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THERMAL BEHAVIOUR OF NEW HYDRAZINIUM(1+) HEXAFLUOROZIRCONATE AND -HAFNATE

D. GANTAR, A. RAHTEN

'Jozef Stefan' Institute, 'Edvard Kardelj' University of Ljubljana, 61000 Ljubljana, (Yugoslavia)

and B. VOLAVSEK

Faculty of Technical Sciences, University of Maribor, 62000 Maribor (Yugoslavia)

SUMMARY

Two new hydrazinium(1+) fluorocomplexes, $(N_2H_5)_2ZrF_6$ and $(N_2H_5)_2HfF_6$ were prepared and characterized by chemical analysis, vibrational spectroscopy and X-ray powder photography. They are isostructural and the diffraction data were indexed on the basis of a monoclinic cell. Study of their thermal behaviour by TG, DTG, DTA and DSC measurements showed that they decomposed in stages. $(N_2H_5)_2ZrF_6$ decomposed in three steps through $(NH_4)_2ZrF_6$ and NH_4ZrF_5. The thermal decomposition of $(N_2H_5)_2HfF_6$ was more complex: in the first step $(NH_4)_2HfF_6$ with some $N_2H_5HfF_5$ was obtained, and in the second NH_4HfF_5. The intermediates were identified by chemical analysis and vibrational spectroscopy.

INTRODUCTION

In the sixties the hydrazinium(2+) fluorometalates $N_2H_6MF_6$ and $(N_2H_6)_3M_2F_{14}$ (M = Zr, Hf) were isolated from aqueous solutions [1,2] . However, the corresponding hydrazinium(1+) compounds have not been prepared so far. Various methods can be used for the preparation of hydrazinium(1+) fluorometalates, among which the reaction of the corresponding hydrazinium(2+) salts with hydrazine is very common. In the present study we synthesized $(N_2H_5)_2ZrF_6$ and $(N_2H_5)_2HfF_6$ and investigated their properties, particularly their thermal behaviour.

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EXPERIMENTAL

The hydrazinium(1+) fluorometalates, $(N_2H_5)_2MF_6$ (M = Zr, Hf), were prepared by the reactions of the hydrazinium(2+) hexafluorozirconate and -hafnate with hydrazine hydrate:

$$N_2H_6MF_6 + N_2H_4 \cdot H_2O \longrightarrow (N_2H_5)_2MF_6 + H_2O$$

M = Zr, Hf

The chemical analysis of the products is summarized below:

$(N_2H_5)_2ZrF_6$: Found: N_2H_4, 23.3; Zr, 33.6; F, 41.5.
Calcd.: N_2H_4, 23.62; Zr, 33.62; F, 42.01.

$(N_2H_5)_2HfF_6$: Found: N_2H_4, 17.9; Hf, 49.5; F, 31.2.
Calcd.: N_2H_4, 17.87; Hf, 49.78; F, 31.79.

For thermal analysis a Mettler TA 1 thermoanalyzer was used. In a typical run a 100 mg sample was used; in a macrothermogravimetric decomposition this was increased to 500 mg: both were referenced against a 100 mg sample of α- Al_2O_3. Platinum crucibles (1 ml) were used, the heating rate of the furnace was 1 ^oC min^{-1}, and the decompositions were carried out in a dry argon atmosphere with a flow rate of 5 lh^{-1}. The DTG range was 10 mg min^{-1} and the DTA range was 200 μV.

Heat flow as a function of temperature was determined with a differential scanning calorimeter (Mettler, DSC-20). DSC recordings were made in a closed aluminium cell with a pin hole on its surface and in a flowing argon atmosphere. From 8-9 mg of sample was employed at a heating rate of 10 ^oC min^{-1}. ΔH was determined by graphical integration using a Mettler TC 10A processor.

