

A novel organically templated three-dimensional open framework vanadium tellurite: $(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3)_2\text{V}_2\text{Te}_6\text{O}_{18}$

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Abstract

A novel organically templated vanadium tellurite $(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3)_2\text{V}_2\text{Te}_6\text{O}_{18}$ (**1**) has been hydrothermally synthesized and characterized by elemental analyses, IR, thermal stability analysis, magnetic susceptibilities and single crystal X-ray diffraction. Compound **1** crystallizes in the monoclinic system, space group $P2_1/n$, $a = 8.891(2)\text{Å}$, $b = 8.834(2)\text{Å}$, $c = 15.906(4)\text{Å}$, $\beta = 94.789(4)^\circ$, $V = 1181.5(5)\text{Å}^3$, $Z = 2$, $R_1[I > 2\sigma(I)] = 0.0187$, $wR_2[I > 2\sigma(I)] = 0.0482$. Compound **1** exhibits a novel three-dimensional (3D) vanadium tellurite anion framework composed of vanadium, tellurium, and oxygen atoms through covalent bonds, with the $[\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3]^{2+}$ cations residing in the channels.

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1. Introduction

A large variety of inorganic open framework networks have been reported during the last few years, most of which are metal silicates, phosphates, carboxylates [1–4]. Recently, great efforts have been made to prepare open framework structures using other anionic units. Some metal selenites [5–7] with two- or three-dimensional structures have been successfully prepared. Compared with selenium, crystals containing tellurium (IV) with extended structures have been less explored. We are interested in the tellurite-based frameworks because the lone pair of electrons can act as an invisible structure-directing agent, which may give rise to a number of important physical properties such as second harmonic generation (SHG) behavior [8–10]. In addition to the usual $\{\text{TeO}_3\}$ trigonal pyramid-like sulfites and selenites, tellurites also form $\{\text{TeO}_4\}$ folded square and

$\{\text{TeO}_5\}$ square pyramidal geometry [11–14]. It is notable that vanadium can also adopt various coordination behaviors. Thus their coordination chemistry is of interest since they should be a source of new and interesting solid-state phases. This unusual rich chemistry has led us to investigate the synthesis and chemistry of vanadium tellurites. In this paper, we report the hydrothermal synthesis and characterization of a novel organically templated vanadium tellurite $(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3)_2\text{V}_2\text{Te}_6\text{O}_{18}$ (**1**). The first coordination-complex-linked vanadium tellurites, $M(\text{phen})\text{V}_2\text{TeO}_8$ ($M = \text{Cu}, \text{Ni}$) [15], have been reported recently, which exhibit a two-dimensional (2D) networks with double-chain-like ribbons. Compound **1**, however, is a novel example of organically templated vanadium tellurite with 3D structure, belonging to the new family of open framework tellurites. In the past years, some inorganic vanadium tellurite phases have been reported [16–23], but none of them are organically templated. Furthermore, compound **1** is tellurium-rich vanadium tellurite compared with those reported.

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2. Experimental

2.1. Synthesis and characterization

All chemicals were of analytical reagent grade and commercially purchased, and used without further purification. The elemental analyses were performed on a PLASMA-SPEC(I) ICP atomic emission spectrometer. IR spectra were recorded in the range 400–4000 cm^{-1} on an Alpha Centaur FT/IR spectrophotometer using KBr pellets. TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 $^\circ\text{C min}^{-1}$. Magnetic susceptibility data were collected over the temperature range 2–300 K at a magnetic field of 10,000 Oe on a Quantum Design MPMS-5 SQUID magnetometer.

In a typical synthesis procedure for **1**, a mixture of 0.4788 g of TeO_2 , 0.1577 g of NaVO_3 , 0.42 ml of ethylenediamine and 9 ml of H_2O was stirred in air for 1 h. The mixture was then sealed in a 16-ml Teflon-lined stainless steel autoclave, which was heated to 100 $^\circ\text{C}$ for 5 days. After slow cooling to room temperature at 6 $^\circ\text{C h}^{-1}$, the resulting green block crystals **1** were filtered off, washed with distilled water, and dried at ambient temperature. A yield of 87% (based upon tellurium) was observed. $\text{C}_4\text{H}_{20}\text{N}_4\text{O}_{18}\text{Te}_6\text{V}_2$ (1279.7): calcd. C 3.75, H 1.56, N 4.38; found: C 3.70, H 1.60, N 4.30%. FT/IR data (cm^{-1}): 3436(w), 2924(w), 1607(w), 1566(m), 1451(m), 1338(m), 1043(s), 939(vs), 805(s), 769(s), 651(vs), 594(s), 552(vs), 500(s), 457(s).

