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Scientific paper

Hydroxylammonium Tetrafluoridooxidovanadate(V) – $(NH_3OH)[VOF_4]$

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Dedicated to the memory of Prof. Dr. Jurij V. Brenčič.

Abstract

Hydroxylammonium tetrafluoridooxidovanadate(V) has been prepared by reaction of $(NH_3OH)Cl$ and VOF_3 in anhydrous HF solvent and characterised in the solid state by single-crystal X-ray diffraction and Raman spectroscopy. Colourless $(NH_3OH)[VOF_4]$ crystallises in the monoclinic space group $P2_1/n$ with $a = 7.2349(2)$ Å, $b = 5.0351(2)$ Å, $c = 12.8322(4)$ Å, $\beta = 94.843(3)°$, $V = 465.79(3)$ Å^3 and $Z = 4$ at 150 K. The crystal structure of the title compound is comprised of polymeric chain anions, $[VOF_4]_n^{n-}$, interconnected by hydrogen bonds with hydroxylammonium cations, $(NH_3OH)^+$.

Keywords: Fluoridooxidovanadate; Vanadium oxyfluoride; Hydroxylamine; Hydroxylammonium; X-ray crystallography; Anhydrous hydrogen fluoride

1. Introduction

Several hydroxylammonium fluoridometallate salts of the type $(NH_3OH)_x[MF_n]_y$ have been synthesised and structurally characterised. The solid state structures display a variety of anionic types ranging from isolated, 0-dimensional anions (monomers: $[SiF_6]^{2-}$,[1] $[ScF_6]^{3-}$,[2] $[TiF_6]^{2-}$,[3] $[CrF_6]^{3-}$,[4] $[FeF_6]^{3-}$,[5] $[GaF_6]^{3-}$,[6] $[InF_6]^{3-}$,[3] and $[VOF_5]^{3-}$,[7]; dimeric anions: $[Zr_2F_{14}]^{6-}$,[8] $[Hf_2F_{14}]^{6-}$)[9] through 1-dimensional chain species ($[AlF_5]^{2-}$,[10] $[ZrF_6]^{2-}$)[8], to 2-dimensional anionic layers ($[MnF_4]^{2-}$,[2] $[CoF_4]^{2-}$, $[CuF_4]^{2-}$,[11] $[ZnF_4]^{2-}$).[12]

A successful synthetic procedure which leads to these salts was developed in aqueous hydrogen fluoride media, employing a reaction between hydroxylammonium fluoride,[13] $(NH_3OH)F$, and desired metal fluoride. The latter reagent is usually prepared *in situ* by reacting the selected metal or metal oxide with hydrofluoric acid.

However, not all metal oxidation states, and hence anionic species are stable under the foregoing conditions and accessible by the aforementioned synthetic route. This is reflected in the formation of $(NH_3OH)_2[MnF_4]$,[2] $(NH_3OH)_2[CoF_4]$,[11] and $(NH_4)(NH_3OH)_2[VOF_5]$[7] salts with Mn(II), Co(II), and V(IV) fluorido or fluoridooxido anions and not, for instance, Mn(III), Co(III), or V(V) products, respectively. Likewise, this method is not suitable for routine preparation of hydroxylammonium fluoridooxidometallates or respective salts with moisture-sensitive high-oxidation-state anions.

These shortcomings can be overcome by devising a different synthetic procedure, namely the Lewis acid-base reaction of the corresponding metal fluoride or oxyfluoride with $(NH_3OH)F$ in anhydrous HF (aHF). Moreover, hydroxylammonium fluoride could be prepared *in situ* by solvolysis of readily available hydroxylammonium chloride, $(NH_3OH)Cl$, in aHF solvent.[14]

This approach is demonstrated by the synthesis of hydroxylammonium tetrafluoridooxidovanadate(V), $(NH_3OH)^+[VOF_4]^-$, and its characterisation in the solid state by single-crystal X-ray diffraction and Raman spectroscopy reported herein.

2. Experimental

2. 1. General Experimental Procedures

A vacuum line constructed of PTFE (polytetrafluoroethylene), FEP (perfluorinated ethylene propylene), nickel, and equipped with a Monel Helicoid pressure gauge, a soda lime scrubber, liquid nitrogen cooled traps, and a two-stage rotary vane pump was used for the solvent transfer. Other involatile reagents were stored and handled in an argon atmosphere in a glovebox having a maximum water content less than 0.5 ppm (M. Braun, Garching, Germany). A PTFE valve equipped a T-shaped FEP crystallisation vessel which consisted of a larger diameter "reaction" arm constructed from 16-mm i.d. (19-mm o.d.) FEP tubing, to which a narrower "crystallisation" arm constructed from 6-mm i.d. (8-mm o.d.) FEP tube was attached at right angles, was used for synthesis and crystal growth.[15] The solution was stirred in the wider FEP arm with the aid of a PTFE-coated magnetic stir bar. All FEP crystallisation vessels were passivated with F_2 prior to use.

