

Syntheses and crystal structures of the first organically templated metal tellurites

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Abstract

The first organically templated vanadium tellurites, $[\text{H}_2\text{en}][(\text{VO}_2)(\text{TeO}_3)]_2 \cdot \text{H}_2\text{O}$ (**1**, en = ethylenediamine) and $[\text{H}_2\text{pip}][(\text{VO}_2)(\text{TeO}_3)]_2$ (**2**, pip = piperazine) have been synthesized by hydrothermal reactions and structurally characterized. Both compounds feature a $[(\text{VO}_2)(\text{TeO}_3)]^-$ anionic layer containing V_2Te_2 four-member rings and V_4Te_4 eight member rings. The vanadium (V) atom is five coordinated by three tellurite oxygens and two terminal oxygen atoms in a distorted trigonal bipyramidal geometry. The interconnection of the VO_5 polyhedra by bridging tellurite groups leads to a 2D corrugated anionic inorganic layer. The doubly protonated template cations and the lattice water molecules in **1** are located at the interlayer space and are involved in hydrogen bonding. The doubly protonated template cation in **2** is not involved in hydrogen bonding with the anionic inorganic layer.
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1. Introduction

The synthesis of novel open-framework organically templated metal compounds represents a major activity in current solid-state chemistry. They are of scientific interest due to the challenges posed by their syntheses, processing and characterizations. Many of these materials are synthesized in the presence of organic amines as structure-directing agents, which usually occupy the structural voids and are separated from the inorganic skeleton. So far, a remarkable variety of such compounds have been reported [1]. The majority of such work has been dominated by phosphates [1,2], but open-frameworks of metal arsenates [3–5]; germinates [6,7] and carbonates [8] have also been reported. Recently, the studies of compounds with open-framework structures have been extended to the lone pair containing oxo-anions of group 16 elements [9–14]. The stereo-

chemically active lone pair electrons of Se (IV) and Te (IV) have a dramatic effect on their coordination geometries as well as the structures of their metal compounds formed. A number of organically templated transition metal selenites have been reported [9–12]. In the case of vanadium selenites, a series of open-frameworks ranging from 1D, 2D and 3D structures have been reported, including $[\text{H}_2\text{DABCO}]_{0.5}[(\text{V}^{\text{V}}\text{O})(\text{HSeO}_3)(\text{SeO}_3)] \cdot \text{H}_2\text{O}$, $[\text{H}_2\text{en}][(\text{V}^{\text{V}}\text{O})_2(\text{V}^{\text{V}}\text{O})\text{O}_2(\text{SeO}_3)_3] \cdot 1.25\text{H}_2\text{O}$, α - $[\text{H}_2\text{en}][(\text{VO})(\text{SeO}_3)_2]$, β - $[\text{H}_2\text{en}][(\text{VO})(\text{SeO}_3)_2]$ [13].

However, to the best of our knowledge, no organically templated metal tellurites have been structurally characterized and only three vanadium tellurites containing covalently bonded transition metal-organic complex moieties, $M(\text{phen})\text{V}_2\text{TeO}_8$ ($M = \text{Cu}, \text{Ni}$) [15], and $\text{Zn}_2(\text{bipy})_2\text{V}_4\text{TeO}_{14}$ [16], have been reported. Several tellurium (IV) heteropolymolybdates decorated by amino acids have also been prepared [17]. It is noteworthy that both vanadium (V) and tellurium (IV) can adopt a variety of coordination geometry modes [18–20], such as $\{\text{VO}_4\}$ tetrahedron, $\{\text{VO}_6\}$ octahedron,

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{VO₅} square pyramid, {TeO₃} trigonal pyramid and {TeO₄} folded square, which lead to a rich structural chemistry for vanadium tellurites [15]. Furthermore, it is reported that the vanadium tellurite glasses exhibit large third-order nonlinear susceptibility, high infrared transmittance, and semiconducting property, showing special applications in semi-conductive and optical materials [21–26].

Herein we report the hydrothermal syntheses and crystal structures of the first organically templated metal tellurites, namely, [H₂en][(VO₂)(TeO₃)₂·H₂O] (**1**, en = ethylenediamine) and [H₂pip][(VO₂)(TeO₃)₂] (**2**, pip = piperazine), both contain a layered inorganic skeleton.

