PART B
CHAPTER 6
Chapter 6

Direct Synthesis of Potassium Tris(oxalato)manganate(III) Trihydrate, $K_3\text{Mn}(C_2\text{O}_4)_3\cdot3\text{H}_2\text{O}$, and Evidence for the Existence of $\text{Mn}(C_2\text{O}_4)_3\cdot3\text{H}^+$ in Solutions in the Presence of Countercations like $\text{Na}^+$, $\text{Rb}^+$, $\text{Cs}^+$ or $\text{NH}_4^+$

The compound Potassium tris(oxalato)manganate(III) trihydrate, $K_3\text{Mn}(C_2\text{O}_4)_3\cdot3\text{H}_2\text{O}$, is known for quite some time. As mentioned in Chapter 1, this compound is particularly interesting because it has served as a very oft-quoted example whenever the subject of inorganic photochemistry is discussed. However, the literature method of synthesis of the title compound poses some problems. The method involving the reaction of $\text{KMnO}_4$ with oxalic acid and $K_2C_2\text{O}_4$ in the presence of an excess of $K_2\text{CO}_3$ is universally accepted for the synthesis of $K_3\text{Mn}(C_2\text{O}_4)_3\cdot3\text{H}_2\text{O}$. This method not only requires very careful manipulation, but also it uses an excess of potassium carbonate, $K_2\text{CO}_3$, in order to control the pH. The chances of contamination of the end product, owing to the use of $K_2\text{CO}_3$ in such quantities, cannot be ruled out. Our contention was to develop a new synthetic

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route leading to the above-mentioned compound, and also to explore the possibility of synthesis of various other salts of the complex ion \( \left[ \text{Mn}\left(C_2\text{O}_4\right)_3 \right]^{3-} \) with countercations like \( \text{Na}^+ \), \( \text{Rb}^+ \), \( \text{Cs}^+ \) or \( \text{NH}_4^+ \).

It is shown in this Chapter that it is possible to synthesise potassium tris (oxalato)manganate(III) trihydrate, \( K_3\left[\text{Mn}\left(C_2\text{O}_4\right)_3\right]^{3-}3\text{H}_2\text{O} \) in a more nearly quantitative way directly from \( \text{MnO(OH)} \) without making use of any buffer. It will also be shown that \( \left[\text{Mn}\left(C_2\text{O}_4\right)_3\right]^{3-} \) can exist in solutions in the presence of countercations like \( \text{Na}^+ \), \( \text{Rb}^+ \), \( \text{Cs}^+ \) or \( \text{NH}_4^+ \).

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**Experimental**

The chemicals used were all reagent grade products (Sarabhai M., Glaxo, S.D's, E. Merck).

The compound \( \text{MnO(OH)} \) was prepared by the oxidation of \( \text{Mn(OH)}_2 \) with hydrogen peroxide. In a typical preparation, a solution of 2.2g (10 mmol) \( \text{MnSO}_4\cdot4\text{H}_2\text{O} \) in 350 cm\(^3\) of water was treated with 34 cm\(^3\) of a 3% \( \text{H}_2\text{O}_2 \) (30 mmol) solution. An amount of 50 cm\(^3\) of a 0.2M ammonia solution (10 mmol) 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 vacuum.
Synthesis of Potassium Tris(oxalato)manganate(III) Trihydrate,
\[ K_3 \left[ \text{Mn} (C_2O_4)_3 \right] \cdot 3H_2O \]

To a water suspension (20 cm\(^3\)) of 0.89g (10.1 mmol) of MnO(OH) was added a concentrated solution of 2.82g (15.3 mmol) of K\(_2C_2O_4\). The mixture was cooled in an ice bath for ca 15 min, followed by addition of concentrated solution of 1.93g (15.3 mmol) of oxalic acid and the whole was stirred for ca 50 min in an ice bath. The solution, which became cherry-red, was filtered quickly, and an excess of precooled (\(\sim 0^\circ C\)) ethanol (about 1/1 v/v) was added with stirring to obtain the cherry-red \(K_3 \left[ \text{Mn} (C_2O_4)_3 \right] \cdot 3H_2O\). The microcrystalline compound was isolated by quick filtration, washed twice with precooled ethanol, and finally dried in vacuo in the absence of light.

The yield of \(K_3 \left[ \text{Mn} (C_2O_4)_3 \right] \cdot 3H_2O\) was 3.1g (62.5%).

Attempted Preparation of Solid \(A_3 \left[ \text{Mn} (C_2O_4)_3 \right] \cdot 3\) (A = Na, Rb, Cs or \(NH_4\)). Evidence for the Existence of \(\left[ \text{Mn} (C_2O_4)_3 \right]^{-3}\) in Solutions in the Presence of \(Na^+\), \(Rb^+\), \(Cs^+\) or \(NH_4^+\)

The reaction of MnO(OH), alkali-metal or ammonium oxalate, \(A_2C_2O_4\) (A = Na, Rb, Cs or \(NH_4\)), and oxalic acid in the mole ratio 1:1.5:1.5 were carried out in a manner analogous to that described above under the synthesis of potassium tris(oxalato)manganate(III) trihydrate. In each case cherry-red solution was obtained which was found to be stable at ca 0°C in
the dark for a period of at least 7 days. The electronic spectrum of each of the solutions showed characteristic maximum absorption at ca. 19,050 cm\(^{-1}\) providing evidence for the existence of the complex species \(\text{L}_2\text{Mn(C}_2\text{O}_4)_3\text{L}^{-3}\). 

Attempts to isolate \(\text{A}_3\text{L-Mn(C}_2\text{O}_4)_3\text{L}\) (A = Na, Rb, Cs or \(\text{NH}_4\)) in the solid state either by the addition of ethanol or by slow concentration at ca. 0°C under reduced pressure in the dark have resulted in the formation of white decomposition products.

**Elemental Analyses**

Manganese, oxalate, and potassium contents were determined by the methods described in Chapter 2.

Analytical data of \(\text{K}_3\text{L-Mn(C}_2\text{O}_4)_3\text{L}\cdot3\text{H}_2\text{O}\):

- Found: K, 23.81; Mn, 11.41; \(\text{C}_2\text{O}_4\), 53.76.
- Calcd. for \(\text{K}_3\text{L-Mn(C}_2\text{O}_4)_3\text{L}\cdot3\text{H}_2\text{O}\): K, 23.92; Mn, 11.21; \(\text{C}_2\text{O}_4\), 53.86.

Estimated oxidation state of Mn, 3.0;

\(\mu\text{eff} = 4.92 \mu_B\)

**Chemical Determination of the Oxidation State of Manganese**

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

In order to overcome the difficulties involved in the synthesis of the classic oft-quoted, potassium tris(oxalato)manganate(III) trihydrate, $K_3 \text{Mn}(C_2O_4)_3 \cdot 3H_2O$, a direct method has now been improvised. The new method involves two steps. First, the reaction of $\text{MnO(OH)}$ with $1:1.5:1.5$ stoichiometric amounts of $H_2C_2O_4$ and $K_2C_2O_4$ leading to the synthesis of $K_3 \text{Mn}(C_2O_4)_3 \cdot 3H_2O$ in solution.

$$\text{MnO(OH)} + 1.5 \ H_2C_2O_4 + 1.5 \ K_2C_2O_4 \rightarrow K_3 \text{Mn}(C_2O_4)_3 \cdot 3H_2O + 2H_2O$$

Second, isolation of $K_3 \text{Mn}(C_2O_4)_3 \cdot 3H_2O$ in the solid state by the addition of ethanol, which facilitated precipitation. The strategy for the present synthesis was that $\text{MnO(OH)}$ would react with oxalic acid to generate $\text{Mn}^{3+}$, which would be trapped immediately by the $C_2O_4^{2-}$ ions, arising out of $H_2C_2O_4$ and $K_2C_2O_4$, affording the complex $K_3 \text{Mn}(C_2O_4)_3 \cdot 3H_2O$ in the presence of $K^+$. The method is rapid, giving potassium tris(oxalato)manganate(III) trihydrate, $K_3 \text{Mn}(C_2O_4)_3 \cdot 3H_2O$ in a higher yield than the earlier method.

The pink crystalline $K_3 \text{Mn}(C_2O_4)_3 \cdot 3H_2O$ is stable only in the dark. In the presence of light it decomposes to a white product, a property which is typical of the compound. The chemically estimated oxidation state of manganese was found to be $3.0$ in accord with the notion that the metal occurs
in its +3 state. The room temperature magnetic susceptibility measurement yielded a value of the magnetic moment of 4.92 \( \mu_B \) in conformity with that reported in the literature.\(^1\) The IR spectrum of the compound is unambiguous and shows the characteristics of chelated oxalato groups.\(^4\) The electronic spectra of a solution of \( K_3\left[\text{Mn(C}_2\text{O}_4)\right]_3\) showed the maximum absorption, a characteristic of the \( \left[\text{Mn(C}_2\text{O}_4)\right]_3^{3-} \) ion, at 19050 cm\(^{-1}\), while the reflectance spectrum showed a broad band at 9200, a shoulder at 19050, and a peak at 20500 cm\(^{-1}\) assigned\(^5\) to the transitions \( {^5}B_{1g} \rightarrow {^5}A_{1g} \), \( {^5}B_{1g} \rightarrow {^5}B_{2g} \), and \( {^5}B_{1g} \rightarrow {^5}E_g \), respectively, lending support to the identity of the compound.

