Thermochimica Acta, 171 (1990) 185–192
Elsevier Science Publishers B.V., Amsterdam

SYNTHESIS, THERMAL DECOMPOSITION AND VIBRATIONAL SPECTRA OF HYDRAZINIUM(1 +) HEPTAFLUOROZIRCONATE(IV) AND HAFNATE(IV)

A. RAHTEN and S. MILIĆEV *
"J. Stefan" Institute, Ljubljana (Yugoslavia)

(Received 28 March 1990)

ABSTRACT

Two new compounds of Zr^{IV} and Hf^{IV}, $(N_2H_5)_3MF_7$, have been synthesized from aqueous solutions of $(N_2H_6)_3M_2F_{13}\cdot F$ and $N_2H_4\cdot H_2O$. Vibrational spectra show the presence of a dimeric or polymeric anion with a coordination number larger than 6, and two types of $N_2H_5^+$ ion, involved predominantly through their NH_3^+ groups in weak hydrogen bonds. On heating, the compounds start to lose weight above 120 °C (Zr compound) or 110 °C (Hf compound). Decomposition proceeds through $(NH_4)_2MF_6$ and NH_4MF_5 (γ-NH_4ZrF_5) to MF_4 (predominantly α-ZrF_4), and finishes at ca. 350 °C (Zr compound) or 380 °C (Hf compound). Raman spectra of decomposition intermediates show that the composite anionic part transforms through other complex or polymeric fluorozirconate(IV) or hafnate(IV) anions to MF_4, and no simple MF_6^{2-} or MF_5^- anions appear.

INTRODUCTION

A number of hydrazinium fluorometallates have been synthesized from aqueous solutions. Generally, $N_2H_6^{2+}$ compounds crystallize easily, and the Zr and Hf compounds $N_2H_6MF_6$ and $(N_2H_6)_3M_2F_{13}\cdot F$ ($M \equiv Zr$, Hf) have been prepared by this means [1]. Crystallization of $N_2H_5^+$ compounds presents difficulties because of their higher solubility. Nevertheless, it has been achieved, either from aqueous solutions of appropriate concentrations of $N_2H_6MF_6$ and $N_2H_4\cdot H_2O$, and appropriate pH (syntheses of $(N_2H_5)_2MF_6$ [2]); or through thermal decomposition of $N_2H_6MF_6$ (syntheses of $N_2H_5MF_5$ [3]). Further thermal decomposition yields ammonium compounds, $(NH_4)_2MF_6$ [2] and NH_4ZrF_5 [3]. The compounds are synthetically related, and where structure is known, $N_2H_6ZrF_6$ [4], $(N_2H_6)_3M_2F_{13}\cdot F$ [5] and $(NH_4)_2ZrF_6$ [6], dimeric or polymeric fluorozirconate anions based on a deformed bicapped trigonal prism with coordination number 8 are

---

* Author to whom correspondence should be addressed.

0040-6031/90/$03.50

present. The anions are held together by a hydrogen bond network to $N_2H_6^{2+}$ or NH_4^+ cations, and in $(N_2H_6)_3M_2F_{13} \cdot F$ there occur two types of $N_2H_6^{2+}$ ions. The present paper reports on two new members of this series, $(N_2H_5)_3MF_7$.

EXPERIMENTAL

Synthesis

4.5 g of $(N_2H_6)_3Zr_2F_{13} \cdot F$ was dissolved in 50 mL of water, and an aqueous solution of $N_2H_4 \cdot H_2O$ (10%) was added, to achieve a pH value of 5.5. Colourless crystals of $(N_2H_5)_3ZrF_7$, obtained by slow evaporation at room temperature, were filtered and dried over H_2SO_4 in a desiccator. $(N_2H_5)_3HfF_7$ was synthesized analogously. The starting compounds, $(N_2H_6)_3M_2F_{13} \cdot F$ (M ≡ Zr, Hf), were prepared according to a method described elsewhere [1]. The $(N_2H_5)_3ZrF_7$ was determined as: N_2H_4 29.6%, Zr 28.0%, F 41.3% (c.f. required: N_2H_4 29.73%, Zr 28.21%, F 41.12%). The $(N_2H_5)_3HfF_7$ was determined as: N_2H_4 22.9%, Hf 43.5%, F 32.4% (cf. required: N_2H_4 23.41%, Hf 43.47%, F 32.38%).

