.

Infrared spectra were recorded on a Perkin-Elmer model 683 spectrophotometer.

Reflectance spectra of the compounds were recorded against MgO using a Carl Zeiss Jena VSU 2-P instrument.

Magnetic susceptibility measurements were made by the Gouy method using $Hg[Co(NCS)_4]$ as the calibrant.

MnO(OH) was prepared by the literature method (described in Chapter 1).

Elemental Analyses. Manganese, fluoride, Na, K and N were estimated by the methods described in Chapter 1. For estimation of fluoride, only the volumetric method was adopted.

Estimation of SO_4^{2-} (Ref. 9). A known amount of the compound was first treated with 20-25 ml of 0.1 (N) sodium hydroxide solution. The precipitated hydrated manganese oxide

was separated by filtration and carefully washed several times with water, and the combined filtrate and washings was retained for estimation of SO_4^{2-}.

The solution was concentrated by boiling and then neutralised with dilute nitric acid. An amount of 5 ml concentrated hydrochloric acid was added to the solution and the whole was boiled for nearly 40 min. The sulphate content in the resulting solution was then determined gravimetrically as barium sulphate carefully following the procedure described in literature[9].

Chemical Determination of the Oxidation State of Manganese

The chemical determination of the oxidation state of manganese in each of the fluorosulphatomanganate(III) compounds was accomplished by the methods described in Chapter 1, and the result obtained thereof are summarised in Table 4.

Synthesis of Alkali-Metal and Ammonium Trifluoromonosulphatomanganates(III), $A_2[MnF_3(SO_4)]$ (A = Li, Na, K or NH_4).

Three different methods have been developed for the synthesis of the title compounds. Since each of the methods is a general one, only three representative procedures are described.

Method I

Synthesis of Alkali-Metal and Ammonium Trifluoromonosulphatomanganates(III), $A_2[MnF_3(SO_4)]$ (A = Li, Na, K or NH_4).

Solid potassium permanganate and A_2SO_4, taken in the molar ratio 1:1, were mixed intimately by powdering together. The mixed powder was dissolved in a minimum volume of water by gentle warming over a steam-bath (ca 5 min) followed by the addition of 40% hydrofluoric acid, maintaining the molar ratio between $KMnO_4$ and HF at 1:4. The deep-pink solution was then cooled to room temperature and 38% formaldehyde solution was added dropwise with constant stirring until a permanent deep-brown solution (A) was obtained. The solution (A) was concentrated to nearly one-third of its original volume by warming over a steam-bath, and then allowed to cool in a freezer for 2-3 h to obtain crystallised pink-brown alkali-metal and ammonium trifluoromonosulphatomanganates(III), $A_2[MnF_3(SO_4)]$. The compound was separated by filtration, washed with heptane and finally dried in vacuo. While in the case of the sodium salt the solution (A) was concentrated to about 50% of the original volume, in the case of the lithium salt it was not concentrated at all, instead a small amount of ethanol was added to initiate precipitation. This was necessary in order to obtain pure end-products in the two selective cases. The gram amounts of the reagents used and the yields of the compounds are given in Table 1.

Table 1. Amounts of Reagents Used and Yields of Alkali-Metal and Ammonium Trifluoromonosulphatomanganates(III)

Compound	Yield in g (%)	Amount of $KMnO_4$ in g (m mol)	Amount of A_2SO_4 in g(m mol)	Amount of 40% HF in ml (m mol)	Amount of HCHO in g (m mol)
$(NH_4)_2[MnF_3(SO_4)]$	1.3 (87)	1.0 (6.3)	0.83 (6.3)	1.3 (26)	5 (166.5)
$Li_2[MnF_3(SO_4)]$	1.1 (79)	1.0 (6.3)	0.69 (6.3)	1.3 (26.0)	5 (166.5)
$Na_2[MnF_3(SO_4)]$	1.0 (63)	1.0 (6.3)	0.9 (6.3)	1.3 (26.0)	5 (166.5)
$K_2[MnF_3(SO_4)]$	1.6 (89)	1.0 (6.3)	1.1 (6.3)	1.3 (26.0)	5 (166.5)

Method II

Synthesis of Alkali-Metal and Ammonium Trifluoromonosulphatomanganates(III), $A_2[MnF_3(SO_4)]$ (A = Li, Na, K or NH_4).

Freshly prepared MnO(OH), taken as a suspension in water, was dissolved in 40% hydrofluoric acid maintaining the molar ratio of MnO(OH) and HF at 1:4. A concentrated solution of A_2SO_4 (molar ratio of MnO(OH) : A_2SO_4 as 1:1) was added to the above mentioned solution with constant stirring. The mixture was heated over a steam-bath for ca 25 min in order to ensure completion of reaction. The dark brown solution, thus obtained, was worked in a manner analogous to that described under Method I to obtain pink-brown salts of $A_2[MnF_3(SO_4)]$ (A = Li, Na, K or NH_4). The details of the amounts (g) of the reagents used and the yields of the compounds are set out in Table 2.

Method III

Synthesis of Potassium and Ammonium Trifluoromonosulphatomanganates(III), $A_2[MnF_3(SO_4)]$ (A = K or NH_4).

Freshly prepared MnO(OH) was dissolved in 40% hydrofluoric acid, and a solution of $A_2S_2O_8$ (A = K or NH_4) was added to it with gentle stirring (molar ratio of MnO(OH):HF:$A_2S_2O_8$ as 1:4:1). The deep-brown solution, thus obtained, was heated at ca 100 °C with occassional stirring until the volume was reduced to nearly one-fourth of the original volume. The solution was then cooled

Table 2. Amounts of Reagents Used and Yields of Alkali-Metal and Ammonium Trifluoro-monosulphatomanganates(III)

Compound	Yield in g (%)	Amount of MnO(OH) in g (m mol)	Amount of 40% HF in ml(m mol)	Amount of A_2SO_4 in g (m mol)
$(NH_4)_2[MnF_3(SO_4)]$	2.4 (86.0)	1.0 (11.4)	2.3 (46.0)	1.5 (11.4)
$Li_2[MnF_3(SO_4)]$	2.1 (84.0)	1.0 (11.4)	2.3 (46.0)	1.25 (11.4)
$Na_2[MnF_3(SO_4)]$	1.8 (62.0)	1.0 (11.4)	2.3 (46.0)	1.63 (11.4)
$K_2[MnF_3(SO_4)]$	2.8 (85.0)	1.0 (11.4)	2.3 (46.0)	2.0 (11.4)

in a freezer for 2-3 h to obtain the pink-brown crystalline $A_2[MnF_3(SO_4)]$ (A = K or NH_4). The compound was separated by decantation, washed three times with heptane and finally dried by placing between folds of a filter paper. The gram amounts of the reagents used and the yields of potassium trifluoromonosulphatomanganate(III), $K_2[MnF_3(SO_4)]$, and ammonium trifluoromonosulphatomanganate(III), $(NH_4)_2[MnF_3(SO_4)]$, are reported in Table 3.

Table 3. Amounts of Reagents Used and Yields of Potassium Trifluoromonosulphatomanganates(III) and Ammonium Trifluoromonosulphatomanganates(III)

Compound	Yield in g (%)	Amount of MnO(OH) in g (m mol)	Amount of 40% HF in ml(m mol)	Amount of $A_2S_2O_8$ in g (m mol)
$(NH_4)_2[MnF_3(SO_4)]$	2.5 (89)	1.0 (11.4)	2.3 (46)	2.6 (11.4)
$K_2[MnF_3(SO_4)]$	2.8 (85)	1.0 (11.4)	2.3 (46)	3.1 (11.4)

Analytical data, chemically estimated oxidation states of manganese, room-temperature magnetic moment values and structurally important infrared bands are summarized in Table 4. Electronic spectral band positions and their assignments are given in Table 5.

Pyrolysis of Ammonium Trifluoromonosulphatomanganate(III) $(NH_4)_2[MnF_3(SO_4)]$. An amount of 0.5 g of $(NH_4)_2[MnF_3(SO_4)]$ was heated at 340 ± 5 °C in a muffle furnace, by placing the sample in platinum crucible, until a constant weight was reached. The white pyrolysis product was found to be anhydrous $MnSO_4$. Yield 0.31 g (weight loss 37.9%). [Analysis. Found : Mn, 36.41%; SO_4, 63.68%. Calc. for $MnSO_4$: Mn, 36.38%; SO_4, 63.62%. Chemically estimated oxidation state of Mn, 2.1).

RESULTS AND DISCUSSION

It was reported in Chapter 1 that alkali-metal and ammonium pentafluoromanganates(III), $A_2[MnF_5]$, could be easily synthesised by the reduction of $KMnO_4$ with acetylacetone in the presence of alkali-metal and ammonium bifluorides, at the cost of oxidation of acetylacetone[10] to $\alpha,\alpha,\beta,\beta$-tetraacetylethane, $(CH_3CO)_2CH\text{-}CH(CH_3CO)_2$, or by the reaction of MnO(OH), 40% HF and

alkali-metal and ammonium bifluorides under mild conditions. The work has now been extended to the synthesis of mixed fluoro-sulphatomanganates(III) by carrying out reactions in the presence of both F^- and SO_4^{2-} ligands. One of the aims was to see whether sulphate ligand could compete with F^- to form complexes of manganese(III), and if so, what would be the extent of such a competetion. Accordingly, the reaction of $KMnO_4$ with aqueous hydrofluoric acid and alkali-metal or ammonium sulphate in the presence of formaldehyde, or the reaction of MnO(OH) with 40% HF and alkali-metal or ammonium sulphate lead to the synthesis of trifluoromonosulphatomanganates(III) of alkali-metals and ammonium, sufficient in number to leave little doubt that under the appropriate conditions SO_4^{2-} can be made to compete with F^- to form compounds of manganese(III). The yields are very high and the compounds can be synthesised by methods (vide Experimental section) which are simple and straight-forward. The role of formaldehyde in the synthesis involving $KMnO_4$ was to reduce Mn^{7+}. It is evident from the results that, at least under the present conditions, manganese can not be reduced below its tripositive oxidation state, and that the maximum number of SO_4^{2-} ligand that can be brought to coordination with Mn^{3+}, in the presence of F^- ions, is one since the reactions involving higher qunatities of alkali-metal and ammonium sulphates (e.g., Mn : SO_4^{2-} at 1:2) did not alter the results in any way.

In an attempt to study the effect of peroxydisulphate on Mn^{3+} in presence of fluoride ions, we carried out the reaction of MnO(OH) with 40% hydrofluoric acid and $A_2S_2O_8$ (A = K or NH_4). There again, however, the compounds obtained were nothing other than the $A_2[MnF_3(SO_4)]$, thereby enabling us to conclude that in the presence of F^- ions Mn^{3+} can not be oxidised. It appears, from the type of complex species obtained now and that obtained in an earlier work,[11] that most probably MnF_3 is formed first in the reaction media which subsequently undergoes further reaction with SO_4^{2-}, in the present case, to ultimately give the complex $[MnF_3(SO_4)]^{2-}$ ion. The occurrence of the SO_4^{2-} ligand in the complex species obtained from the reaction of MnO(OH), 40% HF and $A_2S_2O_8$ must owe its origin to the process $S_2O_8^{2-} + 2e \longrightarrow 2\ SO_4^{2-}$ as the consequence of electron-transfer between peroxydisulphate, $S_2O_8^{2-}$, and water.

Characterisation and Assessment of Structure. The alkali-metal and ammonium trifluoromonosulphatomanganates(III), $A_2[MnF_3(SO_4)]$, are all pink-brown crystalline compounds stable for prolonged periods. The stability can be ascertained from the periodic estimation of manganese and determination of oxidation state of the metal in the compound. A comparison of stability of the $A_2[MnF_3(SO_4)]$ compounds with the corresponding pentafluoromanganates(III), A_2MnF_5, reveals that the former is comparatively more stable in the presence of air. The enhanced

stability may be attributed to the presence of coordinated SO_4^{2-} group in the title compounds. The $A_2[MnF_3(SO_4)]$ compounds are insoluble in common organic solvents, and in water they decompose rather rapidly thus precluding the molar conductance measurements.

For the reasons already mentioned in Chapters 1 and 2, we emphasize on the results of chemical determination of oxidation states of manganese in the newly synthesised compounds. The chemically estimated oxidation state of manganese was found to lie between 2.9 and 3.1 (Table 4) supporting the contention that manganese in each of the compounds has an oxidation number of +3.

The room temperature (288 K) magnetic moments of the alkali-metal and ammonium trifluoromonosulphatomanganates(III), $A_2[MnF_3(SO_4)]$, have been found to occur between 4.0 and 4.2 BM (1 BM $\simeq$ 0.927×10^{-23} A m^2), much lower than the spin only value for a d^4 system. It is interesting to note that whereas the binary fluoro-complexes of manganese(III), e.g., $A_2[MnF_5]$ show the magnetic moment of about 3.2 BM (strong antiferromagnetic case)[11-13] and the sulphato compounds of manganese(III) exhibit the moment of about 4.8 BM (normal)[5], the magnetic moments of the mixed fluorosulphatomanganates(III) is ca 4.1 BM. It is, therefore, evident that the degree of antiferromagnetic exchange interaction can be controlled by the substitution of two F^- ligands by an SO_4^{2-} ligand in going from $[MnF_5]^{2-}$ to $[MnF_3(SO_4)]^{2-}$.

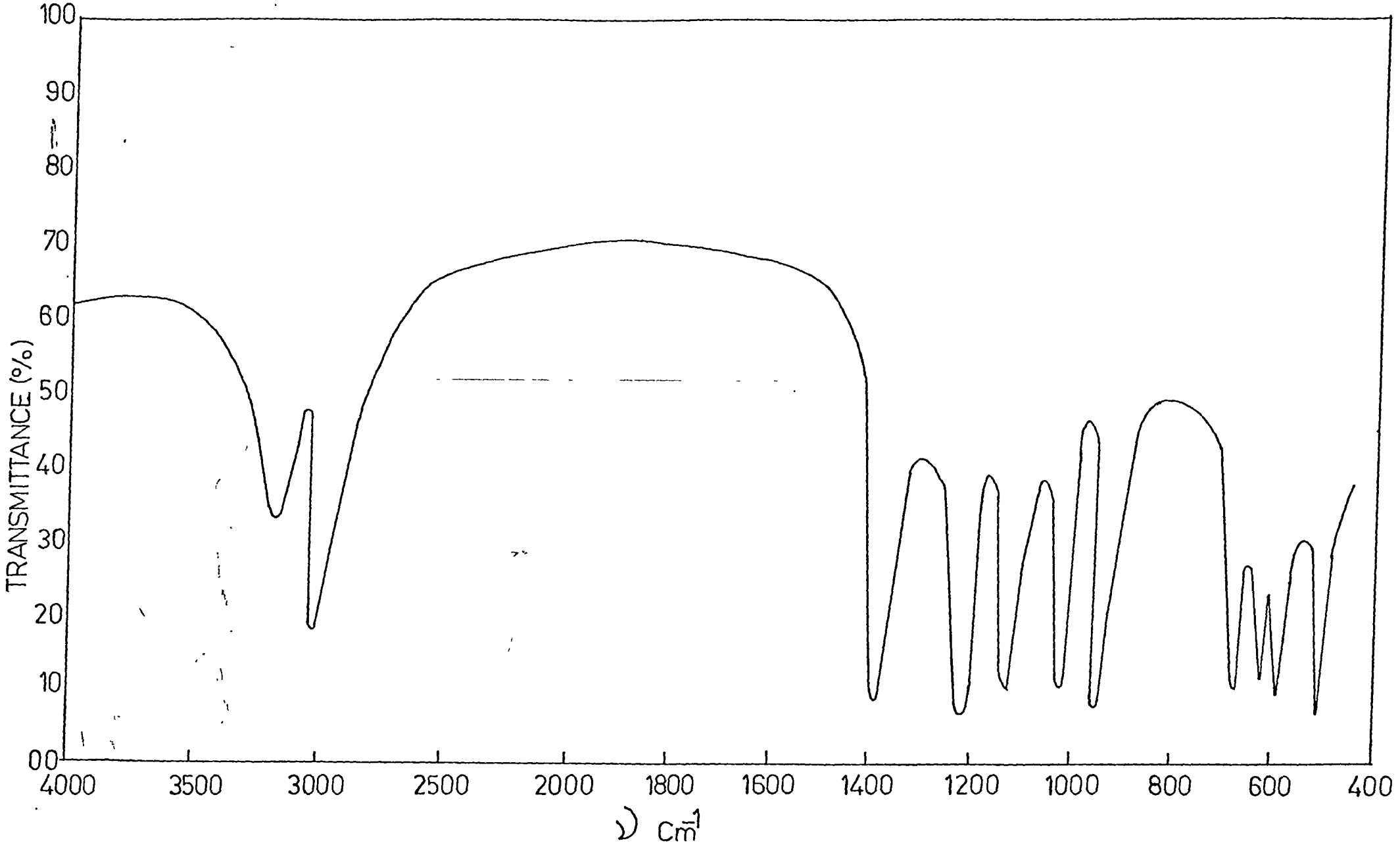
Table 4. Analytical Data, Magnetic Moments, Estimated Oxidation States of Mn, and Structurally Significant IR Bands of $A_2[MnF_3(SO_4)]$ (A = Li, Na, K or NH_4)

Compound	μ in B.M. at 288K	Est. Oxidn. st. of Mn	% found (% calc.) A/N	Mn	F	SO_4	IR Bands in cm^{-1}	Assignments
$(NH_4)_2[MnF_3(SO_4)]$	4.1	3.1	11.4 (11.48)	22.6 (22.51)	23.2 (23.35)	39.4 (39.35)	1225s, 1145s, 1025s .. ν_3 970s .. ν_1 680s, 635s, 605s .. δ	SO
							525s .. $\nu_{(Mn-F)}$	
							3158m .. ν_3 3040s .. ν_1 1400s .. ν_4	NH_4^+ modes
$Li_2[MnF_3(SO_4)]$	4.2	3.0	-	24.8 (24.76)	25.4 (25.69)	43.4 (43.29)	1230s, 1145s, 1030s .. ν_3 975s .. ν_1 685s, 630s, 608s ..	SO
							530s .. $\nu_{(Mn-F)}$	

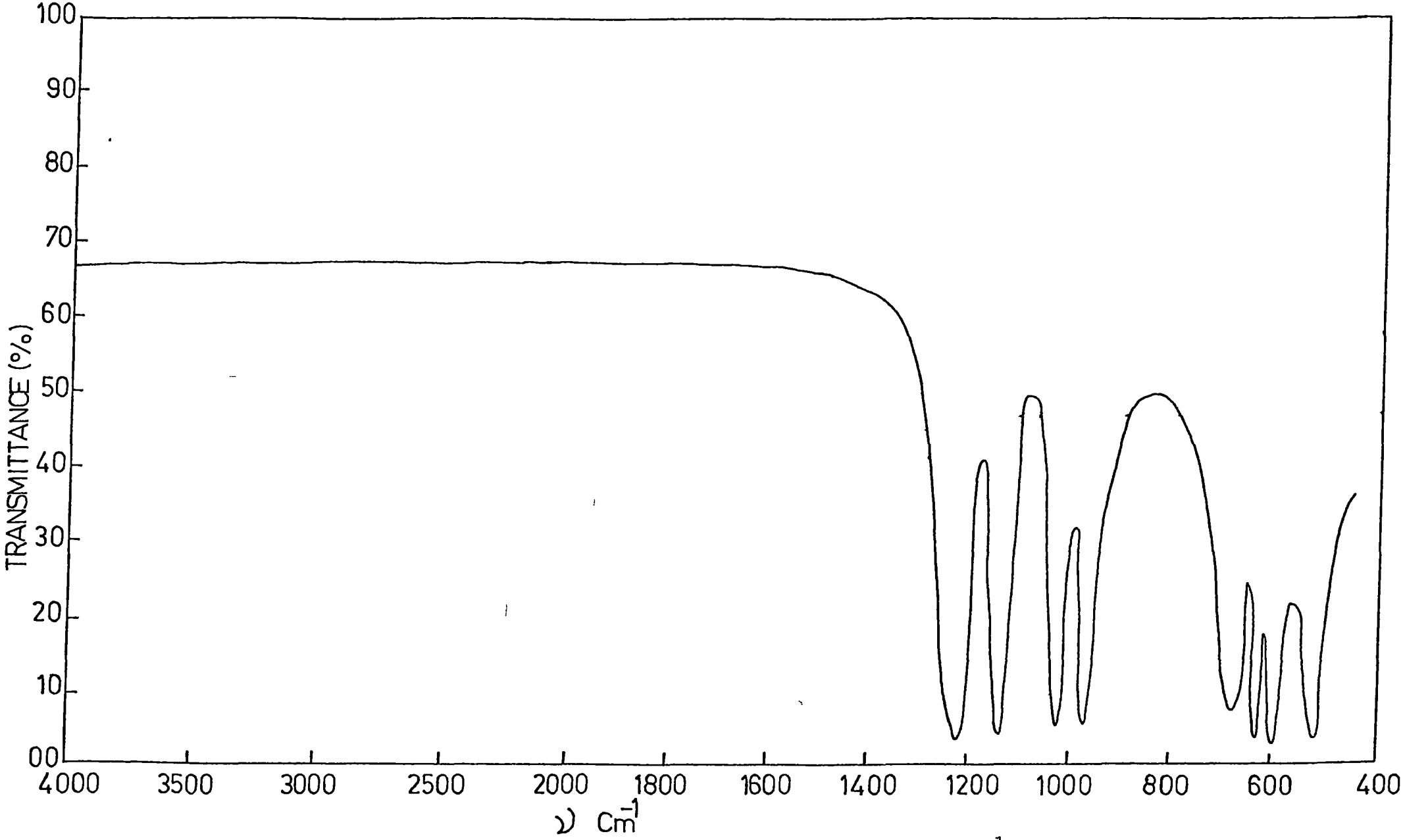
Table 4... contd...../-

Table 4. (contd.....)

$Na_2[MnF_3(SO_4)]$	4.1	2.9	18.2 (18.1)	21.8 (21.63)	22.6 (22.44)	37.6 (37.82)	1230s, 1140s, 1030s .. ν_3 975s .. ν_1 680s, 630s, 605s .. δ	SO
							530s .. ν(Mn-F)	
$K_2[MnF_3(SO_4)]$	4.0	3.1	27.5 (27.32)	19.5 (19.2)	20.1 (19.92)	33.6 (33.56)	1230s, 1145s, 1030s .. ν_3 975s .. ν_1 680s, 630s, 605s .. δ	SO
							525s .. ν(Mn-F)	



IR Spectra of $(NH_4)_2[MnF_3(SO_4)]$ (4000-400 cm^{-1})



IR Spectra of $K_2[MnF_3(SO_4)]$ (4000-400 cm^{-1})

The infrared spectra of the four salts reported in this Chapter resemble each other very closely which suggest that the compounds are similar both structurally and stoichiometrically. The i.r. spectra of the compounds show SO frequencies falling at ca 1230, ca 1145, ca 1030, ca 975, ca 684, ca 635 and ca 605 cm^{-1} and the ν_{Mn-F} at ca 525 cm^{-1}. The pattern suggest a lowering of symmetry[14] of the SO_4^{2-} group from T_d to C_{nv}, and rule out the presence of an ionic SO_4^{2-}. Further the splitting of the ν_3 and δ modes of SO into three bands each (Table 4) enables us to assign a C_{2v} symmetry[15] to the SO_4^{2-} group. Although the ν_{SO} modes appear at relatively higher frequencies than those usually observed for a bridging[15,16] SO_4^{2-}, the possibility of intermolecular sulphato bridging, in the compounds, can not be ruled out. In fact the $K_2[MnF_3(SO_4)]$, which was obtained as a by-product[8] of some other reaction, was shown by X-ray analysis, to have a polymeric structure[8] through bridging SO_4^{2-} group.

The electronic spectra of $A_2[MnF_3(SO_4)]$ (A = K or NH_4) are similar and exhibit three bands at ~ 21,500, ~ 17,900 and ~ 13,600 cm^{-1}, which have been assigned to the transitions[17] $^5B_{1g} \longrightarrow {}^5E_g$, $^5B_{1g} \longrightarrow {}^5B_{2g}$ and $^5B_{1g} \longrightarrow {}^5A_{1g}$ respectively (Table 5). This suggests an appreciable splitting of ^5E_g ground state of manganese(III) in $[MnF_3(SO_4)]^{2-}$ as a consequence of Jahn-Teller effect.

Table 5. Electronic Spectral Data of $(NH_4)_2[MnF_3(SO_4)]$ and $K_2[MnF_3(SO_4)]$

Compound	Band I $^5B_{1g} \rightarrow {}^5A_{1g}$ cm^{-1}	Band II $^5B_{1g} \rightarrow {}^5B_{2g}$ cm^{-1}	Band III $^5B_{1g} \rightarrow {}^5E_g$ cm^{-1}
$(NH_4)_2[MnF_3(SO_4)]$	13,500	17,850	21,300
$K_2[MnF_3(SO_4)]$	13,700	18,200	21,700

Pyrolysis of ammonium trifluoromonosulphatomanganate-(III), $(NH_4)_2[MnF_3(SO_4)]$, at 340 ± 5 °C showed that the compound lost 37.9% wight in ca 45 min to attain a constant weight. The pyrolysis product is white, and it has been found to contain Mn and SO_4^{2-} only. The results of chemical analyses showed the stoichiometry of Mn : SO_4^{2-} as 1:1, and the chemically estimated oxidation state of manganese was found to be 2.1. These results led us to conclude that the pyrolysis product $MnSO_4$. The formation of $MnSO_4$ from $(NH_4)_2[MnF_3(SO_4)]$ requires a loss of 38.14% in weight and agrees very well with the experimentally obtained value.

It appears, therefore, that alkali-metal and ammonium trifluoromonosulphatomanganates(III), $A_2[MnF_3(SO_4)]$, can be synthesised directly from $KMnO_4$ or MnO(OH). The $A_2[MnF_3(SO_4)]$ compounds are relatively more stable than the corresponding $A_2[MnF_5]$ compounds. The complex species, $[MnF_3(SO_4)]^{2-}$, may have a polymeric structure through bridging sulphato groups.

REFERENCES

[1] A. Harriman, Coord. Chem. Rev., 147, 28, 1979.

[2] R. E. Hainin and M. A. Suwyn, Inorg. Chem., 139, 142, 6, 1967.

[3] (a) A. G. R. P. Ubbelohde, J. Chem. Soc., 1605, 1935.
(b) C. G. Barraclough and M. L. Tobe, J. Chem. Soc., 1993, 1961.

[4] N. S. Hush and R. J. N. Hobbs, Progr. Inorg. Chem., 259, 10, 1968.

[5] B. N. Figgis and J. Lewis, Progr. Inorg. Chem., 37, 6, 1964.

[6] H. Hartman and H. L. Schlaefer,
Z. Naturforsch, 760, 6A, 1951.

[7] C. Furlani and A. Ciana, Ann. Chim. (Rome), 286, 48, 1958.

[8] A. J. Edwards, J. Chem. Soc. A, 3074, 1971.

[9] A. I. Vogel, 'A Text Book of Quantitative Inorganic Analysis'
Longman Green & Co., London, 1962, p. 462.

[10] M. N. Bhattacharjee, M. K. Chaudhuri, S. K. Ghosh, Z. Hiese
and N. Roy, J. Chem. Soc. Dalton Trans., 0000, 1983.

[11] M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dalgupta,
A. Kathipri and D. T. Khathing, Synth. React. Inorg. Met.-Org.
Chem, 485, 12, 1982.

[12]S. Emori, M. Inour, M. Kishita and M. Kubo, Inorg. Chem., 1385, 8, 1969.

[13]M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta and D. T. Khathing, J. Chem. Soc. Dalton Trans., 2587, 1981.

[14]K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', 2nd ed., Wiley-Interscience, London, 1970, p. 123.

[15]C. G. Barraclough and M. L. Tobe, J. Chem. Soc., 1993, 1961.

[16]R. Eskenazi, J. Raskovan and R. Levitus, J. Inorg. Nucl. Chem., 521, 28, 1966.

[17]T. S. Davis, J. P. Fackler, Jr., and M. J. Weeks, Inorg. Chem., 1994, 7, 1968.

CHAPTER 4

Alkali-Metal and Ammonium Trifluoromonooxalatomanganates(III), $A_2[MnF_3(C_2O_4)]$ (A = Na, K or NH_4). Synthesis, Characterization and Structural Assessment

Studies involving mixed-ligand fluoro-complexes of manganese(III) are rather scanty. This could be owing to the non-availability of suitable methods for the synthesis of such compounds. One of the very frequently referred compound of Mn^{3+} is potassium tris(oxalato)manganate(III) trihydrate, $K_3[Mn(C_2O_4)_3].3H_2O$, which can be prepared without much difficulties and an extensive work has been done on this compound.[1-4] However, salts of the complex ion, $Mn(C_2O_4)_3^{3-}$, with counter cations other than K^+ or $Co(NH_3)_6^{3+}$ could not be isolated owing to their extreme instability.[1] As a sequel of studies on the chemistry of manganese(III), described in Chapters 1 to 3, it was thought that the stability of oxalatomanganate(III) compounds can be enhanced by the introduction of fluoride ligands into the coordination sphere of Mn^{3+} along with the oxalato group. This will provide not only new compounds of manganese(III)

but also an opportunity to compare their properties with those of the corresponding binary fluoromanganate(III) and binary oxalatomanganate(III) complexes. Further, it was thought that the magnetic properties of mixed fluorooxalatomanganate(III) complexes would be interesting, like those of the fluorosulphato complexes of manganese(III), and might enable us to get a set of internally consistent data concerning the effect of oxalato group on the magnetic behaviour of pentafluoromanganates(III), or the effect of fluoride ligands on the magnetic property of tris(oxalato)manganate(III) complex. In view of the above, studies on mixed fluoro-oxalato complexes of manganese(III) were undertaken. Chapter 4 describes the synthesis and structural assessment of the hitherto unknown alkali-metal and ammonium trifluoromonooxalatomanganates(III), $A_2[MnF_3(C_2O_4)]$.

EXPERIMENTAL

Chemicals used were all reagent grade products (B.D.H., E. Merck or Sarabhai M. Chemicals).

Infrared spectra of the compounds were recorded on a Perkin-Elmer model 683 spectrophotometer.

Electronic spectra were recorded on Beckman model UV -26 spectrophotometer.

Magnetic susceptibility measurements were made by the Gouy method. $Hg[Co(NCS)_4]$ was the calibrant.

MnO(OH) was prepared by the method described in Chapter 1.

Elemental Analyses. Manganese, sodium, potassium, and nitrogen were determined by the methods described in Chapter 1. Fluoride estimation was made by the volumetric method, details of which has been given in Chapter 1.

Estimation of Oxalate ($C_2O_4^{2-}$). An accurately weighed amount of the compound was treated with 25 ml 0.1 (N) sodium hydroxide solution, and then 100 ml water was added to it. The whole was boiled for ca 15 min followed by filtration. The precipitated hydrated manganese oxide was washed several times with water. The filtrate and washings were collected and from which the oxalate content of the compound was determined by the following method.

The combined filtrate and washings was neutralised with dilute sulphuric acid. An amount of 15 ml of concentrated sulphuric acid was added to the solution followed by 2-3 g of boric acid. The resulting solution was then titrated against standard 0.1 (N) potassium permanganate solution maintaining

the temperature of the solution at ca 60 °C.

1 ml of 0.1 (N) potassium permanganate = 0.044 g $C_2O_4^{2-}$ solution.

Chemical Determination of the Oxidation State of Manganese.

The oxidation state of manganese was determined iodometrically by treating a freshly prepared ice-cold potassium iodide solution acidified with dilute sulphuric acid followed by titration of the liberated iodine with a standard sodium thiosulphate solution. The iodine titration was done under ice-cold condition.

Synthesis of Alkali-Metal and Ammonium Trifluoromonooxalatomanganates(III), $A_2[MnF_3(C_2O_4)]$ (A = Na, K or NH_4)

As the methods of syntheses of the sodium, potassium and ammonium trifluoromonooxalatomanganates(III) are similar only a representative method is described.

Freshly prepared MnO(OH) was dissolved in 40% hydrofluoric acid with maintenance of the molar ratio of MnO(OH) and HF at 1:4-5. The resultant solution was warmed at ca 100 °C for about 5 min followed by filtration to remove any undissolved material. The filtrate was cooled to room temperature, and to it was slowly added with occassional stirring a concentrated solution of oxalate $A_2C_2O_4$ (A = Na, K or NH_4), with maintenance

of the molar ratio of MnO(OH) and $A_2C_2O_4$ at 1:1. The colour of the solution changed from dark-brown to deep-pink. The solution was then stirred for a further period of ca 10 min at room temperature (ca 20 °C). Ethyl alcohol was slowly added to the pink solution until precipitate started appearing. An additional amount of ethyl alcohol was then added to the above solution taking care that the total volume of alcohol did not exceed half of that of the original deep-pink solution. The precipitated pink coloured alkali-metal or ammonium trifluoromonooxalatomanganate(III), $A_2[MnF_3(C_2O_4)]$, was separated by filtration under suction, washed 2-3 times with small portions of ethyl alcohol, and finally dried in vacuo. The specific gram amounts of the reagents used and the yields of various alkali-metal and ammonium trifluoromonooxalatomanganates(III) are reported in Table 1.

Analytical data, estimated oxidation states of manganese, magnetic moment values, and IR band positions are set out in Table 2. The electronic spectral band positions and their assignments are given in Table 3.

Table 1. Amounts of Reagents Used and Yields of Alkali-Metal and Ammonium Trifluoro-monooxalatomanganates(III)

Compound	Yield in g (%)	Amount of MnO(OH) in g(m mol)	Amount of 40% HF in ml(m mol)	Amount of $A_2C_2O_4$ in g (m mol)
$(NH_4)_2[MnF_3(C_2O_4)]$	2.4 (90)	1.0 (11.4)	2.5 (50.0)	1.62 (11.4)
$Na_2[MnF_3(C_2O_4)].5H_2O$	3.4 (89)	1.0 (11.4)	2.5 (50.0)	1.53 (11.4)
$K_2[MnF_3(C_2O_4)].H_2O$	3.2 (94)	1.0 (11.4)	2.5 (50.0)	2.1 (11.4)

RESULTS AND DISCUSSION

It has been known for quite some time that manganese(III) forms, under the appropriate condition, deep pink tris(oxalato)-manganate(III), $[Mn(C_2O_4)_3]^{3-}$, ion, in solutions, which can be isolated in the solid state as its potassium salt, i.e., $K_3[Mn(C_2O_4)_3].3H_2O$.[1] It was further reported, in this connection, that attempts to prepare salts of the complex ion, $[Mn(C_2O_4)_3]^{3-}$, with other cations, except for the $Co(NH_3)_6^{3+}$, were futile. However, there seems to be no reported example of mixed fluoro-oxalato compounds of manganese(III).

In the course of studies (Chapter 3) mainly aimed at the synthesis and structural assessment of mixed fluoro-compounds of manganese(III), it was observed that the reaction of MnO(OH) in 40% hydrofluoric acid with alkali-metal or ammonium oxalate, $A_2C_2O_4$, gave a deep-pink coloured solution, at room temperature, and this was found to be stable for quite a long time under that condition. This led us to think that the colour must be owing to some mixed fluoro-oxalato complex of manganese(III). In order to stabilise a manganese(III)-oxalate complex, and also to enable formation of a fluoro-oxalato complex of manganese(III), the present studies were carried out in the presence of an excess of fluoride ions (arising from aqueous HF; Mn:F at 1:4-5),

strongly stabilizing ligands for trivalent manganese (**vide** Chapter 1 and 2). It was further thought, it might be conducive if some coordination positions were blocked by F^- ligands prior to the reaction of alkali-metal or ammonium oxalate. Accordingly the reaction of MnO(OH) in 40% HF with $A_2C_2O_4$ (A = Na, K or NH_4) gave rise to the formation of $[MnF_3(C_2O_4)]^{2-}$ species in the solution. The complex ion was isolated as its alkali-metal or ammonium salt by the addition of alcohol, which facilitated precipitation of the solid compound. A plausible interpretation of this result is that MnO(OH) first reacts with HF to produce MnF_3 in the medium which ultimately undergoes further reaction with $A_2C_2O_4$ such that the formation of $[MnF_3(C_2O_4)]^{2-}$ is favoured.

