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THERMAL PROPERTIES OF HYDRAZINIUM FLUOROMETALLATES OF THE FIRST ROW TRANSITION ELEMENTS

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ABSTRACT

Thermal analyses of hydrazinium fluorometallates of the first row transition elements and zinc are described. The intermediate compounds of the thermal decompositions are either ammonium fluorometallates or adducts of metal fluorides with hydrazine. The end products of the thermal analyses are in all cases metal fluorides, except in the case of the copper compound where elemental copper is obtained.

INTRODUCTION

A number of new hydrazinium fluorometallates were synthesized and characterized during the study of the reactions between hydrazine or its salts with compounds of the first row transition elements and zinc: $N_2H_5ScF_4 \cdot 0.5\ HF \cdot 0.5\ H_2O$, $N_2H_5ScF_4$, $N_2H_6ScF_5$ [1]; $(N_2H_5)_2TiF_6$, $(N_2H_5)_2TiF_6 \cdot 2\ HF$, $N_2H_6TiF_6$ [2]; $(N_2H_5)_3VF_6$ [3]; $N_2H_6VF_5$ [4]; $(N_2H_5)_3CrF_6$ [3]; $N_2H_6CrF_5 \cdot H_2O$ [5]; $(N_2H_5)_2MnF_4$ [6]; $N_2H_6FeF_5$ [6]; $N_2H_5CoF_3$ [7]; $N_2H_5CuF_3$ [8]; $N_2H_5ZnF_3$ [8].

Interestingly enough, using the same approach we were not able to prepare hydrazinium fluoronicollate but only the adduct of $3\ NiF_2 \cdot 2\ N_2H_4$ and $NiF_2 \cdot 2\ N_2H_4 \cdot 2\ H_2O$ [6]. Hydrazinium fluorometallates were prepared:

(a) by the reaction of aqueous solutions of hydrazinium(2+) fluoride with a solution of the corresponding element or its oxide in hydrofluoric acid;

(b) by the addition of an aqueous solution of nitrate of the particular element to a solution of hydrazinium(1+) fluoride, and

(c) by dissolving metal fluoride in molten hydrazinium(2+) fluoride and by removing excess of hydrazinium(2+) fluoride by vacuum sublimation at 70°C.

The results of the chemical analyses of the isolated compounds are given in Table 1. In addition, IR spectroscopy and X-ray powder diffraction methods were also used for characterization of isolated compounds and the products of the thermal analyses.

The structures of $N_2H_6TiF_6$ [9], $(N_2H_5)_2TiF_6 \cdot 2\ HF$ [10] and $(N_2H_5)_3CrF_6$ [11] are known from X-ray structural analyses. The vanadium compound,

TABLE 1

Chemical analysis data of hydrazinium fluorometallates

	Calculated (%)					Found (%)				
	N_2H_4	M	F	HF	H_2O	N_2H_4	M	F	HF	H_2O
$N_2H_5ScF_4 \cdot 0.5\ HF \cdot 0.5\ H_2O$	18.50	29.99	49.43	5.78	5.20	19.0	25.5	48.8	5.6	5.7 *
$N_2H_5ScF_4$	20.81	29.12	49.35			20.7	29.5	49.0		
$N_2H_6ScF_5$	18.42	25.84	54.59			19.2	25.5	53.6		
$(N_2H_5)_2TiF_6$	28.11	21.01	50.00			28.4	21.9	49.8		
$(N_2H_5)_2TiF_6 \cdot 2\ HF$	23.91	17.87	56.71			23.8	17.9	56.6		
$N_2H_6TiF_6$	16.35	24.44	58.11			16.2	24.4	58.1		
$(N_2H_5)_3VF_6$	36.40	19.29	43.16			36.6	18.7	42.6		
$N_2H_6VF_5$	17.45	27.74	51.74			18.1	27.2	51.5		
$(N_2H_5)_3CrF_6$	36.26	19.61	42.99			36.2	19.2	42.9		
$N_2H_6CrF_5 \cdot H_2O$	16.10	25.87	47.71				25.3	47.9		
$(N_2H_5)_2MnF_4$	32.53	27.88	38.57			32.3	27.4	38.2		
$N_2H_6FeF_5$	17.33	30.20	51.37			17.5	30.6	50.2		
$N_2H_5CoF_3$	21.51	39.56	38.26			22.3	38.5	38.1		
$N_2H_5CuF_3$	20.87	41.37	37.11			20.9	40.7	37.6		
$N_2H_5ZnF_3$	20.62	42.06	36.67			20.9	41.7	35.6		

* Calculated from the difference to 100%.

