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Ammoniumbis(hydroxylammonium) Pentafluoridooxidovanadate(IV): Synthesis and Characterisation of a New Fluorovanadate

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Dedicated to the memory of Professor Ljubo Golič

Abstract

Turquoise crystals of a new hydroxylammonium compound with the formula $NH_4(NH_3OH)_2[VOF_5]$ have been synthesized by the reaction of solid NH_3OHF and the aqueous solution of vanadium in HF. The compound crystallizes monoclinic, $P2_1/n$, with cell parameters: a = 10.5658(2) Å, b = 6.6143(1) Å, c = 11.6618(2) Å, β = 96.282(1). Magnetic susceptibility was measured using a SQUID device over a temperature range 2–300 K at magnetic field 10^3 Oe giving the result μ_{eff} = 1.65 BM. The thermal decomposition was studied by TG and DSC analysis. $NH_4(NH_3OH)_2[OF_5V]$ decomposes above 354 K in three steps, obtaining NH_4VOF_3 after the first step and V_2O_5 as the final residue.

Keywords: Hydroxylammonium fluorovanadates, X-ray powder diffraction, X-ray structure determination, thermal analysis

1. Introduction

Hydroxylamine, with the formula NH_2OH, is a derivative of ammonia, with the replacement of one hydrogen atom with an –OH group. Hydroxylammonium fluorometalates with the formula $(NH_3OH)_xMeF_y$ are interesting for the study of hydrogen bonds, since they include all three elements that form strong hydrogen bonds (O, N and F). Although the first hydroxylammonium fluorometallate[1] was reported as early as 1908, only a few compounds were reported up to 1990. In the past decade, our laboratory has reported on the synthesis and properties of a number of new hydroxylammonium fluorometallates of main group[2–7] and transition metals,[8–11] including compounds of Ti, Zr, Hf and Cr. To continue the research into hydroxylammonium fluorometallates of transition metals we decided to study reactions in the system NH_3OHF–V–HF (aq.), since no reports about hydroxylammonium fluorovanadates could be found in the literature.

As already reported in our previous publications, the use of solid NH_3OHF, prepared[12] by adding an ethanol solution of NH_2OH to an aqueous solution of HF, offers some advantages when compared to earlier methods, which used aqueous or ethanolic hydroxylamine solutions. Free hydroxylamine is unstable above 273 K, whereas hydroxylammonium salts of inorganic acids are stable at room temperature, even for prolonged times.

Since the chemistry of hydroxylammonium is similar to that of ammonium and hydrazinium, we also revi-

wed publications reporting the fluorovanadates of ammonium and hydrazinium: Slivnik et al.[13] reported the first preparation of a hydrazinium fluorovanadate, $(N_2H_5)_3VF_6$, and its chemical analysis. The same group later reported[14] the synthesis and characterization of $N_2H_6VF_5$ and conducted thermal analyses on both compounds[15]. Two more vanadium compounds, i.e., $(N_2H_5)_2VF_5 \cdot H_2O$ and $(N_2H_5)_2VF_5$, were reported by Rahten and Milićev[16] in 1997, including a detailed thermal analysis.

Among the ammonium complexes of that type, $(NH_4)_3VF_6$, $(NH_4)_2VF_5$ and NH_4VF_4 have been known for a long time,[17] while the thermal analysis of $(NH_4)_3VF_6$ was studied by Bukovec and Šiftar.[18] The synthesis of ammonium hexafluorovanadate (V), NH_4VF_6 in reaction between $(N_2H_5)_3VF_6$ and excess XeF_2 has been reported by Žemva et al[19]. Besides ammonium fluorovanadates, there are also some known fluorooxovanadates(V), e.g. $(NH_4)_3VO_2F_4$, reported by Buchholz et al.,[20] and three ammonium fluorooxovanadates(IV) –$(NH_4)_3VOF_5$, $(NH_4)_2VOF_4$ and $(NH_4)_2VOF_4 \cdot H_2O$ – which were reported by Demšar and Bukovec, including their thermal analyses in inert and oxidising atmospheres.[21]

