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$[H_xTeV_9O_{28}]^{(5-x)-}$ (x = 1 and 2): Vanadotellurates with Decavanadate Structure

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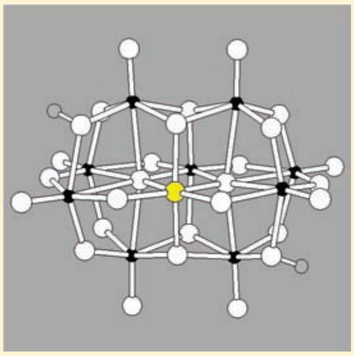
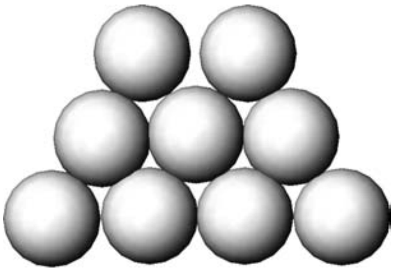
Supporting Information

ABSTRACT: Two new vanadotellurates, $[HTeV_9O_{28}]^{4-}$ and $[H_2TeV_9O_{28}]^{3-}$ have been synthesized and structurally characterized as tetra-*n*-butylammonium (TBA) salts: $TBA_4[HTeV_9O_{28}]\cdot 2CH_3CN$ [triclinic, space group $P\bar{1}$, a = 16.7102(6) Å, b = 17.4680(7) Å, c = 17.9634(7) Å, α = 74.412(1)°, β = 67.494(1)°, γ = 74.160(2)°, Z = 2] and $TBA_3[H_2TeV_9O_{28}]$ [monoclinic, space group $P2_1/c$, a = 13.0013(5) Å, b = 19.157(1) Å, c = 28.453(1) Å, β = 97.222(2)°, Z = 4]. The results of the structural analyses indicate that the four O atoms that bridge two V atoms on the Te side are the most basic ones in the structure. The results of density-functional theory (DFT) calculations support this view.



INTRODUCTION

One main feature of polyoxometalates or anionic molecular oxides is that they provide structurally well-characterized surfaces formed by approximately coplanar, closest-packed O atoms. Decavanadate is composed of 28 oxygen and 10 vanadium atoms and has isosceles trapezoidal surfaces that are made up of nine closest-packed O atoms shown below.[1] Since the identification of protonation



sites provides a good measure of surface charge distribution, different research groups have investigated the protonation sites of this nine-atom array of decavanadate. However, the results obtained so far are somewhat ambiguous. Theoretical calculations suggested the unique O atom at the center of the trapezoid most basic.[2,3] On the other hand, X-ray structural studies of $[HV_{10}O_{28}]^{5-}$ revealed that an O atom on the side is protonated in this anion.[4,5] A total of 27 different salts of diprotonated decavanadate have been structurally characterized. In 15 of them, only the O atoms on the sides are protonated.[6−20] Both the central O and an O atom on the side are protonated in six of them.[11,21−25] In the other seven, only the central O atoms are protonated.[16,26−31] In a hydrated 1,6-hexanediammonium salt of $[H_2V_{10}O_{28}]^{4-}$ only the oxygens on the sides are protonated,[18] while in an unhydrated salt of the same cation only the central oxygens are protonated.[29] These crystal structural studies of protonated decavanadate anions indicate that the protonation sites of $[V_{10}O_{28}]^{6-}$ are significantly affected by hydrogen bonding in the solid state. They also show us that we need a salt of $[HV_{10}O_{28}]^{5-}$ where the cations do not form hydrogen bonds with the molecular oxide anion to determine the most basic oxygen atom in the trapezoidal surface shown above. It is also desirable that the cation is of low surface charge. Cations of high surface charge like alkali metal cations tend to form strong interactions with molecular oxide anions and would affect protonation.[32]

Tetra-*n*-butylammonium (TBA) is ideal in this respect. It does not form hydrogen bonds and has low surface charge. Unfortunately, attempts to isolate TBA salt of either $[V_{10}O_{28}]^{6-}$ or $[HV_{10}O_{28}]^{5-}$ have been unsuccessful.[33] They have always yielded $[V_5O_{14}]^{3-}$ or $[V_{12}O_{32}]^{4-}$,[34,35] although TBA salts of $[H_2V_{10}O_{28}]^{4-}$ and $[H_3V_{10}O_{28}]^{3-}$ are known.[33,36] Recently, we have isolated TBA salts of two vanadotellurates of the decavanadate structure, $[HTeV_9O_{28}]^{4-}$ and $[H_2TeV_9O_{28}]^{3-}$. These compounds gave us an opportunity to study the hitherto elusive protonation sites of the trapezoidal surface. Here we report the results.

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■ EXPERIMENTAL SECTION

Reagents, Solvents, and General Procedures. The following were purchased from commercial sources and used without further purification: $Te(OH)_6$ and V_2O_5 (Mitsuwa Chemical), P_2O_5 (Kishida), and 10% aqueous $[(n\text{-}C_4H_9)_4N]OH$ (Tokyo Kasei). Dimethyl formamide (DMF), diethyl ether, ethyl acetate (Wako), and deuterated dimethylsulfoxide (DMSO-d_6, ISOTEC) were dried over 4 Å molecular sieves. Methanol (Wako) and deuterated acetonitrile (ISOTEC) were dried over 3 Å molecular sieves. Acetonitrile (Kishida) was routinely dried over 3 Å molecular sieves. Dilute hydrochloric acid was prepared from concentrated aqueous HCl (Wako) and standardized against Na_2CO_3 (Takasugi Chemicals).