2.2. Determination of crystal structure

The structure of compound **1** was determined by single-crystal X-ray diffraction. A green single crystal of **1** with dimensions 0.32 \times 0.06 \times 0.04 mm was mounted onto a glass fiber. Data were collected with a Siemens SMART CCD diffractometer using monochromated $\text{Mo-K}\alpha$ ($\lambda = 0.71073$) radiation at 293 K in the range of $2.54^\circ < \theta < 26.17^\circ$. Empirical absorption correction (ω scan) was applied. The structure was solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXTL-97 software. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps. A total of 6225 (2335 unique, $R_{\text{int}} = 0.0211$) reflections were measured. Structure solution and refinement based on 2335 independent reflections with $I > 2\sigma(I)$ and 157 parameters gave $R_1(\omega R_2) = 0.0187(0.0482)$ $\{R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $\omega R_2 = [\sum \omega(F_o^2 - F_c^2)^2 / \sum \omega(F_o^2)^2]^{1/2}\}$. Crystal parameters and details of the data collection and refinement for structure **1** are listed in Table 1. Atomic coordinates and equivalent isotropic displacement parameters of compounds **1** are listed in Table 2. Selected bond lengths of

Table 1
Crystal data and structure refinement for **1**

Empirical formula	$\text{C}_4\text{H}_{20}\text{N}_4\text{O}_{18}\text{Te}_6\text{V}_2$
Formula weight (g mol^{-1})	1279.72
T (K)	293 (2)
λ (\AA)	0.71073
Space group	$P2_1/n$
a (\AA)	8.891 (2)
b (\AA)	8.834 (2)
c (\AA)	15.906 (4)
β ($^\circ$)	94.789 (4)
V (\AA^3)	1181.5 (5)
Z	2
D_{calc} (Mg m^{-3})	3.597
μ (mm^{-1})	8.139
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0187$, $\omega R_2 = 0.0482$
R indices (all data)	$R_1 = 0.0209$, $\omega R_2 = 0.0493$

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad \omega R_2 = \sum [\omega(F_o^2 - F_c^2)] / \sum [\omega(F_o^2)^2]^{1/2}.$$

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**

	x	y	z	$U(\text{eq})$
Te(1)	8022(1)	1457(1)	7471(1)	13(1)
Te(2)	2948(1)	2635(1)	7549(1)	12(1)
Te(3)	4271(1)	-405(1)	9034(1)	14(1)
V	4930(1)	-411(1)	6841(1)	11(1)
O(1)	8253(3)	1777(4)	6348(2)	23(1)
O(2)	8097(3)	3579(3)	7898(2)	19(1)
O(3)	3922(3)	-1021(4)	10,138(2)	19(1)
O(4)	891(3)	2592(3)	7772(2)	15(1)
O(5)	2478(3)	3200(4)	6359(2)	18(1)
O(6)	3149(3)	1469(3)	8945(2)	19(1)
O(7)	4709(3)	-272(4)	5823(2)	23(1)
O(8)	3065(3)	460(3)	7237(2)	13(1)
O(9)	5876(3)	1462(3)	7367(2)	19(1)
N(1)	3051(4)	-4251(5)	10,160(2)	23(1)
N(2)	1205(4)	1838(5)	10,180(2)	23(1)
C(1)	4260(5)	-5036(6)	9716(3)	21(1)
C(2)	469(5)	319(5)	10,385(3)	24(1)

$U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

compound **1** are listed in Table 3 (CCDC reference number 244987).