2. Experimental

Synthesis: $NH_4(NH_3OH)_2[VOF_5]$ was synthesized using vanadium powder (Aldrich), hot 40% HF (Merck) and solid NH_3OHF. The last of these was isolated in an ethanolic solution by the reaction of solid hydroxylammonium chloride with sodium ethylate.[12] NH_2OH has been added to HF, and then cooled to 273 K. White crystals of NH_3OHF were obtained, filtered off, dried and the product was used for further synthesis.

Calculated amounts of NH_3OHF were dissolved (the molar ratios NH_3OHF: V varied from 1 : 1 to 4 : 1) in a solution of 40% HF and vanadium. Turquoise crystalline phase was obtained after the evaporation of the solvent at room temperature.

Methods of characterization: Hydroxylammonium was determined by titration[22] with $KMnO_4$ and fluorine with a fluoride-sensitive electrode with direct calibration, using a TISAB IV buffer to provide a constant background ionic strength. Vanadium was determined by gravimetric methods. Thermal analysis (TG and DSC) was carried out on a METTLER TA 4000 system in the temperature ranges 310–973 K (TG) and 310–673 K (DSC) in air and nitrogen flow (100 mL/min) with a heating rate of 10 K/min, using Al_2O_3 (TG) and gold crucibles (DSC).

The X-ray powder diffraction data for the products were collected with an AXS Bruker/Siemens D5005 diffractometer using $CuK_{\alpha 1}$ radiation at 293 K. The samples were finely ground, placed on a silicone-crystal holder and measured in the range $10° < 2\theta < 70°$ with a step 0.0358° and a scanning speed of 1s/step. The obtained data were analyzed using the EVA program and the PDF datafile.[23]

Magnetic measurements: the magnetic susceptibility of the sample was measured using a superconducting quantum interference device Quantum Design MPMS-XL-5 (SQUID). The data were collected from a 0.0653g sample over the temperature range 2–300 K in a magnetic field of 10^3 Oe. The diamagnetic corrections were made for the $NH_4(NH_3OH)_2[OF_5V]$ using Landolt–Börnstein Tables.[24] The relation for the corrected susceptibility was $\chi_M = \chi_{exp} - \chi_{Di}$ where $\chi_{Di} = -113 \cdot 10^{-6}$ emu/mol.

X-ray structure determination: Diffraction data for $NH_4(NH_3OH)_2[VOF_5]$ were collected on a Nonius KAPPA CCD diffractometer at room temperature (293 ± 2K) using MoK_α radiation. Details of the crystal data, data collection and refinement are given in Table 1.

The structure was solved with the heavy atom method. The hydrogen atoms were located by using difference Fourier synthesis and included in the refinement with positional parameters and individual isotropic displacement parameters. One of the hydroxylammonium ions was found to be disordered and its treatment is explained in detail in the following section. Full-matrix least-squares refinement on *F* with anisotropic displacement parameters of all non-hydrogen atoms and the Regina[25] weighting scheme was applied. The *Xtal3.4*[26] system of crystallographic programs was used for the reduction of data, structure refinement and interpretation as well as the thermal ellipsoids plot. *ATOMS*[27] was used to produce molecular graphics.

3. Results and Discussion

A new compound with the formula $NH_4(NH_3OH)_2[VOF_5]$ was obtained. The chemical analysis of a typical product gave the following results: 7.1% NH_4^+ (calc. 7.3%), 26.8% NH_3OH^+ (calc. 27.4%), 20.5% V^{+4} (calc. 20.6), and 38.8% F^- (calc. 38.3%).

