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Synthesis, thermal decomposition and infrared spectra of two new hydrazinium (1+) fluorovanadates(III), $(N_2H_5)_2VF_5{\cdot}H_2O$ and $(N_2H_5)_2VF_5$

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Abstract

Thermal decomposition of a new compound, $(N_2H_5)_2VF_5{\cdot}H_2O$, prepared from aqueous solutions, gives in inert atmosphere at 93°C the new compound $(N_2H_5)_2VF_5$. The decomposition proceeds further over intermediates, $N_2H_5VF_4$ at 236°C and NH_4VF_4 at 268°C, to the impure VF_3 at 615°C. According to the infrared spectra there are weak hydrogen bonds in all nitrogen compounds. There are different types of $N_2H_5^+$ cations in $(N_2H_5)_2VF_5{\cdot}H_2O$ and $(N_2H_5)_2VF_5$. In $N_2H_5VF_4$, the cation is coordinated over the lone pair of the vanadium atom. By analogy with the spectra of similar compounds, isolated octahedra $[VF_5{\cdot}H_2O]^{2-}$ appear in the structure of $(N_2H_5)_2VF_5{\cdot}H_2O$ and fluorine-bridged chains of $[VF_4F_{2/2}]$ octahedra in $[N_2H_5]_2VF_5$. © 1997 Elsevier Science B.V.

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1. Introduction

Hydrazinium inorganic compounds and complexes have been extensively studied over the last 80 years (see, for instance [1]) and a large number of the fluorometalates of almost all transition elements are known. A variety of structures, various chemical behaviours, various thermal decomposition paths and therefore their potential use make this region of chemistry still interesting and expanding. Till now, only two hydrazinium compounds of vanadium, $N_2H_6VF_5$ [2] and $(N_2H_5)_3VF_6$ [3] have been known, although there is a number of compounds with alkali and NH_4^+ cations [4]. We are now reporting on the syntheses and characterization of two more vanadium compounds, namely, $(N_2H_5)_2VF_5{\cdot}H_2O$ and $(N_2H_5)_2VF_5$. The first, $(N_2H_5)_2VF_5{\cdot}H_2O$, has been prepared from aqueous solutions and the second, $(N_2H_5)_2VF_5$, isolated during the thermal decomposition of the first one.

2. Experimental

2.1. Syntheses

$(N_2H_5)_2VF_5{\cdot}H_2O$ was prepared by the procedure used for analogous compounds of Al, Fe and Cr [5–7]. A 5% aqueous solution of N_2H_4 was added to 10% aqueous $N_2H_6VF_5$ (made according to [2]), until pH=5.5 was reached. A conglomerate of light green crystals of the new compound was crystallized from

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the solution after one to two weeks in air at room temperature. The compound was dried in air and kept in a refrigerator. By thermal decomposition of a 300 mg sample at 100–105°C the well-defined $(N_2H_5)_2VF_5$ was obtained. Chemical analysis: $(N_2H_5)_2VF_5 \cdot H_2O$: theoretically required, N_2H_4 27.86%, V 22.14%, F 41.29%; found, N_2H_4 27.4%, V 21.9%, F 41.3%. $(N_2H_5)_2VF_5$: theoretically required, N_2H_4 30.23%, V 24.02%, F 44.80%; found, N_2H_4 30.7%, V 23.3%, F 45.0%.

Table 2
Thermal decomposition of $(N_2H_5)_2VF_5 \cdot H_2O$ [a]

°C		Thermodynamic effect [b] (°C)	Weight loss% Calc.	Weight loss% Found
93	$(N_2H_5)_2VF_5$	79_{endo}	7.83	6.8
236	$N_2H_5VF_4$	225_{endo}	22.62	23.6
268	NH_4VF_4	260_{exo}	6.53	8.7
615	Impure VF_3	368_{endo}	16.10	16.2

[a] The weight of a sample was 50 mg.
[b] Endo, exo: endothermic and exothermic effects, respectively.