Reactions of \( \text{MnO(OH)} \) with \( \text{A}_2\text{C}_2\text{O}_4 \) (\( \text{A} = \text{Na}, \text{Rb}, \text{Cs} \) or \( \text{NH}_4 \)) and \( \text{H}_2\text{C}_2\text{O}_4 \) gave a cherry-red solution, stable at ca 0°C in the dark, showing the electronic spectral absorption at 19050 cm\(^{-1}\), and allowing to infer the formation and existence of the \( \left[\text{Mn(C}_2\text{O}_4)\right]_3^{3-} \) ion. However, attempts to isolate the corresponding compounds in the solid state resulted in the formation of white decomposition products.

To control photochemical decomposition, it was expected that the stability of the Mn(III) - oxalate system could be enhanced by the presence of \( \text{F}^- \) ions, since fluoro-manganates(III) are stable. It was observed by a co-worker\(^6\) of our laboratory, in line with the contention, that addition
$K_3\left[Mn\left(C_2O_4\right)_3\right] \cdot 3H_2O$
of 40% HF to the afore-mentioned reaction greatly increased the
stability of the solutions as evidenced by their unaltered
colour at **ca.** 20°C in light. Accordingly, the reaction of
MnO(OH) with 40% HF and $A_2C_2O_4$ ($A = \text{Na, K, or NH}_4$) in the
ratio of $\text{MnF}^+:C_2O_4^{2-}$ at 1:4-5:1 at any temperature between
0 and 20°C gave a pink solution from which the deep pink
microcrystalline $A_2 [\text{MnF}_3(C_2O_4)]$ was isolated by the
addition of ethanol.

Thus it appears from the present studies that the
classic oft-quoted $K_3 [\text{Mn}^3(C_2O_4)_3] \cdot 3H_2O$ can be synthesised
in a high yield directly from MnO(OH) without making use
of any buffer. The tris(oxalato)manganate(III) anion,
$[\text{Mn}^3(C_2O_4)_3]^{3-}$ can exist in solutions in the presence of
countercations like Na$^+$, Rb$^+$, Cs$^+$ and NH$_4^+$, but these salts
are not capable of being isolated in the solid state.
Manganese(III)—oxalate system can, however, be stabilised
by fluoride ions.
References


CHAPTER 7
New Mixed-Ligand Fluoro Complexes of Manganese(III). Synthesis and Assessment of Structure of Complexes of the Types

\[ A_3 \left[ \text{MnF}_2 \text{L}_2 \right] \cdot 3\text{H}_2\text{O} \] (L = C\(_2\)O\(_4\)^{2-}, A = K; L = HPO\(_4\)^{2-}, A = Na, K or NH\(_4\)) and A \[ \left[ \text{MnF}_4 \text{L}_n \right] \cdot 3\text{H}_2\text{O} \] (L = EDTA, n = 1, A = K; L = glyH, n = 2, A = Na, K or NH\(_4\))

It has been emphasized in the literature\(^{1-4}\) and also in Chapter 6 of the thesis that fluoride ions can act as stabilizing ligands for tripositive manganese, and fluoromanganates(III) exhibits interesting structural and magnetic properties.\(^{5,6}\)

Consequently this has generated a considerable interest in studies involving synthesis and structural aspects of fluoromanganates(III) over the years.\(^{7-19}\) In contrast, information on mixed-ligand fluoro complexes of manganese(III) are restricted to only few reports.\(^{20-23}\) Mixed-ligand complexes may be important particularly because a combination of suitable ligands might lead to a sharp increase in the stability of Mn(III) in solutions as well as in the solid state. Further, a marked variation in magnetic properties of the mixed-ligand complexes may also be expected since some of the binary fluoromanganates(III) display strong antiferromagnetism whereas other manganese(III) complexes, in general, have straightforward magnetic behaviour.
Recently,\textsuperscript{22} it has been shown that the stability of Mn(III)--oxalate system can be enhanced to a large extent by the partial replacement of oxalate ligands in the complex $\mathrm{Mn(C_2O_4)_3}^{3-}$ ion by $\mathrm{F}^-$ ligands leading to the formation of a stable mono(oxalato)trifluoromanganate(III) species $\mathrm{MnF_3(C_2O_4)}^-$. The magnetic properties of the mixed-fluoro(oxalato)manganates(III), $\mathrm{A_2MnF_3(C_2O_4)}$ were found to be similar to those of $\mathrm{A_2MnF_3(SO_4)}$, but different from both the binary oxalatomanganates(III) and the binary fluoro-manganates(III). In this context it appeared interesting to see the effect of replacing one $\mathrm{C_2O_4}^{2-}$ ligand by two $\mathrm{F}^-$ ligands in the complex ion $\mathrm{Mn(C_2O_4)_3}^{3-}$. A survey of literature reveals that information regarding the dioxalatomanganates(III) is very scanty,\textsuperscript{24,25} apparently owing to instability of such complexes. Similarly, the EDTA (ethylenediamine-tetraacetic acid) complex of Mn(III) is known\textsuperscript{26} to be unstable against heat and light. It was thought that introduction of some $\mathrm{F}^-$ ligands in the coordination sphere of Mn(III) would result into the formation of stable mixed-fluoro-EDTA complex of tripositive manganese. Coordination compounds of transition metals containing orthophosphate ion as the ligand have not been investigated in detail. The multivalent nature of orthophosphate ion and its potential for multidentate coordination were expected to show an interesting variety of coordination modes. It has been reported\textsuperscript{27} that acid orthophosphate
The complex of Mn(III) is known only in solution, although the olive green MnPO₄·H₂O species is well characterised. It may therefore be anticipated that fluoride ion will contribute significantly in stabilizing acid orthophosphate-Mn(III) system providing means for the synthesis and related investigation of fluoro-acid phosphatomanganates(III).

As opposed to aminopolycarboxylate complexes of manganese(III), complexes containing aminomonocarboxylic acid, for instance, glycine (glyH) do not seem to have been studied by previous workers. Here again the problem of stabilization of Mn(III) by glyH alone may not be a reasonable proposition, however, there seems to be a finite possibility of formation of stable mixed-fluoro-glycine complexes of manganese(III).

In view of the above, a research programme aimed at synthesis and structural studies, of mixed-ligand fluoro-manganates(III) was chalked out. The present Chapter of thesis describes the first synthesis, characterization and structural assessment of potassium difluorobis(oxalato)manganate(III) trihydrate, K₃ sweepMn(C₂O₄)₂F₂·3H₂O, potassium tetrafluoro-(ethylenediaminetetraacetic acid)manganate(III) trihydrate, K sweepMn(EDTA)F₄·3H₂O, alkali-metal or ammonium difluorobis-(hydrogen orthophosphato)manganate(III) trihydrates of the type A₃ sweepMn(HPO₄)₂F₂·3H₂O (A = Na, K or NH₄), and alkali-metal
or ammonium tetrafluorobis(glycine)manganate(III) trihydrates
\[
\text{A Mn(glyH)}_2\text{F}_4\text{.3H}_2\text{O (A = Na, K or NH}_4\text{). An attempt has also been made in this Chapter to put in record of a set of internally consistent data concerning the effect of mixed-ligands on the magnetic properties of fluoromanganates(III).}
\]

**Experimental**

Reagent grade chemicals were used (Sarabhai M, Glaxo, E. Merck, S.D's).

The compound MnO(OH) was prepared by the oxidation of Mn(OH)_2 with hydrogen peroxide as described in Chapter 6.

(i) Synthesis of Potassium Difluorobis(oxalato)Manganate(III) Trihydrate, \[ K_3\text{Mn(C}_2\text{O}_4\text{)}_2\text{F}_2\text{.3H}_2\text{O} \]

To an aqueous solution (20 cm\(^3\)) of 1g (6.33 mmol) of KMnO\(_4\), kept in an ice-bath and protected from light, was added an aqueous solution of 3.2 (25.38 mmol) of oxalic acid (H\(_2\)C\(_2\)O\(_4\).2H\(_2\)O). The resulting solution was stirred in an ice-bath for ca 20 min followed by rapid filtration to remove any undissolved residue. To the cherry-red filtrate was added 0.74g (12.74 mmol) of solid potassium fluoride, KF and stirred for a further period of ca 20 min. An equal volume of pre-cooled (0°C) ethanol was added with continuous stirring. A very light pink microcrystalline product that precipitated out at this
stage was filtered off. To the cherry-red filtrate, again an excess of pre-cooled ethanol (twice the volume of the filtrate) was added to obtain the cherry-red coloured microcrystalline 
\[ K_3 \left[ \text{Mn(C}_2\text{O}_4)\right]_2\text{F}_2\cdot7\text{H}_2\text{O} \]. The compound was then isolated by quick filtration, washed twice with pre-cooled ethanol, and finally dried in vacuo over concentrated \( \text{H}_2\text{SO}_4 \) in the absence of light.

The yield of \( K_3 \left[ \text{Mn(C}_2\text{O}_4)\right]_2\text{F}_2\cdot7\text{H}_2\text{O} \) was 1.7g (61%).

(ii) Synthesis of Potassium Tetrafluoro(ethylenediaminetetraacetic acid)Manganate(III) Trihydrate, \( K \left[ \text{Mn(EDTA)}\right]_4\cdot7\text{H}_2\text{O} \)

Freshly prepared \( \text{MnO(OH)} \) was dissolved in 48% HF (2.5 cm\(^3\), 60.0 mmol of HF/0.89g, 10.11 mmol of \( \text{MnO(OH)} \)) and stirred for ca 10 min. The mixture was placed in an ice-bath; to it was added an aqueous solution of 2.96g (10.11 mmol) of ethylenediaminetetraacetic acid (EDTA, \( \text{H}_4\text{Y} \)) slowly with continuous stirring (EDTA was dissolved in water by the addition of 2-3 drops of 10% KOH solution). To the resulting deep pink solution was added 2.35g (40.45 mmol) of solid \( \text{KF} \) (Mn:KF as 1:4) and the solution thus obtained was stirred for a further period of ca 30 min in an ice-bath. The pH was found to be ca 2. The solution was filtered, to remove any undissolved residue, followed by the addition of an equal volume of diethylether to the filtrate with thorough stirring. The organic layer became red-pink in colour with the aqueous layer being practically
colourless. To the above mixture was added an equal volume of
a mixture of ethanol and acetone (1/1, v/v) and the whole was
kept in a freezer for ca 3h. A deep pink coloured oily mass
was formed which was separated by decantation. The oily mass
was treated 3-4 times with acetone, and finally dried in vacuo
to obtain the solid pink coloured \( \text{K Mn(EDTA)F}_4\cdot3\text{H}_2\text{O} \).