The χ vs. T curve, Figs 1, shows a typical Curie-Weiss behaviour. The susceptibility curve can be fitted to the Curie-Weiss law $\chi_M = C / (T + \theta)$, where C is the Curie constant, T is the temperature and θ is the Weiss constant. The best nonlinear plot fitting to the susceptibility data yields $C_M = 0.341$ emu K/mol and $\theta = -0.18$ K.

Since the magnitude of Weiss constant θ is lower than 1 K, the interaction energy between the magnetic moments is considered to be small. Thus, there is neither anti-ferromagnetic nor ferromagnetic ordering in the temperature range for the experimental data. The μ_{eff} from the value of Curie constant is $1.65\mu_B$.

This value is lower as the spin-only moment (1.73 μ_B) expected for an isolated V^{4+} ion. However, when the

Table 1. Crystal data, data collection and refinement summary

Crystal data	
$NH_4(NH_3OH)_2[VOF_5]$	D_x = 2.024 Mg m^{-3}
M_r = 248.09	Mo K_α *radiation*
Monoclinic, $P2_1/n$	Cell parameters from 1182 reflections
a = 10.5658(2) Å	θ = 2.55–27.48°
b = 6.6143(1) Å	μ = 1.294 mm^{-1}
c = 11.6618(2) Å	T = 293(2) K
β = 96.282(1)°	Prism, turquoise
V = 810.10(2) Å^3	0.31 × 0.25 × 0.18 mm
Z = 4	0.672 < T *(transmission factor)* < 0.788
Data collection	
Nonius KAPPA CCD	
ω scans	R_{int} = 0.031
Absorption correction:	θ_{max} = 27.48°
multi–scan(DENZO–SMN)	h = –13 → 13
1434 measured reflections	k = –8 → 8
1849 independent reflections	l = –15 → 15
1633 reflections with I > 2.0$\sigma(I)$	
Refinement	
Software : Xtal 3.4[26]	*Weighting scheme* = Regina[25]
Refinement on F	
R = 0.025	$(\Delta/\sigma)_{max}$ = 0.052
wR = 0.020	$(\Delta/\sigma)_{aver}$ = 0.0015
S = 1.0029	$\Delta\rho_{max}$ = 0.68 eÅ^{-3}
1633 reflections	$\Delta\rho_{min}$ = –0.67 eÅ^{-3}
167 parameters	
10 restraints	

ion is embedded in the crystal field the additional energy levels, which may be populated in accordance with the Boltzmann energy distribution, must be taken into the account. In our case the magnetic moment is independent of the temperature, and the population distribution does not change much in the measured temperature range.

Thus, the difference between the lowest populated energy level and others is $\Delta E_a >> kT$. On the other hand, the Brillouin function fit on Fig. 1b indicates that the Landé factor g < 2, suggesting a deviation from a pure spin magnetic moment.

The susceptibility for an isolated ion is given by the relation $\chi = Ng^2 \mu_B^2 S(S+1)/3kT$ and consequently C = 0,125 g^2 S(S+1) [emu K/mol], here $\mu_B = 9.273 \times 10^{-24}$ J/T, S is the spin, $k_B = 1.3805 \times 10^{-23}$ J/K, N is the Avogadro number, g is the spectroscopic splitting factor, and T the absolute temperature. Using this equation and setting g = 1.9, the value obtained from Brillouin plot, one obtains for the Curie constant C a value of 0.338 emu K/mol and the

