Mixed-metal Fluoride Hydrates and their Thermal-decomposition Products: An Investigation by *X*-Ray, Mössbauer, and Thermal Analysis

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A series of mixed-metal fluoride heptahydrates has been prepared and shown to have the general formula $ABF_5 \cdot 7H_2O$ ($A = Mn^{2+}$, Co^{2+}, or Zn^{2+}; $B = Fe^{2+}$ or Cr^{2+}). Of these, $MnFeF_5 \cdot 7H_2O$ and $FeCrF_5 \cdot 7H_2O$ are reported for the first time. Thermal dehydration of $AFeF_5 \cdot 7H_2O$ and $ZnCrF_5 \cdot 7H_2O$ leads to an intermediate dihydrate $ABF_5 \cdot 2H_2O$. The heptahydrates are isomorphous with one another and the patterns have been indexed with a triclinic *unit cell*, all the parameters of which have been calculated for the AB combinations NiFe, CoFe, NiCr, and CoCr. The *X*-ray pattern of the previously reported anhydrous phase *A* appears during dehydration of $ZnCrF_5 \cdot 7H_2O$ and members of the $AFeF_5 \cdot 7H_2O$ series in flowing hydrogen fluoride. Dehydration of all the members of the iron(III) and chromium(III) series yields *X*-ray patterns of AF_2 in flowing nitrogen and (except $ZnCrF_5 \cdot 7H_2O$) both AF_2 and BF_3 in flowing nitrogen and (except $ZnCrF_5 \cdot 7H_2O$) both AF_2 and BF_3 in flowing hydrogen fluoride. The heptahydrate *X*-ray pattern persists even after complete dehydration of the CoFe, CoCr, ZnFe, and ZnCr mixed-metal fluoride heptahydrates in flowing hydrogen fluoride, CoFe only in flowing nitrogen. Mössbauer spectra indicate that the Fe^{3+} ions occupy two different octahedral sites.

The existence of mixed-metal fluoride hydrates containing bi- and tri-valent cations was first established by Christensen [1] in 1886. He prepared the series $AMn^{III}F_5 \cdot 4H_2O$ ($A = Ni^{II}$, Co^{II}, or Zn), but this number of water molecules in the formula has not been substantiated since. Petersen [2] reported the heptahydrate series $ABF_5 \cdot 7H_2O$ where A represents bi- and B tri-valent cations respectively. He prepared the four possible combinations of $A = Ni^{II}$ or Co^{II} with $B = Cu^{III}$ or Al^{III}, and found them to be isomorphous. The existence and formula of this heptahydrate series was confirmed by Weinland and Koppen [3] in 1899 who prepared other members of the series in which $A = Fe^{II}$, Ni^{II}, Co^{II}, or Zn and $B = Fe^{III}$ or Al^{III}, and by Higley [4] in 1904 who prepared the compound $ZnCrF_5 \cdot 7H_2O$. The present paper is a reinvestigation of fluoride hydrates as likely starting materials for the production of anhydrous fluorides containing cations in different oxidation states. The mixed-valent iron compound $Fe_2F_5 \cdot 7H_2O$ has been recently reinvestigated in a similar manner.[5]

In this paper we report some new members in this series, their preparation and analysis, together with those

[1] O. T. Christensen, *J. prakt. Chem.*, 1887, **35**, 57.
[2] E. Petersen, *J. prakt. Chem.*, 1889, **40**, 58.
[3] R. F. Weinland and O. Koppen, *Z. anorg. Chem.*, 1899, **22**, 266.
[4] G. O. Higley, *J. Amer. Chem. Soc.*, 1904, **26**, 629.
[5] K. J. Gallagher and M. R. Ottaway, *J.C.S. Dalton*, 1975, 978.

previously known, and the results of a detailed study of their thermal-decomposition products by means of a variety of modern techniques including *X*-ray diffraction and Mössbauer spectroscopy. In this study, attention was focused on the iron(III) and chromium(III) series: the corresponding members of the aluminium series were prepared for comparison, but were not further investigated.

EXPERIMENTAL AND RESULTS

Preparation.—The mixed-metal fluoride hydrates were prepared from stock solutions of the appropriate cations, by dissolving the following compounds in 40% hydrofluoric acid (Fison, Analytical Reagent): basic aluminium carbonate, basic chromium(III) fluoride, nickel(II) carbonate (all B.D.H. technical grade), cobalt(II) carbonate, manganese(II) carbonate, basic zinc carbonate (all B.D.H. laboratory grade); freshly prepared iron(III) hydroxide gel; iron powder (99.99% purity; Halewood Chemicals, Colnbrook, Buckinghamshire). Iron(III) hydroxide gel was made by adding ammonia to an aqueous solution of iron(III) nitrate (Fisons, laboratory grade), and filtering and washing the precipitated gel. The solution of iron(III) fluoride was prepared by dissolving iron powder in a closed flask through which nitrogen (99.999% grade, B.O.C.) was passed. This prevents oxidation and thus the precipitation of $Fe_2F_5{\cdot}7H_2O$ from solution.

Each compound was prepared by mixing equimolar solutions of the bi- and tri-valent ions. The mixed fluoride hydrates crystallised out by evaporating the solution at room temperature over a steam-bath, taking care to maintain an atmosphere of N_2 where solutions of Fe^{II} were involved. Crystals so obtained were filtered off and recrystallised after dissolution in 12% HF except in the case of the salts of $Mn^{II}Fe^{III}$ and $Mn^{II}Al^{III}$ because of the low yield. All the preparations were washed after filtration with a little distilled water, ethanol, and then diethyl ether. After drying at room temperature they were stored in a desiccator. The following mixed-metal fluoride hydrates were thus prepared (the bivalent metal is written first) and the colours of the crystalline product were as indicated: MnAl, pink; FeAl, pale green; CoAl, pink; NiAl, pale green; ZnAl, white; FeCr, green; CoCr, dark green; NiCr, green; ZnCr, green; MnFe, fawn; CoFe, pink; NiFe, pale green; ZnFe, white. All such possible combinations are represented except $Mn^{II}Cr^{III}$ as it was not possible to isolate a mixed-metal phase from the equimolar solution of these two ions even by evaporation. The other two manganese(II) combinations were obtained in low yield and one of them, namely $Mn^{II}Fe^{III}$, yielded fawn crystals when evaporated at room temperature and grey crystals when evaporated over a steam-bath. Subsequent analysis (see below) showed that, whereas the room-temperature preparation was the heptahydrate, the high-temperature preparation was the dihydrate $MnFeF_5{\cdot}2H_2O$.

