

## Notes

### Synthesis and crystal structure of a triprotonated decavanadate, $[(C_6H_5CH_2)(CH_3)_3N]_3[H_3V_{10}O_{28}].3H_2O$

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The title compound,  $[(C_6H_5CH_2)(CH_3)_3N]_3[H_3V_{10}O_{28}].3H_2O$ , has been obtained by treating  $V_2O_5$  with  $H_2O_2$  in presence of benzyltrimethylammonium chloride and characterised. The crystal structure of the compound has been determined. The protonation sites on the cage surface of the decavanadate  $[H_3V_{10}O_{28}]^{3-}$  anion have been clearly identified. Intermolecular O-H...O hydrogen bonds involving the surface protons leads to the formation of an unprecedented zigzag chain of the  $[H_3V_{10}O_{28}]^{3-}$  anions.

**Keywords:** Coordination chemistry, Supramolecular chemistry, Polyoxometallates, Triprotonated decavanadate, Protonated compounds, Hydrogen-bonded chains, X-ray diffraction, Crystal structure, Vanadium

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Polyoxometalates (POMs) can either donate or accept electrons, and hence are useful acid and oxidation catalysts in various reactions. Moreover, their catalytic features can be controlled at a molecular level. In view of their attractive properties, polyoxometalates are economically and environmentally important in both academic as well as industrial research<sup>1</sup>. Environmentally benign oxidants including molecular oxygen or  $H_2O_2$  can be used as the oxidizing agents in conjunction with POMs. The ion-pair complexes of oligomeric anions and phase-transfer cations have been investigated as catalysts as well as stoichiometric reagents in oxidation reactions. Vanadium(V) POMs are dominated by the decavanadate anion,  $[V_{10}O_{28}]^{6-}$ , which is a stable species in acidic aqueous solutions and has been known for long to undergo protonation in multiple steps depending on the acidity of the solution used in its preparation. In the acidic pH range of 2-6, differently protonated decavanadate ions,  $[H_nV_{10}O_{28}]^{(6-n)-}$ , are formed. Tetraalkylammonium cations have been utilized for the construction of hydrogen-bonded aggregates of protonated

decavanadate anions in the solid state<sup>2</sup>. Different cations have been shown to produce different types of hydrogen-bonded self-assemblies. These studies have also demonstrated that the degree of protonation in the crystalline state is dependent on the size of the counter cations.

Crystal structure of the decavanadate  $[V_{10}O_{28}]^{6-}$  is well known<sup>3,4</sup>. However, crystal structures of only a limited number of protonated decavanadate species,  $[H_nV_{10}O_{28}]^{(6-n)-}$ , where  $n = 2, 3$  or  $4$ , have been reported<sup>5-7</sup>. The triprotonated decavanadate anion has been identified as a salt of quaternary ammonium and phosphonium cations. It has been found that the hydroxyl groups on the surface of the protonated oxovanadium cage are involved in intercage hydrogen bonding. In all known cases these hydrogen bonds lead to dimerization of the triprotonated decavanadate anions. However, the number of hydrogen bonds as well as the nature of the dimer formed appears to be dependent on the counter-cation used. In connection with our interests on the use of vanadium based reagents in oxidation reactions under phase transfer conditions, we have been interested in the protonated decavanadate species. Herein we report the results of studies including crystal structure analysis on  $[(C_6H_5CH_2)(CH_3)_3N]_3[H_3V_{10}O_{28}].3H_2O$  wherein the  $[H_3V_{10}O_{28}]^{3-}$  ions display a novel hydrogen-bonded chain structure.

### Experimental

$V_2O_5$  and 30%  $H_2O_2$  were obtained from E. Merck (India).