Starting from 0.89g of MnO(OH) the yield of
\( \text{K Mn(EDTA)F}_4\cdot3\text{H}_2\text{O} \) obtained was 1.35g (25.8%).

(iii) Synthesis of Difluorobis(hydrogen orthophosphato-)
Manganate(III) Trihydrates, \( \text{A}_3\text{Mn(HPO}_4\text{)}_2\text{F}_2\cdot3\text{H}_2\text{O} \)
(\( \text{A} = \text{Na}, \text{K or NH}_4 \))

To an aqueous suspension (25 cm\(^3\)) of 0.89g (10.11 mmol)
of MnO(OH) was added alkali-metal or ammonium fluoride,
AF (\( \text{A} = \text{Na}, \text{K or NH}_4 \)), with the maintenance of MnO(OH) to AF
ratio at 1:3, and the resulting mixture was stirred for ca 5 min.
To it was added 8 cm\(^3\) (142.9 mmol) of orthophosphoric acid,
\( \text{H}_3\text{PO}_4 \) (88-93\%, wt. per cm\(^3\) at 20°C, 1.75g), slowly with
continuous stirring to obtain a violet colour solution.
Stirring was continued, for a further period of ca 10 min.
To the violet solution, obtained as above, equal volumes
(in each case equal to that of the violet solution) of ethanol
and acetone were added with continuous stirring. This resulted
in the precipitation of pink-brown microcrystalline
The compound was separated by filtration, and purified by washing 3-4 times with acetone, and finally dried in vacuo over concentrated H₂SO₄.

The yields of Na₃\(\text{Mn(HP}_4\text{O)}_2\text{F}_2\cdot\text{3H}_2\text{O}\), K₃\(\text{Mn(HP}_4\text{O)}_2\text{F}_2\cdot\text{3H}_2\text{O}\), and (NH₄)₃\(\text{Mn(HP}_4\text{O)}_2\text{F}_2\cdot\text{3H}_2\text{O}\) were 2.2g (53%), 2.4g (52%), 2.1g (53%), respectively.

(iv) Synthesis of Ammonium and Alkali-Metal Tetrafluorobis-(glycine)Manganate(III) Trihydrates, A\(\text{Mn(glyH)}_2\text{F}_4\cdot\text{3H}_2\text{O}\),
(A = Na, K or NH₄)

An amount of 0.89g (10.11 mmol) of freshly prepared MnO(OH) was dissolved by the addition of 2.0 cm\(^3\) (40.0 mmol) of 40% HF, maintaining the molar ratio between MnO(OH) and HF at 1:4. The solution was stirred for ca 10 min followed by the addition of 1.52g (20.2 mmol) of glycine, keeping MnO(OH):glycine ratio at 1:2, and the resulting solution was stirred for a period of ca 15 min. To this was added a stipulated amount of A₂CO₃ (A = Na, K or NH₄) (MnO(OH):A₂CO₃ as 1:0.5) with stirring. The whole was then concentrated over a steam bath followed by the slow addition of acetone whereupon pink microcrystalline, A\(\text{Mn(glyH)}_2\text{F}_4\cdot\text{3H}_2\text{O}\) (A = Na, K or NH₄) was precipitated out. The compound was isolated by centrifugation, washed 3 times with acetone, and then dried in vacuo over concentrated H₂SO₄.
The yields of Na Mn(glyH)$_2$F$_4$·3H$_2$O, K Mn(glyH)$_2$F$_4$·3H$_2$O, and (NH$_4$)$_2$Mn(glyH)$_2$F$_4$·3H$_2$O were 3.16 g (87.3%), 3.5 g (92%) and 3 g (85%), respectively.

Elemental Analyses

Determination of manganese, fluoride, oxalate, phosphate, and C, H and N, and sodium and potassium contents of the various compounds described in this Chapter have been made by the methods already described in Chapter 2.

The analytical data for K$_3$Mn(C$_2$O$_4$)$_2$F$_2$·3H$_2$O and K Mn(EDTA)F$_2$·3H$_2$O are given in Table 1, while those for A$_3$Mn(HPO$_4$)$_2$F$_2$·3H$_2$O (A = Na, K or NH$_4$), and A Mn(glyH)$_2$F$_4$·3H$_2$O (A = Na, K or NH$_4$) are reported in Tables 2 and 3, respectively.

Chemical Determination of Oxidation State of Manganese

The oxidation state of manganese was determined chemically by iodometry. An accurately weighed amount of the manganese compound was added to an ice-cold potassium iodide solution acidified with dilute sulphuric acid and kept in the dark for about 10 min. The liberated iodine was then titrated with a standard sodium thiosulphate solution using starch as the indicator.
Table 1. Analytical Data of $K_3$ Mn($C_2O_4$)$_2$F$_2\cdot 3H_2O$ and $K$ Mn(EDTA)$F_4\cdot 3H_2O$

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<th>Compound</th>
<th>Found % (Calcd. %)</th>
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<td>K     Mn     F     $C_2O_4$  C    H    N</td>
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<tr>
<td>$K_3$ Mn($C_2O_4$)$_2$F$_2\cdot 3H_2O$</td>
<td>26.75 12.51 8.82 39.65 10.87 1.38</td>
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<td>(26.64) (12.48) (8.83) (39.96) (10.91) (1.36) -</td>
</tr>
<tr>
<td>$K$ Mn(EDTA)$F_4\cdot 3H_2O$</td>
<td>7.73 10.77 14.81 -</td>
</tr>
<tr>
<td></td>
<td>(7.57) (10.64) (14.72) (23.26) (4.26) (5.42)</td>
</tr>
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Table 2. Analytical Data of $A_3 \left[ \text{Mn(HPO}_4\text{)}_2 \right] F_2 \cdot 3H_2O$

(A = Na, K or NH₄)

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<td>A or N</td>
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<tr>
<td>(NH₄)₃</td>
<td>10.72  (10.69)</td>
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<tr>
<td>Mn(HPO₄)₂F₂ • 3H₂O</td>
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</tr>
<tr>
<td>Na₃</td>
<td>17.21 (16.91)</td>
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<tr>
<td>Mn(HPO₄)₂F₂ • 3H₂O</td>
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Table 3. Analytical Data of A Mn\textsubscript{2}F\textsubscript{4}·3H\textsubscript{2}O

\( (A = \text{Na}, \text{K} \text{ or} \text{NH}_4) \)

<table>
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<th>Compound</th>
<th>Found % (Calcd. %)</th>
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<td>(NH\textsubscript{4}) Mn\textsubscript{2}F\textsubscript{4}·3H\textsubscript{2}O</td>
<td>15.73</td>
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<td>Na Mn\textsubscript{2}F\textsubscript{4}·3H\textsubscript{2}O</td>
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<tr>
<td>K Mn\textsubscript{2}F\textsubscript{4}·3H\textsubscript{2}O</td>
<td>10.55</td>
</tr>
</tbody>
</table>
Results and Discussion

The main problem, that one encounters in the synthesis of manganese(III) complexes from aqueous solutions, lies in the ease with which Mn(III) disproportionate to Mn(IV) and Mn(II). \(^{29,30}\) Synthesis of manganese(III) compounds may not, however, be difficult provided the above-mentioned disproportionation process is inhibited. It is evident from earlier work done in the laboratory, where the present work was carried out, that manganese(III) can be well stabilized in an acidic medium containing fluoride ions, and accordingly some binary fluoro- and mixed-ligand fluoro-complexes of manganese(III) were synthesised. \(^{16,21,22}\) Apart from fluoride, ligands like oxalate, phosphate, carboxylates etc also seem to form complexes with manganese(III) in solutions with varying stabilities. \(^{31}\)

It was therefore rational to think that mixed fluoromanganate(III) complexes containing oxalate, EDTA, acidphosphate or an amino-acid like glycine could be stabilized in solutions and thence isolated in the solid state to get an access to a host of manganese(III) complexes. Potassium permanganate, KMnO\(_4\), or a manganese compound already containing manganese in its +3 state can be chosen as a source of the metal depending upon the redox property of the ligand itself. If a ligand is capable of reducing manganese(VII), KMnO\(_4\) can be taken as a starting material, where as in the cases where ligands donot
posses such a property a manganese(III) compound may be suitable. Oxalic acid is known to reduce manganese(VII) ultimately to manganese(II). This reduction is assisted by heat. It was believed that such a reduction of manganese(VII), if carried out at a relatively lower temperature (say \(\sim 0^\circ\text{C}\)) particularly in the presence of a limited amount of fluoride ions using an excess of oxalic acid might lead to the synthesis of mixed-fluorooxalatomanganates(III). In accord with this a reaction of \(\text{KMnO}_4\) with potassium fluoride, \(\text{KF}\), and oxalic acid in the ratio of 1:2:4 at \(0^\circ\text{C}\) in the dark followed by the addition of ethanol has led to the successful synthesis of potassium difluorobis(oxalato)manganate(III) trihydrate,

\[
\text{K}_3\left[\text{Mn}(\text{C}_2\text{O}_4)_2\text{F}_2\right]\cdot3\text{H}_2\text{O}
\]

\[
\text{KMnO}_4 + 4\text{H}_2\text{C}_2\text{O}_4 + 2\text{KF} \longrightarrow \text{K}_3\left[\text{Mn}(\text{C}_2\text{O}_4)_2\text{F}_2\right] + 4\text{CO}_2 + 4\text{H}_2\text{O}
\]

Success of the above synthesis lies on:

(i) maintaining of a low temperature (\(0^\circ\text{C}\)) of the reaction;

(ii) using of the appropriate amounts of both oxalate and fluoride, remembering that while a part of \(\text{C}_2\text{O}_4^{2-}\) is utilised to reduce manganese(VII) to manganese(III), the rest is used for coordinating to the metal center;

(iii) avoiding an excess of fluoride ions in the medium to check the formation of \(\text{MnF}_5^{2-}\); and

(iv) carrying out of the reaction in the dark.
The role of ethanol was to bring about precipitation of the desired product. An alternative route starting with MnO(OH) (a manganese(III) compound) was not found suitable since an already known\textsuperscript{22} compound $K_2 \overset{\text{MnF}_3 (C_2O_4)}{\to}$ was obtained instead of the compound looked for.

