

# Structural studies of decavanadate compounds with organic molecules and inorganic ions in their crystal packing

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## Abstract

The formation of decavanadates containing amine counter-ions is explored to get a better insight into the resulting crystal packing. From mixtures containing the Schiff base  $H_2(SO_3\text{-sal})_2en$  and vanadate, two different compounds containing decavanadate units have been characterised by X-ray diffraction. The structure of **1** consists of  $[V_{10}O_{28}]^{6-}$  monomers united by  $K^+$ , ethylenediamine cations and  $H_2O$  molecules, which act as bridging atoms between the layers, forming a three-dimensional array. The structure of **2** contains vanadium triprotonated decavanadate anions,  $[H_3V_{10}O_{28}]^{3-}$ , in one-dimensional vertical chains, bonded by interdecavanadate hydrogen bonds. The interchain region is populated by  $(H_2en)^{2+}$  cations and  $H_2O$  molecules, which form a network of hydrogen bonds. From the filtrate solution of the reaction mixture containing  $V^{IV}OSO_4$ , D,L-diaminopropionic acid and salicylaldehyde, which also contained triethylamine, a diprotonated decavanadate **3** was obtained. Compound **3** consists of decavanadate vertical dimers, surrounded by triethylammonium cations that preclude the interaction between the dimers. Bond valence calculations were used to confirm the degree of protonation of the decavanadate anions.

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**Keywords:** Decavanadates; Crystal structure; Supramolecular array; Hydrogen bonds

## 1. Introduction

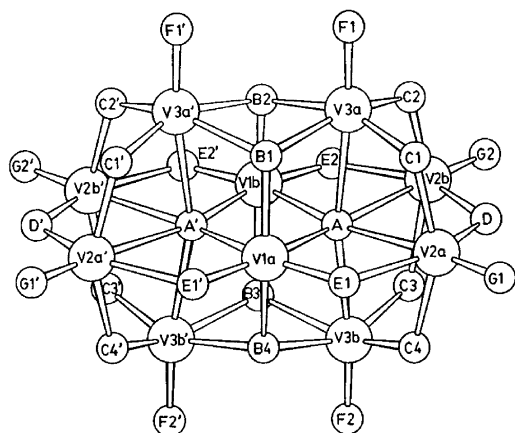
Polyoxometalates (POMs) have been attracting considerable attention due to their possible application in many fields such as catalysis, biology, medicine and materials science [1–4]. The variety of its structural, catalytic and magnetic properties might lead to the development of new materials with novel properties. The physical and chemical properties of polyoxometalates are mainly based on their size, mass, electron- and proton-transfer/storage abilities, thermal stability, lability of “lattice oxygen” and high Brønsted acidity.

The vanadium polyoxometalates have been extensively studied in solution and in the solid state [5–7]. In solution, the acidification under pH 6 leads to the formation of yellow solutions containing the decavanadate core,  $[V_{10}O_{28}]$ , which can be found in several protonation states, e.g.,  $H_2V_{10}O_{28}^{4-}$ ,  $HV_{10}O_{28}^{5-}$  and  $V_{10}O_{28}^{6-}$  [8]. The structure of the decavanadate core is well established and consists of an arrangement of ten edge-shared  $VO_6$  octahedra with approximate  $D_{2h}$  symmetry (see Scheme 1). The protonation sites have been determined in several cases mainly by bond valence calculations, since the direct determination of the location of the hydrogen atoms by X-ray diffraction requires data of sufficient quality. Due to their higher basicity when compared to the terminal oxygens, the doubly and triply bonded oxygens (Ob and Oc, see Scheme 1) are those more susceptible to protonation.

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Scheme 1. Structure of a decavanadate, with the atom labelling scheme.

In the solid state the protons of the polyoxometalate crystals are important in defining the crystal packing through the H-bonds, as the oxygen atoms can act as proton acceptors or donors. The intermolecular interactions between the different units establish reliable connections, which determine the supramolecular structure and can have the origin in Coulombic, van der Waals forces, H-bonds, etc. [1]. These are in general still weak enough to enable the reversible decomposition of the primary building units or the re-organisation into different polymorphisms. The predictable self-organisation of molecules into one- two- or three-dimensional frameworks is of utmost importance in crystal engineering [1]. For such structures, hydrogen bonding can act as supramolecular cement.