Infrared spectra in the mid-IR region (4000-450  $cm^{-1}$ ) were recorded on a Perkin-Elmer RX1 FTIR spectrophotometer for both KBr pellet and nujol mull. <sup>1</sup>H NMR spectrum was recorded in Bruker ACF 200 MHz spectrometers in DMSO. Thermogravimetric data were obtained using a Netzsch STA 409PC TG-DTA instrument in the temperature range ambient to 210°C at the heating rate of 10°C  $min^{-1}$ . Crystal structure analyses are based on single crystal X-ray diffraction data obtained using a Bruker CCD instrument.

### Preparation of $[(C_6H_5CH_2)(CH_3)_3N]_3[H_3V_{10}O_{28}].3H_2O$

Vanadium pentoxide  $V_2O_5$  (0.587 g, 3.24 mmol) was added slowly to the required amount of 30%

hydrogen peroxide to make a saturated solution. The colour of the solution became reddish brown and the pH of the solution was recorded to be 2.2. The resulting solution was filtered through Whatman No. 1 filter paper. This filtrate was slowly added to a solution of 0.320 g benzyltrimethylammonium chloride (1.72 mmol) in 20 mL of deionized water with continuous stirring. A pale yellow coloured precipitate appeared. The precipitate was recovered by filtration under suction. It was then dried under vacuum over fused CaCl<sub>2</sub> and recrystallized from water. Yield = 75%. IR data (KBr disc) cm<sup>-1</sup>: 3366 (symmetric O-H stretching); 2989 and 1471 (symmetric >CH<sub>2</sub>, -CH<sub>3</sub> stretching); 1628 (conjugated cyclic system); 972 (V-O vibration); 838, 777 and 729 (asymmetric vibrations of V-O-V bridge); 605 (symmetric vibration of V-O-V bridge). <sup>1</sup>H NMR data (DMSO-D<sub>6</sub>, 200 MHz, TMS) δ: 7.6 (s, 5H), 4.6 (s, 2H), 3.0 (s, 9H). TG weight loss (30-210°C): ~3.8%.

#### Molecular and crystal structure of the compound

[(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)(CH<sub>3</sub>)<sub>3</sub>N]<sub>3</sub>[H<sub>3</sub>V<sub>10</sub>O<sub>28</sub>].3H<sub>2</sub>O was determined by single crystal X-ray diffraction technique. To obtain the compound in crystalline form, the reaction product was dissolved in deionized water and the resulting orange-yellow solution gave well formed crystals of the title compound upon standing. A crystal of suitable size was mounted on glass fibre for intensity data collection at room temperature using graphite monochromatized Mo-Kα radiation on a Bruker SMART CCD diffractometer. The crystal was found to be stable against thermal/oxidative decomposition and X-radiation induced decay. The structure was solved by direct method (SHELXS) and refined by full-matrix least squares techniques (SHELXL) with SHELX-97 using the WinGX platform available for personal computers<sup>8,9</sup>. The hydrogen atoms in the anionic part were clearly located in the difference Fourier map and refined with isotropic atomic displacement parameters. The hydrogen atoms belonging to the cations were placed at calculated positions using available options of SHELXL-97 and were refined using a riding model by giving thermal parameters equivalent to either 1.5 (methyl hydrogen atoms) or 1.2 (all other hydrogen atoms) times the thermal parameter of the carbon atoms to which they were attached. All other atoms were refined with anisotropic displacement parameters. The hydrogen atoms for the three water molecules present as solvent of crystallization could

not be located. The crystallographic data are presented in Table 1. The structural diagrams were drawn using ORTEP-III<sup>10</sup> for Windows<sup>11</sup>, PLUTON<sup>12</sup>, and Mercury<sup>13</sup>.