The cherry-red $K_3 \overset{\text{Mn}(C_2O_4)_{2}F_2 \cdot 3H_2O}{\to}$ compound was obtained in a microcrystalline form and was found to be unstable both in the solid state as well as in a solution. The compound is relatively less stable than the potassium tris (oxalato)manganate(III) trihydrate, $K_3 \overset{\text{Mn}(C_2O_4)_{3} \cdot 3H_2O}{\to}$ (described in Chapter 6). Owing to its instability neither molar conductance nor even a satisfactory magnetic susceptibility measurement could be made. The chemically estimated oxidation state of manganese, determined iodometrically immediately after synthesising a sample of the compound, was found to be 3.1 in conformity with the occurrence of manganese(III). The electronic spectrum of a freshly prepared sample of the compound, recorded immediately after making a solution in water containing a small amount of HF, shows bands at 11950, 19800, and 22220 cm$^{-1}$ which have been assigned to $^5_{B1g} \rightarrow ^5_{A1g}$, $^5_{B1g} \rightarrow ^5_{E2g}$, and $^5_{B1g} \rightarrow ^5_{Eg}$ transitions, respectively, suggesting a distorted octahedral environment of manganese(III)$^{32,33}$ in the compound. The observed pattern also points to an appreciable splitting of the $^5_{Eg}$ ground state.
of Mn\(^{3+}\) probably owing to Jahn-Teller effect. The IR spectrum of the compound shows absorptions characteristic for the presence of coordinated oxalate and fluoride ligands (Table 4). Ionic oxalate has a planar, symmetrical structure with all C-O bonds of equal length. For a chelated oxalate, all the C-O vibrations become infrared active, with asymmetric (O-C-O) stretching shifting to higher frequency and the symmetric stretching to lower.\(^{34}\) The oxalato modes for the present compound occur in the region 1680-1750 cm\(^{-1}\) and at 1435 cm\(^{-1}\) the positions stipulated for a chelated \(\text{C}_2\text{O}_4^{2-}\) group\(^{35}\) leading us to state that the oxalate ligand in \(\text{K}_3\text{LiVIn}(\text{C}_2\text{O}_4)_2\text{F}_2\cdot3\text{H}_2\text{O}\) is bonded to manganese in a chelated fashion. A comparison of the IR spectrum of the present compound with that of \(\text{K}_2\text{LiMnF}_3(\text{C}_2\text{O}_4)_2\cdot3\text{H}_2\text{O}\) shows a distinct difference in so far as the mode of coordination of oxalate is concerned. Unlike the presence of a bridging \(\text{C}_2\text{O}_4^{2-}\) group in \(\text{K}_2\text{LiMnF}_3(\text{C}_2\text{O}_4)_2\cdot3\text{H}_2\text{O}\) the \(\text{C}_2\text{O}_4^{2-}\) ligands in \(\text{K}_3\text{LiVIn}(\text{C}_2\text{O}_4)_2\text{F}_2\cdot3\text{H}_2\text{O}\) occur as chelated ones. The band at 490 cm\(^{-1}\) originates from the presence of coordinated fluoride and is attributed to \(\nu(\text{Mn-F})\). The absence of any splitting of this band as well as appearance of no other band close to 490 cm\(^{-1}\) suggest\(^{36,37}\) that the two F\(^{-}\) ligands occupy positions trans to each other around manganese(III), and the complex species \(\text{K}_3\text{LiVIn}(\text{C}_2\text{O}_4)_2\text{F}_2\cdot3\text{H}_2\text{O}\) most likely has a distorted octahedral structure with a D\(_{4h}\) symmetry. The two additional bands occurring at 3460 and
Table 4. Structurally Significant IR Bands of
\[ K_3 \overset{\text{Mn(C}_2\text{O}_4)_2 \text{F}_2}{\text{F}_2 \cdot 3\text{H}_2\text{O}} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR cm(^{-1})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ K_3 \overset{\text{Mn(C}_2\text{O}_4)_2 \text{F}_2}{\text{F}_2 \cdot 3\text{H}_2\text{O}} ]</td>
<td>1730m</td>
<td>( \nu_{\text{as}} (C=O) \cdot \nu_7 )</td>
</tr>
<tr>
<td>1680s</td>
<td>( \nu_{\text{as}} (C=O) - \nu_1 )</td>
<td></td>
</tr>
<tr>
<td>1435s</td>
<td>( \nu (C-O+C-C) \cdot \nu_2 )</td>
<td></td>
</tr>
<tr>
<td>1315s</td>
<td>( \nu (C-O) \cdot \nu_8 )</td>
<td></td>
</tr>
<tr>
<td>780s</td>
<td>( \delta (O-C-O) + \nu_9 )</td>
<td></td>
</tr>
<tr>
<td>460m</td>
<td>ring def. + ( \nu_{10} )</td>
<td></td>
</tr>
<tr>
<td>430m</td>
<td>ring def. + ( \nu_{11} )</td>
<td></td>
</tr>
<tr>
<td>490m</td>
<td>( \nu (\text{Mn-F}) )</td>
<td></td>
</tr>
<tr>
<td>3460m</td>
<td>( \nu (\text{O-H}) )</td>
<td></td>
</tr>
<tr>
<td>1640s</td>
<td>( \delta (\text{H-O-H}) )</td>
<td></td>
</tr>
</tbody>
</table>
$K_3\left[\text{Mn(C}_2\text{O}_4)_2\text{F}_2\right] \cdot 3\text{H}_2\text{O}$
1640 cm\(^{-1}\) resemble in their shapes and positions to those observed for other fluoromanganate(III) complexes\(^{16}\) containing uncoordinated water, and accordingly these modes have been assigned to \(\nu(\text{O-H})\) and \(\delta(\text{H-O-H})\), respectively.

It is evident therefore that potassium difluorobis-(oxalato)manganate(III) trihydrate, K\(_3\) \(\sqrt[3]{\text{Mn} (\text{C}_2\text{O}_4)_2 \text{F}_2 \cdot 3\text{H}_2\text{O}}\), can be synthesised by the method developed now (vide Experimental). The compound is not very stable. The complex species \(\sqrt[3]{\text{Mn} (\text{C}_2\text{O}_4)_2 \text{F}_2 \cdot 3}\) containing coordinated fluorides and chelated oxalato groups most probably has a distorted octahedral structure.

The problems regarding the stability of manganese(III)-EDTA system has been already stressed earlier in this Chapter. In view of the earlier problems\(^{26}\) and also because of our interest in mixed-ligand fluoromanganates(III), the synthesis of mixed-fluoro-EDTA-manganese(III) complexes was undertaken. A redox reaction between Mn(VII) and EDTA was not considered to be a viable method. Thus a reaction of MnO(OH) in 40% HF with a solution of ethylenediaminetetraacetic acid (EDTA) containing a very small amount of KOH, and potassium fluoride, KF, in the ratio of Mn:EDTA:KF as 1:1:4, was carried out in a manner described in the experimental section. The product isolated from this was found to be pink microcrystalline K \(\sqrt[3]{\text{Mn}(\text{EDTA}) \text{F}_4 \cdot 3\text{H}_2\text{O}}\). That the condition described
herein for the synthesis of the above compound is appropriate was ascertained from the results of similar reactions carried out under higher pH (≈ 7 or slightly above). The products obtained from such reactions were found to be contaminated ones. It is necessary to mention that an higher amount of fluoride, higher than the one used in the present case, is detrimental because this leads to the formation of $\text{MnF}_5^{2-}$.

Potassium tetrafluoro(ethylenediaminetetraacetic acid) manganate(III) trihydrate, $K\text{Mn(EDTA)}F_4\cdot7\text{H}_2\text{O}$, is stable, unlike the $K_3\text{Mn(C}_2\text{O}_4)_2\text{F}_2\cdot7\text{H}_2\text{O}$, and can be stored for a prolong period, and its stability can be ascertained by estimating manganese and recording its IR spectrum. The chemically estimated oxidation state of manganese in this compound was found to be 3.0, while the room temperature magnetic susceptibility measurement gave a value of the magnetic moment as 4.92 $\mu_B$ (at 300K). These two results unambiguously showed the occurrence of manganese(III) in the compound under discussion.

