

New organically templated vanadium tellurites: $(\text{H}_2\text{pn})[\text{V}_2\text{TeO}_8]$ (pn is propane-1,3-diamine)

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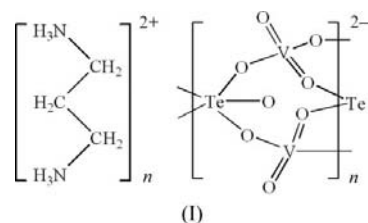
The title compound, poly[propane-1,3-diaminium hexa- μ -oxido-dioxidotellurium(IV)divanadium(V)], $(\text{C}_3\text{H}_{12}\text{N}_2)[\text{V}_2\text{O}_8\text{Te}]$ or $(\text{H}_2\text{pn})[\text{V}_2\text{TeO}_8]$ (pn is propane-1,3-diamine), contains a two-dimensional anionic layer and the diprotonated pn cation for charge compensation. The anionic layer consists of pyrovanadates and $[\text{TeO}_3]$ pyramids, which are linked alternately through corner-sharing to form a one-dimensional chain. These one-dimensional chains are crosslinked through two weak Te—O bonds, constructing an anionic layer. Hydrogen bonds are observed involving the diprotonated pn cation and the O atoms of the anionic framework.

Comment

A large variety of inorganic open-framework compounds have been reported during the past decade, most of which are metal silicates, phosphates and carboxylates (Cheetham *et al.*, 1999; Yu & Xu, 2006; Natarajan & Mandal, 2008). Recently, studies of such materials have been extended to include using oxotellurites as anionic units. The stereochemically active lone-pair electrons of Te^{IV} can act as a structure-directing agent, exerting a significant influence on the Te coordination geometries, as well as on the structures of the compounds formed with other metals, and subsequently on their physical properties (Rao *et al.*, 2006; Kim *et al.*, 2007; Mao *et al.*, 2008). It is noteworthy that vanadium can also adopt various coordination behaviors (Chiang & Chuang, 2005). The variety in the coordination chemistry of tellurium(IV) and vanadium suggests that a great deal of flexibility is possible in any framework architecture formed by them and indicates the potential for a variety of open-framework topologies.

Most inorganic open-framework materials are prepared under mild conditions in the presence of organic amines as structure-directing agents. The protonated organic amines usually occupy the structural voids and contribute to the stability of the framework through hydrogen bonding. This has

promoted the formation of various interesting three-dimensional open-framework, two-dimensional layer and one-dimensional chain structures (Cheetham *et al.*, 1999; Yu & Xu, 2006; Natarajan & Mandal, 2008). So far, four organically templated vanadium tellurites, including one three-dimensional, $(\text{H}_2\text{en})_2[\text{V}_2\text{Te}_6\text{O}_{18}]$, and three two-dimensional, $(\text{H}_2\text{en})-[(\text{VO}_2)(\text{TeO}_3)]_2 \cdot \text{H}_2\text{O}$, $(\text{H}_2\text{pip})[(\text{VO}_2)(\text{TeO}_3)]_2$ and $(\text{H}_2\text{en})-[\text{VTeO}_5]$ (en is ethylenediamine and pip is piperazine), have been reported (Feng & Mao, 2005; Gao *et al.*, 2005; Jung *et al.*, 2006). In our previous work, we have obtained several vanadium selenites and molybdenum tellurites (Lian *et al.*, 2004; Hou *et al.*, 2005, 2006). For the present work, we used propane-1,3-diamine (pn) as a structure-directing agent, and prepared a new organically templated vanadium tellurite, *viz.* $(\text{H}_2\text{pn})[\text{V}_2\text{TeO}_8]$, (I), which contains a layered inorganic skeleton.