Recently, Ferreira da Silva *et al.* [7] published a survey concerning the donor–acceptor intermolecular interactions in decavanadate anions, and systematised the solid-state supramolecular motifs. Coulombic interactions play an important role when the decavanadates are unprotonated and the cations are small. As they become protonated, the van der Waals forces and H-bonding interactions become more important, leading to four main supramolecular motifs: monomers, dimers, one- and two-dimensional arrays. The role of the cations and solvent molecules is determinant: small, spherical cations generally favour monomers and large linear cations favour one-dimensional arrays; the solvent, particularly water, due to its high H-bond capacity, is also important in the observed supramolecular motifs [7,9,10].

POMs have also been investigated as compounds of pharmaceutical interest, namely as antiviral and anticancer agents, and biological action. In this context, the interaction of POMs with the enzymes and cellular membranes is a relevant theme. Vanadate oligomers have also been studied [11,12], namely its effect on the

activity of the sarcoplasmic reticulum  $\text{Ca}^{2+}$  pump [13] and its interaction with myosin [14,15].

Therefore, the study of polyoxovanadates containing organic molecules is important, particularly the role of the organic cations in the structure of the decavanadates and how the organic moiety and the decavanadate units interact. In this work, ethylenediamine and triethylammonium are the organic molecules, and  $\text{K}^+$  the inorganic ion that binds the decavanadate anions to form one- two- and three-dimensional solid structures. We investigate the protonation of the decavanadate anions, the network of H-bonds and the assembly patterns constructed by the H-bonding.

## 2. Experimental

### 2.1. $\text{Na}_2\text{H}_2(\text{SO}_3\text{-sal})_2\text{en}$

The Schiff base was prepared according to a literature procedure [16] ( $\text{SO}_3\text{-sal}$  = salicylaldehyde-5-sulfonate). Yield: 87%. *Anal. Calc.* for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_8\text{S}_2\text{Na}_2$ : C, 40.7; H, 3.0; N, 5.9; S, 13.4. Found: C, 40.68; H, 2.99; N, 5.93, S, 13.57%.

### 2.2. $(\text{H}_2\text{en})_2\text{K}_2[\text{V}_{10}\text{O}_{28}] \cdot 4\text{H}_2\text{O}$ (1)

The vanadate stock solution was prepared by dissolving  $\text{NaVO}_3$  in KOH solution of known molarity. The ligand  $\text{Na}_2\text{H}_2(\text{SO}_3\text{-sal})_2\text{en}$  (0.17 g, 0.36 mmol) was dissolved in water (5 mL) and 30 mL of the aqueous vanadate solution (0.012 M) was added. The pH was set to  $\sim 5$  by addition of HCl *conc.* The colour of the solution changed from yellow to green. The solution was stored at  $\sim 5^\circ\text{C}$  for two days. Yellow crystals were collected and characterised by X-ray diffraction.

### 2.3. $(\text{H}_2\text{en})_3(\text{en})[\text{H}_3\text{V}_{10}\text{O}_{28}]_2 \cdot 7\text{H}_2\text{O}$ (2)

The crystals were obtained by a similar procedure as 1 but at pH  $\sim 4$ . *Anal. Calc.* for  $\text{C}_8\text{H}_{58}\text{N}_8\text{O}_{63}\text{V}_{20}$ : C, 4.1; H, 2.4; N, 5.0. Found: C, 4.19; H, 2.55; N, 5.0%.

### 2.4. $[(\text{C}_2\text{H}_5)_3\text{NH}]_4[\text{H}_2\text{V}_{10}\text{O}_{28}]$ (3)

The crystals were obtained from a methanolic solution containing D,L-diaminopropionic acid (1 mmol, 0.14 g), salicylaldehyde (2.2 mmol, 0.23 mL), vanadyl sulfate (1 mmol, 0.2531 g) and triethylamine (used to set the pH at  $\sim 5$ ). The solution was kept at ambient temperature and a few days later brown crystals were collected and characterised by X-ray diffraction. *Anal. Calc.* for  $\text{C}_{24}\text{H}_{66}\text{N}_4\text{O}_{28}\text{V}_{10}$ : C, 22.65; H, 5.8; N, 4.4; C/N = 5.18. Found: C, 21.07; H, 4.86; N, 4.07;

C/N = 5.15%; therefore, the product analysed was contaminated by some other (possibly inorganic) material.