Infrared spectra of the solids pressed between CsBr discs were obtained using a Perkin-Elmer 521 spectrometer. The Raman spectra of the samples in a Pyrex tube were recorded on a Spex 1401 double monochromator instrument with exciting radiation from the 5145 Å line of a Coherent Radiation Laboratories (model Ar) ion laser.

X-ray powder diffraction data were obtained with a Debye-Scherrer type camera and CuK_α radiation. The diffraction photographs were indexed using a Haendler program [3] on an IBM-1130 computer.

Hydrazine was determined potentiometrically [4], total fluorine by a modified distillation method [5], ammonium by a Kjeldahl method [6] and metals gravimetrically [7].

RESULTS AND DISCUSSION

The decomposition of $(N_2H_5)_2ZrF_6$ starts at 100°C (Fig. 1). The endothermic DTA peaks at 98°, 110°, 130° and 136°C, which are not accompanied by weight loss, can be accounted for by phase changes in the sample. Between 146° and 220°C decomposition is strongly exothermic with DTA peaks at 194°, 199°, 210° and 294°C and a DTG minimum at 214°C. Up to 220°C the sample loses 13.6% of its weight, corresponding to the loss of a mole of hydrogen and a mole of nitrogen per mole of starting material (theoretical weight loss is 11.07%). The intermediate is $(NH_4)_2ZrF_6$ (found: NH_4, 14.4; calcd. for $(NH_4)_2ZrF_6$: NH_4, 14.95). In the temperature interval between 220° and 271°C a further 11.1% weight loss

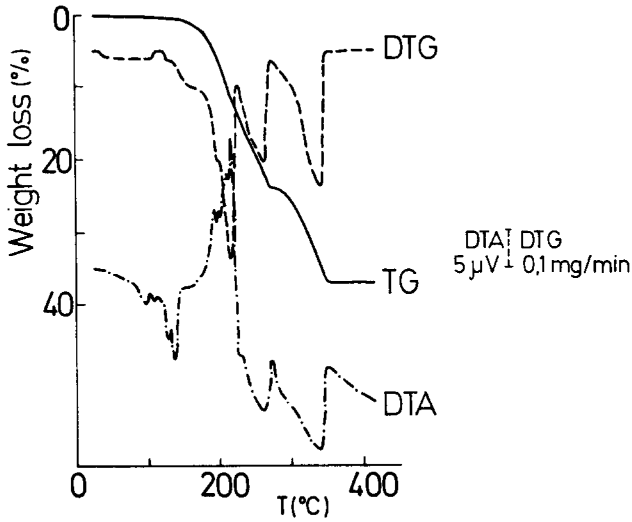

Fig. 1. TG, DTG and DTA curves of $(N_2H_5)_2ZrF_6$.

occurs (theoretical weight loss for the formation of NH_4ZrF_5 is 13.65%) and this is accompanied by an endothermic DTA peak and a DTG minimum at 262°C. The intermediate NH_4ZrF_5 is isolated at 271°C (found: NH_4, 8.1; calcd. for NH_4ZrF_5: NH_4, 8.23). In the last step the decomposition is endothermic with a DTA peak and a DTG minimum at 340°C. Up to 415°C the cumulative weight loss is 37.7%, which correlates well with the theoretical value (38.37%) for the formation of ZrF_4.

The decomposition may be described in terms of the equations:

$$(N_2H_5)_2ZrF_6 \longrightarrow (NH_4)_2ZrF_6 + H_2 + N_2 \tag{1}$$

$$(NH_4)_2ZrF_6 \longrightarrow NH_4ZrF_5 + 1.5H_2 + 0.5N_2 + HF \tag{2}$$

$$NH_4ZrF_5 \longrightarrow ZrF_4 + 1.5H_2 + 0.5N_2 + HF \tag{3}$$

The thermal decomposition of $(N_2H_5)_2HfF_6$ begins at 105°C (Fig. 2). Up to this temperature DTA peaks at 70°, 82° and 95°C are observed, as in the case of $(N_2H_5)_2ZrF_6$. In the first step up to 219°C the sample loses 8.4% of its weight