The crystals in all the preparations were quite small, being less than 0.5 mm in their largest dimension. Under a low-powered optical microscope they appeared to have triclinic morphology and, as is often the case with hydrated salts, displayed complex intergrowths and deformed faces. No attempts were made to grow large single crystals, although it has been reported in the early literature [1,2] that this is possible.

The mixed-metal fluoride heptahydrates were moderately soluble in water with the possible exception of $MnFeF_5{\cdot}7H_2O$ and $MnAlF_5{\cdot}7H_2O$. The low yield of the latter from HF suggests that their solubility products may be closer to those of the single-metal fluorides. The low yield did not permit solubility tests to be carried out. Crystals of heptahydrates were stable in the air; they are markedly lustrous and intensely coloured.

During an attempt to prepare pure manganese(II) difluoride tetrahydrate by evaporating a solution of manganese(II) ions in concentrated HF a brown crust appeared which, on isolation, yielded the *X*-ray powder pattern of the heptahydrate together with faint reflections of an unidentified compound or compounds. Since no other metal was present it was concluded that the major constituent was the compound $Mn_2F_5{\cdot}7H_2O$ analogous to $Fe_2F_5{\cdot}7H_2O$. Because of the small quantities available this compound was not studied further.

Since these mixed-metal fluoride heptahydrates were found to be isostructural by *X*-rays they should form solid solutions. In order to ascertain whether this was so, equimolar quantities of NiFe and CoFe hydrates were dissolved in HF. Crystals were obtained by evaporation as before and these analysed as $(Ni_{0.56}Co_{0.44})FeF_5{\cdot}7H_2O$ (see next section for analysis details).

Analysis.—The fluorine content was determined on the dehydrated products as the hydrates did not give consistent results. The procedure involving conversion into SiF_4 as previously described [5] was used. The accuracy of this method is $\pm 0.2\%$ fluorine. Iron was determined by titration with cerium(IV) sulphate after reduction with tin(II) chloride.[5] Nickel was determined by the dimethylglyoxime method and cobalt and zinc by the pyridine–thiocyanate method.[6] All these metal contents were redetermined with Southern Analytical model A1750 atomic-absorption spectrophotometer to an accuracy of *ca.* $\pm 0.5\%$, by dissolving a weighed amount in a known volume of water so that the concentration lay in the upper range of the

TABLE 1

Chemical analyses of some $ABF_5{\cdot}7H_2O$ preparations

	Analysis (% by wt.) [a]			
AB	A	B	F	H_2O
FeCr	16.7, 16.8 (17.0)	15.8 (15.8)	28.8 (28.9)	38.6 (38.35)
CoCr	17.4, 17.6 (17.75)	15.5 (15.65)	28.5 (28.6)	38.2 (38.0)
NiCr	17.3, 17.8 (17.7)	15.7 (15.65)	28.5 (28.6)	38.7 (38.0)
ZnCr	18.9, 19.3 (19.3)	15.2 (15.35)	27.9 (28.05)	38.0 (37.3)
CoFe	18.1, 17.9 (17.55)	16.2, 16.7 (16.65)	27.7 (28.3)	37.5 (37.55)
NiFe	17.3, 17.6 (17.5)	16.3, 16.5 (16.65)	26.9 (28.3)	38.0 (37.55)
Co_xNi_yFe [b]	Co 8.0, 8.0 Ni 9.6, 9.5 (17.5)	16.7, 16.6 (16.6)	28.2 (28.3)	38.0 (37.6)
ZnFe	19.2, 19.2 (19.1)	16.1, 16.1 (16.3)	27.0 (27.75)	37.0 (36.85)

[a] Where two values are given, the first was obtained from a wet analysis and the second from atomic-absorption spectroscopy (see text). Calculated values are given in parentheses. [b] The analysis yields a formula $Co_{0.44}Ni_{0.56}FeF_5{\cdot}7H_2O$.

[6] A. I. Vogel, 'Textbook of Quantitative Inorganic Analysis,' Longmans, 1960.

TABLE 2

The unit-cell dimensions of four heptahydrates

	$NiFeF_5 \cdot 7H_2O$	$CoFeF_5 \cdot 7H_2O$	$NiCrF_5 \cdot 7H_2O$	$CrCrF_5 \cdot 7H_2O$
$10^{10}a$/m	6.506	6.506	6.495	6.533
$10^{10}b$/m	8.942	8.991	8.885	8.907
$10^{10}c$/m	10.433	10.464	10.391	10.446
α/°	106.30	106.38	106.16	106.02
β/°	123.11	122.42	123.44	123.14
γ/°	83.02	83.02	83.20	83.25

calibration graph. The calibration graph was obtained for the widest range in which it is linear, namely zero concentration to 100 times the sensitivity for the particular metal as given by Price.[7] The final value taken was the average of four determinations for each method. The water content was determined by isothermal dehydration at 300 °C in flowing hydrogen fluoride as this method gave more reliable and consistent results than either thermal analysis, or isothermal dehydration in flowing nitrogen. Because of the difficulty of determining Cr^{3+} by wet methods, chromium was determined by atomic absorption only and the figures quoted are also the mean from two independent determinations.

Analyses of the preparations except those containing manganese and/or aluminium are shown in Table 1. The low yield of the MnFe and MnAl preparations precluded a complete analysis but the results of thermal analysis indicated that the MnFe salt analysed as the heptahydrate $MnFeF_5 \cdot 7H_2O$ when prepared by evaporation at ambient temperature, but as the dihydrate $MnFeF_5 \cdot 2H_2O$ when prepared by evaporation over a steam-bath. In the case of the MnAl combination both the high- and low-temperature hydrate preparations analysed as $MnAlF_5 \cdot 2H_2O$.

