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# A New Vanadium (V) Coordination Based on $[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}]_n^{2n-}$ Polymeric Chains and Diethylammonium Cations, Synthesis, Crystal Structure, Vibrational and Optical Properties

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**Abstract** An original vanadium (V) oxyfluoride, containing a polymeric  $[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}]_n^{2n-}$  chains and diethylammonium cations, has been synthesized by slow evaporation from aqueous solutions and characterized by single-crystal X-ray diffraction and vibrational spectroscopies (IR and Raman).  $(\text{Hdea})_2[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}] \cdot \text{H}_2\text{O}$  (dea: diethylamine) crystallizes in the monoclinic system, space group C2/c. The structure can be described as a succession of equivalent layers perpendicular to **b**. The anionic  $[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}]_n^{2n-}$  polymeric chain is composed of trigonal bipyramidal  $\text{VO}_4\text{F}$  polyhedra and fumaric acid ( $\text{H}_2\text{C}_4\text{O}_4$ ) groups sharing O2 corners. The cohesion of the structure is provided by a network hydrogen-bonding. The IR and Raman spectra exhibit characteristic bands of all groups present in the structure. Additionally UV–Vis diffuse reflectance spectrum was recorded in order to investigate the band gap nature. The measurements show that this compound exhibit semiconducting behavior with an optical band gap of 3.51 eV.

**Keywords** Polymeric · X-ray diffraction · IR and Raman spectroscopies · Diethylamine · Fumaric acid

**Electronic supplementary material** The online version of this article (doi:[10.1007/s10876-014-0811-4](https://doi.org/10.1007/s10876-014-0811-4)) contains supplementary material, which is available to authorized users.

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## Introduction

The interest in coordination chemistry of vanadium has increased in the last decades because of its catalytic and medicinal importance [1–4]. A wide range of structural variations associated with their diverse reactivity are also making them the center of continuous research activities [5–7]. Oxide-fluoride transition metal compounds have been interesting for magnetism [8–12], nonlinear properties such as piezoelectricity [12]. Detailed studies of the vanadium fluorides and oxyfluorides by Lightfoot, Zubieta and others demonstrate a complex structural chemistry, including oligomeric, chain and ladder building blocks [9–29]. Vanadium complexes with organic ligands are often less toxic and can have improved aqueous solubility and lipophilicity [30]. The most important oxidation states of vanadium are +3, +4 and +5 and the V(V) compounds are the most commonly observed in the form of compounds of the vanadate ion,  $\text{VO}_4^{3-}$  [31–37]. Additionally these ions vanadium exhibits tetrahedral, square pyramidal, trigonal-bipyramidal and octahedral coordination [38–40].

Fumaric acid containing a single double C=C bond is a good candidate linker molecule that can generate various framework topologies by coordinating either as monodentate and/or as a multidentate ligand. In that respect, the coordination chemistry of fumaric dicarboxylic acid,  $^-\text{OOC}-\text{CH}=\text{CH}-\text{COO}^-$ , has been widely investigated. Many examples of several metal derivatives of this dicarboxylic acid possessing interesting structures with or without other organic ligands have been reported [41–45]. Their use as bridging ligands has generated metal–organic coordination polymers with diverse and interesting structural features [46–52]. Coordination polymers are particularly interesting because they exhibit various applications in catalysis, electrical conductivity, magnetism, luminescence, non-linear optics, molecular electronics, medicine, sensing and zeolitic behavior (For interesting reviews concerning the chemistry, applications of coordination polymers, see Ref. [53] [54–62]). Our research interest covers the structural, vibrational, thermal and other physico-chemical properties of clusters and coordination polymers (See for example Ref. [63]). [64–69]. We present herein the synthesis, characterization, crystal structure of a new oxyfluoride  $(\text{Hdea})_2[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}]\cdot\text{H}_2\text{O}$ .

## Experimental

### Materials and Physical Measurements

The chemicals and solvents used in this work were of analytical grade, available commercially, and were used without further purification.