The reaction is best monitored by IR spectroscopy. This was accomplished by isolating a small amount of the compound followed by recording its IR spectrum. The observance of bands owing to coordinated $C_2O_4^{2-}$ and a band at ca 490 cm^{-1} owing to ν_{Mn-F} indicated the completion of the reaction. It is evident that, under the present condition, the maximum number of fluoride and oxalate ligands coordinated to the manganese(III) centre is 3 and 1 respectively.

Characterization and Assessment of Structure. The alkali-metal and ammonium trifluoromonooxalatomanganates(III) are all pink micro-crystalline products. While the ammonium

salt of the complex ion is anhydrous, $(NH_4)_2[MnF_3(C_2O_4)]$, the sodium and potassium salts are hydrated, $Na_2[MnF_3(C_2O_4)].5H_2O$ and $K_2[MnF_3(C_2O_4)].H_2O$. It is notable that in the present case the three salts can be isolated without any specific difficulty. All the three salts of trifluoromonooxalatomanganate(III) ion are much more stable than the corresponding potassium tris-(oxalato)manganate(III), $K_3[Mn(C_2O_4)_3].3H_2O$, and can be stored in sealed polyethylene envelopes for a period of 25-30 days. However, they can be stored in dark for prolonged periods. The stability of the compounds can be ascertained from their unaltered colour, and can be checked by periodic estimation of manganese and oxalate contents and chemical determination of the oxidation state of manganese. The estimation of oxidation states of manganese, in the present series of compounds, should be best done at ice-bath temperatures to eliminate any interference from oxalate. The estimation of oxidation state of manganese, in such compounds, is considered to be of extreme importance in order to decide about the actural oxidation number of the metal since the magnetic moments in many such cases, of which the present series of compounds are no exception, are not straight forward. The chemically determined oxidation states of manganese was found to lie between 3 and 3.1 lending support to the contention that manganese, in each of the compounds, has the oxidation number of +3.

The room temperature magnetic moments of alkali-metal and ammonium trifluoromonooxalatomanganates(III) were found to fall between 4.2 and 4.3 BM. It is evident that the values are lower than that of a normal manganese(III) (d^4 case) compound. A comparison of magnetic moment values of the present series of compounds with those of the alkali-metal and ammonium pentafluoromanganates(III), A_2MnF_5, (vide Chapter 1) compounds, and that of the potassium tris(oxalato)manganate(III),[1] $K_3[Mn(C_2O_4)_3].3H_2O$, reveals that the magnetic moments of $A_2[MnF_3(C_2O_4)]$ compounds are higher than those of the corresponding A_2MnF_5 compounds (strong antiferromagnetic cases), but lower than that of $K_3[Mn(C_2O_4)_3].3H_2O$ (normal). This, therefore, suggests the lowering in antiferromagnetic exchange interaction in going from A_2MnF_5 to $A_2[MnF_3(C_2O_4)]$ as a result of replacement of two F^- ligands by an oxalato ligand per formula unit. Alternatively, it can be said that there is a definite hike in the antiferromagnetic exchange interaction in going from $K_3[Mn(C_2O_4)_3].3H_2O$ to $A_2[MnF_3(C_2O_4)]$ owing to the introduction of three F^- ligands in place of two $C_2O_4^{2-}$ ligands. It may be mentioned that the magnetic moments of the present series of compounds closely resemble those of the alkali-metal and ammonium trifluoromonosulphatomanganates(III), $A_2[MnF_3(SO_4)]$, leading us to believe that there may be some sort of structural similarity between $A_2[MnF_3(SO_4)]$ and $A_2[MnF_3(C_2O_4)]$ compounds.

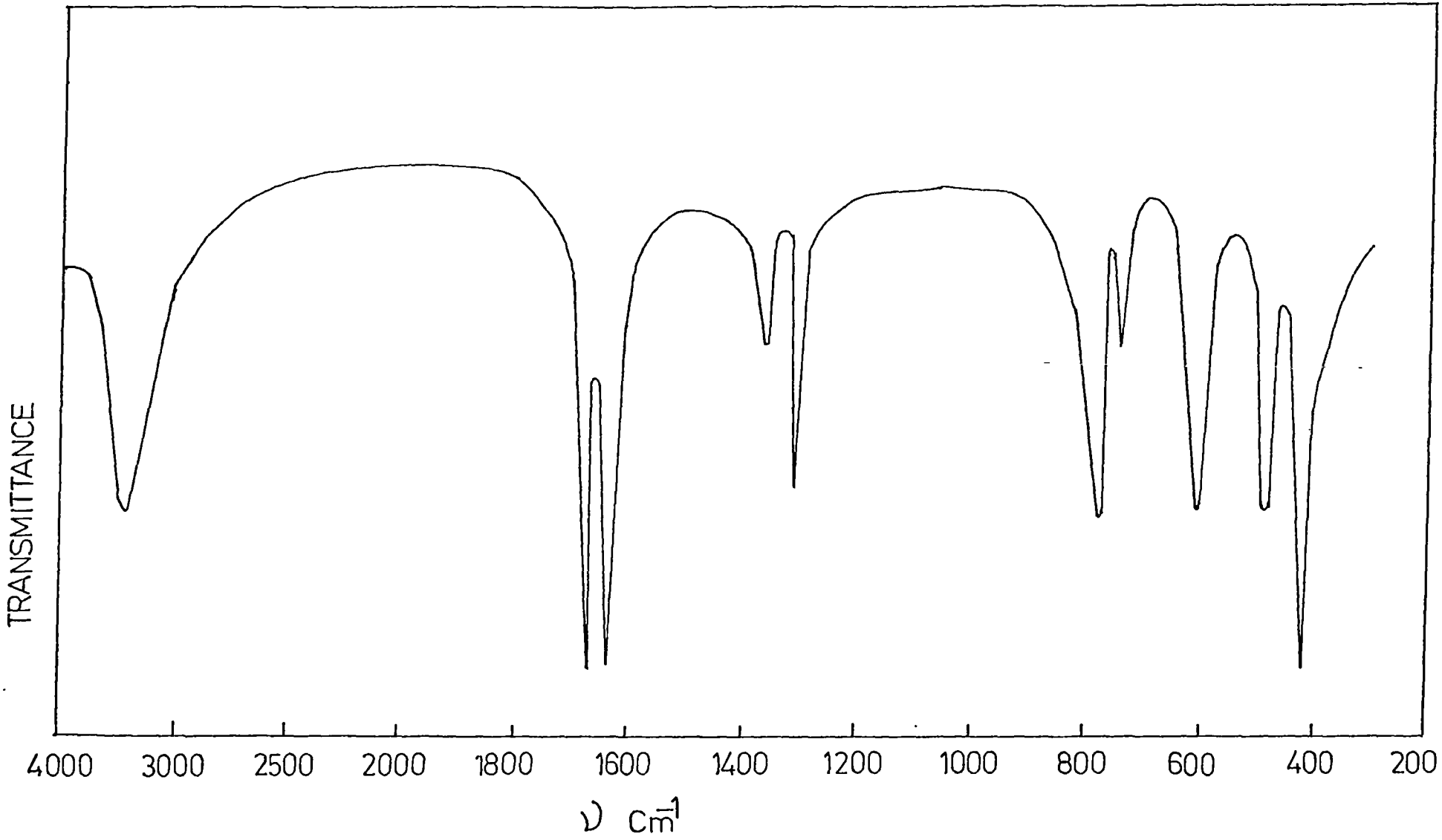
Table 2. Analytical Data, Estimated Oxidation State of Mn, Magnetic Moment Values and IR Bands of $(NH_4)_2[MnF_3(C_2O_4)]$, $Na_2[MnF_3(C_2O_4)].5H_2O$ and $K_2[MnF_3(C_2O_4)].H_2O$

Compound	Estimated Oxidation state of Mn	μ_{eff} BM (302K)	%found (% calc.)				IR Bands cm^{-1}	Assignments
			A/N	Mn	C_2O_4	F		
$(NH_4)_2[MnF_3(C_2O_4)]$	3.1	4.2	11.4 (11.86)	23.2 (23.31)	37.6 (37.3)	24.4 (24.15)	1670s ..	ν_{as}(O-C-O)
							1365w, 1320m ..	ν_s(O-C-O)
							778m, 750w ..	δ(O-C-O)
							425s ..	ν(Mn-O)
							490m ..	ν(Mn-F)
							3160m ..	ν_3
							3040s ..	ν_1
							1400s ..	ν_2
								NH_4^+ modes

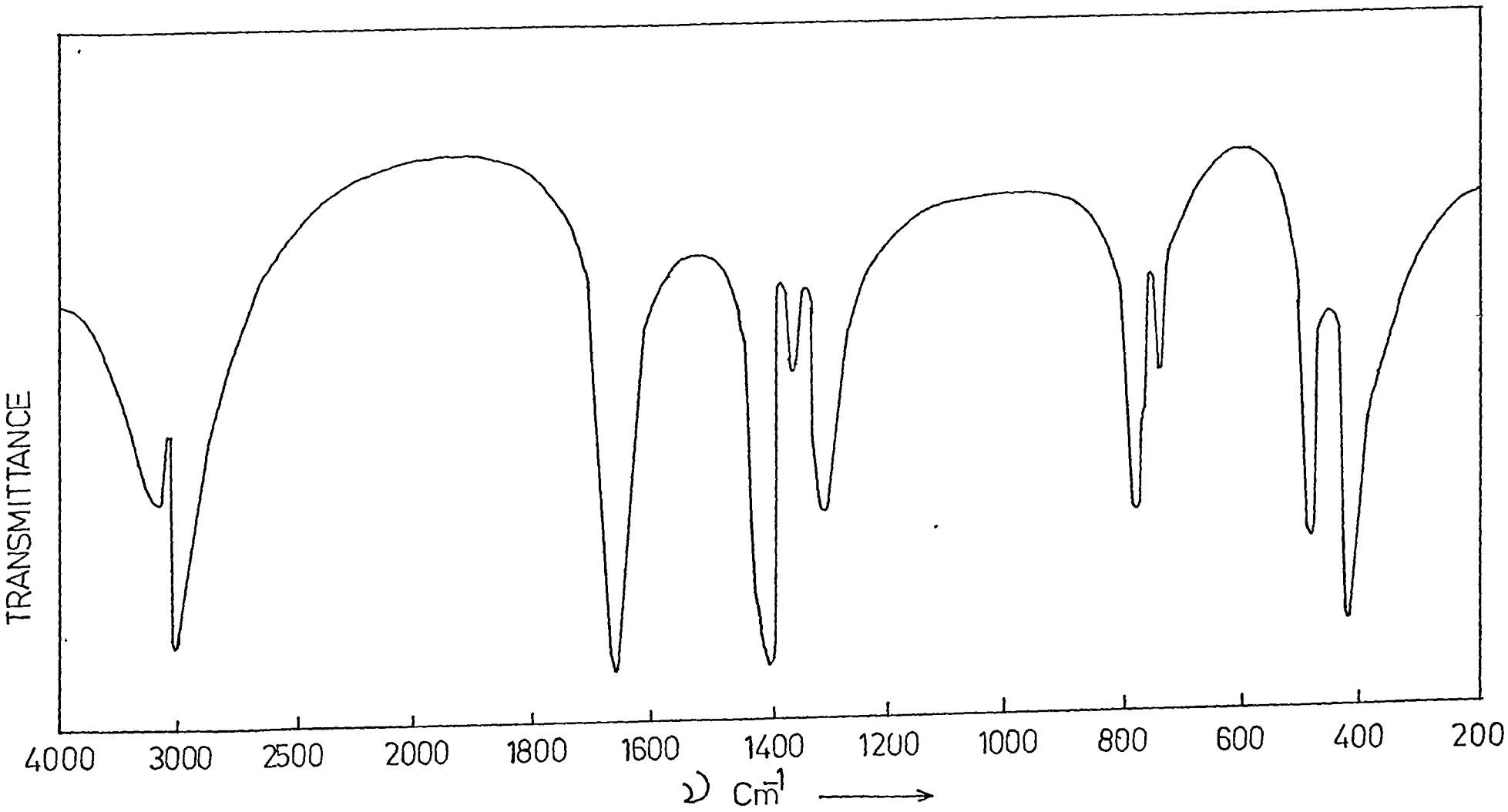
Table 2. contd...../-

Table 2. (contd..)

Compound		μ_{eff}	A/N	Mn	C_2O_4	F	IR	Assignments
$Na_2[MnF_3(C_2O_4)].5H_2O$	3.0	4.3	13.9	16.7	26.5	17.2	1670s ..	ν_{as}(O-C-O)
			(13.69)	(16.37)	(26.19)	(16.96)	1365w, 1320w ..	ν_s(O-C-O)
							778m, 755w ..	δ(O-C-O)
							425s ..	ν(Mn-O)
							495m ..	ν(Mn-F)
							3455m ..	ν(O-H) H_2O modes
							1640s ..	δ(H-O-H) H_2O modes
							600m ..	crystal water
$K_2[MnF_3(C_2O_4)].H_2O$	3.1	4.3	26.1	18.8	29.7	19.4	1672s ..	ν_{as}(O-C-O)
			(26.35)	(18.58)	(29.73)	(19.26)	1365w, 1320m ..	ν_s(O-C-O)
							778m, 750w ..	δ(O-C-O)
							425s ..	ν(Mn-O)
							490m ..	ν(Mn-F)
							3460m ..	ν(O-H) H_2O modes
							1640s ..	δ(H-O-H) H_2O modes
							605m ..	crystal water



IR Spectra of $K_2[MnF_3(C_2O_4)].H_2O$ (4000-2000 cm^{-1})



IR Spectra of $(NH_4)_2[MnF_3(C_2O_4)]$ (4000-200 cm^{-1})

The lower magnetic moments of $A_2[MnF_3(C_2O_4)]$ compounds may owe their origin to the existence of antiferromagnetic exchange interaction between the contiguous manganese(III) ion through —Mn—F—Mn— chain, and the complex species may have a polymeric structure.

The infrared spectra of $(NH_4)_2[MnF_3(C_2O_4)]$, $Na_2[MnF_3(C_2O_4)].5H_2O$ and $K_2[MnF_3(C_2O_4)].H_2O$, recorded both in nujol and KBr media, resemble each other very closely, as far as the manganese-fluoride and manganese-oxalate bands are concerned, indicating thereby that the complexes are similar both structurally and stoichiometrically. While the band at ca 490 cm^{-1} has been assigned to ν_{Mn-F} mode, those at ca 1670, ca 1360, ca 1320, ca 780 and at ca 750 cm^{-1} have been assigned to various modes (Table 2) of the coordinated oxalato group.[6-9] The spectral pattern and the observed bands for $C_2O_4^{2-}$ suggest the possibility of a bridging bidentate $C_2O_4^{2-}$ group[8] rather than a chelated[8] one. In particular the absence of any band between 1680 and 1750 cm^{-1} and shifting of the single $\nu_{as}(O-C-O)$ band to lower frequencies indicate that the oxalato ligand in the present compounds is probably not acting as a chelated[8,9] ligand. It has been exphasised in the literature[6-9] that a band at ca 1720 cm^{-1} is a very good evidence for the occurrence of a chelated oxalato group. However, this point can be more conclusively decided through X-ray analysis. The bands at ca 1670s, at ca 1360w and 1320 m, at ca 780 m and 750 w have been assigned, in line with the

elegant studies of Curtis,[6-8] to ν_{as}(O-C-O), ν_{s}(O-C-O) and δ (O-C-O) respectively. The two bands at ca 3455 and ca 1640 cm^{-1} in the spectra of the sodium and potassium salts are similar in their shapes and positions to those generally observed for uncoordinated water in many manganese(III) fluoro complexes[10,11] and have been unambiguously assigned as ν_{O-H} and δ_{H-O-H} mode of water. The ν_{O-H} band at ca 3455 cm^{-1} in the infrared spectra of the hydrates is typical of lattice water, rather than coordinated water.[8] The absence of ν_{O-H} and δ_{H-O-H} modes in the spectrum of the ammonium salt support the contention that the salt is anhydrous, $(NH_4)_2[MnF_3(C_2O_4)]$. These extra vibrations, in the case of the ammonium salts, at 3160, 3040 and 1400 have been assigned to the ν_3, ν_1 and ν_2 modes of NH_4^+(Ref.12).

The solution electronic spectra of $(NH_4)_2[MnF_3(C_2O_4)]$ and $K_2[MnF_3(C_2O_4)].H_2O$, recorded between 14,500 and 28,000 cm^{-1} in the presence of a very small amount of 40% HF (required for stabilising the compounds), are similar showing to bands at ca 19,500 and ca 22,500 cm^{-1}. The bands have been assigned to the transitions[13] $^5B_{1g} \longrightarrow {}^5B_{2g}$ and $^5B_{1g} \longrightarrow {}^5E_g$ respectively (Table 3). Although recording could not be made below 14,000 cm^{-1} owing to some limitations of the instrument, the appearance of two bands at $\sim$ 19,500 and at $\sim$ 22,500 cm^{-1} indicates an appreciable splitting of ^5E_g ground state of manganese(III) in $[MnF_3(C_2O_4)]^{2-}$ as a consequence of Jahn-Teller effect.

Table 3.. Electronic Spectral Data of $(NH_4)_2[MnF_3(C_2O_4)]$ and $K_2[MnF_3(C_2O_4)]\cdot H_2O$.

Compound	$^5B_{1g} \longrightarrow {}^5B_{2g}$ cm^{-1}	$^5B_{1g} \longrightarrow {}^5E_g$ cm^{-1}
$(NH_4)_2[MnF_3(C_2O_4)]$	19,500	22,500
$K_2[MnF_3(C_2O_4)]\cdot H_2O$	19,800	22,700

Thus, it appears from the present work that the stability of oxalatomanganate(III) complexes can be definitely enhanced through the formation of mixed ligand fluorooxalatomanganate(III) complexes. The complex species, $[MnF_3(C_2O_4)]^{2-}$, may have a polymeric structure trhough a —Mn-F—Mn— bridging but the probability of oxalato bridging can not also be ruled out.

REFERENCES

[1] G. H. Cartledge and W. P. Ericks, J. Am. Chem. Soc., 2061, 2063, 2065, 58, 1936.

[2] J. W. Ladbury and C. F. Cullis, Chem. Rev., 403, 58, 1958.

[3] A. Harriman, Coord. Chem. Rev., 156, 28, 1979.

[4] E. L. Simmons and W. W. Wendlandt, J. Inorg. Nucl. Chem., 2325, 27, 1965.

[5] A. I. Vogel, 'A Text Book of Quantitative Inorganic Analysis' 3rd ed., Longman Green & Co., 1962, p. 284.

[6] N. F. Curtis, J. Chem. Soc., 4109, 1963.

[7] N. F. Curtis, J. Chem. Soc., 2644, 1964.

[8] N. F. Curtis, J. Chem. Soc. A, 1584, 1968.

[9] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', 2nd ed., Wiley-Interscience, London, 1970, p. 244.

[10] A. J. Edwards, J. Chem. Soc. A, 3074, 1971.

[11] M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta and D. T. Khathing, J. Chem. Soc. Dalton Trans., 2587, 1981.

[12] M. K. Chaudhuri and S. K. Ghosh, Inorg. Chem., 4020, 21, 1982.

[13] T. S. Davis, J. P. Fackler, Jr., and M. J. Weeks, Inorg. Chem., 1994, 7, 1968.

CHAPTER 5

Direct Synthesis and Mass Spectrometric Studies of Tris(acetylacetonato)manganese(III), $Mn(C_5H_7O_2)_3$ *

Complexes with 1,3-diketones, particularly with acetylacetone, have been reported for all of the non-radioactive metallic and metalloid elements in the periodic table.[1] Since β-ketoenol complexes have been very commonly used commodity in chemistry laboratories, and many of them can be purchased commerciably, many text and reference books provide with information regarding them. However, interest on the synthetic, chemical and physico-chemical studies involving such compounds never seem to be diminishing.

Tris(acetylacetonato)manganese(III), $Mn(C_5H_7O_2)_3$, is one such compound which was reported as early as 1900[2], and since

* The work described in this Chapter has been published: J. Chem. Soc. Dalton Trans., 669, 1982.

then a number of reports[3-14] relating to its synthesis and structural studies, have been published. The compound acts as an oxidant[15] and can bring about coupling of phenols.[16] In the presence of donors such as $(CH_3)_2SO$, tris(acetylacetonato)manganese(III) initiates the free-radical polymerisation of acrylonitrile and styrene.[17] Shigematsu and Tabushi[18] reported that manganese can be quantitatively extracted, from its alkaline peroxide solutions, with acetylacetone and chloroform. The brilliant dark brown-black crystalline $Mn(C_5H_7O_2)_3$ is monomeric in nature and has no appreciable trigonal distortion.[19] A comparison of the infrared spectra of some Jahn-Teller resistant acetylacetonato complexes of metals with that of $Mn(acac)_3$ enabled Forman and Orgel[7] to conclude that the Jahn-Teller effect is operative in $Mn(acac)_3$. Later Fackler et al.[19] explained the mode of Jahn-Teller distortions through the results of their crystal field calculations. The compound thus represent a unique behaviour.

Tris(acetylacetonato)manganese(III), $Mn(C_5H_7O_2)_3$, can be synthesised by air or chlorine oxidation of a basic solution of Mn^{2+} in the presence of acetylacetone (acacH). However, this method has not been used in practice because of the deleterious effect of alkali on the end product, as well as the chances of its contamination by chloride ions. Instead, the synthesis due to Cartledge[20] and Charles[21] involving the oxidation of Mn^{2+} with

$KMnO_4$ in the presence of acetylacetone (acacH) have been employed. The success of this method depends markedly on the pH. The reaction mixture requires to be regulated at pH ca 5 by the addition of a large amount of sodium acetate. The use of sodium acetate in such quantities must surely contaminate the end product. In view of this it was thought worthwhile to develope a direct method of synthesis of the title compound. Further, it was felt necessary to find out an appropriate condition for studying the compound mass spectrometrically, since it has been reported in the literature[22] that attempts to obtain good mass spectra of $Mn(C_5H_7O_2)_3$ have not always been successful.

This Chapter describes a direct method of synthesis of tris(acetylacetonato)manganese(III), $Mn(C_5H_7O_2)_3$, which does not require buffer. Chapter 5 also presents the results, of mass spectrometric studies of $Mn(C_5H_7O_2)_3$, obtained by making use of the direct insertion technique.

EXPERIMENTAL

Reagent grade (B.D.H., Loba Chemie, E. Merck) potassium permanganate and acetylacetone were used in the synthesis.

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

The mass spectrum was recorded on a Varian MAT CH-5 mass spectrometer. The sample was introduced directly in the ionisation chamber using a direct insertion probe. The operation conditions were electron energy, 70 eV (1 eV $\approx$ 1.60 x 10^{-19} J); source temperature, 20 ^{o}C; resolution 10,000; and accelerating voltage, 8 kV. The mass spectrometric observations were made with the field of ionising current sufficiently strong to trap primary ions.

Infrared spectral band positions and their assignments are summarised in Table 1, while the essential features of the mass spectrum run at 20 ^{o}C are given in Table 2.

Elemental Analyses. Quantitative estimation of manganese was accomplished by the method already described in Chapter 1. C and H contents of the compound were determined by microcrystalline methods.

Chemical Determination of the Oxidation State of Manganese in $Mn(C_5H_7O_2)_3$. The oxidation state of manganese in the compound was determined iodometrically by reduction of a known amount of the compound with acidified potassium iodide solution followed by titration of the liberated iodine with standard sodium thiosulphate solution.

Synthesis of Tris(acetylacetonato)manganese(III), $Mn(C_5H_7O_2)_3$. A quantity of 5.0 g (31.7 m mol) of powdered potassium permanganate, $KMnO_4$, was dissolved in the minimum volume of water by slight warming over a steam-bath and the solution then filtered. Distilled acetylacetone (22.0 g, 220.0 mmol) was added to the solution with vigorous stirring. The mixture was stirred for a further period of about 5 min over a steam-bath and then allowed to cool at room temperature for ca 10 min. The dark brown-black shiny crystals of $Mn(C_5H_7O_2)_3$ were filtered off and washed 3-4 times with small amounts of acetylacetone-water mix (1:1) and finally dried in vacuo. The compound thus obtained was very pure and gave 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 petrol (b.p. 40-60 °C), and then cooling at ca 0 °C. The compound does not have a sharp melting point but decomposes at ca 155 °C. This method may also be used for large-scale synthesis.

Analysis

Found: C, 51.1; H, 6.10; Mn, 15.7. Calc. for $C_{15}H_{21}MnO_6$: C, 51.15; H, 6.00; Mn, 15.6%.

The molecular weight was found to be 352 mass spectrometrically.

The chemically estimated oxidation state of manganese, in the compound, was found to be +3.

RESULTS AND DISCUSSION

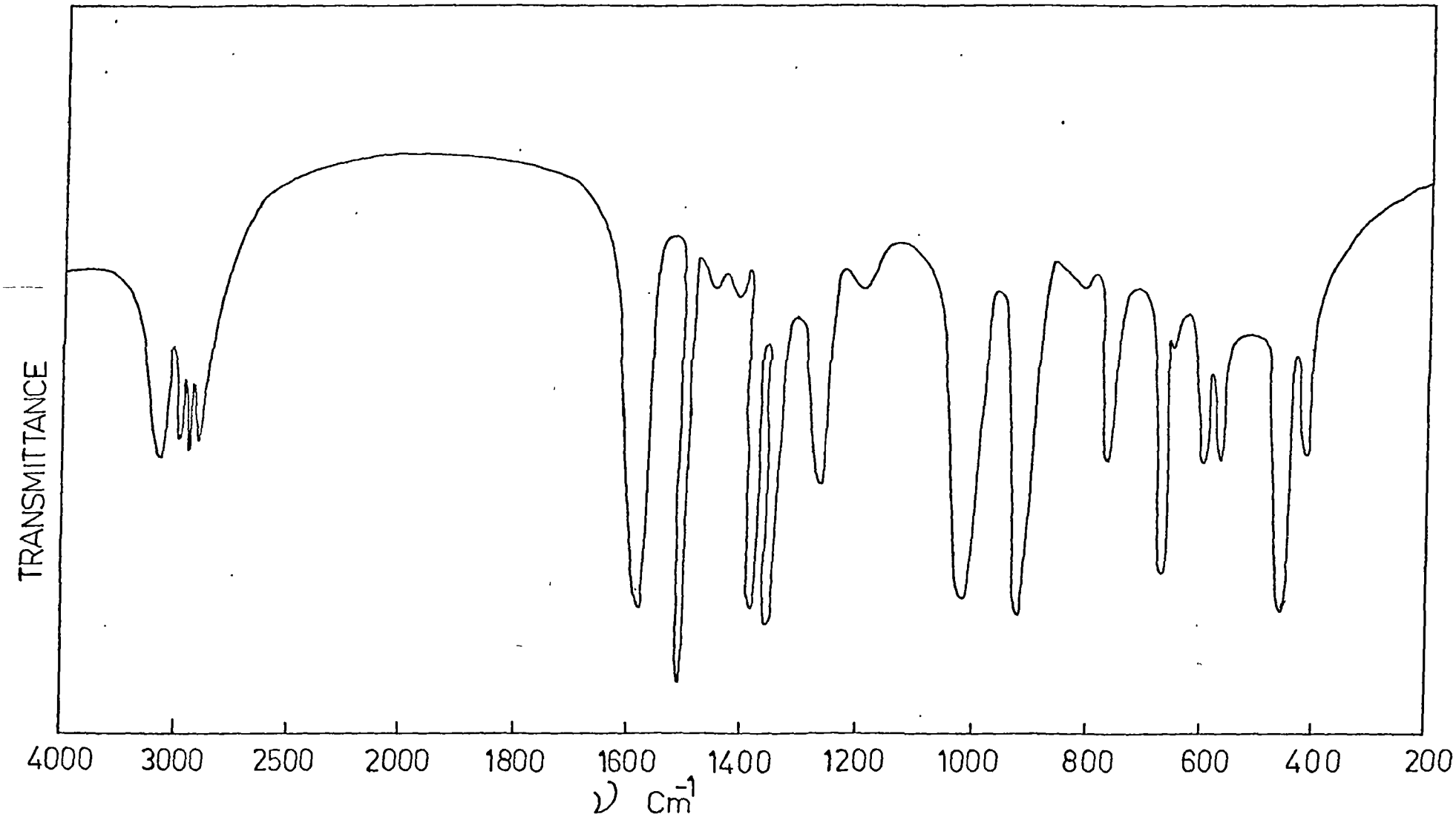
In Chapter 1 the role of acetylacetone as a reducing agent, in the reduction of Mn^{7+}, has been emphasized. The use of this concept has now been extended to the synthesis of $Mn(C_5H_7O_2)_3$. The method described (vide Experimental section) leads to the rapid synthesis of tris(acetylacetonato)manganese(III) in a very high yield, and analogous procedures have also been used successfully, in our laboratories, for the synthesis of $Cr(C_5H_7O_2)_3$ from CrO_3[24] and $[Ni(C_5H_7O_2)_2(H_2O)_2]$ from NiO(OH).[25] It is evident that, if planned properly, gram quantities of $Mn(C_5H_7O_2)_3$ can be synthesised in less than 1 h without using any buffer. The reduction of MnO_4^- by acetylacetone and the subsequent formation of the tris-chelate owing to the presence of an excess of acetylacetone (acacH) appear to be the driving forces for the reaction. It is interesting to note that although the present synthesis does not involve any buffer, the course of the reaction is such that it automatically maintains the pH desired for the successful formation of $Mn(C_5H_7O_2)_3$. The pH of the solution measured immediately after the formation of the compound was found to be ca 5. This value concurs exactly with that maintained by the addition of a large amount of sodium acetate in the syntheses of Cartledge[20] and Charles.[21]

In order to understand the mechanism for the present synthesis, an attempt was made to isolate the oxidation product of acetylacetone (acacH). Work up of the mother liquor, obtained after separating $Mn(C_5H_7O_2)_3$, afforded a crystalline organic compound which has been identified as $\alpha,\alpha,\beta,\beta$-tetraacetylethane, $(CH_3CO)_2CH\text{-}CH(CH_3CO)_2$[25]. This leads us to conclude that in the electron-transfer reaction between Mn^{+7} and acacH, acetylacetone is oxidised to $(CH_3CO)_2CH\text{-}CH(CH_3CO)_2$. In view of the products isolated from the reaction of Mn^{7+} and acetylacetone, and the pH of the reaction medium, we feel that acetylacetone first undergoes ionization giving $(CH_3CO)_2CH^-$ ($acac^-$) and H^+ (cf. the observed pH) followed by the oxidation of $(CH_3CO)_2CH^-$ ion to the $(CH_3CO)_2CH^\bullet$ radical (with corresponding reduction of the metal), which dimerises to yield $\alpha,\alpha,\beta,\beta$-tetraacetylethane, $(CH_3CO)_2CH\text{-}CH(CH_3CO)_2$.

Characterisation. Tris(acetylacetonato)manganese(III) is a dark brown-black crystalline compound, unstable in air but capable of being stored in a sealed container for months. The compound is slightly soluble in water but the dissolution is accompanied by decomposition. Freshly synthesised $Mn(C_5H_7O_2)_3$ does not show a sharp melting point but decomposes around 155 ^oC. The infrared spectrum (Table 1) of the compound is unambiguous and shows the characteristics of chelated acetylacetonates ($acac^-$), in agreement with the reported spectrum[23].

Table 1. Infrared Spectral Bands and Their Assignments

IR Bands (cm^{-1})		Assignments[23]
3065 m	.....	$\nu_{(CH)}$
2995 m 2965 m 2925 m	.....	$\nu_{(CH_3)}$
1575 s	.....	Partial C=O stretching
1510 vs	.....	C=C stretching
1455 w 1425 w	.....	CH_3 asymmetrical bending
1380 s 1355 s	.....	CH_3 symmetrical bending
1255 m	.....	C=C stretching + C-CH_3 stretching, ν_2.
1180 vw	.....	C-H in-plane bending
1015 s	.....	CH_3 rocking
925 s	.....	C-CH stretching + C=O stretching, ν_3.
800 w 775 m	.....	C-H out of plane bending
670 s	.....	Ring deformation + Mn-O stretching, ν_4.
655 sh	.....	out of plane deformation
592 m 566 m	.....	Mn-O stretching, ν_5.
450 s	.....	C-CH_3 bending + Mn-O stretching.
410 m	.....	In plane O-Mn-O bending.



IR Spectra of Mn $(C_5H_7O_2)_3$ (4000-200)cm^{-1})

The M-O stretching vibrations of acetylacetonato complexes of transition metals are very important since they provide direct information about the strength of the M-O bands. The band at 592 cm^{-1} in the present case has been assigned to Mn-O stretching mode of vibration in line with the argument of Pinchas et al.[23]

The molecular weight, determined mass spectrometrically, was found to be 352 suggesting that compound is monomeric. This agrees well with the crystal structures of various forms of $Mn(C_5H_7O_2)_3$ which also showed the presence of discrete $Mn(C_5H_7O_2)_3$ molecules.[19,26] Chemical determination of the oxidation state of manganese in the synthesised compound gave +III, providing further support for the identity of the compound.

Mass Spectrometric Studies. It was reported in the literature[22] that attempts to obtain good mass spectra of tris(acetylacetonato)manganese(III) have not always been successful. It appears from the available information that the spectra of $Mn(acac)_3$ markedly depend on the method of sample introduction. From our earlier experience,[27] we favoured the direct insertion technique, and introduced the sample straight into the ionisation chamber without any prior heating.

The spectrum run at 20 ^{o}C (Table 2) showed a molecular ion signal of moderate intensity (18%) at m/Z 352 and a base peak at m/Z 253 due to $[Mn(C_5H_7O_2)_2]^+$. It is observed that the

Table 2. Mass Spectral Data for $Mn(C_5H_7O_2)_3$

(a) Major Peaks

Assignments	m/Z	Intensity(%)
$[Mn(C_5H_7O_2)_3]^+$	352	18
$[Mn(C_5H_7O_2)_2]^+$	253	100
$[Mn(C_5H_7O_2)(C_4H_4O_2)]^+$	238	34
$[Mn(C_5H_7O_2)]^+$	154	74
$[Mn(C_4H_4O_2)]^+$	139	5
Mn^+	55	0

(b) Metastable Transitions

m/Z*			Fragment
observed	calculated	Process	Lost
181.8	181.84 ..	352 ⟶ 253 ..	$C_5H_7O_2$
223.9	223.89 ..	253 ⟶ 238 ..	CH_3
99.6	99.65 ..	238 ⟶ 154 ..	$C_4H_4O_2$
125.6	125.46 ..	154 ⟶ 139 ..	CH_3

molecular ion $[Mn(C_5H_7O_2)_3]^+$. loses one $C_5H_7O_2$ group to give $[Mn(C_5H_7O_2)_2]^+$ which then loses a CH_3 unit followed by the loss of $C_4H_4O_2$ to yield the fragment ion $[Mn(C_5H_7O_2)]^+$ at m/Z 154. The ion $[Mn(C_5H_7O_2)]^+$ loses a CH_3 unit first and then probably $C_4H_4O_2$. In view of the observed signals, the most probable fragmentation pathway may be given as in Scheme 1.

$$[Mn(C_5H_7O_2)_3]^+ \longrightarrow [Mn(C_5H_7O_2)_2]^+ \longrightarrow$$

$$[Mn(C_5H_7O_2)(C_4H_4O_2)]^+ \longrightarrow [Mn(C_5H_7O_2)]^+$$

$$\longrightarrow [Mn(C_4H_4O_2)]^+ \longrightarrow Mn^+.$$

Scheme 1

In order to obtain further information, metastable transitions were also studied. The metastable peaks at m/Z^* 181.8, 223.9, 99.6 and 125.6, indeed, support the proposed fragmentation path. Thus, the mass spectrometric results adduce further support to the identity and purity of the compound, conform to the monomeric nature of $Mn(C_5H_7O_2)_3$, and compare very well with those reported by Westmore and coworkers.[6]

It may be concluded that tris(acetylacetonato)manganese(III), $Mn(C_5H_7O_2)_3$, can be synthesised directly from $KMnO_4$ without making use of any buffer. A good mass spectrum of $Mn(C_5H_7O_2)_3$ can be obtained by the direct insertion technique.