## 2.5. FTIR

IR spectra were recorded on a BioRad FTS 3000 MX FTIR spectrometer and a Bruker Vector 22 Spectrophotometer (in La Coruña).

## 2.6. X-ray crystal structure determinations

Three-dimensional X-ray data were collected on a Bruker SMART 1000 CCD diffractometer by the  $\phi$ - $\omega$  scan method. Data were collected at room temperature. Reflections were measured from a hemisphere of data collected of frames, each covering  $0.3^\circ$  in  $\Omega$ . Of the reflections measured, 4906 for **1**, 14 985 for **2** and 30642 for **3**, all of which were corrected for Lorentz and polarisation effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections, 2914, 8750 and 7830 independent reflections exceeded the significance level  $|F|/\sum(|F|) > 4.0$ , respectively. Complex scattering factors were taken from the program package SHELXTL [17]. The structures were solved by direct methods and refined by full-matrix least-squares methods on  $F^2$ . The hydrogen atoms were included in calculated positions and refined by using a riding mode, except the hydrogen

atoms H(1H), H(2H), H(1N), H(2N), H(3N), H(3H), H(4H) H(4N), H(5N) and H(6N) for **1**, and H(1WA), H(1WB), H(1SA), H(1SB), H(1SC), H(2SA), H(2SB), H(2SC), H(2WA), H(2WB), H(3WA), H(3WB), H(3SA), H(3SB), H(3SC), H(4SA), H(4SB), H(4WA), H(4WB), H(5WA), H(5WB), H(5SA), H(5SB), H(5SC), H(6WA), H(6WB), H(6SA), H(6SB), H(6SC), H(7WA), H(7SA), H(7SB), H(7SC), H(8SA), H(8SB), H(8SC), H(8WA), H(9WA), H(9WB), H(10A), H(10B), H(11A), H(11B), H(13A), H(13B) and H(14A) for **2**, and H(2N) and H(3N) for **3**, which were first located in a difference density map, and fixed to the distance obtained from the corresponding heteroatom. H(14B), H(21), H(42), and H(46) for **2**, and H(1V) and H(2V) for **3** were located in a difference density map and left to refine freely. Some hydrogen atoms were not localised (in **2**, hydrogen atoms of the O(12W) water molecule, and in **3**, two hydrogen atoms bonded to nitrogen atoms N(1) and N(4) in triethylammonium cations). Refinement converged with allowance for thermal anisotropy of all non-hydrogen atoms, except C(20), C(23) and C(24) in **3**. The structure of **3** presents disorders in the  $C_2H_5$  groups of the triethylammonium cations. These disorders have been resolved in some cases and several atomic sites have been observed and refined with anisotropic atomic displacement parameters. The site occupancy factors for N(1A), C(1A) and C(2A) were 0.602(12), for C(7A) 0.102(16) and for C(13A) 0.36(6).