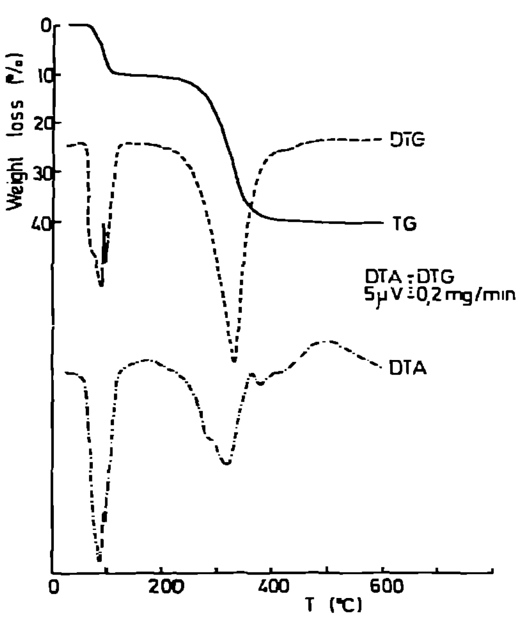
$(N_2H_5)_3VF_6$, is isomorphous with $(N_2H_5)_3CrF_6$. For other isolated compounds we have not yet succeeded in the preparation of the proper monocrystals for X-ray structure determination. Mössbauer effect measurements have been carried out on hydrazinium(2+) pentafluoroferrate [12]. The results confirmed the (3+) oxidation state of iron and octahedral arrangement of fluoride ions around it.

The thermal properties of the isolated compounds were investigated with a Mettler thermoanalyzer TA-1 [13] in an atmosphere of argon. Experimental conditions were as follows: sample weight 100 mg (1000 mg), reference substance, 100 mg α-Al_2O_3; Pt crucibles, 1 ml (3.3 ml); TD-1 (TD-Ma) crucible holder; flow rate, 5 l h^{-1}; and heating rates, 1 and 4°C min^{-1}.

RESULTS

The initial temperature of the thermal decomposition of $N_2H_5ScF_4 \cdot 0.5\ HF \cdot 0.5\ H_2O$ is 68°C (Fig. 1). Up to 125°C it loses water and hydrogen fluoride with DTG minima at 89 and 95°C. The intermediate obtained at 135°C is $N_2H_5ScF_4$, which decomposes further with increasing temperature into scandium(III) fluoride, with a DTG minimum at 330°C. The decomposition is concluded at 470°C.

The initial temperature of the thermal decomposition of $N_2H_5ScF_4$ is 105°C (Fig. 2). With increasing temperature the compound decomposes with one endothermal step, with a DTG minimum at 323°C. At 470°C scandium(III) fluoride is obtained.



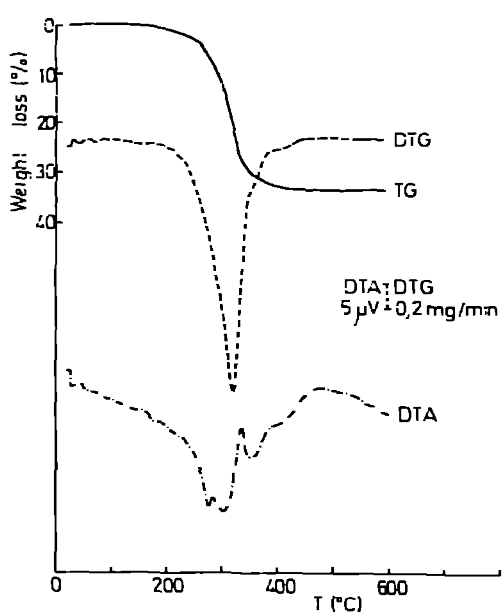


Fig. 1. TG, DTG and DTA curves of $N_2H_5ScF_4 \cdot 0.5\ HF \cdot 0.5\ H_2O$.

Fig. 2. TG, DTG and DTA curves of $N_2H_5ScF_4$.

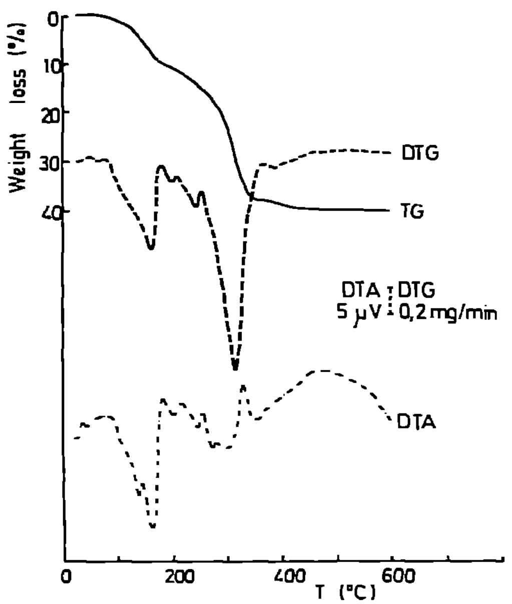


Fig. 3. TG, DTG and DTA curves of $N_2H_6ScF_5$.

$N_2H_6ScF_5$ decomposes in two endothermal steps (Fig. 3). The initial temperature of the first step of thermal decomposition is 70° C. $N_2H_6ScF_5$ transforms into $N_2H_5ScF_4$ upon heating up to 180°C, with a DTG minimum at 165°C, by losing 1 mole of hydrogen fluoride. In the second step the intermediate $N_2H_5ScF_4$ decomposes into scandium(III) fluoride as described above.