2. 2. Reagents

Hydroxylamine hydrochloride, $(NH_3OH)Cl$, (Alfa Aesar, 99%) and vanadium oxytrifluoride, VOF_3, (Aldrich, 99%) were used as received. The solvent, aHF, was prepared by treating commercial anhydrous HF (Linde, Fluorwasserstoff 3.5) with K_2NiF_6 (Ozark-Mahoning, 99%) for at least 12 h prior to use. ***Caution****: Anhydrous HF must be handled with great care in a well-ventilated fume hood and protective gear must be worn at all times.*

2. 3. Synthesis and Crystallisation of $(NH_3OH)[VOF_4]$

In a typical experiment, $(NH_3OH)Cl$ (70 mg, 1.01 mmol) and VOF_3 (126 mg, 1.02 mmol), were weighed into the larger diameter arm of a FEP-crystallisation vessel, and aHF solvent (2.0 mL) was condensed at liquid nitrogen temperature into the same arm. Upon warming of the frozen reaction mixture, vigorous evolution of HCl gas occurred, which was removed on a vacuum line. A clear, pale yellow solution resulted which was decanted from the larger diameter reaction arm of the T-shaped crystallisation vessel into the narrower crystallisation arm. The latter was left at room temperature while the former was slowly cooled. Due to the steadily increasing temperature gradient (up to 35–45 °C), aHF evaporated from the crystallisation arm into the reaction arm in the course of 3–4 weeks. The resulting white crystalline material was transferred to a glovebox where a portion of the crystals were poured from the FEP tube onto a watch glass and covered with a protective layer of perfluorinated oil (ABCR, AB102850, perfluorodecalin, 98%, *cis* and *trans*). Suitable plate-like colourless crystals were selected under a polarizing microscope outside the glovebox, mounted on a glass capillary pin with the aid of Baysilone-paste, and quickly transferred onto the goniometer head with magnetic base, where it was cooled by a cold nitrogen stream. The product decomposes rather slowly in air, but undergoes a rapid reaction and effervesces upon contact with water.

2. 4. Single-crystal X-ray Structure Determination

X-ray diffraction data were collected with the *CrysAlis PRO*[16] software package on an Agilent New Gemini, Dual, diffractometer equipped with an Atlas CCD area detector using graphite-monochromatised Mo $K\alpha$ radiation at 150 K. An analytical absorption correction was applied to the data set. Using *Olex2*,[17] the structure was solved by the charge-flipping algorithm using the structure solution program *Superflip*[18] and refined with *SHELXL* (v. 2014/7)[19] software by least squares minimisation. Hydrogen atoms were located in a difference Fourier map and isotropically refined. While atoms H1–H3 were well behaved, the H4-atom displayed a short H4–N1 distance (0.73 Å), therefore, a distance restraint (DFIX) of 0.91 Å with a sigma value of 0.02 Å was employed. Small residual electron density minima and maxima are located 0.78 Å from V1 and 0.73 Å from O1, respectively. The figures were prepared using *DIAMOND* program.[20] Details of the data collection, data processing, and refinement are given below (Table 1). The supplementary crystallographic data (CIF file) may be obtained from the Fachinformationszentrum Karlsruhe (FIZ), D–76344 Eggenstein-Leopoldshafen, Germany, on quoting the deposition number CSD-429634 for $(NH_3OH)[VOF_4]$.

2. 5. Raman Spectroscopy

Raman spectra were obtained from a crystalline sample that was powdered and transferred into a quartz capillary under an inert atmosphere and flame-sealed. Spectra were measured at room temperature in the range 50–3900 cm^{-1} on a Horiba Jobin-Yvon LabRAM HR Raman microscope using He–Ne laser excitation (632.8 nm, 25 mW).

Table 1. Crystal data and structure refinement summary

Compound	**$(NH_3OH)[VOF_4]$**
Fw	176.98
T (K)	150
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	7.2349(2)
b (Å)	5.03513(16)
c (Å)	12.8322(4)
β (°)	94.843(3)
V (Å^3)	465.79(3)
Z	4
ρ_{calc} (g/cm^3)	2.524
λ (Å)	0.71073
μ (mm^{-1})	2.141
Reflns./indep./with $[I > 2\sigma(I)]$	3232/1139/1066
R_{int}, R_{sigma}	0.0180, 0.0218
Data/restraints/parameters	1139/1/90
S	1.063
R_1, wR_2 $[I > 2\sigma(I)]$	0.0180, 0.0436
R_1, wR_2 [all data]	0.0197, 0.0444
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (eÅ^{-3})	–0.327, 0.273