The infrared spectrum was recorded at room temperature on a Perkin Elmer Spectrum™ 100 FT-IR spectrometer in the  $4,000\text{--}500\text{ cm}^{-1}$  region. A Raman spectrum was measured with a LABRAMHR 800 triple monochromator in the region  $1,600\text{--}200\text{ cm}^{-1}$ . The Optical absorption spectra were measured at room temperature using a T90 + -UV-Vis spectrometer within the range of  $300\text{--}700\text{ nm}$ .  $\text{BaSO}_4$  was used as a reference material.

**Table 1** Crystal data, structure solutions and refinements for  $(\text{Hdea})_2[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}] \cdot \text{H}_2\text{O}$

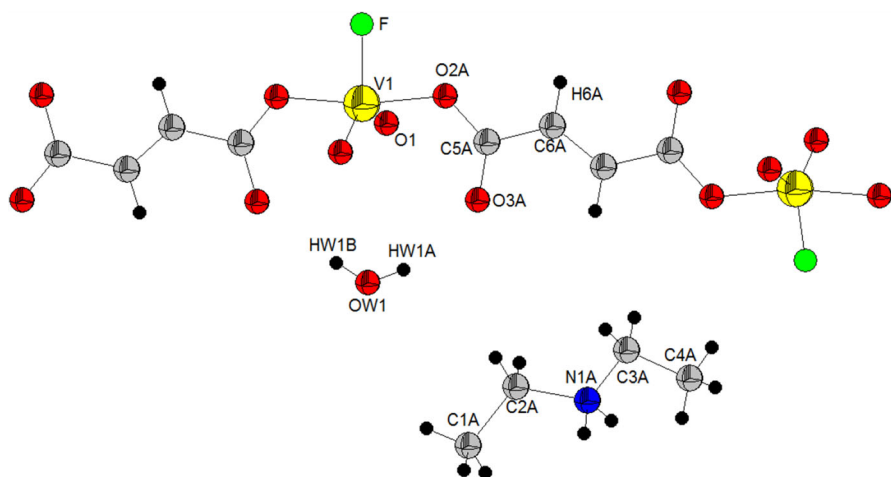
Compound	$(\text{H}_{12}\text{C}_4\text{N})_2[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}] \cdot \text{H}_2\text{O}$
Empirical formula	$\text{C}_{12}\text{H}_{28} \text{N}_2\text{FO}_7\text{V}$
Formula weight	380.29 g mol <sup>-1</sup>
Temperature	293 (2) K
Wavelength	$\lambda = 0.71073 \text{ \AA}$
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	$a = 11.563 (1) \text{ \AA}$ $b = 14.978 (1) \text{ \AA}$ $c = 11.415 (2) \text{ \AA}$ $\beta = 106.140 (6)^\circ$
Volume	1899.0 (4) Å <sup>3</sup>
Z	4
calculated density	1.330 g cm <sup>-3</sup> 0.56 mm <sup>-1</sup>
F(000)	800
$\theta$ range for data collection	2.3°–25.0°
Limiting indices	$-13 \leq h \leq 13$ $-13 \leq k \leq 17$ $-13 \leq l \leq 8$
No. of coll. ref	6790
No. of indep. Ref.	1665 [ $R_{\text{int}} = 0.034$ ]
No. of Ref with $ I  > 2\sigma(I)$	1244
Goodness-of-fit	1.02
Final R indices $ I  > 2\sigma(I)$	$R_1 = 0.052$ ; $wR = 0.157$
Parameters	207
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$	0.42/−0.41 e Å <sup>-3</sup>
Measurement	Bruker APEX II Kappa CCD
CCDC ID	1013244

### Synthesis of $(\text{Hdea})_2[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}] \cdot \text{H}_2\text{O}$

The title compound was synthesized through the reaction of 2.3 g of diethylamine, 0.4 g of vanadium (V) oxide and 0.6 g of fumaric acid in 20 ml of water. The reaction mixture is stirred until homogenized. The pH of this mixture was adjusted to 8 using a hydrofluoric acid. Green crystals were separated after a few months by slow evaporation at room temperature.