$(N_2H_5)_2TiF_6$ begins to lose weight at 155°C (Fig. 4). It decomposes into a

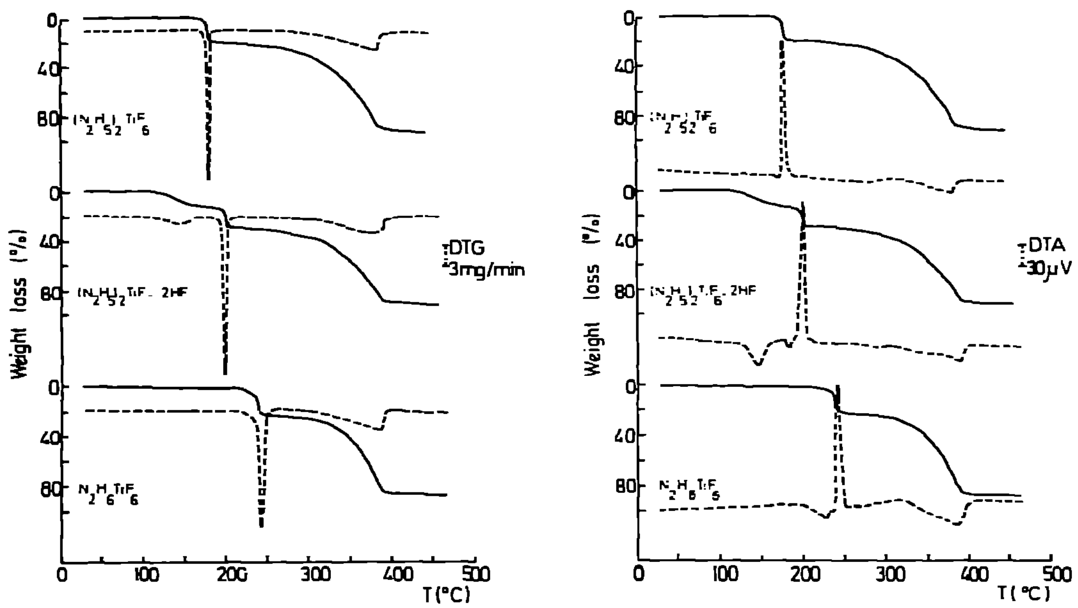
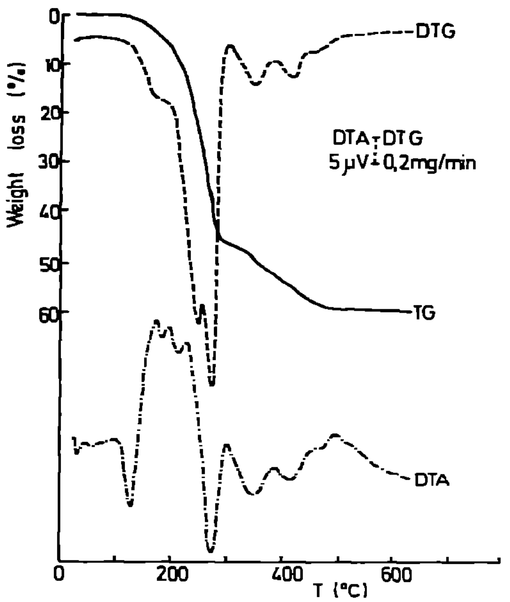


Fig. 4. TG, DTG and DTA curves of hydrazinium fluorotitanates.



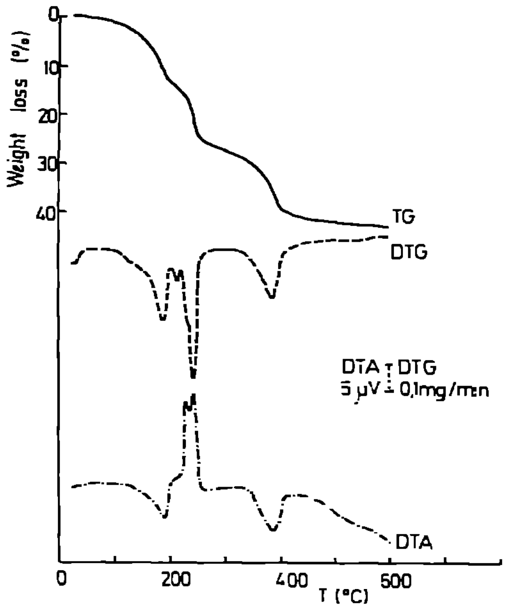


Fig. 5. TG, DTG and DTA curves of $(N_2H_5)_3VF_6$.

Fig. 6. TG, DTG and DTA curves of $N_2H_6VF_5$.

mixture of ammonium penta- and hexafluorotitanate(IV) in the molar ratio 2 : 1 in an almost explosive exothermal decomposition step, with the DTG minimum at 185°C.