## Results and discussion

### Synthesis and properties

The title compound, [(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)(CH<sub>3</sub>)<sub>3</sub>N]<sub>3</sub>[H<sub>3</sub>V<sub>10</sub>O<sub>28</sub>].3H<sub>2</sub>O, has been obtained in 75% yield by reacting V<sub>2</sub>O<sub>5</sub> with H<sub>2</sub>O<sub>2</sub> in presence of benzyl-

Table 1—Crystal data and structure refinement for [(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)(CH<sub>3</sub>)<sub>3</sub>N]<sub>3</sub>[H<sub>3</sub>V<sub>10</sub>O<sub>28</sub>].3H<sub>2</sub>O

Identification code	H3V10O28	
Empirical formula	C30 H51 N3 O31 V10	
Formula weight	1459.14	
Temperature	293(2) K	
Wavelength	0.71073 Å	
(Mo-Kα)		
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 13.1493(3)$ Å	$\alpha = 70.7420(10)^\circ$
	$b = 13.5237(3)$ Å	$\beta = 83.4330(10)^\circ$
	$c = 15.2264(3)$ Å	$\gamma = 84.1900(10)^\circ$
<i>V</i>	2533.55(9) Å <sup>3</sup>	
<i>Z</i>	2	
Density (calculated)	1.913 g cm <sup>-3</sup>	
Absorption coefficient	1.851 mm <sup>-1</sup>	
F(000)	1460	
Crystal size	0.48 × 0.30 × 0.15 mm <sup>3</sup>	
Theta range for data collection	1.56 to 27.92°	
Index ranges	-17 < <i>h</i> < 17, -17 < <i>k</i> < 17, -19 < <i>l</i> < 19	
Reflections collected	38322	
Independent reflections	11734 [R(int) = 0.0233]	
Completeness to $\theta = 27.92^\circ$	96.9 %	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	11734 / 0 / 679	
Goodness-of-fit on F <sup>2</sup>	1.033	
Final R indices [I > 2σ(I)]	R1 = 0.0292, wR2 = 0.0821	
R indices (all data)	R1 = 0.0377, wR2 = 0.0884	
Largest diff. peak and hole	0.732 and -0.446 e.Å <sup>-3</sup>	

\*R and R<sub>w</sub> values are for all unique and observed data with F<sub>o</sub> ≥ 4σ(F<sub>o</sub>); R = Σ||F<sub>o</sub> - |F<sub>c</sub>|| / Σ|F<sub>o</sub>|; R<sub>w</sub> = {Σ[w(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)<sup>2</sup>] / Σ[w(F<sub>o</sub><sup>2</sup>)<sup>2</sup>]}<sup>1/2</sup> where w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (aP)<sup>2</sup> + bP] with P = [2F<sub>c</sub><sup>2</sup> + Max(F<sub>o</sub><sup>2</sup>, 0)]/3.

trimethylammonium chloride in an aqueous medium. Salts of the triprotonated decavanadate anion have earlier been prepared in nonaqueous<sup>14</sup> as well as aqueous media<sup>15</sup>. The aqueous procedure has been applied further via addition of quaternary ammonium and phosphonium salts to acidified aqueous  $\text{Na}_3\text{VO}_4$  to obtain products in 20-35% yield. The compound  $[\text{CuCl}(\text{phen})_2]_3[\text{H}_3\text{V}_{10}\text{O}_{28}] \cdot 7\text{H}_2\text{O}$ , on the other hand, was prepared by reaction of an acidic aqueous solution of  $\text{KVO}_3$  with an aqueous solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  containing 1,10-phenanthroline (phen) and  $\text{KCl}$ <sup>16</sup>. The independent procedure adopted by us to form  $[\text{H}_3\text{V}_{10}\text{O}_{28}]^{3-}$  is very simple and clearly quite productive. Considering that no oxidation of vanadium in  $\text{V}_2\text{O}_5$  is called for to generate  $[\text{H}_3\text{V}_{10}\text{O}_{28}]^{3-}$ , the role of  $\text{H}_2\text{O}_2$  remains uncertain; however, its presence is believed to induce the protonation under the reaction conditions used by us. In spite of the large size of the cation, this species is moderately soluble in water.