### X-ray Crystallography

A suitable single crystal of the title compound was chosen for the structure determination and refinement. It was selected under a polarizing microscope and



**Fig. 1** Atom numbering scheme for the  $(\text{Hdea})_2[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}]\cdot\text{H}_2\text{O}$  compound (For clarity, one position of disordered atoms are shown)

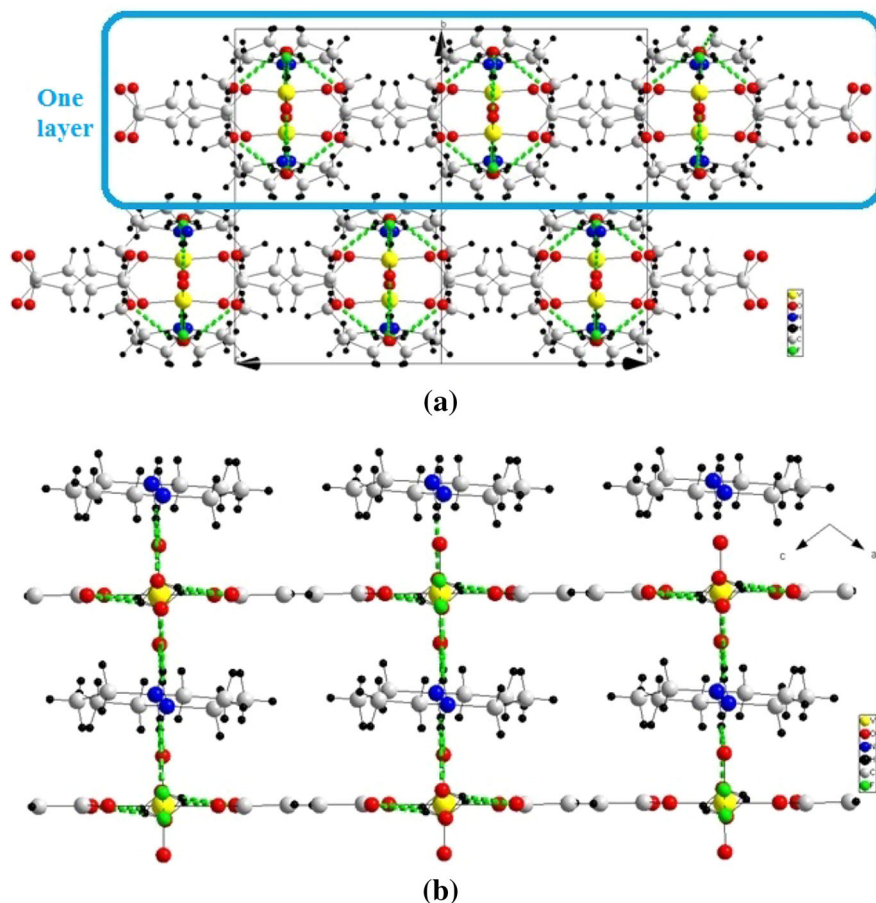
was mounted on a glass fibre. The data collected at room temperature using a Bruker APEX II Kappa CCD diffractometer with graphite-monochromated MoK $\alpha$  radiation [70]. The structure was determined by direct methods, completed by Fourier difference syntheses with SIR97 [71], and refined against  $F^2$  using SHELX-2013 [72] included in the WingX software package [73]. No higher symmetry or unit cells were found by examination with PLATON [74]. The diethylammonium cations and the fumaric acid have occupancy disorders, all its O, N, C, H atoms occupied two adjacent positions. This disordered model has been refined by using supplementary instruction (PART, SIMU, DELU, ISOR and FVAR). Each of fluor and Ow atoms occupied two equivalents positions per a symmetry operation (twofold rotation axis at  $z = 1/4$ ) with an occupancy of 0.5. Non-hydrogen atoms were refined anisotropically. All C-bound and N-bound H atoms of the organic cations and the fumaric acid were placed at calculated positions and refined with isotropic displacement parameters, riding on their parent atoms [ $\text{C}-\text{H} = 0.93, 0.96$  and  $0.97 \text{ \AA}$ , and  $\text{N}-\text{H} = 0.97$ ]. The O-bound H atoms were located in difference maps and refined. Crystal data and details on data collection and refinement are summarized in Table 1. The atomic coordinates and the displacement parameters are reported in Tables S1 and S2. DIAMOND-2 [75] package was used for molecular graphics.

