

Silver(I) Tetrafluoridooxidovanadate(V) – Ag[VOF₄]

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Dedicated to the memory of Prof. Dr. Marija Kosec.

Abstract

Silver(I) tetrafluoridooxidovanadate(V) which contains the polymeric chain anion, [VOF₄]_nⁿ⁻, has been prepared in reaction between AgNO₃ and VOF₃ in anhydrous HF solvent and characterised in the solid state by single-crystal X-ray diffraction and Raman spectroscopy. Pale yellow crystals of Ag[VOF₄] crystallise in a monoclinic *P*2₁/*c* space group with *a* = 5.5452(4) Å, *b* = 5.0071(3) Å, *c* = 13.6511(11) Å, β = 100.543(3)°, and *V* = 372.63(5) Å³ at 200 K with *Z* = 4. The most intense feature in the Raman spectrum is the V=O stretching band of the anion at 1008 cm⁻¹. Solid-state conformational isomerism exists between [VOF₄]_nⁿ⁻ anions in crystal structures of Ag[VOF₄] and previously reported and structurally characterised K[VOF₄] and Cs[VOF₄] salts.

Keywords: Vanadium oxyfluoride; Fluoridooxidovanadates; Vanadium; Silver; Crystal structure; Anhydrous hydrogen fluoride

1. Introduction

Vanadium(IV) fluoridooxido anions of the type [V_xO_xF_y]_nⁿ⁻, where *x* < *y*, which are built from {VOF₃}-octahedra, display a rich structural variety. Examples of monomeric (octahedral^{1–3} – [VOF₅]_nⁿ⁻, trigonal bipyramidal⁴ – [VOF₄]_nⁿ⁻, square pyramidal⁴ – [VOF₄]_nⁿ⁻), oligomeric (edge-sharing dimer^{1,5–9} – [V₂O₂F₇]_nⁿ⁻, face-sharing dimer^{5,10,11} – [V₂O₂F₈]_nⁿ⁻; tetramers (two structural isomers)¹ – [V₄O₄F₁₄]_nⁿ⁻) and polymeric (1-D: zigzag *cis*-chain^{6,12–15} – [VOF₄]_nⁿ⁻; zigzag *trans*-chain¹⁶ – [VOF₄]_nⁿ⁻; zigzag ribbon¹⁷ – [VOF₃]_nⁿ⁻; ladder^{18–20} – [VOF₃]_nⁿ⁻; alternating ladder¹⁹ – [VOF₃]_nⁿ⁻; 2-D: layers (two structural isomers)^{19,21} – [V₂O₂F₅]_nⁿ⁻) species have been reported.

In the case of vanadium(V) far fewer compounds of this type have been synthesised and structurally characterised and these mainly consist of monomeric (octahedral^{22–27} – [VOF₅]_nⁿ⁻), several oligomeric (corner-sharing dimer^{28,29} – [V₂O₂F₉]_nⁿ⁻, edge-sharing dimer^{26,30} – [V₂O₂F₈]_nⁿ⁻; corner-sharing cyclic trimer²⁸ – [V₃O₃F₁₂]_nⁿ⁻) and one higher-dimensional type, 1-D anion (zigzag *cis*-chain^{31,32} – [VOF₄]_nⁿ⁻).

From this comparison it is evident that fluoridooxidovanadium(V) species are underrepresented and specifically, there is a relative paucity of known polymeric anions.

Silver(I)-vanadium(V) oxyfluorides, especially silver- and oxygen-rich phases such as Ag₄V₂O₆F₂³³ and

Ag₃VO₂F₄³⁴ have been investigated as possible promising new cathode materials for lithium batteries. Therefore, it is important to explore the phases that occur over a range of Ag^I/V^V/O/F compositions.

In the present and on-going studies from this laboratory, anions formed by the reactions of vanadium trifluoride oxide, VOF₃, with various metal fluorides in anhydrous hydrogen fluoride (aHF) are being investigated. The present work reports the synthesis and characterisation by single-crystal X-ray diffraction and Raman spectroscopy of the fluorine-rich phase, silver(I) tetrafluoridooxidovanadate(V) – Ag[VOF₄].