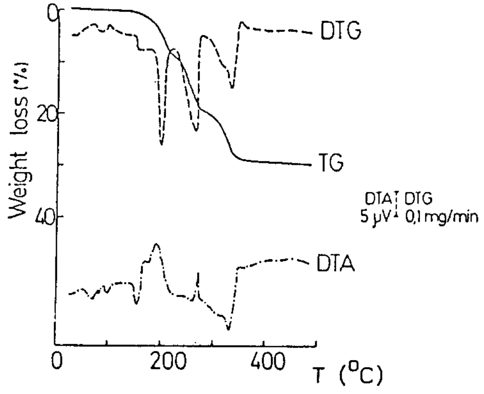

Fig. 2. TG, DTG and DTA curves of $(N_2H_5)_2HfF_6$

corresponding to the formation of $(NH_4)_2HfF_6$ (theoretical value is 8.37%). However, some $N_2H_5HfF_5$ is also present as is proved by chemical analysis (found: N_2H_4, 4.5) and the vibrational spectrum of the first step intermediate. This step is accompanied by an endothermic DTA peak at 153°C and an exothermic DTA peak at 200°, and a DTG minimum at 200°C. In the second step between 219° and 271°C the decomposition is exothermic with a DTA peak and a DTG minimum at 270°C. Between 105° and 271°C the sample loses 19.1% of its weight and this corresponds to the formation of NH_4HfF_5 (theoretical weight loss is 18.70%; found: NH_4, 6.3; calcd. for NH_4HfF_5: NH_4, 6.18). Further decomposition is endothermic with a DTA peak and a DTG minimum at 332°C. The cumulative weight loss of the sample up to 357°C amounts to 29.0%, corresponding to the formation of HfF_4 (theoretical weight loss is 29.03%).

The first step of the thermal decomposition of $(N_2H_5)_2HfF_6$ is more complex in comparison to that of $(N_2H_5)_2ZrF_6$. Similar behaviour was also observed in the second step of the thermal decomposition of $N_2H_6MF_6$ (M = Zr, Hf) [8]. The decomposition is accompanied by exothermic and endothermic effects, and the intermediate, besides $(NH_4)_2HfF_6$, still contains $N_2H_5HfF_5$. In the next two steps NH_4HfF_5 and HfF_4, as with the zirconium compound, are formed.

In the DSC curves for $(N_2H_5)_2ZrF_6$ and $(N_2H_5)_2HfF_6$ similar endothermal and exothermal effects take place in the range 40-500°C. The total area integrated between the DSC curves and the baseline from 40-500°C showed that the decompositions to metal tetrafluoride in total were endothermal, but ΔH for the decomposition of $(N_2H_5)_2ZrF_6$ was higher than for $(N_2H_5)_2HfF_6$. The effects clearly show that the both decompositions occur at the same way; however, pure $(NH_4)_2HfF_6$ could not be isolated under the conditions used on a thermoanalyser.

The vibrational spectra of starting materials and of the intermediate compounds isolated in the thermal decomposition were recorded. They are given in Tables 1 and 2.

The bands observed in the Raman and the absorptions in the infrared spectra between 940 and 1700 cm^{-1} are assigned to the $N_2H_5^+$ ion, and between 3100 and 3330 cm^{-1} to NH_4^+. For the anionic part of the vibrational spectra the bands in the 380-570 cm^{-1} interval are assigned to metal-fluorine stretching and in the 200-355 cm^{-1} interval to bending vibrations (metals Zr, Hf). The observed vibrational spectra are in accordance with the literature [9,10,11] .