3. Results and discussion

The single-crystal X-ray diffraction analysis reveals that compound **1** exhibits a novel 3D framework constructed from VO_5 square pyramids, TeO_3 trigonal pyramids and TeO_4 folded squares through corner- and/or edge-shared oxygen atoms. The asymmetric unit of compound **1** (Fig. 1) shows that there are one vanadium (V) environment and three different tellurium (IV) environments in this structure. The V site shows a

Table 3
Selected bond lengths (Å) and angles (°) for **1**

Te(1)–O(1)	1.836(3)	Te(1)–O(9)	1.901(3)
Te(1)–O(2)	1.904(3)	Te(2)–O(4)	1.891(3)
Te(2)–O(8)	1.896(3)	Te(2)–O(5)	1.962(3)
Te(2)–O(6)	2.418(3)	Te(3)–O(6)	1.860(3)
Te(3)–O(3)	1.880(3)	Te(3)–O(5)#1	2.004(3)
Te(3)–O(3)#2	2.322(3)	V–O(7)	1.620(3)
V–O(9)	1.938(3)	V–O(4)#1	1.947(3)
V–O(2)#3	1.961(3)	V–O(8)	1.963(3)
O(1)–Te(1)–O(9)	96.20(14)	O(1)–Te(1)–O(2)	101.98(14)
O(9)–Te(1)–O(2)	91.94(12)	O(4)–Te(2)–O(8)	96.06(11)
O(4)–Te(2)–O(5)	93.10(12)	O(8)–Te(2)–O(5)	89.48(12)
O(4)–Te(2)–O(6)	79.57(11)	O(8)–Te(2)–O(6)	81.40(11)
O(5)–Te(2)–O(6)	167.56(11)	O(6)–Te(3)–O(3)	100.02(13)
O(6)–Te(3)–O(5)#1	94.13(13)	O(3)–Te(3)–O(5)#1	86.94(12)
O(6)–Te(3)–O(3)#2	87.11(12)	O(3)–Te(3)–O(3)#2	76.82(13)
O(5)#1–Te(3)–O(3)#2	163.67(11)	O(7)–V–O(9)	112.68(15)
O(7)–V–O(4)#1	111.14(15)	O(9)–V–O(4)#1	136.15(14)
O(7)–V–O(2)#3	105.92(15)	O(9)–V–O(2)#3	84.86(12)
O(4)#1–V–O(2)#3	85.09(12)	O(7)–V–O(8)	104.96(14)
O(9)–V–O(8)	84.73(12)	O(4)#1–V–O(8)	82.49(12)
O(2)#3–V–O(8)	149.08(13)	Te(1)–O(2)–V#4	118.89(15)
Te(3)–O(3)–Te(3)#2	103.18(13)	Te(2)–O(4)–V#5	115.87(14)
Te(2)–O(5)–Te(3)#5	122.62(14)	Te(3)–O(6)–Te(2)	114.17(14)
Te(2)–O(8)–V	120.55(14)	Te(1)–O(9)–V	115.58(14)

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1/2, y - 1/2, -z + 3/2$; #2 $-x + 1, -y, -z + 2$; #3 $-x + 3/2, y - 1/2, -z + 3/2$; #4 $-x + 3/2, y + 1/2, -z + 3/2$; #5 $-x + 1/2, y + 1/2, -z + 3/2$; #6 $-x + 1, -y - 1, -z + 2$; #7 $-x, -y, -z + 2$.

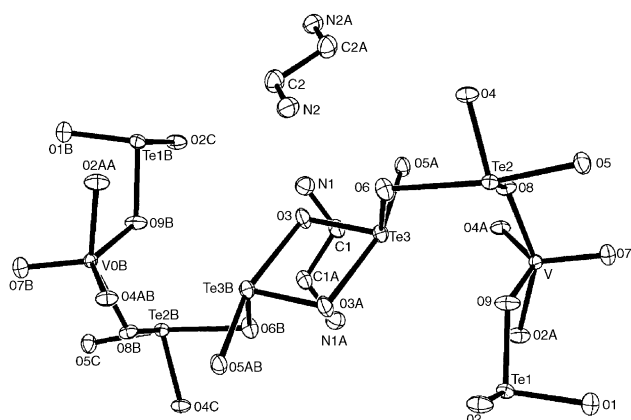


Fig. 1. ORTEP drawing of compound **1** with thermal ellipsoids at 50% probability. The hydrogen atoms are omitted for clarity.