Table 1  
Crystal data and structure refinement for **1–3**

|   | <b>1</b>                      | <b>2</b>                   | <b>3</b>                      |
|---|-------------------------------|----------------------------|-------------------------------|
| Formula                                     | $C_4H_{28}K_2N_4O_{32}V_{10}$ | $C_8H_{58}N_8O_{63}V_{20}$ | $C_{24}H_{66}N_4O_{28}V_{10}$ |
| Fw  | 1231.9                        | 1202.77                    | 1370.22                       |
| T (K)                                       | 293(2)                        | 293(2)                     | 298(2)                        |
| Radiation (Mo K $\alpha$ ) ( $\text{\AA}$ ) | 0.71073                       | 0.71073                    | 0.71073                       |
| Crystal system                              | triclinic                     | triclinic                  | monoclinic                    |
| Space group                                 | $P\bar{1}$                    | $P\bar{1}$                 | $P2_1/c$                      |
| <i>Unit cell dimensions</i>                 |                               |                            |                               |
| a ( $\text{\AA}$ )                          | 8.4252(6)                     | 12.2036(5)                 | 19.1420(9)                    |
| b ( $\text{\AA}$ )                          | 10.2669(8)                    | 15.2437(7)                 | 14.3818(9)                    |
| c ( $\text{\AA}$ )                          | 10.6423(8)                    | 18.2206(8)                 | 19.4517(12)                   |
| $\alpha$ ( $^\circ$ )                       | 103.1700(10)                  | 95.2750(10)                |                               |
| $\beta$ ( $^\circ$ )                        | 98.0210(10)                   | 95.2250(10)                | 115.0740(10)                  |
| $\gamma$ ( $^\circ$ )                       | 114.0150(10)                  | 101.5190(10)               |                               |
| V ( $\text{\AA}^3$ )                        | 790.35(10)                    | 3286.3(2)                  | 4850.3(5)                     |
| F(000)                                      | 604                           | 2392                       | 2776                          |
| Z   | 2                             | 2                          | 8                             |
| $D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )    | 2.588                         | 2.445                      | 1.876                         |
| $\mu$ ( $\text{mm}^{-1}$ )                  | 3.199                         | 2.834                      | 1.922                         |
| $R_{\text{int}}$                            | 0.0163                        | 0.0290                     | 0.0293                        |
| No. of reflections collected                | 4906                          | 14 985                     | 30 642                        |
| No. of independent reflections              | 2914                          | 8750                       | 7830                          |
| Goodness-of-fit on $F^2$                    | 1.084                         | 0.993                      | 1.039                         |
| Final R indices                             | $R_1 = 0.0304$                | $R_1 = 0.0470$             | $R_1 = 0.0461$                |
| $[I > 2\sum(I)]^a$                          | $wR_2 = 0.0820$               | $wR_2 = 0.1089$            | $wR_2 = 0.1273$               |
| Final R indices (for all data) <sup>a</sup> | $R_1 = 0.0388$                | $R_1 = 0.1001$             | $R_1 = 0.0778$                |
|   | $wR_2 = 0.0864$               | $wR_2 = 0.1309$            | $wR_2 = 0.1437$               |

<sup>a</sup>  $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ ,  $wR_2 = \{\sum[w(|F_o|^2 - |F_c|^2)|^2]/\sum[w(F_o^4)]\}^{1/2}$ .

Minimum and maximum final electron densities were:  $-0.705$  and  $0.784 \text{ e \AA}^{-3}$  for **1**,  $-0.703$  and  $0.772 \text{ e \AA}^{-3}$  for **2** and  $-0.744$  and  $0.935 \text{ e \AA}^{-3}$  for **3**. Crystal data and details on data collection and refinement are summarised in Table 1.

### 3. Results and discussion

From aqueous solutions containing V(V) and the Schiff base  $\text{H}_2(\text{SO}_3\text{-sal})_2 \text{ en}$  at pH 4–5, two different decavanadate crystals were obtained containing ethylenediamine as the organic counter ion. Schiff bases are a very important class of ligands in several areas including biological systems; nevertheless, in aqueous or alcoholic solutions they are susceptible to hydrolysis. The formation of compounds **1** and **2** is an evidence of that tendency, as the ligand decomposed, yielding ethylenediamine, which acts as the organic counter ion of the decavanadate anions. The degree and speed of hydrolysis depend on the nature of the Schiff base, its concentration, the pH, the solvent, the temperature, and the presence (or absence) of metal ions.

In aqueous solution, vanadates tend to oligomerise forming mono, di, tetra, penta and decanuclear species in different protonation states, and the equilibria depend on several factors including pH and ionic strength [8,18]. From solutions containing approximately the same composition and concentration of initial species, two different structures were obtained and characterised by X-ray diffraction studies, in which the common units are the decavanadate anion and the presence of ethylenediamine cations. It is possible that the presence of the  $\text{SO}_3\text{-sal}$  and the ethylenediamine may slow down the formation of the solid, thereby the formation of crystals.