$(NH_4)_2ZrF_6$ and $(NH_4)ZrF_5$, which were used for comparing vibrational spectra, were prepared according to a method described elsewhere [7].

Thermoanalysis

100 mg samples were heated at 1° C min^{-1} in a stream of dried argon (5 l h^{-1}) using a Mettler TA-1 thermoanalyser. The reference sample was 100 mg of α-Al_2O_3. The DTG range was 10 mg min^{-1}, and the DTA range was 100 μV. 150–250 mg samples were used for isolating intermediates.

Vibrational spectroscopy

IR spectra were taken as Nujol and fluorolube mulls on KBr or CsBr plates using a Perkin–Elmer FTIR 1710 spectrometer (4000–300 cm^{-1}, resolution 4 cm^{-1}). Raman spectra of samples in glass capillaries were excited in back-scattering geometry with the 5145 Å line of an Ar^+-ion laser (Coherent Radiation model I-52-3, 2 W) using a home-made instrument with a Spex-1401 double monochromator.

Powder data

Debye–Scherrer X-ray diffraction patterns were obtained from a sample sealed in a glass capillary with graphite monochromatized Cu $K\alpha$ radiation using an Enraf (Delft) instrument. Intensities were estimated visually.

RESULTS AND DISCUSSION

The thermal decomposition patterns are presented in Fig. 1. The path (Table 1) was determined by weight loss, chemical analysis, and in the case of the Zr compound, by comparison with known X-ray powder patterns (Table 2) and IR spectra (Table 3). The powder and decomposition data for the two compounds are very similar, so we conclude that they undergo essentially the same mechanism of thermal decomposition. A small endothermic effect at 78 °C for both compounds is ascribed to a phase transition. The compounds start to lose weight above 120 °C (Zr compound) or 110 °C (Hf compound). The violence of the first exothermic step, in which the hydrazinium(1 +) ion most probably disproportionates into NH_3, NH_4^+ and N_2, makes it difficult to isolate pure $(NH_4)_2MF_6$. The product includes traces of $N_2H_5^+$, according to the IR spectra and chemical analysis (which indicates up to 0.6% of N_2H_4 in weight, depending on the experiment). In the next two endothermic steps NH_4F and NH_4MF_5 (γ-NH_4ZrF_5) are evolved; and finally MF_4 compounds are formed. In the case of the Zr compound, a mixture of modifications is obtained, with a predominance of α-ZrF_4.

Vibrational spectra are shown in Fig. 2 and Table 4. The assignments were made according to data from the literature (see ref. 9 for the hydrazinium cation, and refs, 5, 7 and 10 for the fluorometallic anion). The spectra of the two compounds correspond closely, as has been observed previously for Zr and Hf compounds of the same stoichiometry [5,10a]. They differ significantly only in the position of IR bands at 498 cm^{-1} for the Zr and 477 cm^{-1} for the Hf compound. This discrepancy is probably due to a