The asymmetric unit of (I) contains two crystallographically unique V atoms, one Te atom and eight O atoms, as well as one doubly protonated pn cation (Fig. 1). All atoms reside on general positions. Atoms V1 and V2 both have a slightly distorted tetrahedral environment (Table 1) with V—O bond lengths of 1.602 (2)–1.8085 (18) Å and O—V—O angles in the range 107.03 (11)–113.49 (10)°. The V1- and V2-centered tetrahedra are joined to form a pyrovanadate unit by sharing a vertex at atom O6. Atom Te1 has a pyramidal coordination geometry with one terminal atom (O1) and two bridging atoms (O2 and O3). The lone pair of electrons occupies an apical position. The Te—O_{terminal} bond (Te1—O1) is shorter

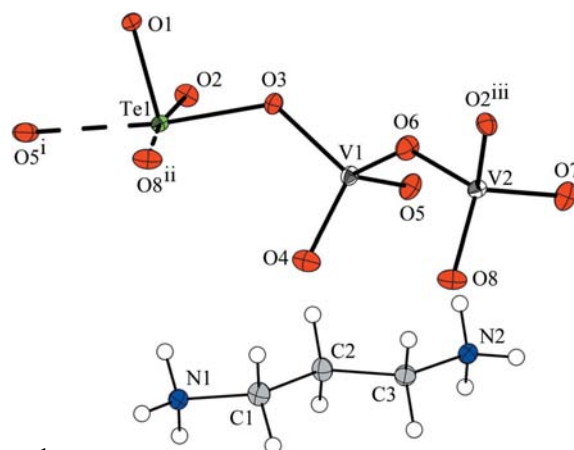


Figure 1

The asymmetric unit and some symmetry-related atoms of (I), shown with 30% probability displacement ellipsoids. The weak Te—O bond is drawn as a dashed line. [Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 2, -y + 1, -z + 1$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.]

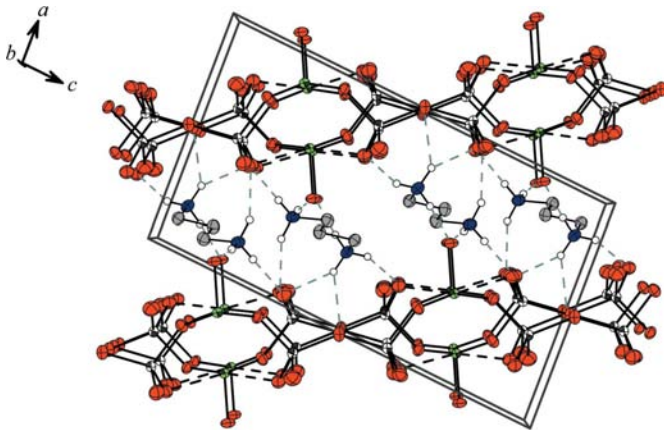


Figure 2
The packing of (I), with hydrogen-bond interactions (gray) and weak Te—O bonds (black) drawn as dashed lines.

than the Te—O_{bridging} bonds (Te1—O2 and Te1—O3; Table 1). Bond-valence-sum calculations give values of 4.10 for Te1, and 5.10 and 5.12 for V1 and V2, respectively (Brown & Shannon, 1973), consistent with the oxidation states of +4 for Te and +5 for V.

The pyrovanadate unit and [TeO₃] pyramid are bridged by atoms O2 and O3 into an alternating sequence, forming a [V₂TeO₈]_n²ⁿ⁻ chain along the [101] direction. As shown in Fig. 2, the [V₂TeO₈]_n²ⁿ⁻ chains are further situated abreast on the (20 $\bar{2}$) plane, and each chain connects with two adjacent chains through two weak Te—O bonds, namely Te1—O5ⁱ [2.421 (2) Å] and Te1—O8ⁱⁱ [2.646 (2) Å; symmetry codes are given in Table 1], forming a two-dimensional [V₂TeO₈]_n²ⁿ⁻ anionic inorganic skeleton. The importance of weak Te—O bonds had also been observed in another two-dimensional vanadium tellurite, (H₂en)[VTeO₅]₂ (Jung *et al.*, 2006), which has a one-dimensional anionic chain similar to that of NaVTeO₅ (Darriet *et al.*, 1972), if one disregards the weak Te—O bonds [2.466 (3) Å].

The interlayer space is occupied by H₂pn cations. In order to balance the negative charge of the anionic framework, the two terminal amine groups of the propane-1,3-diamine molecules are protonated. Both of the protonated NH₃ groups act as hydrogen-bond donors to form six hydrogen bonds in which five O atoms of the anionic layers act as acceptors (Table 2). The two shortest hydrogen bonds, with short O...N contact distances of 2.717 (3) and 2.789 (3) Å, and nearly linear N—H...O angles, involve terminal atom O1 of the [TeO₃] pyramid. These moderately strong hydrogen bonds may play a key role in the formation of the uncommon Te-centered polyhedron in the solid state, and they undoubtedly enhance the stability of the layered architecture.