The electronic spectrum of the compound, recorded in the region 11000-40000 cm$^{-1}$ immediately after making a solution exhibited bands at 22200, 19800, and 11800 cm$^{-1}$ assigned to $5B_{1g} \rightarrow 5E_g$, $5B_{1g} \rightarrow 5B_{2g}$ and $5B_{1g} \rightarrow 5A_{1g}$ transitions, respectively. This feature is similar to that observed for $K_3\text{Mn(C}_2\text{O}_4)_2\text{F}_2\cdot7\text{H}_2\text{O}$ and also for other manganese(III)
complexes suggesting thereby that the complex species $\text{Mn(EDTA)}F_4\cdot3H_2O$ may have a distorted octahedral structure. The infrared spectral band positions along with their assignments are set out in Table 5. It is notable that the absence of any band in the region 1590-1650 cm$^{-1}$ points to the occurrence of the EDTA ligand as an unionized one and accordingly rules out the possibility of coordination of EDTA through its O atoms. This view is further supported by the observation of bands at 1738 and 1723 cm$^{-1}$ attributed to antisymmetric (O-C-O) stretchings arising from the presence of -COOH groups. This therefore suggests that the EDTA ligand is coordinated to the manganese(III) center through nitrogen only. Since the reactions were carried out in an acidic condition, protons from the carboxylic acid groups of EDTA could not be removed as this is now more evident from the IR spectrum of the newly synthesised compound. The frequencies at 444 and 390 cm$^{-1}$ have been assigned to $\nu$(Mn-N) modes, and those at 298 and 245 cm$^{-1}$ to $\delta$(N-Mn-N) further support the notion concerning the presence of N-bonded EDTA in present case. Another important feature of the IR spectrum of $K\text{Mn(EDTA)}F_4\cdot3H_2O$ is the appearance of two bands at 562 and 494 cm$^{-1}$ due to $\nu$(Mn-F) vibrations of the coordinated fluoride ligands. The additional bands at 3440 and 1640 cm$^{-1}$ assignable to $\nu$(O-H) and $\delta$(H-O-H), respectively, are
Table 5. Structurally Significant IR Bands of $\text{K Mn(EDTA)F}_4 \cdot 3\text{H}_2\text{O}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR cm$^{-1}$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K Mn(EDTA)F}_4 \cdot 3\text{H}_2\text{O}$</td>
<td>1738, 1723</td>
<td>$\nu_{as}(\text{C}=\text{O})$</td>
</tr>
<tr>
<td></td>
<td>440, 390</td>
<td>$\nu$(Mn-N)</td>
</tr>
<tr>
<td></td>
<td>298, 245</td>
<td>$\delta$(N-Mn-N)</td>
</tr>
<tr>
<td></td>
<td>562, 494</td>
<td>$\nu$(Mn-F)</td>
</tr>
<tr>
<td></td>
<td>3450</td>
<td>$\nu$(O-H)</td>
</tr>
<tr>
<td></td>
<td>1660</td>
<td>$\delta$(H-O-H)</td>
</tr>
</tbody>
</table>
$\text{K} \left[ \text{Mn(EDTA)} \right]_4 \cdot 3\text{H}_2\text{O}$
typical for the presence of lattice water supporting the view that the water molecules are not coordinated to the metal center.

It is evident from the above results that a stable mixed-ligand fluoro-EDTA-manganese(III) complex, $K \left[ \text{Mn(EDTA)} F_4 \right] \cdot 3H_2O$ can be synthesised from the reaction of MnO(OH) with 48% HF, EDTA and KF. The complex species $\left[ \text{Mn(EDTA)} F_4 \right]^{2-}$ most probably has a distorted octahedral structure.

As mentioned in the opening section of this Chapter, we were also interested to synthesise mixed-fluoromanganate(III) containing acid phosphate as the heteroligand. The synthetic strategy for achieving this goal was somewhat different from the one adapted for that of $K \left[ \text{Mn(EDTA)} F_4 \right] \cdot 3H_2O$. Instead of dissolving MnO(OH) in 48% HF, a mixture of MnO(OH) and AF (A = Na, K or NH$_4$) was dissolved in orthophosphoric acid ($H_3PO_4$), while the Mn:F$^-$ ratio was maintained at 1:3. The reaction took place as indicated by the appearance of a violet colour of the reaction solution. Addition of a mixture of ethanol and acetone (1/1, v/v) gave pink-brown microcrystalline $A_3 \left[ \text{Mn(HPO}_4\right)_2 F_2 \right] \cdot 3H_2O$ (A = Na, K or NH$_4$). Thus it is clear that the synthesis of the desired compound could be achieved without making use of hydrofluoric acid. The method is a straight one and leads to the synthesis of a series of salts of the complex ion $\left[ \text{Mn(HPO}_4\right)_2 F_2 \right]^{3-}$.
The $A_3 \left[ Mn(HPO_4)_2 F_2 \right] \cdot 3H_2O$ (A = Na, K or NH$_4$) compounds are quite stable, in the absence of moisture, for a long period. The stability of the compounds were ascertained in a manner similar to that described earlier for the $K \left[ Mn(EDTA)F_2 \right] \cdot 3H_2O$ case. The compounds donot dissolve in water instead they decompose. The chemically determined oxidation state of manganese was found to lie between 2.9 and 3.1 in conformity with the occurrence of manganese(III) in each of them. The room temperature magnetic moments of the compounds lying in the range 4.8-4.9 $\mu_B$ give further support with regard to the presence of manganese(III) in the newly synthesised compounds. The observed magnetic moments are normal for a d$^4$ system and donot indicate any antiferromagnetic exchange interaction in the compounds.

Owing to their instability in water, solution electronic spectra could not be recorded. The reflectance spectra of $A_3 \left[ Mn(HPO_4)_2 F_2 \right] \cdot 3H_2O$ (A = Na, K or NH$_4$) resemble each other very closely showing absorptions at ca 11000, ca 18200 and ca 20800 cm$^{-1}$ owing, respectively, to the transitions $^5B_{1g} \rightarrow ^5A_{1g}$, $^5B_{1g} \rightarrow ^5B_{2g}$, and $^5B_{1g} \rightarrow ^5E_g$. These absorptions are quite representative for a distorted octahedral manganese(III) complex.
The IR spectra of phosphato complexes of metals are generally complex particularly because of the broadness of peaks and poor resolution of the spectra making it difficult to precisely identify the peak positions let alone their assignments. These problems become more pronounced when phosphate occurs as an acid phosphate and more so when lattice water is also present in the same compound. The presence of lattice water and hydrogen bonding largely effect the internal modes of vibrations of the anion with the $\nu$(O-H) shifting appreciably to lower frequencies. These difficulties were also encountered for the present compounds. The IR spectra of $A_3\left[Mn(HPO_4)_2\right]_2F_2\cdot7.3H_2O$ (A = Na, K, or NH$_4$) complexes, though poorly resolved, indicate the presence of coordinated acid phosphate ligand. A strong but broad absorption in the region 1050-1250 cm$^{-1}$, and a weak broad absorption at 2750-2925 cm$^{-1}$ were observed in the IR spectrum of each of the compounds. These are regarded as characteristics for the presence of coordinated acid orthophosphate ligands causing us to infer that the complexes under discussion contain $HPO_4^{2-}$ coordinated through O atoms to the manganese(III) center. This view is further supported by the observance of a medium intensity band at ca 350 cm$^{-1}$ which has been assigned to $\nu$(Mn-O) stretching mode originating from the coordination of $HPO_4^{2-}$ ligands through their O atoms. The band at ca 510 cm$^{-1}$ has been assigned to the $\nu$(Mn-F) mode arising from the
presence of coordinated fluoride ligands. The IR spectra also show bands at ca 1640 and around 3450 cm\(^{-1}\) attributed to \(\delta(H-O-H)\) and \(\nu(O-H)\) modes of uncoordinated water similar to those observed for the other manganese(III) compounds described in this Chapter. The weak nature and broadness of the \(\nu(O-H)\) mode in addition to its lowering point to the involvement of hydrogen bonding as expected.

The results of pyrolytic studies involving \(K_3\mathcal{L}_2\text{Mn}(\text{HPO}_4)_2\text{F}_2\cdot3\text{H}_2\text{O}\) show that the compound first loses water molecules in two steps. While one molecule of \(H_2\text{O}\) was lost at 120°C the rest two molecules of \(H_2\text{O}\) were lost at 190-200°C. It is believed that a relatively higher temperature, required for the removal of last two molecules of water was probably because of their involvement in hydrogen bonding. The dehydrated material on being heated at 300°C underwent a loss in its weight corresponding to the loss of two molecules of HF. The formation of HF owes its origin to the occurrence of \(\text{HPO}_4^{2-}\), from which the \(H^+\) is abstracted by a \(F^-\) ligand followed by the loss of HF. The above observations further support the formulation of the compounds.

Thus mixed-fluoromanganates(III) containing acid phosphate of the type \(A_3\mathcal{L}_2\text{Mn}(\text{HPO}_4)_2\text{F}_2\cdot3\text{H}_2\text{O}\) (\(A = \text{Na}, \text{K}\) or \(\text{NH}_4\)) can be obtained under the experimental conditions described herein. The complexes are stable. It appears from
the results of various physical studies that the complex species \( \left[ \text{Mn(HPO}_4\right]_{2}^2\text{F}_2\text{]}^{3-} \) may have a distorted octahedral structure.

In our attempts to synthesise mixed- ligand fluoro-
manganate(III) containing glycine, a freshly prepared sample of MnO(OH) was allowed to react with 40% HF and glycine (glyH) with the ratio of Mn:F\(^-\):glyH being maintained at 1:4:2. In order to provide counter cations, alkali-metal or ammonium carbonate, in lieu of the corresponding alkali-metal or ammonium fluoride, was added to the reaction solutions. The use of alkali-metal or ammonium fluoride had to be avoided in order to inhibit the formation of \( \left[ \text{MnF}_5\text{]}^{2-} \) species instead of the desired one. Another point of importance in the context of the synthesis of mixed-fluoro(glycine)manganate(III) complexes is that the reaction solution requires concentration prior to precipitating out the compounds by the addition of acetone. The compounds synthesised in this way were found to be A \( \left[ \text{Mn(glyH)}_2\text{F}_4\text{]}^{7.3\text{H}_2\text{O}} \) with A being Na, K or NH\(_4\).