2. Experimental section

All chemicals were obtained from commercial sources and used without further purification. Elemental analyses were performed on a Vario EL III elemental analyzer. Te, and V analyses were carried out with an ICPQ-100 spectrometer. IR spectra were recorded on a Magna 750 FT-IR spectrometer photometer as KBr pellets in the range of 4000–400 cm⁻¹. Thermogravimetric analyses were carried out with a NETZSCH STA 449C unit, at a heating rate of 10 °C/min under a nitrogen atmosphere. The XRD powder patterns were collected on a Philips X'Pert-MPD diffractometer using graphite-monochromated CuK α radiation in the angular range $2\theta = 5\text{--}70^\circ$ with a step size of 0.02° and a counting time of 3 s per step.

2.1. Synthesis and characterization

Synthesis of [H₂en][(VO₂)(TeO₃)₂·H₂O] **1:** In a typical synthesis, a mixture of V₂O₅ (0.184 g), Na₂TeO₃ (0.114 g), ethylenediamine (0.06 ml), ethanol (5 ml) and H₂O (5 ml) in a molar ratio of 1:0.5:1:86:278 was stirred under ambient conditions until it was homogeneous. The resultant mixture was sealed into an autoclave equipped with a Teflon liner (25 ml) and then heated at 110 °C for 5 days. The initial and final pH values of the solution did not show any appreciable change and were close to 8.0. After cooling over 24 h, light yellow plate crystals and indefinite yellow powder were obtained. The crystalline products were selected by hand, washed with deionized water, and dried at room temperature. Crystals of compound **1** were collected in a yield of 21.2% based on Te. Elemental analysis for compound **1**, C₂H₁₂N₂V₂Te₂O₁₁: V, 16.01; Te, 41.28; C, 3.65; H, 2.15; N, 4.62 (%). Calcd.: V, 16.93; Te, 43.18; C, 3.99; H, 2.01; N, 4.65 (%). IR data (KBr, cm⁻¹): 3435 (m), 2924 (m), 1599 (w), 1518 (w), 908 (vs), 731 (s), 622 (s), 494 (m).

Synthesis of [H₂en][(VO₂)(TeO₃)₂·H₂O] **2:** Compound **2** was synthesized by hydrothermal reactions in

a similar procedure as that for compound **1** except that reactant mixture was V₂O₅ (0.181 g), Na₂TeO₃ (0.111 g), PIP (PIP = piperazine) (0.044 g), ethanol (5 ml) and H₂O (5 ml) in a molar ratio of 1:0.5:0.5:86:278. The initial and final pH values of the reaction mixture are about 7.0 and 7.5, respectively. Crystals of compound **2** were collected in a yield of 12.5% based on Te. Elemental analysis for compound **2**, C₄H₁₂N₂V₂Te₂O₁₀: V, 16.21; Te, 41.53; C, 7.56; H, 2.16; N, 4.51 (%). Calcd.: V, 16.83; Te, 42.17; C, 7.94; H, 2.00; N, 4.63 (%). IR data (KBr, cm⁻¹): 3468 (m), 2928 (w), 1431 (w), 1086 (s), 911 (vs), 721 (m), 630 (s), 582 (m), 459 (s).

2.2. Determination of crystal structures

Single crystals with dimensions of 0.60 × 0.10 × 0.10 mm³ for **1** and 0.10 × 0.06 × 0.04 mm³ for **2** were used for structural analyses. Data collections were performed on a Siemens Smart CCD diffractometer with a graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Intensity data were collected by the narrow frame method at 293 K. Both data sets were corrected for Lorentz and Polarization factors as well as for absorption by SADABS program [27]. The space groups were determined uniquely to be *C2/c* for both compounds **1** and **2**, based on systematic absences as well as *E*-value statistics, which gave satisfactory refinements for both compounds. Both structures were solved by the direct methods and refined by full-matrix least squares fitting on *F*² by SHELXS-97 [27]. All hydrogen atoms, except that for lattice water molecule in **1**, were located at geometrically calculated positions. The hydrogen atom of the lattice water molecule in **1** was calculated from difference Fourier maps. The data collection and refinement parameters are summarized in Table 1, atomic coordinates and equivalent thermal parameters, and selected bond lengths and angles are listed in Tables 2 and 3, respectively.