The presence of three molecules of water as solvent of crystallization has been confirmed by thermogravimetric (TG) studies. The dehydration curve of  $[(\text{C}_6\text{H}_5\text{CH}_2)(\text{CH}_3)_3\text{N}]_3[\text{H}_3\text{V}_{10}\text{O}_{28}] \cdot 3\text{H}_2\text{O}$  shows (please see supporting information) that the

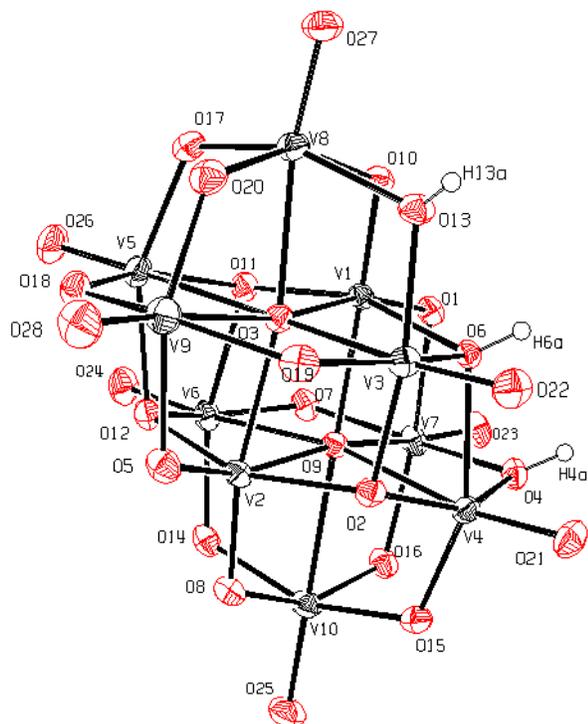


Fig. 1—ORTEP diagram of the complex part of  $[\text{H}_3\text{V}_{10}\text{O}_{28}]^{3-}$  anion.

observed weight loss of 3.82% in the 30-210°C range corresponds very well with the expected loss of all the water molecules present in  $[(\text{C}_6\text{H}_5\text{CH}_2)(\text{CH}_3)_3\text{N}]_3[\text{H}_3\text{V}_{10}\text{O}_{28}] \cdot 3\text{H}_2\text{O}$  (calc. wt. loss = 3.72%). Furthermore, the dehydration weight loss as given by TG data is consistent with the composition obtained from single crystal X-ray structure analysis (as discussed below).

Crystal structure of  $[(\text{C}_6\text{H}_5\text{CH}_2)(\text{CH}_3)_3\text{N}]_3[\text{H}_3\text{V}_{10}\text{O}_{28}] \cdot 3\text{H}_2\text{O}$  has been determined by single crystal X-ray diffraction. It was found to crystallize in the triclinic space group  $\bar{P}1$ . The asymmetric unit in the crystal structure consists of one formula unit. The structure of the  $[\text{H}_3\text{V}_{10}\text{O}_{28}]^{3-}$  anion is shown in Fig. 1. The crystal packing diagram is depicted in Fig. 2.

The crystallographically determined structure of the anionic  $[\text{H}_3\text{V}_{10}\text{O}_{28}]^{3-}$  part in  $[(\text{C}_6\text{H}_5\text{CH}_2)(\text{CH}_3)_3\text{N}]_3[\text{H}_3\text{V}_{10}\text{O}_{28}] \cdot 3\text{H}_2\text{O}$  consists of a  $[\text{V}_{10}\text{O}_{28}]^{6-}$  cage<sup>3</sup> having three of its bridging oxo anions protonated. All ten V(V) centres in the trianion,  $[\text{H}_3\text{V}_{10}\text{O}_{28}]^{3-}$  are six-coordinate and distorted octahedral. The distorted nature of the  $\text{VO}_6$  octahedra can be seen from the V-O bond distances listed in Table 2. The V-O-V and O-V-O angles (provided as supporting information) also corroborate this fact. By taking the V3 atom in (Fig. 1 & Table 2) as an example, it may be stated that all six observed V-O distances are different. The distances range from 1.594(1) Å to 2.252(1) Å. Such