distorted VO_5 square pyramid geometry, with terminal oxygen (O (7)) in the apical position and four bridging oxygen atoms linking to four tellurium atoms. The Te (1) atom adopts severely distorted trigonal pyramid coordination geometry with a terminal oxygen O (1) and two bridging oxygen atoms O (2) and O (9) which connect with two vanadium centers, respectively. Both Te (2) and Te (3) sites are tetraordinated by oxygen atoms and exhibit TeO_4 folded square geometries, only

with some differences between bond lengths and bond angles. The geometry of TeO_4 in compound **1** can be explained by VSEPR theory as an AX_4E trigonal bipyramid [24,25], in which the lone pair electrons occupy one equatorial position. The four oxygen atoms around Te (2) center connect with two vanadium sites and two Te (3) centers through corner-sharing mode. As to the Te (3) O_4 folded square, two of the oxygen atoms bridge two Te (2) sites, and the remaining two are shared with another Te (3) atom via edge-sharing mode, forming a $\text{Te(3)}_2\text{O}_6$ group. The Te_2O_6 group in compound **1** is similar to that in $\alpha\text{-TeO}_2$ [26] and NaVTeO_5 [18], but different from the Te_2O_6 group (formed through corner-shared mode) in compound **11** $\{(\text{UO}_2)_2[\text{Te}_2\text{O}_5(\text{OH})(\text{Te}_2\text{O}_6)]\} \cdot 2\text{H}_2\text{O}$ [27].

The connection of the alternating $\text{Te(3)}_2\text{O}_6$ groups and Te(2)O_4 units through corner-shared oxygen atoms results in a parallelogram-like 20-membered rings comprised of six Te (3) atoms, four Te (2) atoms, and ten oxygen atoms. The 20-membered rings connect with each other using mutual oxygen atoms, forming a 2D layer along the bc -plan, as shown in Fig. 2(a). Two adjacent 2D layers are connected together by zigzag chains along the b -axis, as shown in Fig. 2(b). The zigzag chains are composed of V, Te (1) and oxygen atoms with Te (1) atoms locating at the middle position of the zigzag chains, and V atoms at the apexes of the turning of the zigzag chains. These zigzag chains are arranged paralleled to each other between the 2D layers with the O (4) and O (8) atoms in the zigzag chains linking to Te (2) sites in the 2D layers. This connectivity leads to the formation of a 3D anionic inorganic framework.

Two distinct $[\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3]^{2+}$ cations are observed in the 3D anionic inorganic framework, filling in the channels along the c -axis, as shown in Fig. 3. Channels along the b -axis and $[110]$ direction also can be observed in compound **1**. Fig. 4(a) exhibits the two distinct ethylenediamine molecules more clearly, which are placed in two dissimilar cage-like frameworks constructed from V, Te and O atoms. The upside and underside of the cage-like frameworks are both formed by a 16-membered ring, which are composed of four Te atoms, four V atoms and eight O atoms, as shown in Fig. 4(b). Two 16-membered rings are linked by two Te_2O_6 groups as pillars. It is notable that there are different connectivity behavior and orientation of the Te_2O_6 groups between the two dissimilar cage-like frameworks, as shown in Fig. 4(a). This connecting manner leads to the formation of two distinct $[\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3]^{2+}$ cations, each of which donates eight hydrogen bonds to the inorganic framework ranging from 2.818 to 3.259 Å.

Bond valence calculations [28] indicate that both V and Te atoms are in the +4 oxidation state: the calculated total bond valences for the Te atoms are in the range of 3.855 to 3.992 and that for V atoms is 4.096.