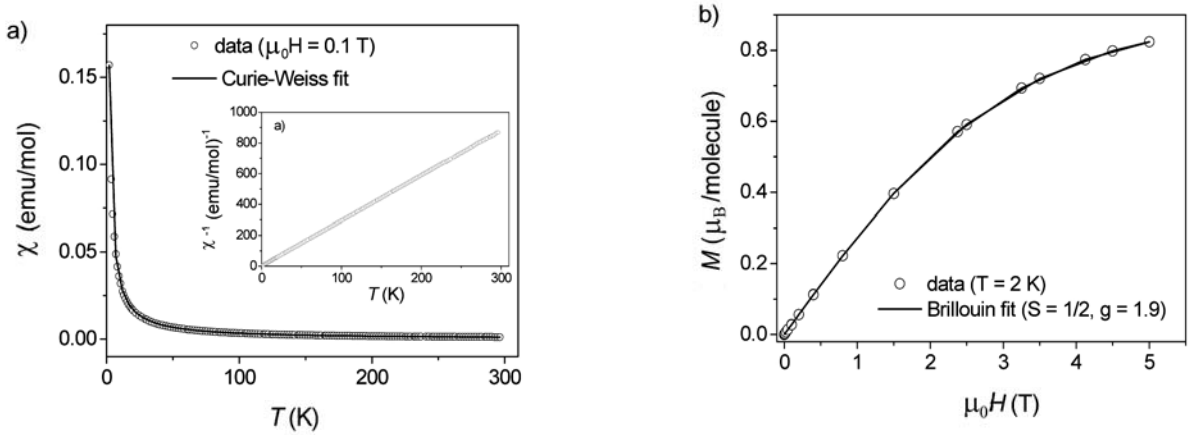

Figure 1. a) Molar susceptibility χ as a function of temperature measured in magnetic field 0,1 T for the $NH_4(NH_3OH)_2[VOF_5]$. Full line represents a Curie-Weiss fit. Inverse susceptibitilty χ^{-1} is linear with T (inset) showing paramagnetic behaviour. **b**) Magnetization M at a constant temperature 2 K as a function of magnetic field H follows a Brillouin function (full line).

corresponding magnetic moment $\mu_{eff} = 2.828\ C^{1/2} = 1.64\ \mu_B$. This value is close to the measured value and indicates an orbital contribution to the V^{4+} magnetic moment. The magnetic measurements indicate that the oxidation sate of vanadium in the compound is 4+.

On the other hand the bond valence sum for vanadium was calculated as reported by Brese and O'Keeffe using the relation $v_{ij} = \exp[(R_{ij}–d_{ij})/b]$ where d_{ij} is the bond length, b is constant equal to 0.37 and R_{ij} is the bond valence parameter from Ref. 27. The bond – valence sum should be approximately equal to the valence of the cation examined and is given by $V_{ij} = \chi v_{ij}$. The bond – valence sum calculated for vanadium using the bond - valence parameters $R(V^{4+})$ was 3.99 what is close to the expected value, in agreement with magnetic measurements and supports the finding of the structure analysis.

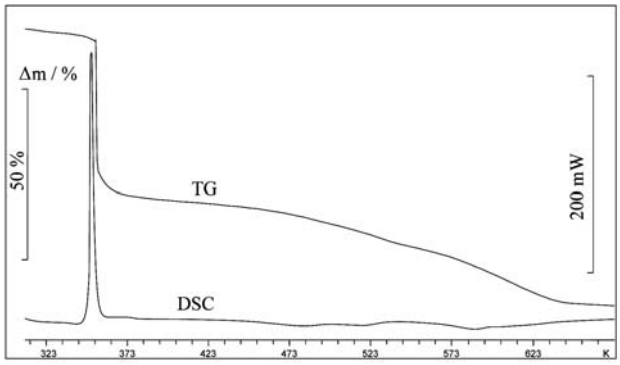

Figure 2. Thermal analysis of $NH_4(NH_3OH)_2[VOF_5]$: TG = Thermogravimetric analysis, DSC = Differential Scanning Calorimetry

The thermal decomposition of the compound in a nitrogen atmosphere is shown on Figure 2. The small initial drift on the TG curve can be attributed to the loss ob adsorbed water and HF. The onset point of thermal decomposition of the title compound is at 354 K. Up to 368 K the sample loses 44.2% of its starting mass with a peak temperature at 356 K. The DSC curve shows a significant exothermic peak at the same temperature. In the second temperature interval between 368 K and 668 K the sample loses another 22.8% of its mass. At 673 K, 67% of the initial mass is lost and the mass of the residue does not change anymore.