2. Experimental

2.1. General Experimental Procedures

The solvent, aHF, was transferred on a vacuum line constructed of PTFE (polytetrafluoroethylene), FEP (perfluorinated ethylene propylene) and nickel as described previously.³⁵ All non-volatile 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). The compound was synthesised and crystals were grown in a T-shaped FEP crystallisation vessel equipped with a PTFE valve which consisted of a larger diameter “reaction” arm constructed from 16-mm i.d.

(19-mm o.d.) FEP tubing, to which a 6-mm i.d. (8-mm o.d.) FEP tube was attached at right angles and which was used as narrower “crystallisation” arm.²⁶ The wider FEP arm also contained a PTFE-coated magnetic stirring bar. All crystallisation vessels were passivated with F₂ prior to use.

2. 2. Reagents

Silver nitrate, AgNO₃, (Kemika, 99.7%) and vanadium oxytrifluoride, VOF₃, (Aldrich, 99%) were used without further purification. The solvent, aHF, was prepared by treating commercial anhydrous HF (Linde, Fluorwasserstoff 3.5) with K₂NiF₆ (Ozark-Mahoning, 99%) for at least 12 h prior to use. **Caution:** aHF must be handled with great care in a well-ventilated fume hood and protective gear must be worn at all times.

2. 3. Synthesis/Crystallisation of Ag[VOF₄]

The reagents, AgNO₃ (100 mg, 0.59 mmol) and VOF₃ (75 mg, 0.61 mmol), were weighed into the larger diameter arm of the FEP-crystallisation vessel. The solvent aHF (2.0 mL) was condensed at liquid nitrogen temperature into the same arm. After the reaction mixture had been warmed to room temperature, a light yellow precipitate immediately formed. The resulting suspension was agitated for 1.5 h on a laboratory shaker in order to ensure saturation of the solution. The clear, colourless solution was decanted from the larger diameter reaction arm of the T-shaped crystallisation vessel into the narrower crystallisation arm. The former was cooled to ~10 °C while the latter was left at room temperature (25–26 °C). Because of the temperature gradient, aHF evaporated from the crystallisation arm into the reaction arm. Light-yellow crystals already appeared after 1 h and were isolated the next day, after only a small amount of mother liquor remained in narrow arm. The remaining solution was carefully decanted back into the reaction arm and frozen with liquid nitrogen. Meanwhile, the narrow FEP arm containing the crystals was heat-sealed off and transferred to a glovebox where the crystals were immersed in perfluorinated oil (ABCR, AB102850, perfluorodecalin, 98%, *cis* and *trans*). A suitable crystal was selected under a microscope outside the glovebox and quickly transferred into the cold nitrogen stream of the X-ray diffractometer.

2. 4. X-ray Structure Determination

X-ray diffraction data were collected using the *CrystalClear*³⁶ software package on a Rigaku AFC7 diffractometer equipped with a Mercury CCD area detector using graphite-monochromatised Mo K α radiation at 200 K. The data were corrected for Lorentz and polarisation effects. A multi-scan absorption correction was applied to the data set. The structure was solved by direct methods using the *SIR-92* program³⁷ implemented in the program

package *teXsan*³⁸ and refined with *SHELXL-97*³⁹ software (program packages *teXsan* and *WinGX*).⁴⁰ The figures were prepared using *DIAMOND* software.⁴¹ 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-427626 for Ag[VOF₄] (http://www.fiz-karlsruhe.de/request_for_deposited_data.html).

Table 1. Crystal data and structure refinement summary

Compound	Ag[VOF ₄]
<i>F</i> _w	250.81
<i>T</i> (K)	200
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	5.5452(4)
<i>b</i> (Å)	5.0071(3)
<i>c</i> (Å)	13.6511(11)
β (°)	100.543(3)
<i>V</i> (Å ³)	372.63(5)
<i>Z</i>	4
ρ_{calc} (g/cm ³)	4.469
λ (Å)	0.71069
μ (mm ⁻¹)	7.725
Reflns. # / Reflns. # [<i>I</i> > 2 σ (<i>I</i>)]	2140/790
Data/parameters	815/65
<i>R</i> _{int}	0.03
GOI indicator	1.171
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0251
<i>wR</i> ₂ (all) ^b	0.0645
Min., max. $\Delta\rho$ (eÅ ⁻³)	–1.313, 0.869

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

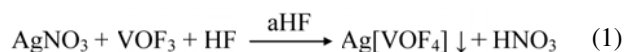
2. 5. Raman Spectroscopy

The Raman spectrum of a powdered crystalline sample flame-sealed in a quartz capillary was obtained at room temperature on Horiba Jobin-Yvon LabRAM HR spectrometer using 632.8-nm He-Ne laser excitation at 25 mW.