Analytical Procedures. Elemental analyses were performed by Toray Research Center Inc., Shiga, Japan. Infrared spectra were recorded from mineral oil (Nujol) mulls between KRS plates on a Shimadzu FTIR-8400 spectrometer. Absorptions are described as follows: very strong (vs), strong (s), medium (m), weak (w), and shoulder (sh). NMR spectra were recorded on a Varian Inova spectrometer. ^{1}H NMR spectra were recorded at 299.966 MHz and referenced internally against TMS. ^{51}V NMR spectra were recorded at 78.855 MHz and referenced externally against $VOCl_3$. ^{125}Te NMR spectra were recorded at 94.735 MHz. They were referenced externally against aqueous 1.0 M $Te(OH)_6$ instead of highly toxic and difficult to handle $(CH_3)_2Te$. The chemical shift of $(CH_3)_2Te$ is −707 ppm on this scale.

Preparation of $TBA_4[HTeV_9O_{28}]$. $Te(OH)_6$ (0.355 g, 1.55 mmol) was dissolved in 15.0 mL of aqueous 10% TBAOH (6.16 mmol). To this solution was added 1.26 g of V_2O_5 (6.93 mmol), and the mixture was stirred for 3 h. Orange-yellow microcrystals that formed were collected by filtration and dried under vacuum over P_2O_5 to yield 2.20 g of crude product (1.10 mmol, 71.4% on V). This crude material was then dissolved in 22.0 mL of acetonitrile. After the solution was centrifuged to separate a small amount of insoluble material, 66.0 mL of diethylether was added to the supernatant deep orange solution with stirring. Orange-yellow microcrystals formed immediately. The microcrystals were collected by filtration and dried under vacuum over P_2O_5 to yield 2.13 g (1.06 mmol, 69.0% on V) of the product. Anal. Calcd for $C_{64}H_{145}N_4O_{28}TeV_9$: C, 38.34; H, 7.29; N, 2.79. Found: C, 38.01; H, 7.23; N, 2.59. IR (Nujol mull, 1000−400 cm^{-1}): 989 (s), 971 (vs), 868 (m), 841 (m), 777 (s), 739 (s), 628 (w), 584 (m), 554 (m), 515 (m), 494 (sh), 457 (w), 436 (w). ^{1}H NMR (CD_3CN, TMS): δ (ppm) 0.98 (t, $CH_3CH_2CH_2CH_2N$), 1.42 (m, $CH_3CH_2CH_2CH_2N$), 1.67 (m, $CH_3CH_2CH_2CH_2N$), 3.19 (m, $CH_3CH_2CH_2CH_2N$), 4.82 (s, br, $HTeV_9O_{28}$). ^{51}V NMR (CD_3CN, $VOCl_3$): δ (ppm) −447 (1 V), −470 (1 V), −478 (1 V), −493 (1 V), −507 (3 V), −516 (1 V), −524 (1 V). ^{125}Te NMR (CD_3CN, 1.0 M $Te(OH)_6$ in H_2O): δ (ppm) 136.2 (s). Single crystals suitable for X-ray structural analysis were prepared by dissolving microcrystalline $TBA_4[HTeV_9O_{28}]$ in 2.0 mL of acetonitrile, adding 2.0 mL of diethylether to the solution with stirring, and allowing the solution to stand at ambient temperature. Plate-shaped orange crystals formed in 24 h.

Preparation of $TBA_3[H_2TeV_9O_{28}]$. To a solution of $TBA_4[HTeV_9O_{28}]$ (1.91 g, 0.953 mmol, in 20.0 mL of DMF) was added 0.923 mL of aqueous 1.05 M HCl (0.966 mmol), and the solution was stirred for 15 min. Ethyl acetate (120 mL) was then added to the solution with stirring to form a yellow precipitate, which was collected by filtration and dried under vacuum over P_2O_5 to yield 1.74 g of the product. Crystallization was accomplished by dissolving 0.50 g of the product in 10 mL of acetonitrile, removing a tiny amount of insoluble solid by centrifuge, and adding 17.5 mL of diethyl ether to the supernatant solution without stirring to make a second layer. Yellow block-shaped crystals appeared in 18 h. Anal. Calcd for $C_{48}H_{110}N_3O_{28}TeV_9$: C, 32.69; H, 6.29; N, 2.38; Te, 7.2; V 26.0. Found: C, 32.70; H, 6.17; N, 2.16; Te, 7.6; V, 25.9. IR (Nujol mull, 1000−400 cm^{-1}): 999 (s), 991 (s), 979 (vs) 879 (m), 867 (s), 851 (s), 797 (s), 739 (s), 616 (m), 583 (s), 541 (w), 525 (w), 499 (w), 431 (m). ^{1}H NMR (CD_3CN, TMS): δ (ppm) 0.97 (t, $CH_3CH_2CH_2CH_2N$), 1.38 (m, $CH_3CH_2CH_2CH_2N$), 1.64 (m, $CH_3CH_2CH_2CH_2N$), 3.14 (m, $CH_3CH_2CH_2CH_2N$), 7.05 (s, br, $H_2TeV_9O_{28}$). ^{51}V NMR (CD_3CN, $VOCl_3$): δ (ppm) −441 (1 V), −501 (2 V), −513 (2 V), −515 (1 V), −520 (2 V), −539 (1 V), −543 (1 V).