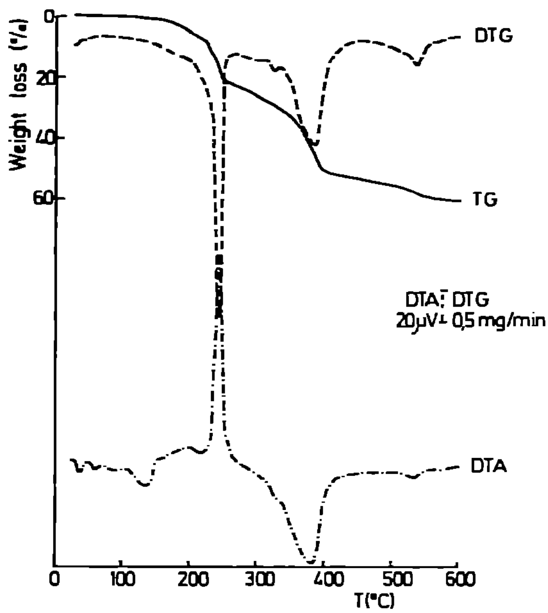
The initial temperature of the thermal decomposition of $(N_2H_5)_2TiF_6 \cdot 2\ HF$ is 80°C (Fig. 4). In the first endothermal step up to 180°C it loses 2 moles of hydrogen fluoride per mole of the starting compound. $(N_2H_5)_2TiF_6$ thus obtained decomposes in an exothermal step, with a DTG minimum at 195°C, into a mixture of ammonium penta- and hexafluorotitanate(IV) with a molar ratio of 2 : 1.

The initial temperature of the thermal decomposition of $N_2H_6TiF_6$ is 180°C (Fig. 4). With increasing temperature an almost explosive exothermal effect occurs at 240°C, the residue being ammonium pentafluorotitanate(IV).

$(N_2H_5)_3VF_6$ begins to lose weight at 90°C (Fig. 5). After two DTG minima at 252 and 277°C an intermediate NH_4VF_4 is obtained at 305°C. The thermal decomposition of the sample is concluded at 503°C, the residue being vanadium(III) fluoride.

Thermal analysis of $N_2H_6VF_5$ was carried out at a heating rate of 1°C min^{-1} (Fig. 6). The decomposition of the sample was so vigorous at higher heating rates that some of the sample was blown out of the crucible. $N_2H_6VF_5$ decomposes into hydrazinium(1+) tetrafluorovanadate, with a DTG minimum at 190°C. In the next step of thermal decomposition this intermediate decomposes in an exothermal reaction into ammonium tetrafluorovanadate(III). At 437°C the residue of impure vanadium(III) fluoride is obtained.

The thermal properties of hydrazinium fluorochromates were studied by Bukovec [5], who found that the hydrazinium(2+) pentafluorochromate



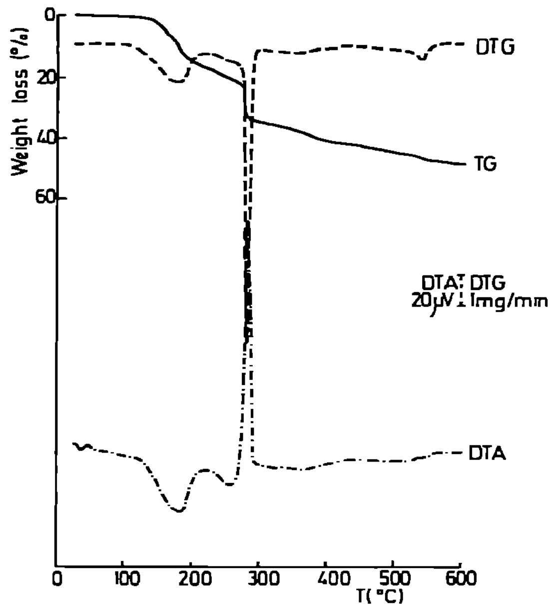


Fig. 7. TG, DTG and DTA curves of $(N_2H_5)_3CrF_5$.

Fig. 8. TG, DTG and DTA curves of $N_2H_6CrF_5 \cdot H_2O$.

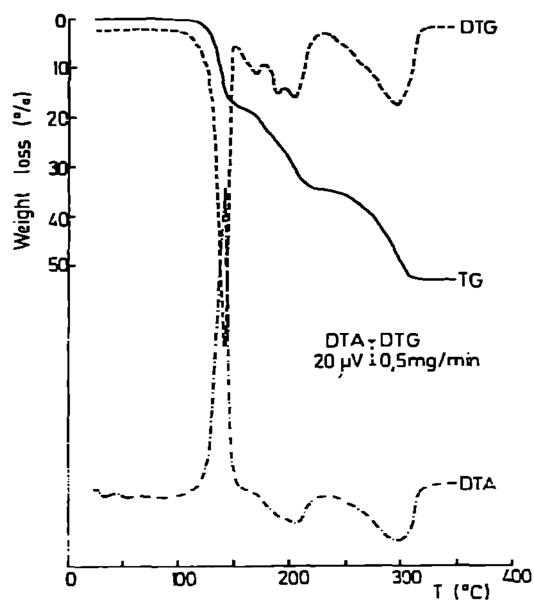
monohydrate decomposes via hydrazinium(1+) tetrafluorochromate(III) into impure chromium(III) fluoride.