This study shows that weak Te—O bonds, as well as hydrogen bonds, have an important effect on the formation of the structure of the final product.

Experimental

The reactants NaVO₃·2H₂O (0.314 g, 2 mmol), Na₂TeO₃ (0.442 g, 2 mmol) and propane-1,3-diamine (0.17 ml, 2 mmol) were added to

water (7 ml). The mixture, a gel, was placed in a 25 ml Teflon-lined stainless steel vessel and heated at 363 K for 60 h. After slow cooling to room temperature, pale-brown block-shaped crystals of (I) suitable for X-ray analysis were isolated from the solution by filtration.

Crystal data

(C ₃ H ₁₂ N ₂)[V ₂ O ₈ Te]	$V = 1105.5 (4) \text{ \AA}^3$
$M_r = 433.63$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 8.6312 (17) \text{ \AA}$	$\mu = 4.31 \text{ mm}^{-1}$
$b = 8.4130 (17) \text{ \AA}$	$T = 293 \text{ K}$
$c = 15.301 (3) \text{ \AA}$	$0.12 \times 0.10 \times 0.06 \text{ mm}$
$\beta = 95.71 (3)^\circ$	

Data collection

Rigaku Mercury CCD area-detector diffractometer	10515 measured reflections
Absorption correction: multi-scan (RAPID-AUTO; Rigaku, 1998)	2534 independent reflections
$T_{\min} = 0.626$, $T_{\max} = 0.782$	2292 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.048$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$	145 parameters
$wR(F^2) = 0.052$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.70 \text{ e \AA}^{-3}$
2534 reflections	$\Delta\rho_{\text{min}} = -1.86 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Te1—O1	1.8263 (17)	V1—O3	1.7888 (17)
Te1—O2	1.9343 (18)	V1—O6	1.8031 (19)
Te1—O3	1.9742 (18)	V2—O7	1.6339 (19)
Te1—O5 ⁱ	2.421 (2)	V2—O8	1.645 (2)
Te1—O8 ⁱⁱ	2.646 (2)	V2—O6	1.7954 (19)
V1—O4	1.602 (2)	V2—O2 ⁱⁱⁱ	1.8085 (18)
V1—O5	1.6957 (19)		
O1—Te1—O2	95.69 (8)	O3—Te1—O5 ⁱ	169.43 (7)
O1—Te1—O3	91.40 (8)	O1—Te1—O8 ⁱⁱ	85.15 (7)
O2—Te1—O3	87.92 (8)	O2—Te1—O8 ⁱⁱ	171.16 (7)
O1—Te1—O5 ⁱ	85.91 (7)	O3—Te1—O8 ⁱⁱ	83.26 (7)
O2—Te1—O5 ⁱ	82.19 (7)	O5 ⁱ —Te1—O8 ⁱⁱ	106.65 (7)

Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 2, -y + 1, -z + 1$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1C...O1 ⁱ	0.89	1.90	2.789 (3)	175
N1—H1E...O8 ^{iv}	0.89	1.98	2.803 (3)	153
N1—H1D...O7 ^v	0.89	1.96	2.846 (3)	174
N2—H2C...O5 ^{vi}	0.89	2.02	2.846 (3)	154
N2—H2E...O7 ^{vi}	0.89	2.26	2.944 (3)	134
N2—H2D...O1 ^{viii}	0.89	1.83	2.717 (3)	173
N2—H2E...O6 ^{viii}	0.89	2.40	3.077 (3)	133

Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + 1, -y + 1, -z + 1$; (v) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (vi) $-x + 1, -y, -z + 1$; (vii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (viii) $x - 1, y, z$.

Carbon-bound H atoms were positioned geometrically and were included in the refinement in the riding-model approximation [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $C-H = 0.97 \text{ \AA}$]. H atoms bonded to N atoms were positioned geometrically and were included in the refinements as rotating groups [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$ and $N-H = 0.89 \text{ \AA}$]. The deepest hole of residual electron density lies 0.04 \AA from atom Te1.

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3204). Services for accessing these data are described at the back of the journal.

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