3. Results and Discussion

3. 1. Synthesis

The only previously reported and structurally characterised hydroxylammonium fluoridovanadate is the vanadium(IV) double salt, $(NH_4)(NH_3OH)_2[VOF_5]$,[7] which formed as a product of partial decomposition of $(NH_3OH)^+$ ion and aerial mono-oxygenation of vanadium in aqueous HF. An altogether different synthetic procedure was therefore employed for the synthesis of hydroxylammonium vanadium(V) oxyfluoride, $(NH_3OH)[VOF_4]$. The latter was synthesised by a Lewis acid-base reaction in which the Lewis acid, VOF_3, accepts a fluoride ion from the base, $(NH_3OH)F$, which is formed *in situ* by solvolysis of $(NH_3OH)Cl$ in aHF. This reaction produces hydrogen chloride gas which is sparingly soluble in anhydrous hydrogen fluoride.[21]

$$(NH_3OH)Cl + VOF_3 + HF \xrightarrow{aHF} (NH_3OH)[VOF_4] + HCl\uparrow$$

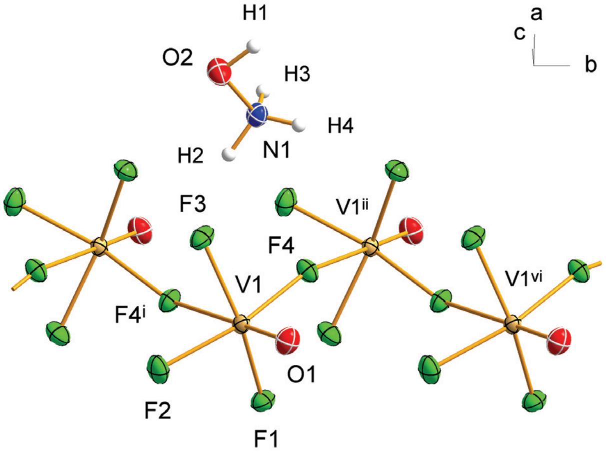

Figure 1. The asymmetric unit is composed of a $(NH_3OH)^+$ cation and a VOF_4-unit which has been expanded to reveal a zigzag $[VOF_4]_n^{n-}$ chain anion comprised of *cis*-corner sharing $[VOF_3F_{2/2}]$ octahedra. Thermal ellipsoids are drawn at the 70% probability level and hydrogen atoms are depicted as small spheres of arbitrary radius.

3. 2. Crystal Structure

The title compound crystallises in the monoclinic space group $P2_1/n$ with all atoms of the asymmetric unit (V1, F1–F4, O1, O2, N1, and H1–H4) occupying general positions (Wyckoff 4*e*) (Figure 1). The $(NH_3OH)[VOF_4]$ salt has a 1-dimensional polymeric anion and this group of hydroxylammonium fluoridometallate salts is, along with the family possessing oligomeric anions, the least populated. The $^{1}_{\infty}([VOF_4]^-)$ anion is a zigzag *cis*-corner sharing chain, whereas essentially linear chains of *trans*-corner sharing AlF_6-octahedra and *trans*-perpendicular-edge sharing ZrF_8-units have been observed in the crystal structures of $(NH_3OH)_2[AlF_5]$[10] and $(NH_3OH)_2[ZrF_6]$,[8] respectively. It is also noteworthy that the described compound represents a rare example of a structurally characterised hydroxylammonium fluoridometallate having a 1:1 cation-anion stoichiometry, whereas 3:1 and 2:1 salt-types prevail.

The central vanadium(V) cation of the $[VOF_4]^-$ anion is coordinated by five fluorine and one oxygen atom to form a distorted $[VOF_3F_{2/2}]$ octahedron with a short V=O (1.5662(10) Å) and a long bridging *trans*-$V–F_b$ (2.3306(7) Å) bonds. Equatorial bridging *cis*-$V–F_b$ distance (1.8540(8) Å) is, as expected, elongated in comparison with the three terminal $V–F_t$ bonds (1.8094(7)–1.8315(7) Å). The bond valence sum calculation on vanadium gives 5.01, in agreement with the expected value of 5 valence units.[22] The "roof effect" or the repulsion of the axial oxido ligand exerted on the equatorial fluorido ligands is manifested by the deviation of *cis*-O–V–F angles (99.20(4)–101.07(4)°) from 90° (Table 2).

The consequence of the described arrangement of oxido and fluorido ligands is the axial displacement of vanadium ion (by 0.3157(5) Å) from the least-square plane of four equatorial fluorido ligands of the $[VOF_5]$ octahedral unit towards the O-atom. This so-called intrinsic primary C_4 [001] out-of-centre distortion[23] is typical of early d^0 transition metal fluoridomonooxido anions.[24] Thus, the polar $^{1}_{\infty}([VOF_4]^-)$ zigzag *cis*-corner sharing chains are oriented antiparallel with respect to each other along the *b*-crystallographic axis and, as a result, a centrosymmetric material is formed (Figure 2).

Three different anions with the empirical formula VOF_4^- have been described in the literature, namely, the edge-sharing dimer[25,15] – $[V_2O_2F_8]^{2-}$, the corner-sharing cyclic trimer[26] – $[V_3O_3F_{12}]^{3-}$, and the polymeric zigzag *cis*-chain[27–29] – $[VOF_4]_n^{n-}$. The other three examples of structurally characterised $^{1}_{\infty}([VOF_4]^-)$ anions display bond lengths comparable to those observed in $(NH_3OH)[VOF_4]$ (Table 2): $Cs[VOF_4]$:[27] V=O 1.529(12) Å, $V–F_t$ 1.783(10) Å and 1.788(6) Å, $V–F_b$ 1.793(10) and 2.312(10) Å; $K[VOF_4]$:[28] V=O 1.572(8) Å, $V–F_t$ 1.786(7)–1.804(7) Å, $V–F_b$ 1.875(7) and 2.333(7) Å; $Ag[VOF_4]$:[29] V=O 1.571(3) Å, $V–F_t$ 1.798(2)–1.822(2) Å, $V–F_b$ 1.857(2) and 2.287(2) Å.