Crystallographic data (excluding structure factors) for the two structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 266805 and 266806. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336-033; E-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

[H₂en][(VO₂)(TeO₃)₂·H₂O] (**1**, en = ethylenediamine) and [H₂pip][(VO₂)(TeO₃)₂] (**2**, pip = piperazine) represent the first organically templated metal tellurites. Both of them were synthesized under a slightly basic condition. Their structures are similar and feature 2D anionic layers of [(VO₂)(TeO₃)₂]⁻ with the template

Table 1
Crystal data and structure refinements for compounds **1** and **2**

Compound	1	2
Formula	C ₂ H ₁₂ N ₂ V ₂ Te ₂ O ₁₁	C ₄ H ₁₂ N ₂ V ₂ Te ₂ O ₁₀
Fw	597.22	605.24
space group	C2/c	C2/c
a/Å	22.771(9)	21.006(4)
b/Å	5.0812(18)	5.8584(12)
c/Å	11.569(5)	11.427(2)
α/°	90	90
β/°	111.926(7)	112.36(3)
γ/°	90	90
V, Å ³	1241.7(8)	1300.5(5)
Z	4	4
D _{calcd} , g cm ⁻³	3.195	3.091
μ, mm ⁻¹	6.168	5.886
Crystal size	0.60 × 0.10 × 0.10 mm	0.10 × 0.06 × 0.04 mm
F(000)	1104	1120
Reflections Collected	4427	4763
Independent reflections	1402 [R(int) = 0.0226]	1500 [R(int) = 0.0269]
Observed reflections [I > 2σ(I)]	1329	1431
Data/restraints/parameters	1402/0/92	1500/0/91
GOF on F ²	1.054	1.168
R ₁ , wR ₂ (I > 2σ(I)) ^a	0.0169/0.0442	0.0344/0.0761
R ₁ , wR ₂ (all data)	0.0182/0.0449	0.0377/0.0780

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

Table 2
Atomic coordinates (× 10⁴) and displacement parameters (Å² × 10³) for compounds **1** and **2**

Atom	x	y	z	U(eq) ^a
Compound 1				
V(1)	3479(1)	989(1)	2112(1)	6(1)
Te(1)	2217(1)	4875(1)	884(1)	5(1)
O(1)	4183(1)	2341(3)	2574(1)	10(1)
O(2)	3517(1)	-1961(3)	1582(2)	11(1)
O(3)	1461(1)	5047(3)	1199(2)	8(1)
O(4)	2658(1)	2397(3)	2101(1)	8(1)
O(5)	1842(1)	2349(3)	-421(1)	7(1)
O(1W)	5000	-1561(5)	2500	13(1)
N(1)	4258(1)	-4474(4)	325(2)	10(1)
C(1)	4719(1)	-5902(5)	-75(2)	10(1)
Compound 2				
V(1)	1467(1)	4183(2)	2915(1)	8(1)
Te(1)	2742(1)	438(1)	4054(1)	9(1)
N(1)	4387(3)	5279(10)	5291(6)	25(1)
C(1)	4632(3)	2980(9)	5078(5)	13(1)
C(2)	5015(3)	3070(10)	4226(5)	15(1)
O(1)	1458(2)	6671(7)	3556(4)	18(1)
O(2)	693(2)	3073(8)	2358(4)	17(1)
O(3)	2302(2)	2670(7)	2824(3)	12(1)
O(4)	3188(2)	2465(7)	5444(3)	9(1)
O(5)	3558(2)	319(7)	3721(3)	10(1)

^a U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond lengths (Å) and angles (°) for compounds **1** and **2**