3. Results and Discussion

3. 1. Synthesis

The title compound, silver(I) tetrafluoridoxydovanadate(V), Ag[VOF₄], can be conveniently synthesised as a pale yellow, air-sensitive solid, by reaction of AgNO₃ and VOF₃ in aHF (eq. 1). Nitrates undergo solvolysis in aHF solvent generating fluoride anions (eq. 2),^{42,43} which are, in this case, necessary for the formation of tetrafluoridoxydovanadate(V) species from the Lewis acid VOF₃.



3. 2. Crystal Structure

Single crystals suitable for X-ray diffraction were grown from a saturated HF solution. All atoms of the asymmetric unit of the $\text{Ag}[\text{VOF}_4]$ crystal structure – Ag1, V1, O1, and F1–F4, reside on general positions (Wyckoff 4e) of the monoclinic space group, $P2_1/c$.

The polymeric zigzag chain anion $[\text{VOF}_4]_n^{n-}$ is built from *cis*-corner sharing $[\text{VOF}_3\text{F}_{2/2}]$ octahedra, connected by asymmetric fluorine bridges (Figure 1). The basic oc-

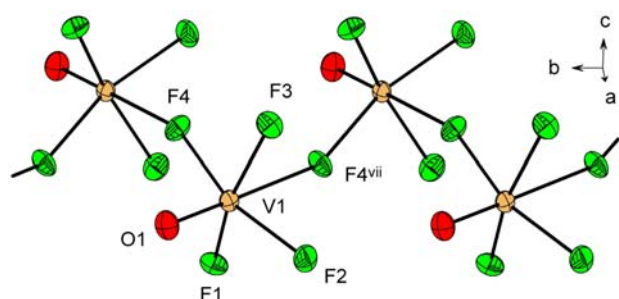


Figure 1. The zigzag $(\text{VOF}_4)_n^{n-}$ chain anion consisting of *cis*-corner sharing $[\text{VOF}_3\text{F}_{2/2}]$ octahedra (thermal ellipsoids are shown at the 50% probability level).

tahedral $[\text{VOF}_5]$ unit is characterised by a short $\text{V}=\text{O}$ bond (1.571(3) Å) and a long bridging *trans*- $\text{V}-\text{F}$ bond (2.287(2) Å) where the bridge fluorine is donated by the neighbouring $\{\text{VOF}_4\}^-$ unit. The equatorial bridging $\text{V}-\text{F}$ distance (1.857(2) Å) is slightly elongated in comparison with terminal $\text{V}-\text{F}$ bond lengths (1.798(2)–1.822(2) Å). The repulsion of the axial oxido ligand exerted on the equatorial fluoro ligands or the “roof effect” is demonstrated by the more open *cis*- $\text{O}-\text{V}-\text{F}$ angles (99.3(1)–101.4(1)°) (Table 2). The aforementioned $[\text{VOF}_5]$ octahedral unit displays intrinsic primary C_4 [001] out-of-centre distortion,⁴⁴ typical for d^0 early transition metal fluoridomonooxido anions.⁴⁵ This distortion leads to the formation of polar $^\infty[\text{VOF}_4]^-$ chains that are oriented antiparallel to each other along the *b*-crystallographic axis, resulting in a centrosymmetric material (Figure 2).

The other two examples of structurally characterised $[\text{VOF}_4]^-$ anions display comparable bond lengths ($\text{K}[\text{VOF}_4]$:³² $\text{V}=\text{O}$ 1.572(8) Å, $\text{V}-\text{F}_t$ 1.786(7)–1.804(7) Å, $\text{V}-\text{F}_b$ 1.875(7) and 2.333(7) Å; $\text{Cs}[\text{VOF}_4]$:³¹ $\text{V}=\text{O}$ 1.529(12) Å, $\text{V}-\text{F}_t$ 1.783(10) Å and 1.788(6) Å, $\text{V}-\text{F}_b$ 1.793(10) and 2.312(10) Å).

