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A Vanadium Tellurate, $(NH_4)_2[VO_2]_2[TeO_4(OH)_2]$, Containing Two Edge-Shared Square-Pyramidal VO_5 Groups

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A new ammonium vanadium tellurate, $(NH_4)_2[VO_2]_2[TeO_4(OH)_2]$ (**1**), was hydrothermally synthesized and characterized by single-crystal X-ray diffraction, elemental analysis, IR spectroscopy, and TG analysis. Compound **1** crystallizes in the monoclinic system, space group $P2_1/n$: $a = 8.9112(18)$ Å, $b = 15.151(3)$ Å, $c = 15.187(3)$ Å, $\beta = 97.91(3)°$, $V = 2030.9(7)$ Å^3, $Z = 8$, R1 ($I > 2\sigma(I)$) = 0.0295, wR2 (all data) = 0.0631. The structure of **1** consists of infinite anionic chains, $\{[VO_2]_2[TeO_4(OH)_2]\}^{2-}$, of edge-sharing VO_5 square pyramids and $TeO_4(OH)_2$ octahedra. Two VO_5 square pyramids are joined together by sharing their edge to form a V_2O_8 binuclear unit. The V_2O_8 and $TeO_4(OH)_2$ units are alternatively connected to each other by sharing their edges to complete infinite zigzag anionic $\{[VO_2]_2[TeO_4(OH)_2]\}^{2-}$ chains. The structure contains an extended network of O—H···O hydrogen bonds between the chains. The network of intermolecular hydrogen bonding results in layers parallel to the *ab* plane. Ammonium cations are hydrogen-bonded either to the oxygen atoms of the anionic chains or to each other in a complex arrangement.

Introduction

Vanadium compounds have been widely studied because of their biological importance and ion exchange and catalytic properties. The chemistry of vanadate ions in aqueous solution is well established, and a variety of vanadate ions can be obtained by controlling the pH, concentration, reaction time, and temperature. The aqueous chemistry of vanadium in oxidation states greater than +3 gives more than 10 isopolyvanadate species in acidic, neutral, and basic aqueous solutions. The basic building units of various polyvanadate ions vary from tetrahedron to trigonal pyramid, square pyramid, and octahedron.

Schindler et al. noted that [5]-coordinated $V^{5+}O_5$ polyhedra with [1 + 4]- and [2 + 3]-coordinations can adopt a square-pyramidal or trigonal-bipyramidal geometry.[1] Zavalij et al. reported a crystal-chemical and topographical analysis of a variety of vanadium oxides with open structures and classified V^{5+} polyhedra into three groups: square pyramids with one vanadyl bond ([1 + 4]), trigonal bipyramids with one vanadyl bond ([1 + 4]), and distorted trigonal bipyramids with two vanadyl bonds ([2 + 3]).[2] Therefore, $V^{5+}O_5$ with two vanadyl oxygen atoms is expected to adopt a (distorted) trigonal-bipyramidal instead of a square-pyramidal geometry. Quantitative geometrical comparisons between a square pyramid and trigonal bipyramid were made by Addison et al.; the angular structural parameter $\tau = (\beta - \alpha)/60$ was defined as an index of the degree of trigonality in five-coordinated molecules.[3]

To date, several ternary and quaternary vanadium tellurium oxides, $V_2Te_2O_9$, $VTeO_4$, $V_4Te_4O_{18}$, $MVTeO_5$ (M = Li, Na, K, Cs), $CsV_3Te_2O_{12}$, and $CsVTeO_6$ have been reported, most of which include tellurite(IV) anions.[4–9] Only the $CsVTeO_6$ phase with a pyrochlore-related structure contains Te^{6+}—O tellurate(VI) anions.[9] As part of a systematic study of the synthesis and crystal chemistry of vanadium tellurium oxides that contain Te(VI), we synthesized a new ammonium vanadium tellurate, $(NH_4)_4\{(VO_2)_2[Te_2O_8(OH)_2]\}\cdot 2H_2O$, which consists infinite anionic chains, $\{(VO_2)_2[Te_2O_8(OH)_2]\}^{4-}$, of

