

A new organically templated vanadium tellurite: $(\text{H}_2\text{dien})[(\text{VO}_2)(\text{TeO}_3)]_2 \cdot 2\text{H}_2\text{O}$ (dien is diethylenetriamine)

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Received 16 August 2009

Accepted 2 September 2009

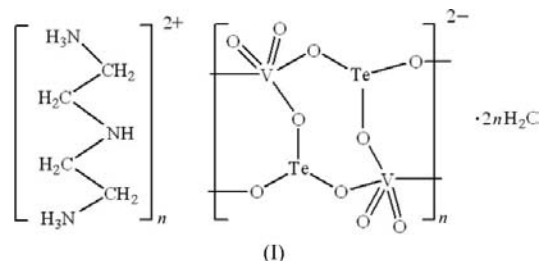
Online 19 September 2009

A new organically templated vanadium tellurite, poly[2,2'-imino-diethanaminium [hexa- μ_2 -oxido-tetraoxidoditellurium(IV)-divanadium(V)] dihydrate], $\{(\text{C}_4\text{H}_{15}\text{N}_3)[\text{Te}_2\text{V}_2\text{O}_{10}] \cdot 2\text{H}_2\text{O}\}_n$, features the interconnection of distorted $[\text{VO}_5]$ trigonal bipyramids by bridging $[\text{TeO}_3]$ pyramids, leading to a two-dimensional corrugated anionic layer with an interlayer distance of about 13.47 Å. The interlayer space is occupied by doubly protonated diethylenetriamine cations (H_2dien) and guest water molecules. The two terminal amino groups of H_2dien are protonated, while the middle amino group, located on a twofold rotation axis, is not protonated. All the three amino groups and water molecules are involved in hydrogen-bonding interactions. The compound represents a new member in the series $(\text{H}_2\text{am})[(\text{VO}_2)(\text{TeO}_3)]_2 \cdot x\text{H}_2\text{O}$, where H_2am represents a doubly protonated diamine. Similarities and differences between the structures of members of the series are discussed.

Comment

A large variety of inorganic open-framework compounds have been reported during the last decade, most of which are metal silicates, phosphates and carboxylates (Cheetham *et al.*, 1999; Yu *et al.*, 2006; Natarajan *et al.*, 2008). Recently, the studies of such materials have extended to using the oxotellurites as anionic units. The stereochemically active lone-pair electrons of Te^{IV} can act as an invisible structure-directing agent, having a dramatic effect on the coordination geometries, as well as on the structures, of the compounds formed with different metals (Rao *et al.*, 2006; Kim *et al.*, 2007; Mao *et al.*, 2008). In addition to the usual $[\text{TeO}_3]$ pyramid, like sulfite or selenites, tellurites can also form $[\text{TeO}_4]$ folded-square and $[\text{TeO}_5]$ square-pyramidal geometries. Vanadium can also adopt various coordination geometries. The oxidation state of vanadium may vary among +3, +4 and +5, and the coordination polyhedron can be

tetrahedral, square pyramidal, trigonal bipyramidal or octahedral (Chiang *et al.*, 2005). The variety in the coordination chemistry of tellurium(IV) and vanadium suggests a great deal of flexibility in any framework architecture and the potential for a variety of open-framework topologies.



Most inorganic open-framework materials are prepared under hydro/solvothermal conditions with the aid of organic amines. The protonated organic amines usually occupy the structural voids as charge compensation and contribute to the stability of the framework structure through hydrogen bonding (Cheetham *et al.*, 1999; Yu *et al.*, 2006; Natarajan *et al.*, 2008). Reports of organically templated vanadium tellurites are still rare. Only four such materials, namely $(\text{H}_2\text{en})[\text{VTeO}_5]$, $(\text{H}_2\text{en})_2[\text{V}_2\text{Te}_6\text{O}_{18}]$, $(\text{H}_2\text{en})[(\text{VO}_2)(\text{TeO}_3)]_2 \cdot \text{H}_2\text{O}$ and $(\text{H}_2\text{pip})[(\text{VO}_2)(\text{TeO}_3)]_2$ (Feng & Mao, 2005) (en is ethylenediamine and pip is piperazine), with two- or three-dimensional open frameworks, have been reported (Feng *et al.*, 2005; Gao *et al.*, 2005; Jung *et al.*, 2006). Recent reports suggest that the use of a diamine or a triamine seems to be more effective than monoamines in the construction of open-architecture zinc phosphates (Choudhury *et al.*, 2000). As an extension of our previous work on metal selenites and tellurites (Lian *et al.*, 2004; Hou *et al.*, 2005, 2006), we are examining the role of multiple amines in the V/Te/O system. In this paper, we describe the synthesis and crystal structure of a new organically templated vanadium tellurite, poly[2,2'-imino-diethanaminium [hexa- μ_2 -oxido-tetraoxido-ditellurium(IV)-divanadium(V)] dihydrate], $(\text{H}_2\text{dien})[(\text{VO}_2)(\text{TeO}_3)]_2 \cdot 2\text{H}_2\text{O}$ (dien is diethylenetriamine), (I), which features two-dimensional anionic layers, with the template cations located in the interlayer space.