REFERENCES

[1]J. P. Fackler, Jr., Progr. Inorg. Chem., 361, 7, 1966.

[2]F. Gach, Monatsch, 98, 21, 1900.

[3]H. A. Jahn and E. Teller,
Proc. Roy. Soc. London, 200, 161, 1937.

[4]H. A. Jahn, Proc. Roy. Soc. London, 117, 164, 1938.

[5]D. N. Barnum, J. Inorg. Nucl. Chem., 183, 22, 1961.

[6]G. M. Bancroft, C. Reichert and J. B. Westmore,
Inorg. Chem., 870, 7, 1968.

[7]A. Forman and L. E. Orgel, Mol. Phys., 362, 2, 1959.

[8]B. Morosin and J. R. Brathovde, Acta. Cryst., 807, 13, 1960.

[9]T. S. Piper and R. L. Carlin, Inorg. Chem., 260, 2, 1963.

[10]J. P. Fackler, Jr., T. S. Davis and I. D. Chawla,
Inorg. Chem., 130, 4, 1965.

[11]R. J. Irving and R. A. Schutz,
J. Chem. Soc. Dalton Trans., 2414, 1973.

[12]K. Isobe, K. Takeda, Y. Nakamura and S. Kawaguchi,
Inorg. Nucl. Chem. Lett., 1283, 9, 1973.

[13] K. Isobe and S. Kawaguchi, Bull. Chem. Soc. Jpn., 250, 48, 1975.

[14] J. P. Collman, Angew. Chem. Intern. Ed. Engl., 132, 4, 1965.

[15] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', 3rd ed., Wiley-Eastern, New Delhi, 1976, p. 850.

[16] M. J. S. Dewar and T. Nakaya, J. Am. Chem. Soc., 7134, 90, 1968.

[17] C. H. Bamford and A. N. Ferrar, J. Chem. Soc. Chem. Commun., 315, 1970.

[18] T. Shigematsu and M. Tabushi, J. Chem. Soc. Japan, Pure Chem. Sect., 814, 83, 1962.

[19] J. P. Fackler, Jr. and A. Avdeef, Inorg. Chem., 1864, 13, 1974.

[20] G. H. Cartledge, J. Am. Chem. Soc., 4416, 73, 1951, U.S. Patent, 2,556,316.

[21] R. G. Charles, Inorg. Syntheses, 183, 7, 1963.

[22] C. G. McDonald and J. S. Shannon, Aust. J. Chem., 1545, 19, 1966.

[23] S. Pinchas, B. L. Silver and I. Laulight, J. Chem. Phys., 1506, 46, 1967.

[24] M. K. Chaudhuri, N. Roy and D. T. Khathing, Synth. React. Inorg. Met.-Org. Chem, 715, 12, 1982.

[25] M. N. Bhattacharjee, M. K. Chaudhuri, S. K. Ghosh, Z. Hiese and N. Roy, J. Chem. Soc. Dalton Trans., 0000, 1983.

[26]B. R. Stults, R. S. Marianelli and V. W. Day, Inorg. Chem., 1853, 18, 1979.

[27]M. K. Chaudhuri, H. S. Dasgupta, N. Roy and D. T. Khathing, Org. Mass. Spectrum., 303, 16, 1981.

CHAPTER 6

Synthesis and Structural Assessment of Alkali-Metal and Ammonium Trifluoroaquomanganates(II), $A[MnF_3(H_2O)]$ (A = Na, K, Rb, Cs or NH_4)*

The divalent manganese resembles the trivalent iron in respect of its d^n configuration. Both Mn^{2+} and Fe^{3+} have a d^5 configuration, and it is Mn^{2+}, of the two, which seems to have been more extensively studied spectroscopically.[1,2] It is well known that the Mn^{2+} ion exists as $[Mn(H_2O)_6]^{2+}$ in an aqueous solution, and anhydrous salts and complexes of manganese(II) are generally prepared by either dry reactions or carrying out the reactions in non-aqueous media.[3]

Manganese(II) forms two types of fluoro-complexes,[4] viz., tetrafluoromanganates(II) and trifluoromanganates(II). The tetrafluoromanganate(II), MnF_4^{2-}, ion has a tetrahedral

* The work described in this Chapter has been published: Ind. J. Chem., 21A, 977 (1982).

structure, while in the trifluoromanganate(II), MnF_3^-, manganese(II) finds itself in an octahedral environment. A considerable amount of work was done on trifluoromanganates(II)[5-15] particularly involving the structure and magnetic properties of such compounds. The X-ray diffraction studies of NH_4^+, K^+ and Rb^+ salts of the MnF_3^- ion showed that the compounds have perovskite structures, sometimes with some modifications.

It is now well established that F^- ion is one of the most important ligands used for stabilising manganese(III), and it is also generally believed that the reduction of a higher valent manganese below its +3 state, through electron-transfer reactions, in the presence of F^- ligands, would be a rather difficult task,[16-18] although the +2 oxidation state of manganese is a more familiar one. Moreover, complex formation tendency of Mn^{2+} seems to be comparatively less pronounced than that of Mn^{3+} (Ref. 19). In the course of our studies on fluoro and mixed-fluoro compounds of manganese (Chapters 1 to 5), we thought it would be very interesting if we could succeed in the synthesis of fluoromanganate(II) complexes directly by the reduction of Mn^{7+}, in the presence of F^- ions, by making use of a strong reducing agent. Accordingly, the reactions among $KMnO_4$, alkali-metal and ammonium bifluorides, AHF_2 (A = Na, K, Rb, Cs or NH_4), and hydrazine hydrate, $N_2H_4.H_2O$, were carried in aqueous media.

The present Chapter reports the results of the reactions among $KMnO_4$, AHF_2 and $N_2H_4.H_2O$ leading to the synthesis of alkali-metal and ammonium trifluoromonoaquomanganates(II), $A[MnF_3(H_2O)]$ (A = Na, K, Rb, Cs or NH_4), and also the characterisation and structural assessment of $A[MnF_3(H_2O)]$ compounds.

EXPERIMENTAL

The chemicals used were all reagent grade products. Alkali-metal and ammonium bifluorides were prepared by the methods developed in our laboratory[20] and the procedure has already been described in Chapter 1.

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

Molar conductance measurements were made using a Philips PR 9500 conductivity bridge.

Magnetic susceptibility measurements were made by the Gouy method using $Hg[Co(NCS)_4]$ as the calibrant.

Elemental Analyses. Manganese, fluoride, sodium, potassium and nitrogen estimations were accomplished by the methods described in Chapter 1.

Chemical Determination of the Oxidation States of Manganese. The oxidation state of manganese in each of the newly synthesised compounds was determined chemically by the methods already described in the previous Chapters.

Synthesis of Alkali-Metal and Ammonium Trifluoromonoaquomanganates(II), $A[MnF_3(H_2O)]$ (A = Na, K, Rb, Cs or NH_4). Since the methods of syntheses of sodium, potassium and ammonium trifluoromonoaquomanganates(II) are similar, only a representative method is described.

An excess of alkali-metal or ammonium bifluoride, AHF_2 (A = Na, K or NH_4), was mixed with solid $KMnO_4$ by powdering together in an agate mortar. The thoroughly mixed powder was dissolved in the minimum volume of water by slightly warming over a steam-bath, and then filtered. The filtrate was collected in a polyethylene beaker and an excess of hydrazine hydrate, $N_2H_4.H_2O$, was added, all at a time, with constant stirring. A highly exothermic reaction set in and readily gave a light pinkish-white microcrystalline product in a very high yield, with the mother liquor becoming colourless. The reaction container was cooled to room temperature, and the compound was separated by centrifugation, purified by washing with heptane, and finally dried in vacuo. The $Rb[MnF_3(H_2O)]$ and $Cs[MnF_3(H_2O)]$ have been prepared from the $(NH_4)[MnF_3(H_2O)]$ compound, and for

which separate methods have been given. The specific amounts of the reagents used and the yields of $(NH_4)[MnF_3(H_2O)]$, $Na[MnF_3(H_2O)]$ and $K[MnF_3(H_2O)]$ are set out in Table 1.

Table 1. Amounts of Reagents Used and Yields of $A[MnF_3(H_2O)]$ (A = Na, K or NH_4)

Compound	Yield in g (%)	Amount of $KMnO_4$ in g (m mol)	Amount of AHF_2 in g (m mol)	Amount of $N_2H_4 \cdot H_2O$ in ml
$NH_4[MnF_3(H_2O)]$	0.4 (85)	0.5 (3.16)	1.1 (19.3)	3.0
$Na[MnF_3(H_2O)]$	0.4 (83)	0.5 (3.16)	1.2 (19.4)	3.0
$K[MnF_3(H_2O)]$	0.5 (93)	0.5 (3.16)	1.5 (19.2)	3.0

Synthesis of Rubidium Trifluoroaquomanganate(II), $Rb[MnF_3(H_2O)]$. A quantity of 0.3 g (2.0 m mol) of $NH_4[MnF_3(H_2O)]$ was dissolved in the minimum volume of 20% hydrofluoric acid. To this solution 0.23 g (1.0 m mol) of powdered Rb_2CO_3 was added, in portions, with stirring. Immediately after the addition was over, the light pinkish white $Rb[MnF_3(H_2O)]$ appeared. The compound thus obtained was separated by centrifugation, and purified by washing with heptane and finally dried in vacuo. The yield of $Rb[MnF_3(H_2O)]$ was 0.4 g (91%).

Synthesis of Cesium Trifluoroaquomanganate(II), $Cs[MnF_3(H_2O)]$. This compound was synthesised in a manner analogous to that of $Rb[MnF_3(H_2O)]$. The metathesis reaction was carried out with 0.3 g (2.0 m mol) of $NH_4[MnF_3(H_2O)]$ and 0.19 g (1.0 m mol) of Cs_2CO_3. The yield of $Cs[MnF_3(H_2O)]$ was 0.6 g (91%).

Analytical data, room temperature magnetic moment values, chemically estimated oxidation states of manganese and structurally significant infrared bands are summarised in Table 2.

RESULTS AND DISCUSSION

It has been generally believed that F^- ion is a very potential stabilising ligand for Mn^{3+} (Ref. 16, 18), and as such it would be rather difficult to reduce a higher valent manganese species further below its +3 state, particularly in the presence of an excess of F^- ions. We, however, thought that this barrier could be overcome by the use of a drastic condition for the reduction. With this in view, the reduction of potassium permanganate, $KMnO_4$, in the presence of an excess of alkali-metal or ammonium bifluoride, AHF_2, was performed using hydrazine hydrate, $N_2H_4.H_2O$, a strong reducing agent. On addition of hydrazine hydrate to a solution of a mixture of $KMnO_4$ and AHF_2, the temperature of the medium went up to 80-90 ^oC. This temperature was strategically maintained in order to facilitate the reduction of Mn^{7+} to Mn^{2+}. Analysis of the product obtained thereof indicated that the contention was fulfilled. Thus, the method (vide Experimental section) lead to the synthesis of alkali-metal and ammonium trifluoroaquomanganates(II), $A[MnF_3(H_2O)]$ sufficient in number leaving little doubt that reduction of Mn^{7+} with hydrazine hydrate could be developed for the synthesis of other types of compounds of manganese(II). The

yields of $A[MnF_3(H_2O)]$ compounds are very high and gram quantities of such compounds can be prepared, using this simple method, in a very short time. It is now evident that the by the use of somewhat forcing conditions, fluoro complexes of Mn^{2+} can be synthesized from aqueous media although the formation constants, in aqueous solutions, of fluoromanganates(II) are very low.[5,21] The alkali-metal and ammonium bifluorides, AHF_2, here act as the sources of fluoride ions. In some earlier work (Chapter 1), the role of AHF_2 as the source of fluoride, in the syntheses of fluorometalates, was emphasised. In fact it appears that the success of the present method depends not only on the role played by $N_2H_4.H_2O$ in the electron-transfer process, but also quite appreciably on the presence of both H^+ and F^- in the solution arising from AHF_2. The overall reaction leading to the formation of $A[MnF_3(H_2O)]$ may be expressed as follows:

$$4\ KMnO_4 + 13\ AHF_2 + 5\ N_2H_4.H_2O \longrightarrow 4\ A[MnF_3(H_2O)] + 5\ N_2 + 17\ H_2O + HF + 4\ KF + 9AF.$$

The alkali-metal and ammonium trifluoroaquomanganates(II) are all very light pinkish-white microcrystalline products, and they attack glass in the presence of moisture. They do not dissolve in common organic solvents, and in water they decoompose. The $A[MnF_3(H_2O)]$ compounds, however, dissolve in aqueous hydrofluoric acid.

The chemically estimated oxidation states of manganese is found to lie between 2.05 and 2.12 (Table 2), lending strong support to the contention that manganese in each of the compounds has an oxidation number of +2. The attempts to measure the molar conductances of the $A[MnF_3(H_2O)]$ compounds, in water, was unsuccessful. The observed values were higher than that expected for a uni-uni valent type of electrolyte. The higher molar conductance values indicate some sort of decomposition of the compounds probably as a consequence of the enhanced ionic character of the Mn—F bonds.

The i.r. spectra of the series of five salts of the trifluoroaquomanganate(II) ion resemble each other very closely. The typical features of the spectra are a strong absorption at ca 410 cm^{-1}, a broad weak band at ca 1640 cm^{-1}, a medium intensity band at ca 3350 cm^{-1}, and a medium intensity band at ca 710 cm^{-1}. These bands have been assigned to ν_{Mn-F}, and δ_{H-O-H}, ν_{O-H} and the rocking mode of water respectively. The occurrence of the ν_{Mn-F} at a much lower frequency, compared to those of the MnF_5^{2-} and MnF_6^{3-} species[9,18] suggests that the Mn-F bonds in $[MnF_3(H_2O)]^-$ complex have enhanced ionic character. However, from the fact, that the ν_{Mn-F} has been observed in the present case at ca 410 cm^{-1}, it is certain that a definite degree of covalency exists in the Mn—F bonds. Similar observation was made by Peacock and Sharp in the case of $KMnF_3$.[9]

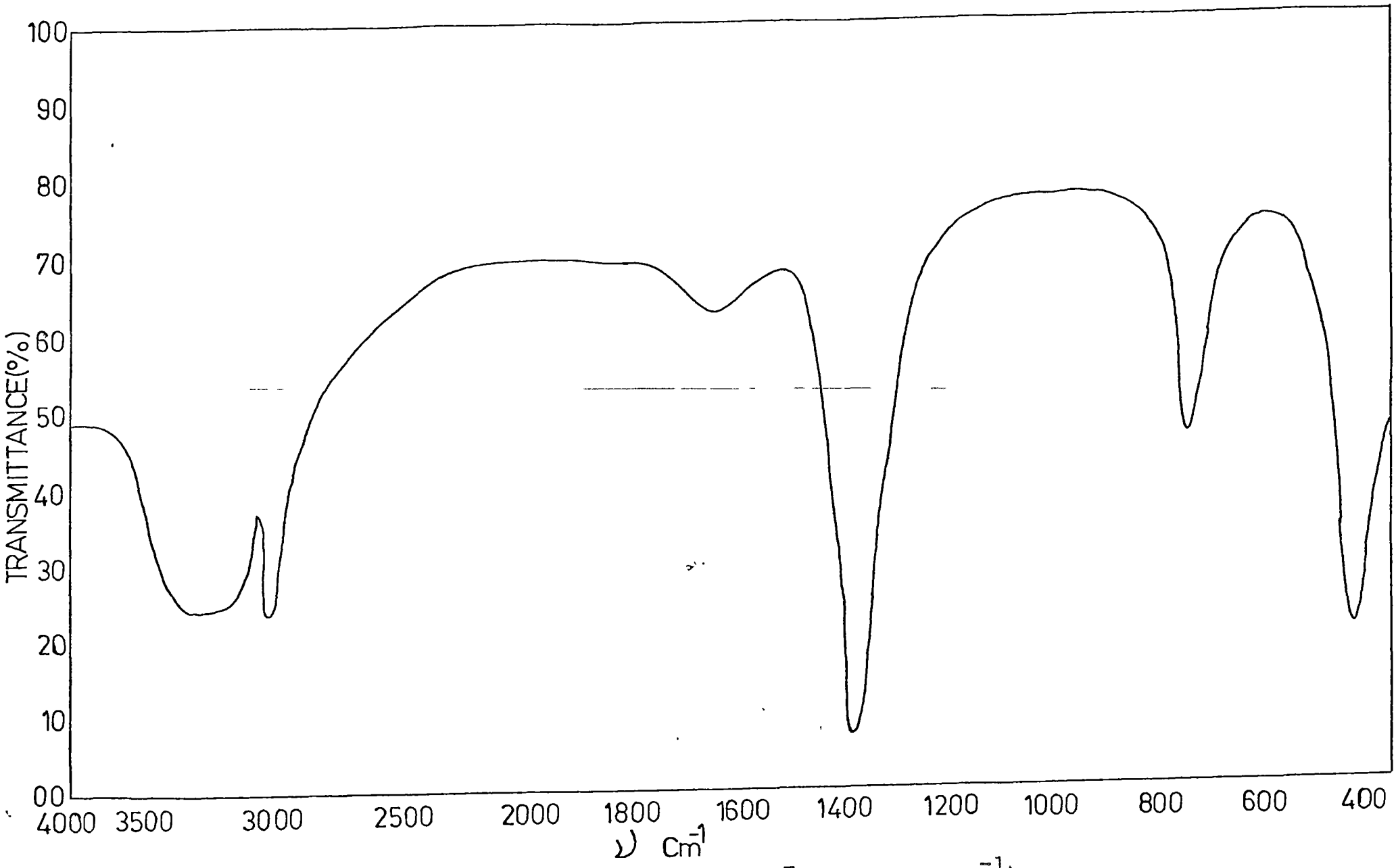
Table 2. Analytical Data, Magnetic Moment Values, Estimated Oxidation States of Manganese, and IR Bands of $A[MnF_3(H_2O)]$ (A = Na, K, Rb, Cs or NH_4)

Compound	μ_{eff}/BM at 290 K	Estimated Oxidation states of Mn	% found (% calc.) A/N	Mn	F	IR Bands cm^{-1}	Assignments
$NH_4[MnF_3(H_2O)]$	5.3	2.05	9.61 (9.46)	37.52 (37.16)	38.21 (38.51)	410s 707m 1635vw,br. 3355m,br	.. $\nu_{(Mn-F)}$ .. rocking mode of water $\delta_{(H-O-H)}$ $\nu_{(O-H)}$
666							
$Na[MnF_3(H_2O)]$	5.2	2.11	15.52 (15.03)	36.34 (35.95)	37.68 (37.25)	408s 712m 1643vw,br. 3345m,br	.. $\nu_{(Mn-F)}$ .. rocking mode of water $\delta_{(H-O-H)}$ $\nu_{(O-H)}$

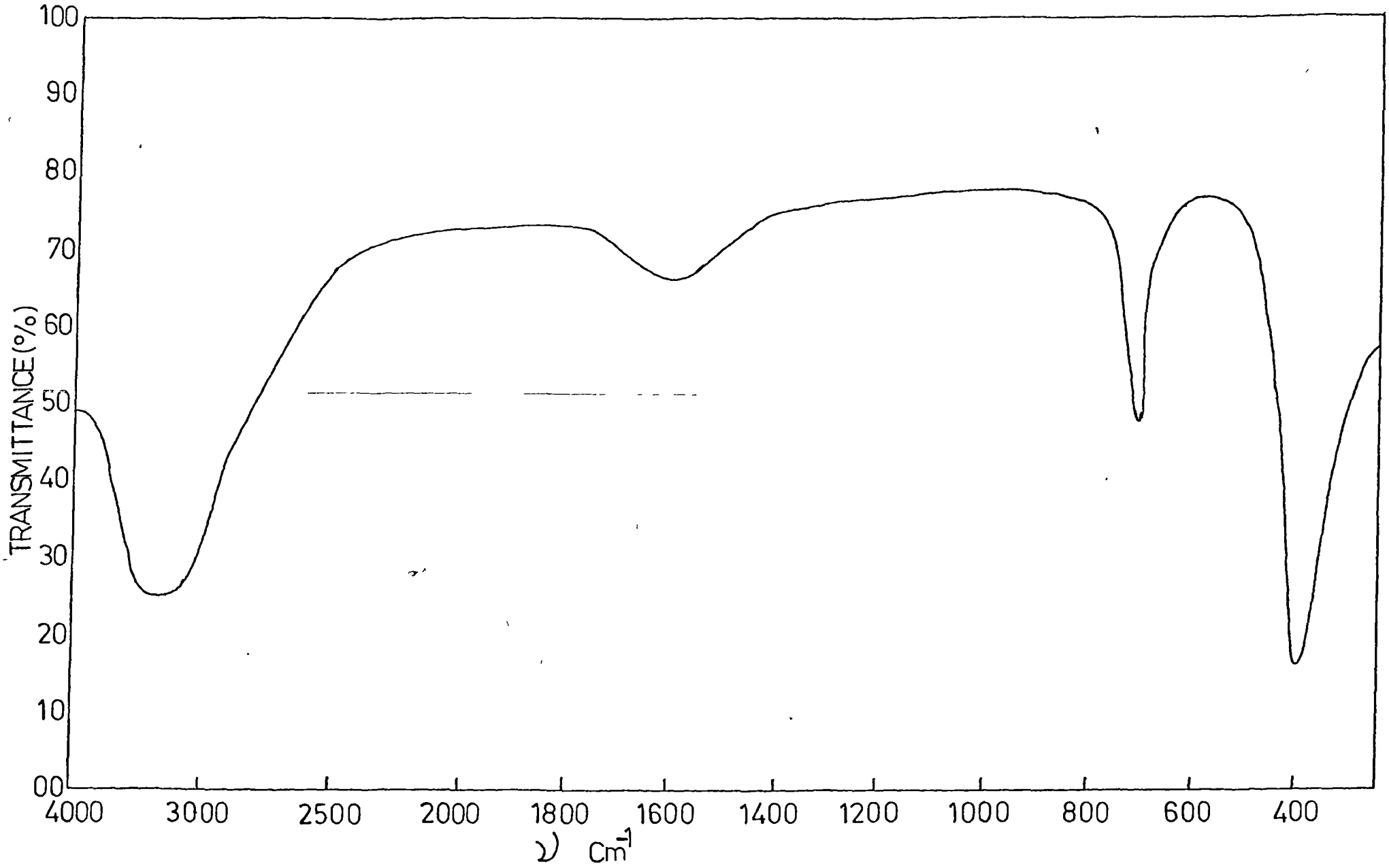
Table 2. contd...../-

Table 2. (contd.....)

$K[MnF_3(H_2O)]$	5.2	2.12	23.43	32.89	33.51	412s	...	ν(Mn-F)
			(23.08)	(32.54)	(33.73)	712m	...	rocking mode of water
						1640vw,br.		δ(H-O-H)
						3350m,br..		ν(O-H)
$Rb[MnF_3(H_2O)]$	5.3	2.08	40.52	25.73	26.83	410s	...	ν(Mn-F)
			(39.68)	(25.52)	(26.45)	712m	...	rocking mode of water
						1638vw,br.		δ(H-O-H)
						3345m,br..		ν(O-H)
$Cs[MnF_3(H_2O)]$	5.3	2.12	51.61	21.38	21.48	408s	...	ν(Mn-F)
			(50.55)	(20.92)	(21.68)	710m	...	rocking mode of water
						1640vw,br.		δ(H-O-H)
						3350m,br..		ν(O-H)



IR Spectra of $NH_4[MnF_3(H_2O)]$ (4000-400 cm^{-1})



IR Spectra of $K[MnF_3(H_2O)]$ (4000-400 cm^{-1})

The very weak nature of the δ_{H-O-H} band observed at ca 1640 cm^{-1} definitely indicates the presence of coordinated water.[22,23] Moreover, the appearance of a medium intensity band at ca 710 cm^{-1}, which is generally attributed to the rocking mode of coordinated water, adduces strong evidence for the presence of coordinated water in the present series of compounds. Further evidence regarding the presence of coordinated water was obtained from the pyrolysis studies of $K[MnF_3(H_2O)]$ (taken as a representative). Pyrolysis of $K[MnF_3(H_2O)]$ at 125-130 °C for a period of 3 h did not practically show any change in the weight of the compound. The i.r. spectra of the compound recorded both before and after heating did not exhibit any change in the spectral pattern.

The room temperature magnetic moments of alkali-metal and ammonium trifluoroaquomanganates(II) were found to occur between 5.2 and 5.3 BM, well below the anticipated value for a high-spin d^5-system. This, however, is not too surprising because somewhat similar observations were made in the cases of many fluoromanganate complexes.[18,24,25] Considerably lower magnetic moments presumably owe their origin not to spin-pairing, but to antiferromagnetic exchange interaction between contiguous Mn^{2+} ions through —Mn—F—Mn— chains. This, therefore indicate a polymeric structure of the complex species $[MnF_3(H_2O)]^-$.

It may be concluded that fluoromanganates(II) of the type $A[MnF_3(H_2O)]$ can be directly synthesised, from aqueous media, by the reduction of Mn^{7+}, in the presence of AHF_2, with hydrazine hydrate. The complex species $[MnF_3(H_2O)]^-$ may have a polymeric structure.

REFERENCES

[1] N. S. Huss and R. J. M. Hobbs, Progr. Inorg. Chem., 372, 10, 1970.

[2] O. G. Holmes and D. S. McClure, J. Chem. Phys. 1686, 26, 1957.

[3] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemisiry' 3rd ed., Wiley-Eastern, New Delhi, 1976, p. 846.

[4] R. D. W. Kemmitt and R. D. Peacock, 'The Chemistry of Manganese, Technetium and Rhenium', in Pergamon Texts in Inorganic Chemistry, Vol. 22, Pergamon Press, Oxford, 1975, p. 784.

[5] R. Colton and J. H. Canterford, 'Halides of the First Row Transition Metals', Wiley, 1969, p. 212.

[6] A. Zalkin, K. Lee and D. H. Templeton, J. Chem. Phys., 697, 37, 1962.

[7] S. Ogawa, J. Phys. Soc. Jpn., 1475, 15, 1960.

[8] K. Knox, Acta Cryst., 1115, 14, 1959.

[9] R. D. Peacock and D. W. A. Sharp, J. Chem. Soc., 2762, 1959.

[10] K. Hirakawa, K. Hirakwap and T. Hashimoto, J. Phys. Soc. Japan, 2063, 15, 1960.

[11]A. L. Heegow, O. Beckman and A. M. Portis, Phys. Rev., 1652, 123, 1961

[12]S. Ogawa, J. Phys. Soc. Jpn., 1115, 14, 1959.

[13]K. Lee, A. M. Portis and G. L. Witt, Phys. Rev., 144, 132, 1963.

[14]A. Mehra and P. Venkateswarlu, J. Chem. Phys., 2334, 47, 1967.

[15]R. L. Martin, R. S. Nyholm and N. C. Stephenson, Chem. Ind. (London), 83, 1956.

[16]W. Massa, Inorg. Nucl. Chem. Lett., 253, 13, 1977.

[17]P. Bukovec and V. Kaucic, J. Chem. Soc., 945, 1977.

[18]M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta and D. T. Khathing, J. Chem. Soc. Dalton Trans., 2587, 1981.

[19]C. W. Wood and A. K. Holliday, 'Inorganic Chemistry' Butterworths, London, 1967, p. 336.

[20]M. K. Chaudhuri and P. K. Choudhury, Chem. Ind. (London), 88, 1979.

[21]Ref. 3, p. 848.

[22]J. R. Thornback and G. Wilkinson, J. Chem. Soc. Dalton Trans., 110, 1978.

[23]A. R. Chakravorty and A. Chakraborty, Inorg. Chem., 275, 20, 1981.

[24]S. Emori, M. Inoue, M. Kishita and M. Kubo, Inorg. Chem., 1385, 8, 1969.

[25]R. S. Nyholm and A. G. Sharpe, J. Chem. Soc., 3579, 1952.

CHAPTER 7

Alkali-Metal and Ammonium Fluoromonooxalatomanganates(II), $A[MnF(C_2O_4)].nH_2O$ (A = Na, n = 2; A = K or NH_4, n = 0). Synthesis and Physico-Chemical Studies

It was mentioned in the preceding Chapter that manganese(II) generally forms two types of fluoro complexes, viz., tetrafluoromanganates(II), and trifluoromanganates(II). It has been also known that manganese(II) forms a oxalato coomplex, e.g., $K_2Mn(C_2O_4)_2.2H_2O$,[1] which is fairly stable under the ordinary conditions.[1,2] Although many of the fluoromanganates(II) show abnormal magnetic properties (Chapter 6), the binary oxalato-manganate(II) complex, $K_2Mn(C_2O_4)_2.2H_2O$, seems to behave like a normal manganese(II) complex. In view of this, and also since there appears to be no reported example of mixed fluoro-oxalato complex of manganese(II), it was thought worthwhile to synthesise mixed ligand fluoro-oxalatomanganate(II) complexes and compare their properties with those of the binary fluoro and binary oxalato complexes of manganese(II) to get more insight

into the chemistry of bivalent manganese. It was also our interest to see whether the oxalato group(s), in such compounds, binds the manganese(II) centre(s) in a chelated or in a bridging bidentate manner.

The present Chapter reports the synthesis of alkali-metal and ammonium fluoromonooxalatomanganates(II), $A[MnF(C_2O_4)].nH_2O$ ($A = Na$, $n = 2$; $A = K$ or NH_4, $n = 0$), and the results of physicochemical studies of the newly synthesised fluoromonooxalatomanganate(II) complexes.

EXPERIMENTAL

All chemicals were of reagent grade.

Infrared spectra were recorded on a Perkin-Elmer Model 683 spectrophotometer separately in KBr and in nujol media.

Magnetic susceptibility measurements were made by the Gouy method. $Hg[Co(NCS)_4]$ was the calibrant.

MnO(OH) was prepared by the method described in Chapter 1.

Elemental Analyses. Manganese, fluoride, sodium, potassium and nitrogen were estimated by the methods described in

Chapter 1. The oxalate content of each of the compounds was determined by the method described in Chapter 4.

Chemical Determination of the Oxidation States of Manganese. The oxidation state of manganese in each of the newly synthesised compounds was determined by the method described in Chapter 4.

Synthesis of Alkali-Metal and Ammonium Fluoromonooxalatomanganates(II). Two general methods have been developed for the synthesis of the title compounds.

Method I

Powdered potassium permanganate, $KMnO_4$, was dissolved in the minimum amount of water and 40% hydrofluoric acid was added to it. The solution was filtered. To the filtrate, a solution of alkali-metal or ammonium oxalate, $A_2C_2O_4$, made by dissolving it in the minimum volume of water, was added under constant stirring. The molar ratio among $KMnO_4$, HF and $A_2C_2O_4$ was maintained at 1:3:3.5. The reaction mixture thus obtained was then heated at ca 100 °C with constant stirring until the solution becomes colourless giving a white microcrystalline alkali-metal or ammonium fluoromonooxalatomanganate(II), $A[MnF(C_2O_4)]$. Heating may be continued for a further period of a few minutes in order to ensure complete precipitation of the product. The $A[MnF(C_2O_4)]$ compound was separated by filtration, washed

2-3 times with ethyl alcohol and finally dried in vacuo over phosphorous pentoxide.

The specific gram amounts of the reagents used and yields of alkali-metal and ammonium fluoromonooxalatomanganates(II) are given in Table 1.

Table 1. Amounts of Reagents Used and Yields of Alkali-Metal and Ammonium Fluoromonooxalatomanganates(II)

Compound	Yield in g (%)	Amount of $KMnO_4$ in g (m mol)	Amount of 40% HF in ml(m mol)	Amount of $A_2C_2O_4$ in g (m mol)
$NH_4[MnF(C_2O_4)]$	0.5 (84)	0.5 (3.16)	0.5 (10)	1.5 (11.27)
$Na[MnF(C_2O_4)]\cdot 2H_2O$	1.2 (86)	0.5 (3.16)	0.5 (10)	1.5 (11.2)
$K[MnF(C_2O_4)]$	1.1 (87)	1.0 (6.33)	1.0 (20)	4.1 (22.28)

Method II

To an aqueous suspension of freshly prepared MnO(OH) (30-35 ml of water per gram of MnO(OH)) , 40% hydrofluoric acid was added with stirring. The solution was filtered. Alkali-metal or ammonium oxalate, $A_2C_2O_4$, solution, made by dissolving the stipulated amount in the minimum volume of water, was added to the filtrate with vigorous stirring. The molar ratio of MnO(OH), HF and $A_2C_2O_4$ was maintained at 1:1.75:1.5. The dark pink coloured solution thus obtained was heated on a steam-bath (ca 100 °C) with occassional stirring until the solution became colourless giving microcrystalline alkali-metal or ammonium fluoromonooxalatomanganate(II), $A[MnF(C_2O_4)]$. The solution was cooled to room temperature and the compound was separated by filtration. The compound was washed 2-3 times with alcohol and finally dried in vacuo over phosphorous pentoxide.

The specific gram amounts of the reagents used and yields of the $A[MnF(C_2O_4)]$ compounds are set out in Table 2.

The analytical data, estimated oxidation states of manganese, room temperature magnetic moment values and infrared spectral bands of alkali-metal and ammonium fluoromonooxalatomanganates(II) are summarised in Table 3.

Table 2. Amounts of Reagents Used and Yields of Alkali-Metal and Ammonium Fluoromono-oxalatomanganates(II)

Compound	Yield in g (%)	Amount of MnO(OH) in g (m mol)	Amount of 40% HF in ml(m mol)	Amount of $A_2C_2O_4$ in g (m mol)
$NH_4[MnF(C_2O_4)]$	1.85 (90)	1.0 (11.4)	1.0 (20)	2.43 (17.11)
$Na[MnF(C_2O_4)].2H_2O$	1.1 (88)	0.5 (5.68)	0.5 (10)	1.15 (8.58)
$K[MnF(C_2O_4)]$	0.95 (83)	0.5 (5.68)	0.5 (10)	1.56 (8.48)

RESULTS AND DISCUSSION

Synthesis. It has been reported in one of the previous Chapters (Chapter 4) that the manganese(III)-oxalate system can be stabilised in the presence of F^- ions in aqueous media, and a number of salts of the mixed fluorooxalatomanganate(III) ion can be isolated in the solid state. The stability of trifluoromonooxalatomanganate(III) complexes isolated from such a solution have been found to be more than that of the binary oxalatomanganate(III) complex, $K_3[Mn(C_2O_4)_3].7.3H_2O$.