Table 1
Powder diffraction data of the new compounds, $(N_2H_5)_2VF_5 \cdot H_2O$ and $(N_2H_5)_2VF_5$

$(N_2H_5)_2VF_5 \cdot H_2O$		$(N_2H_5)_2VF_5$	
d (Å)	I	d (Å)	I
6.45	m–s	6.42	vs
5.71	s	5.57	m
5.57	w	5.21	m
5.33	s	4.07	m
4.92	w	3.92	m
4.64	vw	3.48	vw
4.36	s	3.41	vw
4.26	w	3.37	s
4.20	s	3.26	vw
3.97	m–s	3.21	m–s
3.67	m	3.13	m–s
3.55	m	2.921	w
3.49	w	2.726	m
3.38	w	2.632	m
3.33	m	2.534	m
3.22	w	2.473	m
3.05	s	2.403	m
3.01	w	2.355	m
2.853	m	2.300	m
2.736	w–m	2.241	m
2.673	m–s	2.189	m
2.573	m	2.142	vw
2.533	m	2.095	vw
2.484	m	2.018	vw
2.451	m	1.955	m
2.408	w	1.912	w
2.317	w	1.894	w
2.263	m–s	1.874	m
2.236	m–s	1.791	vw
2.186	w	1.704	vw
2.130	w	1.672	m
2.095	m		
2.072	m		
2.045	w		

Intensities: s – strong; m – medium; w – weak and v – very.

2.2. Powder data

Debye–Scherrer X-ray powder diffraction patterns in sealed Pyrex capillaries were obtained using graphite monochromatized CuK_α radiation on a Seifert 3000S X-ray generator. Intensities were estimated visually. The data for the new compounds, $(N_2H_5)_2VF_5 \cdot H_2O$ and $(N_2H_5)_2VF_5$, are given in Table 1.

2.3. Thermal analysis

Results of thermal analysis are given in Table 2 and Fig. 1. Samples of 50 mg of $(N_2H_5)_2VF_5 \cdot H_2O$ were heated on a Mettler thermoanalyzer in 0.9 ml Pt crucibles at the rate of 1°C/min in a stream of dry argon, 5 L/h. The reference samples were 50 mg of α-Al_2O_3. DTG range was 5 mg min^{-1} and DTA range was 100 µV. The intermediates were isolated by repeating the decomposition under the same conditions, but starting with larger quantities of $(N_2H_5)_2VF_5 \cdot H_2O$ (200–400 mg) in 0.9 and 3.3 ml Pt crucibles and stopping, because of larger mass, at temperatures which were 10–15°C higher than those specified in Table 2. The intermediates were identified by chemical analysis, powder diffraction data and by comparing the infrared spectra, when available (see Ref. [2]). The first intermediate, which is the new compound, $(N_2H_5)_2VF_5$, mentioned in Section 2.1, was isolated at 100–105°C; $N_2H_5VF_4$ was isolated at 248°C, required, N_2H_4 20.03%, F 47.50%; found, N_2H_4 18.0%, NH_4 1.8%, F 46.1%; NH_4VF_4 was isolated at 285°C, required, NH_4 12.44%; found, NH_4 11.0%. Impure VF_3 was obtained as the end product at 615°C.

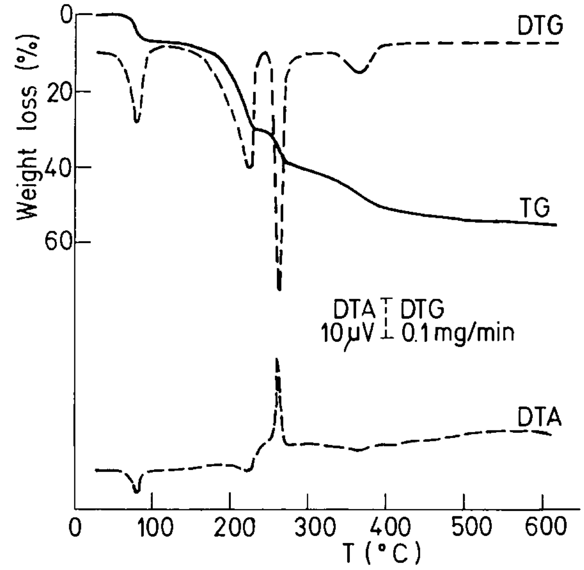

Fig. 1. Thermal decomposition of $(N_2H_5)_2VF_5{\cdot}H_2O$.

2.4. *Infrared spectra*

Infrared spectra were taken on a Perkin–Elmer FTIR 1710 infrared spectrophotometer (resolution 4 cm^{-1}) as Nujol and fluorolube mulls on plates of CsBr and NaCl.