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Table 1. Crystal Structure and Refinement Details for **1**

empirical formula	$H_{10}N_2O_{10}Te_1V_2$
formula wt	427.58
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a (Å)	8.9112(18)
b (Å)	15.151(3)
c (Å)	15.187(3)
β (deg)	97.91(3)
V (Å^3)	2030.9(7)
Z	8
ρ_{calcd} (g cm^{-3})	2.797
μ (cm^{-1})	47.0
F(000)	1616
T (K)	150(2)
λ (Å)	0.710 73
cryst size (mm^3)	0.05 × 0.15 × 0.20
θ range for data collection (deg)	3.01–27.48
index ranges	$-10 \le h \le 11$; $-19 \le k \le 19$; $-19 \le l \le 19$
no. of rflns collected	19 243
no. of indep rflns	4649 (R(int) = 0.0499)
GOF on F^2	1.007
R1[a] ($I > 2\sigma(I)$)	0.0295
wR2[b] (all data)	0.0631
max, min $\Delta\rho$ (e/Å^3)	0.811, −0.922

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ (based on reflections with $I > 2\sigma(I)$). [b] $wR2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0236P)^2 + 0.00P]$, $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$.

edge-sharing VO_6 octahedra and $TeO_5(OH)$ octahedra.[10] Here we report the synthesis and structure of a second phase with Te(VI), $(NH_4)_2[VO_2]_2[TeO_4(OH)_2]$, (**1**), which possesses infinite zigzag anionic chains, $\{[VO_2]_2[TeO_4(OH)_2]\}^{2-}$, containing edge-sharing square-pyramidal V_2O_8 and octahedral $TeO_4(OH)_2$ units. This compound is a rare example of a square-pyramidal VO_5 structure with two vanadyl oxygen atoms in each apical and basal position.

Experimental Section

Materials and General 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 10 °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. Semiquantitative analyses of the compounds were performed with JEOL JSM-5200 scanning electron microscope (SEM) equipped with an EDAX Genesis energy dispersive spectroscopy (EDS) detector. Element analyses of the compounds were carried out using a ThermoQuest CE EA1110 instrument for C, H, and N.

