Synthesis, Structural Assessment and Reactivity Studies on Some Schiff base and Mixed-Ligand-Fluoro Complexes of Manganese(III)

Abstract

The present thesis deals with the results of studies involving the syntheses, assessment of structures and physico–chemical studies of some mixed-ligand fluoro complexes of manganese(III) and synthesis, structural assessment and reactivity studies of mono and binuclear manganese(III) Schiff base complexes. The thesis comprises of a total of seven chapters. The results described in chapters 3-6, deals with the studies on mixed-ligand fluoro complexes of manganese(III), while chapter 7 deals with the results of studies on manganese(III) Schiff base chemistry.

**Chapter 1** presents a brief introduction pertaining to the work embodied in the thesis. The importance of and the interest in the studies of manganese(III) chemistry in general, and mixed-ligand fluoro and Schiff base complexes of manganese(III) in particular, are highlighted in this chapter. The problem encountered in stabilizing manganese(III) in aqueous medium, and the importance of fluoride ligand in stabilizing this particular oxidation level of the metal both in solution as well as in solid state have been accentuated in this chapter. Peculiarities encountered with structure and properties of some mixed-ligand fluoro and carboxylato complexes of manganese(III) are highlighted. This chapter also incorporates the importance of work on chosen aspects of manganese(III)-Schiff base chemistry.

**Chapter 2** describes the details of the methods of elemental analyses, and the instruments / equipment used for characterization, structural assessment and reactivity studies of the newly synthesized compounds.

Stabilization of manganese(III) in aqueous medium. Synthesis, spectral characterization and structural assessment of new mixed-ligand fluoromanganate(III) containing hydroxy carboxylic, dicarboxylic acids as co-ligands constitute the subject matter of **Chapter 3**.