In the course of our earlier studies (vide Chapter 4) mainly aimed at the synthesis and structural assessment of fluorooxalatomanganese compounds, it was observed that heating of the reaction mixture at ca 100 °C changed the deep pink colour of the solution owing to trifluoromonooxalatomanganate(III) to colourless, simultaneously precipitating a white microcrystalline compound. A similar observation was also made by heating (at ca 100 °C) a solution of $KMnO_4$, 40% HF and alkali-metal or ammonium oxalate, $A_2C_2O_4$, and thought that the white compound must be a fluorooxalato complex of manganese(II). Accordingly, in line with our contention, the reactions among $KMnO_4$, 40% HF and $A_2C_2O_4$, and among MnO(OH), 40% HF and $A_2C_2O_4$

gave rise to the formation $[MnF(C_2O_4)]^-$ species, in each case, which was isolated as its alkali-metal or ammonium salt. A plausible interpretation of this result is that a relatively higher temperature (ca 100 °C) probably helps to reduce the higher valent manganese to Mn^{2+} such that the formation of $[MnF(C_2O_4)]^-$ is favoured. One point that requires attention is that an appreciable amount of $C_2O_4^{2-}$ ions must be present in the reaction media such that a part of it is utilised in the electron-transfer process between the higher valent manganese and $C_2O_4^{2-}$, and another part is used for coordination to the Mn^{2+} centre. Although there is no direct evidence for the most probable mechanism, considering the potential of $C_2O_4^{2-}$ as a reducing agent, it is felt that oxalate ions assisted by the enhanced temperature, are responsible for the reduction of higher valent manganese to Mn^{2+}, in the present cases.

The reaction is best monitored by noting the decolourization of the reaction mixture with the progress of heating, and determination of oxidation state of manganese chemically. It is evident that mixed ligand fluorooxalatomanganate(II) complexes can be synthesised from aqueous media, and that, at least under the present condition, the number of F^- ion that could be brought to coordination with manganese(II), containing one coordinated $C_2O_4^{2-}$ group, is one.

Characterization and Assessment of Structure. The alkali-metal and ammonium fluoromonooxalatomanganates(II) are all white microcrystalline products. They are very sparingly soluble in water and insoluble in common organic solvents. In the presence of moisture they attack glass slowly. The chemical determination of the oxidation state of manganese in the compounds show that the values lie between 2.1 and 2.2 supporting the contention that manganese, in each of the compounds, has an oxidation number of +2.

The room temperature magnetic moments of the $A_2[MnF(C_2O_4)_2].nH_2O$ (A = Na, n = 2; A = NH_4 or K, n = 0), compounds were found to occur between 3.8 and 3.9 BM, the values remarkably lower than that of a normal Mn^{2+} (d^5) compound. A comparison of magnetic moments of the present series of compounds with those of the fluoro complexes of manganese(II), described earlier in this thesis, (vide Chapter 6), and with $K_2[Mn(C_2O_4)_2].2H_2O$[1] reveal that the newly synthesised mixed fluorooxalatomanganate(II) complexes have the moments much lower than those of the fluoromanganates(II), and comparatively more lower than that of $K_2[Mn(C_2O_4)_2].2H_2O$.[1] The lower values are attributed to the existence of a strong antiferromagnetic exchange interaction between the contiguous manganese(II) ions probably through —Mn—F—Mn— chains. This indicates a polymeric structure of the complex ion. It is evident from

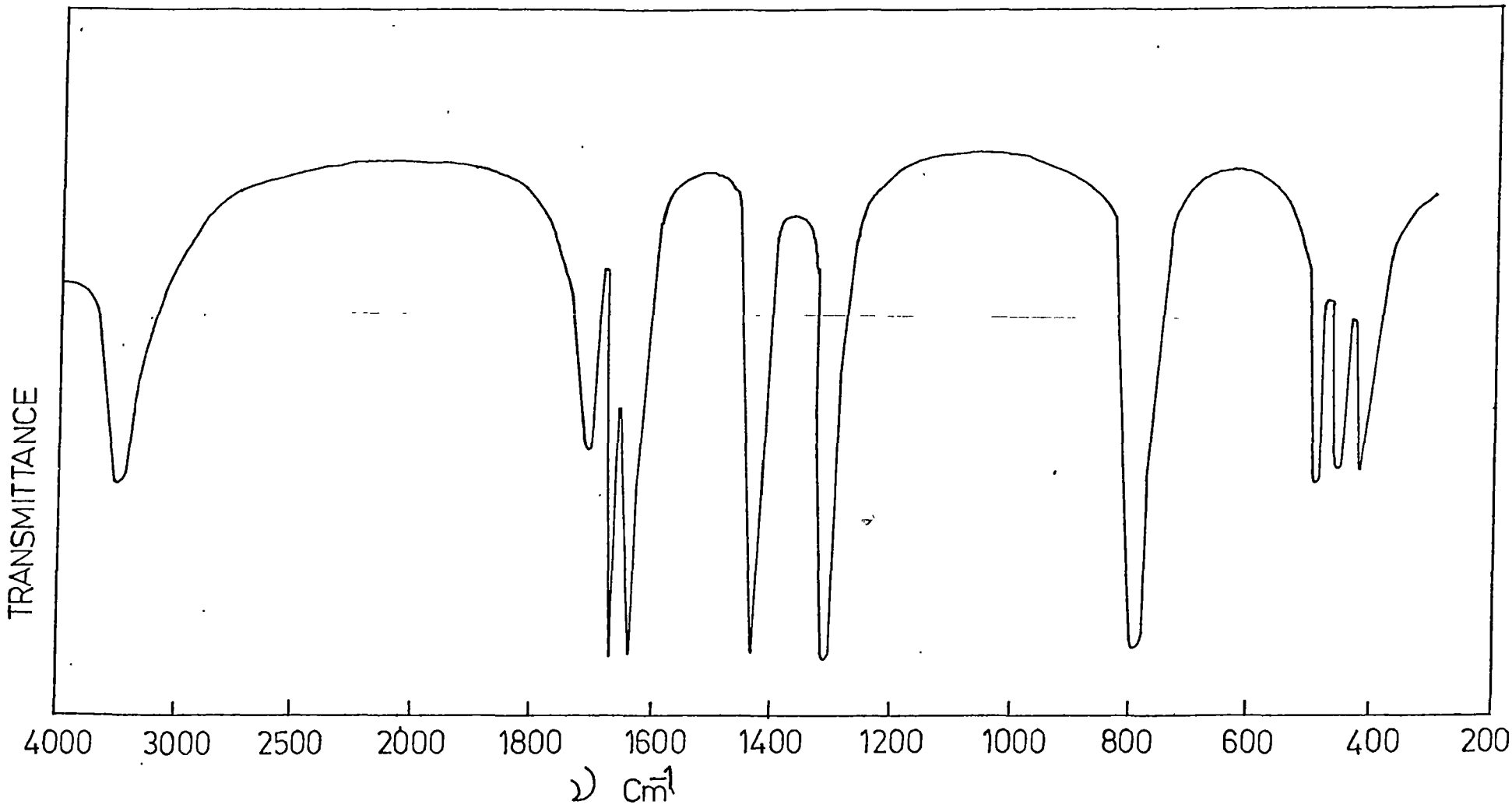
Table 3. Analytical Data, Estimated Oxidation State of Mn, Magnetic Moment Values, and IR Bands of $NH_4[MnF(C_2O_4)_2]$, $Na[MnF(C_2O_4)_2]$ and $K[MnF(C_2O_4)_2]$

Compound	Estimated Oxidation state of Mn	μ_{eff}/BM (292K)	%found (%calcd.) A/N	Mn	C_2O_4	F	IR Bands in cm^{-1}	Assignments
$NH_4[MnF(C_2O_4)_2]$	2.1	3.8	7.72 (7.78)	30.7 (30.56)	48.4 (48.9)	10.8 (10.56)	1705m	... ν_{as}(C=O) .. ν_7
							1670s	... ν_{as}(C=O) .. ν_1
							1430s	... ν(C-O + C-C) ν_2
							1310s	... ν(C-O) + δ(O-C=O) .. ν_8
							790s, 740m	... δ(O-C=O)+.. ν_9 ν(Mn-O)
							460m	... ring def. ν_{10} + δ(O-C=O)
							425m	... ring def. ν_{11} + ν(Mn-O)
							490m	... ν(Mn-F)
							3160m, 3040s, 1400s	... ν_3, ν_1, ν_2 NH_4^+ modes

Table 3. contd...../-

Table 3. (contd....)

$Na[MnF(C_2O_4)]2H_2O$	2.2	3.9	10.2	25.2	39.6	8.8	1705m ...	$\nu_{as}(C=O)$ .. ν_7
			(10.4)	(24.9)	(39.8)	(8.6)	1675s ...	$\nu_{as}(C=O)$ .. ν_1
							1435s ...	$\nu(C=O + C-C)$ ν_2
							1315s ...	$\nu(C-O)$ + .. ν_8 $\delta(O-C=O)$
							795s ...	$\delta(O-C=O)$ + ν_9 $\nu(Mn-O)$
							460m ...	ring def. + ν_{10} $\delta(O-C=O)$
							430m ...	ring def. + ν_{11} $\nu(Mn-O)$
							495m ...	$\nu(Mn-F)$
							3460m ...	$\nu(O-H)$
							1640s ...	$\delta(H-O-H)$
$K[MnF(C_2O_4)]$	2.1	3.8	19.2	27.7	43.5	9.8	1710m ...	$\nu_{as}(C=O)$ .. ν_7
			(19.4)	(27.36)	(43.78)	(9.45)	1675s ...	$\nu_{as}(C=O)$ .. ν_1
							1435s ...	$\nu(C=O + C-C)$ ν_2
							1310s ...	$\nu(C=O)$ + .. ν_8 $\delta(O-C=O)$
							795s ...	$\delta(O-C=O)$ + ν_9 $\nu(Mn-O)$
							465m ...	ring def. + ν_{10} $\delta(O-C=O)$
							430m ...	ring def. + ν_{11} $\nu(Mn-O)$
							495m ...	$\nu(Mn-F)$



IR Spectra of $Na[MnF(C_2O_4)].2H_2O$ (4000-200 cm^{-1})

the above-mentioned results that the degree of antiferromagnetic exchange interaction increases in going from fluoro to mixed fluorooxalato complexes of manganese(II).

The IR spectra of the series of three salts resemble each other very closely (Table 3) indicating that the compounds are similar both structurally and stoichiometrically. The spectra of the compounds showed absorptions in the regions typical for a coordinated $C_2O_4^{2-}$ group,[3-6] viz., at 1705-1710, 1670-1675, 1430-1435, 1310-1315, 790-795, 460-465, 425-430 cm^{-1}. The spectral pattern is different from that of the trifluoromonooxalatomanganate(III) complexes (vide Chapter 4). The bands have been unambiguously assigned[3-6] as the $\nu_{as}(C=O)$ (ν_7), [1705-1710 cm^{-1}]; $\nu_{as}(C=O)$ (ν_1), [1670-1675 cm^{-1}], $\nu(C-O + C-C)$ (ν_2), [1430-1435 cm^{-1}]; $\nu(C-O) + \delta(O-C=O)$ (ν_8), [1310-1315 cm^{-1}]; $\delta(O-C=O) + \nu(Mn-O)$ (ν_9), [790-795 cm^{-1}]; ring deformation + $\delta(O-C=O)$ (ν_{10}) [460-465 cm^{-1}] ring deformation + $\nu(Mn-O)$ (ν_{11}), [425-430 cm^{-1}] modes of coordinated oxalato group. Since the various modes, owing to the oxalato group, occur exactly in the regions stipulated for the chelated $C_2O_4^{2-}$ group, we infer that oxalato ligands in the complexes are bonded in a bidentate chelated manner. The absorptions in the region 490-495, are straightforward and have been assigned as the ν_{Mn-F} modes arising from the presence of fluoride ion coordinated to the manganese(II) centre. Its

position, however, indicates the possibility of a bridging fluoride than a terminal one. The two extra vibrations at 3460m and at 1640 s cm^{-1}, in the spectrum of the sodium salt, resemble in their shapes and position, those observed for the presence of uncoordinated water in many fluoromanganate complexes[7,8] and have been assigned to the ν_{O-H} and δ_{H-O-H} modes of uncoordinated water. Three vibrations, over and above the ones observed for the coordinated $C_2O_4^{2-}$ and coordinated F^- ligands, at 3160m, 3040s, and 1400s cm^{-1} in the spectrum of $NH_4[MnF(C_2O_4)_2]$ have been assigned to the ν_3, ν_1 and ν_4 modes of NH_4^+.

Thus, it appears from the present work that mixed fluoro-oxalatomanganate(II) complexes have magnetic moments much lower than those of fluoromanganate(II) complexes and considerably more lower than that of $K_2[Mn(C_2O_4)_2].2H_2O$. The oxalato ligand is bonded to the Mn^{2+} centre in a bidentate chelated manner, and the complex species $[MnF(C_2O_4)_2]^-$ may have a polymeric structure through a —Mn—F—Mn— bridging.

REFERENCES

[1] N. Goldenberg, Trans. Farad. Soc., 847, 36, 1940.

[2] C. K. Jorgenson, 'Inorganic Complexes', Academic Press, New York, 1963.

[3] N. F. Curtis, J. Chem. Soc., 4109, 1963.

[4] N. F. Curtis, J. Chem. Soc., 2644, 1964.

[5] N. F. Curtis, J. Chem. Soc. A, 1584, 1968.

[6] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', 2nd ed., Wiley-Interscience, London, 1970, p. 244.

[7] A. J. Edwards, J. Chem. Soc. A, 3074, 1971.

[8] M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta and D. T. Khathing, J. Chem. Soc. Dalton Trans., 2587, 1981.

CHAPTER 8

Bis(acetylacetonato)manganese(II) Dihydrate, $Mn(C_5H_7O_2)_2 \cdot 2H_2O$. A New Synthesis and Mass Spectrometric Studies

---

Acetylacetonato complexes of transition metals are important in their own rights. Bis(acetylacetonato) complexes of all the members in the series Mn^{2+} — Cu^{2+} have been known.[1] It has also been reported that the bis(acetylacetonato) chelates of Cu^{2+} and Ni^{2+} are most stable towards dissociation in aqueous solutions and heat, while the acetylacetonato complexes of Mn^{2+} and Fe^{2+} are unstable.[2] The $Co(acac)_2$, however, shows an intermediate behaviour.

Like tris(acetylacetonato)manganese(III), $Mn(C_5H_7O_2)_3$, bis(acetylacetonato)manganese(II), $Mn(C_5H_7O_2)_2$, has been known for a long time. The most widely recommended method of synthesis[3] of $Mn(acac)_2$ involves the use of a large amount of sodium acetate as a buffer, and an appreciably high amount of ammonia as a proton acceptor. The use of these two reagents in such

amounts may contaminate the end-product.[4] In view of this, and in a continuation to our work on the chemistry of manganese(II) we thought it interesting to develope a new method for the synthesis, of bis(acetylacetonato)manganese(II), which would not require any buffer and ammonia, and study the compound mass spectrometrically.

The present Chapter reports a new synthesis of $Mn(C_5H_7O_2)_2$ and also the results of mass spectrometric studies of the compound.

EXPERIMENTAL

All chemicals were of reagent grade (B.D.H., Loba Chemie, E. Merck).

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

The mass spectra were recorded on a Varian MAT CH-5 mass spectrometer. The sample was introduced directly in the ionisation chamber using a direct insertion probe. The operation conditions were electron energy, 70 eV (1 eV $\approx 1.60 \times 10^{-19}$ J);

source temperature 50, 100 and 150 °C; resolution 10,000; and accelerating voltage, 8 kV. The mass spectrometric observations were made with the field of ionising current sufficiently strong to trap primary ions.

Infrared spectral band positions and their assignments are set out in Table 1, while the essential features of the mass spectra run at 100 °C are reported in Table 2.

Elemental Analyses. Manganese was estimated by the method described in Chapter 1. C and H were estimated by micro-analytical methods.

Synthesis of Bis(acetylacetonato)manganese(II) Dihydrate, $Mn(C_5H_7O_2)_2.2H_2O$. A solution of 2 g (10.1 m mol) of $MnCl_2.4H_2O$ in about 15 ml water was treated with about 5-7 ml of 0.1 (M) sodium hydroxide. The precipitated hydrated manganese hydroxide was then centrifuged and washed several times with water until free from chloride.

The hydrated manganese(II) hydroxide was transfered to a small conical flask. A small amount of water was added to make a water suspension of $Mn(OH)_2$. To this was added 2.5 ml of 38% formaldehyde solution followed by the addition of 2.05 g (20.5 m mol) of distilled acetylacetone. The mixture was stirred for a maximum period of about 10 min, and the yellow coloured

$Mn(C_5H_7O_2)_2.2H_2O$ was obtained. The compound was separated by quick filtration, washed 2-3 times with small portions of ethyl alcohol and finally dried in vacuo over phosphorous pentoxide for 3-4 h. The compound, $Mn(C_5H_7O_2)_2.2H_2O$, was stored in a sealed container. The yield obtained was 2.3 g (77%). If desired the compound can be recrystallised from ethanol.

Analysis

Found: C, 41.54; H, 6.33; Mn, 18.8. Calc. for $C_{10}H_{18}MnO_6$: C, 41.52; H, 6.23; Mn, 19.03%.

RESULTS AND DISCUSSION

In Chapter 5, the direct synthesis of tris(acetylacetonato)-manganese(III), $Mn(acac)_3$, has been described.[7] The compound, $Mn(C_5H_7O_2)_3$, was synthesised by the reaction of MnO_4^- with acetylacetone by exploiting the electron-transfer reaction between them. The weak acidity of acetylacetone (acacH) in a polar medium, and the reaction of acetylacetone (Hacac) with manganese(II) hydroxide, $Mn(OH)_2$,

$$Mn(OH)_2 + 2\ Hacac \longrightarrow Mn^{2+} + 2\ acac^- + 2\ H_2O \quad \ldots(1)$$

$$Mn^{2+} + 2\ acac^- \longrightarrow Mn(acac)_2 \quad \ldots \quad \ldots \quad (2)$$

constitute the basis of the present synthesis. Analogous methods have been used with success for the synthesis of $Co(acac)_3$ from CoO(OH) and $Mn(acac)_3$ from MnO(OH). This method (vide Experimental section) does not require any buffer, and it also does not make use ammonia unlike the method recommended in the literature.[3] The pH of the solution, required for the successful formation of $Mn(acac)_2$, was maintained by the ionisation of Hacac (cf. pH 5) in the reaction medium. There is a strong tendency of $Mn(acac)_2$ to get oxidized,[2] particularly when it is wet. Moreover, the hydrated manganese(II) hydroxide is slowly oxidised by air. Therefore it was necessary for us to use a small amount of formaldehyde to check the unwanted oxidation of Mn^{2+}. The reasons why formaldehyde was chosen for the purpose are that formaldehyde is obtained as a solution, and the oxidation products of formaldehyde can not contaminate the end-product. The method is quite rapid and can be scaled up to higher quantities.

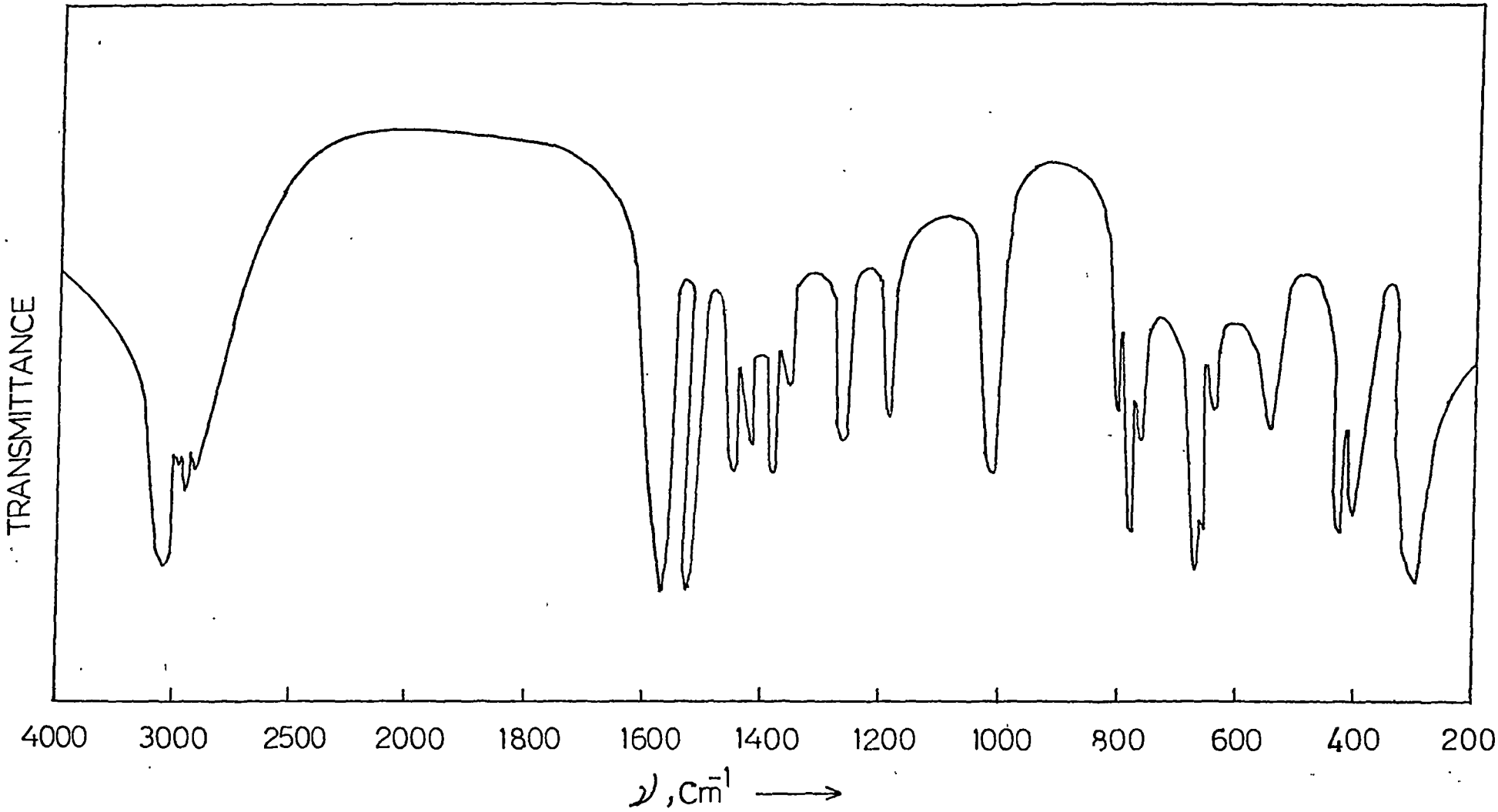
Characterization. Bis(acetylacetonato)manganese(II) dihydrate, $Mn(C_5H_7O_2)_2.2H_2O$, is a yellow coloured compound, soluble in many organic solvents. The compound is not stable in air, particularly in the presence of moisture. However, it can be stored in sealed capsules for prolonged periods. The dihydrated compound can be dehydrated by heating, in vacuum, at ca. 65 °C.[3]

The infrared spectrum of the compound (Table 1) is unambiguous and exhibit the typical pattern of chelated acetylacetonates ($acac^-$) in agreement with those of various $M(acac)_2$[5,6] compounds.

Mass Spectrometric Studies. The mass spectra of $Mn(acac)_2.2H_2O$ was studied by direct insertion technique. The sample was introduced into ionisation chamber using a direct insertion probe without any prior heating. The spectra were recorded with the temperature of ionization chamber being maintained at 50°, 100° and 150°C respectively. The optimum temperature for the record of a good spectrum of the compound was found to be 100 °C, since the spectrum obtained at 50 °C was showing very poorly developed signals owing to various fragment ions, and that 150 °C showed some pyrolysis effect. The essential features of the spectrum run at 100 °C are summarised in Table 2. The molecular ion peak was observed at m/Z 253 followed by a strong peak at m/Z 238 assigned to the fragment ion $[Mn(C_5H_7O_2)(C_4H_4O_2)]^+$. A comparison of the present spectrum with that of $Mn(C_5H_7O_2)_3$ (Chapter 5) reveals that while the molecular ion in the csse of $Mn(acac)_3$ loses an acac• unit, that of $Mn(C_5H_7O_2)_2$ loses a methyl group. The most dominant ion peak was observed at m/Z 154 (100 %) owing to the fragment ion $[Mn(C_5H_7O_2)]^+$ with the major fragmentation pathway being $[Mn(C_5H_7O_2)_2]^+ \longrightarrow [Mn(C_5H_7O_2)(C_4H_4O_2)]^+ \longrightarrow$

Table 1. Infrared Spectral Bands and Their Assignments

IR Bands (cm^{-1})			Assignments[5,6]
3065	...	...	ν(CH)
2990 2960 2920	...	...	$\nu(CH_3)$
1570	...	...	$\nu(C{:::}C)$ + $\nu(C{:::}O)$ combination
1530	...	...	$\nu(C{:::}O)$ + $\nu(C{:::}C)$
1450	...	...	δ(OH) + $\nu(C{:::}C)$
1430	...	...	$\delta_a(CH_3)$
1390 1360	...	...	$\delta_s(CH_3)$
1270	...	...	$\nu(C\text{-}CH_3)$ + $\nu(C{:::}C)$
1190	...	...	δ(CH) + $\nu(C\text{-}CH_3)$
1020	...	...	$\rho_r(CH_3)$
935	...	...	$\nu(C{:::}C)$ + $\nu(C{:::}O)$
801 780 771	...	...	π(CH)
670 665	...	...	$\nu(C\text{-}CH_3)$ + ring deformation + ν(Mn-O)
650	...	...	$\chi(CH_3\text{—}C\lessdot{C \atop O})$
550	...	...	ring deformation + ν(Mn-O)
435	...	...	ν(Mn-O) + $\nu(C\text{-}CH_3)$
410	...	...	ring deformation
300	...	...	ν(Mn-O)



IR Spectra of $Mn(C_5H_7O_2)_2$ (4000-200 cm^{-1})

Table 2. Mass Spectral Data for $Mn(C_5H_7O_2)_2$

(a) Major Peaks

Assignments	m/Z	Intensity (%)
$[Mn(C_5H_7O_2)_2]^+$	253	88
$[Mn(C_5H_7O_2)(C_4H_4O_2)]^+$	238	62
$[Mn(C_5H_7O_2)(C_3H_5O)]^+$	211	12
$[Mn(C_5H_7O_2)]^+$	154	100
$[Mn(C_4H_4O_2)]^+$	139	4
$[Mn(C_5H_5O)]^+$	136	3
$[MnOH]^+$	72	6
$[MnCH_3]^+$	70	14
Mn^+	55	10

(b)

m/Z* observed	m/Z* calculated	Process	Fragment Lost
223.0	222	253 → 238	CH_3
99.65	99.5	238 → 154	$C_4H_4O_2$
125.46	125	154 → 139	CH_3
21.76	21.5	139 → 55	$C_4H_4O_2$

$[Mn(C_5H_7O_2)]^+ \longrightarrow [Mn(C_4H_4O_2)]^+ \longrightarrow Mn^+$. The metastable peaks at m/Z* 222, 99.5, 125 and at 21.5 strongly support the fragmentation path. A relatively strong signal at m/Z 70 (14%) has been assigned to $[MnCH_3]^+$ ion. This provides evidence for easy methyl migration from carbon to manganese, presumably favoured by the formation of a new bond between the metal atom and CH_3. Similar observation has been made very recently by Chaudhuri and Ghosh[8] in the case of $Fe(acac)_3$. The mass spectrum suggests that the compound exists in its monomeric form in the vapor state and resemble those recorded earlier.[9,10]

It appears, from the results described in this Chapter, that bis(acetylacetonato)manganese(II) dihydrate, $Mn(acac)_2.2H_2O$, can be synthesised without making use of any buffer, or ammonia. Its mass spectrum provides evidences for its existence as a monomer in the vapour state, and for rearrangement to $Mn-CH_3$ species.

REFERENCES

[1] J. P. Fackler, Jr., Progr. Inorg. Chem., 361, 7, 1966.

[2] R. G. Charles and M. A. Pawlikowski, J. Phys. Chem., 440, 62, 1958.

[3] R. G. Charles, Inorg. Syntheses, 164, 6, 1960.

[4] W. C. Fernelius and B. E. Bryant, Inorg. Syntheses, 108, 5, 1957.

[5] M. Mikami, I. Nakagawa and T. Shimanouchi, Spectrochim. Acta, 1037, 20A, 1967.

[6] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compound', 2nd ed., Wiley-Interscience, London, 1970, p.249.

[7] M. N. Bhattacharjee, M. K. Chaudhuri and D. T. Khathing, J. Chem. Soc. Dalton Trans., 669, 1982.

[8] M. K. Chaudhuri and S. K. Ghosh, J. Chem. Soc. Dalton Trans., 0000, 1983.

[9] C. G. McDonald and J. S. Shannon, Aust. J. Chem., 1545, 19, 1966.

[10] G. M. Bancroft, C. Reichert and J. B. Westmore, Inorg. Chem., 870, 7, 1968.

PART II

Studies Involving A New Chromium (VI) Reagent, PYRIDINIUM FLUOROCHROMATE (VI), $C_5H_5NHCrO_3F$ (PFC)

CHAPTER 9

Oxidation of Organic Substrates Involving a New and Efficient Oxidant, Pyridinium Fluorochromate(VI), $C_5H_5NHCrO_3F$ (PFC)*

Mechanisms of the oxidation reactions of chromium(VI), particularly involving chromic acid, are in many cases rather fairly well understood as a result of the pioneering work of Westheimer and his coworkers[1,2] and of some others.[3,4] It is generally believed[5] that the mode and nature, rate and type of oxidation reactions vary in many cases with the nature of the chromium(VI) species and the solvent used. Accordingly a number of newer chromium(VI) reagents were prepared, and the oxidations involving them were studied. These include the oxidations involving CrO_3-3,5-dimethylpyrazol complex,[6] chromium(VI) oxide-pyridine complex,[7] CrO_3-acetone complex,[8,9] CrO_3-dipyridine complex,[10-14] CrO_3-2,2'-dipyridyl complex,[15] pyridinium dichromate[16-19] and chromic anhydride-tertiary amine complex[11,20] and may be some

* The work described in this Chapter has been published: Synthesis (Stuttgart), 588 (1982).

more. However, these reagents do not always prove to be very satisfactory particularly when some specific oxidations like oxidations of alcohols containing not only an acid-sensitive group but also a double bond, oxidation of a thio ether group, and oxidations of strained hydrocarbon rings etc. are desired.

Thus there is continued interest in the development of new chromium(VI) reagents for the effective and selective oxidation of organic substrates, in particular alcohols, under mild conditions. Of the large number of "mild" oxidising agents available many prove impractical when the reactions are performed on a larger (mol) scale. In recent years, significant improvement were achieved by the use of pyridinium chlorochromate(VI), $C_5H_5NHCrO_3Cl$(PCC).[21-24] Although PCC has been gaining importance, it has dome inherent problems, e.g., PCC is quite acidic and thus precludes its use in the cases of oxidations of acid sensitive organic substrates. Some-times the use of PCC requires buffering of the reaction media.

Recently we have synthesised a new chromium(VI) compound, pyridinium fluorochromate(VI), $C_5H_5NHCrO_3F$ (PFC), with a view to explore its synthetic utility. In this Chapter the results of investigation of the synthetic potential of the new chromium(VI) reagent, pyridinium fluorochromate(VI), $C_5H_5NHCrO_3F$, and its advantages over similar oxidising agents have been reported.

EXPERIMENTAL

The chemicals used for the synthesis of pyridinium fluorochromate(VI), $C_5H_5NHCrO_3F$ (PFC), were all reagent grade products.

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

Molar conductance measurement was made using a Philips PR 9500 conductivity bridge.

pH measurements were made with a Systronic Digital pH meter 335.

Preparation of Pyridinium Fluorochromate(VI), $C_5H_5NHCrO_3F$ (PFC). Chromium(VI) oxide (CrO_3; 15.0 g, 0.15 mol) is dissolved in water (25 ml) in a polyethylene 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 *ca* 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 *ca* 1 h; Yield: 27.9 g (93.5 %); m.p. 106-108 °C.

Analysis

Found: C, 30.12; H, 3.07; Cr, 26.17; F, 9.58; N, 6.96. Calc. for $C_5H_6CrFNO_3$: C, 30.16; H, 3.04; Cr, 26.12; F, 9.54; N, 7.04%

IR (KBr): 908 ($\tilde{\nu}_1$), 640 ($\tilde{\nu}_2$), 340 ($\tilde{\nu}_3$), 952 ($\tilde{\nu}_4$), 373 ($\tilde{\nu}_5$), 262 ($\tilde{\nu}_6$) cm^{-1}.

Molar conductance of 0.001 molar solution of pyridinium fluorochromate(VI) in water: Λ_M (25 °C) = 128 ohm^{-1} cm^2 mol^{-1}.

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

Oxidation of Organic Substrates (Alcohols 1, Fused Ring Hydrocarbons 3) with Pyridinium Fluorochromate (PFC): General Procedure. The oxidation reaction is carried out in a dry round-bottom flask fitted with a reflux condenser and an 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, maintaining the molar ratio of substrate to oxidant at 1:1.25-1.5 in the case of alcohols (1) and 1:2.5 in the case of polycyclic arenes (3) (Table 1). The mixture is stirred for the time indicated in the Table 1 (The progress of the reaction may be followed by

T.L.C. on silica gel using benzene/ethylacetate (90/10) as the 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 details of oxidations are set out in Table 1.

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

Oxidation of 4-Hydroxy-tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (1f); A Typical Procedure. In a 250 ml round-bottom flask fitted with reflux condenser and stirrer was placed a suspension of pyridinium fluorochromate (PFC) (16.15 g, 81.2 m mol) in dichloromethane (30 ml). To this, a solution of 4-hydroxy-tricyclo[5.2.1.$0^{2,6}$]-deca-3,8-diene[25] (1f ; 8.0 g, 54.05 m mol) in dichloromethane (40 ml) was added with vigorous stirring which was continued for 90 min. The reaction was monitored by T.L.C. on silica gel using benzene/ethyl acetate (90/10) as the eluent. To the resultant mixture, dry ether (100 ml) was added and the mixture was filtered through a short silica gel column (7 cm x 2 cm^2). The contents of the column were thoroughly washed with ether (3 x 40 ml) and filtered. The combined filtrates were evaporated on a steam-bath and the oily residue, which solidified on standing, was

recrystallised from pentane. Yield of the colourless crystalline 4-oxotricyclo[5.2.1.$0^{2,6}$]-deca-3,8-diene (2f) was 7.3 g (92%); m.p. 79-80 °C (lit.,[26] m.p. 80 °C).

RESULTS AND DISCUSSION

Pyridinium fluorochromate(VI), $C_5H_5NHCrO_3F$ (PFC), is easily prepared in 93-94% yield by the reaction among pyridine, aqueous 40% hydrofluoric acid, and chromium(VI) oxide in a molar ratio of 1:1.5:1. It is believed that chromium(VI) oxide first react with F^- ion, in the acidic medium, to form fluorochromate(VI) ion, CrO_3F^-, which is then precipitated by the counter cation $C_5H_5NH^+$ (pyH^+), obtained by the addition of pyridine (C_5H_5N) in the acidic medium. The orange crystalline, pyridinium fluorochromate(VI), reagent can be stored in a sealed polythene bag for long periods without decomposition. The stability of the reagent can be ascertained by the determination of the chromium(VI) content iodometrically. The molar conductance of the compound in water was found to be 128 obm^{-1} cm^2 mol^{-1} suggesting an uni-uni valent electrolytic nature in accordance with the formula shown. This result adduce further support to the stability of the compound. The infrared spectrum of $C_5H_5NHCrO_3F$

(PFC) is similar to that of potassium fluorochromate(VI),[27,28] as far as the bands owing to the CrO_3F^- are concerned.

Pyridinium fluorochromate(VI) is soluble in water, dimethyl formamide, and acetone; it is comparatively less soluble in dichloromethane and only sparingly soluble in benzene, carbon tetrachloride, chloroform, and hexane.

We have investigated the synthetic potential of pyridinium fluorochromate(VI), $C_5H_5NHCrO_3F$ (PFC), and found that this reagent has certain advantages over similar oxidizing agents in terms of amounts of the oxidant and solvent required, short reaction times, and high yields of the products. Further, pyridinium fluorochromate(VI) does not react with acetonitrile which is a suitable medium for studying oxidation kinetics and mechanism. It is notable that the acidity of pyridinium fluorochromate(VI) (pH of a 0.01 molar solution: 2.45) is less pronounced than that of pyridinium chlorochromate (pH of 0.01 molar solution: 1.75).