The irregular coordination environment of silver cation is comprised of nine atoms which belong to six $\{\text{VOF}_4\}^-$ units of three $[\text{VOF}_4]_n^{n-}$ chain anions (Figure 3). Eight $\text{Ag}-\text{F}$ distances range from 2.397(2) to 3.094(2) Å, while the length of $\text{Ag}-\text{O}$ contact is 2.640(3) Å (Table 2). Similar, albeit somewhat narrower range of silver-fluorine distances (2.472(8)–2.947(10) Å) has also been reported in the case of $\text{AgSb}_2\text{F}_{11}$ compound.⁴⁸

Table 2. Selected interatomic distances and angles and bond valence sums.

Distances (Å) ^a							
V1–O1	1.571(3)	V1–F3	1.822(2)	Ag1–F1 ⁱⁱ	2.508(2)	Ag1–F3	2.397(2)
V1–F1	1.798(2)	V1–F4	1.857(2)	Ag1–F1 ^v	2.938(2)	Ag1–F3 ⁱⁱⁱ	2.656(2)
V1–F2	1.818(2)	V1–F4 ^{vii}	2.287(2)	Ag1–F2	3.094(2)	Ag1–F4 ⁱⁱⁱ	2.536(2)
				Ag1–F2 ⁱ	2.402(2)	Ag1–O1 ^{iv}	2.640(3)
				Ag1–F2 ^v	2.894(2)		
Angles (°) ^a							
O1–V1–F1	101.39(12)	O1–V1–F3	99.33(12)	O1–V1–F4 ^{vii}			179.20(11)
O1–V1–F2	100.32(13)	O1–V1–F4	99.32(12)	V1–F4–V1 ^{ix}			151.26(11)
Bond Valence Sums (valence units – vu) ^b							
Atom	O1	F1	F2	F3	F4	Σcations	
Ag1	0.116	0.148 0.046	0.197 0.052 0.030	0.199 0.099	0.137	1.02	
V1	1.872	0.788	0.747	0.739	0.672 0.210	5.03	
Σanions	1.99	0.98	1.03	1.04	1.02		

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

^b Bond valence sum calculations were done using the following parameters: $b = 0.37$ Å; $R_0 = 1.80$ Å (Ag–F), 1.842 Å (Ag–O), 1.71 Å (V–F), 1.803 Å (V–O).^{46,47}

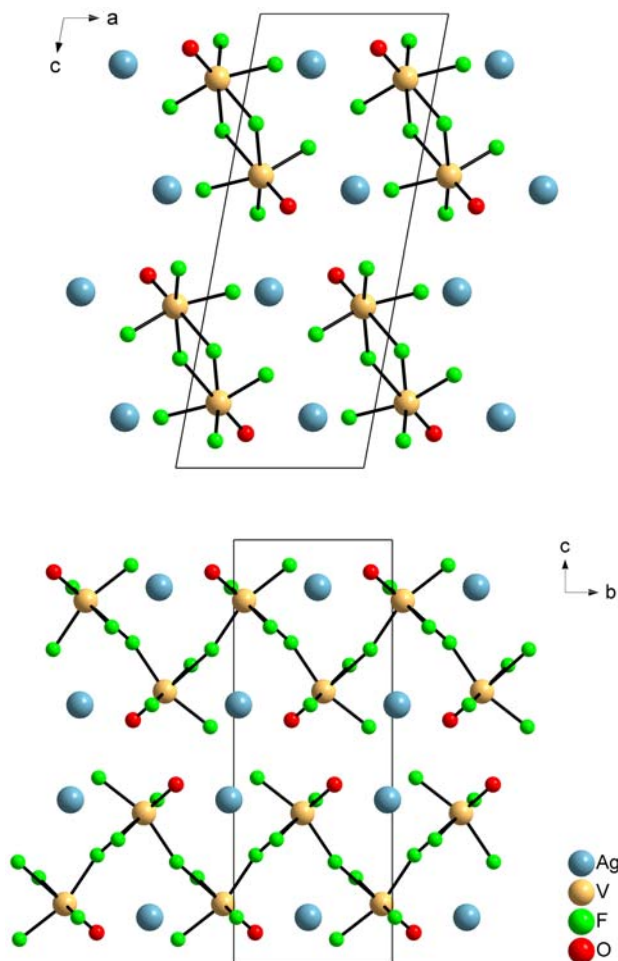


Figure 2. Packing in the unit cell of Ag[VOF₄] viewed along *b*- and *a*-crystallographic axis, respectively.