Mixed fluorides of aluminium and bivalent metals prepared by evaporation of their fluorides in HF are,

TABLE 3

Intensities and d values of X-ray powder reflections of four $A^{II}B^{III}F_5 \cdot 7H_2O$ compounds

	$NiFeF_5 \cdot 7H_2O$			$CoFeF_5 \cdot 7H_2O$			$NiCrF_5 \cdot 7H_2O$			$CoCrF_5 \cdot 7H_2O$		
		$10^{10}d$/m			$10^{10}d$/m			$10^{10}d$/m			$10^{10}d$/m	
hkl	I/I_1	obs.	calc.	I/I_1	obs.	calc.	I/I_1	obs.	calc.	I/I_1	obs.	calc.
$10\bar{1}$			6.41	1	6.41	6.40			6.40			6.44
$11\bar{2}$	10	4.76	4.76	10	4.78	4.77	10	4.75	4.75	10	4.76	4.76
$1\bar{1}0$	10	4.68	4.70	10	4.70	4.71	10	4.67	4.66	10	4.70	4.70
110	10	4.51	4.52	10	4.55	4.55	10	4.49	4.48	10	4.53	4.52
020	10	4.29	4.29	10	4.31	4.31	10	4.26	4.26	10	4.27	4.28
002	10	4.22	4.22	10	4.26	4.27	10	4.19	4.19	10	4.23	4.24
$1\bar{1}\bar{2}$	10	3.797	3.801	10	3.801	3.804	10	3.797	3.797	10	3.808	3.812
$02\bar{2}$	8	3.489	3.491	8	3.519	3.521	8	3.467	3.469	8	3.484	3.484
012	1	3.450	3.452	1	3.480	3.482			3.428			3.456
$12\bar{1}$	1	3.340	3.339			3.348			3.332			3.345
$20\bar{2}$	9	3.203	3.203	9	3.207	3.199	8	3.200	3.201	8	3.218	3.218
$20\bar{1}$	3	3.130	3.129	2	3.135	3.139	1	3.115	3.119			3.143
$12\bar{3}$	2	3.100	3.088			3.101			3.071			3.082
$21\bar{1}$	2	2.990	2.989	1	3.000	3.001			2.973			2.996
$21\bar{3}$			2.930	1	2.930	2.926			2.925			2.937
$12\bar{2}$	4	2.856	2.856	3	2.865	2.863	2	2.847	2.848	2	2.853	2.851
003	5	2.816	2.815	5	2.838	2.844	2	2.790	2.793	3	2.851	2.819
$13\bar{2}$	6	2.800	2.800	6	2.813	2.810	3	2.778	2.781	4	2.785	2.786
$13\bar{1}$	3	2.772	2.773	1	2.780	2.784			2.749			2.759
200	8	2.722	2.723	7	2.751	2.744	4	2.708	2.708	5	2.725	2.733
$02\bar{3}$	2	2.690	2.692	2	2.717	2.719	2	2.671	2.673			2.690
121	1	2.643	2.645	1	2.663	2.668			2.622	1	2.643	2.643
$2\bar{1}0$	1	2.622	2.625			2.643			2.614			2.635
$22\bar{1}$	4	2.589	2.591	4	2.602	2.604	3	2.573	2.574	3	2.592	2.591
210	1	2.563	2.567	1	2.640	2.643			2.549			2.572
$1\bar{3}0$			2.572	1	2.582	2.585			2.563	1	2.573	2.572
130	6	2.495	2.492	6	2.506	2.508	4	2.470	2.472	6	2.484	2.485
112			2.455	2	2.482	2.485	2	2.434	2.432	1	2.455	2.457
$1\bar{3}1$	3	2.450	2.448	1	2.458	2.463			2.434			2.445
$20\bar{4}$	6	2.414	2.410	6	2.415	2.408	6	2.407	2.406	8	2.409	2.142
$22\bar{2}$	6	2.400	2.399	6	2.402	2.401	6	2.399	2.398			2.409
$22\bar{4}$	2	2.385	2.382	2	2.382	2.385	1	2.373	2.375	1	2.380	2.377
$03\bar{3}$	1	2.331	2.327	1	2.348	2.348			2.311	1	2.318	2.323
$23\bar{2}$	1	2.309	2.311	1	2.320	2.319			2.297			2.306
220	3	2.255	2.260	3	2.274	2.277	1	2.243	2.242	1	2.255	2.260
041	4	2.217	2.219	4	2.230	2.231	1	2.202	2.206	1	2.210	2.211
$1\bar{3}2$	3	2.173	2.175	1	2.189	2.196	1	2.160	2.163	1	2.172	2.175
040	3	2.145	2.144	3	2.155	2.155	2	2.129	2.131	2	2.134	2.138
$02\bar{4}$	5	2.123	2.123	6	2.143	2.145	4	2.104	2.108	4	2.121	2.123
004	3	2.110	2.111	2	2.132	2.133			2.095			2.114
$14\bar{3}$	1	2.092	2.091	1	2.100	2.102			2.077			2.083
$31\bar{4}$	5	2.052	2.052	5	2.052	2.048	3	2.049	2.055	2	2.053	2.052
$3\bar{1}\bar{2}$	4	2.032	2.032	4	2.034	2.035	3	2.030	2.030	2	2.039	2.042
$3\bar{1}\bar{3}$	1	2.003	2.003	1	2.000	2.001	1	2.000	2.002	1	2.010	2.013

[7] W. J. Price, 'Analytical Atomic Absorption Spectroscopy,' Heyden and Son Ltd., London, 1974 (corrected 1972 edn.).