The new reagent pyridinium fluorochromate(VI), $C_5H_5NHCrO_3F$ (PFC), in dichloromethane oxidizes (Table 1) primary alcohols (1a-d) and secondary alcohols (1e) to the corresponding aldehydes or ketones (2) in very high yields. The reagent has also been successfully applied to the oxidation of benzoin (1g) and a tricyclic allylic alcohol (1f) to benzil(2g)

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

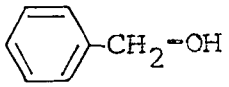
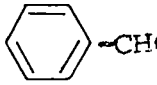
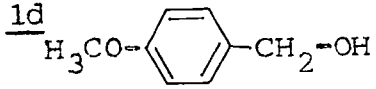
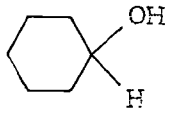
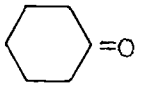
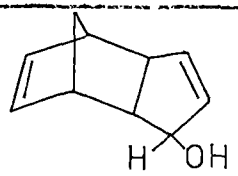
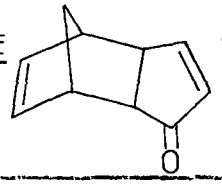
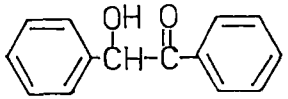
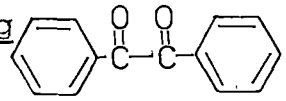
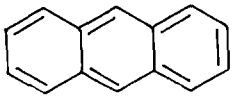
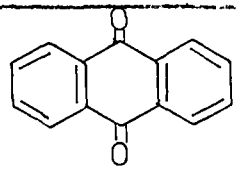
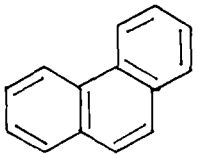
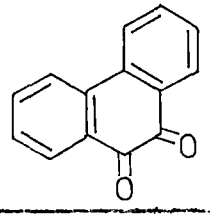
Substrate	Substrate/ Oxidant (mol mol)	Solvent	Reaction time	Product[a]	Yield (%)	m.p. or b.p./torr °C found (reported)
1a $n\text{-}C_4H_9OH$	1/1.5	CH_2Cl_2	2 h	2a $m\text{-}C_3H_7\text{-}CHO$	94	bp. 74°/760 (bp. 75°/760)[29]
1b $n\text{-}C_7H_{15}\text{-}OH$	1/1.5	CH_2Cl_2	1 h	2b $n\text{-}C_6H_{13}\text{-}CHO$	84	bp.152°/760 (bp.153°/760)[30]
1c 	1/1.25	CH_2Cl_2	45 min	2c 	90	bp. 63°/10 (bp. 62°/10)[31]
1d 	1/1.25	CH_2Cl_2	50 min	2d 	90	bp.248°/760 (bp.259.5/760)[32]

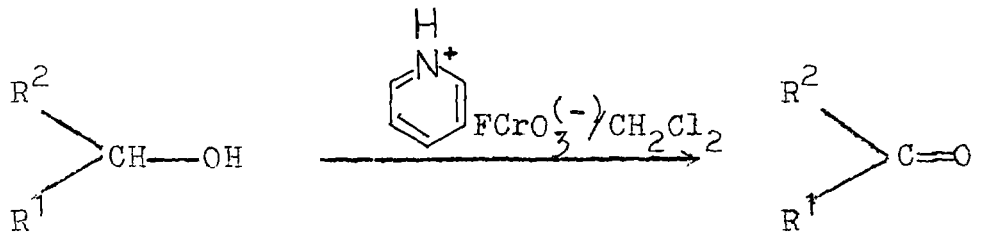
Table... contd...../-

Table. (contd...)

1e		1/1.5	CH_2Cl_2	3.5 h	2e		89	bp. 153-154°/760 (bp. 155.4°/760)[33]
1f		1/1.5	CH_2Cl_2	1.5 h	2f		92-93	mp. 79-80° (mp. 80°)[26]
1g		1/1.5	CH_2Cl_2	2.5 h	2g		98	mp. 95° (mp. 95°)[34]
3a		1/2.5 1/2.5	CH_2Cl_2 AcOH	4.0 h 1.5 h	4a		68 98	mp. 274° (mp. 275°)[35]
3b		1/2.5 1/2.5	CH_2Cl_2 AcOH	5.0 h 2.0 h	4b		52 72	mp. 205 (mp. 206.5-207.5)[36]

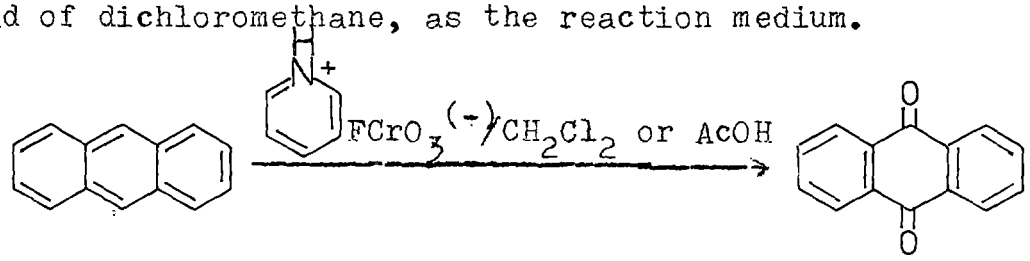
[a] The purity of the liquid products was found to be 98% by G. L. C. analysis.

and a tricyclic enone (2f), respectively.



1 2

Pyridinium fluorochromate(VI) (PFC) 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 oxidising agents under mild conditions and they may even be raised to 98% and 72% by using acetic acid, instead of dichloromethane, as the reaction medium.



3a 4a

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

Thus, the results hitherto obtained with pyridinium fluorochromate, $C_5H_5NHCrO_3F$(PFC), are very satisfactory and suggest the new reagent as a valuable addition to the existing oxidizing agents

REFERENCES

[1] F. H. Westheimer, Chem. Rev., 419, 45, 1949.

[2] (a) W. Watanabe and F. H. Westheimer, J. Am. Chem. Soc., 61, 71, 1949.

(b) G. T. E. Graham and F. H. Westheimer, J. Am. Chem. Soc., 3030, 80, 1958.

[3] J. O. Edwards, Chem. Rev., 455, 50, 1952.

[4] K. B. Wiberg and T. Mill, J. Am. Chem. Soc., 3022, 80, 1958.

[5] K. B. Wiberg, 'Oxidation in Organic Chemistry', Part A, Academic Press, New York, 1965, p. 71.

[6] E. J. Corey and G. W. J. Fleet, Tetrahedron Lett., 4499, 1973.

[7] J. R. Holum, J. Org. Chem., 4814, 26, 1961.

[8] K. Bowden, I. M. Heilbern, E. R. H. Jones and B. C. L. Weeden, J. Chem. Soc., 39, 1949.

[9] A. Bowers, T. G. Hatsall, E. R. H. Jones and A. J. Lemin, J. Chem. Soc., 2555, 1953.

[10] J. C. Collins, W. W. Hess and F. J. Frank, Tetrahedron Lett., 3363, 1968.

[11]H. H. Sisler, J. D. Bush and O. E. Accountius, J. Am. Chem. Soc., 3827, 70, 1948.

[12]H. H. Sisler, M. El-Jadir and D. H. Busch, J. Inorg. Nucl. Chem., 257, 16, 1961.

[13]H. H. Sisler, W. C. L. Ming, E. Metter and F. R. Hurley J. Am. Chem. Soc., 446, 75, 1953.

[14]F. Holloway, M. Cohen and F. H. Westheimer, J. Am. Chem. Soc., 65, 75, 1951.

[15]F. S. Guziec, Jr. and F. A. Luzzio, Synthesis, 691, 1980.

[16]J. C. Collins and W. W. Hess, Org. Syntheses, 5, 52, 1972.

[17]A. K. Sharma, T. Ku, A. D. Dawson and D. Swern, J. Org. Chem., 2758, 40, 1975.

[18]K. Omura and D. Swern, Tetrahedron, 1651, 34, 1978.

[19]E. J. Corey and G. Schmidt, Tetrahedron Lett., 399, 1979.

[20]G. I. Poos, G. E. Aoth, R. E. Beyher and L. H. Sarett, J. Am. Chem. Soc., 425, 75, 1953.

[21]E. J. Corey and J. W. Suggs, Tetrahedron Lett., 2647, 1975.

[22]E. J. Corey and D. L. Boger, Tetrahedron Lett., 2461, 1978.

[23]G. Piancatelli, A. Scettri and M. D'Auria, Tetrahedron Lett., 2199, 1977.

[24]W. G. Dauben and D. M. Michno, J. Org. Chem.,682, 42, 1972.

[25]R. B. Woodward and T. J. Katz, Tetrahedron, 70, 5, 1959.

[26]L. A. Paquette and J. S. Ward, J. Org. Chem., 3569, 37, 1972.

[27]R. Colton and J. H. Canterford, 'Halides of the First Row Transition Metals', John Wiley and Sons, New York, 1969, p. 190.

[28]M. K. Chaudhuri, H. S. Dasgupta and N. Roy, Ind. J. Chem., 1227, 20A, 1981.

[29]A. E. Tschitschibabin, Ber. Dtsch. Chem. Ges., 188, 37, 1904.

[30]N. Zelinsky, Ber. Dtsch. Chem. Ges., 2800, 34, 1901.

[31]L. E. Hinkel, E. E. Ayling and W. H. Morgan, J. Chem. Soc., 2793, 1932.

[32]L. E. Hinkel, E. E. Ayling and W. H. Morgan, J. Chem. Soc., 2797, 1932

[33]M. L. Sherril, J. Am. Chem. Soc., 1991, 52, 1930.

[34]Beilstein, 747, 7.

[35]Beilstein, 782, 7.

[36]Beilstein, 797, 7.

CHAPTER 10

Kinetics and Mechanism of the Oxidation of Alcohols with Pyridinium Fluorochromate(VI), $C_5H_5NHCrO_3F$ (PFC) *

Studies of various mechanistic aspects of chromium(VI) oxidations have been always very rewarding.[1] A chromium(VI) oxidant, being a multielectronic reagent, offers a number of fascinating possibilities for reactions. Thus most chromium(VI) oxidations of one-equivalent reductants proceed through chromium(V) and chromium(IV), and reduction of either chromium(VI) or chromium(V) may be rate-limiting. Consequent upon this, two general classes of kinetic pathways have been suggested[2]: (i) involving a series of one-electron changes, and (ii) involving multi-electron processes. Since the reduction of chromium(VI) to chromium(III) can occur through different mechanisms, depending on the nature of reducing agents and

* This work has been published:
Bull. Chem. Soc. Jpn., 0000, 57, 1984.

the reaction conditions, a considerable amount of work was done on the studies of kinetic features of oxidation reactions involving various chromium(VI) reagents.[3-9]

The development of pyridinium chlorochromate(VI), $C_5H_5NHCrO_3Cl$ (PCC) (Corey's reagent) as a very successful reagent for various oxidations has generated much interest and many papers have been published on the results of kinetic and mechanistic studies involving pyridinium chlorochromate.[10-14] We have recently developed a new chromium(VI) rea-gent[15] pyridinium fluorochromate(VI), $C_5H_5NHCrO_3F$ (PFC) and found several advantages of our reagent over similar oxidizing agents in respects of amounts of oxidant and solvent required, considerably short reaction times, and high yields (vide Chapter 9). The mechanism of oxidations involving this important reagent has now been studied.

The present Chapter, indeed the last Chapter of the thesis, describes the kinetics of oxidation of three typical alcohols viz., benzyl alcohol, ethanol and cyclohexanol, studied in medium acetonitrile-nitrobenzene (1:1, v/v) evaluates the reaction constants and discusses the probable mechanism.

EXPERIMENTAL

All chemicals used were reagent grade products.

Purification of Solvents and Substrates. The solvents and the substrates were purified and dried by the literature methods.[16,17]

(i) Acetonitrile. Acetonitrile was distilled three times over P_2O_5 in an all glass appratus containing a P_2O_5 packed guard tube. The distillate thus obtained was then distilled over anhydrous K_2CO_3 to remove traces of P_2O_5, and finally distilled without any drying agent. The fraction boiling at 78-79.5 °C was collected. (UV: λ_{max} at 161 nm).

(ii) Nitrobenzene. The reagent grade nitrobenzene was dried by keeping over anhydrous calcium chloride for ca 24 h in a well-stoppered round bottom flask. The dried solvent was separated by decantation and distilled. The fraction of the liquid boiling at 207-209 °C was collected. (VU: λ_{max} at 252 nm, 280 nm and 330 nm).

(iii) Ethyl Alcohol. Reagent grade ethanol and freshly burnt quicklime (~1 lit. ethanol: 250 g quicklime) were refluxed on a steam-bath for ca 6 h, and then allowed to stand

for 8-10 h. The cold and dry liquid was then filtered through a packed glass wool column. The filtrate was finally distilled by heating over a steam-bath and taking utmost care to prevent absorption of moisture. The first few ml of the distillate was rejected. The fraction boiling at 75 ^{o}C was collected for further studies.

(iv) Benzyl Alcohol. An amount of 100 ml of benzyl alcohol was mixed with an equal volume of ether in a 500 ml separating funnel and shaken well twice with 20 ml portions of a saturated sodium bisulphite solution in order to remove any benzaldehyde. The organic layer was washed with 20 ml of a 10% sodium carbonate solution to ensure complete removal of the bisulphite. The organic layer was then washed with 25 ml of water. The washed organic liquid was dried over anhydrous magnesium sulphate in a stoppered erlenmeyer flask and then filtered. The filtrate was distilled at a lower temperature, to first remove ether, and then at a higher temperature. The fraction boiling at 203-204 ^{o}C was collected as the pure benzyl alcohol.

(v) Cyclohexanol. Reagent grade cyclohexanol was first treated with anhydrous K_2CO_3 and then allowed to settle. The organic liquid was separated by decantation and refluxed for 10-15 min over dehydrated lime. It was then cooled and filtered and finally distilled under vacuum. The fraction

boiling at 87-89 °C (18 mm pressure) was collected as the pure cyclohexanol.

Preparation of the Oxidant Pyridinium Fluorochromate(VI) $C_5H_5NHCrO_3F$ (PFC). The oxidising agent $C_5H_5NHCrO_3F$ (PFC) was prepared by the method[15] already described in Chapter 9.

Apparatus for Kinetic Measurements

For kinetic measurements standard (Corning Class A) glass apparatus were used. The oxidation reactions were carried out using an electrically operated thermostatic water-bath having all arrangement to maintain constant temperature (± 0.1 K). A sensitive and accurate thermometer having finer graduations was used for temperature measurements.

Monitoring of Kinetic Runs. The progress of each kinetic run was monitored by determining the amount of unreacted chromium(VI) at each interval of time. This was accomplished by quenching off the reaction, of an exactly known amount of the reaction solution, withdrawn from the main reaction container at a definite interval of time, and then estimating the unreacted chromium(VI) content by iodometry. The iodometric titrations were made under a CO_2-atmosphere. The quenching off of the reaction was done by pouring the aliquot to an ice-water mixture.

On sub-tration of the amount of chromium(VI) unreacted from that originally taken gave the amount of chromium(VI) used up in the oxidation at each interval of time. These values were made use of in the calculations of rate constants.

Kinetic Runs and Rate Measurements. General Procedure.

For kinetic measurements, the reactions were performed under pseudo-first order conditions by maintaining a large excess (x 5 or greater) of alcohol over pyridinium fluorochromate (VI) (PFC). The reactions were carried out at a constant temperature (± 0.1 K). The medium of reactions was always 1:1 (v/v) acetonitrile:nitrobenzene unless otherwise stated. Acetonitrile-nitrobenzene was chosen as the solvent because it was observed[15] (also Chapter 9) that acetonitrile did not react with the oxidant (PFC). The reaction mixtures were homogeneous for the total period of kinetic investigation.

For each kinetic run, fresh solutions of the oxidant, and the substrate were separately prepared in a 25 ml scale. The solutions were heated in the thermostatic bath, maintained at a particular temperature, for ca 30 min. An amount of 20 ml of each of the two solutions were mixed together for a particular run. The progress of the oxidation reaction was followed by withdrawing 5 ml portions of the reaction solution at an interval of 5 min.

Computations of the rate constants were made from the plot of log[oxidant] against time ([oxidant] = [x_t - x_∞], where x_t represents the amount of unreacted oxidant at time t, and x_∞ represents the amount of unreacted oxidant after a long time (24 h, taken to be an infinite time). For some cases, the results were checked by least-square calculations and found to be extremely satisfactory. The values reported are the mean of at least duplicate runs are reproducible to within ± 4%.

Dependence of reaction rate an solvent composition were studied with varying compositions of the solvent media. Dielectric constants for the varying proportions of acetonitrile-nitrobenzene mixtures were estimated from the dielectric constants of the pure solvents[18] and are set out in Table 3. A constant ionic strength could not be maintained owing to the nonaqueous nature of the reaction medium. It may, however, be mentioned that the variation in ionic strength did not bring about any change[19] in the oxidation of benzyl alcohol by chromic(VI) oxide in an aqueous acidic medium.

The uncatalysed reactions were studied with varying temperatures of 303, 308, 313 and 318 K (error limit ± 0.1 K) respectively for all the three alcohols (Table 4). The frequency factors were determined on the basis of the results

obtained thereof. The activation parameters were evaluated by the standard procedure[20] within allowable average error limit (at 303 K) (Table 5).

Calculations[20-22]

(i) Rate Constants. The first order rate constants for reactions were found out by making use of the first-order rate equation. For the sake of simplicity, the equation relating dependent variable x, and the decrease in concentration of reactant in time t has been used. Thus, for a first-order reaction

$$-\frac{dx}{dt} = k(a - x)^n$$

$$\text{or } \ln \frac{a}{(a - x)} = kt$$

$$\text{or } k = \frac{1}{t} \ln \frac{a}{(a - x)} \quad \ldots \quad \ldots \quad (1)$$

/ where, a represents initial concentration of oxidant, x represents the amount of unreacted oxidant, and (a - x) represents the fall in oxidant concentration in time t /

In the logarithmic form the equation (1) becomes,

$$k = \frac{2.303}{t} \log \frac{a}{(a - x)} \quad \ldots \quad \ldots \quad (2)$$

If it is assumed that x represents the amount of unreacted oxidant after the infinite time (24 h), and x_o and x_t

represent those before starting and after an interval of time t respectively, the equation (2) can then be transformed to

$$k = \frac{2.303}{t} \log \frac{(x_o - x_\infty)}{(x_t - x_\infty)}$$

since, $a \propto x_o - x_\infty$ and $x \propto x_o - x_t$,

$$a - x \propto x_t - x_\infty$$

Hence,

$$t = \frac{2.303}{k} \log (x_o - x_\infty) - \frac{2.303}{k} \log (x_t - x_\infty)$$

Thus, a plot of $\log (x_t - x_\infty)$ versus t gives a straight line, the slope of which corresponds to 2.303/k. Accordingly, from the slope, the value of k (the rate constant) is found out.

(ii) Thermodynamic Activation Parameters

(a) Activation Energy (E_a). Since a plot of log k against 1/T was nearly linear with a negative slope, the Arrhenius equation was applied to the present cases. Thus,

$$k = A. e^{-E_a/RT}$$ (where A stands for frequency factor or Pre-Exponential factor)

$$\text{or} \quad \ln k = \ln A - E_a/RT$$

$$\text{or} \quad \ln k = -E_a/RT + \ln A$$

$$\text{or} \quad \log k = -\frac{E_a}{R \times 2.303} \times \frac{1}{T} + \ln A$$

If log k is plotted against $10^3/T$, then,

$$\text{slope} = -\frac{E_a \times 10^{-3}}{R \times 2.303} \quad \text{(a negative slope)}$$

Therefore,

$$E_a = \frac{\text{slope} \times 2.303 \times R}{10^{-3}}$$

$$= \frac{\text{slope} \times 2.303 \times 8.3143}{0.001} \text{ J/mole}$$

$$(\because R = 8.3143 \text{ J/mole})$$

or,

$$E_a = \text{slope} \times 2.303 \times 8.3143 \text{ kJ/mole}$$

(b) Frequency Factor (A). The frequency factor was calculated by putting the value of activation energy (E_a) in the following equation :

$$\log k = \log A - \frac{E_a}{2.303\ RT}$$

$$\text{or} \quad \log A = (\log k + E_a/2.303\ RT)\ \text{sec}^{-1}$$

(c) Enthalpy of Activation ($\Delta H^{\#}$). This was obtained from the thermodynamic equation:

$$\Delta H^{\#} = E_a - RT$$

(d) Entropy of Activation ($\Delta S^{\#}$). The entropy of activation was obtained by using the thermodynamic equation for transition state.

$$k = \frac{KT}{h} e^{-\Delta H^{\#}/RT} \cdot e^{\Delta S^{\#}/R}$$

$$\text{or } \log k = \left(\log \frac{KT}{h} - \frac{\Delta H^{\#}}{RT} + \frac{\Delta S^{\#}}{R}\right)$$

By putting the values of k, K, T, h and $\Delta H^{\#}$ in the above equation, the value of entropy of activation was calculated.

(c) Free Energy of Activation ($\Delta G^{\#}$). The free energy of activation was calculated using the following simple thermodynamic equation:

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$

Product Analysis. The oxidation products benzaldehyde, acetaldehyde and cyclohexanone were characterized by spectral analyses (IR and UV), and estimated quantitatively as their 2,4-dinitrophenylhydrazones.

The melting points of 2,4-dinitrophenylhydrazone derivatives of benzaldehyde, acetaldehyde and cyclohexanone were 236 °C (lit.[23] 237), 146 °C (lit.[23] 144-146 °C) and 160 °C (lit.[23] 160 °C) respectively.

RESULTS AND DISCUSSION

The oxidation of benzyl alcohol, ethanol and cyclohexanol by PFC in 1:1 (v/v) acetonitrile-nitrobenzene leads to the formation of benzaldehyde, acetaldehyde and cyclohexanone respectively in very high yields (>90%), showing no indication of further oxidation of the carbonyls conforming to the earlier synthetic studies involving pyridinium fluorochromate(VI), $C_5H_5NHCrO_3F$, (PFC) (Chapter 9).

The stoichiometry of various oxidations studied herein were estimated by the reaction of the respective alcohol with an excess of oxidant (PFC) followed by estimating the unreacted chromium(VI). In some runs, however, an excess of alcohols were used followed by the estimation of the carbonyl product. The stoichiometry of the reactions can be represented as follows:

$$3\ RCH_2OH + 2\ Cr^{6+} \longrightarrow 3\ RCHO + 6\ H^+ + 2\ Cr^{3+}$$

The stoichiometry of the reactions with cyclohexanol was determined in an analogous manner,

$$3\ C_6H_{11}OH + 2\ Cr^{6+} \longrightarrow 3\ C_5H_{10}CO + 6\ H^+ + 2\ Cr^{3+}$$

Like the analogous pyridinium chlorochromate(VI), $C_5H_5NHCrO_3Cl$ (PCC)[10-12] reactions, all the three alcohols

studied in the present case were found to be first order with respect to time, because the first order rates were constant at different times. The reactions were also observed to be clearly first order with respect to the oxidant (PFC), as the rate constants were found to be practically unaltered for most of the reaction times (Table 1) with varying concentration of oxidant. The most prominent difference in the oxidations involving PCC[10-12] and those involving PFC (present studies) is that the order of the reactions of the three alcohols with respect to the substrate concentrations was found to be practically constant enabling us to infer that the rates are almost independent of substrate concentrations. However, a small but steady increase in the rate constant values for all the three alcohols with increasing concentrations of the substrate has been observed (Table 2) and a plot of log k_{obs} against log [substrate] shows that the rates increase in very small fractions with the sequential increase in substrate concentration. This most probably implies that complex formation between the substrate and oxidant is taking place in present cases.

Our attempts to study the acid-catalyzed oxidations of the three alcohols were unsuccessful. Attempted acid-catalysed reactions involving p-Toluenesulfonic acid or benzoic acid, and varying proportions of solvent compositions were observed to be too fast to measure the rate.

Table 1. Oxidant Dependence of the Reaction Rate

[Oxidant]	$k_1/10^{-4}$ s^{-1}		
10^{-3} mol dm^{-3}	[Ethanol]	[Benzyl Alcohol]	[Cyclo-Hexanol]
1	6.765 ...	8.413 ...	9.233
		$(0.075)^{10}$	
2	6.77 ...	7.95 ...	9.5
	$(0.10)^{11}$	$(0.075)^{10}$ ...	
3	6.62 ...	8.41 ...	9.34
		$(0.072)^{10}$	
4	6.56 ...	8.27 ...	9.59
	$(0.973)^{11}$	$(0.077)^{10}$ ..	
5	6.64 ...	8.21 ...	9.60
		$(0.076)^{10}$	

PCC Oxidation data are in parentheses.

T = 303 K ; [Ethanol] = 0.1 mol dm^{-3}

[Benzyl alcohol] = 0.01 mol dm^{-3}

[Cyclohexanol] = 0.01 mol dm^{-3}

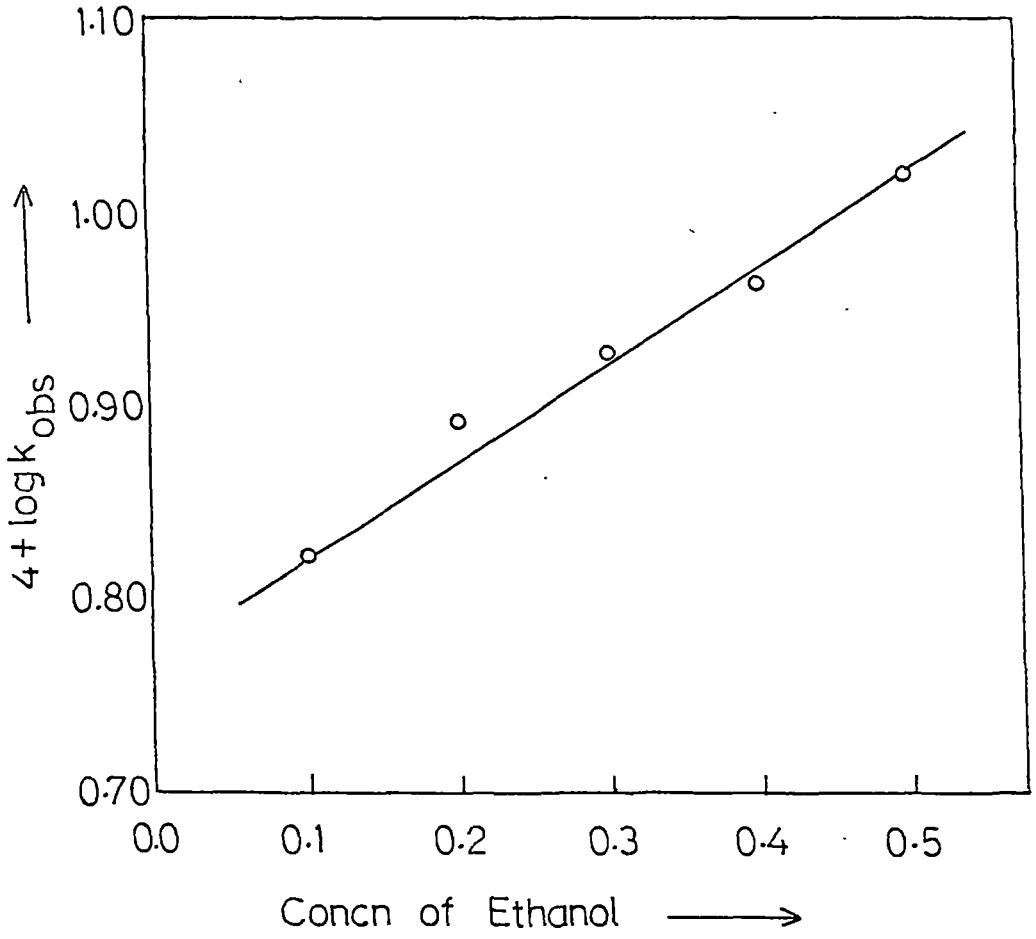
Table 2. Substrate Dependence of the Reaction Rate

Ethanol		Benzyl Alcohol		Cyclohexanol	
Concn. $moldm^{-3}$	$k_1/10^{-4}s^{-1}$	Concn. $moldm^{-3}$	$k_1/10^{-4}s^{-1}$	Concn. $moldm^{-3}$	$k_1/10^{-4}s^{-1}$
0.1	6.765 (0.10)[13]	0.01	8.413 (0.075)[a10]	0.01	9.233
0.2	7.87 (0.207)[13]	0.02	9.66 (0.152[a])[10]	0.02	13.89
0.3	8.55	0.03	10.1	0.03	15.79
0.4	9.16 (0.41)[13]	0.04	10.52 (0.306[a])[10]	0.04	17.78
0.5	10.6	0.05	11.54		

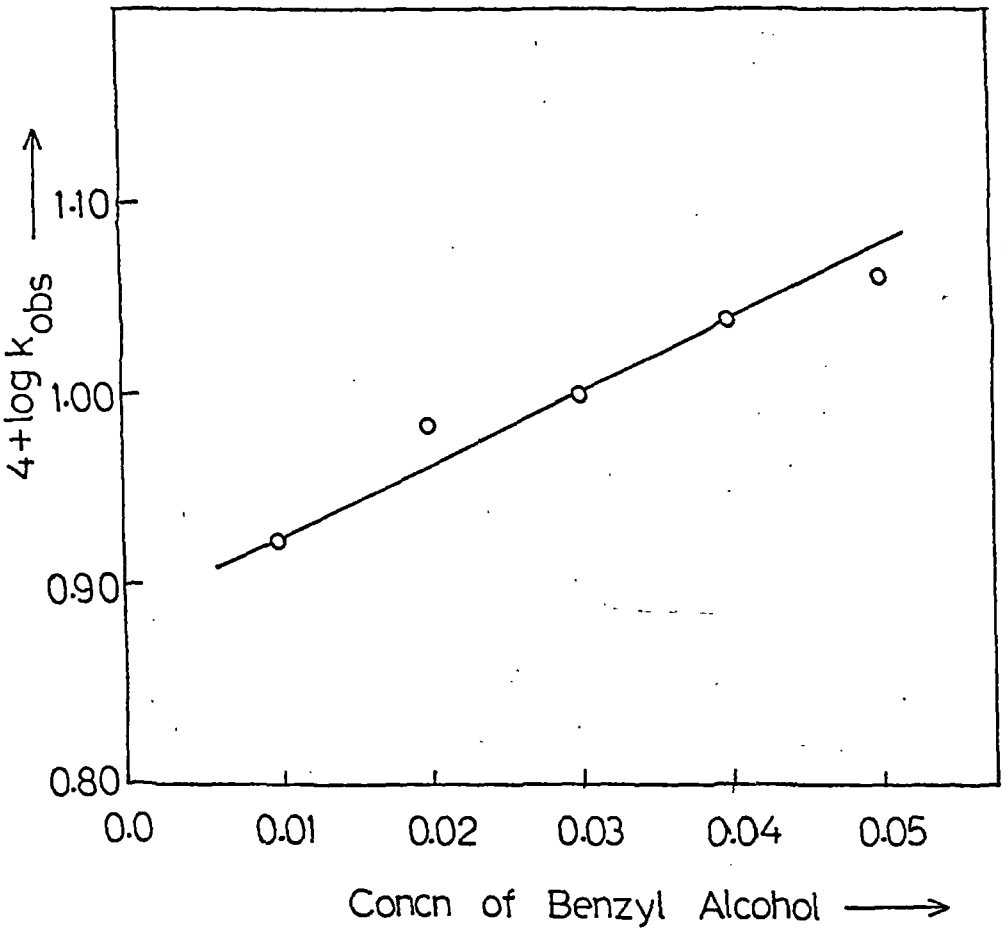
PCC Oxidation data are in parentheses;

a, values at 298 K

$[PFC] = 0.001$ mol dm^{-3}; T = 303 K



Plot of log k_{obs} vs. [Ethanol]



Plot of log k_{obs} vs. [Benzyl Alcohol]

The results of uncatalyzed reactions with varying composition of the solvent components (Table 3) shows that the reaction rate decreases with increase in dielectric constant (though small) of the medium suggesting that the more polar solvents may require larger reaction times for the oxidation reactions. A plot of log k_1 against the inverse of dielectric constants of the media is a straight line with positive slope and implies the occurrence of an interaction between a dipole and a positive ion,[24] and also indicates the probable involvement of a protonated Cr^{6+} species, in the presence of an acid, in the rate determining step. However, since the range of dielectric constants varies between 35.6 and 36.7 showing a large increase in the rate, the observed change could as well be solvent specific rather than owing to the effect of change in dielectric constant.