Bond valence sum calculations resulted in expected values for both cations (Ag⁺: 1.02 vu; V⁵⁺: 5.03 vu) and anions (O²⁻: 1.99 vu; F⁻: 0.98–1.04 vu) and therefore, additionally confirm the correctness of the obtained structure (Table 2).

Although all three known isoformulaic monovalent metal tetrafluoridooxidovanadium(V) salts are structurally similar (K[VOF₄]³²: *P*2₁/*c*, *a* = 5.603(3) Å, *b* = 13.536(8) Å, *c* = 5.444(2) Å, β = 95.87(5)°; Cs[VOF₄]³¹: *Pnma*, *a* = 5.484(1) Å, *b* = 6.342(2) Å, *c* = 14.034(3) Å),

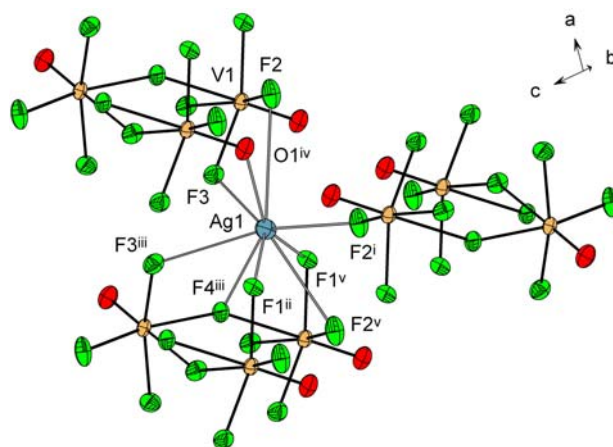


Figure 3. Silver coordination environment in the structure of Ag[VOF₄] compound (50% probability ellipsoids).

geometries of the ¹_∞([VOF₄]⁻) anions are different in all three examples. The view along the anion's running axis reveals a solid state conformational isomerism (Figure 4) that is also apparent from different angles around the asymmetric fluorine bridges and different distances between neighbouring vanadium atoms (Table 3). Curiously, the V...V distance or the repeat distance of the anion chain corresponds to the length of one of the unit cell axes (Table 3). The depicted shape of the anion in the crystal structure of Ag[VOF₄] resembles a dimeric edge-sharing [V₂O₂F₈]²⁻ dianion.^{26,30} Although the ...V–F–V–F–V... chains of the [VOF₄]⁻ anions have a zigzag and bent zigzag geometry in the case of the Cs⁺ and K⁺ salts, respectively, the chain in Ag⁺ compound is best described as a helix (Figure 3).



Figure 4. Solid-state conformational isomerism of [VOF₄]⁻ anions in the crystal structures of Cs[VOF₄] (viewed along the *a*-axis),³¹ K[VOF₄] (viewed along the *c*-axis),³² and Ag[VOF₄] (viewed along the *b*-axis), respectively. Coordinates for the crystal structures of alkali salts have been obtained from the literature.⁴⁹

Table 3. Selected geometric parameters for [VOF₄]⁻ anions ^a

	Cs[VOF ₄] ³¹	K[VOF ₄] ³²	Ag[VOF ₄]
V...V (F _b)...V / Å	4.096(3)	3.884(7)	4.0159(8)
V...V / Å	5.484(1) = <i>a</i>	5.444(2) = <i>c</i>	5.0071(3) = <i>b</i>
V–F _b –V / °	172.5(6)	134.4(5)	151.26(11)
F _b –V–F _b / °	83.1(1)	80.0(5)	80.63(4)

^a Distances between neighbouring vanadium atoms (fluorine bridged and non-bridged), and angles around bridges (fluorine- and vanadium-centred). The non-bridging V...V distance corresponds to the length of one of the unit cell axes.

