The Direct Synthesis of Alkali-metal Pentafluoromanganates(III)

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The reduction of potassium permanganate with acetylacetone in the presence of an excess of alkali-metal difluoride AHF_2 (A = NH_4, Na, K, or Cs) readily gives pentafluoromanganates(III), $A_2[MnF_5]$ (A = NH_4 or Na) or $A_2[MnF_5]\cdot H_2O$ (A = K or Cs) in almost quantitative yield. Characterisation of the compounds was made from the results of i.r. spectral studies, chemical analyses, magnetic susceptibility measurements, and chemical determination of oxidation states of manganese in the various compounds.

ALTHOUGH alkali-metal pentafluoromanganates(III) have been known for some time, there has been no easy and simple synthetic method available to date. The reaction between MnF_3 in hydrofluoric acid and alkali-metal fluoride AF[1] has been generally used for the synthesis of alkali-metal pentafluoromanganates(III). The present paper reports a general synthesis of the title compounds that does not require MnF_3.

EXPERIMENTAL

Potassium permanganate and acetylacetone were reagent-grade products. The difluorides AHF_2 were synthesised by the method developed in this laboratory.[2] Infrared spectra were recorded on a Perkin-Elmer model 125 spectrophotometer. Magnetic susceptibility measurements were made by the Gouy method using $Hg[Co(CNS)_4]$ as calibrant. The oxidation state of manganese in each of the pentafluoromanganates(III) was determined chemically by the reduction of a known amount of the compounds with aqueous acidic iron(II) solution followed by estimation of the excess of unoxidised Fe^{II} in the solution.

Synthesis of Alkali-metal Pentafluoromanganates(III) $A_2[MnF_5]$ (A = NH_4 *or* Na) *and Pentafluoromanganate*(III) *Monohydrates* $A_2[MnF_5]\cdot H_2O$ (A = K *or* Cs).—Since the methods of syntheses of the pentafluoromanganates(III) are similar, only a representative method is given.

An excess of difluoride AHF_2 was intimately mixed with solid $K[MnO_4]$ by powdering together in an agate mortar. The finely mixed powder was dissolved in a minimum volume of water and filtered. The filtrate was collected in a Polythene beaker and an excess of acetylacetone was added with constant stirring. An exothermic reaction set in and readily gave a rose-pink coloured microcrystalline product in almost quantitative yield with the mother-liquor becoming colourless. The compound was separated by centrifugation and purified by washing with heptane and finally dried *in vacuo*. In the case of the sodium salt, the powdered mixture $K[MnO_4]$–$NaHF_2$ was dissolved in water by slightly warming over a boiling water bath in order to avoid using a large volume of water, otherwise necessary, owing to the lower solubility of $NaHF_2$. If properly planned, the whole process takes no more than 30—40 min. The specific amounts (g) of the reagents used and the yields of the compounds are given in the Table 1; however, the method can be scaled up to higher quantities as well.

TABLE 1

Amounts of reagents used and yields of alkali-metal pentafluoromanganates(III)

Compound	Yield/g (%)	Amount of $KMnO_4$/g (mmol)	Amount of AHF_2/g (mmol)	Amount of acetyl-acetone/g (mmol)
$[NH_4]_2[MnF_5]$	0.34 (97.1)	0.3 (1.9)	1.0 (17.5)	3.0 (30)
$Na_2[MnF_5]$	0.32 (86.5)	0.3 (1.9)	1.1 (17.7)	4.0 (40)
$K_2[MnF_5]\cdot H_2O$	0.44 (93.6)	0.3 (1.9)	1.0 (12.8)	3.0 (30)
$Cs_2[MnF_5]\cdot H_2O$	0.78 (95.1)	0.3 (1.9)	2.3 (13.4)	3.0 (30)

Analytical data, room-temperature magnetic-moment values, structurally important i.r. bands, and chemically estimated oxidation states of manganese are given in Table 2.

RESULTS AND DISCUSSION

Direct Synthesis.—The methods described lead to the synthesis of pentafluoromanganates(III) of alkali metals, sufficient in number to leave little doubt that reductions with acetylacetone could be developed for the synthesis of compounds of other transition metals. The yields are almost quantitative and gram quantities of pentafluoromanganates(III) can be synthesised directly from $K[MnO_4]$ in about 30—40 min with very simple apparatus and without the use of hydrogen fluoride or even hydrofluoric acid. The difluorides AHF_2 here act as fluorinating agents. In previous papers [2,3] we have emphasised the potential of alkali-metal difluorides as fluorinating agents. The strategy for the present synthesis was that the reduction of Mn^{VII} by a relatively mild reducing agent like acetylacetone in the presence of F^- (stabilising species for Mn^{3+}) should enable the synthesis of pentafluoromanganates(III). In fact it appears that the success of the method largely depends on the presence of both H^+ and stabilising F^- ligands in the solution phase arising from AHF_2.