TABLE 4

X-Ray powder data for $MnFeF_5 \cdot 2H_2O$, a dihydrate prepared from solution, and $NiFeF_5 \cdot 2H_2O$, a dihydrate prepared by thermal decomposition of the heptahydrate

$MnFeF_5 \cdot 2H_2O$		$NiFeF_5 \cdot 2H_2O$	
$10^{10}d$ (obs.)/m	I/I_1	$10^{10}d$ (obs.)/m	I/I_1
5.73	10	5.58	10
5.04	8	4.90	8
3.78	1	3.76	2
3.70	8	3.62	9
3.36	1	3.32	2
3.20	9	3.13	8
3.15	9	3.09	7
3.11	9	3.05	7
3.00	2	2.835	7
2.962	1	2.670	1
2.863	8	2.485	1
2.727	2	2.445	1
2.448	3	2.401	2
2.396	3	2.348	1
2.366	3	2.288	2
2.350	6	2.165	5
2.284	1	2.111	5
2.211	7	2.091	5
2.166	7	2.073	1
2.149	7	1.947	1
2.117	7	1.852	6
2.075	2	1.813	8
2.001	4	1.781	1
1.985	4	1.758	2
2.907	7	1.748	4
1.891	8	1.674	2
1.847	8	1.662	2
1.819	5	1.649	2
1.797	7	1.636	2
1.784	7	1.605	2
1.708	3	1.594	2
1.704	4	1.561	3
1.688	2	1.542	3
1.681	2	1.528	2
1.674	2		
1.649	1		
1.637	2		
1.628	7		
1.598	7		
1.578	7		
1.561	4		
1.553	4		
1.536	1		
1.518	4		
1.498	1		
1.480	7		

however, isomorphous with mixed-metal heptahydrates indicating that they have the composition $AAlF_5 \cdot 7H_2O$.

X-Ray Diffraction.—All the preparations and products of thermal decomposition were examined by powder diffractometry on a Guinier–De Wolff camera (ENRAF-Nonius Ltd., Delft) using Fe-K_α radiation or Cu-K_α radiation in the case of chromium compounds. None of the preparations yielded single crystals suitable for structural determination by *X*-rays.

The *X*-ray diffraction patterns of all the heptahydrates were very similar to one another and to that of $Fe_2F_5 \cdot 7H_2O$. All the dihydrates also displayed powder-diffraction patterns which were very similar to one another but markedly different from the heptahydrate pattern. As may be expected from the analysis described in the previous section, the $Mn^{II}Fe^{III}$ preparations yielded two different *X*-ray patterns according to the temperature of crystallisation. Room-temperature crystallisation yielded crystals with the heptahydrate pattern, whilst high-temperature crystallisation yielded crystals with a pattern corresponding to those of other dihydrates obtained by partial dehydration of the heptahydrates. The pattern also corresponds to that of $Fe_2F_5 \cdot 2H_2O$ previously described.[5] The $Mn^{II}Al^{III}$ preparations yielded the dihydrate pattern whether prepared at low or high temperatures, in agreement with the analytical data.

Since these heptahydrates are isomorphous with triclinic $Fe_2F_5 \cdot 7H_2O$, it has been possible to index their complex powder patterns without the aid of single-crystal diffractometry. This has been done by initially assuming the same unit cell determined for $Fe_2F_5 \cdot 7H_2O$ by single-crystal methods [5] and by progressively modifying the six unit-cell parameters (each time calculating *d* values for the proposed cell) until the calculated *d* values corresponded to those observed. The powder-diffraction data used had been corrected for film shrinkage during processing using ammonium alum as an internal standard.

Powder-diffraction patterns of $NiFeF_5 \cdot 7H_2O$, $CoFeF_5 \cdot 7H_2O$, $NiCrF_5 \cdot 7H_2O$, and $CoCrF_5 \cdot 7H_2O$ were indexed with triclinic unit cells whose parameters are given in Table 2. The *d* values as calculated from these parameters are listed in Table 3 together with the observed *d* values and intensities. The dihydrate pattern on the other hand could not be indexed as single crystals were not available. The observed *d* values and intensities of $MnFeF_5 \cdot 2H_2O$, a dihydrate prepared from solution, and $NiFeF_5 \cdot 2H_2O$, a dihydrate prepared by thermal decomposition of the heptahydrate, are listed in Table 4.

Thermal Decomposition–Thermal Analysis.—Decomposition studies were carried out on a Linseis thermoanalyser

TABLE 5

Thermal-analysis data for the mixed-metal fluoride heptahydrates in flowing nitrogen

		1st Dehydration stage					
AB	Thermogram type (see Figure 1)	θ_c/°C	Loss in weight (%)	Water loss (mol per mol ABF_5)	2nd Dehydration stage, θ_c/°C	Total loss in weight (%)	Total water loss (mol per mol ABF_5)
MnFe	(*a*)	74—140	27.9	5.14	155—463	40.2	7.41
CoFe	(*a*)	110—177	27.3	5.10	177—370	40.0	7.46
NiFe	(*b*)	115—240	33.6	6.27	240—290	42.8	7.98
ZnFe	(*a*)	97—167	27.5	5.23	167—290	40.4	7.68
FeCr	(*c*)	92—226	34.3	6.27	226—298	39.9	7.29
CoCr	(*c*)	130—225	35.2	6.49	225—480	42.6	7.84
NiCr	(*c*)	120—295	34.1	6.29	295—457	43.2	7.97
ZnCr	(*b*)	105—260	32.0	6.01	260—608	42.2	7.92
FeAl	(*a*)	100—155	29.1	4.92	155—285	39.6	6.68
CoAl	(*b*)	80—155	33.2	5.67	155—330	44.2	7.53

which provided simultaneous traces of thermal gravimetric analysis (t.g.a.), differential thermal gravimetry (d.t.g.), and differential thermal analysis (d.t.a.) and was accurate to ± 0.25 mg for the particular operating conditions selected. Sample weights were in the range 30—50 mg and were heated at a rate of 10 °C min^{-1} in flowing nitrogen (99.999%, B.O.C.).