## Result and Discussion

### Structural Study

The asymmetric unit of  $(\text{Hdea})_2[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}]\cdot\text{H}_2\text{O}$  contains one-half  $[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}]^{2-}$  anion, one diethylammonium  $(\text{C}_4\text{H}_{12}\text{N})^+$  cation and one water molecule



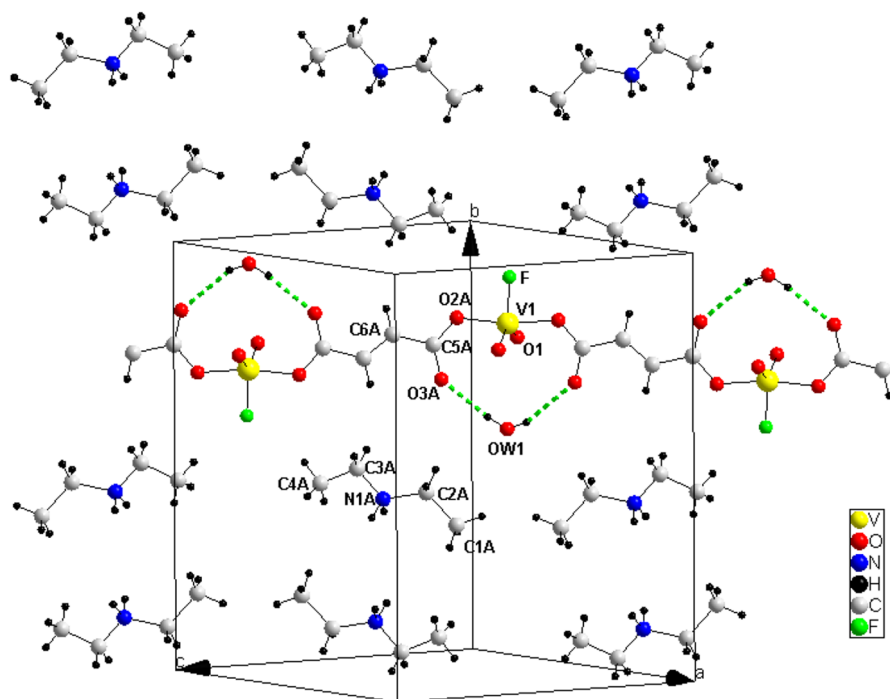


**Fig. 2** **a** Crystal packing of  $(\text{Hdea})_2[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}]\cdot\text{H}_2\text{O}$  compound along  $[101]$  direction **b** Projection along the **b**-axis of a layer in the  $(\text{Hdea})_2[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}]\cdot\text{H}_2\text{O}$  compound. The drawing shows the intermolecular hydrogen bonds contacts which are represented by *dotted line* (For clarity, one position of disordered atoms are shown)

having 0.5 occupancy (Fig. 1). The structure can be described as a succession of equivalent layers perpendicular to **b** (Fig. 2a), no hydrogen bonding is observed between these layers. Each layer consists of alternating of ribbons parallel to  $[10\bar{1}]$  (Fig. 2b). One of ribbons contains an infinite polymeric  $[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}\cdot\text{H}_2\text{O}]_n^{2n-}$  chain. The other contains organic  $(\text{C}_4\text{H}_{12}\text{N})^+$  cations. The  $[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}\cdot\text{H}_2\text{O}]_n^{2n-}$  ribbons are linked through the diethylammonium groups via N–H–O and O–H–O and N–H–F hydrogen bonds. All hydrogen bonds are weak with a range of D–A bond lengths from 2.83 (2) to 3.24 (2) Å [76] (Table S3, Fig. 2). In addition, the succession of layers shows that one polymeric ribbon and two adjacent ribbons of organic molecules intersect the **b**-axis (Fig. 3).

The anionic  $[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}]_n^{2n-}$  polymeric chain is composed of trigonal-bipyramidal  $\text{VO}_4\text{F}$  polyhedra and fumaric acid ( $\text{H}_2\text{C}_4\text{O}_4$ ) groups sharing O2 corners.