The structure of (I) (Fig. 1) is built up from strictly alternating distorted $[\text{VO}_5]$ trigonal bipyramids and $[\text{TeO}_3]$ pyra-

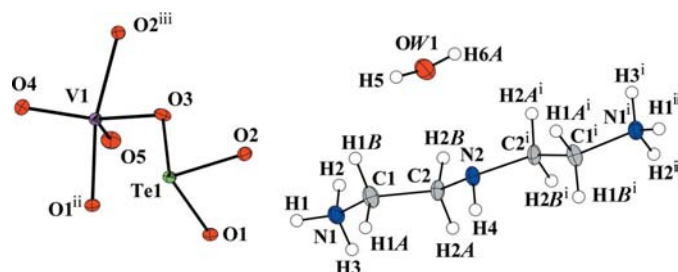


Figure 1

A view of the asymmetric unit and some symmetry-related atoms of compound (I), showing the atom-numbering scheme (30% probability displacement ellipsoids). Only one of the disordered H6 positions is shown. [Symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.]

mids linked through shared vertices, giving rise to a corrugated inorganic anionic layer parallel to the *bc* plane that is like those observed in the previously reported compounds (H₂en)[(VO₂)(TeO₃)₂·H₂O, (II), and (H₂pip)[(VO₂)(TeO₃)₂], (III) (Feng & Mao, 2005). Indeed, the three compounds represent a series with the same space group and similar *b*- and *c*-axis dimensions, with the length of the *a* axis dependent on the size of the templating cation. There are some notable differences between the structures. Although the *M*—O bond lengths and O—*M*—O bond angles of (I) are comparable with those of (II) and (III), the amplitude of the corrugated anionic layer [5.1596 (4) Å, equal to the *b*-axis length] of (I) is less than in (III) [5.858 (2) Å], and is close to that of (II) [5.081 (2) Å]. This dissimilarity might be derived from the different forms of the templating cations, *i.e.* the ring shape of piperazine *versus* the linear shapes of ethylenediamine and diethylenetriamine. Although the layers themselves are essentially the same among the three compounds, they stack differently. In (I), the layers stack with no offset in the *c* direction (Fig. 2), while in (II) and (III) there are sizeable offsets of about 4.25 and 4.00 Å, respectively, between two adjacent layers along the equivalent direction. This offset is reflected in the β angle of (I) [90.06 (4)°] *versus* those of (II) and (III), which are both about 112°. In addition, the interlayer distance of (I) (half the *a*-axis length, or about 13.47 Å) is significantly greater than those of (II) (*circa* 11.38 Å) and (III) (*circa* 10.50 Å) due to the different sizes of the templates and how they are positioned, as well as the different levels of hydration.

The interlayer space is occupied by templated H₂dien cations and the guest water molecules. In order to balance the negative charge of the anionic framework, the two terminal amino groups of the diethylenetriamine molecules are protonated, while the middle amino group is not protonated. The protonated NH₃ group acts as the hydrogen donor to form hydrogen bonds with two O atoms from the anionic layers and