Table 1. Crystallographic Data for $TBA_4[HTeV_9O_{28}]\cdot 2CH_3CN$ and $TBA_3[H_2TeV_9O_{28}]$

	$TBA_4[HTeV_9O_{28}]\cdot 2CH_3CN$	$TBA_3[H_2TeV_9O_{28}]$
empirical formula	$C_{68}H_{151}N_6O_{28}TeV_9$	$C_{48}H_{110}N_3O_{28}TeV_9$
fw	2087.04	1763.45
space group	$P\bar{1}$	$P2_1/c$
a/Å	16.7102(6)	13.0013(5)
b/Å	17.4680(7)	19.1571(10)
c/Å	17.9634(7)	28.4531(13)
α/deg	74.412(1)	90
β/deg	67.494(1)	97.222(2)
γ/deg	74.160(2)	90
V/Å^3	4579.9(3)	7030.5(6)
Z	2	4
T/K	150(1)	150(1)
λ/Å	0.71073	0.71073
ρ_{calcd}/g cm^{-1}	1.508	1.666
μ/mm^{-1}	1.260	1.624
$R\ [F_o^2 > 2\sigma(F_o^2)]^a$	0.0614	0.0443
R_w [all data]^b	0.2051^c	0.0960^d

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$. [c] $a = 0.0973$, $b = 16.5511$. [d] $a = 0.0185$, $b = 16.7457$.

Crystal Structure Determinations. Single-crystal diffraction data for $TBA_4[HTeV_9O_{28}]\cdot 2CH_3CN$ and $TBA_3[H_2TeV_9O_{28}]$ were measured on a Rigaku R-Axis Rapid diffractometer using Mo Kα radiation. The structures were solved by the direct methods and refined by full-matrix least-squares with the SHELX-97 program suite.[37] Crystallographic parameters are summarized in Table 1. Selected bond distances in $TBA_4[HTeV_9O_{28}]\cdot 2CH_3CN$ and $TBA_3[H_2TeV_9O_{28}]$ are listed in Table 2 and 3, respectively. The structure of $[HTeV_9O_{28}]^{4-}$ is shown in Figure 1 and that of $[H_2TeV_9O_{28}]^{3-}$ in Figure 2. There are two crystallographically independent $[HTeV_9O_{28}]^{4-}$ anions in a unit cell of $TBA_4[HTeV_9O_{28}]\cdot 2CH_3CN$. Each anion has a crystallographic inversion center, and only half of it is crystallographically independent. The Te atom in each anion is completely disordered with a V atom over two central V atom sites, which are related by an inversion center (see Figure 1). In $TBA_3[H_2TeV_9O_{28}]$ crystal, the whole $[H_2TeV_9O_{28}]^{3-}$ anion is crystallographically independent. However, the Te atom is also disordered over two central V atom positions. The refinement of the occupancies for these sites converged with the values 0.610(1) (Te_1 in Figure 2) and 0.390(1) (Te_2 in Figure 2). The final stage of the structure refinement was performed by fixing these parameters at 0.61 and 0.39, respectively.

Density-Functional Theory (DFT) Calculations. The $[TeV_9O_{28}]^{5-}$, $[HTeV_9O_{28}]^{4-}$, and $[H_2TeV_9O_{28}]^{3-}$ anions were subjected to first-principles calculations based on the density-functional theory (DFT) using the Gaussian03 program.[38] All DFT calculations were carried out using the B3LYP exchange-correlation functionals[39] and the def2-TZVP basis sets.[40]

■ RESULTS AND DISCUSSION

The vanadotellurate of the decavanadate structure $[HTeV_9O_{28}]^{4-}$ was first obtained by reacting $[TeO_4]^{2-}$ and $[(V_{12}O_{32})\supset MeCN]^{4-}$.[41] Later we found out that the same anionic molecular