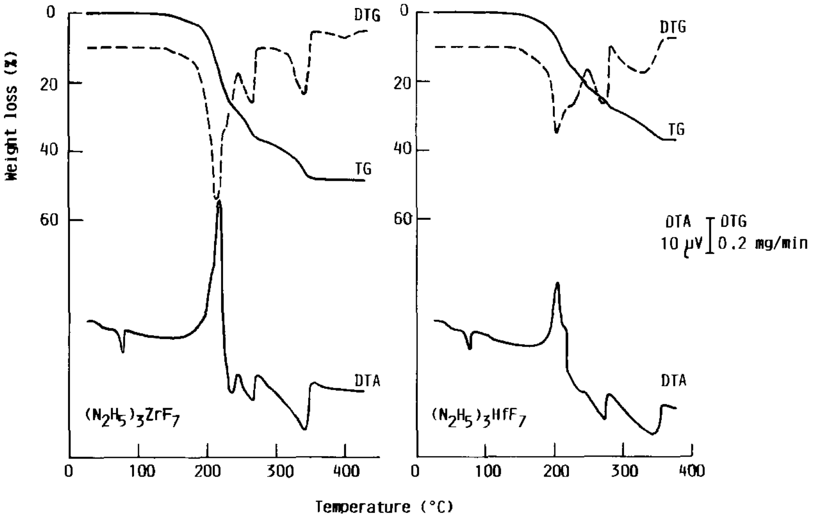

Fig. 1. Thermal decomposition of $(N_2H_5)_3ZrF_7$ and $(N_2H_5)_3HfF_7$.

TABLE 1

Thermal decomposition of $(N_2H_5)_3ZrF_7$ and $(N_2H_5)_3HfF_7$

$(N_2H_5)_3ZrF_7$				$(N_2H_5)_3HfF_7$		
Temperature of DTA peaks (°C)	Calculated weight loss (%)	Measured [a] weight loss (%)		Calculated weight loss (%)	Measured [a] weight loss (%)	Temperature of DTA peaks (°C)
			$(N_2H_5)_3MF_7$			
			↓			
220	25.4	27.6	$(NH_4)_2MF_6$	20.0	19.6	205
			↓			
268	36.8	36.6	NH_3MF_5 [b]	29.0	27.7	276
			↓			
342	48.3	48.2	MF_4	38.0	36.7	344

[a] Using a Mettler TA-1 thermoanalyser.

[b] γ-NH_4ZrF_5.

mass effect in an anti-symmetric stretching mode, as has been suggested for the similar difference which is observed between the spectra of $(N_2H_6)_3Zr_2F_{13} \cdot F$ (M = Zr, Hf) [5]. (498 cm^{-1} may be calculated from 477 cm^{-1} by the simple diatomic model approximation.) The strongest Raman metal–fluorine band in both compounds and in their decomposition products (tentatively assigned to a breathing mode of the anion) has a frequency well below those for the breathing modes of the octahedral ZrF_6^{2-} (585 cm^{-1}) and HfF_6^{2-} (589 cm^{-1}) ions [10]. Comparing the spectra with the spectra of other dimeric and polymeric fluorozirconates and hafnates [7] and with the spectra and structures of $(N_2H_6)_3M_2F_{13} \cdot F$ [5] and $(NH_4)_2ZrF_6$ [6,7], which are the starting compounds and the first decomposition products, respectively, we conclude that both $(N_2H_5)_3MF_7$ compounds contain a complex or polymeric anion of similar type with a coordination number larger than 6. These are transformed during thermal decomposition through other complex or polymeric anionic structures to ZrF_4 or HfF_4.

The activity of the N–N stretching band in the Raman and IR spectra clearly shows the presence of $N_2H_5^+$ ions [9a] in both $(N_2H_5)_3MF_7$ compounds. The position of the band and the relatively low frequencies of the N–H deformations place the spectra in the first group of hydrazinium(1 +) fluorometallates, according to ref. 9a. The N–N band is split for ca. 16 cm^{-1} into two components of comparable strength. Splitting of this kind is not common (see e.g. ref. 9a), but has also been observed in the spectra of the starting compound, $(N_2H_6)_3Zr_2F_{13} \cdot F$. As the band is sensitive to the environment, (see e.g. refs. 9a and 11), the splitting has been explained in terms of the presence of two types of $N_2H_6^{2+}$ ion in the crystal [5]. That the band is also split for $(N_2H_5)_3ZrF_7$ may indicate, similarly, two types of $N_2H_5^+$ ion, which are involved in different hydrogen bond interactions.