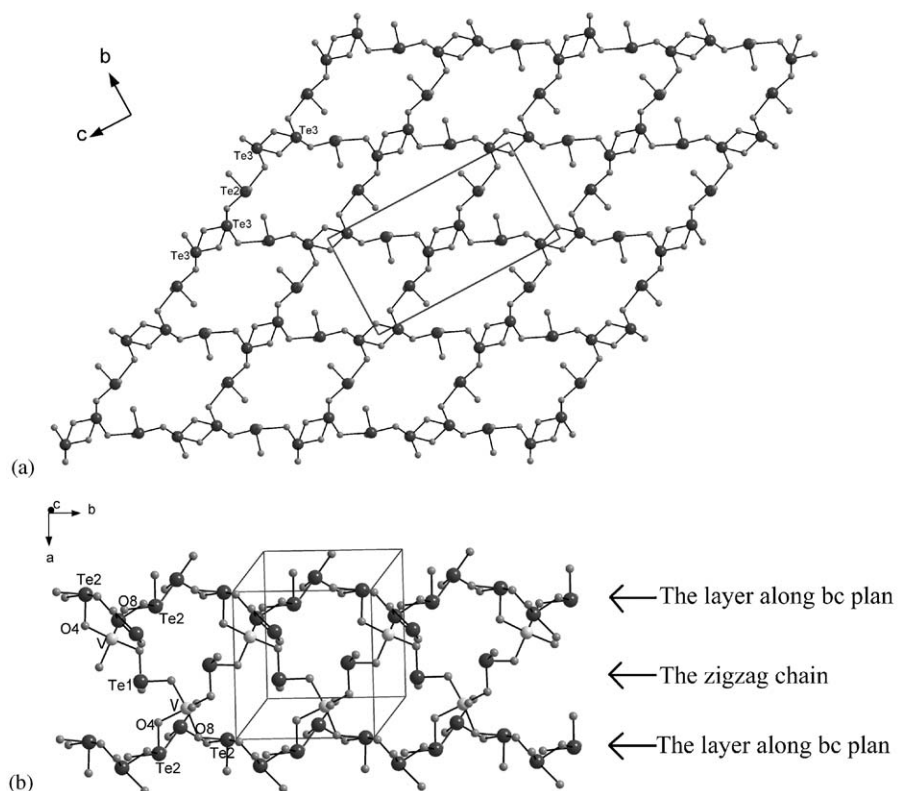


Fig. 2. (a) View of 2D layer structure along the [100] direction. (b) View of the zigzag chains along the *b*-axis.

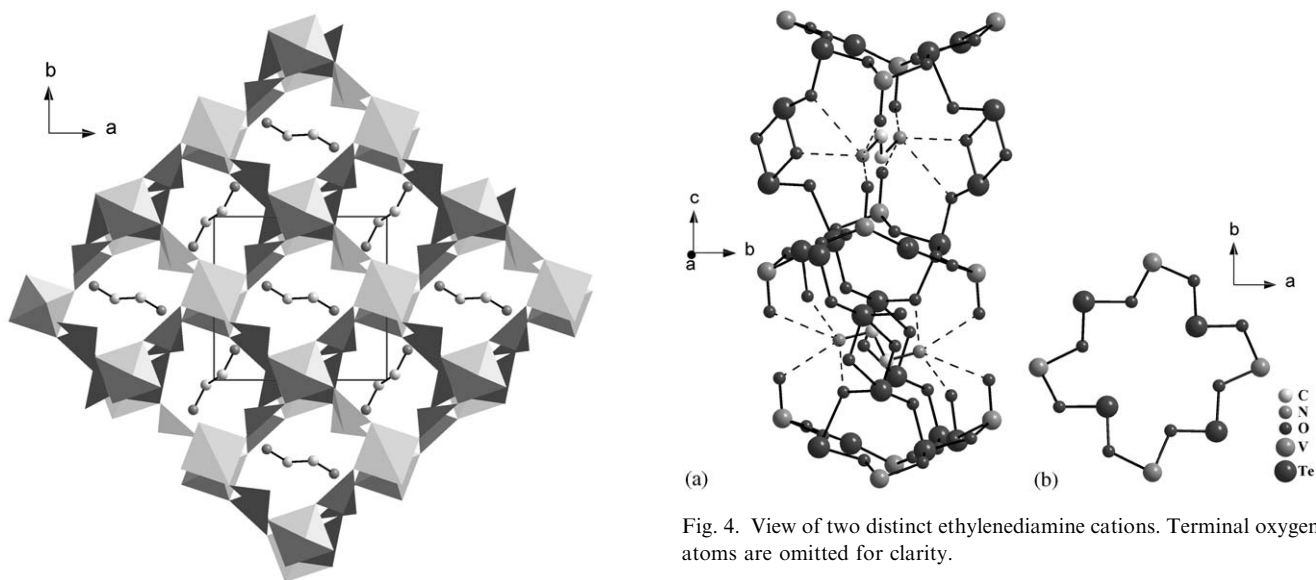


Fig. 3. Compound **1** as view along the *c*-axis. Template hydrogen atoms have been removed for clarity. TeO₄ units: dark grey; VO₅ units: light grey; C atoms: light grey; N atoms: medium grey.