The alkali-metal or ammonium tetrafluorobis(glycine)-manganate(III) trihydrates A \( \left[ \text{Mn(glyH)}_2\text{F}_4\text{]}^{7.3\text{H}_2\text{O}} \) (A = Na, K or NH\(_4\)), were obtained as pink microcrystalline products. They are stable in the absence of moisture. Like the fluorophosphatomanganate(III) described above, these compounds are also insoluble in common organic solvents. The chemically
estimated oxidation state of manganese in the compounds was found to lie between 2.9 and 3.1 in conformity with the occurrence of manganese(III) in each of the compounds. The results of magnetic susceptibility measurements on A $\text{Mn(glyH)}_2\text{F}_4\cdot3\text{H}_2\text{O}$ (A = Na, K or NH$_4$) gave the magnetic moments falling in the range 4.78 to 4.80 $\mu_B$ (300K). These values are normal for d$^4$ systems occurring in an octahedral or a distorted octahedral environment.

Owing to their instability in water, solution electronic spectra could not be recorded. The reflectance spectra of the compounds exhibit bands at ca 12000, ca 19800 and ca 21300 cm$^{-1}$. The observed pattern is rather typical of an octahedral or a distorted octahedral Mn$^{3+}$ complex, and the bands have been accordingly assigned to the transitions $^5\text{B}_1\text{g} \rightarrow ^5\text{A}_1\text{g}$, $^5\text{B}_1\text{g} \rightarrow ^5\text{B}_2\text{g}$, and $^5\text{B}_1\text{g} \rightarrow ^5\text{E}_g$, respectively. This also indicates an appreciable splitting of $^5\text{E}_g$ ground state of manganese(III) in the complex ion. The significant features of infrared spectra of the compounds are absorptions due to coordinated glycine and fluoride ligands (Table 6). The mode of bonding of glycine to a metal center can be ascertained from the IR spectra of such compounds. The COO stretching band near 1710 cm$^{-1}$ occurs when glycine is coordinated to a metal center in its unionized form, while for an ionized glycine being coordinated shows the COO stretching band near
1610 cm\(^{-1}\). If, however, glycine acts as a chelated ligand an absorption at 1640 cm\(^{-1}\), different from the one mentioned above, becomes a characteristic feature of its IR spectrum. The IR spectra of the present compound show this absorption at ca 1715 cm\(^{-1}\) consistent with the coordination of glycine in its unionized form. It is therefore reasonable to assume that the coordination of glycine has taken place through its nitrogen lone pair electrons. Accordingly, the corresponding \(\nu\)(Mn-N) and \(\delta\)(N-Mn-N) modes have been observed at ca 505 and ca 355 cm\(^{-1}\), respectively. Unfortunately in the present case, the \(\nu\)(Mn-F) mode could not be identified clearly, however, increase in intensity and broadening of the band at ca 505 suggest the overlapping of \(\nu\)(Mn-F) mode with that of the \(\nu\)(Mn-N). The presence of uncoordinated water is unambiguous in the present cases and the corresponding \(\nu\)(O-H) and \(\delta\)(H-O-H) modes of water were observed in positions similar to those observed in various other cases containing lattice water making any further discussion redundant. It is evident from the IR spectra that glycine in the present complexes coordinate to the metal center in its unionized form through its nitrogen atom. This also appears reasonable in view of an acidic condition maintained for the syntheses of the present series of compounds.
Table 6. Structurally Significant Infrared Bands of
\( A {\text{Mn}}(\text{glyH})_{2}{\text{F}}_{4}{\text{.3H}_{2}{\text{O}}} \) (A = Na, K or NH\(_4\))

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR cm(^{-1})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{NH}_4) ( {\text{Mn}}(\text{glyH})_2{\text{F}}<em>4{\text{.3H}</em>{2}{\text{O}}}))</td>
<td>1715</td>
<td>(\nu_{\text{as}}(\text{COOH}))</td>
</tr>
<tr>
<td></td>
<td>1596</td>
<td>(\delta(\text{NH}_2))</td>
</tr>
<tr>
<td></td>
<td>1445</td>
<td>(\delta(\text{CH}_2))</td>
</tr>
<tr>
<td></td>
<td>1411</td>
<td>(\nu(\text{C=O}))</td>
</tr>
<tr>
<td></td>
<td>1335</td>
<td>(\rho_w(\text{CH}_2))</td>
</tr>
<tr>
<td></td>
<td>1256</td>
<td>(\rho_t(\text{NH}_2))</td>
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<tr>
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<td>(\rho_r(\text{NH}_2))</td>
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<tr>
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<td>1027</td>
<td>(\rho_w(\text{NH}_2))</td>
</tr>
<tr>
<td></td>
<td>913</td>
<td>(\rho_r(\text{CH}_2))</td>
</tr>
<tr>
<td>888 (\nu_s(\text{CCN})) 871</td>
<td>(\delta(\text{C=O}))</td>
<td></td>
</tr>
<tr>
<td>740</td>
<td>(\pi(\text{C=O}))</td>
<td></td>
</tr>
<tr>
<td>606</td>
<td>(\nu(\text{Mn-N}) + \nu(\text{Mn-F}))</td>
<td></td>
</tr>
<tr>
<td>505 br</td>
<td>(\delta(\text{N-Mn-N}))</td>
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</tr>
<tr>
<td>355</td>
<td>(\nu(\text{O-H}))</td>
<td></td>
</tr>
<tr>
<td>3445</td>
<td>(\delta(\text{H-O-H}))</td>
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</tr>
</tbody>
</table>

continued..
$\text{NH}_4\left[\text{Mn(glyH)}_2\text{F}_4\right] \cdot 3\text{H}_2\text{O}$
<table>
<thead>
<tr>
<th>Compound</th>
<th>IR cm(^{-1})</th>
<th>Assignment</th>
</tr>
</thead>
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continued...
Table 6 continued

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<th>Compound</th>
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<td>505</td>
<td>(\vee(\text{Mn-N}) + \vee(\text{Mn-F}))</td>
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<td>355</td>
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<td>3425</td>
<td>(\vee(\text{O-H}))</td>
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<tr>
<td></td>
<td>1645</td>
<td>(\delta(\text{H-O-H}))</td>
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</table>
$K\left[\text{Mn(glyH)$_2$F}_4\right]\cdot3\text{H}_2\text{O}$
Considering the results of chemical determination of oxidation state of manganese, magnetic susceptibility measurements, reflectance, and infrared spectral studies that the complex species has the formula $\text{Mn(glyH)}_2F_4$ with the manganese(III) being in a distorted octahedral environment.

To conclude this Chapter the following points may be emphasized that,

(i) a number of mixed-ligand fluoro complexes of Mn(III) containing O- and N-donor ligands have been synthesised by proper choice of the reaction conditions;

(ii) all the newly synthesised compounds have been synthesised in aqueous media;

(iii) of all the compounds reported in this Chapter $K_3\text{Mn(C}_2\text{O}_4)_2F_2\cdot3H_2O$ is the only example which is a very unstable one, while the rest are stable for prolong period in the absence of moisture; and

(iv) the magnetic moments of all the newly synthesised complexes, except $K_3\text{Mn(C}_2\text{O}_4)_2F_2\cdot3H_2O$ for which magnetic susceptibility could not measured owing to its instability, are normal unlike those of the $A_2\text{MnF}_3(SO_4)_2$ and $A_2\text{MnF}_3(C_2\text{O}_4)_2$ ($A =$ alkali metal or NH$_3$) complexes.

Moreover, a comparison of magnetic properties of the binary fluoro complexes of manganese(III) namely $A_2\text{MnF}_5$ with those of the newly synthesised compounds described in the present work shows that whereas $A_2\text{MnF}_5$ compounds
exhibit strong antiferromagnetic interactions, the magnetic
moments of $K \mathbf{Mn(EDTA)F}_4 \cdot 3\text{H}_2\text{O}$, $A_3 \mathbf{Mn(HPO}_4)_2 F_2 \cdot 3\text{H}_2\text{O}$ and
$A \mathbf{Mn(glyH)}_2 F_4 \cdot 3\text{H}_2\text{O}$ have been found to be normal expected
for (d$^4$) manganese(III) systems. In view of the present results
we tend to also believe that manganese(III) compounds involving
$\mathbf{Mn-...Mn-...}$ interactions either through bridging
fluoride or through double bridges like in the cases
$A_2 \mathbf{MnF}_3 (\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ and $A_2 \mathbf{MnF}_3 (\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$ lead to the
operation of super exchange phenomenon giving rise to anti-
ferromagnetism to a variable extent. Further the synthesis of
stable manganese(III) complexes $K \mathbf{Mn(EDTA)F}_4 \cdot 3\text{H}_2\text{O}$ and
$A \mathbf{Mn(glyH)}_2 F_4 \cdot 3\text{H}_2\text{O}$, provides evidence for the capability
of manganese(III) complexes containing N-donor ligands being
synthesised. The examples of manganese(III) complexes containing
nitrogen donor ligands are scanty. $^{45,46}$
References


28. Ref 27, p 829.


38. Ref 37, p 238.
44. Ref. 37, p 232.
Molecular Complexes of Manganese(III). Synthesis And Physico-Chemical Studies of $\text{Mn(o-phen)}_3(H_2O)\cdot2H_2O$, $\text{Mn(bipy)}_3(H_2O)\cdot2H_2O$, And $\text{Mn(urea)}_2F_3\cdot3H_2O$

Fluoride assisted stabilization of manganese(III) in aqueous solutions ultimately allowing the synthesis of a good number of mixed-ligand fluoromanganate(III) complexes has been described in the previous Chapter. A few molecular mixed-ligand chloro complexes of manganese(III) were reported by earlier workers, and the only molecular mixed ligand fluoro complex of manganese(III) known to our knowledge is $\text{Mn(o-phen)}_3(H_2O)\cdot2$. It was also reported that the corresponding 2,2'-bipyridine complex could not be synthesised. As a sequel of the studies described in Chapter 7, we were curious also to synthesise molecular mixed-ligand fluoro complexes of manganese(III) and to study their properties. In view of this attention was directed to synthesise the proposed type of manganese(III) compounds.