Compound 1			
V(1)–O(2)	1.6342(17)	V(1)–O(1)	1.6392(16)
V(1)–O(3)#1	1.966(2)	V(1)–O(4)	1.9971(17)
V(1)–O(5)#2	2.0021(16)	Te(1)–O(4)	1.8769(15)
Te(1)–O(3)	1.890(2)	Te(1)–O(5)	1.9216(15)
Hydrogen bonds:			
O(1) ... O(1W)	2.741(3)	O(1W)... O(1)#3	2.741(3)
O(1W)... N(1)	2.864(3)	N(1)–H(1c)... O(1w)	152.8
O(1w)–H(1wa) ... O(1)#3	165.6		
O(2)–V(1)–O(1)	108.96(8)	O(2)–V(1)–O(3)#1	98.96(7)
O(1)–V(1)–O(3)#1	94.71(8)	O(2)–V(1)–O(4)	120.41(8)
O(1)–V(1)–O(4)	130.63(8)	O(3)#1–V(1)–O(4)	79.08(7)
O(2)–V(1)–O(5)#2	94.08(8)	O(1)–V(1)–O(5)#2	95.60(7)
O(3)#1–V(1)–O(5)#2	159.76(7)	O(4)–V(1)–O(5)#2	80.98(6)
Compound 2			
V(1)–O(1)	1.634(4)	V(1)–O(2)	1.637(4)
V(1)–O(5)#1	1.966(4)	V(1)–O(4)#2	1.985(4)
V(1)–O(3)	2.003(4)	Te(1)–O(3)	1.884(4)
Te(1)–O(5)	1.892(4)	Te(1)–O(4)	1.918(4)
O(1)–V(1)–O(2)	110.5(2)	O(1)–V(1)–O(5)#1	97.09(18)
O(2)–V(1)–O(5)#1	95.84(18)	O(1)–V(1)–O(4)#2	94.15(18)
O(2)–V(1)–O(4)#2	97.24(18)	O(5)#1–V(1)–O(4)#2	158.54(15)
O(1)–V(1)–O(3)	125.22(19)	O(2)–V(1)–O(3)	124.3(2)
O(5)#1–V(1)–O(3)	78.88(15)	O(4)#2–V(1)–O(3)	79.70(15)

Symmetry transformations used to generate equivalent atoms:

For **1**: #1 - x + 1/2, y - 1/2, -z + 1/2; #2 - x + 1/2, -y + 1/2, -z; #3 - x + 1, y, -z + 1/2.

For **2**: #1 - x + 1/2, y + 1/2, -z + 1/2; #2 - x + 1/2, -y + 1/2, -z + 1.

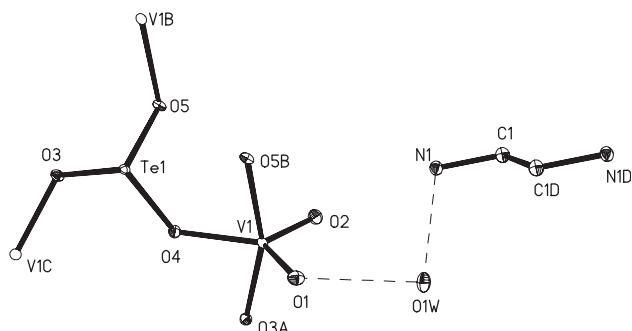


Fig. 1. ORTEP representation of the selected unit in compound **1**. The thermal ellipsoids are drawn at 50% probability. Hydrogen bonds are drawn as dash lines. Symmetry codes for the generated atoms: (a) $-x + 1/2, y - 1/2, -z + 1/2$; (b) $-x + 1/2, -y + 1/2, -z$; (c) $-x + 1/2, y + 1/2, -z + 1/2$; (d) $-x + 1, y, -z + 1/2$.

cations located at the interlayer space. As show in Fig. 1, the asymmetric unit of **1** consists of 10 non-hydrogen atoms, 7 of which belong to the inorganic framework and 3 of them belong to the template cation and the lattice water. The vanadium atom is five-coordinated by two terminal oxygen anions and three oxygen atoms from three tellurite groups. The coordination geometry around the vanadium atom can be described as a distorted trigonal bipyramid, which is different from the tetrahedral ones reported in the organically covalent bonded vanadium tellurium (IV) compounds [15,16]. The V–O (terminal) bonds are significantly shorter than those of V–O (tellurite) (Table 3). The tellurium atom is in a ψ -TeO₃ tetrahedral coordination geometry with the fourth coordination site occupied by the lone pair electrons, such geometry is different from the ψ -TeO₄ trigonal bipyramidal geometry reported in the organically covalent bonded vanadium tellurium (IV) compounds [15,16]. The Te–O bond lengths vary from 1.890(2) to 1.9212(17) Å. Each tellurite group is tridentate and bridges to three vanadium atoms. Bond valence calculations indicate the vanadium and tellurium atom are in the oxidation state of +5 and +4, respectively. The calculated total bond valences for V(1) and Te(1) are 4.95 and 3.74, respectively [28].