**Fig. 3** Crystal packing of (Hdea)<sub>2</sub>[(H<sub>2</sub>C<sub>4</sub>O<sub>4</sub>)VO<sub>2</sub>F]·H<sub>2</sub>O compound showing succession of layers (For clarity, one position of disordered atoms are shown)

The vanadium atom is five-coordinate in an O<sub>4</sub>F trigonal-bipyramidal coordination, as evidenced by the value of  $\tau$  (0.61).  $\tau$  is defined as  $(\beta - \alpha)/60$  [77], where  $\alpha$  and  $\beta$  are the largest angles subtended at the vanadium atom. For an ideal square-pyramidal geometry  $\tau$  is 0, and for an ideal trigonal-bipyramidal geometry  $\tau$  is 1. The vanadium is in the +5 oxidation, as confirmed by valence sum calculations. This assignment of oxidation state is consistent with the overall charge balance of the compound and confirmed by the bond strength calculations around vanadium atoms using the following equation proposed by Brown for vanadium oxide compound:  $S_i = \exp[(R_0 - R_i)/B]$ , where  $S_i$  is the bond valence of bond 'i',  $R_0$  is a constant dependent upon the bonded elements,  $R_i$  is the bond length of bond 'i', and B equals 0.37.  $R_0(V^V-O) = 1.803$  and  $R_0(V^V-F) = 1.71$  [78, 79]. The vanadium (V) site is surrounded by two terminal oxo-groups with a short V=O distance of 1.767 (2) Å, two oxygen donors from fumaric acid ligands with a long V–O distance between 1.81 (2) Å and 2.15(1) Å and the fluorine atom (1.620 (5) Å). As expected, The V–F<sub>terminal</sub> bond distance, in the trigonal-bipyramidal VO<sub>4</sub>F polyhedron, is shorter than those in related fluorovanadate (Hdea)<sub>4</sub>(V<sub>7</sub>O<sub>19</sub>F)·0.42H<sub>2</sub>O compound [80]. Indeed, the (V<sub>7</sub>O<sub>19</sub>F)<sup>4−</sup> cluster present the fluor (V–F<sub>3br</sub>) in center.

The O–V–O angles vary from 87.1 (4) to 170.2 (8)°. The V–O bonds and O–V–O angles of the [(H<sub>2</sub>C<sub>4</sub>O<sub>4</sub>)VO<sub>2</sub>F]<sub>n</sub><sup>2n−</sup> are in agreement with those reported in literature [14, 81, 82]. Selected bond lengths and bond angles are listed in Table 2.

**Table 2** Selected bond and angle lengths and BVS calculations for  $(\text{Hdea})_2[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}]\cdot\text{H}_2\text{O}$

Bond length (Å)		Bond angles (°)			
Polyhedron V(1)O <sub>4</sub> F					
V1–O1	1.767 (2)	F–V1–O1	98.5 (2)	F–V1–O2A <sup>a</sup>	84.6 (6)
V1–O1 <sup>a</sup>	1.767 (2)	F <sup>a</sup> –V1–O1	128.4 (2)	F <sup>a</sup> –V1–O2A <sup>a</sup>	86.0 (6)
V1–O2A	1.81 (2)	F–V1–O1 <sup>a</sup>	128.4 (2)	O1–V1–O2A <sup>a</sup>	91.7 (6)
V1–O2A <sup>a</sup>	1.81 (2)	F <sup>a</sup> –V1–O1 <sup>a</sup>	98.5 (2)	O1 <sup>a</sup> –V1–O2A <sup>a</sup>	92.2 (6)
V1–F	1.620 (5)	O1–V1–O1 <sup>a</sup>	133.2 (1)	F–V1–O2A	86.0 (6)
	Σs <sub>i</sub> <sup>*</sup> = 5.44	F <sup>a</sup> –V1–O2A	84.6 (6)	O1–V1–O2A	92.2 (6)
		O2A <sup>a</sup> –V1–O2A	170.2 (8)	O1 <sup>a</sup> –V1–O2A	91.7 (6)
C5A–O3A	1.238 (13)	O3A–C5A–O2A	125.8 (14)	O3A–C5A–C6A	115.8 (13)
C5A–O2A	1.275 (14)	C6A <sup>b</sup> –C6A–C5A	127.3 (12)	O2A–C5A–C6A	118.4 (13)
C5A–C6A	1.476 (16)	C5A–O2A–V1	126.3 (12)		
C6A–C6A <sup>b</sup>	1.34 (2)				
N1A–C3A	1.39 (4)	C3A–N1A–C2A	121 (2)		
N1A–C2A	1.58 (3)	C3B–N1B–C2B	113.1 (10)		
N1B–C3B	1.46 (2)	N1A–C3A–C4A	109 (3)		
N1B–C2B	1.54 (2)	C1A–C2A–N1A	119 (3)		
C1A–C2A	1.57 (4)	N1B–C3B–C4B	110.6 (10)		
C1B–C2B	1.51 (1)	C1B–C2B–N1B	111.7 (7)		
C4B–C3B	1.47 (1)				
C4A–C3A	1.45 (3)				