Table 2. Selected Distances in $TBA_4[HTeV_9O_{28}]\cdot 2CH_3CN$

anion 1		anion 2	
$Te_1/V_{1A}-O_{A1}$	2.017(2)	$Te_2/V_{1B}-O_{A2}{}^{i}$	2.032(2)
$Te_1/V_{1A}-O_{A1}{}^{i}$	2.054(2)	$Te_2/V_{1B}-O_{A2}$	2.061(2)
$Te_1/V_{1A}-O_{B1}$	1.931(2)	$Te_2/V_{1B}-O_{B3}$	1.906(2)
$Te_1/V_{1A}-O_{B2}{}^{i}$	1.930(2)	$Te_2/V_{1B}-O_{B4}{}^{i}$	1.945(2)
$Te_1/V_{1A}-O_{E1}$	1.792(2)	$Te_2/V_{1B}-O_{E3}$	1.789(2)
$Te_1/V_{1A}-O_{E2}$	1.798(2)	$Te_2/V_{1B}-O_{E4}$	1.780(2)
$V_{2A}-O_{A1}{}^{i}$	2.389(2)	$V_{2C}-O_{A2}$	2.422(2)
$V_{2A}-O_{C1}$	1.870(2)	$V_{2C}-O_{C5}$	1.897(2)
$V_{2A}-O_{C4}{}^{i}$	1.911(2)	$V_{2C}-O_{C8}{}^{i}$	1.880(2)
$V_{2A}-O_{D1}$	1.814(2)	$V_{2C}-O_{D2}$	1.821(2)
$V_{2A}-O_{E1}$	2.025(2)	$V_{2C}-O_{E3}$	2.053(2)
$V_{2A}-O_{G1}$	1.592(3)	$V_{2C}-O_{G3}$	1.594(2)
$V_{2B}-O_{A1}$	2.422(2)	$V_{2D}-O_{A2}{}^{i}$	2.411(2)
$V_{2B}-O_{C2}{}^{i}$	1.840(2)	$V_{2D}-O_{C6}{}^{i}$	1.851(2)
$V_{2B}-O_{C3}$	1.964(2)	$V_{2D}-O_{C7}$	1.924(3)
$V_{2B}-O_{D1}{}^{i}$	1.833(2)	$V_{2D}-O_{D2}{}^{i}$	1.841(2)
$V_{2B}-O_{E2}$	2.042(2)	$V_{2D}-O_{E4}$	2.045(2)
$V_{2B}-O_{G2}$	1.605(2)	$V_{2D}-O_{G4}$	1.597(2)
$V_{3A}-O_{A1}{}^{i}$	2.315(2)	$V_{3C}-O_{A2}$	2.298(2)
$V_{3A}-O_{B1}$	2.034(2)	$V_{3C}-O_{B3}$	2.031(2)
$V_{3A}-O_{B2}$	2.023(2)	$V_{3C}-O_{B4}$	2.054(2)
$V_{3A}-O_{C1}$	1.788(2)	$V_{3C}-O_{C5}$	1.791(2)
$V_{3A}-O_{C2}$	1.850(2)	$V_{3C}-O_{C6}$	1.843(2)
$V_{3A}-O_{F1}$	1.613(2)	$V_{3C}-O_{F3}$	1.604(2)
$V_{3B}-O_{A1}$	2.293(2)	$V_{3D}-O_{A2}{}^{i}$	2.272(2)
$V_{3B}-O_{B1}$	2.062(2)	$V_{3D}-O_{B3}$	2.055(2)
$V_{3B}-O_{B2}$	2.010(2)	$V_{3D}-O_{B4}$	2.019(2)
$V_{3B}-O_{C3}$	1.887(2)	$V_{3D}-O_{C7}$	1.857(2)
$V_{3B}-O_{C4}$	1.768(2)	$V_{3D}-O_{C8}$	1.789(2)
$V_{3B}-O_{F2}$	1.606(2)	$V_{3D}-O_{F4}$	1.590(2)

Atoms labeled with a superscripted i are related to those labeled without it by the crystallographic inversion center at (0, 1/2, 1/2) for anion 1 and at (1/2, 0, 0) for anion 2. See also Figure 1.