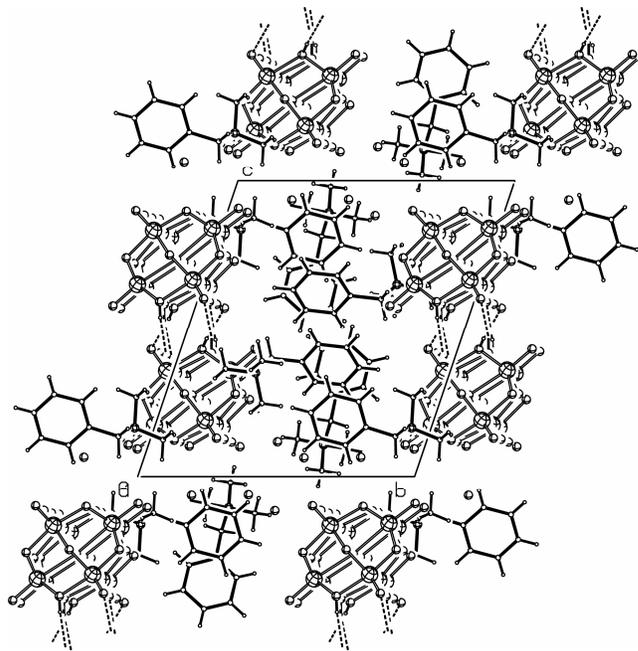


Fig. 2—Crystal packing diagram for  $[(\text{C}_6\text{H}_5\text{CH}_2)(\text{CH}_3)_3\text{N}]_3[\text{H}_3\text{V}_{10}\text{O}_{28}] \cdot 3\text{H}_2\text{O}$ .

Table 2—Various types of V–O bonds [Å] in [(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)(CH<sub>3</sub>)<sub>3</sub>N]<sub>3</sub>[H<sub>3</sub>V<sub>10</sub>O<sub>28</sub>].3H<sub>2</sub>O.

<i>O<sub>terminal</sub> – V</i>					
V(4)-O(21)	1.5911(15)	V(3)-O(22)	1.5936(15)	V(7)-O(23)	1.6100(14)
V(6)-O(24)	1.5945(15)	V(10)-O(25)	1.5992(15)	V(5)-O(26)	1.5959(16)
V(8)-O(27)	1.6077(15)	V(9)-O(28)	1.5966(16)		
<i>μ-O – V</i>					
V(1)-O(1)	1.7094(13)	V(7)-O(1)	2.0339(14)	V(9)-O(5)	2.0250(15)
V(2)-O(5)	1.6896(14)	V(7)-O(7)	1.7791(14)	V(6)-O(7)	1.8699(14)
V(10)-O(8)	2.0369(14)	V(2)-O(8)	1.6777(14)	V(1)-O(10)	1.6821(14)
V(8)-O(10)	2.0355(14)	V(10)-O(14)	1.8518(15)	V(6)-O(10)	1.7964(15)
V(4)-O(15)	1.7327(14)	V(10)-O(15)	1.9347(15)	V(7)-O(16)	1.8385(14)
V(10)-O(16)	1.8133(14)	V(8)-O(17)	1.7844(15)	V(5)-O(17)	1.8641(15)
V(5)-O(18)	1.8032(15)	V(9)-O(18)	1.8551(16)	V(3)-O(19)	1.7393(15)
V(9)-O(19)	1.9478(16)	V(8)-O(20)	1.8360(15)	V(9)-O(20)	1.8088(15)
<i>μ<sub>3</sub>-O – V</i>					
V(2)-O(2)	1.9625(13)	V(3)-O(2)	1.9235(13)	V(4)-O(2)	1.9378(13)
V(1)-O(11)	1.8282(13)	V(5)-O(11)	2.0114(14)	V(6)-O(11)	2.0429(14)
V(2)-O(12)	1.9109(14)	V(5)-O(12)	1.9792(14)	V(6)-O(12)	1.9651(14)
<i>μ<sub>6</sub>-O – V</i>					
V(1)-O(3)	2.0831(13)	V(2)-O(3)	2.1408(13)	V(3)-O(3)	2.2522(13)
V(5)-O(3)	2.3280(13)	V(8)-O(3)	2.2774(13)	V(9)-O(3)	2.3468(13)
V(1)-O(9)	2.0879(13)	V(2)-O(9)	2.1174(13)	V(6)-O(9)	2.3123(13)
V(7)-O(9)	2.2913(13)	V(10)-O(9)	2.3699(13)	V(4)-O(9)	2.2556(13)
<i>μ-OH – V</i>					
V(4)-O(4)	1.9348(15)	V(7)-O(4)	1.9920(15)	V(3)-O(13)	1.9350(15)
V(8)-O(13)	2.0133(16)				
<i>μ<sub>3</sub>-OH – V</i>					
V(1)-O(6)	2.0749(14)	V(3)-O(6)	2.1211(14)	V(4)-O(6)	2.1106(14)