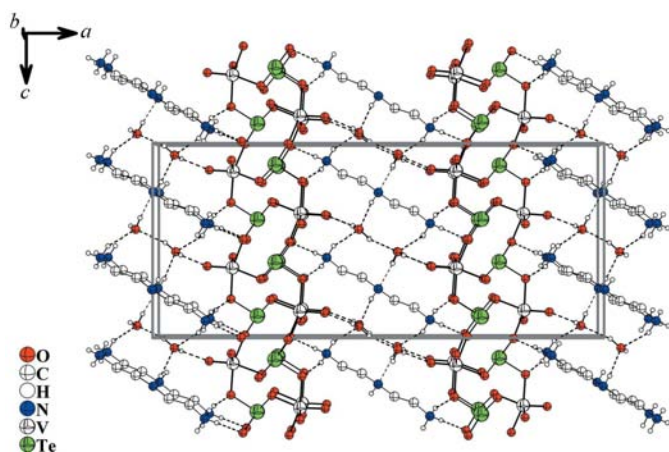


Figure 2
A crystal packing diagram for compound (I). All atoms are shown as isotropic spheres of arbitrary size. H atoms bonded to C atoms have been omitted for clarity. The hydrogen-bonding interactions between the amine groups, water molecules and the anionic layers are shown as dashed lines.

one water molecule. The N2 atom is located on a twofold rotation axis and its attached H4 atom is statistically distributed on the two corners of the N2-centred polyhedron. One of the H atoms on the water molecule is also disordered across two positions. Thus, the hydrogen bonds involving the N2—H4 and OW1—H6 groups can readily be divided into two symmetrically related sets (Figs. 3a and 3b). N2—H4 serves as a hydrogen-bond donor to form a hydrogen bond with OW1ⁱ [symmetry code: (i) 1 - *x*, *y*, ½ - *z*], and N2 simultaneously acts as a hydrogen-bond acceptor with H6B on OW1 (Fig. 3a). The alternate arrangements of N2—H4ⁱ and OW1—H6A lead to the interactions N2—H4ⁱ···OW1, OW1ⁱ—H6Bⁱ···N2 and OW1—H6B···OW1^{vi} (Fig. 3b) [symmetry code: (vi) 1 - *x*, -*y*, 1 - *z*].

This study shows that the [(VO₂)(TeO₃)₂] layer can be produced with a variety of amine templates of different shapes and sizes. The specific details of the stacking of the layers, as well as the degree of hydration of the material, depend on the template used.

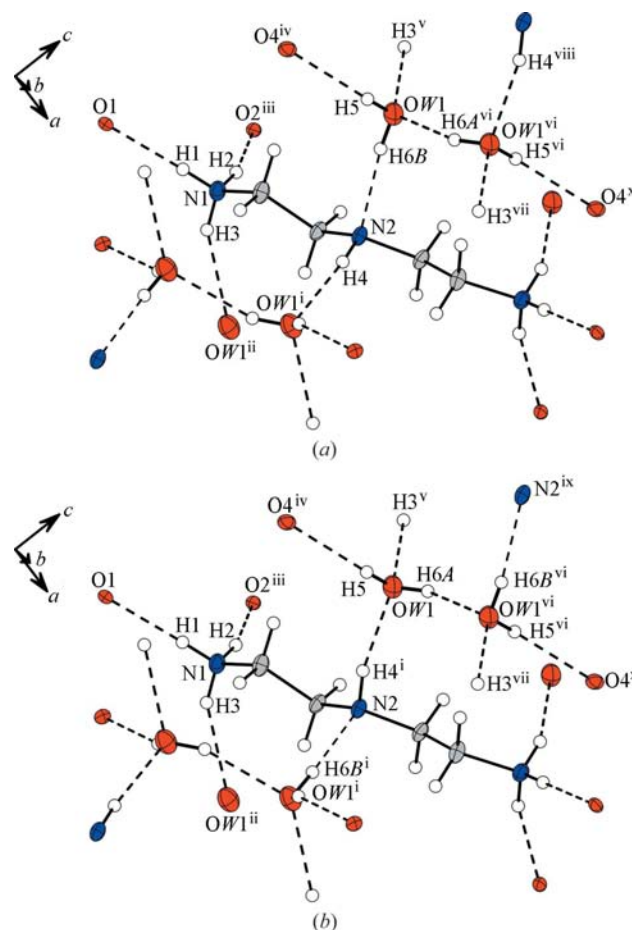


Figure 3
The hydrogen-bonding interactions involving the disordered N2—H4 and OW1—H6 groups are divided into two symmetrically related sets (top and bottom). The diagram also shows the hydrogen-bonding interactions involving the protonated NH₃ groups. [Symmetry codes: (i) 1 - *x*, *y*, ½ - *z*; (ii) *x*, 1 - *y*, -½ + *z*; (iii) *x*, 1 + *y*, *z*; (iv) ½ - *x*, -½ + *y*, ½ - *z*; (v) *x*, 1 - *y*, ½ + *z*; (vi) 1 - *x*, -*y*, 1 - *z*; (vii) 1 - *x*, -1 + *y*, ½ - *z*; (viii) *x*, -*y*, ½ + *z*; (ix) 1 - *x*, 1 - *y*, 1 - *z*; (x) ½ + *x*, ½ - *y*, ½ + *z*.]