Table 3. Selected Distances in $TBA_3[H_2TeV_9O_{28}]$

$Te_1/V_{1A}-O_{A1}$	2.026(2)	$Te_2/V_{1B}-O_{A1}$	2.059(2)
$Te_1/V_{1A}-O_{A2}$	2.028(2)	$Te_2/V_{1B}-O_{A2}$	2.053(2)
$Te_1/V_{1A}-O_{B1}$	1.941(2)	$Te_2/V_{1B}-O_{B2}$	1.904(2)
$Te_1/V_{1A}-O_{B4}$	1.929(2)	$Te_2/V_{1B}-O_{B3}$	1.958(2)
$Te_1/V_{1A}-O_{E1}$	1.801(2)	$Te_2/V_{1B}-O_{E3}$	1.758(2)
$Te_1/V_{1A}-O_{E2}$	1.792(2)	$Te_2/V_{1B}-O_{E4}$	1.759(2)
$V_{2A}-O_{A2}$	2.399(2)	$V_{2C}-O_{A1}$	2.397(2)
$V_{2A}-O_{C1}$	1.817(2)	$V_{2C}-O_{C4}$	1.985(2)
$V_{2A}-O_{C8}$	2.004(2)	$V_{2C}-O_{C5}$	1.828(2)
$V_{2A}-O_{D1}$	1.821(2)	$V_{2C}-O_{D2}$	1.811(2)
$V_{2A}-O_{E1}$	2.022(2)	$V_{2C}-O_{E3}$	2.022(2)
$V_{2A}-O_{G1}$	1.589(2)	$V_{2C}-O_{G3}$	1.592(2)
$V_{2B}-O_{A1}$	2.381(2)	$V_{2D}-O_{A2}$	2.423(2)
$V_{2B}-O_{C3}$	2.011(2)	$V_{2D}-O_{C2}$	1.842(2)
$V_{2B}-O_{C6}$	1.814(2)	$V_{2D}-O_{C7}$	1.969(2)
$V_{2B}-O_{D2}$	1.832(2)	$V_{2D}-O_{D1}$	1.803(2)
$V_{2B}-O_{E2}$	2.004(2)	$V_{2D}-O_{E4}$	2.034(2)
$V_{2B}-O_{G2}$	1.592(2)	$V_{2D}-O_{G4}$	1.585(2)
$V_{3A}-O_{A2}$	2.315(2)	$V_{3C}-O_{A1}$	2.339(2)
$V_{3A}-O_{B1}$	2.022(2)	$V_{3C}-O_{B3}$	2.004(2)
$V_{3A}-O_{B2}$	2.020(2)	$V_{3C}-O_{B4}$	2.023(2)
$V_{3A}-O_{C1}$	1.819(2)	$V_{3C}-O_{C5}$	1.816(2)
$V_{3A}-O_{C2}$	1.815(2)	$V_{3C}-O_{C6}$	1.831(2)
$V_{3A}-O_{F1}$	1.591(2)	$V_{3C}-O_{F3}$	1.597(2)
$V_{3B}-O_{A1}$	2.290(2)	$V_{3D}-O_{A2}$	2.301(2)
$V_{3B}-O_{B1}$	2.036(2)	$V_{3D}-O_{B3}$	1.978(2)
$V_{3B}-O_{B2}$	1.984(2)	$V_{3D}-O_{B4}$	2.039(2)
$V_{3B}-O_{C3}$	1.882(2)	$V_{3D}-O_{C7}$	1.810(2)
$V_{3B}-O_{C4}$	1.814(2)	$V_{3D}-O_{C8}$	1.877(2)
$V_{3B}-O_{F2}$	1.597(2)	$V_{3D}-O_{F4}$	1.596(2)

oxide can be synthesized by reacting $[TeO_4]^{2-}$ with $[V_4O_{12}]^{4-}$ in the presence of HCl.

$$4[TeO_4]^{2-} + 9[V_4O_{12}]^{4-} + 28H^+ \rightarrow 4[HTeV_9O_{28}]^{4-} + 12H_2O$$

The reaction of $Te(OH)_6$ with $[V_4O_{12}]^{4-}$ or V_2O_5 also yields $[HTeV_9O_{28}]^{4-}$.

$$4Te(OH)_6 + 9[V_4O_{12}]^{4-} + 20H^+ \rightarrow 4[HTeV_9O_{28}]^{4-} + 20H_2O$$

$$2Te(OH)_6 + 9V_2O_5 + 8OH^- \rightarrow 2[HTeV_9O_{28}]^{4-} + 9H_2O$$

Different combinations of starting materials yield the same anionic molecular oxide. These results strongly suggest that the formation of $[HTeV_9O_{28}]^{4-}$ is governed by thermodynamics.

The diprotonated anion $[H_2TeV_9O_{28}]^{3-}$ was obtained by reacting $[HTeV_9O_{28}]^{4-}$ with aqueous HCl in DMF. However, attempts to isolate unprotonated anion are so far unsuccessful. The material obtained from the reaction of $[HTeV_9O_{28}]^{4-}$ and TBAOH gave ^{51}V NMR peaks assignable to $[TeV_9O_{28}]^{5-}$ in solution but only together with the $[V_4O_{12}]^{4-}$ peaks of significant intensities. The intensities of the $[V_4O_{12}]^{4-}$ peaks increased when such solution was allowed to stand. Reaction of stoichiometric amounts of $Te(OH)_6$, V_2O_5, and TBAOH (2:9:10) yielded monoprotonated $[HTeV_9O_{28}]^{4-}$, not the unprotonated $[TeV_9O_{28}]^{5-}$.

This apparent instability of $[TeV_9O_{28}]^{5-}$ and stability of $[HTeV_9O_{28}]^{4-}$ and $[H_2TeV_9O_{28}]^{3-}$ in solution is consistent with previous findings.[42,43] The higher charge of Te(VI) would make $[TeV_9O_{28}]^{5-}$ less basic or more acidic than its all V parent $[V_{10}O_{28}]^{6-}$. The $[H_2V_{10}O_{28}]^{4-}$ anion is known to decompose spontaneously in nonaqueous solution,[33] while $[H_3V_{10}O_{28}]^{3-}$ is highly stable in nonaqueous solution.[36] The $[HV_{10}O_{28}]^{5-}$ anion has never been observed in nonaqueous solution. This pattern of stability matches that of vanadotellurate observed here when the higher charge of Te(VI) is taken into consideration.