The free energies of activation of the three reactions were found to lie between 91.82 and 92.65 kJ/mole (Table 5). The near constancy of the values of free energies of activation thus suggest that a similar mechanism is operative in each of the three oxidations. Free energies of the acid-catalysed reactions appear to be lower, as there has been a pronounced increase in the rate of catalyzed reactions. This, therefore, suggests that a protonated Cr^{6+} species may be involved in the rate determining step in the presence of an acid. This is in

Table 3. Dependence of Reaction Rate on Solvent Composition

Nitro-benzene (%)	Aceto-nitrile (%)	Dielectric Constant	[Ethanol] 0.2 mol dm^{-3} $k_1/10^{-5}$ s^{-1}	[Benzyl Alcohol] 0.02 mol dm^{-3} $k_1/10^{-4}$ s^{-1}	[Cyclo-Hexanol] 0.02 mol dm^{-3} $k_1/10^{-4}$ s^{-1}
30	70	36.7	1.01	1.05	3.08
40	60	36.4	1.997	1.77	5.31
50	50	36.16	4.05	3.15	7.2
60	40	35.9	7.97	4.3	10.27
70	30	35.6	15.82	5.51	12.95

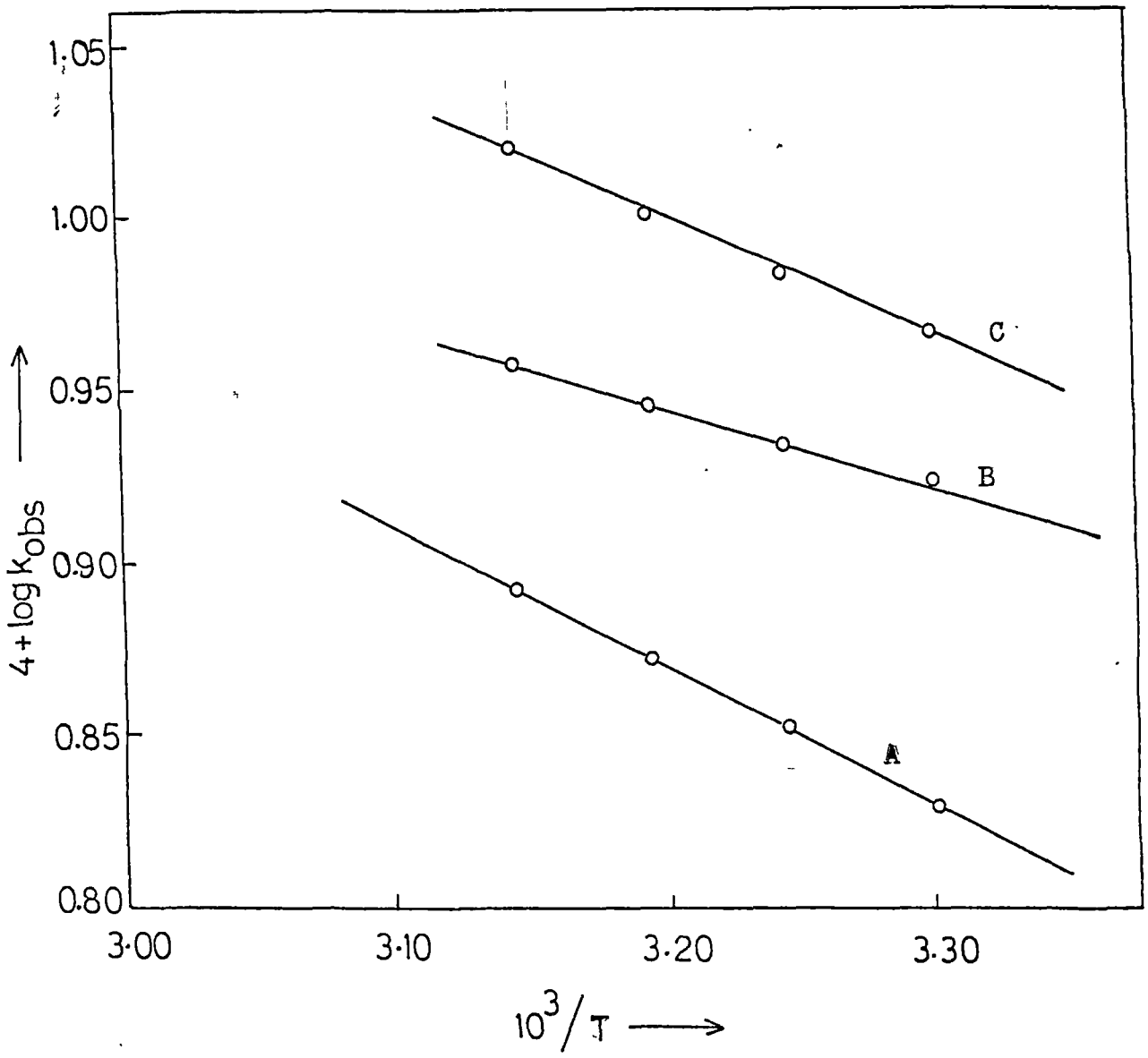
[Oxidant] = 0.002 mol dm^{-3}; T = 303 K

Table 4. Rate Constants for the Uncatalysed Oxidation of Alcohols by Pyridinium Fluorochromate(VI)

Substrate	Concentration of substrate/ (mol dm^{-3})	$k/10^{-4}$ l $mol^{-1}s^{-1}$			
		303 K	308 K	313 K	318 K
Ethanol	0.1	6.765 (1.0)[11]	7.112 (1.4)[11]	7.447 (1.93)[11]	7.798 (2.63)[11]
Benzyl Alcohol	0.01	8.413 (7.5)[10]	8.593 (11.2)[10]	8.811 (15.5)[10]	9.057 (21.6)[11]
Cyclo-hexanol	0.01	9.233 -	9.619 (88.3)[12]	10.0 (133.3)[12]	10.447 (208.3)[12]

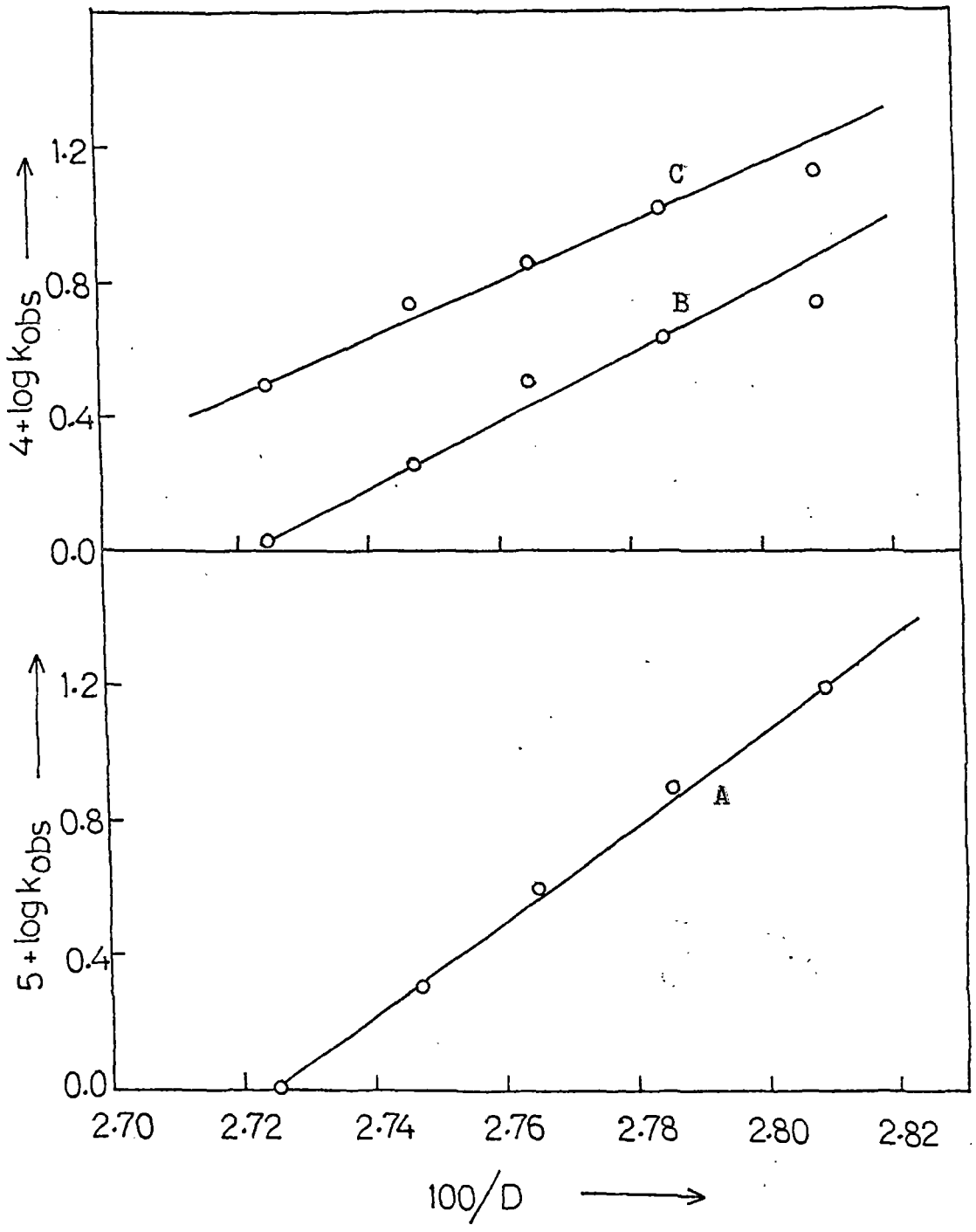
PCC Oxidation data are in parentheses.

$[PFC] = 0.001$ mol dm^{-3}



Plot of log k_{obs} vs. Inverse of Temperature

A = Ethanol; B = Benzyl Alcohol; C = Cyclohexanol



Plot of log k_{obs} vs. Inverse of Dielectric constant

A = Ethanol; B = Benzyl Alcohol; C = Cyclohexanol

Table 5. Activation Parameters for the Oxidation of Alcohols by Pyridinium Fluorochromate(VI)

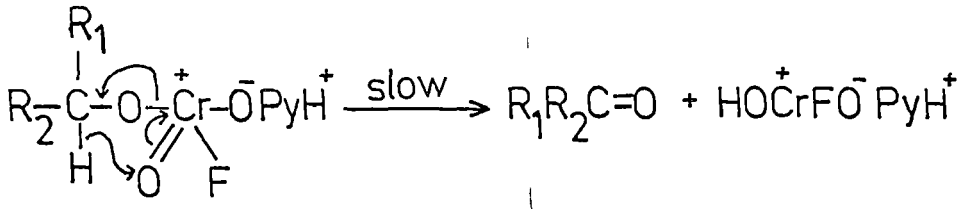
Substrate	$\Delta H^{\#}$/kJ mol^{-1}	$-\Delta S^{\#}$/$Jmol^{-1}K^{-1}$	$\Delta F^{\#}$/$kJmol^{-1}$
Ethanol	7.657 (51.8)[11]	280.51 (153)[11]	92.65 (98.2)[11]
Benzyl Alcohol	3.89 (54.7)[10]	291.33 (125)[10]	92.06 (92.0)[10]
Cyclo-hexanol	6.127 (93.0)[12]	282.98 (- 18)[12]	91.82 (87.4)[12]

PCC Oxidation data in parentheses.

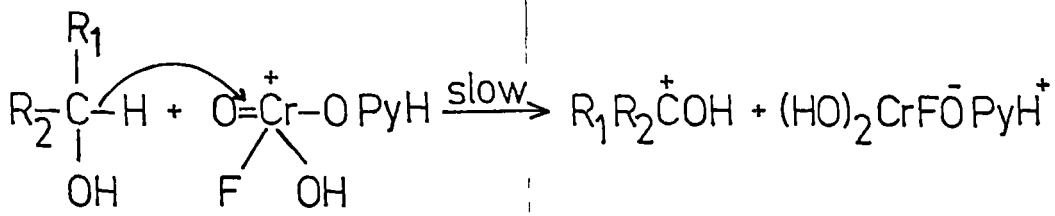
accord with the involvement of such species well established in chromium(VI) oxide oxidations.[25]

The entropy values obtained in the present studies were found to occur between - 280.51 and - 291.33 J mol^{-1} K^{-1}. The large negative entropy values obtained for the present systems, suggest that the solvent molecules are strongly oriented or 'frozen' around the ions thereby resulting in the loss of entropy,[26] the effect being larger in the non-polar solvents. This conforms to the contention that the decrease of polarity of the medium results in increase of the entropy value and the number of unbound molecules in the solution increases.[27] This also accounts for the lowering of rate coefficient values with increasing polarity of the medium. Comparatively greater reactivity of pyridinium fluorochromate, $C_5H_5NHCrO_3F$ (PFC) over that of the corresponding chlorochromate(VI), $C_5H_5NHCrO_3Cl$ (PCC), as shown[15] in the previous Chapter, can now be understood from the relatively higher negative entropy values of the reactions. It is believed that the bonding of F with chromium in PFC facilitates larger charge distribution in the transition state in the cases of PFC oxidation and correlates well with the observed entropy values.

In view of the above results it appears that a hydride transfer mechanism is involved in the rate determining step of the pyridinium fluorochromate(VI), $C_5H_5NHCrO_3F$ (PFC) oxidations.



SCHEME 1



$$R_1R_2\overset{+}{C}OH \xrightarrow{fast} R_1R_2CO + H^+$$

SCHEME 2

$R_1 = H$ & $R_2 = CH_3$ & C_6H_5 for ethanol & benzyl alcohol respectively

&

$R_1R_2 = -(CH_2)_5-$ for cyclohexanol.

It is possible that the hydride transfer may take place either through the prior formation of chromate (Scheme 1), or directly (Scheme 2). The present data also suggest, like the similar oxidations involving chromic acid[25], a chromate ester formation in the rate-determining step (Scheme 1) although the chances of Scheme 2 can not be totally ruled out. It is also expected that the chromate intermediate will be better stabilised in the less polar medium and will enhance the oxidation rate, thus conforming to the observations made by us.

REFERENCES

[1] J. K. Beattie and G. P. Haight, Jr., Progr. Inorg. Chem., 94, 17, 1972.

[2] R. G. Linck, 'Rate and Mechanisms of Oxidation-Reduction Reaction of Metal Ion Complexes' in MTP International Review of Sciences, Inorganic Chemistry, Series 1, Vol. 9, (ed. M. L. Tobe), 1972, p. 346.

[3] F. H. Westheimer, Chem. Rev., 419, 45, 1949.

[4] K. B. Wiberg, 'Oxidation in Organic Chemistry', Part A, Academic Press, New York, 1965, p. 66.

[5] J. H. Espenson, Accounts Chem. Res., 347, 3, 1970.

[6] J. Y. Tong and E. L. King, J. Am. Chem. Soc., 3805, 82, 1960.

[7] J. H. Espenson and E. L. King, J. Am. Chem. Soc., 3328, 85, 1963.

[8] W. Watanabe and F. H. Westheimer, J. Chem. Phys., 61, 17, 1949.

[9] G. P. Haight, Jr., T. J. Huang and B. Z. Shakhashiri, J. Inorg. Nucl. Chem., 2169, 33, 1971.

[10] K. K. Banerjee, J. Chem. Soc. Perkin II, 639, 1978.

[11] K. K. Banerjee, Bull. Chem. Soc. Jpn., 2732, 51, 1978.

[12] G. P. Panigrahi and D. D. Mahapatra, Ind. J. Chem., 579, 19A, 1980.

[13] K. S. Venkataraman, S. Sundaram and N. Venkatasubramanian, Ind. J. Chem., 84, 16B, 1978.

[14] K. K. Banerjee, J. Chem. Res. (M), 2561, 1978.

[15] M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, N. Roy and D. T. Khathing, Synthesis, 588, 1982.

[16] D. D. Perrin, W. L. Armarego and D. R. Perrin, 'Purification of Organic Compounds', Pergamon Press, Oxford, 1966.

[17] A. I. Vogel, 'A Text Book of Practical Organic Chemistry', 3rd. ed., Longman Green & Co., London, 1957.

[18] C. N. R. Rao, 'A Handbook of Chemistry and Physics' Affiliated East-West Press, New Delhi, 1970, p. 169.

[19] G. V. Bakore, K. K. Banerjee and R. Shanker, Z. Phys. Chem., (Frankfurt), 129, 45, 1965.

[20] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism' Wiley-Eastern, New Delhi, 1970.

[21] G. M. Barrow, 'Physical Chemistry', 3rd ed., Internl. Student Ed., McGraw Hill, Tokyo, 1973.

[22]J. L. Latham, 'Elementary Reaction Kinetics', 2nd ed., Butterworth, London, 1969.

[23]Dictionary of Organic Compounds, 4th ed., Vol. I and II, Eyre and Spottiswoode Pub., London, 1965.

[24]E. S. Amiss, 'Solvent Effects on Reaction Rates and Mechanism', Academic Press, New York, 1967, p. 42.

[25]Ref. 4, p. 99.

[26]F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Reaction : A Study of Metal Complexes in Solution' 2nd ed., Wiley-Eastern, New Delhi, 1973, p. 129.

[27]F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', 3rd ed., Wiley-Eastern, New Delhi, 1979, p.169.

LIST OF PUBLICATIONS

Chapter 1

1. "The Direct Synthesis of Alkali-metal Pentafluoromanganates(III)."

   M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta and D. T. Khathing,

   J. Chem. Soc. Dalton Trans., 2587, 1981.

2. "A Convenient Method for the Synthesis of Alkali Metal Pentafluoromanganates(III)."

   M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, A. Kathipri and D. T. Khathing,

   Synth. React. Inorg. Met.-Org. Chem., 485, 12, 1982.

3. "Direct Synthesis of Pentafluoromanganates(III) of the Type, $A_2[MnF_5]$ (A = NH_4, Na or K)."

   M. N. Bhattacharjee and M. K. Chaudhuri,

   Ind. J. Chem, in press.

4. "Ammonium Pentafluoromanganate(III) and Potassium Pentafluoromanganate(III) Monohydrate."

   M. N. Bhattacharjee and M. K. Chaudhuri

   Inorg. Syntheses, Approved by the Review Committee.

Chapter 2

5. "Alkali-Metal Tetrafluoromanganate(III) Monohydrates" $AMnF_4.H_2O$ (A = Rb or Cs)."

   M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta and A. Kathipri, Polyhedron, in press.

Chapter 3

6. "Alkali-Metal Trifluoromonosulphatomanganates(III), $A_2[MnF_3(SO_4)]$ (A = NH_4, Li, Na or K)"
M. N. Bhattacharjee and M. K. Chaudhuri,
Polyhedron, in press.

Chapter 5

7. "Direct Synthesis of Tris(acetylacetonato)manganese(III)".
M. N. Bhattacharjee, M. K. Chaudhuri and D. T. Khathing,
J. Chem. Soc. Dalton Trans., 669, 1982.

Chapter 6

8. "Synthesis of Alkali Metal Trifluoroaquomanganates(II)."
M. N. Bhattacharjee and M. K. Chaudhuri,
Ind. J. Chem., 977, 21A, 1982.

Chapter 9

9. "Pyridinium Fluorochromate : A New and Efficient Oxidant for Organic Substrates."
M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, N. Roy and D. T. Khathing, Synthesis, 588, 1982.

Chapter 10

10. "Kinetics and Mechanism of the Oxidation of Alcohols by Pyridinium Fluorochromate".
M. N. Bhattacharjee, M. K. Chaudhuri and H. S. Dasgupta,
Bull. Chem. Soc. Jpn., 0000, 57, 1984.

SYNTH. REACT. INORG. MET.-ORG. CHEM., 12(5), 485-492 (1982)

A CONVENIENT METHOD FOR THE SYNTHESIS OF ALKALI METAL PENTAFLUOROMANGANATES(III)

Manabendra N. Bhattacharjee, Mihir K. Chaudhuri*, Himadri S. Dasgupta and Athili Kathipri

Department of Chemistry, North-Eastern Hill University, Shillong 793 003, India

Darlando T. Khathing

Department of Physics, North-Eastern Hill University, Shillong 793 003, India

ABSTRACT

Reaction of MnO(OH) and a concentrated solution of AHF_2 ($A = NH_4^+$, Na^+, K^+ or Cs^+) in 40% hydrofluoric acid gives instantaneously rose-pink coloured alkali metal pentafluoromanganate(III), A_2MnF_5 ($A = NH_4^+$ or Na^+), and alkali metal pentafluoromanganate(III) monohydrate, $A_2MnF_5.H_2O$ ($A = K^+$ or Cs^+). Li_2MnF_5 has been synthesised by reacting lithium carbonate with a solution of MnO(OH) in 40% hydrofluoric acid followed by addition of a small amount of alcohol. Characterisation of the compounds and assignment of molecular structure were made from the elemental analyses, chemical determination of oxidation state of manganese in the compounds, magnetic susceptibility measurements and infra red spectral studies.

INTRODUCTION

Alkali pentafluoromanganates(III), a class of structurally important[1-4] compounds of Mn(III), have been known for some time. Although no simple and general method for their synthesis has been reported to date, the one[5] involving the reaction between a solution of MnF_3 in hydrofluoric acid and AF (A = alkali metal) appears to have been used in more than one instance[5,6]. This method uses MnF_3 as one of the starting materials which is difficult to synthesise[7-10] and is unstable under ordinary conditions. In view of this and the current interest in the syntheses and structural studies of fluoromanganates (III) [11-13] we felt it worthwhile to develope an easy general method for the synthesis of the title compounds, to study their composition and to examine their molecular structures by chemical analysis, determination of oxidation state of manganese, magnetic and infrared spectral studies.

In our previous reports[14,15] we have emphasised the importance of alkali metal bifluorides as potential fluorinating agents. We have now extended such studies to the synthesis of the title compounds.

RESULTS AND DISCUSSION

General synthesis — The method (vide Experimental section) involving the reaction among MnO(OH), HF and AHF_2 is a general one and can be applied to the synthesis of all but Li_2MnF_5 for which a slight modification is necessary owing to the extremely low solubility of LiF. The yields of alkali metal pentafluoromanganates(III), obtained by this method, are very high and the process can be scaled up. The overall reaction leading to the synthesis can be expressed as follows:

$$MnO(OH) + HF + 2AHF_2 \longrightarrow A_2MnF_5 + 2H_2O$$

Since an acidic solution prevents pentafluoromanganates(III) from being hydrolysed, the medium was maintained acidic by using a little excess hydrofluoric acid and AHF_2. Freshly prepared MnO(OH) instantaneously reacts with hydrofluoric acid forming MnF_3 which then reacts with alkali metal bifluorides to produce A_2MnF_5.

Characterisation and structural evaluation — All the compounds are rose-pink in colour and are obtained in microcrystalline form. They are insoluble in common organic solvents and decompose in water giving hydrated manganese oxide. However, they can be stored in sealed polythene bags.

The elemental analyses (Table I) suggest the ratio of A:Mn:F in each of the compounds is 2:1:5 with NH_4^+,

TABLE I

Analytical Data, Magnetic Moments and Estimated Oxidation States

Compounds	μ_{eff} at 302°K (BM)	Estimated oxidation state of manganese	Found % (Calc. %)		
			A or N	Mn	F
$(NH_4)_2MnF_5$	3.19	2.9	15.18 (15.06)	29.68 (29.53)	51.32 (51.06)
Li_2MnF_5	3.27	3.1	8.82 (8.47)	33.77 (33.54)	58.13 (57.99)
Na_2MnF_5	3.22	3.0	23.67 (23.48)	28.24 (28.04)	48.61 (48.48)
$K_2MnF_5.H_2O$	3.32	3.0	31.98 (31.77)	22.49 (22.32)	38.75 (38.59)
$Cs_2MnF_5.H_2O$	3.29	3.1	61.31 (61.28)	12.74 (12.67)	21.72 (21.90)

Li^+ and Na^+ salts of the type A_2MnF_5 whilst the K^+ and Cs^+ salts are monohydrates of the type $A_2MnF_5.H_2O$. Estimation of oxidation states of manganese in all these compounds by chemical methods suggests a +3 oxidation state of the metal, supporting the above formulations. This was of particular importance as the fluoromanganates(III), even at room temperature, might exhibit antiferromagnetic behaviour[2,16,17] leading to confusion with regard to the actual oxidation state of the metal.

The structure and composition of the ammonium salt has been the subject of some debate[1,18], although the species consisting of chains of tetragonally elongated octahedra linked through bridging fluoride ions is generally favoured. Based on the results of replicate chemical analyses and infra red spectral studies, the present work also confirms that the ammonium salt is $(NH_4)_2MnF_5$ and not $(NH_4)_2MnF_4(OH)$. Repeated chemical analyses always conform to the Mn:F ratio as 1:5 and the infra red spectrum of the compound neither showed any absorption in the δ_{M-O-H} region (1200-900 cm^{-1}) nor absorbed at $\sim$ 3600 cm^{-1} which is typical for ν_{O-H}[19]. The absorptions at 3040(s), 3157(m) and 1400(s) cm^{-1} have been assigned as ν_1, ν_3 and ν_4 modes, respectively, of NH_4^+ and correlate very well with those of the analogous ammonium pentachloromanganate(III)[20]. The bands at 614(m) and 563(s) cm^{-1} have been assigned to ν_3 and ν_4 vibrational modes[21] of Mn-F.

The infra red spectra of the whole series of compounds show that they are all identical structurally and stoichiometrically. The only difference lies in NH_4^+, Li^+ and Na^+ salts being anhydrous while the K^+ and Cs^+ salts are monohydrates. Typical of all spectra are the two absorptions at $\sim$ 615 and at $\sim$ 565 cm^{-1} which imply the presence of octahedral or distorted octahedral[21] MF_6^{n-} and have been assigned as ν_3 and ν_4 modes of Mn-F vibrations. Thus, it is evident that Mn^{3+} in MnF_5^{2-} displays the Jahn-Teller effect, assumes a distorted

octahedral structure with each octahedron being linked to its nearest neighbour through a bridging fluoride ion, and conforms to the crystal structure of $K_2MnF_5.H_2O$ reported by Edwards[4]. The K^+ and Cs^+ salts show two extra bands at $\sim$ 1640 and at $\sim$ 3460 cm^{-1} which have been assigned to the δ_{H-O-H} and ν_{O-H} vibrational modes of uncoordinated water, are in accord with the earlier observations[15,21] and also agree with the crystal structure[4] of $K_2MnF_5.H_2O$.

The effective magnetic moments of the compounds at 302°K lie between 3.19 and 3.32 BM. This observation can be very well correlated with the proposed structure mentioned above. The lowering of magnetic moment is not to be attributed to spin-pairing but to super exchange interaction between the contiguous Mn^{3+} ions through -Mn-F-Mn- chains. The agreement in the values of the magnetic moments of the NH_4^+, Li^+, Na^+, K^+ salts and the value of the hitherto unreported moment of $Cs_2MnF_5.H_2O$ lend credence to the contention that the compounds are isostructural.

EXPERIMENTAL

The chemicals used were all reagent grade. MnO(OH) was prepared by the literature method[22]. Alkali metal bifluorides have been synthesised by the method developed in this laboratory[14]. Infra red spectral measurements were made on a Perkin-Elmer model 125 spectrophotometer. Magnetic susceptibility measurements were made by the Gouy method using $Hg[Co(NCS)_4]$ as the calibrant.

The oxidation state of manganese in each of the compounds was determined chemically by the reduction of a known amount of the compound with aqueous acidic Fe(II) solution followed by estimation of the excess of unoxidised Fe(II) in the solution.

Synthesis — Since the methods of synthesis of A_2MnF_5 (A = NH_4^+ or Na^+) and $A_2MnF_5.H_2O$ (A = K^+ or Cs^+)

are very similar, only a representative method is given. A slightly different method had to be adopted for the synthesis of Li_2MnF_5, for which a separate method is described.

Alkali metal pentafluoromanganates(III), A_2MnF_5 ($A = NH_4^+$ or Na^+), and alkali metal pentafluoromanganates(III) monohydrate, $A_2MnF_5.H_2O$ ($A = K^+$ or Cs^+) — To a suspension of 1.0g (11.4 m mol) MnO(OH) in a minimum volume of water, 0.5ml of 40% hydrofluoric acid is added dropwise with constant stirring whereupon the MnO(OH) completely dissolves giving a dark brown solution (A). A concentrated solution of the respective bifluoride AHF_2 ($A = NH_4^+$, Na^+, K^+ or Cs^+) in a small amount of 40% hydrofluoric acid is added directly to the solution(A) with stirring whereby a rose-pink coloured, microcrystalline product appears immediately. The product, A_2MnF_5 or $A_2MnF_5.H_2O$, is separated by centrifugation, washed with heptane until it is free from acid, and finally dried in vacuo.

The details of amounts of reagents used and yields of various alkali pentafluoromanganates(III) are given in Table II.

TABLE II

Amounts of the Reagents Used and Yields of Alkali Metal Pentafluoromanganates(III)

Compound	Yield in g	Amount of MnO(OH) in g	Amount of 40% hydrofluoric acid in ml	Amount of AHF_2 (A=NH_4, Na, K or Cs) in g
$(NH_4)_2MnF_5$	1.9(89.2%)	1.0(11.4mmol)	2.0(40mmol)	1.5(26.3mmol)
Na_2MnF_5	1.8(80.0%)	1.0(11.4mmol)	2.5(50mmol)	1.6(25.8mmol)
$K_2MnF_5.H_2O$	2.5(88.7%)	1.0(11.4mmol)	2.2(44mmol)	2.1(26.9mmol)
$Cs_2MnF_5.H_2O$	2.2(88.4%)	0.5(5.7mmol)	1.2(24mmol)	2.3(13.4mmol)

Lithium pentafluoromanganate(III), Li_2MnF_5 — To a suspension of 1.0g (11.4 m mol) of MnO(OH) in a minimum volume of water, 6.0ml (120 m mol) of 40% hydrofluoric acid is added with constant stirring and a dark brown solution is obtained. To this solution 1.7g (23 m mol) of lithium carbonate is added in several portions with constant stirring. An amount of 2-2.5ml ethanol is added to the solution, all at a time with vigorous stirring, and a rose-pink coloured product is obtained. The product, Li_2MnF_5, is immediately separated by centrifugation, washed several times with heptane to make it free from acid, and finally dried in vacuo. The yield of Li_2MnF_5 is 1.2g (63.8%).

REFERENCES

1. R. Dingle, Inorg. Chem., 4, 1287 (1965).
2. S. Emori, M. Inoue, M. Kishita and M. Kubo, Inorg. Chem., 8, 1385 (1969).
3. D. R. Sears and H. L. Hoard, J. Chem. Phys., 50, 1066 (1969).
4. A. J. Edwards, J. Chem. Soc.(A), 2653 (1971).
5. E. Muller and P. Koppe, Z. anorg. Chem., 68, 160 (1910).
6. I. G. Ryss and B. S. Vitokhnovskoya, Zh. Neorg. Khim., 3, 1185 (1958).
7. H. J. Emeléus and G. L. Hurst, J. Chem. Soc., 396 (1964).
8. E. E. Aynsley, R. D. Peacock and P. L. Robinson, J. Chem. Soc., 1622 (1950).
9. A.G. Sharpe and A. A. Woolf, J. Chem. Soc., 798 (1951).
10. M. A. Hepnorth and K. H. Jack, Acta. Cryst., 10, 345 (1957)
11. P. Bukovec and V. Kaucic, J. Chem. Soc., 945 (1977).
12. W. Massa, Inorg. Nucl. Chem. Lett., 13, 253 (1977).
13. V. Kaucic and P. Bukovec, J. Chem. Soc., 1512 (1979).
14. M. K. Chaudhuri and P. K. Choudhury, Chem. Ind. (London), 88 (1979)

15. M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta and D. T. Khathing, J. Chem. Soc. Dalton, in press.
16. R. S. Nyholm and A. G. Sharpe, J. Chem. Soc., 3579 (1952).
17. M. K. Chaudhuri, J. C. Das and H. S. Dasgupta, J. Inorg. Nucl. Chem., 43, 85 (1981).
18. N. S. Hush and R. J. M. Hobbs, "Progress in Inorganic Chemistry" (edited by F.A. Cotton), Vol. 10, 1968, p. 259.
19. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd Edition, Wiley-Interscience, 1970, p. 168.
20. C. F. Bell and D. N. Waters, J. Inorg. Nucl. Chem., 39, 773 (1977).
21. R. D. Peacock and D. W. A. Sharp, J. Chem. Soc., 2762, (1959).
22. G. Brauer (Ed.), "Handbook of Preparative Inorganic Chemistry", Vol.2, Academic Press, London, 1965, p.1457.

Received: 16 November 1981
Accepted: 8 February 1982

Referee I: C. C. Patel
Referee II: J. W. Vaughn

The Direct Synthesis of Alkali-metal Pentafluoromanganates(III)

By **Manabendra N. Bhattacharjee, Mihir K. Chaudhuri,* and Himadri S. Dasgupta,** Department of Chemistry, North-Eastern Hill University, Shillong-793003, India
Darlando T. Khathing, Department of Physics, North-Eastern Hill University, Shillong–793003, India

The reduction of potassium permanganate with acetylacetone in the presence of an excess of alkali-metal difluoride AHF_2 (A = NH_4, Na, K, or Cs) readily gives pentafluoromanganates(III), $A_2[MnF_5]$ (A = NH_4 or Na) or $A_2[MnF_5]\cdot H_2O$ (A = K or Cs) in almost quantitative yield. Characterisation of the compounds was made from the results of i.r. spectral studies, chemical analyses, magnetic susceptibility measurements, and chemical determination of oxidation states of manganese in the various compounds.

ALTHOUGH alkali-metal pentafluoromanganates(III) have been known for some time, there has been no easy and simple synthetic method available to date. The reaction between MnF_3 in hydrofluoric acid and alkali-metal fluoride AF [1] has been generally used for the synthesis of alkali-metal pentafluoromanganates(III). The present paper reports a general synthesis of the title compounds that does not require MnF_3.

EXPERIMENTAL

Potassium permanganate and acetylacetone were reagent-grade products. The difluorides AHF_2 were synthesised by the method developed in this laboratory.[2] Infrared spectra were recorded on a Perkin-Elmer model 125 spectrophotometer. Magnetic susceptibility measurements were made by the Gouy method using $Hg[Co(CNS)_4]$ as calibrant. The oxidation state of manganese in each of the pentafluoromanganates(III) was determined chemically by the reduction of a known amount of the compounds with aqueous acidic iron(II) solution followed by estimation of the excess of unoxidised Fe^{II} in the solution.

Synthesis of Alkali-metal Pentafluoromanganates(III) $A_2[MnF_5]$ (A = NH_4 *or* Na) *and Pentafluoromanganate*(III) *Monohydrates* $A_2[MnF_5]\cdot H_2O$ (A = K *or* Cs).—Since the methods of syntheses of the pentafluoromanganates(III) are similar, only a representative method is given.

An excess of difluoride AHF_2 was intimately mixed with solid $K[MnO_4]$ by powdering together in an agate mortar. The finely mixed powder was dissolved in a minimum volume of water and filtered. The filtrate was collected in a Polythene beaker and an excess of acetylacetone was added with constant stirring. An exothermic reaction set in and readily gave a rose-pink coloured microcrystalline product in almost quantitative yield with the mother-liquor becoming colourless. The compound was separated by centrifugation and purified by washing with heptane and finally dried *in vacuo*. In the case of the sodium salt, the powdered mixture $K[MnO_4]$–$NaHF_2$ was dissolved in water by slightly warming over a boiling water bath in order to avoid using a large volume of water, otherwise necessary, owing to the lower solubility of $NaHF_2$. If properly planned, the whole process takes no more than 30—40 min. The specific amounts (g) of the reagents used and the yields of the compounds are given in the Table 1; however, the method can be scaled up to higher quantities as well.

Analytical data, room-temperature magnetic-moment values, structurally important i.r. bands, and chemically estimated oxidation states of manganese are given in Table 2.

TABLE 1

Amounts of reagents used and yields of alkali-metal pentafluoromanganates(III)

Compound	Yield/g (%)	Amount of $KMnO_4$/g (mmol)	Amount of AHF_2/g (mmol)	Amount of acetyl-acetone/g (mmol)
$[NH_4]_2[MnF_5]$	0.34 (97.1)	0.3 (1.9)	1.0 (17.5)	3.0 (30)
$Na_2[MnF_5]$	0.32 (86.5)	0.3 (1.9)	1.1 (17.7)	4.0 (40)
$K_2[MnF_5]\cdot H_2O$	0.44 (93.6)	0.3 (1.9)	1.0 (12.8)	3.0 (30)
$Cs_2[MnF_5]\cdot H_2O$	0.78 (95.1)	0.3 (1.9)	2.3 (13.4)	3.0 (30)

RESULTS AND DISCUSSION

Direct Synthesis.—The methods described lead to the synthesis of pentafluoromanganates(III) of alkali metals, sufficient in number to leave little doubt that reductions with acetylacetone could be developed for the synthesis of compounds of other transition metals. The yields are almost quantitative and gram quantities of pentafluoromanganates(III) can be synthesised directly from $K[MnO_4]$ in about 30—40 min with very simple apparatus and without the use of hydrogen fluoride or even hydrofluoric acid. The difluorides AHF_2 here act as fluorinating agents. In previous papers [2,3] we have emphasised the potential of alkali-metal difluorides as fluorinating agents. The strategy for the present synthesis was that the reduction of Mn^{VII} by a relatively mild reducing agent like acetylacetone in the presence of F^- (stabilising species for Mn^{3+}) should enable the synthesis of pentafluoromanganates(III). In fact it appears that the success of the method largely depends on the presence of both H^+ and stabilising F^- ligands in the solution phase arising from AHF_2.

Characterisation.—The pentafluoromanganates(III) are all rose-pink coloured crystalline products, unstable in water, and they attack glass in the presence of moist air.

The chemically estimated oxidation states of manganese lie between 2.9 and 3.1 (Table 2), lending strong credence to the contention that manganese in each of these compounds has an oxidation number of +3. It is interesting to note that the NH_4^+ and Na^+ salts are anhydrous, of the type $A_2[MnF_5]$, whilst the K^+ and

TABLE 2

Analytical data, magnetic moments, estimated oxidation states, and structurally significant i.r. bands of $A_2[MnF_5]$ (A = NH_4 or Na) and $A_2[MnF_5]\cdot H_2O$ (A = K or Cs)

Compound	$\mu_{eff.}$[a]/B.M.	Estimated ox. state of Mn	Analysis [b]/% A	Mn	F	I.r.(cm^{-1})	Assignments	
$[NH_4]_2[MnF_5]$	3.19	3.0	15.15 [c]	29.65	51.1	614m	ν(Mn–F)	ν_3
			(15.05) [c]	(29.55)	(51.05)	564s	ν(Mn–F)	ν_4
						3 040s	ν(N–H)	ν_1
						3 157m	ν(N–H)	ν_3
						1 400s	ν(N–H)	ν_4
$Na_2[MnF_5]$	3.21	2.9	23.5	28.25	48.45	615m	ν(Mn–F)	ν_3
			(23.5)	(28.05)	(48.5)	565s	ν(Mn–F)	ν_4
$K_2[MnF_5]\cdot H_2O$	3.30	3.0	31.8	22.4	38.7	616m	ν(Mn–F)	ν_3
			(31.75)	(22.3)	(38.6)	565s	ν(Mn–F)	ν_4
						3 460s	ν(O–H)	
						1 635m	δ(H–O–H)	
$Cs_2[MnF_5]\cdot H_2O$	3.20	3.1	61.3	12.7	21.85	614m	ν(Mn–F)	ν_3
			(61.3)	(12.65)	(21.9)	564s	ν(Mn–F)	ν_4
						3 458s	ν(O–H)	
						1 640m	δ(H–O–H)	

[a] Measured at 302 K. [b] Calculated values in parentheses. [c] Analysis for N.