It is interesting to note that the $^{1}_{\infty}([VOF_4]^-)$ anion apparently possess sufficient degree of conformational flexibility to the extent that it can accommodate and efficiently pack into a crystal lattice with monovalent cations of various sizes (Ag^+, K^+, Rb^+, Cs^+) as well as different shapes ($H_3N^+–OH$). However, in the aforementioned salts, the zigzag *cis*-chain $[VOF_4]^-$ anions adopt different solid-state conformations,[29] and in the present hydroxylammonium salt, a "helical" geometry is observed, which is identical to that of the conformer described in the $Ag[VOF_4]$ crystal structure. This is reflected in the good agreement between geometric parameters of $^{1}_{\infty}([VOF_4]^-)$

Table 2. Selected interatomic distances and angles.

Distances (Å)		**Angles** (°)			
V1–O1	1.5662(10)	O1–V1–F1	101.07(4)	V1–F4–V1^{ii}	150.89(4)
V1–F1	1.8094(7)	O1–V1–F2	99.83(5)	F1–V1···V1^{ii}–F1^{ii}	–157.19(3)
V1–F2	1.8100(8)	O1–V1–F3	99.72(4)	N1–O2–H1	98.7(16)
V1–F3	1.8315(7)	O1–V1–F4	99.20(4)	O2–N1–H2	105.0(14)
V1–F4	1.8540(8)	O1–V1–F4^{i}	178.84(4)	O2–N1–H3	109.7(12)
V1–F4^{i}	2.3306(7)	F1–V1–F3	159.09(4)	O2–N1–H4	108.9(17)
N1–O2	1.4111(14)	F2–V1–F4	160.96 (4)	H2–N1–H3	112(2)
V1···(F4)···V1^{ii}	4.0521(4)	F2–V1–F4^{i}	79.03(3)	H2–N1–H4	113(2)
V1···V1^{vi}	5.03513(16)	F4–V1–F4^{i}	81.932(14)	H3–N1–H4	108(2)

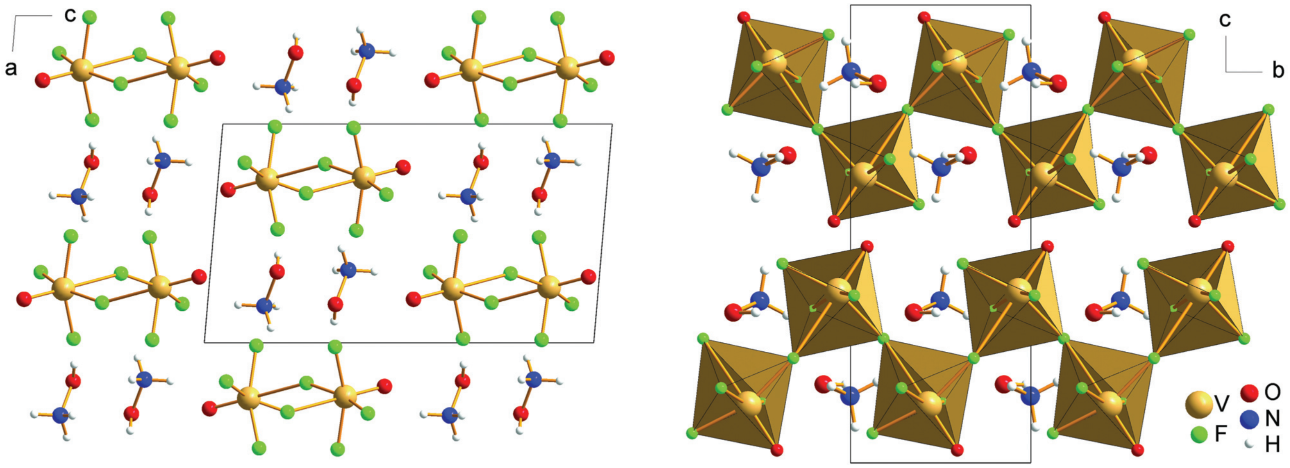

Figure 2. Packing in the unit cell of $(NH_3OH)[VOF_4]$ viewed along *b*- and *a*-crystallographic axes, respectively. Note the resemblance of $[VOF_4]^-$ anion depicted in [010] direction to the dimeric and centrosymmetric edge-sharing $[V_2O_2F_8]^{2-}$ dianion,[25,15] as well as the packing similarities between the crystal structures of $(NH_3OH)[VOF_4]$ and $Ag[VOF_4]$.[29]

anion described herein (Table 2) and those reported for the Ag^+ salt (V···(F_b)···V 4.0159(8) Å; V···V 5.0071(3) Å; V–F_b–V 151.3(1)°).[29]