The general features of thermal decomposition of the mixed-metal fluoride heptahydrates resemble those of the dehydration of $Fe_2F_5 \cdot 7H_2O$ previously reported.[5] The decomposition took place in two stages, both of which exhibited endothermic d.t.a. peaks. In the first stage, loss of water was accompanied by the formation of the dihydrate, a distinct phase with a characteristic *X*-ray

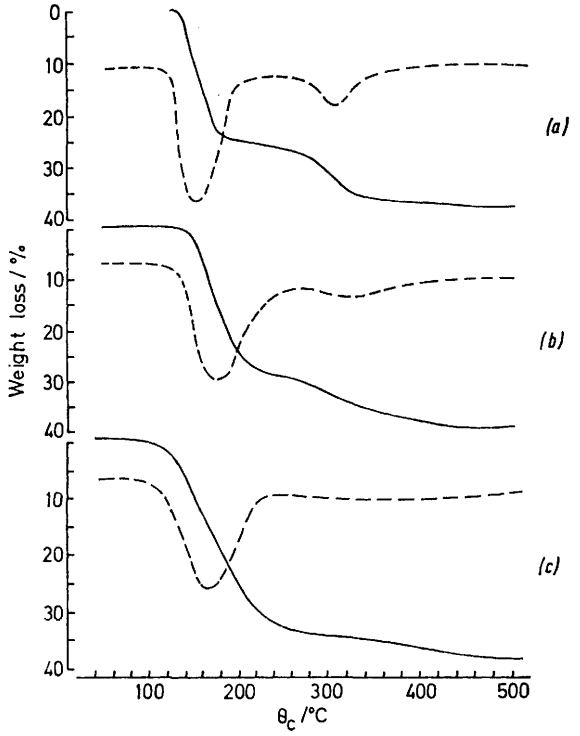


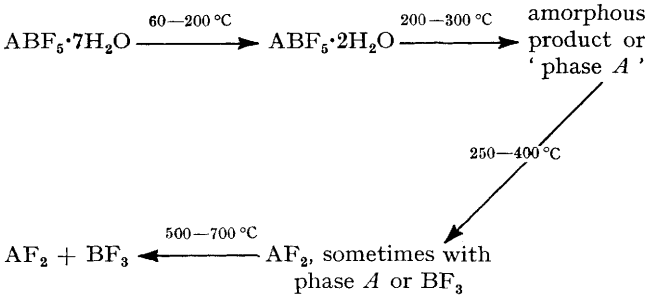
FIGURE 1 Three types of thermograms in the mixed-metal fluoride heptahydrates characterised by: (*a*) $CoFeF_5 \cdot 7H_2O$, two well resolved dehydrations; (*b*) $NiFeF_5 \cdot 7H_2O$ two partially resolved dehydrations; and (*c*) $FeCrF_5 \cdot 7H_2O$, one dehydration stage merging into a slow and indistinct dehydration process. (— — —) D.t.g., (——) t.g.

diffraction pattern, and in the second stage the remaining water was lost to form anhydrous products. There were, however, differences in detail. The temperature at which the first dehydration commenced varied between 60 and 130 °C; the rate and thus the temperature spread also varied. Similarly the temperature and rate of dehydration of the intermediate dihydrate varied considerably. These variations may be seen in Table 5. It will be observed that the thermal behaviour of the $AAlF_5$ hydrates closely resembles that of the $AFeF_5$ hydrates. The two dehydration stages of $ACrF_5$ hydrates were not sufficiently well resolved to enable accurate water losses for the individual stages to be measured (although the total water loss can still be accurately assessed). An additional feature of this compound was that the two stages occurred at much higher temperatures than in the other mixed-metal fluoride heptahydrates. When the first dehydration for the other heptahydrates could be accurately measured [*i.e.* in type (*a*) thermograms as illustrated in Figure 1] it always corresponded to a loss of 4.9—5.10 mol per mol of ABF_5. The total loss corresponded to 6.7—7.7 mol of water. The excessively high values for the total weight in some heptahydrates is probably due to the appreciable volatility of the anhydrous fluorides produced. The fastest dehydrations and, therefore, the most narrow d.t.a. and d.t.g. peaks were observed in the thermograms of $Mn^{II}Fe^{III}F_5 \cdot 2H_2O$.

By terminating the decomposition after the first water loss and examining the product by *X*-ray powder diffraction the intermediate dihydrate could be isolated free from crystalline impurities, except in the case of $A^{II}Cr^{III}$ heptahydrates which did not yield the dihydrate *X*-ray pattern if the decomposition was interrupted after the loss of five water molecules. This observation is consistent with the absence of a horizontal plateau in the thermogram [see Figure 1(*c*)]. The *d* spacings and *X*-ray intensities of the dihydrate $NiFeF_5 \cdot 2H_2O$ obtained after the first dehydration step of $NiFeF_5 \cdot 7H_2O$ was complete are given in Table 4. These parameters correspond very closely with those of the dihydrate $MnFeF_5 \cdot 2H_2O$ (see Table 4) obtained by crystallisation from solution as described in the *Preparation* section.

The products obtained by complete dehydration in nitrogen were examined by *X*-ray diffraction. When dehydration was complete below *ca.* 400 °C the products showed very low crystallinity, but those obtained from compounds which were dehydrated at higher temperatures yielded better defined patterns although the degree of crystallinity was still low. The products from $ZnFe^{III}$ and $ZnCr^{III}$ hydrates yielded ill defined diffraction patterns similar to those which resulted from dehydration of $Fe_2F_5 \cdot 7H_2O$ indicating that, as in the case of the latter, the main constituent from dehydration was ' Phase *A* ' (see ref. 5 for *X*-ray powder data of this phase). The patterns showed that trace amounts of the anhydrous bivalent metal fluoride were also present. Because of the poor crystallinity they were not studied further. Above 500 °C, products in general yielded the pattern of the trivalent metal fluoride.

The decomposition behaviour of the heptahydrates may be summarised in the following reaction scheme. The



diffraction patterns sometimes indicated the presence of the heptahydrate long after the decomposition to anhydrous products, as revealed by the t.g.a. curve indicating that water molecules had simply vacated their lattice sites leaving a heptahydrate skeleton structure of cations and fluoride ions in virtually the same positions as they occupied in the heptahydrate structure.

The heptahydrate $(Ni_{0.56}Co_{0.44})FeF_5 \cdot 7H_2O$ yielded a thermogram intermediate between $NiFeF_5 \cdot 7H_2O$ and $CoFeF_5 \cdot 7H_2O$. The two dihydrates which were obtained by crystallisation from solution namely, $MnFeF_5 \cdot 2H_2O$ and $MnAlF_5 \cdot 2H_2O$, displayed only one dehydration stage which was accompanied by a weight loss corresponding to two water molecules per formula weight, and in both cases the thermal curves were identical to those of the heptahydrates after the first dehydration stage. The colour of the anhydrous products was always intermediate between those of the two fluoride components.