Thermoanalytical measurements were repeated on hydrazinium fluorochromates in order to compare the thermal properties of hydrazinium fluorochromates with other hydrazinium fluorometallates both taken under identical conditions.

The initial temperature of the thermal decomposition of $(N_2H_5)_3CrF_6$ is 84°C (Fig. 7). After a very strong exothermal effect at 240°C a mixture of $(NH_4)_2CrF_5$ and $(NH_4)_3CrF_6$ was obtained. In the temperature interval 250—450°C this mixture decomposes into an intermediate with the molar ratio of the components $NH_4 : Cr : F = 0.9 : 1 : 4.0$. In the final step impure chromium(III) fluoride is obtained.

The initial temperature of the thermal decomposition of $N_2H_6CrF_5 \cdot H_2O$ is 68°C (Fig. 8). Up to 235°C it loses 1 mole of water and 1 mole of hydrogen fluoride and transforms, with a DTG minimum at 185°C, into $N_2H_5CrF_4$. This product further decomposes in a strongly exothermal step (DTG minimum being at 283°C) into an intermediate with the molar ratio of the components $NH_4 : Cr : F = 0.8 : 1 : 2.9$. The end product is again impure chromium(III) fluoride.

$(N_2H_5)_2MnF_4$ begins to lose weight at 110°C (Fig. 9). After an exothermal effect at 141°C and an endothermal effect at 208°C, ammonium trifluoromanganate(II) is obtained at 220°C. This intermediate further decomposes into pure manganese(II) fluoride which is obtained at 320°C, with a DTG minimum at 297°C.



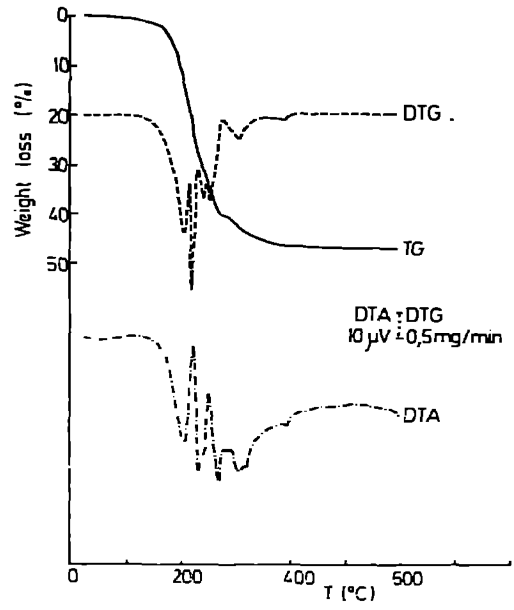
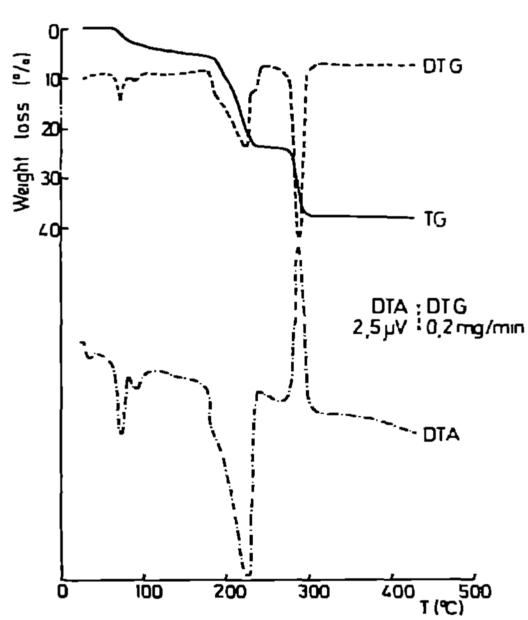


Fig. 9. TG, DTG and DTA curves of $(N_2H_5)_2MnF_4$.

Fig. 10. TG, DTG and DTA curves of $N_2H_6FeF_5$.

$N_2H_6FeF_5$ starts to decompose at 127°C (Fig. 10). No intermediate with a definite composition could be isolated. The products obtained at various temperatures of the thermal decomposition were in all cases mixtures of



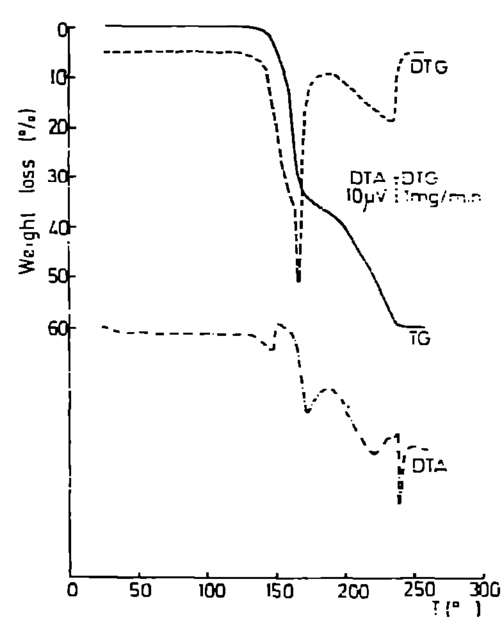


Fig. 11. TG, DTG and DTA curves of $N_2H_5CoF_3$.