Cs^+ salts are monohydrates, $A_2[MnF_5]\cdot H_2O$, even though their methods of synthesis are the same. The i.r. spectra of the series of four salts, now obtained through a unique method, resemble each other very closely. The occurrence of two vibrations at relatively low wavenumber in the i.r. spectra implies the presence of octahedral or distorted octahedral MF_6^{n-}, and in keeping with this there are two readily identifiable ν(Mn–F) bands at *ca.* 615 and *ca.* 565 cm^{-1} [*cf.* the analysis of ν(M–F) in MF_6^{n-} complexes].[4,5] This is in conformity with the crystal structure of $K_2[MnF_5]\cdot H_2O$ as reported by Edwards.[6] The K^+ and Cs^+ salts show two extra vibrational bands at *ca.* 1 640 and 3 460 cm^{-1}, typical for δ(H–O–H) and ν(O–H) owing to the presence of one molecule of unco-ordinated water in each compound. The absorptions at 3 157m, 3 040s, and 1 400s cm^{-1} in the spectrum of $[NH_4]_2[MnF_5]$ correlate very well with those observed recently for $[NH_4]_2[MnCl_5]$ [7] and have been assigned as ν_3, ν_1, and ν_4 of NH_4^+. The room-temperature magnetic moments of the NH_4^+, Na^+, and K^+ salts and the hitherto unreported magnetic moment of the Cs^+ salt have been found to occur between 3.19 and 3.30 B.M.* and agree very well with those reported previously.[8-10] Considerably lower moments presumably owe their origin to antiferromagnetic exchange interaction between contiguous manganese(II) ions through a –Mn–F–Mn– chain in keeping with the reported structure of $K_2[MnF_5]\cdot H_2O$.[6]

* Throughout this paper: 1 B.M. $\approx 0.927 \times 10^{-23}$ A m^2.

[1/231 *Received*, 12*th February*, 1981]

REFERENCES

[1] E. Muller and P. Koppe, *Z. Anorg. Chem.*, 1910, **68**, 160.
[2] M. K. Chaudhuri and P. K. Choudhury, *Chem. Ind.* (*London*), 1979, 88.
[3] M. K. Chaudhuri, H. S. Dasgupta, S. K. Ghosh, and D. T. Khathing, *Synth. React. Inorg. Metal-Org. Chem.*, in the press.
[4] R. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.*, 1959, 2762.
[5] M. K. Chaudhuri and N. Roy, *Synth. React. Inorg. Metal-Org. Chem.*, in the press.
[6] A. J. Edwards, *J. Chem. Soc. A*, 1971, 2653.
[7] C. F. Bell and D. N. Waters, *J. Inorg. Nucl. Chem.*, 1977, **39**, 773.
[8] S. Emori, M. Inoue, M. Kishita, and M. Kubo, *Inorg. Chem.*, 1969, **8**, 1385.
[9] R. S. Nyholm and A. G. Sharpe, *J. Chem. Soc.*, 1952, 3579.
[10] M. K. Chaudhuri, J. C. Das, and H. S. Dasgupta, *J. Inorg. Nucl. Chem.*, 1981, **43**, 85.

Poly 508/902

Polyhedron Vol No pp 1984
Printed in Great Britain

0277-5387/84 $3.00 + .00

NOTE

ALKALI-METAL TRIFLUOROMONOSULPHATOMANGANATES (III) $A_2[MnF_3(SO_4)]$ (A = NH_4, Li, Na or K)

M. N. BHATTACHARJEE and M. K. CHAUDHURI*
Department of Chemistry, North-Eastern Hill University, Shillong 793 003, India

(*Received* 19 *May* 1983; *accepted* 10 *October* 1983)

Abstract—Pink-brown crystalline alkali-metal trifluoromonosulphatomanganates(III), $A_2[MnF_3(SO_4)]$ (A = NH_4, Li, Na or K), have been synthesised in high yields by reacting $KMnO_4$ or MnO(OH) with 40% HF and A_2SO_4 or by the reaction of MnO(OH) with 40% HF and $A_2S_2O_8$ (A = NH_4 or K). The chemically estimated oxidation state of manganese occurs between 2.9 and 3.0 and the room temperature magnetic moments lie in the range 4.0–4.2 BM. $(NH_4)_2[MnF_3(SO_4)]$ on being pyrolysed at 340°C yields $MnSO_4$.

Although the tripositive oxidation state is quite common for many first-row transition metals, manganese presents a different story probably because of its strong oxidising power and photolytic instability.[1] However, the known compounds of manganese(III) have received widespread attention primarily because of their interesting structural,[2–10] photochemical[1] and magnetic properties.[10,11] Our interest in this area involves synthesis, characterization and structural assessment of compounds of manganese(III). In two previous reports[12,13] we presented the direct synthesis and structural assessment of alkali-metal pentafluoromanganates(III). Their limitation is that all Mn-ligand interactions are only between Mn and F. This paper reports the synthesis, characterization and structural assessment of the mixed fluorosulphato compounds of manganese(III) and presents a set of internally consistent data concerning the effect of sulphate ligand on the magnetic properties of fluoromanganates(III).

EXPERIMENTAL

Reagent grade chemicals were used. MnO(OH) was prepared by the literature method.[14] IR spectra were recorded on a Perkin–Elmer model 125 spectrophotometer. Reflectance spectra were recorded against MgO using a Carl Zeiss Jena VSU 2–P instrument. Magnetic susceptibility measurements were made by the Gouy method. $Hg[Co(NCS)_4]$ was the calibrant.

Synthesis of alkali-metal trifluoromonosulphatomanganates(III), $A_2[MnF_3(SO_4)]$(A = NH_4, Li, Na or K)

Method I. Reaction of $KMnO_4$ with A_2SO_4 (A = NH_4, Li, Na or K), 40% HF and formaldehyde—an intimately mixed powder of $KMnO_4$ and A_2SO_4 (mole ratio 1:1) was dissolved in a minimum amount of water by gentle warming, followed by the addition of 40% hydrofluoric acid maintaining the molar ratio between $KMnO_4$ and HF at 1:4. The resultant solution was then cooled to room temperature and 38% formaldehyde solution was added dropwise with stirring until a deep-brown solution (A) was obtained. The solution (A) was concentrated, over a steam-bath, to nearly one-third of its original volume, and then allowed to cool in a freezer for 2–3 hr to obtain crystallised pink–brown $A_2[MnF_3(SO_4)]$. The compound was separated by filtration, washed with heptane and finally dried *in vacuo*. While in the case of the sodium salt the solution (A) was concentrated by about 50%, in the case of the lithium salt it was not concentrated at all, instead a small amount of alcohol was added to initiate precipitation.

Method II. Reaction of MnO(OH) with A_2SO_4 (A = NH_4, Li, Na or K) and 40% HF—freshly prepared MnO(OH) was dissolved in 40% HF and a concentrated solution of A_2SO_4 was added to it (mole ratio of MnO(OH):HF:A_2SO_4 at 1:4:1) under stirring. The mixture was heated over a steam-bath for *ca* 25 min. The dark brown solution thus obtained was worked up in a manner analogous to that described under Method I to obtain pink-brown $A_2[MnF_3(SO_4)]$ (A = NH_4, Li, Na or K).

*Author to whom correspondence should be addressed

Method III. Reaction of MnO(OH) with $A_2S_2O_8$ (A = NH_4 or K) and 40% HF—This reaction was done in a similar manner as described under Method II maintaining the molar ratio of MnO(OH):HF:$A_2S_2O_8$ as 1:4:1.

The yields of NH_4^+, Li^+ and K^+ salts of trifluoromonosulphatomanganate(III), $[MnF_3(SO_4)]^{2-}$, lie between 80 and 90%, while that of Na^+ salt is around 60%.

Elemental analysis and chemical determination of oxidation state of manganase—Manganese was determined by complexometric titration with EDTA using Erio T as the indicator,[15(a)] fluoride was estimated volumetrically,[15(b)] and sulphate gravimetrically as barium sulphate.[15(c)]

The oxidation state of manganese was determined chemically by the reduction of a known amount of the compound with aqueous acidic iron(II) solution followed by the estimation of unoxidized Fe^{2+} in the solution.

Analytical data, estimated oxidation states of manganese, magnetic moment values and ir bands are summarized in Table 1, while reflectance spectral band positions and their assignments are set out in Table 2.

Pyrolysis of $(NH_4)_2[MnF_3(SO_4)]$—An amount of 0.5 g of $(NH_4)_2[MnF_3(SO_4)]$ was heated at 340 ± 5°C until a constant weight was reached. The white pyrolysis product was found to be $MnSO_4$. Yield 0.31 g (weight loss 37.9%). (Found: Mn, 36.4; SO_4, 63.7. Calc. for $MnSO_4$: Mn, 36.38; SO_4, 63.62%. Estimated oxidation state of Mn, 2.1).

RESULTS AND DISCUSSION

It was reported recently that alkali-metal pentafluoromanganates(III) could by synthesized either by the reduction of $KMnO_4$ with acetylacetone[12] in the presence of alkali-metal bifluorides, AHF_2, through the oxidation of acetylacetone[16] to α, α, β, β-tetra-acetylethane, or by the reaction of MnO(OH), 40% HF and AHF_2.[13] The reaction of $KMnO_4$ with 40% HF and alkali-metal sulphates, A_2SO_4, in the presence of formaldehyde, or the reaction of MnO(OH), 40% HF and A_2SO_4 has now led to the synthesis of trifluoromonosulphatomanganates(III) of alkali-metals in very high yields. The role of formaldehyde was to reduce Mn(VII). It is evident from the results that, under the conditions de-

Table 1. Analytical data, magnetic moments, estimated oxidation states, and structurally significant IR bands of $A_2[MnF_3(SO_4)]$ (A = NH_4, Li, Na or K)

Compound	μ in B.M. (288 K)	Estimated oxidation state of Mn	Analysis[a] (%) A	Mn	F	SO_4	$\tilde{\nu}$/cm^{-1}	Assignments
$(NH_4)_2[MnF_3(SO_4)]$	4.1	3.1	11.4[b] (11.48)	22.6 (22.51)	23.2 (23.35)	39.4 (39.35)	1225(s), 1145(s), 1025(s)	$\tilde{\nu}_3$ SO
							970(s)	$\tilde{\nu}_1$ SO
							680(s), 635(s), 605(s)	δ SO
							525(s)	$\tilde{\nu}$(Mn-F)
							3158(m)	$\tilde{\nu}_3$ (N-H
							3040(s)	$\tilde{\nu}_1$ (N-H
							1400(s)	$\tilde{\nu}_4$ (N-H
$K_2[MnF_3(SO_4)]$	4.2	3.0		24.8 (24.76)	25.4 (25.69)	43.4 (43.29)	1230(s), 1145(s), 1030(s)	$\tilde{\nu}_3$ SO
							975(s)	$\tilde{\nu}_1$ SO
							685(s), 630(s), 608(s)	δ SO
							500(s)	$\tilde{\nu}$(Mn-F)
$Na_2[MnF_3(SO_4)]$	4.1	2.9	18.2 (18.1)	21.8 (21.63)	22.6 (22.44)	37.6 (37.82)	1230(s), 1140(s), 1030(s)	$\tilde{\nu}_3$ SO
							975(s)	$\tilde{\nu}_1$ SO
							680(s), 630(s), 605(s)	δ SO
							530(s)	$\tilde{\nu}$(Mn-F)
$Li_2[MnF_3(SO_4)]$	4.0	3.1	27.5 (27.32)	19.5 (19.2)	20.1 (19.92)	33.6 (33.56)	1230(s), 1145(s), 1030(s)	$\tilde{\nu}_3$ SO
							975(s)	$\tilde{\nu}_1$ SO
							635(s), 605(s)	δ SO
							525(s)	$\tilde{\nu}$(Mn-F)

a, Calculated values in parentheses; b, Analysis for N.

Table 2. Electronic Spectral Data of $(NH_4)_2[MnF_3(SO_4)]$ and $K_2[MnF_3(SO_4)]$

Compound	Band I $^5B_{1g} \rightarrow {}^5A_{1g}$ cm^{-1}	Band II $^5B_{1g} \rightarrow {}^5B_{2g}$ cm^{-1}	Band III $^5B_{1g} \rightarrow {}^5E_g$ cm^{-1}
$(NH_4)_2[MnF_3(SO_4)]$	15,500	17,800	21,700
$K_2[MnF_3(SO_4)]$	15,700	18,200	21,700

scribed, manganese is reduced not below Mn^{3+}, and that a maximum of one SO_4^{2-} is coordinated to the Mn^{3+} centre since a higher amount of A_2SO_4 did not alter the results. The fact, that the reaction of MnO(OH), 40% HF and $A_2S_2O_8$ (A = NH_4 or K) also afforded only $A_2[MnF_3(SO_4)]$, enables us to conclude that peroxydisulphate cannot oxidise Mn^{3+} in the presence of F^- ions. The process $S_2O_8^{2-} + 2e \rightarrow 2SO_4^{2-}$, as a consequence of electron-transfer between $S_2O_8^{2-}$ and water, must be the origin of SO_4^{2-} in this case.

Characterisation and Assessment of Structures—$A_2[MnF_3(SO_4)]$ are all pink-brown crystalline compounds, stable for prolonged periods. They are relatively more stable than the corresponding A_2MnF_5 compounds and the enhanced stability must owe its origin to the presence of SO_4^{2-} ligand. The $A_2[MnF_3(SO_4)]$ compounds are insoluble in organic solvents, and in water they decompose, thus precluding molar conductance measurements. The chemically estimated oxidation state of manganese, falling between 2.9 and 3.1 (Table 1), supports the contention that manganese, in each of the compounds, is in its +3 state. It is interesting to note that while the mangnetic moments of A_2MnF_5 compounds occur at *ca.* 3.2 BM (strong antiferromagnetic case)[11-13] and those of sulphato compounds of manganese(III) fall at *ca.* 4.8 BM (normal),[17] the magnetic moments of $A_2[MnF_3(SO_4)]$ compounds lie between 4.0 and 4.2 BM. It is evident that the degree of antiferromagnetic exchange interaction can be controlled by the replacement of two F^- ligands by an SO_4^{2-} ligand in going from $[MnF_5O]^{2-}$ to $[MnF_3(SO_4)]^{2-}$.

The IR spectra of the compounds show the SO frequencies at *ca.* 1230, *ca.* 1145, *ca.* 1030, *ca.* 975, *ca.* 684, *ca.* 635 and at *ca.* 605 cm^{-1}, and the ν_{Mn-F} at *ca.* 525 cm^{-1}. The pattern suggest a lowering of symmetry[18] of the SO_4^{2-} group from T_d to C_2 and rule out the presence of an ionic SO_4^{2-}. Further the splitting of the ν_3 and δ modes of SO into three bands each (Table 1) enables us to assign a C_{2v} symmetry[19] to the SO_4^{2-} group. Although the ν_{SO} modes appear at relatively higher frequencies than those usually observed for a bridging[19,20] SO_4^{2-}, the possibility of inter molecular sulphato bridging cannot be ruled out. The reflectance spectra of $A_2[MnF_3(SO_4)]$ (A = NH_4 or K) exhibit three bands at ~ 21,500, ~ 17,900 and ~ 13,600 cm^{-1}, which have been assigned to the transitions[21] $^5B_{1g} \rightarrow {}^5E_g$, $^5B_{1g} \rightarrow {}^5B_{2g}$ and $^5B_{1g} \rightarrow {}^5A_{1g}$ respectively. This suggests an appreciable splitting of ^5E_g ground state of Mn^{3+} ion in $[MnF_3(SO_4)]^{2-}$ as a consequence of the Jahn-Teller effect. Pyrolysis of $(NH_4)_2[MnF_3(SO_4)]$ at *ca.* 340°C loses 37.9% weight to yield $MnSO_4$.

Acknowledgement—We thank the University for award of a U.G.C. fellowship to M.N.B., and the Department of Atomic Energy, Government of India, for the financial assistance (Sanction No. 37/16/82-G).

REFERENCES

1. A. Harriman *Coord. Chem. Rev.* 1979, 28, 147.
2. D. R. Scarfe, J. F. Ward, *J. Chem. Phys.* 1969, 50, 1066.
3. A. J. Edwards, *J. Chem. Soc., A* 1971, 2653.
4. M. Bartlett and G. J. Palenik, *J. Chem. Soc. D*, 1970, 416.
5. P. C. Healy and A. H. White, *J. Chem. Soc. Dalton Trans.* 1972, 1883.
6. A. Avdeef, J. A. Costamagna and J. P. Fackler, Jr., *Inorg. Chem.* 1974, 13, 1854.
7. J. P. Fackler, Jr., and A. Avdeef, *Inorg. Chem.* 1974, 13, 1864.
8. R. J. Butcher and E. Sinn, *J. Chem. Soc., Dalton Trans.* 1975, 2517.
9. B. Stults, R. S. Marianelli and V. W. Day, *Inorg. Chem.* 1979, 18, 1853.
10. H. Aghabozorg, G. J. Palenik, R. C. Stoufer and J. Summers, *Inorg. Chem.* 1982, 21, 3903.
11. S. Emori, M. Inoue, M. Kishita and M. Kubo, *Inorg. Chem.* 1969, 8, 1385.
12. M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta and D. T. Khathing, *J. Chem. Soc., Dalton Trans.* 1981, 2587.
13. M. N. Bhattacharjee, M. K. Chaudhuri, H. S.

Dasgupta, A. Kathipri and D. T. Khathing, *Synth. React,. Inorg. Met.-Org. Chem.* 1982, 12, 485.

14. G. Brauer (Editor) *Handbook of Preparative Inorganic Chemistry*, Vol. 2. p. 1457. Academic Press, London (1965).
15. A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, (a) p. 434; (b) p. 296; (c) p. 462. Longman Green, (1964).
16. M. N. Bhattacharjee, M. K. Chaudhuri, S. K. Ghosh, Z. Hiese and N. Roy, *J. Chem. Soc., Dalton Trans.* in press.
17. B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.* 1964, 6, 37.
18. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd Edn., p. 123. Wiley-Interscience, London (1970).
19. C. G. Barraclough and M. L. Tobe, *J. Chem. Soc.* 1961, 1993.
20. R. Eskenazi, J. Raskovan and R. Levitus, *J. Inorg. Nucl. Chem.* 1966, 28, 521.
21. T. S. Davis, J. P. Fackler, Jr., and M. J. Weeks, *Inorg. Chem.*, 1968, 7, 1994.

Direct Synthesis of Tris(acetylacetonato)manganese(III)

By **Manabendra N. Bhattacharjee** and **Mihir K. Chaudhuri,*** Department of Chemistry, North-Eastern Hill University, Shillong 793 003, India
Darlando T. Khathing, Department of Physics, North-Eastern Hill University, Shillong 793 003, India

A concentrated solution of $K[MnO_4]$ undergoes a ready reaction with acetylacetone, in the absence of any buffer, giving a very high yield of the title compound, $[Mn(acac)_3]$. The pH of the solution, recorded immediately after the formation of crystalline $[Mn(acac)_3]$, was found to be *ca.* 5. Electron impact induced mass spectrometry showed the compound to be monomeric.

TRIS(ACETYLACETONATO)MANGANESE(III), $[Mn(acac)_3]$, has been known for a long time. The compound can be synthesised by air or chlorine oxidation of a basic solution of Mn^{2+} in the presence of acetylacetone. However, this method has not been used in practice because of the deleterious effect of alkali on the end product, as well as the chances of its contamination by chloride ions. Instead, the syntheses due to Cartledge [1] and Charles [2] involving the oxidation of Mn^{2+} with $K[MnO_4]$ in the presence of acetylacetone (Hacac) have been employed. The success of this method depends markedly on the pH. The reaction mixture requires to be regulated at pH *ca.* 5 by the addition of a large amount of sodium acetate. The use of sodium acetate in such quantities must surely contaminate the end product. In the course of our studies on the synthesis of manganese(III) compounds directly from $K[MnO_4]$,[3] we have developed a method for the synthesis of $[Mn(acac)_3]$ which does not require buffer. This note reports the direct synthesis of $[Mn(acac)_3]$.

EXPERIMENTAL

Reagent-grade potassium permanganate and acetylacetone were used in the synthesis. Infrared spectra were recorded on a Perkin-Elmer model 125 spectrophotometer. The oxidation state of manganese in the compound was determined iodometrically by reduction of a known amount of the compound with acidified potassium iodide solution followed by titration of the liberated iodine with standard sodium thiosulphate solution.

The mass spectrum was 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, 20 °C; resolution, 1 000; and accelerating voltage, 8 kV. The essential features of the mass spectrum run at 20 °C are given in the Table. The mass spectrometric observations were made with the field of ionising current sufficiently strong to trap primary ions.

Synthesis of Tris(acetylacetonato)manganese(III), $[Mn(acac)_3]$.—A quantity of powdered $K[MnO_4]$ (5.0 g, 31.7 mmol) was dissolved in the minimum volume of water by slight warming over a steam-bath and the solution then filtered. Distilled acetylacetone (22.0 g, 220.0 mmol) was added to the solution with vigorous stirring. The mixture was stirred for *ca.* 5 min over a steam-bath and then allowed to cool for *ca.* 10 min. The dark brown-black shiny crystals of $[Mn(acac)_3]$ were filtered off and washed several times with small amounts of acetylacetone–water (1 : 1) and finally dried *in vacuo*. 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 (b.p. 40—60 °C) and then cooling at *ca.* 0 °C. The yield obtained was 9.7 g (87%). The compound does not have a sharp melting point but decomposes at *ca.* 155 °C. This method may also be used for large-scale synthesis (Found: C, 51.1; H, 6.10; Mn, 15.7. Calc. for $C_{15}H_{21}MnO_6$: C, 51.15; H, 6.00; Mn, 15.6%). The molecular weight was found to be 352 mass spectrometrically.

† Throughout this note: 1 eV ≈ 1.60 × 10^{-19} J.

Mass spectral data for $[Mn(acac)_3]$

(*a*) Major peaks

Assignment	*m/z*	Intensity (%)
$[Mn(C_5H_7O_2)_3]^+$	352	18
$[Mn(C_5H_7O_2)_2]^+$	253	100
$[Mn(C_5H_7O_2)(C_4H_4O_2)]^+$	238	34
$[Mn(C_5H_7O_2)]^+$	154	74
$[Mn(C_4H_4O_2)]^+$	139	5
Mn^+	55	0

(*b*) Metastable transitions

m/z Observed	*m/z* Calculated	Process	Fragment lost
181.8	181.84	352 → 253	$C_5H_7O_2$
223.9	223.89	253 → 238	CH_3
99.6	99.65	238 → 154	$C_4H_4O_2$
125.6	125.46	154 → 139	CH_3

RESULTS AND DISCUSSION

Direct Synthesis.—In our previous paper [3] we emphasised the role of acetylacetone as a reducing agent in the reduction of Mn^{VII}. We have now extended the use of this concept to the synthesis of $[Mn(acac)_3]$. The method described leads to the rapid synthesis of tris(acetylacetonato)manganese(III) in very high yield and analogous procedures have also been used successfully for the synthesis of $[Cr(acac)_3]$ from CrO_3 and $[Ni(acac)_2(H_2O)_2]$ from NiO(OH). Gram quantities of $[Mn(acac)_3]$ can be synthesised in less than 1 h without using any buffer. The reduction of $[MnO_4]^-$ by acetyl-

acetone and the subsequent formation of the tris chelate owing to the presence of an excess of acetylacetone (Hacac) appear to be the driving forces for the reaction. Although the present synthesis does not involve any buffer, the course of the reaction is such that it automatically maintains the pH desired for the successful formation of $[Mn(acac)_3]$. The pH of the solution measured immediately after the formation of the compound was found to be *ca.* 5. This value concurs exactly with that maintained by the addition of a large amount of sodium acetate in the syntheses of Cartledge [1] and Charles.[2] It is not possible to propose a mechanism for the present synthesis in the absence of full details of the oxidised products of acetylacetone.

Characterisation.—Tris(acetylacetonato)manganese(III) is a dark brown-black crystalline compound, unstable in air but capable of being stored in a sealed container for months. The compound is slightly soluble in water but dissolution is accompanied by decomposition. Freshly prepared $[Mn(acac)_3]$ does not show a sharp melting point but decomposes around 155 °C. The i.r. spectrum of the compound is unambiguous and shows the characteristics of chelated acctylacetonates ($acac^-$), in agreement with the reported spectrum.[4] The molecular weight, determined mass spectrometrically, was found to be 352 suggesting that the compound is monomeric. This agrees well with the crystal structures of various forms of $[Mn(acac)_3]$ which also showed the presence of discrete $[Mn(acac)_3]$ molecules.[5,6] Chemical determination of the oxidation state of manganese in the synthesised compound gave +III, providing further support for the identity of the compound.

Mass Spectrometric Studies.—Attempts to obtain good mass spectra of $[Mn(acac)_3]$ have not always been successful.[7] It appears that the spectra of tris(acetylacetonato)metalates markedly depend on the method of sample introduction. We favoured the direct insertion probe and introduced the sample into the ionisation chamber without any prior heating. The other conditions were similar to those maintained in our earlier experiments.[8]

The spectrum run at 20 °C (Table) showed a molecular ion signal of moderate intensity (18%) at *m/z* 352 and a base peak at *m/z* 253 due to $[Mn(acac)_2]^+$, the major fragmentation path being $[Mn(C_5H_7O_2)_3]^+ \longrightarrow [Mn(C_5H_7O_2)_2]^+ \longrightarrow [Mn(C_5H_7O_2)(C_4H_4O_2)]^+ \longrightarrow [Mn(C_5H_7O_2)]^+ \longrightarrow [Mn(C_4H_4O_2)]^+ \longrightarrow Mn^+$. The metastable peaks observed at *m/z* * 181.8, 223.9, 99.6, and 125.6 support the proposed fragmentation path and closely resemble those reported by Westmore and coworkers.[9]

[1/1076 *Received, 7th July,* 1981]

REFERENCES

[1] G. H. Cartledge, *J. Am. Chem. Soc.*, 1951, **73**, 4416; U.S. P. 2,556,316/1951.
[2] R. G. Charles, *Inorg. Synth.*, 1966, **7**, 183.
[3] M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, and D. T. Khathing, *J. Chem. Soc., Dalton Trans.*, 1981, 2587.
[4] S. Pinchas, B. L. Silver, and I. Laulight, *J. Chem. Phys.*, 1967, **46**, 1506.
[5] J. P. Fackler, Jun., and A. Avdeef, *Inorg. Chem.*, 1974, **13**, 1864.
[6] B. R. Stults, R. S. Marianelli, and V. W. Day, *Inorg. Chem.*, 1979, **18**, 1853.
[7] C. G. McDonald and J. S. Shannon, *Aust. J. Chem.*, 1966, **19**, 1545.
[8] M. K. Chaudhuri, H. S. Dasgupta, N. Roy, and D. T. Khathing, *Org. Mass Spectrom.*, 1981, **16**, 303.
[9] G. M. Bancroft, C. Reichert, and J. B. Westmore, *Inorg. Chem.*, 1968, **7**, 870.

Indian Journal of Chemistry
Vol 21A, October 1982, pp 977-979

Synthesis of Alkali Metal Trifluoroaquomanganates(II)

MANABENDRA N BHATTACHARJEE & MIHIR K CHAUDHURI*
Department of Chemistry, North Eastern Hill University, Shillong 793003

Received 12 *April* 1982, *revised and accepted* 26 *June* 1982

The electron transfer reaction between hydrazine hydrate and $KMnO_4$ in the presence of alkali metal bifluorides, AHF_2 (A $=NH_4$, Na or K) readily gives light pinkish-white alkali metal trifluoroaquomanganates(II), $A[MnF_3(H_2O)]$ in very high yields The corresponding Rb^+ and Cs^+ salts have been obtained by reacting 20% hydrofluoric acid solution of $NH_4[MnF_3(H_2O)]$ with Rb_2CO_3 and Cs_2CO_3 respectively The compounds have been characterised by elemental analyses, chemical determination of oxidation states of manganese in the compounds, room temperature magnetic susceptibility measurements, pyrolysis and infrared spectral studies

There is a growing current interest in the study of fluoro-manganese chemistry[1-6] It is now well established that F^- ions stabilise Mn^{3+} and it is also generally believed that the reduction of higher valent manganese below +3 state through electron transfer reactions in the presence of F^- ligands is rather a difficult task[1-5], eventhough +2 oxidation state of manganese is a more common one Moreover, complex formation tendency of Mn^{2+} seems to be comparatively less pronounced than that of Mn^{3+} (ref 7) In view of this and in continuation of our work on the synthesis and structural assessment of fluoromanganates[4,5], we thought it important to carry out the electron transfer reaction between $KMnO_4$ and a strong reducing agent, like hydrazine hydrate (N_2H_4 H_2O) in the presence of alkali metal bifluorides and to synthesise and characterise fluoro-manganates(II) directly from Mn^{7+} This paper incorporates results of such an investigation

Materials and Methods

All the chemicals used were reagent grade products Alkali metal bifluorides, AHF_2 were synthesised by the method developed in this laboratory[8]

The oxidation state of manganese in each of the alkali metal trifluoroaquomanganates(II) was determined chemically by the reaction of a known amount of the compound with aqueous acidic Fe^{2+} solution followed by estimation of unreacted Fe^{2+} in solution

Synthesis of alkali metal trifluoroaquomanganates(II), $A[MnF_3(H_2O)]$—Ammonium, sodium and potassium trifluoroaquomanganates(II) were synthesised by the following general method

Alkali metal bifluoride, AHF_2 (A $=NH_4$, Na or K) (19 3 m mol) and solid $KMnO_4$ (3 16 m mol) were mixed, powdered and dissolved in a minimum volume of water by slightly warming over a steam-bath and filtered The filtrate was collected in a polythene beaker and an excess of hydrazine hydrate (3 ml) added in one lot with constant stirring A highly exothermic reaction set in and readily gave a light pinkish-white microcrystalline product with the mother liquor becoming colourless The reaction mixture was cooled to room temperature, solid separated by centrifugation and purified by washing with *n*-heptane and finally dried *in vacuo* The yield was between 80 and 90%

Synthesis of rubidium trifluoroaquomanganate(II), $Rb[MnF_3(H_2O)]$—$NH_4[MnF_3(H_2O)]$ (2 m mol) was dissolved in a minimum volume of 20% hydrofluoric acid to get a clear solution To this solution was added powdered Rb_2CO_3 (1 m mol) in portions with stirring After addition was over, the light pinkish-white $Rb[MnF_3(H_2O)]$ appeared, which was separated by centrifugation and purified by washing with *n*-heptane and finally dried *in vacuo*, yield 91%

Synthesis of cesium trifluoroaquomanganate(II), $Cs[MnF_3(H_2O)]$—The above metathesis reaction was carried out with $NH_4[MnF_3(H_2O)]$ (2 m mol) and Cs_2CO_3 (1 m mol) to get $Cs[MnF_3(H_2O)]$ in 91% yield

Results and Discussion

The experimental conditions employed for the synthesis of various alkali metal trifluoroaquo-manganates successfully brought about the reduction of manganese below its +3 state, inspite of difficulties recorded earlier[1-5] On the addition of N_2H_4 H_2O to excess of alkali metal bifluorides and potassium permanganate the temperature went up to about 80-90°C This temperature was strategically maintained in order to facilitate the reduction of manganese below its +3 state The analysis of the reaction products shows the reduction of manganese below its +3 state Thus the method leading to trifluoroaquomanganates(II) of alkali metals indicates that hydrazine hydrate reductions could be developed for the synthesis of other types of compounds of manganese in its +2 state

starting from Mn^{7+} and also compounds of other transition metals starting from their stable higher oxidation states. The yields obtained by this method are very high. It is also evident that by the use of forcing conditions the fluoro complexes of Mn^{2+} can be synthesised eventhough their formation constants in aqueous solutions are very low[9-11]. The alkali metal bifluorides, AHF_2, here act as fluorinating agents. In our previous papers[4,5,8,12] we emphasised the role of AHF_2 as fluorinating agents. In fact it appears that the success of the method depended not only on the role played by $N_2H_4.H_2O$ but also quite appreciably on the presence of both H^+ and F^- in the solution phase arising from AHF_2. The overall reaction leading to the formation of $A[MnF_3(H_2O)]$ may be expressed by Eq. (1)

$$4KMnO_4 + 13AHF_2 + 5N_2H_4.H_2O \rightarrow 4A[MnF_3(H_2O)] + 5N_2 + 17H_2O + HF + 4KF + 9AF \quad \ldots (1)$$

The alkali metal trifluoroaquomanganates(II) are all very light pinkish-white microcrystalline products and they attack glass in the presence of moisture. They are not soluble in common organic solvents. $A[MnF_3(H_2O)]$ dissolves in water to some extent but the dissolution is accompanied by dissociation or decomposition. The compounds dissolve highly in hydrofluoric acid.

The chemically estimated oxidation states of manganese lie between 2.05 and 2.12 (Table 1), lending strong support to the contention that manganese in each of the compounds has an oxidation number of +2. We emphasise on the chemical determination of oxidation state of manganese in such compounds because the observed magnetic moment values (measured on a Gouy balance with $Hg[Co(NCS)_4]$ as the calibrant) are often lower than the expected values owing to their pronounced antiferromagnetic behaviour. The attempts to measure the molar conductance of various $A[MnF_3(H_2O)]$ compounds in water were unsuccessful. The observed values were higher than that expected for a uni-uni valent type of electrolyte. The higher molar conductance values indicate some sort of decomposition of the compounds or the enhanced ionic character of the Mn-F bonds.

The IR spectra of ammonium, sodium, potassium, rubidium and cesium trifluoroaquomanganates(II), (recorded on a Perkin-Elmer model 125) are almost identical. The typical features of the spectra are the occurrence of a strong absorption ~410, a weak and broad band ~1640, a medium intensity broad band ~3350 and a medium intensity band ~710 cm^{-1}, assignable to νMn-F, $\delta H-O-H$, $\nu O-H$ and rocking modes of water arising out of coordinated fluoride and water respectively. The occurrence of νMn-F at a much lower frequency compared to those of MnF_5^{2-} and MnF_6^{3-} species[4,5,13], suggests that the Mn-F bonds in $[MnF_3(H_2O)]^-$ have enhanced ionic character than those in MnF_5^{2-} and MnF_6^{3-}. However, from the fact that the νMn-F has been observed in the present cases ~410 cm^{-1}, it is certain that a definite degree of covalency exists in the Mn-F bonds. Similar observation was made by Peacock and Sharp[13] in the case of $KMnF_3$. The very weak nature of the $\delta H-O-H$ band points to the presence of coordinated water[14,15]. Moreover, the appearance of medium intensity band ~710 cm^{-1} which is generally attributed to the rocking mode of coordinated water adduces strong evidence for the presence of coordinated water in the compounds. Further evidence with regard to the presence of coordinated water was obtained from the pyrolysis studies of $K[MnF_3(H_2O)]$, taken as a representative. Pyrolysis of the compound at 125-30°C for 3 hr virtually did not show any change in weight of the compound. The IR spectra of the compound recorded before and after heating also did not indicate any change in the spectral pattern.