The interconnection of VO₅ polyhedra by bridging TeO₃ groups results in the corrugated inorganic anionic layers of [(VO₂)(TeO₃)][−] (Fig. 2), which contain alternating V₂Te₂ and V₄Te₄ polyhedral rings (Fig. 2). The lone pair electrons of the tellurium (IV) atoms are oriented toward the voids of the V₄Te₄ polyhedral rings. The interlayer distance is estimated to be 11.3 Å. The two negative charges of the two such inorganic layers are compensated by the doubly protonated ethylenediamine cation. These templated cations located at interlayer space are being placed on the eight origins and the body center of the unit cell. The lattice water molecule forms hydrogen bonds with one terminal oxygen (O(1)) of the VO₅ polyhedron (O(1)...O(1W) 2.741(3) Å,

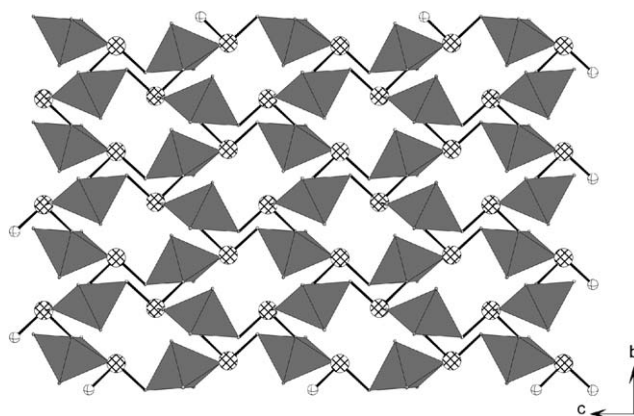


Fig. 2. A $\langle 400 \rangle$ [(VO₂)(TeO₃)][−] anionic layer containing V₂Te₂ and V₄Te₄ polyhedral rings. The VO₅ polyhedra are shaded in gray. Te and O atoms are drawn as hatched and crossed circles, respectively.

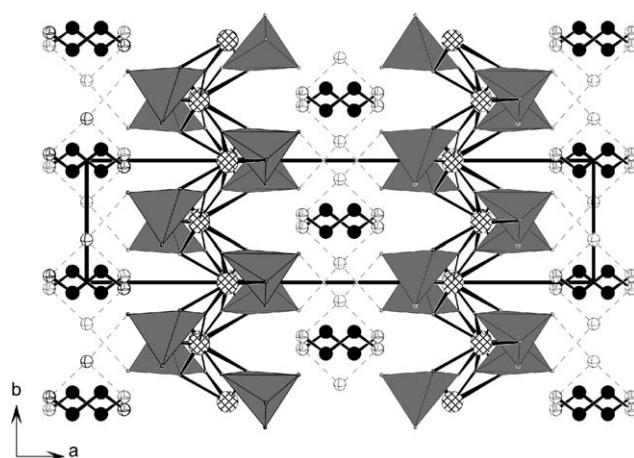


Fig. 3. View of the structure of compound **1** along c -axis. The VO₅ polyhedra are shaded in gray. Te, N, C and O atoms are drawn as hatched, octahed, black and crossed circles, respectively. Hydrogen bonds are drawn as dash lines.

O(1W)...O(1) (symmetry code: $1 - x, y, 1/2 - z$) 2.741(3) Å) and the amine group of the template cation (O(1W)...N(1) 2.864(3) Å). The N(1)–H(1c)...O(1w) and O(1w)–H(1wa)...O(1) (symmetry code: $1 - x, y, 1/2 - z$) hydrogen bond angles are 152.8 and 165.6°, respectively (Table 3). Hence the interconnection of the inorganic layers with the lattice waters and the template cations via above hydrogen bonds results in a 3D network structure (Fig. 3).

When piperazine was used as the template molecule, compound **2** was isolated. As shown in Fig. 4, the asymmetric unit of **1** consists of 10 non-hydrogen atoms, 7 of which belong to the inorganic framework and 3 of them belong to the template cation. The structure of [H₂pip][(VO₂)(TeO₃)]₂ **2** consists of a similar [(VO₂)(TeO₃)][−] layer as that in **1**. The coordination geometries around the vanadium and tellurium atoms are same as that in **1**. Different from that in compound