TABLE 2

Powder diffraction data for $(N_2H_5)_3ZrF_7$, $(N_2H_5)_3HfF_7$, and thermal decomposition products [a]

$(N_2H_5)_3ZrF_7$		$(N_2H_5)_3HfF_7$		Product at 245 °C		$(NH_4)_2ZrF_6$		Product at 280 °C		γ-NH_4ZrF_5	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
6.11	vs	6.08	vs	7.11	w			7.51	m		
5.82	vs	5.81	vs			6.73	10	6.80	vs	6.80	100
5.31	m	5.33	m	6.47	m			5.76	w		
5.13	m	5.13	m	5.82	vs	5.82	100	5.19	m	5.16	60
4.62	s	4.62	s			5.07	10	4.38	vw		
3.98	m	3.97	m	4.44	w			3.96	m	3.96	60
3.57	vs	3.56	vs	4.27	w			3.79	m		
3.29	m–s	3.28	m	4.03	w			3.54	m–s	3.54	60
3.19	vw			3.87	m	3.86	60	3.41	m	3.42	60
3.14	w–m	3.13	m	3.72	m					3.40	60
		3.06	w	3.57	m			3.17	w		
		3.00	vw,dif	3.36	s	3.36	60	3.10	w		
2.955	vw	2.931				3.35	30	2.804	m	2.800	30
2.859	vw	2.849	m	3.22	s	3.22	80	2.510	vw	2.463	60
2.698	w–m	2.697	m			2.975	10	2.427	vw		
2.541	m	2.535	m			2.924	30	2.260	m	2.265	30
2.411	m	2.414	w	2.907	w	2.908	30	2.177	vw	2.175	10
2.351	w	2.350	w	2.798	vw			2.140	vw		
2.303	m	2.299	m			2.741	10	2.101	vw		
2.266	w	2.262	w	2.542	vw			2.045	w		
2.203	m	2.203	m	2.525	m	2.529	30	1.964	w	1.965	20
2.172	vw	2.171	vw			2.412	10	1.921	m–s	1.920	30
2.097	m	2.093	m			2.331	10	1.898	m–s	1.901	20
2.043	m	2.041	m	2.318	s	2.323	60	1.853	m–s	1.847	80
		2.014	w			2.207	60	1.770	w	1.771	20
		1.987	vw	2.193	m	2.191	60			1.717	20
1.962	w	1.960	vw			2.164	10			1.695	20
1.934	w	1.933	w			2.144	10				
1.841	vw			2.114	m	2.120	10				
1.813	vw	1.808	vw			2.084	10				
1.784	vw	1.782	vw	2.007	m	2.014	30				
1.759	w–m	1.757	m			1.945	20				
1.730	m	1.729	m	1.935	m	1.934	30				
1.643	w–m					1.918	60				
1.619	w–m			1.908	s	1.910	30				
				1.829	m–s	1.834	60				
				1.769	vw	1.772	20				

---

[a] Powder data for $(NH_4)_2ZrF_6$ and γ-NH_4ZrF_5 were taken from ASTM cards (see ref. 8). Intensities for $(N_2H_5)_3ZrF_7$, $(N_2H_5)_3HfF_7$, and the decomposition products were estimated visually: s, strong; m, medium; w, weak; v, very; dif, diffuse.