Synthesis of $(NH_4)_2[VO_2]_2[TeO_4(OH)_2]$, (1). Hydrothermal reactions were carried out in 23 mL capacity Teflon-lined stainless steel Parr hydrothermal reaction vessels at 150 °C for 3 days. V_2O_5 (0.27 g, 1.5 mmol), H_6TeO_6 (0.69 g, 3.0 mmol), NH_4OH (0.42 mL, 3.0 mmol), and H_2O (5 mL) were allowed to react. The solution pH values before and after the reaction were ~7 and ~8, respectively. The product was filtered, and colorless polyhedral crystals were found together with an unidentified brown powder. The yield of the product, **1**, was 42%, based on vanadium. The products are stable in air and water and are insoluble in common polar and nonpolar solvents, including water. EDS analysis confirmed the presence of V and Te. The elemental analyses gave the following results Anal. Found: V, 22.8; Te, 29.0; N, 6.40; H, 2.26. Calcd for $(NH_4)_2[VO_2]_2[TeO_4(OH)_2]$: V, 22.8; Te, 29.8; N, 6.55; H, 2.34.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Te(1)−O(5)	1.891(2)	Te(2)−O(1)	1.893(2)
Te(1)−O(18)	1.894(2)	Te(2)−O(3)	1.893(2)
Te(1)−O(6)	1.895(2)	Te(2)−O(19)	1.901(2)
Te(1)−O(7)	1.909(2)	Te(2)−O(2)	1.908(2)
Te(1)−O(8)	1.928(2)	Te(2)−O(4)	1.925(2)
Te(1)−O(20)	1.938(2)	Te(2)−O(17)	1.928(2)
Te(1)−V(2)	3.0592(8)	Te(2)−V(3)	3.0722(8)
Te(1)−V(4)	3.0860(8)	Te(2)−V(1)	3.0737(8)
V(1)−O(12)	1.623(2)	V(2)−O(15)	1.603(2)
V(1)−O(11)	1.633(2)	V(2)−O(10)	1.649(2)
V(1)−O(8)#1	1.944(2)	V(2)−O(2)	1.941(2)
V(1)−O(1)	1.969(2)	V(2)−O(5)	1.950(2)
V(1)−O(4)	2.030(2)	V(2)−O(7)	2.043(2)
V(3)−O(9)	1.610(2)	V(4)−O(14)	1.621(2)
V(3)−O(13)	1.636(2)	V(4)−O(16)	1.629(2)
V(3)−O(7)	1.946(2)	V(4)−O(4)#2	1.944(2)
V(3)−O(3)	1.968(2)	V(4)−O(6)	1.970(2)
V(3)−O(2)	2.051(2)	V(4)−O(8)	2.041(2)
O(5)−Te(1)−O(18)	86.79(10)	O(1)−Te(2)−O(3)	173.55(9)
O(5)−Te(1)−O(6)	173.41(9)	O(1)−Te(2)−O(19)	96.84(10)
O(18)−Te(1)−O(6)	97.66(10)	O(3)−Te(2)−O(19)	86.69(10)
O(5)−Te(1)−O(7)	78.72(9)	O(1)−Te(2)−O(2)	97.75(9)
O(18)−Te(1)−O(7)	165.01(10)	O(3)−Te(2)−O(2)	78.97(9)
O(6)−Te(1)−O(7)	97.11(9)	O(19)−Te(2)−O(2)	165.29(10)
O(5)−Te(1)−O(8)	96.91(9)	O(1)−Te(2)−O(4)	78.26(9)
O(18)−Te(1)−O(8)	92.72(11)	O(3)−Te(2)−O(4)	96.27(9)
O(6)−Te(1)−O(8)	78.09(9)	O(19)−Te(2)−O(4)	92.05(11)
O(7)−Te(1)−O(8)	92.78(11)	O(2)−Te(2)−O(4)	92.74(11)
O(5)−Te(1)−O(20)	94.19(10)	O(1)−Te(2)−O(17)	90.54(10)
O(18)−Te(1)−O(20)	91.00(13)	O(3)−Te(2)−O(17)	94.82(10)
O(6)−Te(1)−O(20)	90.60(10)	O(19)−Te(2)−O(17)	90.67(12)
O(7)−Te(1)−O(20)	86.32(11)	O(2)−Te(2)−O(17)	87.32(11)
O(8)−Te(1)−O(20)	168.47(9)	O(4)−Te(2)−O(17)	168.71(10)
O(12)−V(1)−O(11)	108.40(13)	O(15)−V(2)−O(10)	106.52(12)
O(12)−V(1)−O(8)#1	101.73(11)	O(15)−V(2)−O(2)	100.77(12)
O(11)−V(1)−O(8)#1	99.21(11)	O(10)−V(2)−O(2)	99.85(10)
O(12)−V(1)−O(1)	99.55(11)	O(15)−V(2)−O(5)	102.28(11)
O(11)−V(1)−O(1)	98.68(10)	O(10)−V(2)−O(5)	98.39(10)
O(8)#1−V(1)−O(1)	146.12(9)	O(2)−V(2)−O(5)	145.02(9)
O(12)−V(1)−O(4)	122.31(11)	O(15)−V(2)−O(7)	123.83(12)
O(11)−V(1)−O(4)	129.30(11)	O(10)−V(2)−O(7)	129.62(11)
O(8)#1−V(1)−O(4)	72.29(9)	O(2)−V(2)−O(7)	71.14(9)
O(1)−V(1)−O(4)	74.09(8)	O(5)−V(2)−O(7)	74.21(9)
O(9)−V(3)−O(13)	106.34(13)	O(14)−V(4)−O(16)	108.72(13)
O(9)−V(3)−O(7)	101.28(12)	O(14)−V(4)−O(4)#2	98.47(11)
O(13)−V(3)−O(7)	100.02(10)	O(16)−V(4)−O(4)#2	102.52(12)
O(9)−V(3)−O(3)	102.08(11)	O(14)−V(4)−O(6)	99.24(10)
O(13)−V(3)−O(3)	98.67(10)	O(16)−V(4)−O(6)	99.67(11)
O(7)−V(3)−O(3)	144.45(9)	O(4)#2−V(4)−O(6)	145.31(9)
O(9)−V(3)−O(2)	123.89(12)	O(14)−V(4)−O(8)	130.95(11)
O(13)−V(3)−O(2)	129.75(11)	O(16)−V(4)−O(8)	120.34(12)
O(7)−V(3)−O(2)	70.86(9)	O(4)#2−V(4)−O(8)	72.05(9)
O(3)−V(3)−O(2)	73.91(8)	O(6)−V(4)−O(8)	73.79(9)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $x - 1, y, z$; (#2) $x + 1, y, z$.