3. Results and discussion

The new compound, $(N_2H_5)_2VF_5{\cdot}H_2O$, thermally decomposes, under the selected conditions, in well-defined steps permitting the isolation of the intermediates (Fig. 1 and Table 2). Infrared spectra (Fig. 2 and Table 3) of the compounds offer some interesting information.

3.1. *Hydrazinium cations*

In all the three hydrazinium compounds, the stretching band of the environment sensitive NN bond is split, which indicates the presence of $N_2H_5^+$ cations [8] with different hydrogen bondings. The frequencies in the first two compounds at ca. 980 and 960 cm^{-1} correspond to the isolated cations. In the spectrum of $N_2H_5VF_4$ the bands are shifted to higher frequencies (1017 and 1026 cm^{-1}, see Fig. 2), which is the evidence for the coordination of the $N_2H_5^+$ ions through the nitrogen lone pair to the central vanadium atom [8,9].

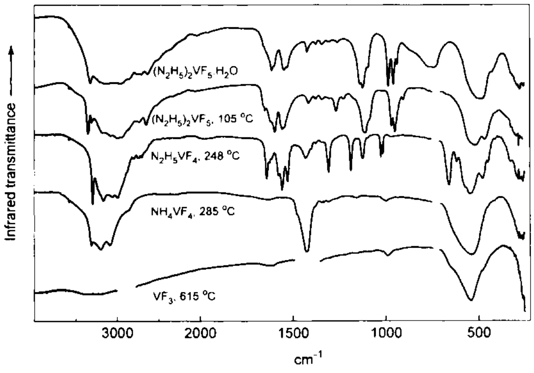

Fig. 2. Infrared spectra of the compounds in the order of isolation.

3.2. *Hydrogen bonding*

Already weak hydrogen bonding in the hydrazinium compounds is gradually weakened along the decomposition series. The centre of H-bond absorption and its width at half height are in the spectrum of $(N_2H_5)_2VF_5{\cdot}H_2O$ at ca. 2980 and 1000 cm^{-1}, in $(N_2H_5)_2VF_5$ at 2990 and 780 cm^{-1}, and in $N_2H_5VF_4$ at 3090 and 450 cm^{-1}. Reason for this is the presence of water in the first compound and in the last one the coordination of $N_2H_5^+$ ions weakens both the hydrogen bond donor capacity of $N_2H_5^+$ and the already weak hydrogen bond acceptor capacity of coordinated fluorine. The numbers for NH_4VF_4 are 3190 and 400 cm^{-1}.

3.3. *Fluorovanadate anions*

The spectra of both $(N_2H_5)_2VF_5{\cdot}H_2O$ and $(N_2H_5)_2VF_5$ in the region of vibrations of the fluorovanadate ion are similar to the spectra of comparable hydrazinium(1+) and ammonium compounds of Al, Fe and Cr fluorides of the same stoichiometry (see Refs. [5,6,10], and the literature cited within). By analogy, this indicates isolated octahedral $[VF_5{\cdot}H_2O]^{2-}$ units in the structure of $(N_2H_5)_2VF_5{\cdot}H_2O$ and the $[VF_4F_{2/2}]$ chains of fluorovanadate octahedra connected through the bridging fluorine atoms in $(N_2H_5)_2VF_5$.

Table 3
Infrared spectra [a] of $(N_2H_5)_2VF_5{\cdot}H_2O$ and $(N_2H_5)_2VF_5$ in cm^{-1}

$(N_2H_5)_2VF_5{\cdot}H_2O$	$(N_2H_5)_2VF_5$	Assignment [b]
3328 vs	3357 vs	$(NH)_s$ and $(OH)_s$ for $(N_2H_5)_2VF_5{\cdot}H_2O$ or $(NH)_s$ for $(N_2H_5)_2VF_5$
	3312 m	
3215 sh	3182 sh	
3145 vs, br	3081 sh	
	3002 vs, br	
2964 vs, br	2962 sh	
2866 sh	2880 sh	
2759 m	2736 m	
2711 m		
2632 m	2652 m	
2040 w	2062 w	Combination bands
1961 vw		
	1651 sh	
1614 s	1620 sh	$(NH_2)_d$
1604 sh	1597 vs	
1547 s	1558 s	$(NH_3^+)_d$
1532 sh	1548 sh	
1422 w-m	1415 w-m	
1377 w	1377 w	
1344 w	1344 w	$(NH_2)_r$
1305 w	1303 vw	
1260 w	1267 m	
	1227 w	
	1170 vw	
1138 sh	1116 sh	$(NH_3^+)_r$
1123 vs	1109 vs	
1096 sh	1089 sh	
985 vs	969 s	
959 vs	950 vs	$(NN)_s$
939 m	905 w	
863 sh		
765 sh		water libration in $[VF_5{\cdot}H_2O]^{2-}$
742 m-s, br		
	519 vs, br	$(VF_5^+)_s$ in $[VF_4F_{2/2}]^{2-}$
	466 s	
490 vs, br		$(VF_5)_s$ in $[VF_5{\cdot}H_2O]^{2-}$
428 sh		
277 m	294? m	$(VF)_d$