There are two crystallographically independent $[HTeV_9O_{28}]^{4-}$ anions in crystalline $TBA_4[HTeV_9O_{28}]\cdot 2CH_3CN$. Figure 1 shows the structures of both of them together with the labeling scheme. Apart from slight differences in interatomic distances and angles, the anions have an identical structure. The Te atoms are disordered and statistically distributed over two crystallographically equivalent sites related by inversion symmetry in both anions. The structure of the $[HTeV_9O_{28}]^{4-}$ anion is basically the same as that of decavanadate, $[V_{10}O_{28}]^{6-}$.[1] In $[HTeV_9O_{28}]^{4-}$ one of the central V atoms of $[V_{10}O_{28}]^{6-}$ is replaced with a Te atom. Replacement of a central V atom with a heteroatom has also been observed for $[H_2PtV_9O_{28}]^{5-}$.[44]

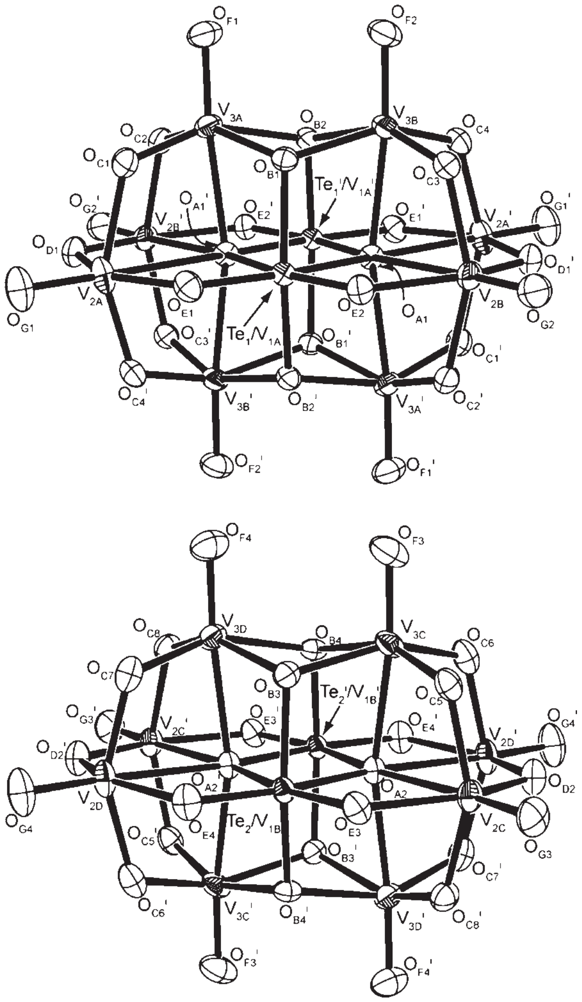


Figure 1. Structures and labeling of two crystallographically independent $[HTeV_9O_{28}]^{4-}$ anions in $TBA_4[HTeV_9O_{28}]\cdot 2CH_3CN$. The ellipsoids are drawn to encompass 50% probability levels. Atoms labeled with a superscripted i are related to those labeled without it by the crystallographic inversion center at (0, 1/2, 1/2) for anion 1 (top) and at (1/2, 0, 0) for anion 2 (bottom).

The $[HTeV_9O_{28}]^{4-}$ anions are protonated, just as the formula tells. Although we could not locate the protons directly from the diffraction data, their location can be reasonably inferred from bond valence sum calculations for both anions.[45,46] The bond valence sums for O_{C3} in anion 1 is 1.5 and that for O_{C7} in anion 2 is 1.6. The values are significantly smaller than those of the other O atoms and the ideal value of 2, suggesting that these oxygens are the ones that are protonated.

The observation discussed above suggests that O_C oxygens that bridges two V atoms are the most basic in the $[TeV_9O_{28}]^{5-}$ anion. However, there is another question that should be addressed. The $[HTeV_9O_{28}]^{4-}$ anion appears to be centrosymmetric in the crystals because of the disorder, but in reality the anion does not have a center of symmetry. Thus not all eight O_C oxygens are equivalent. They should be divided into two groups; those on the Te side, O_C(Te), and the others on the opposite V side, O_C(V). Which are more basic? The X-ray diffraction results of $[HTeV_9O_{28}]^{4-}$ failed to answer this question. Fortunately, however, the structural analysis of the diprotonated anion $[H_2TeV_9O_{28}]^{3-}$ gave us some insights on this matter.

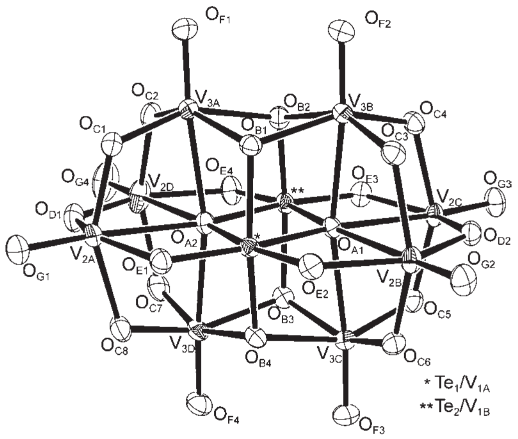


Figure 2. Structure and labeling of the $[H_2TeV_9O_{28}]^{3-}$ anion in $TBA_3[H_2TeV_9O_{28}]$. The ellipsoids are drawn to encompass 50% probability levels.