Single-Crystal Structure Determination. Single-crystal data were collected on a Rigaku R-AXIS RAPID diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å, T = 150 K): An empirical absorption correction was applied. The structure was solved by direct methods using SHELXS97 and refined on F^2 by full-matrix least squares using SHELXL97.[11,12] All the hydrogen atoms associated with the ammonium cations,

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Table 3. Selected Hydrogen Bond Lengths (Å) and Angles (deg) for **1**

D−H···A	H···A	D···A	D−H···A
N(1)−H(11)···O(5)	1.830(1)	2.919(1)	165.49(2)
N(1)−H(13)···O(9)	1.873(8)	2.835(18)	162.31(2)
N(2)−H(21)···O(10)	1.957(25)	2.815(36)	176.84(2)
N(2)−H(22)···O(6)	1.788(3)	2.793(4)	173.05(2)
N(2)−H(23)···O(11)	1.979(29)	2.863(42)	167.73(2)
N(3)−H(31)···O(11)	1.878(24)	2.814(36)	166.54(2)
N(3)−H(32)···O(1)	1.777(2)	2.818(3)	175.31(2)
N(3)−H(34)···O(10)	2.303(30)	2.896(41)	155.47(3)
N(4)−H(41)···O(3)	2.020(1)	2.928(2)	168.97(2)
N(4)−H(42)···O(15)	2.104(15)	2.920(22)	149.17(2)
N(4)−H(43)···O(13)	2.181(28)	2.924(37)	176.75(2)
O(18)−H(18)···O(17)	1.887(19)	2.685(29)	164.18(2)
O(19)−H(19)···O(20)	1.927(20)	2.716(31)	161.11(2)
O(20)−H(20)···O(12)	2.072(1)	2.795(3)	146.99(2)

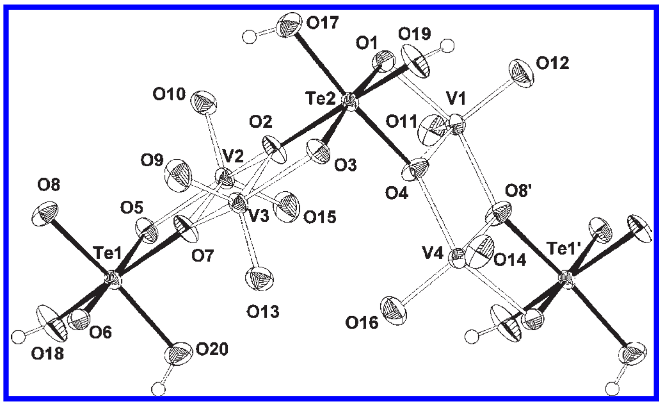

Figure 1. View of a fragment of the $\{[VO_2]_2[TeO_4(OH)_2]\}^{2-}$ chain. Ellipsoids are drawn at the 50% probability level. The empty small circles are H atoms.