The present Chapter deals with the synthesis, characterization, and structural assessment of three molecular mixed ligand fluoro complexes of manganese(III).
Experimental

Roagent grade chemicals were used (Sarabhai M, S.D's, E. Merck, Glaxo, Sisco).
The compound MnO(OH) was prepared by the oxidation of Mn(CH)₂ with hydrogen peroxide as described in Chapter 6.

(i) Synthesis of Trifluoroaquoo(1,10-phenanthrolino)-Manganese(III) Dihydrate, $\text{Mn} \cdot \text{O} \cdot \text{OH} \cdot \text{F} \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{O}$

An aqueous suspension (20 cm³) of freshly prepared 0.89g (10.11 mmol) of MnO(OH) was dissolved in 3 cm³ (72 mmol) of 48% HF with continuous stirring. To the clear solution an ethanolic solution of 1,10-phenanthroline (2.0g, 10.11 mmol) was added slowly, maintaining Mn:o-phen ratio at 1:1. The solution was stirred for ca 20 min, whereupon a dull orange compound started appearing. Stirring was continued for a further period of ca 10 min followed by the addition of about 10 cm³ of ethanol (ethanol was added to achieve nearly complete precipitation of the product). The compound $\text{Mn} \cdot \text{O} \cdot \text{OH} \cdot \text{F} \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{O}$ was filtered, and washed 3 to 4 times with ethanol, dried in vacuo over concentrated H₂SO₄.

Yield of $\text{Mn} \cdot \text{O} \cdot \text{OH} \cdot \text{F} \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{O}$ was found to be 2.5g (71.4%).
(ii) Synthesis of Trifluoroaquo(2,2'-bipyridine)Manganese(III) Dihydrate \( \text{Mn(bipy)}F_3(H_2O) \cdot 2H_2O \)

Freshly prepared 0.89g (10.11 mmol) of MnO(OH) was dissolved in 3 cm\(^3\) (72 mmol) of 48% HF with stirring to obtain a clear solution. To the above reaction solution was added a concentrated ethanolic solution of 1.58g (10.11 mmol) of 2,2'-bipyridine and the whole was stirred for ca 10 min, a reddish-brown colour was developed. This was then concentrated over a steam bath to nearly half of its original volume. Acetone (half of the original volume) was added slowly, to the above concentrated solution, which precipitated out dull orange \( \text{Mn(bipy)}F_3(H_2O) \cdot 2H_2O \). The compound was isolated by filtration, followed by washing with acetone 2 to 3 times and dried in vacuo over concentrated H\(_2\)SO\(_4\).

Yield of the compound \( \text{Mn(bipy)}F_3(H_2O) \cdot 2H_2O \) was 2g (61.4%).

(iii) Synthesis of Trifluorobis(urea)Manganese(III) Trihydrate, \( \text{Mn(urea)}_2F_3\cdot 3H_2O \)

An aqueous suspension of 0.89g (10.11 mmol) of freshly prepared MnO(OH) was dissolved by the slow addition of 3 cm\(^3\) (72 mmol) of 48% HF with continuous stirring. To the clear reaction solution 1.82g (30.36 mmol) of solid urea was added slowly with the maintenance of Mn:urea ratio at 1:3, and stirring was continued for a further period of ca 20 min.
The resultant reddish-brown solution was concentrated over a steam bath, and to the concentrated reaction mixture was added acetone slowly, when chocolate colour microcrystalline \( \text{Mn(urea)}_2.F_3\cdot.3\text{H}_2\text{O} \) precipitated out. The compound was filtered, and purified by washing 2-3 times with acetone. The product \( \text{Mn(urea)}_2.F_3\cdot.3\text{H}_2\text{O} \) was dried in vacuo over concentrated H\(_2\)SO\(_4\). Yield of \( \text{Mn(urea)}_2.F_3\cdot.3\text{H}_2\text{O} \) was found to be 1.2g (41.5%).

**Elemental Analyses**

Quantitative estimations of manganese, fluoride, carbon, hydrogen, and nitrogen were accomplished by the methods described in Chapter 2.

The results of elemental analyses and chemically estimated oxidation state of manganese in the newly synthesised compounds are reported in Table 1.

**Chemical Determination of oxidation state of Manganese**

The estimation of oxidation state of manganese was made chemically by the method already described in Chapter 7.
Table 1. Analytical Data of $\left[\text{Mn(o-phen)}\right]_3\left(\text{H}_2\text{O}\right)_2\cdot\text{H}_2\text{O}$, $\left[\text{Mn(bipy)}\right]_3\left(\text{H}_2\text{O}\right)_2\cdot\text{H}_2\text{O}$, and $\left[\text{Mn(urea)}\right]_2\text{F}_3\cdot\text{H}_2\text{O}$

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<td>$\left[\text{Mn(o-phen)}\right]_3\left(\text{H}_2\text{O}\right)_2\cdot\text{H}_2\text{O}$</td>
<td>2.9</td>
<td>Mn 15.77 16.81 41.54 4.11 8.12 (15.87) (16.47) (41.63) (4.04) (8.09)</td>
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<td>$\left[\text{Mn(bipy)}\right]_3\left(\text{H}_2\text{O}\right)_2\cdot\text{H}_2\text{O}$</td>
<td>3.0</td>
<td>F 17.51 17.62 37.32 4.37 8.82 (17.06) (17.69) (37.28) (4.35) (8.69)</td>
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<tr>
<td>$\left[\text{Mn(urea)}\right]_2\text{F}_3\cdot\text{H}_2\text{O}$</td>
<td>3.1</td>
<td>C 18.92 19.81 8.43 4.85 19.64 (19.21) (19.93) (8.39) (4.89) (19.58)</td>
</tr>
</tbody>
</table>
Results and Discussion

In the context of some studies involving manganese(III), it was suggested in 1982\(^3\) that MnO(OH) when dissolved in 40% HF produced MnF\(_3\) in solution. It was thought in the present context that a further reaction of MnF\(_3\), generated in situ, with ligands like 1,10-phenanthroline, 2,2'-bipyridine or urea, which are capable of acting as neutral ligands for transition metal would be a reasonable strategy for the synthesis of the kind of compounds looked for. Accordingly a solution of MnO(OH) in 48% hydrofluoric acid was reacted separately with o-phen, bipy and urea (vide Experimental), from which

\[ \text{L-Mn(o-phen)F}_3\text{(H}_2\text{O)}\text{.2H}_2\text{O, 1, L-Mn(bipy)F}_3\text{(H}_2\text{O)}\text{.2H}_2\text{O, 2,}\]

and \[ \text{L-Mn(urea)F}_3\text{.3H}_2\text{O, 3,}\]

respectively, were obtained in high yields. While \[ \text{L-Mn(o-phen)F}_3\text{(H}_2\text{O)}\text{.2H}_2\text{O}\]

was precipitated out from a dilute solution, the other two compounds required concentration of the reaction solution by heating on a steam bath followed by the addition of acetone required for bringing about precipitation of the compounds. These results again support the view concerning the formation of MnF\(_3\) in the reaction of MnO(OH) with aqueous hydrofluoric acid. The methods described are direct and the strategy used herein can be used as a paradigm for the synthesis of similar mixed-ligand fluoromanganate(III) compounds to provide a rather easy access to them.
Whereas $\text{Mn(o-phen)}_3\text{F}_3\cdot 2\text{H}_2\text{O}$, 1, and $\text{Mn(bipy)}_3\text{F}_3\cdot 2\text{H}_2\text{O}$, 2, were dull orange in colour, the $\text{Mn(urea)}_2\text{F}_3\cdot 3\text{H}_2\text{O}$, 3, was obtained as a chocolate colour product. The compounds are stable and can be stored in polyethylene sample containers. Their stability can be ascertained by estimation of manganese and also by chemical determination of its oxidation state. The compounds slowly decompose in water, however, they dissolve partly in polar organic solvents. The chemically estimated oxidation state of manganese was found to lie in the range 2.9 to 3.1 (Table 1) suggesting the occurrence of manganese(III) in each of the compounds. Chemical determination of oxidation state of the metal in such compounds is very crucial particularly because their magnetic moments may not always be very straightforward leading to confusion concerning the formal oxidation state of the central metal atom.