TABLE 3

IR spectra of thermal decomposition products of $(N_2H_5)_3ZrF_7$ in cm^{-1} [a], and assignments

Product at 245 °C	$(NH_4)_2ZrF_6$	Product at 280 °C	NH_4ZrF_5	Assignment [b]
3241 s	3225 s	3202 s	3202 s	$\nu_3(NH_4^+)$
3094 m–s	3094 m–s	3094 m–s	3094 m–s	Overtone and combination bands
2036 vw,br	2042 vw,br	2030 vw,br	2015 vw,br	
1810 vw,br	1810 vw,br		1812 vw,br	
1710 w–m	1710 w–m			
1690 sh	1690 sh	1689 w	1691 w	
1420 s	1415 vs	1435 vs	1435 vs	$\nu_4(NH_4^+)$
562 sh	566 m			ν(Zr–F)
		492 vs,br	492vs,br	
471 vs,br	471 vs,br			
		388 m	388 m	
343 m	345 m			δ(Zr–F)
		306 s	304 s	

[a] Intensities: s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad.
[b] Assignment according to ref. 7. Vibrations of the anion: ν stretching, δ deformation.

The wide IR N–H stretching absorption centred at ca. 2950 cm^{-1}, with an approximate width of 1100 cm^{-1} at half height, shows frequencies at somewhat lower values than those for N_2H_5Cl (estimated at ca. 2950–3000 cm^{-1} from ref. 9c), and at appreciably higher values than those for N_2H_5F (estimated at ca. 2600 cm^{-1} from ref. 9d), indicating weaker hydrogen bonding. The spectra show three Raman bands in the region of NH_2

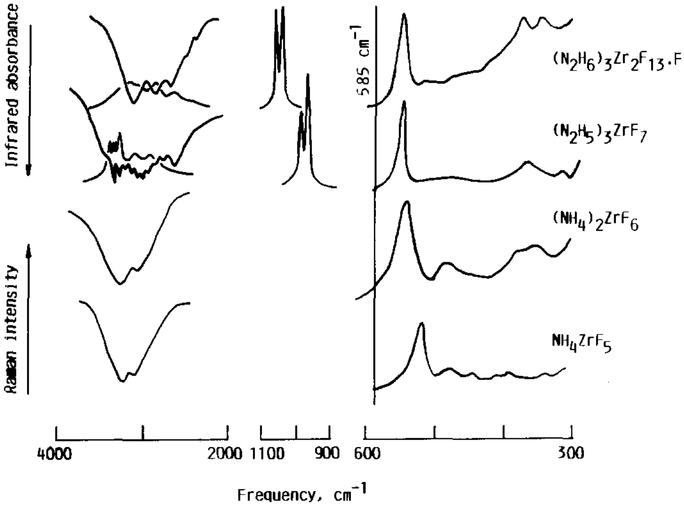

Fig. 2. Raman and IR spectra of $(N_2H_5)_3ZrF_7$, compounds corresponding to its decomposition products, and $(N_2H_6)_3Zr_2F_{13}\cdot F$. 585 cm^{-1}: frequency of ν_1 in octahedral ZrF_6^{2-} ions.

TABLE 4

Vibrational spectra [a] of $(N_2H_5)_3ZrF_7$ and $(N_2H_5)_3HfF_7$ in cm^{-1}, and assignments

$(N_2H_5)_3ZrF_7$		$(N_2H_5)_3HfF_7$		Assignment [b]
IR	R	IR	R	
3430 sh		3430 sh		
	3332(2)		3328(2)	
3295 vs	3292(2)	3295 s	3291(2)	$\nu(NH_2)$
3235 vs	3215(3)	3235 s	3216(3)	
3187 s				
3144 vs		3143 s		
	3092(1) br		3087(1) br	
3038 vs	3033(1) br	3038 vs	3028(1) br	
2966 vs	2959(1) br	2965 vs	2963(1) br	
2894 s	2883(?) br		2850(?) br	$\nu(NH_3^+)$
2834 s				
2764 s				
2613 s		2623 s		
2089 m–w		2097 m–w		Combination bands
2030 sh				
1650 sh	1663(3)	1650 sh	1663(3)	$\delta(NH_2)$
1608 s	1610(2)	1607 s	1612(2)	
1559 m		1555 m		$\delta(NH_3^+)$
		1534 m		
1495 s	1498(1)	1495 s	1502(1)	
1480 m		1482 sh		
		1437 m		
1414 m,br	1417(1)	1416 m–s	1416(2)	$\rho(NH_2)$
1376 m		1377 m		
1344 m		1344 m		
1303 w		1304 w		
1250 m	1242(?)	1249 m		
1226 sh		1230 sh		
1138 m	1133(1)	1135 m	1138(2)	$\rho(NH_3^+)$
1093 vs	1100(3)	1094 vs	1102(3)	
	1082(1)		1083(1)	
976 m	973(5)	976 m	973(8)	$\nu(N-N)$
954 vs	959(10)	958 vs	961(10)	
	543(6)		551(6)	
498 s,br		477 s,br		$\nu(Zr-F)$
	487(?)		482(?)	
440 s,br		438 s,br		
	362(2)		373(2)	
	305(1)			$\delta(Zr-F)$
	253(1)		252(1)	
	198(1)		200(1)	Lattice modes
	157(1)		160(1)	