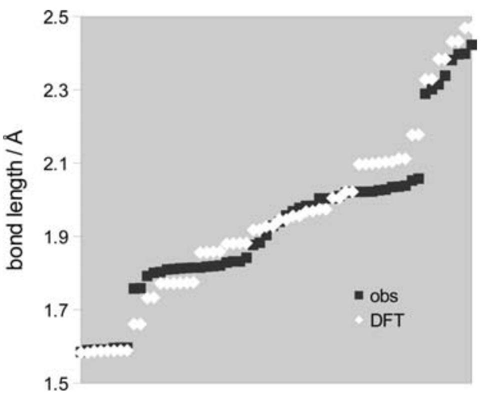


Figure 3. Comparison of observed and calculated bond lengths of the $[H_2TeV_9O_{28}]^{3-}$ anion.

Figure 2 shows the structure of $[H_2TeV_9O_{28}]^{3-}$ together with the labeling scheme. The decavanadate structure is maintained upon protonation. Here again the Te atom is disordered with the central V atom (V_1), but not totally statistically. The occupation of the Te atom is 0.61 at one site (Te_1) and 0.39 at the other (Te_2). As a result the $[H_2TeV_9O_{28}]^{3-}$ anion lacks crystallographic inversion symmetry. The protons could not be located directly from the diffraction data but here again their location can be inferred from bond valence sum calculations. The bond valence sums for O_{C3} and O_{C8} are 1.4 and significantly smaller than those of most of the other oxygen atoms in the anion and the ideal value of 2. The sums for two other oxygens, O_{C4} and O_{C7}, are also somewhat small at 1.6. These values strongly suggest that the protons are attached to these oxygen atoms. On a closer inspection, the values tell us more about the protonation sites. The two oxygens that have the lowest bond valence sums, O_{C3} and O_{C8}, are located on the side where the occupancy of the Te atom is higher at 0.61. Those that have a slightly higher value, O_{C4} and O_{C7}, are on the side where the occupancy of the Te atom is lower at 0.39. This probably suggests that the two protons of the $[H_2TeV_9O_{28}]^{3-}$ anion are actually attached to the O_C oxygens that are on the Te side, O_C(Te), and not those on the V side, O_C(V).

The results of DFT calculations support the discussion above. The calculations performed on the $[H_2TeV_9O_{28}]^{3-}$ anion that

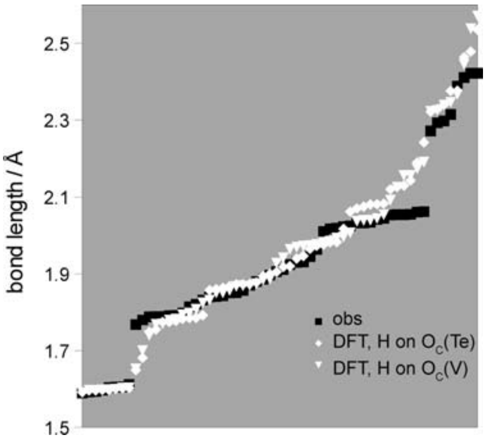
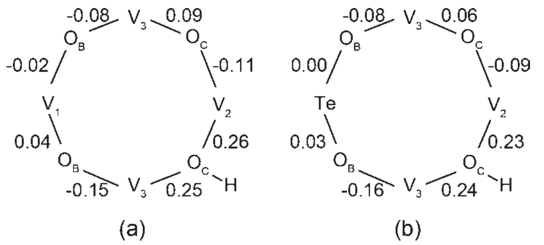


Figure 4. Comparison of observed and calculated bond lengths of the $[HTeV_9O_{28}]^{4-}$ anion.

Scheme 1



has the protons attached on a pair of diagonal O_C(Te) oxygens reproduced the observed bond lengths very well (Figure 3). In addition, two sets of calculations were performed on the $[HTeV_9O_{28}]^{4-}$ anion. The proton was assumed to be on an O_C(Te) in one set and on an O_C(V) in the other. Both reproduced experimental bond lengths very well (Figure 4). However, the total energy of the $[HTeV_9O_{28}]^{4-}$ anion that has a proton on an O_C(Te) oxygen was lower than that of the anion that is protonated at an O_C(V) oxygen by 0.215 eV or 20.7 kJ mol^{-1}. This value is comparable to the enthalpies of hydrogen bonds and explains why protonation sites of decavanadate in crystals are readily affected by hydrogen bonds.

Why does the proton favor O_C(Te) oxygens over O_C(V) oxygens? Klemperer's theory of bond length alternation gives us some clue.[36,47] Protonation of an O_C(Te) would be expected to lengthen the V−O bond to this oxygen atom and establish a pattern of trans bond length alternation in the eight-membered V_4O_4 ring to which this oxygen atom belongs. In fact, such a pattern is clearly visible if we compare the optimized structures of $[TeV_9O_{28}]^{5-}$ and $[HTeV_9O_{28}]^{4-}$ that is protonated at O_C(Te) [Scheme 1(a)]. Similarly, the charge would be expected to delocalize through the trans bond length alternation of the corresponding eight-membered ring if an O_C(V) oxygen is protonated. In this case, however, a Te atom is included in the ring. Octahedral TeO_6 is known to be relatively rigid, and Te−O bonds longer than 2.0 Å or shorter than 1.8 Å are extremely rare.[48,49] Thus, the Te atom would hinder the charge delocalization through the trans bond length alternation if it is included in the eight-membered ring. Again, comparison of the optimized structures of $[TeV_9O_{28}]^{5-}$ and $[HTeV_9O_{28}]^{4-}$ that are protonated at O_C(V) shows that this indeed is the case [Scheme 1(b)].