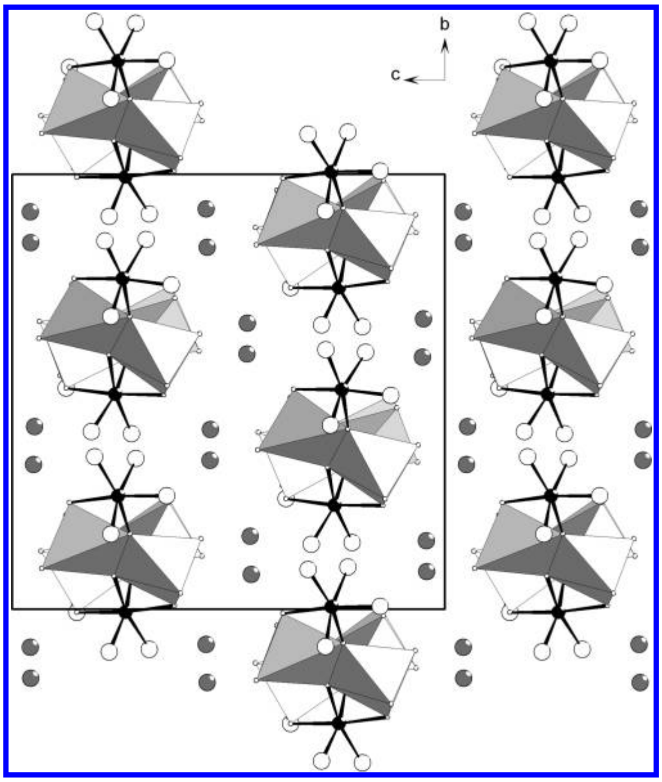

Figure 2. View of **1** showing the interchain packing along the *a* axis. The black circles, empty circles, and light gray polyhedra are Te, O, and VO_5 units, respectively. NH_4^+ groups, shown as gray circles, occupy the interchain sites. H atoms are omitted for clarity.

except for N(4), were located in a Fourier difference map and were refined freely. The remaining H atom in the tellurate anions was positioned geometrically, and the O−H distance and Te−O−H angle were fixed. 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 given in Table 2. Hydrogen-bonding distances and angles are given in Table 3. The highest peak (0.81 Å) and the deepest hole (0.92 Å) are observed from Te(1). The crystallographic files in CIF format have been deposited with FIZ Karlsruhe as CSD No. 419431 for $(NH_4)_2[VO_2]_2[TeO_4(OH)_2]$. The data may be obtained free of charge by contacting FIZ Karlsruhe at +49 7247 808 666 (fax) or crysdata@fiz-karlsruhe.de (e-mail). For drawings of the crystal structure the program Diamond (Crystal Impact, Bonn, 1995) was used.

Results

Crystal Structure. The structure of **1** is built up of infinite $\{[VO_2]_2[TeO_4(OH)_2]\}^{2-}$ chains separated by NH_4^+ cations (Figure 1). Two crystallographically distinct tellurium atoms are coordinated by five oxygen atoms and an OH group to form a slightly distorted octahedron with distances in the ranges of 1.891(2)−1.939(2) and 1.892(2)−1.931(2) Å for Te(1) and Te(2), respectively. A bond valence sum (BVS) calculation gives values of 6.13 and 6.15 for Te(1) and Te(2), respectively, indicating an oxidation state of +6.00. There are four crystallographically independent vanadium atoms each in a distorted-square-pyramidal geometry. Each vanadium atom has two short V=O bonds (1.624(3) and 1.633(2) Å for V(1), 1.607(3) Å and 1.649(2) for V(2), 1.612(3) and 1.635(2) Å for V(3), 1.617(2) and 1.630(3) Å for V(4)) in a cis configuration and three V−O bonds in the ranges of 1.945(2)−2.031(2), 1.941(2)−2.044(2), 1.947(2)−2.052(2), and 1.946(2)−2.041(2) Å for V(1), V(2), V(3), and V(4), respectively.