The variable-temperature magnetic susceptibility of compound **1** was measured from 2 to 300 K and displayed in Fig. 5, plotted as thermal variation of χ_M and $1/\chi_M$. The molar magnetic, χ_M , increases as temperature is lowered, which indicates paramagnetic

Fig. 4. View of two distinct ethylenediamine cations. Terminal oxygen atoms are omitted for clarity.

behavior in **1**. The inverse susceptibility plot as a function of temperature is linear, closely following the Curie–Weiss law [$\chi_M = C/(T - \theta)$] with $C = 0.346 \text{ emu K mol}^{-1}$ and $\theta = -3.747 \text{ K}$. At 300 K the magnetic moment (μ_{eff}) per vanadium, determined from the equation $\mu_{\text{eff}} = 2.828 (\chi_M T)^{1/2}$, is $1.65 \mu_B$, which is slightly lower than that expected for an isolated tetravalent system with $\mu_{\text{eff}} = 1.73 \mu_B$. Magnetic susceptibility confirmed the valences of the vanadium

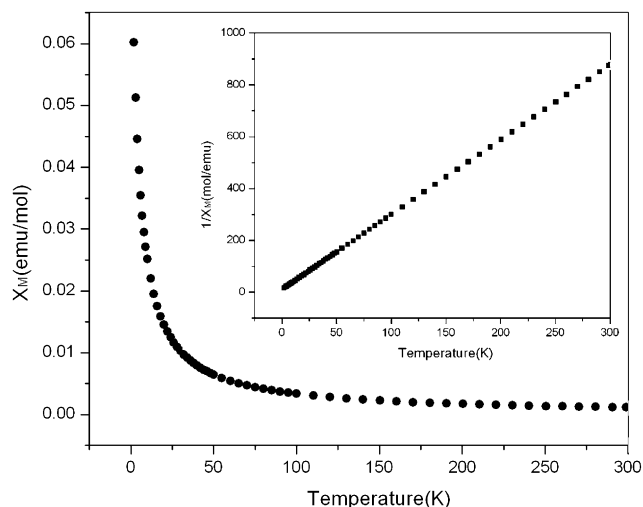


Fig. 5. Thermal variation of χ_M for compound **1**. The inset shows the inverse susceptibility with a linear regression based on the Curie–Weiss law.

atoms to be +4 for compound **1**. It can be concluded that ethylenediamine acts not only as a templating agent, but also as a reducing agent, which is responsible for the reduction of V^{5+} to V^{4+} .

In the infrared spectrum of compound **1**, the strong bands at 939 cm^{-1} is assigned to the stretching vibrations of the terminal $V=O$ bonds, and the bands at 805 and 769 cm^{-1} are due to the stretching vibrations of $V-O-V$ bonds. The peaks round 651 , 594 , 552 and 500 cm^{-1} are probably ascribed to the vibrations of $V-O$, $Te-O$ or $Te-O-V$ bonds. Bands in the $1043\text{--}2924\text{ cm}^{-1}$ regions are attributed to the characteristic peaks of the ethylenediamine groups.

Thermogravimetric measurements of compound **1** show that the diprotonized ethylenediamine molecules released in the region $250\text{--}300^\circ\text{C}$ with a weight loss of 9.45% (calc. 9.38%). In the range of $300\text{--}1000^\circ\text{C}$, another two steps of weight loss of 54.97% and 20.05% are corresponding to the release of tellurium dioxides (sublimation), which is probably due to the different coordination behavior of tellurium atoms. The experimental value for the release of tellurium dioxides is consistent with the sublimation of all tellurium in compound **1** (calc. 74.83%).

4. Conclusion

In conclusion, we have hydrothermally synthesized a novel vanadium tellurite using ethylenediamine as the structure-directing agent. The successful synthesis of

compound **1** demonstrated that it is possible to assemble open framework of vanadium tellurite using organic species as the template under suitable conditions.

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