The results of room temperature (300K) magnetic susceptibility measurements showed that the compounds are paramagnetic with the magnetic moments of $\text{Mn(o-phen)}_3\text{F}_3\cdot 2\text{H}_2\text{O}$, 1, $\text{Mn(bipy)}_3\text{F}_3\cdot 2\text{H}_2\text{O}$, 2, and $\text{Mn(urea)}_2\text{F}_3\cdot 3\text{H}_2\text{O}$, 3, being 5.0, 4.9 and 4.3 $\mu_B$, respectively. Thus it is evident that the magnetic moment values of the compounds 1 and 2 are normal, whereas that of the compound 3, is relatively low. This suggests that $\text{Mn(urea)}_2\text{F}_3\cdot 3\text{H}_2\text{O}$ is weakly antiferromagnetic. From the observed magnetic moment values alone, it
may be said that the complex unit in \( \text{L-Mn(o-phen)}F_3(H_2O)\cdot 2H_2O \) and \( \text{L-Mn(bipy)}F_3(H_2O)\cdot 2H_2O \) are very likely monomeric with distorted octahedral structures, but the \( \text{L-Mn(urea)}_2F_3\cdot 3H_2O \) may have a polymeric structure through \(-\text{Mn-F-Mn-}\) interactions enabling super exchange to be operative leading to lowering of magnetic moments as observed. The manganese(III) center in this compound may also find itself in a distorted octahedral environment. The solution electronic spectra also support the view. The electronic spectra of \( \text{L-Mn(o-phen)}F_3(H_2O)\cdot 2H_2O, 1, \) and \( \text{L-Mn(bipy)}F_3(H_2O)\cdot 2H_2O, 2, \) were recorded in DMSO solutions, and of \( \text{L-Mn(urea)}_2F_3\cdot 3H_2O, 3, \) was recorded in a methanol solution. While the spectra of 1 and 2 showed absorptions at 23250, 19000, and 13750 cm\(^{-1}\) assigned to \( ^5B_{1g} \rightarrow ^5E_g, ^5B_{1g} \rightarrow ^5B_{2g} \) and \( ^5B_{1g} \rightarrow ^5A_{1g} \) transitions, respectively, that of 3 exhibited the corresponding bands at 20620, 17240, and 10810 cm\(^{-1}\), respectively. The pattern is typical for manganese(III) occurring in a distorted octahedral environment with appreciable splitting of \( ^5E_g \) ground term of Mn(III). This again adduce support to the notion that each of the compounds 1, 2 and 3, has a distorted octahedral structure.

The IR spectra of \( \text{L-Mn(o-phen)}F_3(H_2O)\cdot 2H_2O, 1, \) and \( \text{L-Mn(bipy)}F_3(H_2O)\cdot 2H_2O, 2, \) showed the characteristics of coordinated o-phen and bipy ligands, respectively.\(^1\),\(^5\)-\(^7\) The Mn-N stretching modes originating from the coordinated
N-heterocyclic ligands for 1 and 2 were observed at 296m and 245s, and 282s and 233m cm\(^{-1}\), respectively,\(^6\)\(^,\)\(^8\) providing further support to the occurrence of coordinated o-phen and bipy ligands in the corresponding compounds. The band at ca 480 cm\(^{-1}\) has been assigned to \(\nu\)(Mn-F) of the coordinated F\(^-\) ligands.\(^9\)\(^,\)\(^10\) A notable feature of the IR spectra of 1 and 2 is the band at ca 725 cm\(^{-1}\) which has been assigned to the rocking mode of coordinated water. This is particularly important because the formula of 1 and 2 contain both coordinated as well as lattice water. Owing to the presence of lattice water the information obtainable from the \(\nu\)(O-H) and \(\delta\)(H-O-H) positions are not very significant in the present cases as far as the distinction between the two kinds of water molecule is concerned. Fortunately the occurrence of rocking mode of water as mentioned above supports the occurrence of coordinated water. Taking into account of the observed magnetic moment values of 1 and 2 together with the results obtained from their IR spectroscopic studies now cause us to infer that while one molecule of water is coordinated to the manganese center in each case, the other two molecules are present as lattice water. Thus the complexes 1 and 2 acquire distorted octahedral structures, and the involvement of polymer formation through a bridging ligand is not required to account for the experimentally obtained results.
The significant features of the IR spectrum of trifluorobis (urea)manganese(III) trihydrate, $\text{Mn(urea)}_2F_3\cdot 3\text{H}_2\text{O}$, 3, are absorptions due to coordinated urea, coordinated fluoride, and lattice water. The important bands arising from coordinated urea were observed at 3424s and 1535s cm$^{-1}$ attributed to $\nu$(NH$_2$) and $\nu$(C=O) vibrational modes,$^{11,13}$ respectively. The fact that $\nu$(NH$_2$) occur in a position stipulated for such a mode$^{12,13}$ of free urea, and a significant lowering of the $\nu$(C=O) frequency compared to that of free urea$^{12,13}$ strongly suggest that the urea ligands are coordinated to the metal center through its oxygen atom only. Therefore it is evident that each of the two urea ligands coordinate in a monodentate manner. Unlike in the cases of 1 and 2, the $\nu$(Mn-F) mode for 3 was observed at 453 cm$^{-1}$. Lowering in position of this mode accompanied by its broadening lead us to believe that the coordinated fluorides might also be involved in bridge formation among the contiguous Mn atoms in the crystal lattice. The complex $\text{Mn(urea)}_2F_3\cdot 3\text{H}_2\text{O}$ may have a distorted octahedral structure attained through $\text{Mn-F-Mn-F-Mn-}$ interactions. Such a proposition is not irrational in view of the earlier reports $\text{MnF}_3(\text{SO}_4)^{2-}$ [ref. 14,15] and $\text{MnF}_3(\text{C}_2\text{O}_4)^{2-}$ [ref. 16]. Moreover, this arrangement will also support the possibility of the compound 3 being slightly antiferromagnetic through super-exchange leading to lowering of magnetic moments as observed,
The bands at 3440 and 1645 cm\(^{-1}\) in the IR spectrum of \(3\) have been assigned to \(\nu(\text{O-H})\) and \(\delta(\text{H-O-H})\) modes, respectively. The absence of any band at ca 720 cm\(^{-1}\), and the positions and shapes of \(\nu(\text{O-H})\) and \(\delta(\text{H-O-H})\) bands further support the occurrence of water molecule as lattice water only. The presence of lattice water in fluoromanganates(III) are well preceded.\(^{10,17}\)

It may be stated therefore that \(\text{[Mn(urea)\textsubscript{2}F_3\textsuperscript{-}3H_2O, 3,}\) may have a distorted octahedral structure involving \(-\text{Mn-F-Mn-F-Mn-}\) interactions and the water molecules are not coordinated to the manganese(III) center.

Thermogravimetric analysis (TGA) of trifluorobis(urea)-manganese(III) trihydrate, \(\text{[Mn(urea)\textsubscript{2}F_3\textsuperscript{-}3H_2O, 3,}\) was carried out in the range 40-800°C. The thermogram of the compound shows that the compound starts losing its weight from about 140°C and continues until 210°C giving a horizontal at 210-240°C. The loss of weight in this process was found to be 19.2% corresponding to the loss of three molecules of \(\text{H}_2\text{O}\) (calc. 18.9) giving anhydrous \(\text{[Mn(urea)\textsubscript{2}F_3\textsuperscript{-}3H_2O, 3,}\) as an intermediate. This undergoes further decomposition in two stages showing horizontals at 330-360°C and 470°C onwards, respectively, with the corresponding weight losses being 40.1% and 62.1% which in turn correspond to the loss of one urea at each stop (Calc. 39.9 and 60.8, respectively), finally
Table 2. Structurally Significant IR bands of \( \text{Mn(urea)}_2 F_3 \cdot 3H_2 O \)

<table>
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<th>Compound</th>
<th>IR cm(^{-1})</th>
<th>Assignment</th>
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<td>( \text{Mn(urea)}_2 F_3 \cdot 3H_2 O )</td>
<td>1535</td>
<td>( \nu(C=O) )</td>
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<tr>
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<td>3424</td>
<td>( \nu(NH_2) )</td>
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<td></td>
<td>1480</td>
<td>( \nu_{as}(CN) )</td>
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<td>1152</td>
<td>( \nu(NCO) )</td>
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<td>( \delta(NCO) )</td>
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</tr>
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<td>( \nu(O-H) )</td>
</tr>
<tr>
<td></td>
<td>1645</td>
<td>( \delta(H-O-H) )</td>
</tr>
</tbody>
</table>
\[ \text{Mn (urea)}_2 \text{F}_3 \cdot 3 \text{H}_2\text{O} \]
producing \( \text{MnF}_3 \). No loss of weight beyond 470°C till 800°C suggest that \( \text{MnF}_3 \) once formed, from \( \text{Mn}(\text{urea})_2\text{F}_3\cdot\text{H}_2\text{O} \) at ca 470°C, does not undergo any change, at least within the range of temperature involved in the present TGA experiment. The mode of thermal decomposition may be depicted in the following way:

\[
\text{L-Mn(urea)}_2\text{F}_3\cdot\text{H}_2\text{O} \xrightarrow{\text{ca}~220°C} \text{L-Mn(urea)}_2\text{F}_3 \xrightarrow{\text{ca}~350°C} \text{MnF}_3 \]

The information gathered from the thermogravimetric analysis (TGA) may be useful in the context of obtaining the intermediates, viz., \( \text{Mn}(\text{urea})_2\text{F}_3 \) and \( \text{Mn}(\text{urea})_2\text{F}_3\), by the pyrolysis of 2 at the temperatures given above, for further studies involving them. Moreover, heating of \( \text{Mn}(\text{urea})_2\text{F}_3\cdot\text{H}_2\text{O} \) at ca 470°C under nitrogen leading to the formation of \( \text{MnF}_3 \) may be an useful way of preparing this compound. The importance of \( \text{MnF}_3 \) as a powerful fluorinating agent is well known.18

In order to evaluate the potentiality of 1, 2 and 3 as oxidants, oxidation reactions involving the newly synthesised compounds were carried out. The results of our initial studies reveal that the compounds can oxidize substrates like benzyl alcohol, anthracene etc. Further studies are now being carried
out by other workers of our laboratory in this direction and the results will be reported elsewhere.
References