Table 1—Analytical Data, Magnetic Moments, Estimated Oxidation States of $A[MnF_3(H_2O)]$ ($A = NH_4$, Na, K, Rb or Cs)

Compound	μ_{eff} (B.M.) 290°K	Oxidation state of Mn	Found (%) (Calc.)		
			A or N	Mn	F
$NH_4[MnF_3(H_2O)]$	5.3	2.05	9.61 (9.46)	37.52 (37.16)	38.21 (38.51)
$Na[MnF_3(H_2O)]$	5.2	2.11	15.52 (15.03)	36.34 (35.95)	37.68 (37.25)
$K[MnF_3(H_2O)]$	5.2	2.12	23.43 (23.08)	32.89 (32.54)	33.51 (33.73)
$Rb[MnF_3(H_2O)]$	5.3	2.08	40.52 (39.68)	25.73 (25.52)	26.83 (26.45)
$Cs[MnF_3(H_2O)]$	5.3	2.12	51.61 (50.55)	21.38 (20.92)	21.48 (21.68)

The room temperature magnetic moments of the alkali metal trifluoroaquomanganates(II), $A[MnF_3(H_2O)]$ lie between 5.2 and 5.3 B.M. well below the expected value for a high-spin d^5-system. This, however, is not too surprising because similar observations were made in the cases of A_2MnF_5 and $A_2MnF_5.H_2O$ (refs 4, 5, 16, 17). Considerably lower moments presumably owe their origin to antiferromagnetic exchange interaction between continuous Mn^{2+} ion probably through $-Mn-F-Mn$-chain in the solid state. The very faint colour of the compounds indicates that they may have octahedral structure but only X-ray study would provide conclusive evidence.

Acknowledgement

The authors thank the UGC, New Delhi for the award of a fellowship to one of them (MNB) and Mr K P Sarma for his cooperation.

References

1 Massa W, *Inorg nucl Chem Lett*, **13** (1977) 253.
2 Bukovec P & Kaucic V, *J chem Soc*, (1977) 945.
3 Kaucic V & Bukovec P, *J chem Soc*, (1979) 1512.
4 Bhattacharjee M N, Chaudhuri M K, Dasgupta H S & Khathing D T, *J chem Soc Dalton Trans*, (1981) 2587.
5 Bhattacharjee M N, Chaudhuri M K, Dasgupta H S, Kathipri A & Khathing D T, *Synth React inorg met-org Chem*, (1982) (in press).
6 Chaudhuri M K, Das J C & Dasgupta H S, *J inorg nucl Chem*, **43** (1981) 85.
7 Wood C W & Holliday A K, *Inorganic chemistry*, (Butterworths, London), 1967, 336.
8 Chaudhuri M K & Choudhury P K, *Chemy Ind*, (1979) 88.
9 Cotton F A & Wilkinson G, *Advanced inorganic chemistry*, (John Wiley, New York), 1972, 848.
10 Foster J J & Gill N S, *J chem Soc (A)*, (1968) 2625.
11 Colton R & Canterford J H, *Halides of the first row transition metals*, (Wiley-Interscience, New York), 1969, 212.
12 Chaudhuri M K, Dasgupta H S, Ghosh S K & Khathing D T, *Synth React inorg met-org Chem*, **12** (1982) 63.
13 Peacock R D & Sharp D W A, *J chem Soc*, (1959) 2762.
14 Thornback J R & Wilkinson G, *J chem Soc Dalton Trans*, (1978) 110.
15 Chakravorty A R & Chakraborty A, *Inorg Chem*, **20** (1981) 275.
16 Emori S, Inoue M, Kishita M & Kubo M, *Inorg Chem*, **8** (1969) 1385.
17 Nyholm R S & Sharpe A G, *J chem Soc*, (1952) 3579.

REPRINT

SYNTHESIS

International Journal
of Methods in Synthetic
Organic Chemistry

1982
No. 7:
July

With Compliments of the Author.

GEORG THIEME VERLAG · STUTTGART · NEW YORK

[1,3-$^{13}C_2$]-Malonsaure-diethylester (3):
Man bereitet bei 0 °C eine Lösung von Lithium-diisopropylamid aus einer 2 2 normalen Lösung (9 2 ml) von Butyllithium in Hexan und Diisopropylamin (2 g), gibt Tetrahydrofuran (10 ml) zu und gibt diese Losung unter Ruhren zu einer eisgekühlten Losung von [1-^{13}C)-Trimethylsilylessigsäure (**2**, 1.06, 8 mmol) in Tetrahydrofuran (10 ml) Anschließend ruhrt man solange (~3 h), bis das Gemisch nur noch schwache Trubung zeigt und das Dilithio-Derivat von **2** praktisch vollkommen gelöst ist[9]. Die Carboxylierung mit $^{13}CO_2$ (aus 1.58 g $Ba^{13}CO_3/H_2SO_4$) erfolgt analog zur Herstellung von **2**. Die erhaltene Reaktionslosung wird auf Eis (10 g) gegossen, das Gemisch mit 10%iger Salzsäure angesäuert, mit Natriumchlorid gesattigt und 15 h kontinuierlich mit Ether extrahiert Der Ether wird abgezogen, der Rückstand in Ethanol (3 ml) aufgenommen, mit einer Spur *p*-Toluolsulfonsaure und mit Chloroform (30 ml) versetzt und in einer Apparatur mit Wasserabscheider unter Ruckfluß gekocht, bis kein Wasser mehr abgeschieden wird. Anschließend wird das Solvens abdestilliert und der Rückstand im Kugelrohr destilliert, Ausbeute an farblosem **3**: 0.96 g (74%, bezogen auf $Ba^{13}CO_3$); Kp· 60 °C/0.1 torr; Reinheit. >90% (gas-chromatographisch)

M S. (Elektronenstoß-Ionisation, 70 eV): $m/e = 162$ (M^+, 4%), 135 (60), 117 (100), 89 (90)

I.R. (CCl_4): $\nu = 1710$, 1695 cm^{-1}.

^{1}H-N.M.R (400 MHz, $CDCl_3$/TMS) $\delta = 4.2$ (qd, 4 H, $J = 7$ und 3 Hz); 3 36 (t[a], 2 H, $J = 7$ 5 Hz); 1 28 ppm (t, 6 H, $J = 7$ Hz).

^{13}C-N.M.R. (20 MHz, $CDCl_3$/TMS) $\delta = 166$ 6 (s, —CO—); 61 5 (s, OCH_2), 41.7 (t[a], $J_{C\,C} = 59$ Hz, —CH_2—); 14.1 ppm (s, CH_3).

[a] Aufgrund der ^{13}C-Einbau-Rate im verwendeten $Ba^{13}CO_3$ (90%) erhalt man 3 mit der Isotopen-Zusammensetzung. $^{13}C_2 = 81\%$, $^{13}C_1 = 18\%$, $^{13}C_0 = 1\%$ Als Folge hiervon liegt das ^{1}H-N M R -Signal der Methylen-Gruppe beim $^{13}C_1$-Ester als Dublett bei $\delta = 3$ 36 vor ($J = 7$ 5 Hz) Im ^{13}C-N M R -Spektrum findet man bei $\delta = 41$ 7 ppm ebenfalls ein Dublett mit $J_{C\,C} = 59$ Hz

Fur die Forderung dieser Arbeit danken wir dem Fonds der Chemischen Industrie und der Deutschen Forschungsgemeinschaft.

Eingang 4. November 1981
(geanderte Fassung 9 Dezember 1981)

* Korrespondenz-Adresse.

[1] N. M Packter: *Biosyntheses of Acetate-derived Compounds*, John Wiley & Sons, New York, 1973, chapter 6.

[2] Siehe z. B. K. N F. Shaw, C. Nolan, *J. Org. Chem* **22**, 1668 (1957).

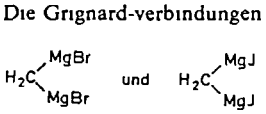
[3] D L. Fitzell, D. P. H Hsich, C. A Reece, J N. Seibert, *J Label Comp.* **11**, 135 (1975)

[4] W. Franke, H Schwarz, H. Thies, J. Chandrasekhar, P. v R Schleyer, W. J. Hehre, M Saunders, P. Walker, *Chem Ber* **114**, 2808 (1981).

[5] M E. Mueller, E. Leete, *J. Org Chem* **46**, 3151 (1981)

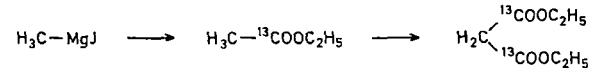
[6] In den *Chemical Abstracts* wird weder [1,3-$^{13}C_2$]-Malonsaure noch ihr Diethylester beschrieben Die Saure ist zu einem extrem hohen Preis kommerziell erhaltlich (z. B. zu DM 2940 00/g bei Merck, Sharp & Dohme, München· „MS-1119").

[7] Die Grignard-verbindungen



reagieren in Ether nicht mit Elektrophilen wie Kohlendioxid. D A. Fidler et al., *J Am Chem. Soc.* **77**, 6634 (1955) [s. a. K Nutzel, in· Houben-Weyl, *Methoden der Organischen Chemie*, 4. Auflage, E. Muller Ed., Band 13/2a, Georg Thieme Verlag, Stuttgart, 1973, p 98] Nach eigenen Versuchen ubersteigt die Ausbeute an Malonsäure nie 10%, selbst dann nicht, wenn Losungsmittelgemische (wie Benzol/Ether) und diverse Aktivierungsmethoden verwendet werden. Ausbeuten von <30% an Malonsaure sollten erhalten werden [F Bertini, P Graselli, G Zubiani, G. Cainelli, *Tetrahedron* **26**, 1281 (1970)], wenn die Grignard-Verbindung von CH_2X_2 mit Mg/Hg hergestellt und CO_2 im Uberschuß eingesetzt wird

Die prinzipiell mogliche Reaktionssequenz



[Lit [4] sowie A. Murray, D L Williams· *Organic Syntheses with Isotopes*, Interscience Publishers, New York, 1958] ist deshalb nicht attraktiv, weil als Zwischenprodukt das fluchtige Ethyl-acetat anfallt; dieses läßt sich bei kleinen Ansatzen nicht ohne Ausbeuteverluste handhaben.

[8] L. H Sommer, J. R. Gold, G. M. Goldberg, N. S. Marans, *J Am. Chem Soc* **71**, 1509 (1949)

[9] P A Grieco, C.-J L Wang, S. D. Burke, *J. Chem Soc Chem. Commun* **1975**, 537.

Pyridinium Fluorochromate; A New and Efficient Oxidant for Organic Substrates

Manabendra N BHATTACHARJEE, Mihir K. CHAUDHURI*, Himadri S DASGUPTA, Nirmalendu ROY

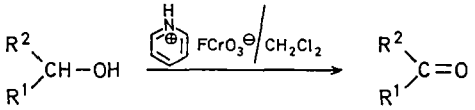
Department of Chemistry, North-Eastern Hill University, Shillong, 793 003, India

Darlando T. KHATHING

Department of Physics, North-Eastern Hill University, Shillong, 793 003, India

There is continued interest in the development of new chromium(VI) reagents[1-5] 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 dichromate[4], and 2,2'-bipyridinium chlorochromate[5]. We have now investigated the synthetic potential of pyridinium fluorochromate, $C_5H_5NHCrO_3F$, 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.

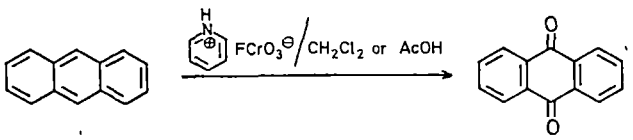


1 **2**

Pyridinium fluorochromate in dichloromethane also oxidizes anthracene (**3a**) and phenanthrene (**3b**) to anthraquinone (**4a**)

0039-7881/82/0732-0588 $ 03 00

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.



3a 4a

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 uni-uni valent 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 fluorochromate[6,7]. 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.

$C_5H_6CrFNO_3$	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): ν = 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: $\Lambda_M(25\,°C) = 128\ ohm^{-1}\ cm^2\ mol^{-1}$.

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:

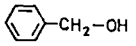
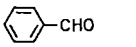
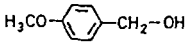
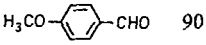
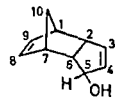
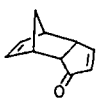
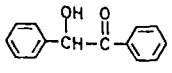
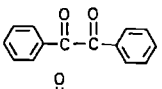
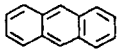
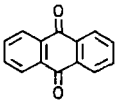
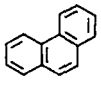
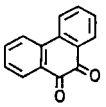
The reaction is carried out in a dry round-bottom flask fitted with reflux-condenser and efficient stirrer. To a vigorously stirred suspension of pyridinium fluorochromate (generally 10 g) in dichloromethane (generally 18 ml), a solution of the substrate in a small amount of dichloromethane is added 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 silica gel 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-diene[17] (**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

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	reported
1a n-C_4H_9–OH	1/1.5	CH_2Cl_2	2 h	**2a** n-C_3H_7–CHO	94	b.p. 74°/760	b.p. 75°/760[10]
1b n-C_7H_{15}–OH	1/1.5	CH_2Cl_2	1 h	**2b** n-C_6H_{13}–CHO	84	b.p. 152°/760	b.p. 153°/760[12]
1c 	1/1.25	CH_2Cl_2	45 min	**2c** 	90	b.p. 63°/10	b.p. 62°/10[8]
1d 	1/1.25	CH_2Cl_2	50 min	**2d** 	90	b.p. 248°/760	b.p. 249.5°/760[9]
1e 	1/1.5	CH_2Cl_2	3.5 h	**2e** 	89	b.p. 153–154°/760	b.p. 155.4°/760[11]
1f 	1/1.5	CH_2Cl_2	1.5	**2f** 	92–93	m.p. 79–80°	m.p. 80°[14]
1g 	1/1.5	CH_2Cl_2	2.5	**2g** 	98	m.p. 95°	m.p. 95°[13]
3a 	1/2.5 1/2.5	CH_2Cl_2 AcOH	4 h 1.5 h	**4a** 	68 98	m.p. 274°	m.p. 275°[15]
3b 	1/2.5 1/2.5	CH_2Cl_2 AcOH	5 h 2 h	**4b** 	52 72	m.p. 205°	m.p. 206.5–207.5°[16]

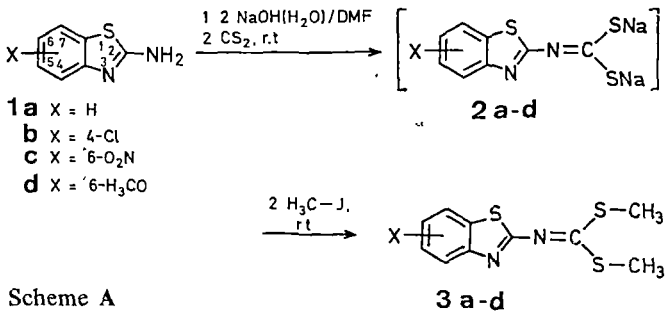
[a] The purity of the liquid products was found to be >98% by G.L.C. analysis.

ml) is added and the mixture is filtered through a short silica gel column (7 cm × 2 cm²). The contents of the column are thoroughly washed with ether (3 × 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. 80 °C).

Received: August 26, 1981
(Revised form: December 14, 1981)

* Address for correspondence.

1 J. C. Collins, W. W. Hess, *Org. Synth.* **52**, 5 (1972).
2 E. J. Corey, J. W. Suggs, *Tetrahedron Lett.* **1975**, 2647.
3 E. J. Corey, D. L. Boger, *Tetrahedron Lett.* **1978**, 2461.
G. Piancatelli, A. Scettri, M. D'Auria, *Synthesis* **1982**, 245.
4 E. J. Corey, G. Schmidt, *Tetrahedron Lett.* **1979**, 399.
5 F. S. Guziec, F. A. Luzzio, *Synthesis* **1980**, 691.
6 R. Colton, J. H. Canterford, *Halides of the First Row Transition Metals*, John Wiley & Sons, New York, 1969, p. 190.
7 M. K. Chaudhuri, H. S. Dasgupta, N. Roy, *Indian J. Chem.*, [A] **20**, 1227 (1981).
8 L. E. Hinkel, E. E. Ayling, W. H. Morgan, *J. Chem. Soc.* **1932**, 2793.
9 L. E. Hinkel, E. E. Ayling, W. H. Morgan, *J. Chem. Soc.* **1932**, 2797.
10 A. E. Tschitschibabin, *Ber. Dtsch. Chem. Ges.* **37**, 188 (1904).
11 M. L. Sherril, *J. Am. Chem. Soc.* **52**, 1991 (1930).
12 N. Zelinsky, *Ber. Dtsch. Chem. Ges.* **34**, 2800 (1901).
13 *Beilstein* **7**, 747.
14 L. A. Paquette, J. S. Ward, *J. Org. Chem.* **37**, 3569 (1972).
15 *Beilstein* **7**, 782.
16 *Beilstein* **7**, 797.
17 R. B. Woodward, T. J. Katz, *Tetrahedron* **5**, 70 (1959).



Scheme A

Table 1. Dimethyl *N*-(2-Benzothiazolyl)-dithiocarbonimidates **3a–d**

Product	Yield [%]	m.p. [°C] (solvent)	Molecular formula[a]	^{1}H-N.M.R. (DMSO-d_6) δ (s, 6H, S—CH$_3$) [ppm]	M.S. *m/e* (M^+)
3a	75	73–74° (CH_3OH)	$C_{10}H_{10}N_2S_3$ (254.4)	2.60	254
3b	80	130–132° (C_2H_5OH)	$C_{10}H_9ClN_2S_3$ (288.8)	2.65	288
3c	60	186–187° (DMF)	$C_{10}H_9N_3O_2S_3$ (299.4)	2.95[b]	299
3d	60	97–98° (CH_3CN/H_2O)	$C_{11}H_{12}N_2OS_3$ (284.4)	2.60	284

[a] Satisfactory microanalyses obtained: C ±0.21, H ±0.16, N ±0.22.
[b] In CF_3COOD solution.

A Facile Synthesis of Dimethyl *N*-(2-Benzothiazolyl)-dithiocarbonimidates and Methyl *N*-(2-Benzothiazolyl)-dithiocarbamates

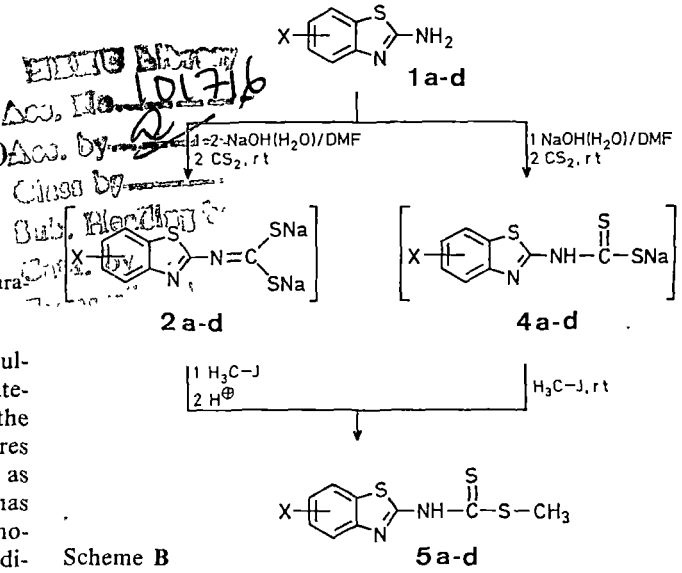
F. MERCHÁN*, J. GARÍN, E. MELÉNDEZ

Departamento de Química Orgánica, Universidad de Zaragoza, Zaragoza, Spain

As a result of our interest in the chemistry of carbon disulfide[1], the reactions of which lead to interesting starting materials for heterocyclic chemistry, we faced the problem of the synthesis of the title compounds **3** and **5**. Similar structures have been obtained from several heterocyclic amines, such as 2-aminothiazole[2] and 2-amino-1,3,4-thiadiazole[3], but it has been reported[4] that no reaction takes place between 2-aminobenzothiazole (**1**) and carbon disulfide under the usual conditions[5,6] (triethylamine, pyridine or potassium hydroxide in water or common organic solvents).

Nevertheless, in the present communication, we report that a sudden reaction between **1** and carbon disulfide is observed when using concentrated aqueous sodium hydroxide and *N*,*N*-dimethylformamide as solvent, this fact being explained by the strongly basic medium so obtained, which causes the amine, despite its poor nucleophilicity, to attack carbon disulfide. When a 2:1 molar ratio of base to **1** is used, the dithiocarbonimidic acid derivatives **2** are obtained which, without isolation, are alkylated to **3** with methyl iodide, according to Scheme A (Table 1).

On the other hand, the dithiocarbamic derivatives **5** can be obtained in two ways (Scheme **B**) (Table 2).



Scheme **B**

We first attempted the reaction using stoichiometric amounts of sodium hydroxide and methyl iodide to give the corresponding compounds **5** via **4**, but dialkylation, leading to products **3**, always took place, as could be expected from similar problems found in the chemistry of dithiocarboxylic acid esters and ketene *S*,*S*-acetals[7], so this procedure was not further investigated. Formation of unwanted products can be avoided in the alternative method, in which intermediate **2** is generated in solution, monoalkylated, and then acidified. In all cases, an excess of carbon disulfide was used to overcome its partial evaporation, due to the exothermic nature of the reaction.

0039-7881/82/0732-0590 $ 03.00

Kinetics and Mechanism of the Oxidation of Alcohols by Pyridinium Fluorochromate

Manabendra N. BHATTACHARJEE, Mihir K. CHAUDHURI,* and Himadri S. DASGUPTA
Department of Chemistry, North-Eastern Hill University, Shillong 793003, India
(Received February 1, 1983)

Pyridinium fluorochromate, $C_5H_5NHCrO_3F$, oxidizes benzyl alcohol, ethanol, and cyclohexanol to benzaldehyde, acetaldehyde, and cyclohexanone, respectively. While each of the oxidation, studied in acetonitrile–nitrobenzene (1 : 1, v/v) medium, is first order with respect to the oxidant, the rate is almost independent of the substrate concentration. The reactions are catalyzed by acid, the acid-catalyzed reactions being very fast, precluded determination of their order in acid medium. The effects of temperatures and solvent compositions were studied and activation parameters evaluated. Probable mechanisms are discussed.

There has been a continued interest in the development of new chromium(VI) reagents[1–6] for the effective oxidation of organic substrates, particularly alcohols, under mild conditions, and significant improvements were achieved, in recent years, by the use of new oxidizing agents.[2–6] We have very recently developed[7] a new reagent pyridinium fluorochromate, $C_5H_5NHCrO_3F$ (PFC) and found several advantages of our reagent over similar oxidizing agents in respects of amounts of oxidant and solvent required, short reaction times, and high yields. The mechanism of oxidations involving this important reagent has not yet been reported. The present paper describes the kinetics of oxidation of three typical alcohols *viz.*, benzyl alcohol, ethanol, and cyclohexanol, studied in medium acetonitrile–nitrobenzene (1 : 1, v/v), evaluates the reaction constants and discusses the probable mechanism.

Experimental

All chemical used were reagent grade products. The solvents were purified and dried by the literature methods.[8] *p*-Toluenesulfonic acid (TsOH) and benzoic acid were used in the attempts to study the acid-catalyzed reactions. Pyridinium fluorochromate, PFC, was synthesized by the method originally described in our previous paper.[7]

The reaction products benzaldehyde, acetaldehyde and cyclohexanone were characterized by spectral analyses and estimated as their 2,4-dinitrophenylhydrazones.

For kinetic measurements, the reactions were performed under pseudo-first-order conditions by maintaining a large excess (×5 or greater) of alcohol over PFC. The reactions were carried out at constant temperature (±0.1 K) and progress of the reactions were followed by iodometric estimation of unreacted chromium(VI), after quenching the reaction. The medium of reactions was always 1 : 1 (v/v) acetonitrile: nitrobenzene, unless otherwise stated. Acetonitrile–nitrobenzene system was chosen as the solvent because it was observed in our previous studies[7] that acetonitrile did not react with PFC. The reaction mixture were homogeneous for the total period of kinetic investigation.

Computations of the rate constants were made from the plot of log[oxidant] against time. The values reported are the mean of at least duplicate runs and are reproducible to within ±4%.

Dielectric constants for the varying proportions of acetonitrile–nitrobenzene mixture were estimated from the dielectric constants of the pure solvents[9] and are set out in Table 3. A constant ionic strength could not be maintained owing to the nonaqueous nature of the reaction medium. It may, however, be mentioned that the variation in ionic strength did not bring about any change[10] in the oxidation of benzyl alcohol by chromium(VI) oxide in aqueous acetic acid medium.

The uncatalyzed reactions were studied with varying temperatures of 303, 308, 313, and 318 K (error limit ±0.1 K) respectively for all the three alcohols (Table 4). The frequency factors were determined on the basis of the results obtained thereof. The activation parameters were evaluated by the standard procedure,[11] within allowable average error limit (at 303 K) (Table 5).

Results and Discussion

The oxidation of benzyl alcohol, ethanol and cyclohexanol by PFC in 1 : 1 (v/v) acetonitrile–nitrobenzene leads to the formation of benzaldehyde, acetaldehyde and cyclohexanone respectively in very high yields (>90%), showing no indication of further oxidation of the carbonyls conforming to our earlier synthetic studies involving PFC.[7]

The stoichiometry of various oxidations studied herein were estimated by the reaction of the respective alcohol with an excess of oxidant (PFC) followed by estimating the unreacted Cr^{VI}. In some runs, however, an excess of alcohols were used followed by the estimation of the carbonyl product. The stoichiometry of the reactions can be represented as follows:

$$3RCH_2OH + 2Cr^{VI} \longrightarrow 3RCHO + 6H^+ + 2Cr^{III}. \quad (1)$$

The stoichiometry of the reactions with cyclohexanol was determined in an analogous manner,

$$3C_6H_{11}OH + 2Cr^{VI} \longrightarrow 3C_3H_{10}CO + 6H^+ + 2Cr^{III}. \quad (2)$$

Like the analogous PCC[12–14] reactions, all the three alcohols studied herein were found to be first order with respect to time, because the first order rates were constant at different times. The reactions were also observed to be clearly first order with respect to the oxidant (PFC) as the rate constants were found to be practically unaltered for most of the reaction times (Table 1) with varying concentration of oxidant. The most prominent difference in the oxidations involving PCC[12–14] and those involving PFC is that the order of the reactions of the three alcohols with respect to the substrate concentrations was found to be practically constant enabling us to infer that the rates are almost independent of substrate concentrations. However, a small but steady increase in the rate constant values for all the three alcohols with increasing concentrations of the substrate

Table 1. Oxidant dependence of the reaction rate
T=303 K

[Oxidant] / 10^{-3} mol dm^{-3}	$k_1/10^{-4}$ s^{-1} [Ethanol] / 0.1 mol dm^{-3}	[Benzyl alcohol] / 0.01 mol dm^{-3}	[Cyclohexanol] / 0.01 mol dm^{-3}
1	6.765	8.413 (0.075)[12]	9.233
2	6.77 (0.10)[13]	7.95 (0.075)[12]	9.5
3	6.62	8.41 (0.072)[12]	9.34
4	6.56 (0.973)[13]	8.27 (0.077)[12]	9.59
5	6.64	8.21 (0.076)[12]	9.60

PCC oxidation data in parentheses.

Table 2. Substrate dependence of the reaction rate
[PFC]=0.001 mol dm^{-3}; T=303 K

Ethanol		Benzyl alcohol		Cyclohexanol	
Concn / mol dm^{-3}	$k_1/10^{-4}$ s^{-1}	Concn / mol dm^{-3}	$k_1/10^{-4}$ s^{-1}	Concn / mol dm^{-3}	$k_1/10^{-4}$ s^{-1}
0.1	6.765 (0.10)[13]	0.01	8.413 (0.075[a])[12]	0.01	9.233
0.2	7.87 (0.207)[13]	0.02	9.66 (0.152[a])[12]	0.02	13.89
0.3	8.55	0.03	10.1	0.03	15.79
0.4	9.16 (0.41)[13]	0.04	10.52 (0.306[a])[12]	0.04	17.78
0.5	10.6	0.05	11.54	—	—

PCC oxidation data in parentheses; a) Values at 298 K.

Table 3. Dependence of reaction rate on solvent composition
[Oxidant]=0.002 mol dm^{-3}; T=303 K

Nitrobenzene (%)	Acetonitrile (%)	Dielectric constant	[Ethanol] / 0.2 mol dm^{-3} $k_1/10^{-5}$ s^{-1}	[Benzyl alcohol] / 0.02 mol dm^{-3} $k_1/10^{-4}$ s^{-1}	[Cyclohexanol] / 0.02 mol dm^{-3} $k_1/10^{-4}$ s^{-1}
30	70	36.7	1.01	1.05	3.08
40	60	36.4	1.997	1.77	5.31
50	50	36.16	4.05	3.15	7.2
60	40	35.9	7.97	4.3	10.27
70	30	35.6	15.82	5.51	12.95

Table 4. Rate constants for the uncatalyzed oxidation of alcohols by pyridinium fluorochromate
[PFC]=0.001 mol dm^{-3}

Substrate	Concentration of substrate/mol dm^{-3}	$k/10^{-4}$ l mol^{-1} s^{-1} [a] 303 K	308 K	313 K	318 K
Ethanol	0.1	6.765 (1.0)[13]	7.112 (1.4)[13]	7.447 (1.93)[13]	7.798 (2.63)[13]
Benzyl alcohol	0.01	8.413 (7.5)[12]	8.593 (11.2)[12]	8.811 (15.5)[12]	9.057 (21.6)[13]
Cyclohexanol	0.01	9.233 —	9.619 (88.3)[14]	10.0 (133.3)[14]	10.447 (208.3)[14]

a) PCC oxidation data in parentheses.

Table 5. Activation parameters for the oxidation of alcohols by pyridinium fluorochromate

Substrate	ΔH^*/kJ mol^{-1} [a]	$-\Delta S^*$/J mol^{-1} K^{-1} [a]	ΔF^*/kJ mol^{-1} [a]
Ethanol	7.657(51.8)[13]	280.51(153)[13]	92.65(98.2)[13]
Benzyl alcohol	3.89 (54.7)[12]	291.33(125)[12]	92.06(92.0)[12]
Cyclohexanol	6.127(93.0)[14]	282.98(−18)[14]	91.82(87.4)[14]

a) PCC oxidations data in parentheses.

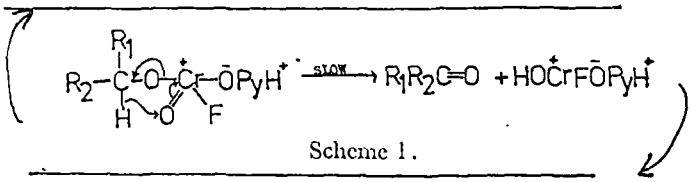
has been observed (Table 2) and a plot of log k_{obsd} against log [substrate] shows that the rates increase in very small fractions with the sequential increase in substrate concentration. This most probably implies that complex formation between the substrate and oxidant is taking place in present cases.

Our attempts to study the acid-catalyzed oxidations of the three alcohols were unsuccessful. Attempted acid-catalyzed reactions involving *p*-Toluenesulfonic acid or benzoic acid, and varying proportions of solvent compositions were observed to be too fast to measure the rate.

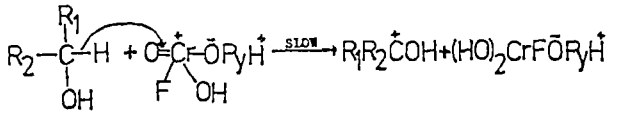
The results of uncatalyzed reactions with varying composition of the solvent components (Table 3) shows that the reaction rate decreases with increase in dielectric constant (though small) of the medium suggesting that the more polar solvents may require larger reaction times for the oxidation reactions. A plot of log k_1 against the inverse of dielectric constants of the media is a straight line with positive slope and implies the occurrence of an interaction between a dipole and a positive ion,[15] and also indicates the probable involvement of a protonated Cr^{VI} species, in the presence of an acid, in the rate determining step. However, since the range of dielectric constants varies between 35.6 and 36.7 showing a large increase in the rate, the observed change could as well be solvent specific rather than owing to the effect of change in dielectric constant.

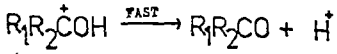
The near constancy of the values of the free energies of activation of the three reactions (Table 5) suggest that a similar mechanism is operative in each of the three oxidations. Free energies of the acid-catalyzed reactions appear to be lower, as there has been a pronounced increase in the rate of catalyzed reactions suggesting thereby that a protonated Cr^{VI} species may be involved in the rate determining step in the presence of an acid. This is in accord with the involvement of such species well established in chromium(VI) oxide oxidations.[16]

The large negative entropy values obtained in the present studies, suggest that the solvent molecules are strongly oriented or 'frozen' around the ions thereby resulting in the loss of entropy,[17] the effect being larger in nonpolar solvents. This conforms to the contention that the decrease of polarity of the medium results in increase of the entropy value and the number of unbound molecules in the solution increases.[18] This also accounts for the lowering of rate coefficient values with increasing polarity of the medium. Comparatively greater reactivity of pyridinium fluorochromate (PFC) over that of the corresponding chlorochromate (PCC), as shown in our previous paper,[7] can now be understood from the relatively higher negative entropy values of the reactions. We believe that the bonding of F with chromium in PFC facilitates larger charge distribution in the transition state in the cases of PFC oxidation and correlates well with the observed entropy values.



Scheme 1.





Scheme 2.

In view of the above results it appears that a hydride transfer mechanism is involved in the rate determining step of the PFC oxidations. It is possible that the hydride transfer may take place either through the prior formation of chromate (Scheme 1), or directly (Scheme 2). The present data also suggest, like the similar oxidations involving chromic acid,[16] a chromate formation in the rate-determining step (Scheme 1) although the chances of Scheme 2 can not be totally ruled out. It is also expected that the chromate intermediate will be better stabilised in the less polar medium and will enhance the oxidation rate, thus conforming to the observations made by us.

The authors wish to thank the University for the award of a fellowship (U. G. C.) to one of them (M. N. B.) and also to Dr. A. K. Sil, for his interest in the work.

References

1) J. C. Collins and W. W. Hess, *Org. Synth.*, **52**, 5, (1972).
2) E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, **1975**, 2647.
3) E. J. Corey and D. L. Boger, *Tetrahedron Lett.*, **1978**, 2461.
4) G. Piancatalli, A. Scettri, and M. D'Auria, *Synthesis*, **1982**, 245.
5) E. J. Corey and G. Schmidt, *Tetrahedron Lett.*, **1979**, 399.
6) F. S. Guziec and F. A. Luzzio, *Synthesis*, **1980**, 691.
7) M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta N. Roy, and D. T. Khathing, *Synthesis*, **1982**, 588.
8) D. D. Perrin, W. L. Armarego, and D. R. Perrin, "Purification of Organic Compounds," Pergamon Press, Oxford (1966).
9) C. N. R. Rao, "A Handbook of Chemistry and Physics," Affiliated East-West Press, New Delhi (1967), p. 169.
10) G. V. Bakore, K. K. Banerjee, and R. Shanker, *Z. Phys. Chem. (Frankfurt)*, **45**, 129 (1965).
11) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley-Eastern, New Delhi (1970), p. 99.
12) K. K. Banerjee, *J. Chem. Soc., Perkin Trans.* 2, **1978**, 639.
13) K. K. Banerjee, *Bull. Chem. Soc. Jpn.*, **51**, 2732, (1978).
14) G. P. Panigrahi and D. D. Mahapatra, *Indian J. Chem.*, **19A**, 579, (1980).
15) E. S. Amiss, "Solvent Effects on Reaction Rates and Mechanism," Academic Press, New York (1967), p. 42.
16) K. B. Wiberg, "Oxidation in Organic Chemistry," Academic Press, New York (1965), Part A, p. 99.
17) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reaction: A Study of Metal Complexes in Solution," 2nd ed, Wiley-Eastern, New Delhi (1973), p. 129.
18) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley-Eastern, New Delhi (1976), p. 169.