[a] Infrared spectra are taken as Nujol and fluorolube mulls; s – strong, m – medium, w – weak, sh – shoulder, b – broad and v – very.

[b] d – deformation, r – rocking and s – stretching.

With the exception of splitting of the VF band at ca. 500 cm^{-1} and absence of water librational band at ca. 759 cm^{-1}, the overall spectrum of the new compound, $(N_2H_5)_2VF_5$, is comparable to the spectrum of the $(N_2H_5)_2VF_5{\cdot}H_2O$. This suggests that the transformation from $(N_2H_5)_2VF_5{\cdot}H_2O$ to $(N_2H_5)_2VF_5$ takes place by simply loosing water accompanied with the slight rearrangement of the fluorine atoms. The similar easy transformation was observed in the reversible interchange of the corresponding two aluminium compounds [5,11]. On the other hand, the conversion of $(N_2H_5)_2VF_5$ to $N_2H_5VF_4$, as reflected in the redistribution of bands in the VF stretching region, is followed with profound structural changes in the configuration of the fluorovanadate ion and with the mentioned coordination of the $N_2H_5^+$ ion.

3.4. *Decomposition of the $N_2H_5VF_4$ intermediate*

The decomposition step at 236°C gives $N_2H_5VF_4$. It is obtained by loosing $N_2H_6F_2$ and N_2H_4 as shown for other hydrazinium(1+) fluorometalates [12]. The compound has not yet been synthesized from solutions but was obtained at somewhat lower temperatures by decomposition of $N_2H_6VF_5$ (180 or 200°C, depending on heating rate, sample weight and other effects [2,12]). It was shown that $N_2H_5VF_4$, obtained from $N_2H_6VF_5$ in such a way, decomposes further by vigorous exothermic disproportionation of $N_2H_5^+$ to NH_3 and N_2, producing NH_4VF_4 at 240 or 270°C. Therefore, we may expect that at 236°C parallel to loosing $N_2H_6F_2$ and N_2H_4 the disproportionation reaction also begins with the consequent appearance of NH_4VF_4. In the spectra of $N_2H_5VF_4$ there is an emerging band at 1431 cm^{-1} assigned to NH_4VF_4. The presence of NH_4VF_4 impurity is also confirmed by the chemical analysis (see Section 2.3). In the similar study of thermal decomposition of $N_2H_6VF_5$ under quasi-isobaric conditions no proper $N_2H_5^+$ compound was found, but NH_4VF_4 with traces of $N_2H_5^+$ ion was isolated [13].

3.5. *NH_4VF_4 and VF_3*

Transformation of $N_2H_5VF_4$ to NH_4VF_4 through disproportionation of $N_2H_5^+$, accompanied by the strong exothermic DTA peak at 260°C, is finished during the next 40°C. The spectrum of the product isolated at 285°C is the spectrum of pure NH_4VF_4. Further decomposition gives impure VF_3. The impurities are partly oxidized and hydrolysed products. The bands of $VF_3 \cdot 3H_2O$ appear in the spectrum. They are quite noticeable in the product isolated at 510°C, but gradually diminish with heating at higher temperatures (products at 580 and at 615°C). The cause for the appearance of impurities is obviously purely instrumental. In this step, NH_4F is evolved. It reacts with the walls of the quartz sample compartment, in which the Pt crucible is placed, producing water (see Ref. [14]). This reacts with the emerging VF_3. A similar situation was also observed in other instances of thermal decomposition of ammonium compounds (see, for instance Ref. [15] or [16]).

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