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

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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

Mihir Kanti Chaudhuri
Signature of the Supervisor

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

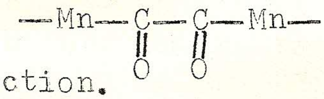
The thesis comprises of two parts and has altogether ten Chapters. While Chapters 1 to 8, based on the studies of synthesis and structural assessment of compounds of manganese +(III) and manganese +(II), constitute Part I of the thesis, Part II, consisting of two Chapters (chapters 9 and 10), contains 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 °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 °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 <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-fluorooxalato-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  $-Mn-\underset{\overset{\|}{O}}{C}-\underset{\overset{\|}{O}}{C}-Mn-$ 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 <u>Chapter 5</u>. 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), $A[MnF(C_2O_4)]$, 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.

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.