Thermal Decomposition–Isothermal Studies.—Samples of the heptahydrate preparations were heated in a platinum boat in flowing nitrogen or hydrogen fluoride gas at selected temperatures in a furnace controlled to ±5 °C. The results are shown in Figure 2 for nitrogen and Figure 3 for hydrogen fluoride. The overall features of the decomposition are similar to those observed during thermal analysis in flowing N_2: two dehydration stages *via* an intermediate dihydrate were followed by disproportionation to the constituent anhydrous fluorides with ' Phase *A* ' sometimes appearing initially as an intermediate dehydration product but disappearing at higher temperatures (Figure 3). As in the case of $Fe_2F_5 \cdot 7H_2O$, flowing HF lowered the decomposition temperature considerably. Thus for $Co^{II}Cr^{III}F_5 \cdot 7H_2O$ and $Zn^{II}Cr^{III}F_5 \cdot 7H_2O$, separation into the component single fluorides had commenced after heating at 120 °C for several hours in flowing HF.

Mössbauer Spectroscopy.—The Mössbauer spectra were obtained for $NiFeF_5 \cdot 7H_2O$ as this compound produced both a sharp *X*-ray diffraction pattern and a well resolved dehydration step to its dihydrate form. The spectra were obtained on ground but undiluted samples in a spectrometer of the Cranshaw type with a 40-mCi ^{57}Co/Rh source at 300 K and a 20-mCi ^{57}Co/Rh source at 4.2 K. Isomer shifts are quoted with respect to zero velocity at the centre

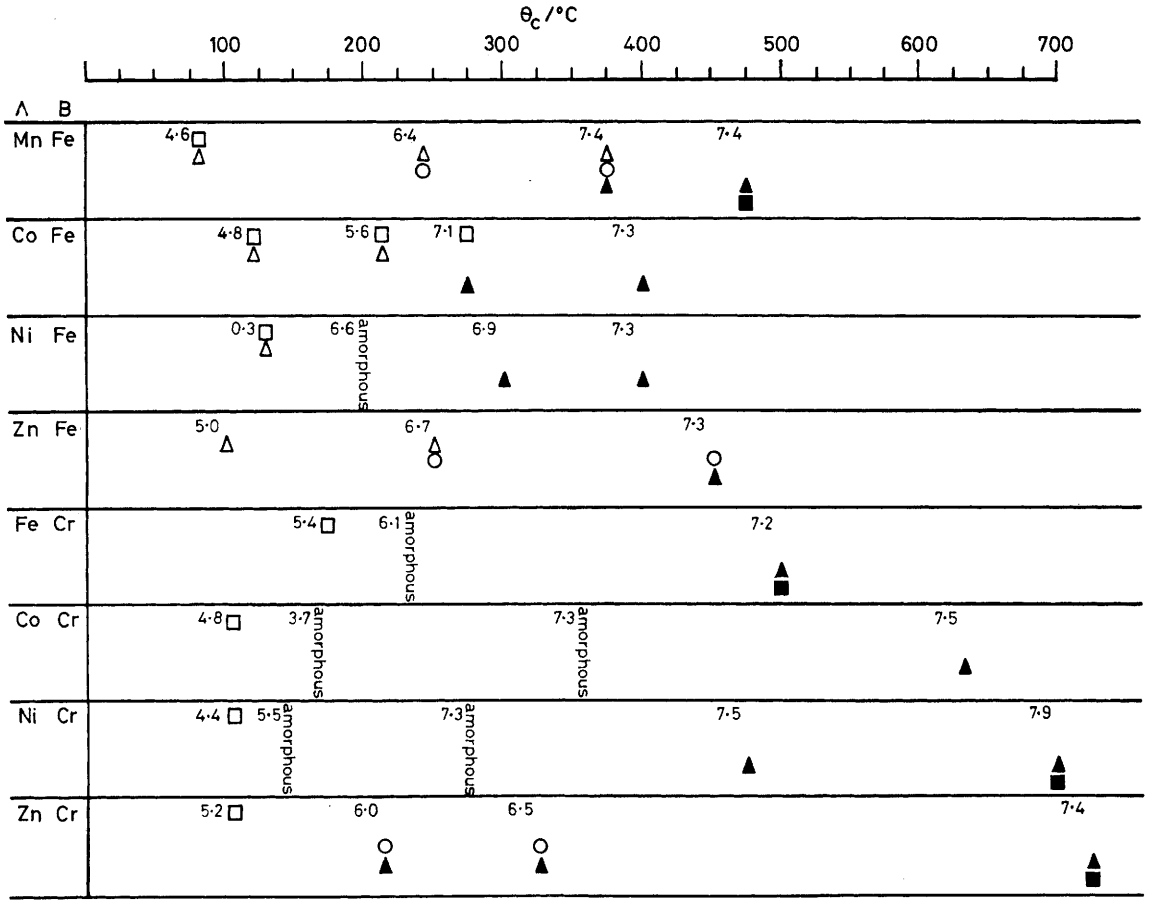


FIGURE 2 Isothermal decomposition in flowing nitrogen of some heptahydrates $ABF_5 \cdot 7H_2O$ for 8 h at room temperatures which have been selected on the basis of the thermal-analysis results. For each temperature, the loss of water in mol per mol $ABF_5 \cdot 7H_2O$ is given and below this figure the resulting phases as observed by *X*-ray diffraction are indicated by (□) $ABF_5 \cdot 7H_2O$, (△) $ABF_5 \cdot 2H_2O$, (○) phase *A*, (▲) AF_2, and (■) BF_3. The observation of a heptahydrate *X*-ray pattern does not necessarily mean that the phase responsible has the composition $ABF_5 \cdot 7H_2O$ (see Discussion section)

of the metallic iron spectrum at 300 K. The spectra were analysed with the Harwell-computer fitting program which allows for the parabolic baseline caused by the geometric effect. The best fits were obtained when the data were fitted to four absorption lines of equal area yielding a χ^2 value of 279 at 300 K and 626 at 4.2 K for 236 degrees of freedom. The lines are considerably broadened, the component half-widths being in the 0.38—0.44 mm s^{-1} region for spectra at both temperatures compared to an expected half-width of 0.23 mm s^{-1}. The absence of a temperature effect on broadening suggests that it is due to some disorder in the crystal. The four lines can be uniquely assigned to

iron(III) ions occupying two kinds of octahedral sites with different electric-field gradients giving rise to two quadrupole doublets.