The products of the thermal decomposition at different temperatures and the final residue were identified by X–ray powder diffraction. The diffraction patterns are shown in Figure 3. At 363 K, after the first significant decomposition step, the diffraction pattern shows that the prevalent product is NH_4VOF_3 (JPCSD card No. 00–041–0653) with some traces of $(NH_4)_3VOF_5$ (JPCSD card No. 00–034–0882). The measured mass loss in the first step ($\Delta m_{meas.} = 44.2\%$) is in good agreement with the value, calculated for the decomposition of $NH_4(NH_3OH)_2[VOF_5]$ to NH_4VOF_3 ($\Delta m_{calc.} = 42.8\%$). The reaction can be described by the equation:

$$3NH_4(NH_3OH)_2[VOF_5] \rightarrow 3NH_4VOF_3 + 2\ NH_4F + 4HF + 2N_2 + 6H_2O$$

Pure $(NH_4)_3VOF_5$ could not be obtained by thermal decomposition, even by lowering the heating rate down to 2 K/min. At 573 K, only NH_4VOF_3 could be observed and

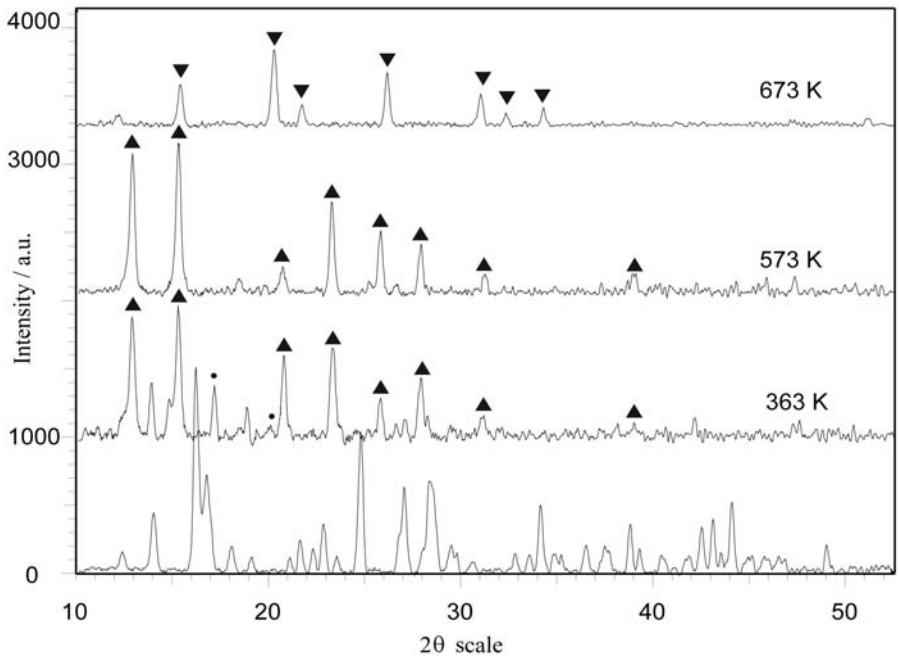

Figure 3. X–ray diffraction patterns of $NH_4(NH_3OH)_2[VOF_5]$ (lowest) and the products of thermal decomposition at different temperatures. (▲) NH_4VOF_3, (●) $(NH_4)_3VOF_5$, (▼) V_2O_5.

the final residue at 673 K could be identified as pure V_2O_5 (JPCSD card No. 00–041–1426). This result suggests that oxidation of V takes place during the heating. The overall measured mass loss ($\Delta m_{meas.}$ = 67.0%) is somewhat higher than the calculated value ($\Delta m_{calc.}$ = 63.3%) for the decomposition of $NH_4(NH_3OH)_2[VOF_5]$ to V_2O_5, the difference can be attributed to the loss of traces of adsorbed water and HF during the initial stages of the decomposition.