The synthesis of alkali-metal or ammonium tetrafluoro(lactato)manganate(III), $A_2\text{[Mn-F}_4\text{(L)}] \quad (L=\text{lactate, } C_3H_5O_3\text{; } A=\text{Na, K, NH}_4)$, alkali-metal tetrafluoro(malato)manga-
nate(III), $A_2[\text{MnF}_4(L)]$ ($L=$ malate, $C_4H_5O_4^-$; $A=\text{Na}$ or $\text{K}$), potassium tetrafluoro(citrate)manganate(III), $K_2[\text{MnF}_4(L)]$ ($L=$ citrate, $C_6H_7O_7^-$) and alkali-metal or ammonium tetrafluoro(malonato)manganate(III)monohydrate, $A_3[\text{MnF}_4(L)].H_2O$ ($L=$ malonate, $C_3H_2O_4^{2-}$; $A=\text{Na}$, $\text{K}$ or $\text{NH}_4$) were achieved from aqueous medium by the reaction of $\text{MnO(OH)}$, 40% HF with corresponding co-ligand in presence of alkali metal carbonate, $A_2\text{CO}_3$ ($A=\text{Na}$, $\text{K}$ or $\text{NH}_4$) maintaining the molar ratio of $\text{MnO(OH)}$: HF: co-ligand: $A_2\text{CO}_3$ as 1:4:1:1 at pH~2. Compounds have been characterized on the basis of chemical analyses, chemical determination of oxidation state of manganese, FTIR, electronic spectroscopic studies, magnetic moment measurements, TGA/DTA, SEM, EDX and by cyclic voltammetry. The newly synthesized complexes are stable in solid state in absence of moisture. The infrared spectra provide evidence for the occurrence of coordinated fluoride and coordinated co-ligand viz. lactate, malate, citrate and malonate. Further the IR spectra suggest that the co-ligand, lactate is bonded to the manganese(III) centre by monodentate carboxylate group and hydroxyl oxygen in overall bidentate fashion. In case of co-ligands malate and citrate bidentate coordination to the metal centre are achieved by involving one of their carboxylate group and the hydroxyl oxygen atom respectively. Whereas in case of malonato complex, both the carboxylate groups of malonate are bonded in monodentate manner giving rise to overall bidentate coordination of the co-ligand. The room temperature magnetic moment values for the complexes lie in the range 4.7 to 5.1 B.M. in conformity with the presence of manganese(III) ion in each of the newly synthesized complexes. The electronic spectra of the compounds suggest that the newly synthesized complexes possess distorted octahedral structures. The scanning electron microscopy (SEM) data show that the surface layers of these complexes are having almost similar morphology and are homogeneous in nature. Energy dispersive X-Ray spectra (EDX) have shown Mn, F, C, O, K, Na, N etc. as the constituent elements of the newly synthesized compounds. Cyclic voltammogram of the malonato complexes in aqueous solution exhibit irreversible redox behaviour due to $\text{Mn(III)}/\text{Mn(II)}$ couple. Aqueous solution of potassium tetrafluoro(citrate)manganate(III),$K_2[\text{MnF}_4(L)]$ ($L=$ citrate, $C_6H_7O_7^-$) complex on treatment with aqueous $\text{H}_2\text{O}_2$ (30%) show effervescence due to liberation of molecular oxygen and subsequently reduced to manganese(II) species.
Chapter 4 of the thesis provides an account of synthesis, characterization, crystal structure and studies of fluorescent properties of polymeric tartrato complex of bivalent manganese. Tartrato bridged polymeric complex of bivalent manganese,\[\text{[Mn}_2\text{(C}_4\text{H}_4\text{O}_6)_2\text{(H}_2\text{O})]\text{2.71 H}_2\text{O}}\] has been synthesized by reacting a freshly prepared aqueous suspension of MnO(OH), 40% HF and tartaric acid in presence of Na\textsubscript{2}CO\textsubscript{3} in stoichiometric amounts of 1: 4: 1: 0.5 in ice-cold condition, which resulted in the formation of an intense brown colour solution. Addition of equal volume of pre-cooled acetone (~20 cm\textsuperscript{3}) to the reaction mixture led to the separation of pink microcrystalline products. The pink microcrystalline product on dissolution in cold water and on standing at room temperature for a period of ca.4-5 days gave diffraction quality reddish brown single crystals of polymeric tartrato complex of bivalent manganese, \[\text{[Mn}_2\text{(C}_4\text{H}_4\text{O}_6)_2\text{(H}_2\text{O})]\text{2.71H}_2\text{O}}\]. Elemental analyses, chemical determination of oxidation state of manganese, FTIR and electronic spectral studies of the intermediate pink microcrystalline compound obtained on addition of acetone indicate the existence of manganese(III)-fluoro-tartrato species with approximate stoichiometry between manganese and fluoride as 1:3. The EDX spectra of the pink microcrystalline product also show the presence of manganese and fluorine in the material. The reddish brown crystalline polymeric tartrato manganese(II) complex has been characterized by elemental analyses, FTIR, electronic spectra, room temperature magnetic susceptibility measurement and on the basis of single crystal X-ray diffraction studies. Infrared spectrum show the characteristic absorptions due to antisymmetric and symmetric vibrations of coordinated carboxylato group, characteristic ν(CO) of coordinated hydroxyl moiety of tartrato ligand and absorption due to lattice water. Compound, \[\text{[Mn}_2\text{(C}_4\text{H}_4\text{O}_6)_2\text{(H}_2\text{O})]\text{2.71 H}_2\text{O}}\] show effective magnetic moment of 5.52 B.M. at room temperature. Single crystal X-Ray diffraction analysis reveals that compound, \[\text{[Mn}_2\text{(C}_4\text{H}_4\text{O}_6)_2\text{(H}_2\text{O})]\text{2.71H}_2\text{O}}\text{ is polymeric in nature, and crystallizes in monoclinic space group P2\textsubscript{1}}\text{. The polymeric structure of the complex consists of corrugated sheets of dimeric [Mn}_2\text{((R,R)-C}_4\text{H}_4\text{O}_6)_2\text{(H}_2\text{O})\text{]}\text{ units and 2.71 water molecules. Three dimensional structures are attained by stacking of corrugated polymeric sheets of dinuclear unit and water molecules. Solid state fluorescence spectrum of the compound at room temperature displayed emissions at 420, 495 and at 575 nm upon excitation at}
275 nm and ascribed to ligand to metal charge transfer transition (LMCT) and intra metal d-d transitions respectively. The compound may find use as fluorescent material.