The Mössbauer parameters (mm s^{-1}) were as follows:

	Isomer shift		Quadrupole splitting	
	300	4.2 K	300	4.2 K
Site 1	0.33	0.43	0.34	0.41
Site 2	0.33	0.43	0.36	0.83

The spectra are shown in Figure 4. The slight asymmetry in the spectrum at 4.2 K is probably due to preferential alignment of the crystals in the particular sample used for measuring the spectrum at this temperature. The resolved lines were too broad to investigate whether the distortion which gives rise to the large quadrupole splitting was tetragonal or rhombic.

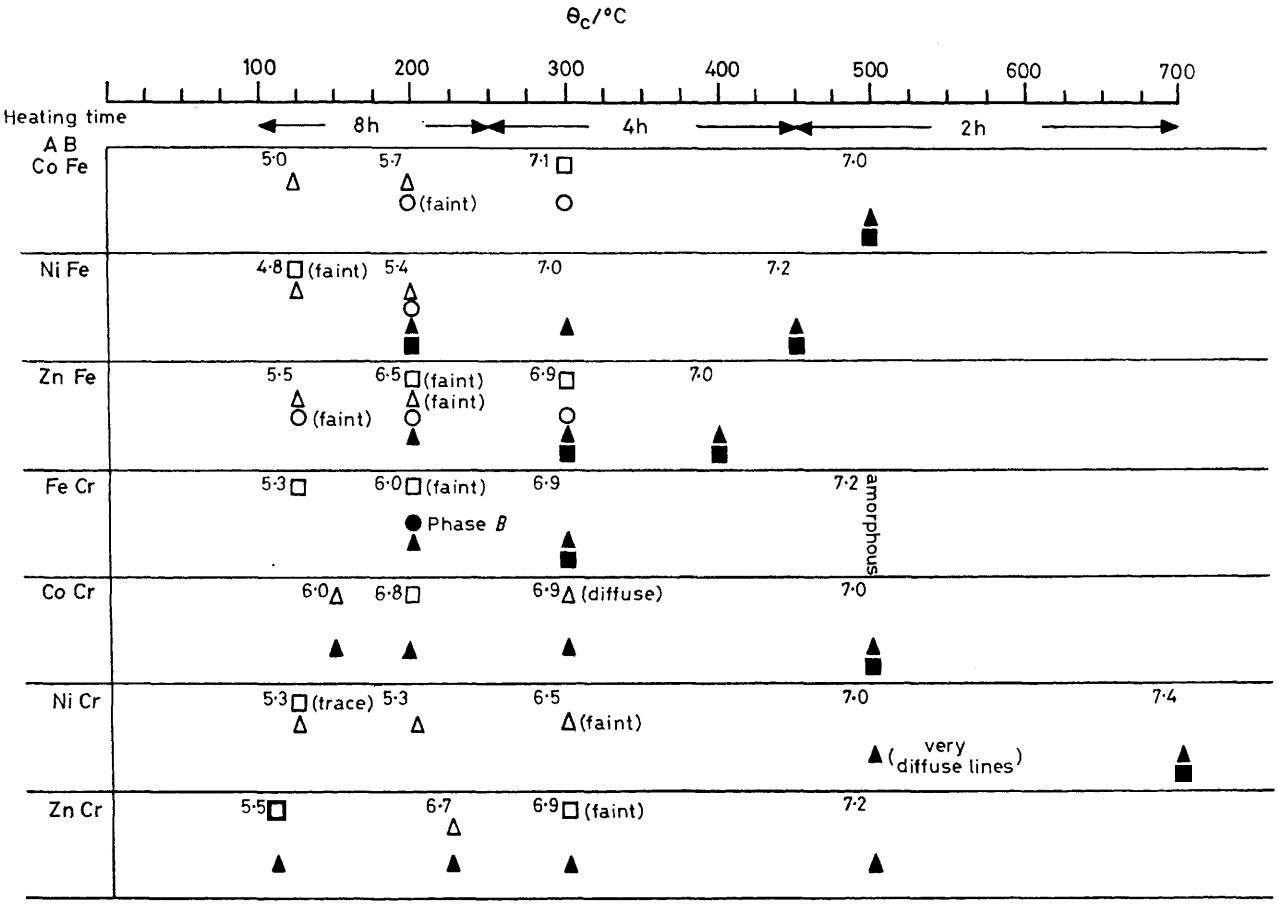


FIGURE 3 Isothermal decomposition in flowing hydrogen fluoride of the same heptahydrates (except $MnFeF_5 \cdot 7H_2O$) and for the same conditions as in Figure 2. Phases: (□) $ABF_5 \cdot 7H_2O$, (△) $ABF_5 \cdot 2H_2O$, (○) phase *A*, (▲) AF_2, (■) BF_3. The terms 'diffuse' and 'faint' refer to the *X*-ray reflections and 'trace' indicates a small proportion of a phase

DISCUSSION

Perhaps the most remarkable feature of the thermal decomposition of the heptahydrates is the persistence in some cases of the heptahydrate *X*-ray pattern after complete dehydration has taken place. The phenomenon occurs for example in $CoFeF_5 \cdot 7H_2O$ under both nitrogen and hydrogen fluoride, in $CoCrF_5 \cdot 7H_2O$, $ZnCrF_5 \cdot 7H_2O$, and $ZnFeF_5 \cdot 7H_2O$ under hydrogen fluoride, and in $MnFeF_5 \cdot 7H_2O$ under nitrogen, and it indicates that a topotactic decomposition has taken place, the main features of the heptahydrate structure being preserved in the product. In each case the heptahydrate pattern is accompanied by patterns of one or more other phases, for example by 'Phase *A*' when $CoFeF_5 \cdot 7H_2O$ is dehydrated under hydrogen fluoride and by CoF_2 when dehydrated under nitrogen. The phenomenon is also observed in some of the other heptahydrates, but only as far as the dihydrate stage, for example in $ACrF_5 \cdot 7H_2O$ compounds in flowing nitrogen and in $FeCrF_5 \cdot 7H_2O$ in flowing hydrogen fluoride. For these cases the heptahydrate pattern is the only pattern present at the dihydrate stage. It then disappears on complete dehydration with a tendency to yield amorphous phases. The persistence of the heptahydrate pattern on complete dehydration is the best evidence for topotactic decomposition as its persistence in material with an overall composition corresponding to $ABF_5 \cdot 2H_2O$ could arise from incomplete decomposition of the original heptahydrate.