The results show some differences, compared to the thermal decomposition of other hydroxylammonium fluorometallates, such as hydroxylammonium fluorotitanates, -zirconates, -hafnates, -galates, and germanates, which decompose at higher temperatures (onset temperatures between 378 and 398 K) and yield metal fluorides as the final residue when heated in nitrogen flow. Hydoxylammonium fluoroindate decomposes[4] into a mixture of InF_3 and InOF while the final product of the thermal analysis of hydroxylammonium fluorochromate[11] in nitrogen is Cr_2O_3. Hydroxylammonium fluorosilicates[5] decompose at lower temperatures (onset temperature 343–348 K), that can be explained with weaker hydrogen bonds (O–H ··· F and N–H ··· F) in silicon compounds, and decompose without solid residue. However, gaseous SiF_4 could be determined as a product by mass spectrometry. Compared with ammonium fluorooxovanadates, studied by Demšar and Bukovec[21], $NH_4(NH_3OH)_2[VOF_5]$ decomposes at lover temperatures, a fact that can be attributed to low thermal stability of hydroxylamine.

The crystal structure of $NH_4(NH_3OH)_2[VOF_5]$ is monoclinic with the unit cell parameters: a = 10.5658(2) Å, b = 6.6143(1) Å, c = 11.6618(2) Å, β = 96.282(1)^0 and V = 810.10(2) Å^3. The structure consists of isolated VOF_5^{3-} octahedra, which are connected by numerous hydrogen bridges to two NH_3OH^+ and one NH_4^+ ions (Fig. 4).

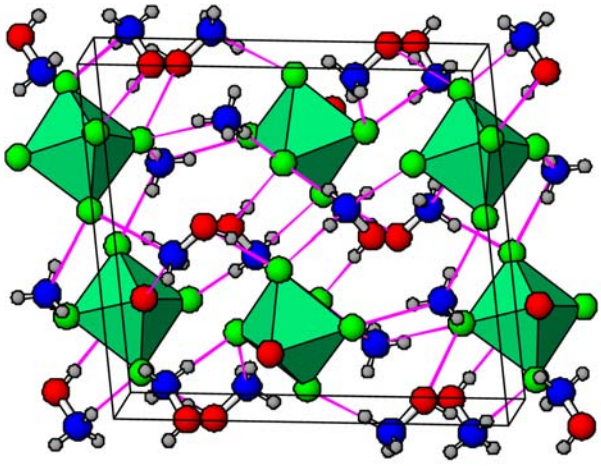

Figure 4. View of the $NH_4(NH_3OH)_2[VOF_5]$ structure (*a* axis up, *c* to the right, *b* into the plane of the paper). Vanadium is in the centre of the octahedron, fluorine, oxygen and nitrogen atoms are green, red and blue respectively, hydrogen bonds are indicated by thin pink lines.

An ordered model gave the R value of about 4.5%, which can be considered rather good, however, there remained a peak in the electron density map of about 2.5 electrons per cubic angstroem, close to the oxygen atom of one of the hydroxylammonium ions. After thorough examination it was found, that this oxygen (O(2)) is disordered over two positions, the predominant one being about 80% populated and the minor one about 20% (labelled O(2a) in Fig. 5 and Tables 2–4). The inclusion of the alternate position of O(2a) lowered the R value down to 2.5% and eliminated the corresponding peak in the final difference electron density map (the highest peak was then about 0.7 eÅ^{-3} close to one of the fluorine atoms in the vanadate ion).