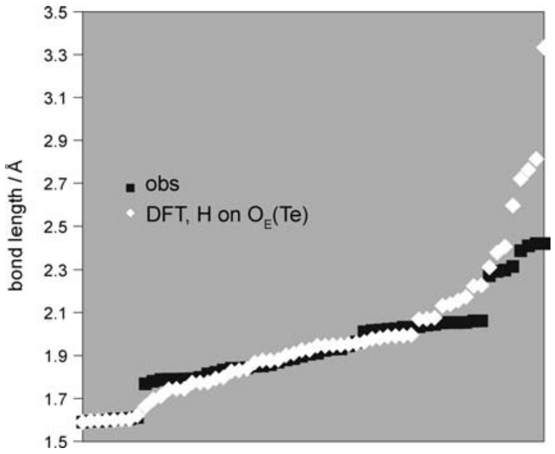


Figure 5. Comparison of observed and calculated bond lengths of the $[HTeV_9O_{28}]^{4-}$ anion.

It is possible that the rigidity of the TeO_6 octahedron is contributing to the preferred protonation at O_C(Te) by another mechanism. The VO_6 octahedra in general are known to be highly flexible, and the coordination octahedra around V_1 in $[V_{10}O_{28}]^{6-}$ are highly distorted with the V_1−O_B bonds bent significantly toward the inside of the anion. The O_B−V_1−O_B angle in $[V_{10}O_{28}]^{6-}$ is as narrow as 156°.[50] Such a drastic distortion is probably not possible for a TeO_6 unit, and displacement of a V_1 atom with a Te atom would make the distance between V_3 and the O_B atom bonded to Te longer. The trans influence of this longer V_3−O_B bond will make the V_3−O_C(V) shorter and the O_C(V) atom less basic. A close inspection of the optimized structure of $[TeV_9O_{28}]^{5-}$ suggested that this probably is the case. The V_3−O_C(V) bond in the optimized $[TeV_9O_{28}]^{5-}$ anion is roughly 0.04 Å shorter than the V_3−O_C bond of $[V_{10}O_{28}]^{6-}$, while the difference of the lengths of the V_3−O_C(Te) bond in $[TeV_9O_{28}]^{5-}$ and V_3−O_C bond of $[V_{10}O_{28}]^{6-}$ is only 0.01 Å and negligible.

It is worth noting that the protonation sites of $[HTeV_9O_{28}]^{4-}$ and $[H_2TeV_9O_{28}]^{3-}$ are different from those of $[H_2PtV_9O_{28}]^{5-}$. In the Pt compound oxygens that connect the Pt atom with one V atom, O_E, are protonated, not the O_C oxygens that bridge two V atoms.[44] We did some calculations on a $[HTeV_9O_{28}]^{4-}$ anion that has the proton attached to an O_E oxygen. Its total energy was 0.128 eV or 12.4 kJ mol^{-1} higher than that of the anion that has the proton on O_C(Te). Moreover, protonation at O_{E1} made the distance between V_{2A} and O_{E1} unreasonably long (3.334 Å). It also makes V_{2A}−O_{A1} (2.813 Å), V_{2B}−O_{A1} (2.763 Å), and V_{3A}−O_{B2} (2.721 Å) bonds extremely long and very different from those observed experimentally (Figure 5). The result means that protonation at O_{E1} would break the V_{2A}−O_{E1} bond and weaken some other bonds significantly. Such breaking and weakening of the bonds is likely to cause decomposition of the $[HTeV_9O_{28}]^{4-}$ anion.

Structural analysis of $[HTeV_9O_{28}]^{4-}$ alone did not allow us to unambiguously determine the protonation site of the vanadotellurate anion. However, by looking at the structure of $[H_2TeV_9O_{28}]^{3-}$ together with that of $[HTeV_9O_{28}]^{4-}$, we were able to conclude unequivocally that O_C(Te) oxygens are protonated in both cases. The DFT calculations supported this conclusion. The DFT calculations also revealed that the difference of basicity between different surface oxygens of the decavanadate framework is comparable to the energy of hydrogen bonds, giving us some insights into why the protonation sites of decavanadate are readily affected by hydrogen bonds. In addition, the DFT results suggested that the $[TeV_9O_{28}]^{5-}$ anion would fall apart if $O_E(Te)$ is protonated, unlike the $[H_2PtV_9O_{28}]^{5-}$ anion that has an analogous structure. The current results, together with the report of $[H_2PtV_9O_{28}]^{5-}$, indicate the existence of a whole series of heterovanadates of the decavanadate structure.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystallographic data for $TBA_4[HTeV_9O_{28}]\cdot 2CH_3CN$ and $TBA_3[H_2TeV_9O_{28}]$, and energies and coordinates of the optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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