The hydroxylammonium cation, $(NH_3OH)^+$, which is isoelectronic with methanol, has an N–O distance (1.4111(14) Å) that is in excellent agreement with the bond length (1.414(2) Å) reported in the crystal structure of hydroxylammonium 4-(ethyloxycarbonyl)-5-oxo-2,5-dihydroisoxazolide, $(NH_3OH)^+(C_6H_6NO_4)^-$, determined at 150 K,[30] and with the N–O bond length (1.416(5) Å) found in the crystal structure of bis(hydroxylammonium) hexachloridoplatinate(IV)–18-crown-6 (1/2), $(NH_3OH)_2[PtCl_6]\cdot 2C_{12}H_{24}O_6$, measured at 100 K.[31] The N–O bond length in $(NH_3OH)[VOF_4]$ also falls well within the range of reported N–O bond distances (1.375(2)–1.416(2) Å; average of 24 values: 1.406(2) Å) for other known hydroxylammonium fluoridometallates that were structurally characterised at room temperature.[1–8, 10–12] Despite the lack of available high-quality, low-temperature X-ray diffraction data on hydroxylamine or its cocrystals, it is evident that the N–O bond in the N-protonated form or hydroxylammonium cation is significantly shortened in comparison with the neutral hydroxylamine molecule.[32] For the latter, the N–O bond distance value in the gas phase is available from the microwave spectroscopy (1.453(2) Å; room temperature)[33] and in the solid state from a single-crystal X-ray diffraction determination which unfortunately suffers from the omission of hydrogen atoms in the refinement which, in turn, is reflected in a large estimated probable error for the N–O bond length (1.476(30) Å; 213 K).[34] The hydroxylammonium cation typically adopts a staggered conformation, however, the energetically soft parameters, namely the H–O–N–H torsion angles, are likely to be to some extent affected by hydrogen bonding interactions. In the present crystal structure, the conformation of the cation is almost midway between staggered (60°) and eclipsed (0°), as demonstrated by the values of the H1–O2–N1–H3 (–80(2)°) and H1–O2–N1–H4 (38(2)°) torsion angles.

The N–H···F type hydrogen bonding usually dominates intermolecular interactions in the solid-state structures of nitrogen base-templated hybrid organic-inorganic fluoride compounds.[35–38] Similarly, the anions in the crystal structure of $(NH_3OH)[VOF_4]$ interact with the cations through a myriad of hydrogen bonds (Table 3). All four hydrogen atoms of the cation are involved in hydrogen bonding interactions, with those residing on nitrogen being bifurcated donors, which is reflected in the deviation of the N–H···F/O hydrogen bonds from linearity. Conversely, in the VOF_4-unit of the anion, just two F-atoms act as a bifurcated acceptors (F1, F3), and all possible acceptors, including oxygen, are utilised, with the exception of the bridging fluorine (F4). The effect of partially charged donors (NH_3^+) and acceptors (VOF_4^-) is demonstrated by the shorter N···F hydrogen bonding distances (2.747(2)–2.952(1) Å) observed in the crystal structure of $(NH_3OH)[VOF_4]$ salt as compared, for instance, to those reported between neutral molecules of either *mer*-$[VF_3(NH_3)_3]$ (2.922(1)–3.267(1) Å)[39] or $[TaF_5(NH_3)_3]$ (2.848(6)–3.519(6) Å).[40]

Table 3. Hydrogen-bond geometry. [a]

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A(°)
O2–H1···F3$^{\mathrm{iii}}$	0.83(2)	1.77(2)	2.5884(13)	167(2)
N1–H2···F1$^{\mathrm{i}}$	0.90(2)	2.03(2)	2.7471(15)	135(2)
N1–H2···F3	0.90(2)	2.28(2)	2.8973(15)	125.5(19)
N1–H3···F2$^{\mathrm{iv}}$	0.87(2)	1.98(2)	2.7665(15)	148.7(18)
N1–H3···O1$^{\mathrm{v}}$	0.87(2)	2.50(2)	3.1360(16)	130.9(16)
N1–H4···F1$^{\mathrm{ii}}$	0.86(2)	2.38(2)	2.9516(14)	125(2)
N1–H4···O2$^{\mathrm{iii}}$	0.86(2)	2.20(2)	2.9433(16)	145(3)

[a] Symmetry transformations for the generation of equivalent atoms: (i) $-x+1/2$, $y-1/2$, $-z+1/2$; (ii) $-x+1/2$, $y+1/2$, $-z+1/2$; (iii) $-x+3/2$, $y+1/2$, $-z+1/2$; (iv) $x+1/2$, $-y+1/2$, $z+1/2$; (v) $x+1/2$, $-y+3/2$, $z+1/2$; (vi) x, $y+1$, z.

In hydroxylammonium fluoridometallates, as well as in other hydroxylammonium salts,[32,41] the shortest, most linear, and hence presumably the strongest hydrogen bond typically involves the hydroxyl group of the cation as a donor and an anion as an acceptor (O···F 2.588(1) Å). In addition to the described cation-anion hydrogen bonding interactions, the cation-cation N–H···O hydrogen bonding is observed which gives rise to hydrogen-bonded zigzag chains oriented along the *b*-crystallographic direction. Each aforementioned cationic chain is surrounded by four parallel $^1_\infty([VOF_4]^-)$ chain anions, and vice versa (Figure 2). In this fashion, conjoined hydrogen bonded ring patterns with the graph-set notations[42] $R^2_1(8)$ and $R^4_4(12)$ connect the *C*3 cationic chain with two neighbouring chain anions in the *bc*-plane (Figure 3), and $R^2_1(6)$, $R^3_3(6)$, and $R^2_2(8)$ rings to the adjoining anions above and below in the direction of the *a*-crystallographic axis.