a wide range in the V3-O distances is due to the fact that the oxygen atoms are all geometrically different – O2, O3, O6, O13, O19, O22 are (μ<sub>3</sub>-O), (μ<sub>6</sub>-O), (μ<sub>3</sub>-OH), (μ-OH), (μ-O), (η<sup>1</sup>-O) respectively. Clearly the oxide and hydroxide anions present as ligands in the complex anion are present in a variety of coordination modes. This is quite remarkable from a coordination chemistry point of view since in six-coordinate complexes, the metal centre is seldom connected to six different ligands. The structure of triprotonated decavanadate cage indeed presents a medley of eight monodentate O<sup>2-</sup>, two μ<sub>6</sub>-O<sup>2-</sup>, three μ<sub>3</sub>-O<sup>2-</sup>, twelve μ-O<sup>2-</sup>, two μ-OH, and one μ<sub>3</sub>-OH ligands in the oxoanion. The V-O distances are longest when the concerned V-O distance corresponds to a bond of V with a μ<sub>6</sub>-O<sup>2-</sup> ligand (O3 and O9). Bonds for the hydroxyl groups are also relatively longer. The shortest V-O distances of ~1.6 Å for the monodentate O<sup>2-</sup> ligands suggest that these bonds have considerable double bond character. All the

V-O distances found in our compound are comparable with published literature values for the decavanadate and protonated decavanadate anions crystallized as salts of a various cations.

The crystal packing diagram shown in Fig. 2 suggests that the organic cations do not have any significant interactions with the anions. The water molecules present as solvent of crystallization may be hydrogen bonded to the anions but since the protons belonging to these molecules could not be located, such interactions have not been shown in Fig. 2. Intermolecular hydrogen bonds between the triprotonated anions are, however, clearly visible through the crystal structure analysis. The hydrogen bond parameters in our crystal structure are given in Table 3. Three distinct hydrogen bonds involving the three protons on the polyoxovanadate cage are observed. As suggested by O...O distances of 2.728(2), 2.744(2) and 2.867(2) Å and O-H...O angles of 174(3), 164(3) and 175(3)° respectively, the

Table 3—Hydrogen bonds for  $[(C_6H_5CH_2)(CH_3)_3N]_3[H_3V_{10}O_{28}]\cdot 3H_2O$ 

D-H...A	$d(D-H)$ (Å)	$d(H...A)$ (Å)	$d(D...A)$ (Å)	$\angle(DHA)$ (°)
O(4)-H(4A)...O(1)#1	0.78(3)	1.95(3)	2.728(2)	174(3)
O(6)-H(6A)...O(23)#1	0.77(3)	1.99(3)	2.744(2)	164(3)
O(13)-H(13A)...O(27)#2	0.72(3)	2.15(3)	2.867(2)	175(3)

Symmetry transformations used to generate equivalent atoms: #1  $-x+1, -y, -z+1$ ; #2  $-x+2, -y, -z+1$