---

[a] IR intensities: s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad. Raman intensities are given in parentheses: (?), very weak.

[b] ν, stretching; δ, deformation; ρ, rocking.

stretching vibrations ($\nu_{1/2} \approx 60$ cm^{-1}), and a series of wider bands ($\nu_{1/2} \approx$ 200 cm^{-1}) of smaller intensity in the region of NH_3^+ stretching. Comparison with the very wide hydrogen-bond influenced bands of NH_3^+ stretching at 3125, 2850 and 2620 cm^{-1} in the Raman spectra of $(N_2H_6)_3M_2F_{13} \cdot F$ [5] suggests that $N_2H_5^+$ ions in $(N_2H_5)_3MF_7$ are predominantly hydrogen-bonded through their NH_3^+ groups.

ACKNOWLEDGEMENTS

The financial support of the Research Community of Slovenia is gratefully acknowledged. We also thank Mrs Borka Sedej for chemical analyses.

REFERENCES

1 J. Slivnik, A. Šmalc, B. Sedej and M. Vilhar, Vestn. Slov. Kem. Drus., 11 (1964) 53; J. Slivnik, B. Jerkovič and B. Sedej, Monatsh. Chem., 97 (1966) 820.
2 D. Gantar, A. Rahten and B. Volavšek, J. Fluorine Chem., 41 (1988) 335.
3 D. Gantar and A. Rahten, J. Fluorine Chem., 34 (1986) 63.
4 B. Kojić-Prodić, S.Šćavničar and B. Matković, Acta Crystallogr., B27 (1971) 638.
5 A. Rahten, I. Leban, S. Milićev and B. Žemva, J. Crystallogr. Spectrosc. Res., 20 (1990) 9.
6 A. Zalkin, D. Eimerl and S.P. Velsko, Acta Crystallogr., C44 (1988) 2050.
7 P.W. Smith, R. Stoessiger and A.G. Turnbull, J. Chem. Soc. (A), (1968) 3013.
8 B. Gaudreau, Rev. Chim. Miner., 2 (1965) 1.
9 (a) S. Milićev and J. Maček, Spectrochim. Acta, 41A (1985) 651; (b) V. Schettino and R.E. Salomon, Spectrochim. Acta, 30A (1974) 1445; (c) J.C. Decius and D.P. Pearson, J. Am. Chem. Soc., 75 (1953) 2436; (d) P. Glavič and D. Hadži, Spectrochim. Acta, 28A (1972) 1963.
10 (a) P.A.W. Dean and D.F. Evans, J. Chem. Soc. (A), (1967) 698; (b) A.P. Lane and D.W.A. Sharp, J. Chem. Soc. (A), (1969) 2942; (c) L.M. Toth and J.B. Bates, Spectrochim. Acta, 30A (1974) 1095.
11 S. Milićev and J. Maček, J. Chem. Soc., Dalton Trans., (1984) 297.