<sup>a</sup>–x, y, –z + 1/2

<sup>b</sup>–x + 1/2, –y + 1/2, –z

\* Valence sums were calculated with the formula  $S_i = \exp[(R_0 - R_i)/B]$  ( $S_i$ , bond valence of bond “i”;  $R_0$ , constant dependent on the bonded element;  $R_i$ , length of bond “i”;  $B = 0.370$ ).  $\Sigma s$ , bond valence sum for vanadium. V, predicted valence for a site.  $R_0(\text{V–O}) = 1.803$  Å,  $R_0(\text{V–F}) = 1.710$  Å

The cationic layers contain non-centrosymmetric diethylammonium  $(\text{C}_4\text{H}_{12}\text{N})^+$  with a range of C–C, C–N and C–O bond lengths from 1.34 (2) to 1.57 (4) Å, from 1.39 (4) to 1.58 (3) Å and from 1.24 (1) to 1.28 (2) Å, respectively. These bond distances are in accordance with those reported in the literature [42, 80].

## Spectroscopic Study

To gain more information on the crystal structure, we have undertaken a spectroscopic study using infrared and Raman spectroscopies. The FTIR spectrum of the title compound  $(\text{Hdea})_2[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}]\cdot\text{H}_2\text{O}$  is shown in Fig. S1. The IR spectrum of  $(\text{Hdea})_2[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}]\cdot\text{H}_2\text{O}$  contains  $\nu_{\text{asy}}(\text{OCO})$  and  $\nu_{\text{sym}}(\text{OCO})$  stretching bands around 1,618 and 1,346  $\text{cm}^{-1}$ , respectively. The relatively large value of  $\Delta_{\text{OCO}}$  ( $\nu_{\text{asy}}(\text{OCO}) - \nu_{\text{sym}}(\text{OCO})$ ) calculated for the complex is 272 in agreement with crystallographically established essentially monodentate of the carboxylato groups. The absence of any strong bands around 1700 indicates that the carboxylate groups of

**Table 3** Assignments of the IR and Raman wave-numbers for (Hdea)<sub>2</sub>[(H<sub>2</sub>C<sub>4</sub>O<sub>4</sub>)VO<sub>2</sub>F]·H<sub>2</sub>O

FT-IR (cm <sup>-1</sup> )	Assignment	Raman (cm <sup>-1</sup> )	Assignment
557	ν (V–F)	250	δ (V=O) terminal
608		360	δ (O–V)
797	ν (V–O)	410	δ (O–V) + ν (V–F)
873		515	ν (O–V)
906	ν (V=O) terminal	556	
951		860	
1044	ν (C–N)	894	
1183	ν (C–O) + ν (C–N)	950	ν (V=O) terminal
1346	ν (C–C) + ν <sub>sym</sub> (OCO)	1045	ν (C–C)
1465	δ (CH)	1158	
1618	ν <sub>asy</sub> (OCO) + δ (NH) + δ (OH)	1257	CH <sub>2</sub> twisting
2837	ν (CH)	1269	
3037		1381	ν <sub>sym</sub> (OCO)
3315	ν (NH) + ν <sub>OH</sub> (H <sub>2</sub> O)	1450	δ (CH)