Characterisation.—The pentafluoromanganates(III) are all rose-pink coloured crystalline products, unstable in water, and they attack glass in the presence of moist air.

The chemically estimated oxidation states of manganese lie between 2.9 and 3.1 (Table 2), lending strong credence to the contention that manganese in each of these compounds has an oxidation number of +3. It is interesting to note that the NH_4^+ and Na^+ salts are anhydrous, of the type $A_2[MnF_5]$, whilst the K^+ and

TABLE 2

Analytical data, magnetic moments, estimated oxidation states, and structurally significant i.r. bands of $A_2[MnF_5]$ ($A = NH_4$ or Na) and $A_2[MnF_5]\cdot H_2O$ (A = K or Cs)

Compound	$\mu_{eff.}$[a]/B.M.	Estimated ox. state of Mn	Analysis [b]/%			I.r.(cm^{-1})	Assignments	
			A	Mn	F			
$[NH_4]_2[MnF_5]$	3.19	3.0	15.15 [c]	29.65	51.1	614m	ν(Mn–F)	ν_3
			(15.05) [c]	(29.55)	(51.05)	564s	ν(Mn–F)	ν_4
						3 040s	ν(N–H)	ν_1
						3 157m	ν(N–H)	ν_3
						1 400s	ν(N–H)	ν_4
$Na_2[MnF_5]$	3.21	2.9	23.5	28.25	48.45	615m	ν(Mn–F)	ν_3
			(23.5)	(28.05)	(48.5)	565s	ν(Mn–F)	ν_4
$K_2[MnF_5]\cdot H_2O$	3.30	3.0	31.8	22.4	38.7	616m	ν(Mn–F)	ν_3
			(31.75)	(22.3)	(38.6)	565s	ν(Mn–F)	ν_4
						3 460s	ν(O–H)	
						1 635m	δ(H–O–H)	
$Cs_2[MnF_5]\cdot H_2O$	3.20	3.1	61.3	12.7	21.85	614m	ν(Mn–F)	ν_3
			(61.3)	(12.65)	(21.9)	564s	ν(Mn–F)	ν_4
						3 458s	ν(O–H)	
						1 640m	δ(H–O–H)	

[a] Measured at 302 K. [b] Calculated values in parentheses. [c] Analysis for N.

Cs^+ salts are monohydrates, $A_2[MnF_5]\cdot H_2O$, even though their methods of synthesis are the same. The i.r. spectra of the series of four salts, now obtained through a unique method, resemble each other very closely. The occurrence of two vibrations at relatively low wavenumber in the i.r. spectra implies the presence of octahedral or distorted octahedral MF_6^{n-}, and in keeping with this there are two readily identifiable ν(Mn–F) bands at *ca.* 615 and *ca.* 565 cm^{-1} [*cf.* the analysis of ν(M–F) in MF_6^{n-} complexes].[4,5] This is in conformity with the crystal structure of $K_2[MnF_5]\cdot H_2O$ as reported by Edwards.[6] The K^+ and Cs^+ salts show two extra vibrational bands at *ca.* 1 640 and 3 460 cm^{-1}, typical for δ(H–O–H) and ν(O–H) owing to the presence of one molecule of unco-ordinated water in each compound. The absorptions at 3 157m, 3 040s, and 1 400s cm^{-1} in the spectrum of $[NH_4]_2[MnF_5]$ correlate very well with those observed recently for $[NH_4]_2[MnCl_5]$ [7] and have been assigned as ν_3, ν_1, and ν_4 of NH_4^+. The room-temperature magnetic moments of the NH_4^+, Na^+, and K^+ salts and the hitherto unreported magnetic moment of the Cs^+ salt have been found to occur between 3.19 and 3.30 B.M.* and agree very well with those reported previously.[8-10] Considerably lower moments presumably owe their origin to antiferromagnetic exchange interaction between contiguous manganese(II) ions through a –Mn–F–Mn– chain in keeping with the reported structure of $K_2[MnF_5]\cdot H_2O$.[6]

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* Throughout this paper: 1 B.M. ≈ 0.927×10^{-23} A m^2.

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