The heptahydrate pattern that persists in the anhydrous material suffers only minor changes in intensity and

a very small diminution in d values in spite of the loss of seven water molecules. This is a very surprising feature. The formula $ABF_5 \cdot 7H_2O$ provides a total of 12 ligands for two cations. As these will require octahedral co-ordination (as revealed by Mössbauer spectroscopy on $Fe_2F_5 \cdot 7H_2O$ which also has the heptahydrate X-ray pattern) the 12 ligands suggest that the most likely arrangement is that of a molecular crystal consisting of two internally neutral complexes, namely $AF_2(OH_2)_4$

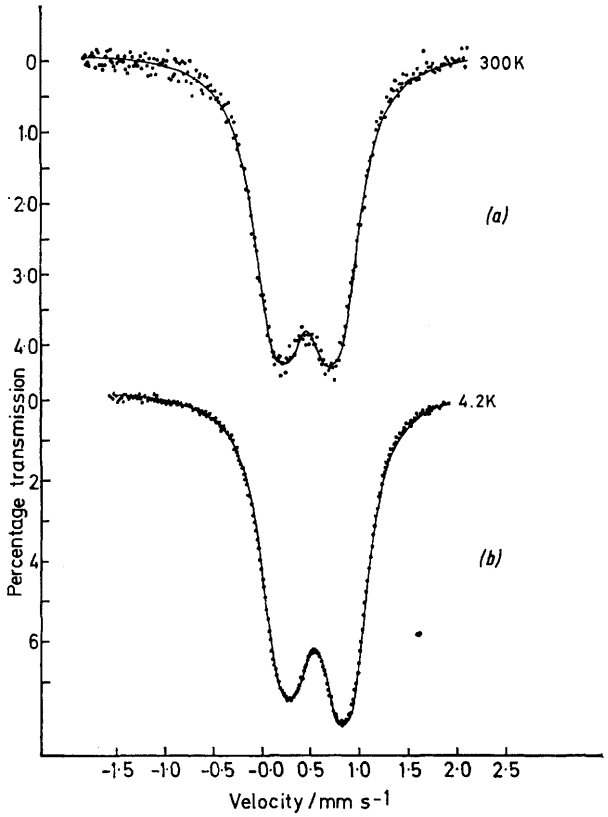


FIGURE 4 Mössbauer spectra of $NiFeF_5 \cdot 7H_2O$ at (*a*) 300 and (*b*) 4.2 K

and $BF_3(OH_2)_3$. The molecular crystal would be stabilised by hydrogen bonds but it is highly unlikely that such a crystal would survive complete dehydration. If, however, another possibility is considered, namely that the fluoride ions formed MF_6 octahedra with corner or edge sharing of F^- to produce a framework in which water molecules filled interstices, the hydrate being stabilised by hydrogen bonding, dehydration could take place without disrupting the framework.

The Mössbauer spectra of $NiFeF_5 \cdot 7H_2O$ indicate that the Fe^{3+} ions occupy two different octahedral sites with different isomer shifts and different quadrupole splittings. Unfortunately, twinning of crystals precluded a structural determination by X-rays, and so these Mössbauer conclusions provide the only structural information available.

A critical appraisal of the structural and bonding features of a mixed fluoride hydrate will be deferred to a discussion in a future publication [8] of the crystal structure of $Cu_3Fe_2F_{12} \cdot 12H_2O$, a member of a related mixed fluoride hydrate series.

' Phase A ' is observed when the dihydrates of all the AFe fluorides are dehydrated in flowing hydrogen fluoride and those of ZnFe, ZnCr, and MnFe only when these are dehydrated in flowing nitrogen. Unfortunately, this phase never occurs on its own, but always in the presence of another phase or phases and so it could not be characterised by chemical analysis. The diffraction pattern has, however, been indicated in the previous paper on $Fe_2F_5 \cdot 7H_2O$. It appears at lower temperatures in flowing hydrogen fluoride than in flowing nitrogen; for example, it occurs at 120 °C during the dehydration of $ZnFeF_5 \cdot 7H_2O$ in flowing hydrogen fluoride compared to 250 °C in flowing nitrogen. In general, flowing hydrogen fluoride tends to lower all the temperatures at which dehydrated phases develop but the effect is not as marked in the mixed-metal fluoride heptahydrates as it is in $Fe_2F_5 \cdot 7H_2O$. Flowing hydrogen fluoride also suppresses the development of amorphous phases. Of the four heptahydrates which produce amorphous products on dehydration in flowing nitrogen only one, $FeCrF_5 \cdot 7H_2O$, yields amorphous products in flowing hydrogen fluoride.

An atmosphere of hydrogen fluoride also favours the formation of dihydrate during thermal decomposition. None of the $ACrF_5$ heptahydrates yields a dihydrate during dehydration in flowing nitrogen; the thermogram shows a single dehydration step and if the dehydration is interrupted after the loss of five water molecules the product does not give an X-ray pattern of the dihydrate. Of these heptahydrates, however, only $FeCrF_5 \cdot 7H_2O$ does not yield the dihydrate in flowing hydrogen fluoride. The absence of a dihydrate in the dehydration of the chromium series is always accompanied by the retention of the $ABF_5 \cdot 7H_2O$ X-ray pattern and it is probable that both phenomena are associated.

The thermogram of $MnFeF_5$ shows that dehydration begins at 66 °C in flowing nitrogen, which is a much lower temperature than that for any of the other heptahydrates, and isothermal dehydration at 80 °C in flowing nitrogen brings about almost complete conversion into the dihydrate, the weight loss corresponding to loss of 4.6 mol of water per mol of $MnFeF_5 \cdot 7H_2O$. It is not surprising therefore that the dihydrate and not the heptahydrate crystallises out when preparations are made from boiling solutions.

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[8] K. J. Gallagher and M. R. Ottaway, unpublished work.