Experimental

NaVO₃·2H₂O (0.314 g, 2 mmol), Na₂TeO₃ (0.442 g, 2 mmol) and diethylenetriamine (0.21 ml, 2 mmol) were dissolved in water (10 ml). The mixture was adjusted to about pH 8 with 2.0 M HCl and stirred for about 10 min. The resulting gel-like mixture was placed in a 25 ml Teflon-lined stainless steel vessel and heated at 363 K for 48 h. After slow cooling to room temperature over a period of 24 h, light-yellow crystals were collected by filtration, washed with distilled water, and dried in air (yield 19%, based on Te).

Crystal data

(C ₄ H ₁₅ N ₃)[Te ₂ V ₂ O ₁₀]·2H ₂ O	$V = 1615.7 (3) \text{ \AA}^3$
$M_r = 658.30$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 26.939 (2) \text{ \AA}$	$\mu = 4.76 \text{ mm}^{-1}$
$b = 5.1596 (4) \text{ \AA}$	$T = 293 \text{ K}$
$c = 11.6242 (12) \text{ \AA}$	$0.20 \times 0.18 \times 0.12 \text{ mm}$
$\beta = 90.06 (4)^\circ$	

Data collection

Rigaku Mercury CCD area-detector diffractometer	7405 measured reflections
Absorption correction: multi-scan (RAPID-AUTO; Rigaku, 1998)	1851 independent reflections
$T_{\min} = 0.450$, $T_{\max} = 0.599$	1732 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	105 parameters
$wR(F^2) = 0.068$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.94 \text{ e \AA}^{-3}$
1851 reflections	$\Delta\rho_{\text{min}} = -2.14 \text{ e \AA}^{-3}$

H atoms bonded to C and N atoms were positioned geometrically and were included in the refinement in the riding-model approximation, with C—H = 0.97 Å and N—H = 0.90 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C or N})$. Atom H4 is statistically distributed across two symmetry-related positions. The water H atoms were located in a difference Fourier map and were included with O—H distances constrained to 0.85 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. Atom H6 atom is statistically distributed across two positions, H6A and H6B, both of which have 50% occupancy.

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3213). Services for accessing these data are described at the back of the journal.

Table 1

Selected geometric parameters (Å, °).

Te1—O3	1.876 (2)	V1—O4	1.637 (2)
Te1—O2	1.892 (2)	V1—O2 ⁱ	1.960 (2)
Te1—O1	1.9174 (19)	V1—O3	2.004 (2)
V1—O5	1.625 (2)	V1—O1 ⁱⁱ	2.0120 (19)
O3—Te1—O2	99.14 (9)	O4—V1—O3	130.58 (10)
O3—Te1—O1	96.33 (10)	O2 ⁱ —V1—O3	78.82 (9)
O2—Te1—O1	91.14 (9)	O5—V1—O1 ⁱⁱ	93.57 (10)
O5—V1—O4	109.73 (12)	O4—V1—O1 ⁱⁱ	94.81 (9)
O5—V1—O2 ⁱ	99.57 (10)	O2 ⁱ —V1—O1 ⁱⁱ	159.12 (9)
O4—V1—O2 ⁱ	95.92 (10)	O3—V1—O1 ⁱⁱ	80.59 (8)
O5—V1—O3	119.64 (11)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1 ⁱ ···O1	0.90	1.95	2.845 (3)	176
N1—H2 ⁱ ···O2 ⁱⁱⁱ	0.90	2.10	2.970 (4)	163
N1—H3 ⁱ ···OW1 ^{iv}	0.90	2.27	3.101 (4)	153
N2—H4 ⁱ ···OW1 ^v	0.90	2.03	2.910 (3)	167
OW1—H5 ⁱ ···O4 ^{vi}	0.85	2.05	2.805 (3)	148
OW1—H6A ⁱ ···OW1 ^{vii}	0.85	2.14	2.935 (5)	155
OW1—H6B ⁱ ···N2	0.85	2.06	2.910 (3)	174

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

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