Fig. 12. TG, DTG and DTA curves of $N_2H_5CuF_3$.

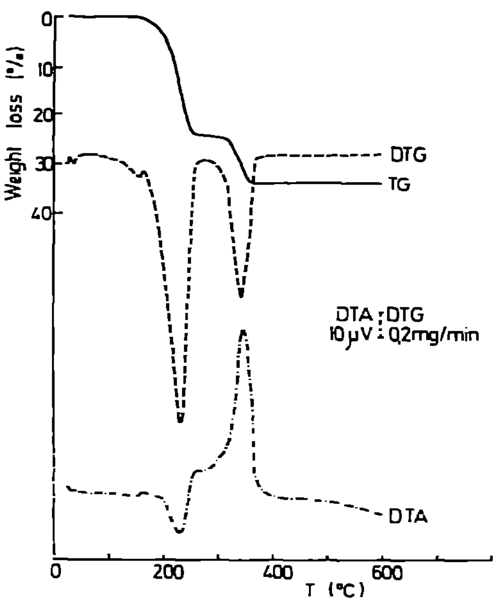


Fig. 13. TG, DTG and DTA curves of $N_2H_5ZnF_3$.

hydrazinium and ammonium fluoroferrates. The end product of the thermal analysis is pure iron(II) fluoride.

$N_2H_5CoF_3$ starts to decompose at 40°C (heating rate 1°C min^{-1}) (Fig. 11). The adduct between cobalt(II) fluoride and hydrazine, 3 $CoF_2 \cdot 2\ N_2H_4$, is the intermediate of the thermal decomposition isolated at 290°C. In the final step this adduct decomposes into cobalt(II) fluoride, the decomposition being accompanied by a strong exothermal effect due to the disproportionation of the coordinate hydrazine.

The initial temperature for the thermal decomposition of $N_2H_5CuF_3$ is 114°C (Fig. 12). At 168°C a strong endothermal effect occurs. The chemical analysis of the copper intermediates, obtained at 188—200°C, showed that the molar ratio between copper and fluorine is Cu : F = 1 : 0.86. At 238°C another DTG peak occurs and the thermal decomposition is complete at 244°C. The end product is pure copper (chemical analysis 99.8% Cu).

$N_2H_5ZnF_3$ starts to decompose at 142°C. The first DTG peak occurs at 237°C (Fig. 13). In the temperature interval 285—300°C an intermediate adduct of zinc difluoride and hydrazine, 2 $ZnF_2 \cdot N_2H_4$, was isolated. With increasing temperature the disproportionation of the hydrazine causes a strong exothermal effect at 345°C. The end product is pure zinc fluoride.

DISCUSSION

Table 2 summarizes the results of the thermal decomposition studies of hydrazinium fluorometallates. On the basis of the observed decomposition, the following decomposition sequences for hydrazinium fluorometallates could be proposed

$$N_2H_5ScF_4 \cdot 0.5\ HF \cdot 0.5\ H_2O \xrightarrow[125^\circ C]{HF,H_2O} N_2H_5ScF_4 \xrightarrow[471^\circ C]{N_2H_6F_2,N_2H_4} ScF_3$$

$$N_2H_5ScF_4 \xrightarrow{N_2H_6F_2,N_2H_4} ScF_3$$

$$N_2H_6ScF_5 \xrightarrow[180^\circ C]{HF} N_2H_5ScF_4 \xrightarrow[465^\circ C]{N_2H_6F_2,N_2H_4} ScF_3$$

$$2\ (N_2H_5)_2TiF_6 \xrightarrow[200^\circ C]{HF,NH_3,N_2} 2\ NH_4TiF_5 + (NH_4)_2TiF_6 \rightarrow \text{sublimes}$$

$$2\ (N_2H_5)_2TiF_6 \cdot 2\ HG \xrightarrow[180^\circ C]{HF} 2\ (N_2H_5)_2TiF_6 \xrightarrow[200^\circ C]{HF,NH_3,N_2}$$

$$2\ NH_4TiF_5 + (NH_4)_2TiF_6 \rightarrow \text{sublimes}$$

$$N_2H_6TiF_6 \xrightarrow[240^\circ C]{HF,NH_3,N_2} NH_4TiF_5 \rightarrow \text{sublimes}$$

$$(N_2H_5)_3VF_6 \xrightarrow[280^\circ C]{HF,NH_3,N_2} NH_4VF_4 \xrightarrow[503^\circ C]{HF,NH_3} VF_3$$