Two short vanadyl oxygen atoms coordinated to each of the vanadium atoms are terminal. One oxygen atom is connected with the $TeO_4(OH)_2$ octahedron (μ_2-O). The remaining other two oxygen atoms are shared with both VO_5 square pyramids and $TeO_4(OH)_2$ octahedra (μ_3-O). In the $TeO_4(OH)_2$ octahedron, four oxygen atoms are shared with two V_2O_8 octahedra and two of the remaining oxygen atoms form an OH group. The two square-pyramidal VO_5 units are connected by sharing an edge to form a V_2O_8 binuclear unit, which is linked by two $TeO_4(OH)_2$ octahedra. The bond lengths of the uncoordinated Te(1)−O(18), Te(1)−O(20), Te(2)−O(19), and Te(1)−O(17) bonds (1.898(2), 1.939(2), 1.902(2), and 1.931(2) Å, respectively) imply that they are protonated (BVS = −1.05, −0.94, −1.04, −0.96 for O(18), O(20), O(19), and O(17), respectively).[13] Bond valence calculations give bond valence sums for V(1), V(2), V(3), and V(4) of 5.07, 5.10, 5.08, and 5.10, respectively, indicating an oxidation state of +5.00.[13] Thus, the structure of the $\{[VO_2]_2[TeO_4(OH)_2]\}^{2-}$ chains can be simply described as alternate connections of the $TeO_4(OH)_2$ unit and the V_2O_8 dimers sharing common edges along the *a* direction.

The structure contains an extended network of O−H···O and N−H···O hydrogen bonds. The OH

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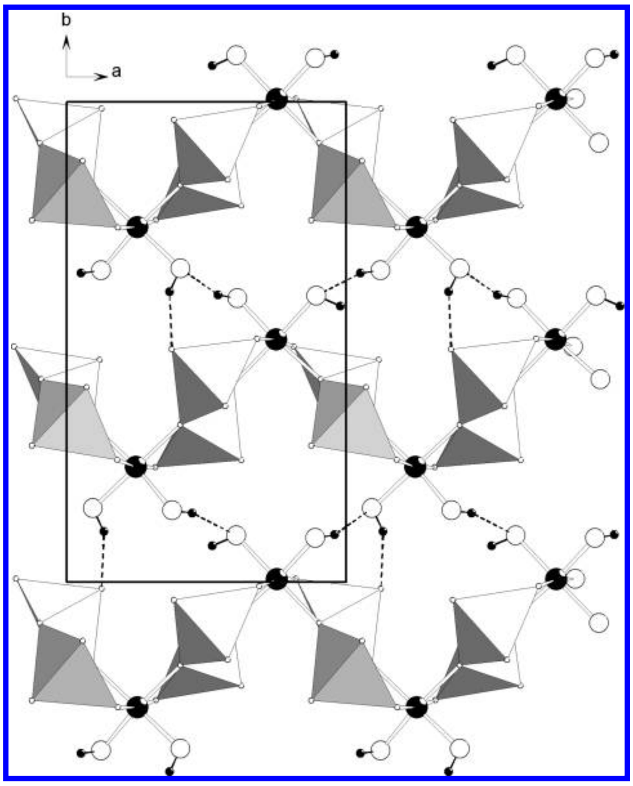


Figure 3. Extended network of O$-$H$\cdots$O hydrogen bonds between the $\{[VO_2]_2[TeO_4(OH)_2]\}^{2-}$ chains. H atoms are represented by small black circles, and the rest of the labeling scheme is the same as that in Figure 2.

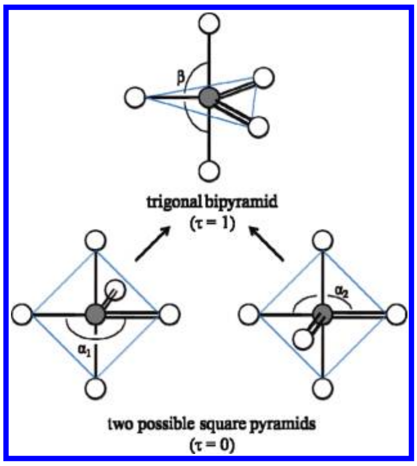
group in the $TeO_4(OH)_2$ octahedron in the $\{[VO_2]_2[TeO_4(OH)_2]\}^{2-}$ chains is linked to adjacent anionic chains by Te$-$OH$\cdots$O$-$V and Te$-$OH$\cdots$O$-$Te hydrogen bonds with O$\cdots$O distances of 2.685, 2.716, 2.795, and 2.725 Å (Figure 3). In this way, the intermolecular hydrogen-bonding network leads to the formation of layers parallel to the *ab* plane.