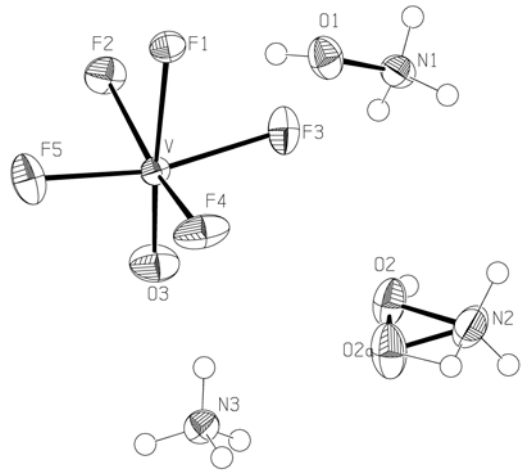

Figure 5. Ellipsoid plot of the asymmetric unit of $NH_4(NH_3OH)_2[VOF_5]$. Ellipsoids are drawn at 50% probability.

The disorder affects of course the whole hydroxylammonium ion, but it was not possible to determine the alternate nitrogen and hydrogen atoms positions as the alternate positions of the nitrogen atom are apparently very close together (less than 0.2 angstroems), which reflects as somewhat larger thermal ellipsoid of N(2), refined as single position (Fig 5). The reason for this disorder was found in the fact that the O(2) atom has two possibilities to form strong hydrogen bonds to fluorine atoms (Table 4). The predominant one to F(3) is 2.56 Å long, while the minor position O(2a) is hydrogen bonded to F(5) of another vanadate ion at a distance of 2.609 Å and to F(4) of yet another vanadate at a distance of 2.703 Å.

As mentioned, it was not possible to find and refine the alternate 20% occupied positions of N(2) and all the corresponding hydrogen atoms. The disorder, however, manifested itself in non-stable refinement of the corresponding hydrogen atoms, which were then restrained to keep the reasonable geometry of the predominant configuration of the disordered hydroxylammonium ion.

The fractional coordinates and the equivalent displacement parameters for non-hydrogen atoms are given

in Table 2, some selected bond lengths and angles can be found in Table 3.

Table 2. Fractional coordinates and equivalent displacement parameters (Å^2) for non-hydrogen atoms of ammonium bis(hydroxylammonium) pentafluoridooxidovanadate(IV). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x/a	y/b	z/c	$U_{(eq)}$
V	–0.23642(2)	0.20312(3)	0.46221(2)	0.0165(1)
F1	0.3079(1)	0.4897(1)	0.5282(1)	0.0228(3)
F2	0.2235(1)	0.3559(1)	0.3184(1)	0.0297(4)
F3	0.4179(1)	0.1651(2)	0.4500(1)	0.0322(4)
F4	0.2604(1)	0.1360(2)	0.6229(1)	0.0381(4)
F5	0.0722(1)	0.3128(2)	0.4849(8)	0.0390(5)
O1	0.0033(1)	–.00773(2)	0.8174(1)	0.0311(5)
O2*	0.5391(1)	0.1124(3)	0.2739(2)	0.0334(1)
O2a*	0.5651(5)	0.1712(1)	0.2076(6)	0.041(4)
O3	0.1940(1)	–0.0169(2)	0.4140(1)	0.0360(5)
N1	–0.0831(1)	–0.2018(2)	0.8691(1)	0.0243(5)
N2	0.4520(1)	0.1800(2)	0.1855(2)	0.0437(8)
N3	0.1685(1)	0.7486(2)	0.6483(1)	0.0238(6)

* O(2) is the predominant position (population 0.778(8)), while O(2a) is minor (population 0.222(8)).

Table 3. Bond distances (Å) and angles (°) for ammonium bis(hydroxylammonium) pentafluoridovanadate(IV) with e.s.d.s. in parentheses.