$$N_2H_6VF_5 \xrightarrow[200^\circ C]{HF} N_2H_5VF_4 \xrightarrow[270^\circ C]{NH_3,N_2} NH_4VF_4 \xrightarrow[437^\circ C]{HF,NH_3} VF_3 \text{ impure}$$

$$2\ (N_2H_5)_3CrF_6 \xrightarrow[250^\circ C]{HF,NH_3,N_2} (NH_4)_2CrF_5 + (NH_4)_3CrF_6 \xrightarrow[552^\circ C]{HF,NH_3} 2\ CrF_3 \text{ impure}$$

$$N_2H_6CrF_5 \cdot H_2O \xrightarrow[235^\circ C]{H_2O,HF} N_2H_5CrF_4 \xrightarrow[550^\circ C]{NH_3,\ N_2} CrF_3 \text{ impure}$$

$$(N_2H_5)_2MnF_4 \xrightarrow[150^\circ C]{NH_3,N_2} (NH_4)_2MnF_4 \xrightarrow[220^\circ C]{NH_3,HF} NH_4MnF_3 \xrightarrow[320^\circ C]{NH_3,\ HF} MnF_2$$

$$N_2H_6FeF_5 \xrightarrow[408^\circ C]{HF,NH_3,N_2} FeF_2$$

$$3\ N_2H_5CoF_3 \xrightarrow[290^\circ C]{HF,N_2H_6F_2} 3\ CoF_2 \cdot 2\ N_2H_4 \xrightarrow[299^\circ C]{N_2H_4} 3\ CoF_2$$

$$N_2H_5CuF_3 \xrightarrow[244^\circ C]{HF,N_2H_6F_2,N_2H_4} Cu$$

$$2\ N_2H_5ZnF_3 \xrightarrow[300^\circ C]{N_2H_6F_2} 2\ ZnF_2 \cdot N_2H_4 \xrightarrow[370^\circ C]{N_2H_4} 2\ ZnF_2$$

The temperatures given are those at which intermediates were isolated, and depend on the heating rate, sample weight and other effects. The decomposition products of the hydrazinium(1+) fluorometallates are related to those of hydrazinium(1+) fluoride, which decomposes on heating, as follows [14]

$$2\ N_2H_5F \rightarrow N_2H_6F_2 + N_2H_4$$

TABLE 2

Chemical analyses of the obtained intermediates of the thermal analyses

Compounds	Intermediates	Temp. (°C)	Weight loss (%)	
			Calc.	Found
$N_2H_5ScF_4 \cdot 0.5\ HF \cdot 0.5\ H_2O$	$N_2H_5ScF_4$	180	10.98	10.30
$N_2H_6ScF_5$	$N_2H_5ScF_4$	185	11.50	11.01
$(N_2H_5)_2TiF_6$	$2\ NH_4TiF_5 + (NH_4)_2TiF_6$	185	24.00	23.40
$(N_2H_5)_2TiF_6 \cdot 2\ HF$	$(N_2H_5)_2TiF_6$	180	14.93	14.81
	$2\ NH_4TiF_5 + (NH_4)_2TiF_6$	195	35.35	34.01
$N_2H_6TiF_6$	NH_4TiF_5	240	17.87	17.90
$(N_2H_5)_3VF_6$	NH_4VF_4	320	45.10	45.95
$N_2H_6VF_5$	$N_2H_5VF_4$	199	15.35	13.15
	NH_4VF_4	242	21.04	21.70
$(N_2H_5)_3CrF_6$	$(NH_4)_3CrF_6 + (NH_4)_2CrF_5$	280	23.97	22.90
$N_2H_6CrF_5 \cdot H_2O$	$N_2H_5CrF_4$	250	19.10	17.65
		300	36.64	35.47
$(N_2H_5)_2MnF_4$	NH_4MnF_3	222	34.04	34.13
$N_2H_5CoF_3$	$3\ CoF_2 \cdot 2\ N_2H_4$	266	20.60	20.21
$N_2H_5CuF_3$		190		36.10
$N_2H_5ZnF_3$	$2\ ZnF_2 \cdot N_2H_4$	252	23.18	23.77

Similarly, the decomposition products of the obtained intermediate ammonium fluorometallates are related to those of ammonium fluoride [15]

$$2\ NH_4F \rightarrow NH_4F \cdot HF + NH_3$$

Hydrazinium fluorometallates of the first row transition elements can be divided into two groups with regard to their thermal properties and the intermediates into which they decompose. $(N_2H_5)_2TiF_6$, $(N_2H_5)_2TiF_6 \cdot 2\ HF$, $N_2H_6TiF_6$, $(N_2H_5)_3VF_6$, $N_2H_6VF_5$, $(N_2H_5)_3CrF_6$, $N_2H_6CrF_5 \cdot H_2O$ and $(N_2H_5)_2MnF_4$, which decompose into intermediate ammonium fluorometallates, form the first group. The second group comprises $N_2H_5CoF_3$, $N_2H_5CuF_3$, and $N_2H_5ZnF_3$, which on thermal decomposition yield adducts of hydrazine with metal fluorides as intermediate products.