The four crystallographically distinct ammonium cations that lie between the chains are hydrogen-bonded to nearby oxygen atoms in the $\{[VO_2]_2[TeO_4(OH)_2]\}^{2-}$ chains in a complex arrangement. No hydrogen bonds between ammonium cations are observed. Hydrogen-bonding details are given in Table 3.

Characterization. The thermogravimetric analysis shows that, upon heating in N_2, **1** exhibits a weight loss of 20.89% in one step between 250 and 350 °C. The observed weight loss is greater than the expected value of 16.37% for the loss of ammonia and water molecules. This may due to a partial reduction of the tellurium and/or vanadium. The final product after heat treatment is a glassy residue that cannot be identified by powder XRD.

Vibrational modes for Te$-$O, V$-$O, and V$=$O are observed at 1140 w, 959 m, 925 m, 911 m, 784 w, 746 m, 709 m, 593 m, and 529 s cm^{-1}. Additional absorption bands for N$-$H, C$-$H, and O$-$H vibrations are observed at 3165 vs, 3016 s, 2819 s, and 1406 s cm^{-1}. These values are in good agreement with those reported previously.[14]

Scheme 1



Discussion

The V$-$O bond lengths fall in the range recently noted for V(V) in [2 + 3]-coordination. As Zavalij et al. noted, five-coordinated vanadium with two vanadyl oxygen atoms will normally have a trigonal-bipyramidal geometry in a cis configuration. For the ideal trigonal bipyramid, the three equatorial oxygen atoms make O$-$V$-$O angles of 120° and the two apical atoms have an angle of 180°. In this case, however, although two vanadyl atoms are both in the equatorial plane and the three equatorial O$-$V$-$O angles are close to 120° (108.4(1), 122.4(1), 129.2(1)° for V(1); 106.5(1), 123.8(1), 129.6(1)° for V(2); 106.5(1), 123.8(1)°, 129.7(1)° for V(3); 108.6(1)°, 120.4(1)°, 130.9(1)° for V(4)), the O$-$V$-$O angles for the two apical oxygen atoms are severely distorted from the ideal 180° (146.1(1)° for V(1), 145.0(1)° for V(2), 144.5(1)° for V(3), 145.4(1)° for V(4)). To quantitatively distinguish square-pyramidal and trigonal-bipyramidal geometries, Addison et al. proposed the angular structural parameter $\tau = (\beta - \alpha)/60$ as an index of the degree of trigonality in five-coordinated molecules. Because each vanadium atom has two short vanadyl bonds, the apex is chosen in two different ways to apply this criterion (Scheme 1).

The angle β is the largest angle, and if α is simply chosen from the second (α_1) and third (α_2) largest angles in the structure, each VO_5 polyhedron has τ values of 0.40 and 0.28 for V(1), 0.35 and 0.26 for V(2), 0.34 and 0.25 for V(3), and 0.42 and 0.24 for V(4). For an ideal trigonal-bipyramidal geometry, τ is equal to 1, whereas τ is 0 for a perfect square-pyramidal structure. Thus, VO_5 polyhedra with $0 \leq \tau \leq 0.5$ and $0.5 < \tau \leq 1$ then can be considered as distorted square pyramids and distorted trigonal bipyramids, respectively. The τ values for the four VO_5 polyhedra in **1** suggests that square pyramidal rather than trigonal bipyramidal is a better description of the coordination geometry. To the best of our knowledge, the title compound is the first inorganic framework example to show a square-pyramidal structure containing two vanadyl oxygen atoms in apical and basal positions.