3. 3. Raman Spectroscopy

Each vanadium oxyfluoride species gives a characteristic Raman spectrum, so vibrational spectroscopy can be used as a fast and reliable method for phase identification in the solid product. The most useful Raman bands are the two strongest bands which, in the case of fluorido-oxidovanadates, are the V=O and V–F stretches. The observed Raman frequencies for Ag[VOF₄] (V=O 1008 cm⁻¹; V–F 621, 595, 570 cm⁻¹) closely correspond to those reported for K[VOF₄] (V=O 1019 cm⁻¹; V–F 643, 618, 577 cm⁻¹)³² and Cs[VOF₄] (V=O 1031 cm⁻¹; V–F 620, 585 cm⁻¹).⁵⁰ Among the three compounds, caesium tetrafluorido-oxidovanadate(V) displays the highest V=O stretch frequency which is in accordance with its observed shortest V=O bond (*vide supra*). Additionally, the observation of only one V=O stretch indicates that there is no vibrational coupling between the {VOF₄}⁻ units of the polymeric anion.

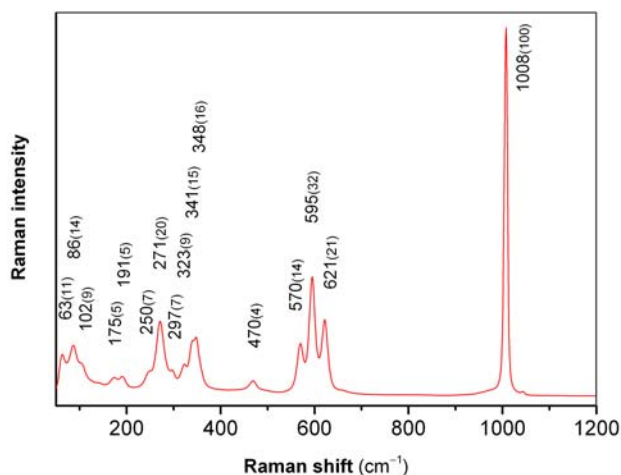


Figure 5. The Raman spectrum of Ag[VOF₄] with denoted values of Raman band frequencies and relative intensities given in parentheses.

4. Conclusions

The formation of the fluorine-rich phase Ag[VOF₄] in the Ag^I/V^V/O/F system from AgNO₃ and VOF₃ in aHF solvent, demonstrates that our previously published synthetic route to metal fluorido-oxidovanadates(V)²⁶ can be extended to include not only metal fluorides as starting materials but also other metal salts that solvolyse in aHF to produce metal cations and fluoride anions. However, metal salts that produce redox-active agents (e.g., bromides), or large quantities of water (e.g., oxides) upon reaction with aHF should be avoided, as these may result in reduction of vanadium(V) species,²⁰ or compounds with the H₃O⁺ cation such as mixed oxonium-metal salts,^{51,52} respectively.

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Povzetek

Srebrov(I) tetrafluoridooksidovanadat(V), ki vsebuje polimerni verižni anion, [VOF₄]_n[−], smo pripravili z reakcijo med AgNO₃ in VOF₃ v brezvodnem HF topilu. Spojino smo v trdnem stanju karakterizirali z rentgensko difrakcijo na monokristalu in Ramansko spektroskopijo. Bledo rumeni kristali Ag[VOF₄] kristalizirajo v monoklinski P2₁/c prostorski skupini z *a* = 5,5452(4) Å, *b* = 5,0071(3) Å, *c* = 13,6511(11) Å, β = 100,543(3)°, in *V* = 372,63(5) Å³ pri 200 K z *Z* = 4. V Ramanskem spektru je najbolj intenziven vrh pri 1008 cm^{−1}, ki pripada vzdolžnemu valenčnemu nihanju V=O vezi aniona. Med [VOF₄][−] anioni, opaženimi v kristalnih strukturah Ag[VOF₄] ter predhodno objavljenima strukturno karakteriziranima solema K[VOF₄] in Cs[VOF₄], je prisotna konformacijska izomerija v trdnem stanju.