TABLE 1

Vibrational spectra (cm^{-1}) of $(N_2H_5)_2ZrF_6$, $(NH_4)_2ZrF_6$ and NH_4ZrF_5

$(N_2H_5)_2ZrF_6$		$(NH_4)_2ZrF_6$		NH_4ZrF_5		Assignment
IR	R	IR	R	IR	R	
	131(6.5)					lattice vibrations
	169(6)		170(6)		172(13)	
	244(9)				242(10)	$(Zr\text{-}F)_b$
	288(3)			288s	294(10)	
			350(17)		352(6.5)	
392m	394(7.5)	383m	383(6)	375m	388(11)	$(Zr\text{-}F)_s$
420s,sh						
480vs	472(5)	477vs	472(11)	478vs	473(22)	
530s,sh	566(58.5)		532(100)		520(100)	
	690(3)		703(7)			$(N\text{-}N)_s$
947vs		943w				
961vs						
972vs,sh	977(100)		968(6)			
1085vs		1082w	1080(4)			$(NH_3^+)_r$
1111vs	1122(6)					
1144s,sh	1142(10)	1145w				
1227w						
1250w	1263(2)					
	1432(2.5)					$(NH_2)_r$
1489vs						
1508s	1516(4)					$(NH_3^+)_d$
1545s	1556(2)					
1600vs	1605(3)					
1634vs	1632(8.5)					
	1651(11)					$(NH_2)_d$
		3130s		3075s,sh		$\nu_3(NH_4^+)$
			3144(10)		3126(6.5)	
		3205s,br		3191s,br		

TABLE 2

Vibrational spectra (cm^{-1}) of $(N_2H_5)_2HfF_6$, the first step intermediates and NH_4HfF_5

$(N_2H_5)_2HfF_6$		$(NH_4)_2HfF_6$, $N_2H_5HfF_5$		NH_4HfF_5		Assignment
IR	R	IR	R	IR	R	
	132(9)					lattice vibrations
	173(4)		188(18)		182(16)	
	248(9)		242(36)		242(52)	$(Hf\text{-}F)_b$
	286(2)	277m		279s	299(26)	
	311(2)					
			354(16)		352(23)	
392m	400(3)	378m	402(19)	378m		$(Hf\text{-}F)_s$
426s,sh	417(3)					
468vs	480(2)	468vs	483(19)	480vs	483(28)	
			539(66)		523(100)	
	568(55)		570(85)			
	685(2.5)		688(19)		700(17)	
960vs						$(N\text{-}N)_s$
970vs,sh	978(100)	972m	975(100)			
			1020(12)			
1108vs		1080m	1048(25)			$(NH_3^+)_r$
1122vs	1122(6)	1110w	1122(27)			
	1145(10.5)					
1142vs,sh						
1250m	1270(2)					
			1338(25)			$(NH_2)_r$
	1431(2.5)		1414(22)			
1505s		1506w				$(NH_3^+)_d$
	1515(4.5)	1528m				
1545s	1554(2)					
1592s	1602(3)	1588m	1594(15)			
1632vs	1630(6.5)	1608w				
		1638w				
	1652(12.5)		1648(28)			$(NH_2)_d$
		3238m,br	3149(34)	3192m,br	3141(47)	$\nu_3(NH_4^+)$

The X-ray powder photographs of $(N_2H_5)_2ZrF_6$ and $(N_2H_5)_2HfF_6$ show that the compounds are isomorphous and crystallize in a monoclinic system. The unit-cell parameters are closely related to those of monoclinic $(N_2H_5)_2TiF_6$ (a = 7.86, b = 9.97, c = 9.20 Å, β = 98°) [12] . The results of indexed diffraction photographs are summarized in Tables 3 and 4.