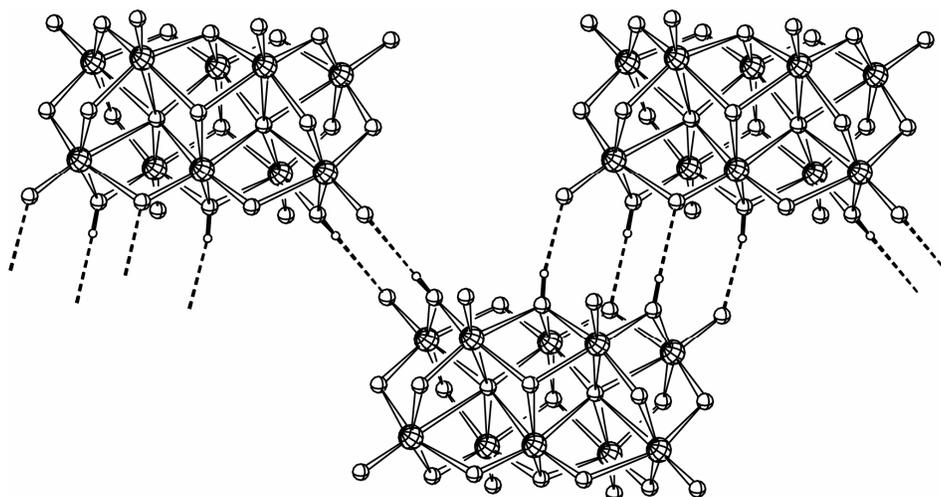


Fig. 3—A portion of the hydrogen bonded chain of triprotonated decavanadate ions in the crystal structure of the compound  $[(C_6H_5CH_2)(CH_3)_3N]_3[H_3V_{10}O_{28}]\cdot 3H_2O$ .

hydrogen bonds are moderately strong. As a result of the presence of these hydrogen bonds the  $[H_3V_{10}O_{28}]^{3-}$  anions are joined together to form zigzag chains running along the crystallographic  $a$  direction (Figs 2 and 3).

The triprotonated decavanadate anions have been identified in several salts and their structures have been determined in the crystalline state<sup>2,5,6,16</sup>. The most prominent feature of these hydrogen-bonded aggregates has been the dimerization of the  $[H_3V_{10}O_{28}]^{3-}$  anions. In all known cases the interanionic hydrogen bonds have been found to be responsible for dimerization. The  $([H_3V_{10}O_{28}]^{3-})_2$  dimer is found in its  $[(C_6H_5)_4P]^+$  salt of the triprotonated decavanadate<sup>5</sup>. The protonation sites in this structure were found to be same as in our species, but unlike in the present case, six hydrogen bonds were found to join two triprotonated decavanadates into a dimer. In the compound  $[(n-C_3H_7)_4N]_3[H_3V_{10}O_{28}]$  reported by Nakamura *et al.*<sup>2</sup> the protonation was found to lead to the formation of vertical dimers involving bifurcated hydrogen bonds.

On the other hand,  $[(n-C_4H_9)_4N]_3[H_3V_{10}O_{28}]$  was shown to form a horizontal dimer. These two structures also form as a result of the formation of six intermolecular hydrogen bonds. Using a complex cation involving  $Cu^{2+}$  yet another dimeric species was obtained by Rakovský *et al.*<sup>16</sup>. In  $[CuCl(phen)_2]_3[H_3V_{10}O_{28}]\cdot 7H_2O$  they found the presence of six hydrogen bonds which dimerize the triprotonated trianions.

Although the above results appear to suggest that there is an influence of the cation on the structure type, in all cases only dimeric species have been found to form in the solid state of the triprotonated decavanadate species. In contrast, it is rather interesting to find that in the present case we have found each triprotonated decavanadate anion in  $[(C_6H_5CH_2)(CH_3)_3N]_3[H_3V_{10}O_{28}]\cdot 3H_2O$  to be linked by four intermolecular hydrogen bonds to one  $[H_3V_{10}O_{28}]^{3-}$  on one side and by two intermolecular hydrogen bonds to another  $[H_3V_{10}O_{28}]^{3-}$  unit on the other side to form a zigzag chain consisting of three  $[H_3V_{10}O_{28}]^{3-}$  anions as the repeating unit (Fig. 3).