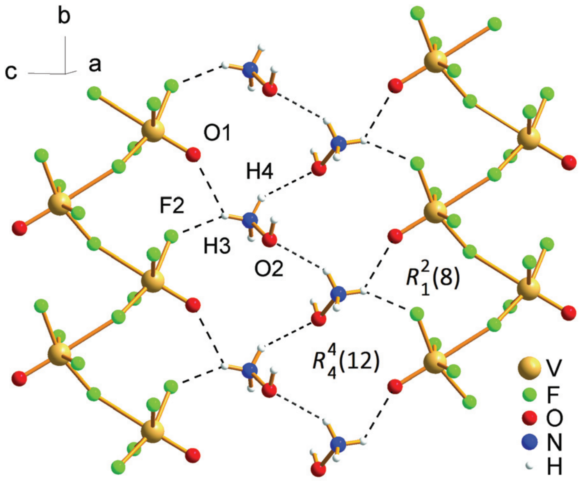

Figure 3. Hydrogen-bonded zigzag cationic chain flanked by two zigzag $^1_\infty([VOF_4]^-)$ anions in the *bc*-crystallographic plane. The hydrogen bonding network is depicted with dashed lines and graph-set notation.[42]

3. 3. Raman Spectroscopy

Hydroxylammonium fluoride-salts that have been studied by Raman spectroscopy include $(NH_3OH)F$,[14] $(NH_3OH)[UF_6]$,[43] and $(NH_3OH)_2[TiF_6]$.[44] Their respective N–O stretching bands of the hydroxylammonium cation were observed at 1017, 1015, and 1014 cm^{-1}. Characteristic V=O and V–F stretches appear in Raman spectra of tetrafluoridooxidovanadate(V) salts: $Cs[VOF_4]$ (V=O 1031 cm^{-1}; V–F 620, 585 cm^{-1}),[45] $K[VOF_4]$ (V=O 1019 cm^{-1}; V–F 643, 618, 577 cm^{-1}),[28] and $Ag[VOF_4]$ (V=O 1008 cm^{-1}; V–F 621, 595, 570 cm^{-1}).[29]

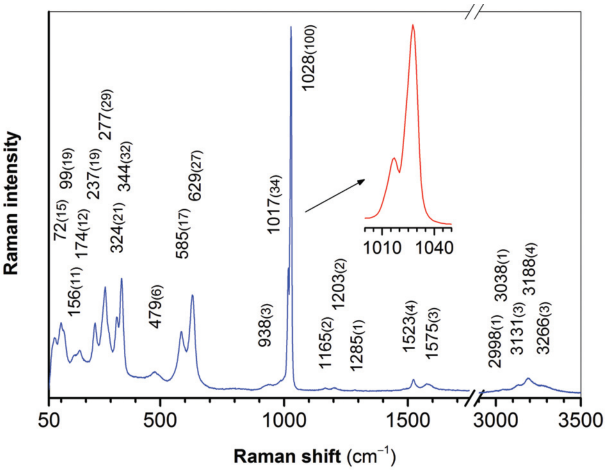

Figure 4. The Raman spectrum of $(NH_3OH)[VOF_4]$ with values of Raman band frequencies and relative intensities (given in parentheses) denoted. The regions (1750–2900 and 3500–3900 cm^{-1}) where no signals were observed are omitted.

The Raman frequencies observed in the case of $(NH_3OH)[VOF_4]$ for both the cation (N–O 1017 cm^{-1}) and the anion (V=O 1028 cm^{-1}; V–F 629, 585 cm^{-1}) are similar to the aforementioned reported values (Figure 4). Weak bands are observed in the O–H and N–H stretching regions, 3200–3000 cm^{-1}, as well as in the H–N–H bending and NH_3^+ rocking or O–H bending mode ranges, 1600–1500 cm^{-1} and 1300–1100 cm^{-1}, respectively.

4. Conclusion

The novel hydroxylammonium salt, hydroxylammonium tetrafluoridooxidovanadate(V), has been synthesised and its crystal structure elucidated at low temperature. The solid-state structure which consists of $(NH_3OH)^+$ cations interconnected by hydrogen bonds with a helical conformation exhibiting $[VOF_4]^-$ chain anions is discussed in detail. In addition, the reported Raman spectrum is in good agreement with the published vibrational spectra of similar compounds. Hydroxylammonium salts with fluoride or oxide fluoride anions of metals in oxidation states that cannot be isolated from aqueous HF solutions, can conveniently be prepared from corresponding Lewis acidic metal fluorides or oxyfluorides and hydroxylammonium chloride in anhydrous HF, as exemplified by the reported synthesis of $(NH_3OH)[VOF_4]$. Furthermore, this procedure bypasses the synthesis and isolation of hydroxylamine and hydroxylammonium fluoride, by formation of the latter Lewis base fluoride *in situ* by the solvolysis of the chloride in aHF.[14] The described synthetic approach could thus be utilised to expand the library of known hydroxylammonium fluoridometallates.

