Synthesis and Structure of a Two-dimensional Vanadium Tellurite, 
\([H_2en][VTeO_5]_2\)

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Abstract. \([H_2en][VTeO_5]_2\) (en = ethylenediamine) was synthesized by a hydrothermal reaction and structurally characterized. The structure of \([H_2en][VTeO_5]_2\) consists of an infinite \(\{VTeO_5\}^-\) layer, which contains VO\(_4\) tetrahedral and TeO\(_5\) square pyramidal units. Two square pyramidal TeO\(_5\) units are connected by sharing an edge to form a Te\(_2\)O\(_8\) binuclear unit. The interlayer space is filled by diprotonated ethylenediammonium cations that link the layers through a network of hydrogen bonds.

**Keywords:** Vanadium; Tellurium; Hydrothermal reaction; Vanadium tellurite; Templates

Introduction

The self-assembly of inorganic molecular building blocks into network structures templated by organic species is of interest as a route to new structured compounds. Most inorganic anionic components are composed of main group 4 and 5 oxy-anions. Accordingly, a large variety of oxoanions such as phosphate, silicate, and gemanate has been investigated \([1 \text{--} 3]\). The organization of such inorganic framework structures is governed by the size, shape, and charge of the non-framework organic components \([4 \text{--} 5]\). These components have often been described as templates or structure-directing agents for the polymerization of other reactants, although the evidence for this is usually indirect.

Recently, several organically templated selenites have been studied in an effort to build structures containing asymmetric coordination environments in the presence of organic cations \([6 \text{--} 9]\). An interesting structural feature of the selenites is that they contain lone pair electrons, which could be important in establishing a route to build non-centrosymmetric structures. Tellurium(IV) oxides can lead to the formation of a stereoactive lone electron pair on the cations, similar to selenites, resulting in an asymmetric coordination environment such as pyramidal “TeO\(_2\)\text{"}, seesaw “TeO\(_4\)\text{"}, and square pyramidal “TeO\(_5\)\text{”} geometry \([10 \text{--} 12]\). Also, tellurites are of importance for their special properties such as non-linear optical properties, and electrical and ionic conductivities. Recently, three organically templated vanadium tellurites, \([H_2en]_2V_2Te_6O_{18}\), \([H_2en][\{VO_2\}(TeO_3)]_2\) \(\cdot\) \(H_2O\) and \([H_2pip][\{VO_2\}(TeO_3)]_2\) (pip = piperazine) have been reported \([13, 14]\). \((H_2en)_2V_2Te_6O_{18}\) has an open framework structure, whereas \([H_2en][\{VO_2\}(TeO_3)]_2\) \(\cdot\) \(H_2O\) and \([H_2pip][\{VO_2\}(TeO_3)]_2\) have 2-dimensional layered structures. \([H_2en]_2V_2Te_6O_{18}\) is constructed from TeO\(_3\) pyramid, TeO\(_3\) seesaw, and VO\(_5\) square pyramidal units through corner- and/or edge-shared oxygen atoms. In \([H_2en][\{VO_2\}(TeO_3)]_2\) \(\cdot\) \(H_2O\) and \([H_2pip][\{VO_2\}(TeO_3)]_2\), the vanadium atom is five coordinated by three tellurite oxygen atoms and two terminal oxygen atoms in a distorted trigonal bipyramidal coordination. The interconnection of the VO\(_5\) polyhedra by bridging pyramidal TeO\(_3\) units construct a 2D corrugated anionic \(\{\{VO_2\}(TeO_3)\}^\text{2\textsuperscript{--}}\) infinite layer. Herein, we report the synthesis and structure of a new organically templated vanadium tellurite, \([H_2en][VTeO_5]_2\) \((\text{en} = \text{ethylenediamine})\), containing VO\(_4\) tetrahedral and TeO\(_5\) square pyramidal units. In the structure each unique TeO\(_5\) binuclear unit formed by sharing two square pyramidal TeO\(_3\) units is connected by six VO\(_4\) polyhedra to complete an anionic inorganic layer, \([\text{Te}_2\text{O}_5(\text{VO}_4)_{6/3}]^\text{2\textsuperscript{--}}\).

Experimental Section

**Materials and methods**

All chemicals used during this work were of reagent grade and used as received from commercial sources without further purification. Thermogravimetric analyses (TGA) were carried out in N\(_2\) at a heating rate of 5 °C/min, using a high-resolution Perkin-Elmer TGA7 Thermal Analyzer. Infrared spectra were recorded on a Hartmann & Braun BOMEM FTIR spectrometer within a range of 400-4000 cm\(^{-1}\) using the KBr pellet method.

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Synthesis

Hydrothermal reactions were carried out in 23-ml capacity Teflon-lined stainless steel Parr hydrothermal reaction vessels at 150 °C for 2 d. V2O5 (0.1365 g, 0.75 mmol), TeO2 (0.480 g, 3.0 mmol), ethylenediamine (0.07 ml, 1.0 mmol) and H2O (5 ml) were allowed to react. The solution PH values before and after the reaction were ~9. The solid products were recovered by vacuum filtration and washed with water. Light brown polyhedral crystals were found. The products are stable in air and water. The yield of the product, \([\text{H}_{2}\text{en}]\text{[VTeO}_5\text{]}_2\) (1), was 64% based on vanadium. The products were insoluble in common polar and non-polar solvents.

A simulated powder X-ray pattern based on the single-crystal structure was in excellent agreement with the X-ray powder data, indicating a single phase reaction. The thermogravimetric analysis shows that upon heating in N2 1 exhibits weight loss of 28.0% in several steps between 260 °C and 900 °C. The observed weight loss is greater than the expected value of 13.2% for the loss of ethylenediamine and water molecules. That may due to a partial reduction of the tellurium and/or vanadium. The final product after heat treatment is glassy residue and cannot be identified by Powder-XRD.