The supramolecular structure obtained by us is thus quite novel because for the first time we have been able to observe the formation of infinite chains by the triprotonated anion in the solid state. The chain structure found by us for  $[\text{H}_3\text{V}_{10}\text{O}_{28}]^{3-}$  is also different from the quadruply hydrogen-bonded chain structure of the previously identified anion  $[\text{H}_4\text{V}_{10}\text{O}_{28}]^{2-}$  (refs 2, 18). The role of cations in determining the supramolecular structure of the triprotonated decavanadate trianion is thus clearly demonstrated by the present work.

In this study, a triprotonated decavanadate species has been synthesised and characterised. X-ray crystallographic studies on the triprotonated decavanadate species having benzyl trimethylammonium,  $[(\text{C}_6\text{H}_5\text{CH}_2)(\text{CH}_3)_3\text{N}]^+$  as the cation show that each  $[\text{H}_3\text{V}_{10}\text{O}_{28}]^{3-}$  anion forms six hydrogen bonds to two other adjacent anions in a (4+2) fashion. The O-H...O hydrogen bonds between the polyoxovanadate cages lead to the formation of unprecedented zigzag chains for  $[(\text{C}_6\text{H}_5\text{CH}_2)(\text{CH}_3)_3\text{N}]_3[\text{H}_3\text{V}_{10}\text{O}_{28}]$  in the crystalline state. The present result confirms that the crystal structure of the protonated decavanadate species is controlled to a large extent by the cations used.

#### Acknowledgement

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#### Supplementary Data

CCDC 724723 contains the crystallographic data for this paper in CIF format. Copies of this information may be obtained free of charge from

<http://www.ccdc.cam.ac.uk>) or from the corresponding author (BKD). TG curves may also be obtained from the authors on request.

#### References

- Hill C L, *Chem Rev*, 98 (1998) 1.
- Nakamura S & Ozeki T, *J Chem Soc, Dalton Trans*, (2001) 472.
- Pacigová S, Rakovsky E, Sivák M & Zák Z, *Acta Cryst, C63* (2007) m419.
- Zhao Q, Du L & Fang R, *Acta Cryst*, E62 (2006) m360.
- Day V W, Klemperer W G & Moltbie, D J, *J Am Chem Soc*, 109 (1987) 2991.
- Arrieta J M, Arnaiz A, Lorente L & Santiago C, *Acta Cryst*, C44 (1988) 1004.
- Duraisamy T, Ramanan A & Vittal J J, *Cryst Eng*, 3 (2000) 237.
- Sheldrick G M, *Acta Cryst*, A64 (2008) 112.
- Farrugia L J, *J Appl Cryst*, 32 (1999) 837.
- Burnett M N & Johnson C K, *ORTEP-III: Oak Ridge Thermal Ellipsoid Plot for Crystal Structure Illustrations, ORNL Report*, (1996) 6895.
- Farrugia L J, *J Appl Cryst*, 30 (1997) 565.
- Spek A L, *Acta Cryst*, A46 (1990) C-34.
- Macrae C F, Edgington P R, McCabe P, Pidcock E, Shields G P, Taylor R, Towler M & van de Streek J, *J Appl Cryst*, 39 (2006) 453.
- Fuchs J, Mahjour S & Palm R, *Z Naturforsch*, 31b (1976) 544.
- Corigliano F & DiPasquale S, *Inorg Chim Acta*, 12 (1975) 99.
- Rakovský E, Joniaková D, Gyepes R, Schwendt & PMička Z, *Cryst Res Technol*, 40 (2005) 719.
- Santiago C, Arnaiz A, Lorente L, Arrieta J M & Germain G, *Acta Cryst*, C44 (1988) 239.
- Wang W, Zeng F, Wang X & Tan M, *Polyhedron*, 15 (1996) 265.