

Synthesis of Alkali Metal Trifluoroaquomanganates(II)

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The electron transfer reaction between hydrazine hydrate and KMnO_4 in the presence of alkali metal bifluorides, AHF_2 ($\text{A} = \text{NH}_4, \text{Na}$ or K) readily gives light pinkish-white alkali metal trifluoroaquomanganates(II), $\text{A}[\text{MnF}_3(\text{H}_2\text{O})]$ in very high yields. The corresponding Rb^+ and Cs^+ salts have been obtained by reacting 20% hydrofluoric acid solution of $\text{NH}_4[\text{MnF}_3(\text{H}_2\text{O})]$ with Rb_2CO_3 and Cs_2CO_3 respectively. The compounds have been characterised by elemental analyses, chemical determination of oxidation states of manganese in the compounds, room temperature magnetic susceptibility measurements, pyrolysis and infrared spectral studies.

There is a growing current interest in the study of fluoro-manganese chemistry¹⁻⁶. It is now well established that F^- ions stabilise Mn^{3+} and it is also generally believed that the reduction of higher valent manganese below +3 state through electron transfer reactions in the presence of F^- ligands is rather a difficult task¹⁻⁵, even though +2 oxidation state of manganese is a more common one. Moreover, complex formation tendency of Mn^{2+} seems to be comparatively less pronounced than that of Mn^{3+} (ref. 7). In view of this and in continuation of our work on the synthesis and structural assessment of fluoromanganates^{4,5}, we thought it important to carry out the electron transfer reaction between KMnO_4 and a strong reducing agent, like hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) in the presence of alkali metal bifluorides and to synthesise and characterise fluoro-manganates(II) directly from Mn^{7+} . This paper incorporates results of such an investigation.

Materials and Methods

All the chemicals used were reagent grade products. Alkali metal bifluorides, AHF_2 were synthesised by the method developed in this laboratory⁸.

The oxidation state of manganese in each of the alkali metal trifluoroaquomanganates(II) was determined chemically by the reaction of a known amount of the compound with aqueous acidic Fe^{2+} solution followed by estimation of unreacted Fe^{2+} in solution.

Synthesis of alkali metal trifluoroaquomanganates(II). $\text{A}[\text{MnF}_3(\text{H}_2\text{O})]$ —Ammonium, sodium and potassium trifluoroaquomanganates(II) were synthesised by the following general method.

Alkali metal bifluoride, AHF_2 ($\text{A} = \text{NH}_4, \text{Na}$ or K) (19.3 mmol) and solid KMnO_4 (3.16 mmol) were mixed, powdered and dissolved in a minimum volume of water by slightly warming over a steam-bath and filtered. The filtrate was collected in a polythene

beaker and an excess of hydrazine hydrate (3 ml) added in one lot with constant stirring. A highly exothermic reaction set in and readily gave a light pinkish-white microcrystalline product with the mother liquor becoming colourless. The reaction mixture was cooled to room temperature, solid separated by centrifugation and purified by washing with *n*-heptane and finally dried *in vacuo*. The yield was between 80 and 90%.

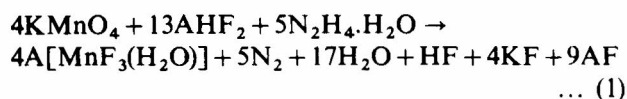
Synthesis of rubidium trifluoroaquomanganate(II). $\text{Rb}[\text{MnF}_3(\text{H}_2\text{O})]$ — $\text{NH}_4[\text{MnF}_3(\text{H}_2\text{O})]$ (2 mmol) was dissolved in a minimum volume of 20% hydrofluoric acid to get a clear solution. To this solution was added powdered Rb_2CO_3 (1 mmol) in portions with stirring. After addition was over, the light pinkish-white $\text{Rb}[\text{MnF}_3(\text{H}_2\text{O})]$ appeared, which was separated by centrifugation and purified by washing with *n*-heptane and finally dried *in vacuo*; yield 91%.

Synthesis of cesium trifluoroaquomanganate(II). $\text{Cs}[\text{MnF}_3(\text{H}_2\text{O})]$ —The above metathesis reaction was carried out with $\text{NH}_4[\text{MnF}_3(\text{H}_2\text{O})]$ (2 mmol) and Cs_2CO_3 (1 mmol) to get $\text{Cs}[\text{MnF}_3(\text{H}_2\text{O})]$ in 91% yield.

Results and Discussion

The experimental conditions employed for the synthesis of various alkali metal trifluoroaquomanganates successfully brought about the reduction of manganese below its +3 state, inspite of difficulties recorded earlier¹⁻⁵. On the addition of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ to excess of alkali metal bifluorides and potassium permanganate the temperature went up to about 80-90°C. This temperature was strategically maintained in order to facilitate the reduction of manganese below its +3 state. The analysis of the reaction products shows the reduction of manganese below its +3 state. Thus the method leading to trifluoroaquomanganates(II) of alkali metals indicates that hydrazine hydrate reductions could be developed for the synthesis of other types of compounds of manganese in its +2 state

starting from Mn^{7+} and also compounds of other transition metals starting from their stable higher oxidation states. The yields obtained by this method are very high. It is also evident that by the use of forcing conditions the fluoro complexes of Mn^{2+} can be synthesised even though their formation constants in aqueous solutions are very low⁹⁻¹¹. The alkali metal bifluorides, AHF_2 , here act as fluorinating agents. In our previous papers^{4,5,8,12} we emphasised the role of AHF_2 as fluorinating agents. In fact it appears that the success of the method depended not only on the role played by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ but also quite appreciably on the presence of both H^+ and F^- in the solution phase arising from AHF_2 . The overall reaction leading to the formation of $\text{A}[\text{MnF}_3(\text{H}_2\text{O})]$ may be expressed by Eq. (1)