However, hydrazinium fluorometallates of two elements of the first row transition elements do not fit in either of these two groups. Scandium fluorometallates decompose into scandium trifluoride without the formation of an intermediate. Hydrazinium pentafluoroferrate decomposes into iron difluoride and, although no definite intermediate could be isolated, chemical analysis of the product obtained at 270°C with a weight loss of 41% shows the presence of both the hydrazine and ammonia. The iron compound can be thus considered as an intermediate between the two groups.

Hydrazine, which is present in these compounds either as hydrazinium(1+)

Calculated (%)			Found (%)			Molar ratio
N_2H_4,NH_4	Me	F	N_2H_4,NH_4	Me	F	N_2H_4,NH_4 : Me : F
20.81	29.12	49.35	20.4	29.4	49.3	0.97 : 1 : 3.99
20.81	29.12	49.35	20.7	29.1	49.2	0.99 : 1 : 4.00
13.88	27.64	58.47	14.2	27.1	57.8	4.17 : 3 : 16.14
28.11	21.01	50.00	27.5	21.0	51.0	1.96 : 1 : 6.12
13.88	27.64	58.47	13.5	27.5	57.9	3.90 : 1 : 15.93
11.21	29.76	59.03	10.2	30.1	58.6	0.90 : 1 : 4.91
12.44	35.14	52.42	12.4	35.1	51.4	1.00 : 1 : 3.93
20.03	31.84	47.50	17.4	31.4	47.2	0.88 : 1 : 4.06
12.44	35.14	52.42	12.2	36.3	52.3	0.95 : 1 : 3.86
22.15	26.01	51.84	20.6	25.6	48.4	2.32 : 1 : 5.17
19.90	32.29	47.19	19.8	31.9	45.6	1.01 : 1 : 3.91
14.31	41.26	45.23	10.2	42.2	45.3	0.70 : 1 : 2.94
13.88	42.27	43.85	13.0	42.1	43.9	0.94 : 1 : 3.01
18.06	49.82	32.12	17.4	48.1	32.4	1.98 : 3 : 6.27
				68.8	18.0	1 : 0.87
13.42	54.75	31.83	13.4	54.8	31.8	1.00 : 2 : 4.00

or (2+) ion, or neutral ligand in the case of adducts, is a strong reducing agent. The oxidation number of the central cation in hydrazinium fluorometallates is, however, lowered during thermal decomposition only in two cases, namely with iron and copper. In the course of thermal analysis the iron in hydrazinium pentafluoroferrate changes its oxidation state from the initial (3+) to (2+) in the end product, which is iron difluoride. In the case of hydrazinium trifluorocuprate a reduction to elemental copper occurs. Table 3 summarizes the data relevant to the end products of the thermal decompositions studied.

In this study of hydrazinium fluorometallates it was found that these compounds could be divided into two groups with regard to their thermal properties. The first group consists of the hydrazinium fluorometallates of titanium, vanadium, chromium and manganese, while the second group is formed by the hydrazinium fluorometallates of cobalt, copper and zinc. Hydrazinium pentafluoroferrate is considered as an intermediate between the two groups. The end products are in most cases metal fluorides, except in the case of the copper compound, where reduction to the metal occurs.

The investigated hydrazinium fluorometallates can be used as starting compounds for the preparation of adducts of hydrazine with metal fluorides, some ammonium fluorometallates and metal fluorides.

TABLE 3

Chemical analyses of the products of the thermal analyses

Compounds	End products	Temp. (°C)	Colour	Weight loss (%)		Calculated (%)		Found (%)	
				Calc.	Found	Me	F	Me	F
$N_2H_5ScF_4 \cdot 0.5\ HF \cdot 0.5\ H_2O$	ScF_3	471	White	41.07	40.00	44.10	55.90	44.2	55.7
$N_2H_6ScF_5$	ScF_3	465	White	41.41	40.4	44.10	55.90	44.4	55.5
$(N_2H_5)_3CrF_6$	CrF_3 impure	552	Green	58.93	58.8	47.71	52.29	46.0	50.5
$N_2H_6CrF_6 \cdot H_2O$	CrF_3 impure	550	Green	45.25	48.0	47.71	52.29	46.2	50.8
$(N_2H_5)_3VF_6$	VF_3	503	Yellow-green	59.13	59.1	47.20	52.80	46.2	52.0
$N_2H_6VF_5$	VF_3 impure	437	Yellow-green	41.21	41.1	47.20	52.80	45.8	50.9
$(N_2H_5)_2MnF_4$	MnF_2	320	Pink	52.84	50.2	59.12	40.88	59.0	40.5
$N_2H_6FeF_5$	FeF_2	408	White	49.25	46.5	59.51	40.49	58.8	40.9
$N_2H_5CoF_3$	CoF_2	299	Rose-red	34.94	37.5	60.80	39.20	60.5	39.2
$N_2H_5CuF_3$	Cu	244	Red	58.63	59.6	100.00		99.8	
$N_2H_5ZnF_3$	ZnF_2	370	White	33.50	34.0	63.24	36.74	63.1	37.0

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