The FTIR spectrum for 1 revealed bands at 1081-1590 and 3130 cm\(^{-1}\), corresponding to N−H, C−H, C−C, and C−N vibrations. The IR spectrum revealed stretching vibrations consistent with Te–O (644 cm\(^{-1}\)) and Te–O–Te (468 cm\(^{-1}\)) vibrations. The strong bands at 938, 879 are due to the ν(V=O) or ν(V−O−V) vibrations. The band around 729 cm\(^{-1}\) is ascribed to the vibration of the V−O or Te−O−V. These values are in good agreement with those reported previously [11, 15].

Single crystal structure determination

Structure determination: Single-crystal data were collected on a Rigaku R-AXIS RAPID diffractometer (graphite-monochromated MoKα radiation, λ = 0.71073 Å, T = 150 K): An empirical absorption correction was applied with (min., max., equivalent transmission factors = 0.69, 1.00). The structure was solved by direct methods using SHELXS97, refined on F\(^2\) by full-matrix least squares using SHELXL97. Hydrogen atoms associated with the ethylenediammonium cations were placed geometrically and refined by riding. All non-hydrogen atoms were refined anisotropically. Further details of the X-ray structural analysis are given in Table 1. Selected bond distances and bond angles are listed in Table 2. Hydrogen bonding distances and angles are listed in Table 3.

Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Centre, CCDC 289500. Copies of the data can be obtained free of charge on application to the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. For drawings of the crystal structure the program Diamond (Crystal Impact, Bonn, 1995) was used.

Results and Discussion

The structure of 1 is built up of infinite \([\text{VTeO}_5\text{]}^-\) layers separated by diprotonated ethylenediammonium cations. Figure 1 shows the coordination environment around the vanadium and tellurium atoms. There is one crystallographically dis-
Fig. 1 View of 1 showing the coordination environment of the tellurium and vanadium atoms (thermal ellipsoids 50%).

Fig. 2 View of the anionic single layer, $\left[\text{TeO}_3\text{VO}_4\right]_2^-$ down the [010] direction. Black, empty circles, and light gray polyhedra are tellurium, oxygen atoms, and VO$_4$ units, respectively.

tinct tellurium atom is coordinated by five oxygen atoms to form a distorted square pyramidal geometry with three short Te–O distances (1.871(3) Å for O(4), 1.949(3) Å for O(1), and 1.964(3) Å for O(3)). Two out of five oxygen atoms are in basal positions (O(1) and O(3)) and one is in apical position (O(4)). The remaining two long Te–O bonds are found in basal positions (Te–O(4); 2.349(3) Å, Te–O(2); 2.466(3) Å). Two square pyramidal TeO$_5$ are connected by sharing an edge (O(4) and O(4')) to form a TeO$_8$ binuclear unit, which possess a center of inversion symmetry. The other three (O(1), O(2), O(3)) out of five oxygen atoms coordinated to Te atoms are bridged by vanadium atoms. The BVS calculation gives a value of 4.07 for Te, indicating an oxidation state of 4.00. In the VO$_4$ tetrahedron, three oxygen atoms are shared with the other tellurium atom as a common corner and the remaining oxygen (O(5)) is terminal. Therefore, in connectivity terms, the layer can be described as consisting of $\left[\text{TeO}_3\text{VO}_4\right]_2^-$ linked to $\left[\text{TeO}_8\right]_{\text{2}}^-$ moieties that form an infinite anionic layer in the ac plane, as illustrated in Figure 2. The layers are built of 4-ring and 6-ring windows of corner-shared VO$_4$ tetrahedra and TeO$_8$ binuclear units. Within the layers, the lone pair on Te$^{4+}$ points approximately in one of either [111] or [111] directions. When taken as a whole, the lone pair polarizations associated with Te$^{4+}$ cancel because Te$^{4+}$ in TeO$_8$ dimer units are at the center of inversion symmetry.

The interlayer space is filled by one crystallographically unique enH$_2$ cation that links the layers through a network of hydrogen bonds, Figure 3. One H$_2$en$^{2+}$ cation contains...
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one crystallographically distinct nitrogen atom due to the center of inversion symmetry. Two different types of N–H⋯O hydrogen bonds link the H$_2$en$^{2+}$ cations and [VTeO$_5$]$^{-}$ layer anions. One hydrogen atom makes H-bonds with the bridged oxygen atom in Te$_2$O$_8$ dimers and the other with a bridged oxygen atom in Te–O–V.

It is interesting to compare the building units of other organically templated vanadium tellurite structures in [H$_2$en]$_2$V$_2$Te$_6$O$_{18}$, [H$_2$en][(VO$_2$)(TeO$_3$)$_2$]·H$_2$O, and [H$_2$pip][(VO$_2$)(TeO$_3$)$_2$] (en = ethylenediamine; pip = piperazine) [13–14]. The structures of these compounds contain TeO$_4$ seesaw, TeO$_3$ pyramid, VO$_5$ square pyramidal, and VO$_5$ trigonal bipyramidal units depending on the reaction conditions and organics used in the synthesis, whereas VO$_4$ tetrahedral and TeO$_3$ square pyramidal units are found in the title compound. Therefore, a variety of structural motif is expected by the combination of TeO$_x$ and VO$_x$ polyhedral units in the presence of various organic cations, and we are currently searching new organically templated vanadium tellurite phases with diverse inorganic framework structures.

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References