The alkali metal trifluoroaquomanganates(II) are all very light pinkish-white microcrystalline products and they attack glass in the presence of moisture. They are not soluble in common organic solvents. $\text{A}[\text{MnF}_3(\text{H}_2\text{O})]$ dissolves in water to some extent but the dissolution is accompanied by dissociation or decomposition. The compounds dissolve highly in hydrofluoric acid.

The chemically estimated oxidation states of manganese lie between 2.05 and 2.12 (Table 1), lending strong support to the contention that manganese in each of the compounds has an oxidation number of +2. We emphasise on the chemical determination of oxidation state of manganese in such compounds because the observed magnetic moment values (measured on a Gouy balance with $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant) are often lower than the expected values owing to their pronounced antiferromagnetic behaviour. The attempts to measure the molar

conductance of various $\text{A}[\text{MnF}_3(\text{H}_2\text{O})]$ compounds in water were unsuccessful. The observed values were higher than that expected for a uni-uni valent type of electrolyte. The higher molar conductance values indicate some sort of decomposition of the compounds or the enhanced ionic character of the Mn-F bonds.

The IR spectra of ammonium, sodium, potassium, rubidium and cesium trifluoroaquomanganates(II), (recorded on a Perkin-Elmer model 125) are almost identical. The typical features of the spectra are the occurrence of a strong absorption ~ 410 , a weak and broad band ~ 1640 , a medium intensity broad band ~ 3350 and a medium intensity band $\sim 710\text{ cm}^{-1}$, assignable to $\nu\text{Mn-F}$, $\delta\text{H-O-H}$, $\nu\text{O-H}$ and rocking modes of water arising out of coordinated fluoride and water respectively. The occurrence of $\nu\text{Mn-F}$ at a much lower frequency compared to those of MnF_3^- and MnF_6^{3-} species^{4,5,13}, suggests that the Mn-F bonds in $[\text{MnF}_3(\text{H}_2\text{O})]^-$ have enhanced ionic character than those in MnF_3^- and MnF_6^{3-} . However, from the fact that the $\nu\text{Mn-F}$ has been observed in the present cases $\sim 410\text{ cm}^{-1}$, it is certain that a definite degree of covalency exists in the Mn-F bonds. Similar observation was made by Peacock and Sharp¹³ in the case of KMnF_3 . The very weak nature of the $\delta\text{H-O-H}$ band points to the presence of coordinated water^{14,15}. Moreover, the appearance of medium intensity band $\sim 710\text{ cm}^{-1}$ which is generally attributed to the rocking mode of coordinated water adduces strong evidence for the presence of coordinated water in the compounds. Further evidence with regard to the presence of coordinated water was obtained from the pyrolysis studies of $\text{K}[\text{MnF}_3(\text{H}_2\text{O})]$, taken as a representative. Pyrolysis of the compound at $125-30^\circ\text{C}$ for 3 hr virtually did not show any change in weight of the compound. The IR spectra of the compound recorded before and after heating also did not indicate any change in the spectral pattern.

Table 1—Analytical Data, Magnetic Moments, Estimated Oxidation States of $\text{A}[\text{MnF}_3(\text{H}_2\text{O})]$

(A = NH_4 , Na, K, Rb or Cs)

Compound	μ_{eff} (B.M.) 290°K	Oxidation state of Mn	Found (%) (Calc.)		
			A or N	Mn	F
$\text{NH}_4[\text{MnF}_3(\text{H}_2\text{O})]$	5.3	2.05	9.61 (9.46)	37.52 (37.16)	38.21 (38.51)
$\text{Na}[\text{MnF}_3(\text{H}_2\text{O})]$	5.2	2.11	15.52 (15.03)	36.34 (35.95)	37.68 (37.25)
$\text{K}[\text{MnF}_3(\text{H}_2\text{O})]$	5.2	2.12	23.43 (23.08)	32.89 (32.54)	33.51 (33.73)
$\text{Rb}[\text{MnF}_3(\text{H}_2\text{O})]$	5.3	2.08	40.52 (39.68)	25.73 (25.52)	26.83 (26.45)
$\text{Cs}[\text{MnF}_3(\text{H}_2\text{O})]$	5.3	2.12	51.61 (50.55)	21.38 (20.92)	21.48 (21.68)

The room temperature magnetic moments of the alkali metal trifluoroaquomanganates(II), $A[MnF_3(H_2O)]$ lie between 5.2 and 5.3 B.M. well below the expected value for a high-spin d^5 -system. This, however, is not too surprising because similar observations were made in the cases of A_2MnF_5 and $A_2MnF_5 \cdot H_2O$ (refs 4, 5, 16, 17). Considerably lower moments presumably owe their origin to antiferromagnetic exchange interaction between continuous Mn^{2+} ion probably through $-Mn-F-Mn-$ chain in the solid state. The very faint colour of the compounds indicates that they may have octahedral structure but only X-ray study would provide conclusive evidence.

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