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6. References

1. M. Kristl, M. Drofenik, L. Golič, *Acta Chim. Slov.* **2002**, *49*, 243–250.
2. M. Kristl, B. Dojer, N. Hojnik, A. Golobič, *J. Fluorine Chem.* **2014**, *166*, 15–21. http://dx.doi.org/10.1016/j.jfluchem.2014.07.006
3. I. Ban, M. Kristl, B. Volavšek, L. Golič, *Monatsh. Chem.* **1999**, *130*, 401–408. http://dx.doi.org/10.1007/PL00010221
4. M. Kristl, M. Drofenik, L. Golič, A. Golobič, *Acta Chim. Slov.* **2003**, *50*, 431–440.
5. B. Dojer, M. Kristl, Z. Jagličić, A. Golobič, M. Kasunič, M. Drofenik, *Acta Chim. Slov.* **2012**, *59*, 789–794.
6. M. Kristl, B. Volavšek, L. Golič, *Monatsh. Chem.* **1996**, *127*, 581–586. http://dx.doi.org/10.1007/BF00817249
7. B. Dojer, M. Kristl, Z. Jagličić, M. Drofenik, A. Meden, *Acta Chim. Slov.* **2008**, *55,* 834–840.
8. I. Ban, L. Golič, S. Milićev, B. Volavšek, *Monatsh. Chem.* **1995**, *126*, 1279–1289. http://dx.doi.org/10.1007/BF00807057
9. I. Ban, B. Volavšek, L. Golič, *Z. Anorg. Allg.* Chem. **2002**, *628*, 695–698. http://dx.doi.org/10.1002/1521-3749(200203)628:3<695::AID-ZAAC695>3.0.CO;2-9
10. M. Kristl, A. Golobič, B. Dojer, M. Drofenik, *Monatsh. Chem.* **2011**, *142*, 755–762. http://dx.doi.org/10.1007/s00706-011-0508-4
11. M. Kristl, B. Dojer, M. Kasunič, A. Golobič, Z. Jagličić, M. Drofenik, *J. Fluorine Chem.* **2010**, *131*, 907–914. http://dx.doi.org/10.1016/j.jfluchem.2010.06.004
12. B. Dojer, A. Golobič, Z. Jagličić, M. Kristl, M. Drofenik, *Monatsh. Chem.* **2012**, *143*, 175–180. http://dx.doi.org/10.1007/s00706-011-0667-3
13. M. Kristl, L. Golič, B. Volavšek, *Monatsh. Chem.* **1994**, *125*, 1207–1213. http://dx.doi.org/10.1007/BF00813806
14. B. Frlec, H. H. Hyman, *J. Inorg. Nucl. Chem.* **1967**, *29*, 2124–2126. http://dx.doi.org/10.1016/0022-1902(67)80481-0
15. M. Lozinšek, E. Goreshnik, B. Žemva, *Z. Anorg. Allg. Chem.* **2012**, *638*, 2123–2128. http://dx.doi.org/10.1002/zaac.201200176
16. *CrysAlis PRO*, v. 1.171.36.32, Agilent Technologies UK Ltd (**2013**), Yarnton, England.
17. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339–341. http://dx.doi.org/10.1107/S0021889808042726
18. L. Palatinus, G. Chapuis, *J. Appl. Cryst.* **2007**, *40*, 786–790. http://dx.doi.org/10.1107/S0021889807029238
19. G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3–8. http://dx.doi.org/10.1107/S2053229614024218
20. K. Brandenburg, *DIAMOND* – Visual Structure Information System, v. 3.1, Crystal Impact GbR (**1997–2005**), Bonn, Germany.
21. M. F. A. Dove, A. F. Clifford: Inorganic Chemistry in Liquid Hydrogen Fluoride, in: G. Jander, H. Spandau, C. C. Addison (Eds.): Chemistry in Nonaqueous Ionizing Solvents, Pergamon Press, Friedr. Vieweg + Sohn, Braunschweig, Germany, **1971**, pp. 119–300.
22. For the bond valence sum calculations the following parameters have been used: b = 0.37 Å; R_0 = 1.71 Å (V–F), 1.803 Å (V–O); (a) I. D. Brown, D. Altermatt, *Acta Crystallogr.* **1985**, *B41*, 244–247. http://dx.doi.org/10.1107/S0108768185002063
    (b) N. E. Brese, M. O'Keeffe, *Acta Crystallogr.* **1991**, *B47*, 192–197. http://dx.doi.org/10.1107/S0108768190011041
23. P. S. Halasyamani, *Chem. Mater.* **2004**, *16*, 3586–3592. http://dx.doi.org/10.1021/cm049297g
24. M. E. Welk, A. J. Norquist, F. P. Arnold, C. L. Stern, K. R. Poeppelmeier, *Inorg. Chem.* **2002**, *41*, 5119–5125. http://dx.doi.org/10.1021/ic025622v
25. T. Kanatani, K. Matsumoto, R. Hagiwara, *Eur. J. Inorg. Chem.* **2010**, 1049–1055. http://dx.doi.org/10.1002/ejic.200901099