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Table 4. Angular Structural Parameter/τ Calculations for Several Oxovanadium Complexes Containing V_2O_8 Dimeric Cores

complex	β	α_1	τ_1	α_2	τ_2	ref
$[V_2O_4(\text{glycolate})_2]^{2-}$	147.75	128.77	0.32	122.91	0.41	15
	147.79	128.57	0.32	123.54	0.40	16
$[V_2O_4(\text{pyridoxinate})_2]$	153.90	128.46	0.42	119.63	0.57	17
$[V_2O_4(\text{2-methylpropanoate})_2]^{2-}$	147.34	131.78	0.26	120.15	0.45	18
	147.50	131.15	0.27	121.81	0.43	19
$[V_2O_4(\text{lactate})_2]^{2-}$	145.56	130.83	0.25	121.75	0.40	19
	148.19	130.87	0.29	121.18	0.45	16
	147.58	126.78	0.35	124.45	0.39	16
	149.54	130.02	0.33	123.65	0.43	20
$[V_2O_4(\text{citrate})_2]^{6-}$	147.90	137.31	0.18	115.83	0.53	21
	145.60	137.72	0.13	115.09	0.50	21
	149.80	128.31	0.36	125.11	0.41	22
	148.45	132.55	0.26	121.33	0.45	20
	148.64	129.12	0.33	123.96	0.41	23
$[V_2O_4(\text{dihydrogen citrate})_2]^{4-}$	149.27	127.06	0.37	124.46	0.41	23
	149.46	130.67	0.31	122.70	0.45	24
	150.10	131.87	0.30	121.26	0.48	24
$[V_2O_4(\text{tetrahydrogen citrate})_2]^{2-}$	148.73	133.90	0.25	118.81	0.50	25
	149.21	130.54	0.31	123.02	0.44	26
$[V_2O_4(\text{2-hydroxy-1,2,3-propane-tricarboxylate})_2]^{4-}$	149.08	126.96	0.37	125.99	0.38	27
	147.68	134.96	0.21	118.82	0.48	27
$[V_2O_4(R,S\text{-homocitrate})_2]^{2-}$	149.43	128.38	0.35	123.56	0.43	28
$[V_2O_4(\text{methyl lactate})_2]^{2-}$	144.90	136.21	0.14	115.22	0.49	29
$[V_2O_4(\text{malate})_2]^{2-}$	146.90	131.16	0.26	121.02	0.43	16
$[V_2O_4(\text{3,5-di-}tert\text{-butylcatecholate})_2]^{2-}$	143.67	134.96	0.15	114.23	0.49	30
	144.52	126.91	0.29	122.80	0.36	30
$[V_2O_4(\text{2-ethyl-2-hydroxybutyrate})_2]^{2-}$	149.34	126.73	0.38	124.79	0.41	31
	149.16	131.43	0.30	121.53	0.46	31
$[V_2O_4(\text{methyl 4,6-}O\text{-benzylidene-}\alpha\text{-D-mannopyranosidato})_2]^{2-}$	143.68	133.28	0.17	117.65	0.43	32
	146.48	128.40	0.30	121.93	0.41	32
$[V_2O_4(\text{adanosinyl})_2]^{2-}$	142.82	141.86	0.02	109.68	0.55	33
	147.39	127.95	0.32	122.36	0.42	33

A search of the Cambridge Structure Database for the double oxovanadyl group V_2O_8 with two O═V═O bonds yields 23 structures.[15−33] In all of the cases, each vanadium atom is chelated by bidentate oxo ligands. Interestingly, the calculated τ values of VO_5 based on the first and second largest angles, β and α_1, for all 23 structures are below 0.5, indicating distorted square pyramids (Table 4). Considerations of the first and third largest angles (different apex setting, α_2) also produce the same results, except for two structures, $[V_2O_4(\text{pyridoxinate})_2]$ and $[V_2O_4(\text{adanosinyl})_2]^{2-}$, with $\tau > 0.5$ (distorted trigonal bipyramid).[17,33]

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Supporting Information Available: Tables and a CIF file giving crystallographic data for **1** and a figure giving a TG curve for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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