TABLE 3

X-ray powder diffraction data for $(N_2H_5)_2ZrF_6$

h k l	$d_{calcd.}$	$d_{obs.}$	I	h k l	$d_{calcd.}$	$d_{obs.}$	I
1 0 0	8.08	8.12	w	1 3-3	2.270	2.262	m
0 1 1	6.90	7.09	vs	3 0 2	2.220	2.221	w
1 1-1	5.51	5.61	vs	-3 0 3	2.195	2.195	w
1 1 1	5.02	4.99	m	1 1 4	2.147	2.152	w
0 0 2	4.74	4.77	m	2 2 3	2.126	2.126	w
0 2 1	4.45	4.56	m	3 3 0	2.101	2.101	w
-1 0 2	4.34	4.40	m	2 4 1	2.055	2.054	m
1 2 0	4.27	4.24	m	3 3 1	2.009	2.005	w
2 0 0	4.04	4.02	m	4 1-1	1.989	1.981	w
1 2 1	3.80	3.80	m	1 5 0	1.956	1.955	vw
2 1-1	3.64	3.66	m	1 5 1	1.904	1.901	w
2 0 1	3.55	3.58	w	1 4 3	1.879	1.875	w
0 2 2	3.45	3.47	m	2 2 4	1.808	1.804	m
2 2 0	3.15	3.16	s	4 3-1	1.737	1.739	m
1 3-1	2.992	2.990	m	1 5-3	1.687	1.684	w
1 1-3	2.946	2.931	m	0 3 5	1.651	1.647	vw
1 0 3	2.820	2.831	vw	2 0 5	1.636	1.634	w
1 1 3	2.716	2.716	w	4 4-1	1.580	1.580	w
0 2 3	2.677	2.685	w	4 4-2	1.543	1.543	vw
1 3 2	2.538	2.536	w	3 4-4	1.520	1.520	vw
1 2 3	2.461	2.462	w	3 5 2	1.492	1.496	vw
3 2-1	2.368	2.370	w	1 4 5	1.462	1.461	vw
1 4 1	2.310	2.316	m				

Indexed on a basis of monoclinic cell with a = 8.15(1) Å, b = 10.08(1) Å, c = 9.56(1) Å, β = 97.5(1)°, V = 778(4) Å^3 .

TABLE 4

X-ray powder diffraction data for $(N_2H_5)_2HfF_6$

h k l	$d_{\text{calcd.}}$	$d_{\text{obs.}}$	I	h k l	$d_{\text{calcd.}}$	$d_{\text{obs.}}$	I
1 0 0	8.09	8.10	w	0 0 4	2.382	2.395	vw
0 1 1	6.92	7.06	vs	2 0 3	2.350	2.353	vw
1 1-1	5.53	5.62	vs	1 4 1	2.310	2.310	w
1 1 1	5.02	4.99	m	3 2 1	2.246	2.255	m
0 0 2	4.76	4.76	m	2 1-4	2.135	2.145	w
0 2 1	4.45	4.55	m	3 3-1	2.100	2.095	w
-1 0 2	4.37	4.38	m	2 4 1	2.056	2.048	w
1 2 0	4.28	4.24	m	4 1-1	1.995	1.997	w
2 0 0	4.05	4.01	m	0 5 1	1.972	1.977	w
1 2 1	3.80	3.79	m	3 1 3	1.898	1.898	vw
2 1-1	3.65	3.64	m	0 1 5	1.873	1.869	vw
2 0 1	3.56	3.57	w	4 2 1	1.799	1.798	m
0 2 2	3.46	3.46	m	0 4 4	1.731	1.732	w
2 2 0	3.15	3.16	s	4 3-2	1.692	1.692	w
1 3-1	2.995	2.988	m	4 2 2	1.677	1.678	w
1 1-3	2.946	2.922	m	3 1-5	1.643	1.643	vw
1 0 3	2.830	2.835	m	1 6-1	1.628	1.628	vw
1 1 3	2.725	2.712	w	4 0 3	1.611	1.612	vw
0 2 3	2.687	2.677	w	4 4 0	1.577	1.576	w
1 2 3	2.468	2.469	m	5 2 0	1.541	1.541	vw

Indexed on the basis of a monoclinic cell with a = 8.17(1) Å, b = 10.08(2) Å, c = 9.62(1) Å, β = 97.8(1)°, V = 784(4) Å^3.

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