Synthesis, spectral characterization and assessment of structures of a number mixed-ligand fluoro manganese(III) complexes containing amino acids as co-ligands, form the subject matter of chapter 5. The new mixed-ligand fluoromanganate(III) complexes containing amino acids viz. aspartic acid, glutamic acid, proline, histidine or cysteine as co-ligands have been synthesized from aqueous medium from the reaction of freshly prepared MnO(OH), 40% HF with corresponding co-ligand in ratio of 1:4:1 at pH ~3 in presence of alkali metal carbonate, A₂CO₃ (A=Na, K or NH₄)/ alkali metal hydroxide, AOH (A= Na, K or NH₄). Complexes have been precipitated by addition of pre-cooled acetone to the reaction mixtures. The compounds are generally stable in solid state, however, undergo slow decomposition in aqueous solution and are practically insoluble in common organic solvents. The compounds have been characterized by chemical analyses, chemical determination of oxidation state of manganese, magnetic susceptibility measurements, FTIR and electronic spectroscopic studies. For some of the selected complexes TGA/DTA and electro chemical studies were also performed.

Infrared spectra of the compounds displayed pattern typical of coordinated amino acids and fluoride ligand. Chemically determined oxidation state of manganese lie between 2.9 to 3.1. The complexes have normal magnetic moments in conformity with the occurrence of high spin d⁴ manganese(III) in each of them. The electronic spectra of the complexes suggest an appreciable splitting of ^5E_g ground state of manganese(III), leading to distorted octahedral structures of the complexes. TGA/DTA data of the complexes agree well with the proposed formulations. Cyclic voltametric study of A₂[MnF₄(L)(H₂O)] (L=proline, A=K) in aqueous solution exhibit quasi-reversible behaviour due to Mn(III)/ Mn(II) couple.

Reported in Chapter 6 synthesis, characterization and physico-chemical studies of molecular mixed-ligand fluoro complexes of manganese(III), namely [Mn(Py)₂F₃(H₂O)], 1, (Py=pyridine); [Mn(en)F₃(H₂O)].3H₂O, 2, (en=ethylenediamine), and [Mn(Imd)₂F₃(H₂O)], 3, (Imd =imidazole).
The compounds were synthesized in aqueous medium from the reaction of a solution of freshly prepared MnO(OH) in 40% HF with pyridine, ethylenediamine or imidazole respectively, maintaining the molar ratio among MnO(OH), HF and the N-donor ligands as 1:4:1. The pH of the reaction was maintained at ca.6 by addition of solid sodium carbonate, Na₂CO₃. The compounds are stable in the solid state in absence of moisture. Characterization of the compounds were made from the results of elemental analyses, chemical determination of the oxidation state of the metal, magnetic susceptibility measurements, infrared and electronic spectroscopic studies. While ethylenediamine occur as bidentate ligand, pyridine and imidazole act as monodentate ligands in the respective compounds. The compounds [Mn(Py)₂F₃(H₂O)], 1, (Py=pyridine); [Mn(en)F₃(H₂O)].3H₂O, 2, (en=ethylenediamine), and [Mn(Imd)₂F₃(H₂O)], 3, (Imd=imidazole) exhibit normal magnetic moments (4.82 to 5.1 B.M.) at room temperature in conformity with the occurrence of high spin manganese(III) in each of them. The complexes are likely to have distorted octahedral structures. TGA/DTA data of [Mn(en)F₃(H₂O)].3H₂O, 2, (en=ethylenediamine) agree with the formulation of the compound.

**Chapter 7** indeed the last chapter, deals with synthesis, characterization, structural elucidation and reactivity studies of mono and binuclear Schiff base complexes of manganese(III).

Two new mononuclear Schiff base complexes viz. [Mn(L¹)(CH₃COO)(H₂O)]₂ and [Mn(L²)(CH₃COO)₂(H₂O)]₂, have been synthesized by reacting manganese(III) acetate with the corresponding Schiff base in methanol solution. Tridentate Schiff base H₂L¹ was obtained by condensation of salicylaldehyde and para aminobenzoic acid, while H₂L² was derived from condensation of acetyl acetone with para aminobenzoic acid.

In addition to the mononuclear complexes, five new phenoxy bridged binuclear Schiff base complexes of manganese(III), [MnL³X]₂ with tetratdentate Schiff base, H₂L³ [H₂L³=N,N'-O-phenylene bis(salicylaldimine)] containing anionic ligands, X [X=NCO⁻, C₆H₅COO⁻, 4-(OH)C₆H₄COO⁻, 4-(NH₂)C₆H₄COO⁻ and 3,5-(O₂N)₂C₆H₃COO⁻] have been synthesized from reaction of manganese(II)acetate, Schiff base, H₂L³ and the corresponding anionic ligand in methanol medium. Schiff base, H₂L³ was obtained
insitu in the reaction medium by condensation of salicylaldehyde and o-phenylenediamine in aqueous methanol.