V–O(3)	1.606(1)	O(3)–V–F(4)	97.73(5)
V–F(4)	1.915(1)	O(3)–V–F(5)	99.68(6)
V–F(5)	1.925(1)	O(3)–V–F(2)	100.24(5)
V–F(2)	1.950(1)	O(3)–V–F(3)	95.55(5)
V–F(3)	1.955(1)	O(3)–V–F(1)	175.66(6)
V–F(1)	2.152(1)	F(4)–V–F(5)	88.74(4)
N(1)–O(1)	1.413(2)	F(4)–V–F(2)	161.97(4)
N(2)–O(2)	1.379(2)	F(4)–V–F(3)	90.90(4)
O(2)–O(2a)	0.933(3)*	F(4)–V–F(1)	81.42(5)
		F(5)–V–F(2)	86.75(4)
		F(5)–V–F(3)	164.68(4)
		F(5)–V–F(1)	84.58(5)
		F(2)–V–F(3)	88.90(4)
		F(2)–V–F(1)	80.78(5)
		F(3)–V–F(1)	80.24(5)

* The disordered position O(2a) is less then 1 Å apart from the predominant one O(2).

Table 4. Hydrogen bond distances (Å).

Bond	Distance
O(2)–F(3)	2.560(2)
O(1) –(F1)	2.575(1)
O(2a) –F(5)	2.609(2)
F(1)–N(1)	2.684(1)
O(2a)–F(4)	2.703(2)
F(2)–N(1)	2.703(1)
N(2)–O(3)	2.711(1)
F(3)–N(1)	2.733(1)
N(3)–F(1)	2.742(1)
N(3)–F(4)	2.768(2)
N(2)–F(5)	2.783(2)
N(3)–F(4)	2.796(1)
N(2)–F(2)	2.831(2)
N(3)–F(5)	2.860(1)

The length of the V–O bond in the structure is 1.606(1) Å and the bond lengths of V–F for the F(2) to F(5) atoms varied from 1.915(1) to 1.955(1) Å. The exception was the V–F(1) bond with a length of 2.152(1) Å, which is the reason why the octahedra are deformed. The angles for O–V–F from 95.55(5) to 100.24(5)` and for F–V–F from 80.78(5) to 90.90(4)` were determined. The N–O lengths are in good agreement with the values, reported in papers for other fluorometallates of hydroxylammine. The hydrogen bond distances N–H ··· F and O–H ··· F (given in Table 3) vary from 2.560 Å for the O(2)–F(3) bond to 2.860 Å for the bond N(3)–F(5), which is in good agreement with literature data for the reported hydroxylammonium fluorometallates, where bond lengths O–H ··· F are in the range 2.503–2.661 Å and N–H ··· F in the range 2.666 Å–2.921 Å are reported.

4. Conclusions

In summary, we have reported the synthesis of a new hydroxylammonium fluorovanadate from aqueous solution. The crystal structure was determined by the x-ray analysis and the thermal decomposition was studied. The title compound decomposes in two steps, yielding NH_4VOF_3 after the first step and V_2O_5 as the final product. However, additional studies will be required before a complete understanding of all reactions taking place during thermal analysis. Magnetic measurements show a typical Curie–Weiss behaviour and the μ_{eff} calculated from the value of Curie constant is $1.65\mu_B$.

The crystallographic data referred to herein have been deposited with the Fachinformationszentrum Karlsruhe (FIZ), D-76344 Eggenstein-Leopoldshafen.

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Povzetek

Z reakcijo med trdnim NH_3OHF in raztopino vanadija v 40% HF smo sintetizirali turkizne kristale nove spojine hidroksilamina s formulo $NH_4(NH_3OH)_2[VOF_5]$. Spojina kristalizira monoklinsko, $P2_1/n$, s parametri osnovne celice: a = 10.5658(2) Å, b = 6.6143(1) Å, c = 11.6618(2) Å, β = 96.282(1). Iz meritev magnetne susceptibilnosti z magnetometrom SQUID v temperaturnem območju 2–300 K pri magnetnem polju 10^3 Oe smo izračunali efektivni magnetni moment μ_{ef} = 1.65 BM. Termični razkroj spojine smo spremljali s TG in DSC analizo. $NH_4(NH_3OH)_2[VOF_5]$ nad temperaturo 354 K razpada v treh stopnjah preko vnesnega produkta NH_4VOF_3 do končnega preostanka V_2O_5.