26. M. Hilbers, M. Leimkühler, R. Mattes, *Z. Naturforsch.* **1989**, *44b*, 383–388. http://dx.doi.org/10.1515/znb-1989-0403
27. G. W. Bushnell, K. C. Moss, *Can. J. Chem.* **1972**, *50*, 3700–3705. http://dx.doi.org/10.1139/v72-585
28. H. Rieskamp, R. Mattes, *Z. Anorg. Allg. Chem.* **1973**, *401*, 158–164. http://dx.doi.org/10.1002/zaac.19734010205
29. M. Lozinšek, E. Goreshnik, B. Žemva, *Acta Chim. Slov.* **2014**, *61*, 542–547.
30. A. R. Kennedy, A. I. Khalaf, C. J. Suckling, R. D. Waigh, *Acta Crystallogr.* **2003**, *E59*, o1410–o1412. http://dx.doi.org/10.1107/S1600536803018828
31. E. Bulatov, A. Afanasenko, T. Chulkova, M. Haukka, *Acta Crystallogr.* **2014**, *E70*, m7–m8. http://dx.doi.org/10.1107/S1600536813032649
32. K.-L. Shi, R.-Q. Wang, T. C. W. Mak, *J. Mol. Struct.* **1987**, *160*, 109–116. http://dx.doi.org/10.1016/0022-2860(87)87009-6
33. S. Tsunekawa, *J. Phys. Soc. Jpn.* **1972**, *33*, 167–174. http://dx.doi.org/10.1143/JPSJ.33.167
34. E. A. Meyers, W. N. Lipscomb, *Acta Crystallogr.* **1955**, *8*, 583–587. http://dx.doi.org/10.1107/S0365110X55001801
35. A. Pevec, *Acta Chim. Slov.* **2015**, *62*, 297–303. http://dx.doi.org/10.17344/acsi.2014.1069
36. I. Abdi, K. Al-Sadhan, A. Ben Ali, *Acta Crystallogr.* **2014**, *E70*, 471–473. http://dx.doi.org/10.1107/S1600536814024155
37. I. M. Shlyapnikov, H. P. A. Mercier, E. A. Goreshnik, G. J. Schrobilgen, Z. Mazej, *Inorg. Chem.* **2013**, *52*, 8315–8326. http://dx.doi.org/10.1021/ic302468j
38. S. Boufas, H. Merazig, A. G. Moliterni, A. Altomare, *Acta Crystallogr.* **2007**, *C63*, m315–m317. http://dx.doi.org/10.1107/S0108270107023815
39. P. Woidy, F. Kraus, *Z. Naturforsch.* **2015**, *70b*, 161–164. http://dx.doi.org/10.1515/znb-2014-0249
40. S. A. Baer, M. Lozinšek, F. Kraus, *Z. Anorg. Allg. Chem.* **2013**, *639*, 2586–2588. http://dx.doi.org/10.1002/zaac.201300342
41. A. Mirčeva, L. Golič, *Acta Crystallogr.* **1995**, *C51*, 798–800. http://dx.doi.org/10.1107/S0108270194013351
42. (a) M. C. Etter, *Acc. Chem. Res.* **1990**, *23*, 120–126. http://dx.doi.org/10.1021/ar00172a005
    (b) M. C. Etter, J. C. MacDonald, J. Bernstein, *Acta Crystallogr.* **1990**, *B46*, 256–262. http://dx.doi.org/10.1107/S0108768189012929
43. B. Frlec, H. H. Hyman, *Inorg. Chem.* **1967**, *6*, 2233–2239. http://dx.doi.org/10.1021/ic50058a023
44. I. Bajc, S. Milićev, B. Volavšek, *Monatsh. Chem.* **1992**, *123*, 321–324. http://dx.doi.org/10.1007/BF00810943
45. J. A. S. Howell, K. C. Moss, *J. Chem. Soc. A* **1971**, 270–272. http://dx.doi.org/10.1039/j19710000270

Povzetek

Spojina hidroksilamonijev tetrafluoridooksidovanadat(V) je bila pripravljena z reakcijo med $(NH_3OH)Cl$ in VOF_3 v brezvodnem HF in okarakterizirana v trdnem stanju z rentgensko difrakcijo na monokristalu in Ramansko spektroskopijo. Brezbarvni kristali $(NH_3OH)[VOF_4]$ kristalizirajo v monoklinski prostorski skupini $P2_1/n$ z dimenzijami osnovne celice a = 7.2349(2) A, b = 5.0351(2) A, c = 12.8322(4) A, β = 94.843(3)°, V = 465.79(3) A^3 in Z = 4 pri 150 K. Kristalno strukturo sestavljajo polimerni verižni anioni, $[VOF_4]_n^{n-}$, ki se z vodikovimi vezmi povezujejo s hidroksilamonijevimi kationi, $(NH_3OH)^+$.