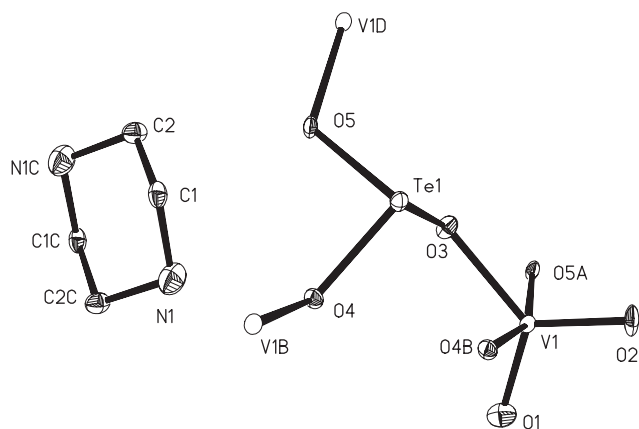


Fig. 4. ORTEP representation of the selected unit in compound **2**. The thermal ellipsoids are drawn at 50% probability. Symmetry codes for the generated atoms: (a) $-x + 1/2, y + 1/2, -z + 1/2$; (b) $-x + 1/2, -y + 1/2, -z + 1$; (c) $-x + 1, -y + 1, -z + 1$; (d) $-x + 1/2, y - 1/2, -z + 1/2$.

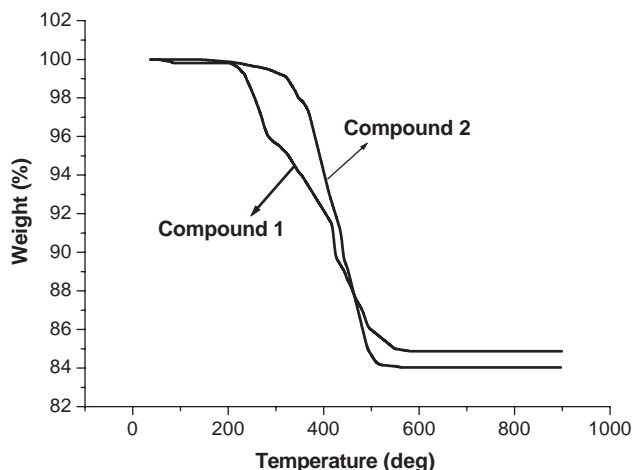


Fig. 5. TGA curves for compounds **1** (black) and **2** (dark gray).

1, the template cation ($\text{NH}_2^+ \text{C}_4\text{H}_8\text{NH}_2^+$) is not involved in hydrogen bonding. Furthermore, its interlayer distance of 10.5 Å is significantly smaller than that of **1**.

The infrared spectra of compounds **1** and **2** have many similar bands. The strong bands at 908 and 911 cm^{-1} are due to the $\nu(\text{V}=\text{O})$ or $\nu(\text{V}-\text{O}-\text{V})$ vibrations. The absorption peaks at 731, 622, 494 cm^{-1} for **1** and 721, 630, 582, 459 cm^{-1} for **2** can be ascribed to the vibrations of V–O, Te–O, and Te–O–V. Bands in the region of 3468–2924 cm^{-1} and 1606–1140 cm^{-1} are due to the bending vibrations of organic template (and the lattice water in the case of compound **1**).

The TGA curves of compounds **1** and **2** are shown in Fig. 5. The TGA curve of **1** exhibits two steps of weight losses. The first weight loss of 3.61% in the range of 220–280 °C corresponds to the release of the lattice water (calculated value, 3.02%). The second step from 290 to 540 °C can be attributed to the loss of the organic

amine. The weight loss of 11.01% is slightly larger than the calculated value of 10.40%. TGA curve of **2** shows only one step of weight loss. It is much more thermally stable than compound **1**. The weight loss occurs in the temperature range of 260–500 °C, corresponding to the loss of the organic amines. The weight loss of 15.41% is slightly larger than the calculated value (14.56%).

For magnetic properties of these two compounds, since vanadium (V) ion and all other structural components are diamagnetic, it is expected that both compounds should be diamagnetic.

4. Conclusions

In summary, the first organically templated vanadium tellurites, $[\text{H}_2\text{en}][(\text{VO}_2)(\text{TeO}_3)_2] \cdot \text{H}_2\text{O}$ (**1**, en = ethylenediamine) and $[\text{H}_2\text{pip}][(\text{VO}_2)(\text{TeO}_3)_2]$ (**2**, pip = piperazine) have been synthesized by hydrothermal reactions and structurally characterized. Both compounds feature a corrugated $[(\text{VO}_2)(\text{TeO}_3)]^-$ anionic layer containing V_2Te_2 four-member rings and V_4Te_4 eight member rings. Our future research efforts will be devoted to the other organically templated metal tellurites that are expected to show a variety of other inorganic skeletons.

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