The ligands $H_2L^1$ and $H_2L^2$ were obtained as yellow microcrystalline solids and characterized by elemental analyses, FTIR and by $^1H$ NMR spectroscopy. However, ligand $H_2L^3$, generated in situ in the reaction medium and was not isolated in the solid state. Mono as well as binuclear Schiff base complexes were characterized on the basis of elemental analyses, molar conductance measurements, FTIR, room temperature magnetic susceptibility measurements and electronic spectroscopic studies. Structure of one of the binuclear complex viz. $[\text{Mn}(L^3)(\text{NCO})]_2$ was assessed by single crystal X-ray diffraction studies.

IR spectra of $[\text{Mn}(L^1)(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ show characteristic absorptions due to coordinated azomethine nitrogen and phenolic oxygen and the carboxylate group. In case of $[\text{Mn}(L^2)(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$ infrared spectral data suggest bidentate coordination of $H_2L^2$ through its imino nitrogen and carboxylate oxygen respectively. IR data also show the existence of coordinated acetato group. In both monomeric complexes coordination of water molecule was also ascertained from infrared spectra. The IR Spectra of binuclear complexes, $[\text{Mn}(L^3)X]_2$ ($X=\text{NCO}^−$, $C_6H_5\text{COO}^−$, 4-$(\text{OH})C_6H_4\text{COO}^−$, 4-$(\text{NH}_2)C_6H_4\text{COO}^−$, 3,5-$(\text{O}_2\text{N})_2C_6H_3\text{COO}^−$) show characteristic absorptions due to coordinated azomethine nitrogen and phenolic oxygen atoms of the Schiff base. In addition, IR Spectra of the compounds also suggest coordination of the anionic ligands namely $\text{NCO}^−$, $C_6H_5\text{COO}^−$, 4-$(\text{OH})C_6H_4\text{COO}^−$, 4-$(\text{NH}_2)C_6H_4\text{COO}^−$, 3,5-$(\text{O}_2\text{N})_2C_6H_3\text{COO}^−$ in the respective complexes. A consistent appearance of a band at ca.755cm$^{-1}$ in all the binuclear complexes is assigned to vibration due to (Mn-O-Mn) moiety originated from interactions of phenoxy oxygen and manganese atoms, resulted in dimeric structure of the complexes. Room temperature magnetic moment values for mononuclear complexes being 5.1 and 5.2 B.M., which are normal as expected for the existence of high spin $d^4$ system of manganese(III). The observed magnetic moment values for the binuclear complexes lie in the range 4.74-4.91 B.M. per manganese centre and support the presence of manganese(III) ion in each of the newly synthesized complexes. Single crystal X-Ray diffraction studies of $[\text{Mn}(L^3)\text{NCO}]_2$ reveals that the
compound crystallizes in monoclinic space group P2\(_1\)/c and contains binuclear manganese entity, wherein two centrosymmetrically related five coordinated metal centers are held by weak phenoxy bridges and the axial position is occupied by nitrogen atom of NCO\(^-\) group which is disordered in two positions with occupancy ratio of 0.697: 0.303. The overall co-ordination geometry around each of the manganese atom is distorted octahedral. Intermolecular hydrogen bonding interactions is operative in the crystal lattice, results in the formation of three dimensional hydrogen bonded supramolecular network. Redox behaviour of the synthesized complexes were ascertained from cyclic voltametric studies. The Schiff base complexes, [Mn(L\(^3\))X\(_2\)] (X=NCO\(^-\), 4-(NH\(_2\))C\(_6\)H\(_4\)COO\(^-\), 3,5-(O\(_2\)N)\(_2\)C\(_6\)H\(_3\)COO\(^-\)) have demonstrated their catalytic potentials in oxidizing selective organic substrates namely cyclohexene and styrene by hydrogen peroxide as the oxidant. The oxidized products were characterized as trans-cyclohexane 1, 2- diol and styrene epoxide respectively.

The results of studies described in chapter 3 have been published and those described in chapters 4, 5, 6 and 7 are under communication.

**Chapter 3**


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**Chapter 7**

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