organic-acid are completely deprotonated. The vibrational frequency of ν(C–O) carboxyl group in this complex is observed at 1,183 cm<sup>-1</sup> [42–44, 83]. The bands located at 906 and 951 cm<sup>-1</sup> correspond to V=O<sub>terminal</sub> stretching mode. The absorption bands near 797 and 873 cm<sup>-1</sup> may be attributed to V–O vibrations, while the stretches of terminal V–F bonds are observed at 557 and 608 cm<sup>-1</sup> [38, 82, 84–86]. The presence of protonated amines and water molecules is shown by the broad band within 3,100–3,500 cm<sup>-1</sup> region and around 1,618 cm<sup>-1</sup>, which may be attributed to (N–H, O–H) stretching and bending, respectively. Additional bands in the region 1,044–1,346 cm<sup>-1</sup> are characteristic for the stretching vibrations of C–N and C–C. The bands in the range 2,837–3,037 cm<sup>-1</sup> and around 1,465 cm<sup>-1</sup> possibly correspond to C–H stretching and bending, respectively [80, 87, 88]. This IR spectrum is in good agreement with the results of X-ray structural analyses.

The structure information was further provided by Raman spectroscopy, as shown in Fig. S2. One medium-frequency Raman peak at 250 cm<sup>-1</sup> are assigned to the bending mode of (V=O)<sub>terminal</sub>. The bands located in the range 360–410 cm<sup>-1</sup> are assigned to the bending vibration of the O–V bonds. In addition, the band situated at 410 cm<sup>-1</sup> can be attributed to the stretches of terminal V–F. The stretches of O–V bonds are located at 515 and 894 cm<sup>-1</sup> while the strong band at 950 cm<sup>-1</sup> is assigned to the terminal oxygen (V=O) stretching mode [80, 89, 90]. Two bands within 1,045–1,158 cm<sup>-1</sup> region are attributed to stretching vibration of the C–C bonds. The Raman spectrum reveals absorptions in the range 1,257–1,269 cm<sup>-1</sup>, which could be attributed to the twisting modes of CH<sub>2</sub>, while the bending vibration of C–H is located at 1,450 cm<sup>-1</sup> [91]. The band situated at 1,381 cm<sup>-1</sup> is assigned to the bridging symmetric vibration ν<sub>sym</sub>(OCO) [92]. The infrared and Raman peaks frequencies are reported in Table 3.

## Optical Properties

The UV–Vis–NIR diffuse reflectance spectrum of  $(\text{Hdea})_2[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}] \cdot \text{H}_2\text{O}$  in the region 300–800 nm is displayed in Fig. S3a. Absorption (K/S) data are calculated from the Kubelkaue-Munk function:  $F = (1 - R)^2/2R = K/S$ ,

where R is the reflectance, K is the absorption, and S is the scattering [84]. In a K/S versus  $\lambda$  (nm) plot, extrapolating the linear part of the rising curve to zero provides the onset of absorption at 3.51 eV for  $(\text{Hdea})_2[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}] \cdot \text{H}_2\text{O}$ . The reflectance spectrum measurement revealed the nature of semiconductor [93–95]. The extended  $[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F} \cdot \text{H}_2\text{O}]_n^{2n-}$  framework of the title compound appears to be responsible for its optical band gap [95]. The band gap is large than those in the vanadium (V) oxide  $\text{V}_2\text{O}_5$  [96, 97]. The UV–Vis absorption spectrum exhibits two absorption bands at 292 and 311 nm corresponding to charge-transfer (CT) transitions of the type  $\pi(\text{O}) \rightarrow d(\text{V})$  (between 250 and approximately 400 nm) (Fig. S3b) [30].

## Conclusion

A new polymeric  $(\text{Hdea})_2[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F}] \cdot \text{H}_2\text{O}$  compound has been synthesized by slow evaporation from aqueous solutions and characterized by IR and Raman spectroscopies. The structure can be described as a succession of equivalent layers perpendicular to **b**. The  $[(\text{H}_2\text{C}_4\text{O}_4)\text{VO}_2\text{F} \cdot \text{H}_2\text{O}]_n^{2n-}$  ribbons are linked through the diethylammonium groups via N–H–O and O–H–O and N–H–F hydrogen bonds. The IR and Raman spectra exhibit characteristic bands of all groups present in the structure. These spectroscopic studies show that the carboxylato group acts as a monodentate ligand and is completely deprotonated; this is in good agreement with the results of X-ray structural analyses. The UV–Vis diffuse reflectance spectrum shows that this compound is a semiconductor material with an optical band gap of 3.51 eV.

## Supplementary data

CCDC 1013244 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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