Compound **3** was obtained from the filtrate solution of the reaction between  $\text{VO}_4^{3-}$ , D,L-diaminopropionic acid and salicylaldehyde. Due to the slow oxidation of the metal ion by diffusion of air into the solution and the presence of triethylamine, a decavanadate was formed containing triethylammonium as counter ions. In the absence of the amino acid and salicylaldehyde, at pH 5 the insoluble vanadyl would precipitate.

In the presence of the additional ligands (aldehyde, and/or diamines), the  $\text{V}^{\text{IV}}\text{O}$ -species is maintained in solution, while  $\text{V}^{\text{IV}}\text{O}$  is slowly oxidised, thereby allowing the slow formation of the required reagents for the formation of the crystals. The  $\text{p}K_{\text{a}}$  values of  $\text{H}_3\text{V}_{10}\text{O}_{28}^{6-}$  are  $\text{p}K_{\text{a}1} \sim 1.2$ ,  $\text{p}K_{\text{a}2} \sim 3.6$  and  $\text{p}K_{\text{a}3} \sim 6.1$  [19], therefore in solution there is a tendency to form protonated decavanadates as the pH is decreased. However, it is known that the solids that precipitate out of solutions do not necessarily correspond to the major species present in the liquid phase. In the present cases, the building of the crystals depends not only on the pH, but also on the availability of the required reagents ( $\text{V}^{\text{V}}$  and

cations), which in turn also depend on the pH and their total concentration, and on the efficiency of the diffusion of  $\text{O}_2$  into the solution.

In the absence of the additional ligands (aldehyde, and/or diamines), no crystals were obtained and we could not characterise the solids that precipitated. Therefore, the factors that control the formation of the crystals depend on the additional ligands present but in a very complex fashion, only indirectly related to the state of the protonation of the decavanadate anions.

#### 3.1. Infrared spectra

The presence of well-differentiated V–O linkages in the crystal structures of compounds **1–3** indicates the possibility of a large number of internal vibrations. The FTIR spectra of compounds **1** and **2** are quite similar, showing two strong bands at  $\sim 950$  and  $975 \text{ cm}^{-1}$  that can be assigned to the stretching of the terminal V–O bonds. Compound **3** shows a very strong band at  $967 \text{ cm}^{-1}$ . The bridging antisymmetric vibrations of V–O–V possibly correspond to the bands at  $\sim 750$  and  $830 \text{ cm}^{-1}$  (and  $840 \text{ cm}^{-1}$  in compounds **1** and **2**), while the symmetric ones are probably at  $530$  and  $595 \text{ cm}^{-1}$  ( $560$  and  $605 \text{ cm}^{-1}$  in compound **3**). The presence of the organic ethylenediaminium cations in compounds **1** and **2** is shown by the presence of bands at  $3478$  and  $1600 \text{ cm}^{-1}$ , that may be attributed to N–H stretching and bending, respectively, and by the  $\nu(\text{C–N})$  bands at  $1050$  and  $1080 \text{ cm}^{-1}$ . In the IR of **3**, there are several bands due to the triethylammonium cations:  $\nu(\text{N–H})$  at  $2492 \text{ cm}^{-1}$ ,  $\nu(\text{CH}_2)_{\text{st}}$  at  $3742 \text{ cm}^{-1}$  and  $\nu(\text{C–N})$  at  $1173 \text{ cm}^{-1}$ . The broad band between  $3600$  and  $3000 \text{ cm}^{-1}$  in **1** and **2** is due to the waters of crystallisation. The different H-bonding network and the presence of the  $\text{K}^+$  cations in **1** explain the differences found in the spectra of **1** and **2**.

#### 3.2. Crystal structures

##### 3.2.1. $(\text{H}_2\text{en})_2\text{K}_2[\text{V}_{10}\text{O}_{28}] \cdot 4\text{H}_2\text{O}$ (**1**)

The X-ray crystal structure of **1** reveals the presence of a decavanadate anion  $[\text{V}_{10}\text{O}_{28}]^{6-}$ , ethylenediamine dications ( $\text{H}_2\text{en}^{2+}$ ),  $\text{K}^+$  and water molecules. The structure of **1** lies across a crystallographic inversion centre and the asymmetric unit contains only half-molecule. Fig. 1 shows the structure and atom-labelling scheme of the decavanadate. The crystallographic inversion centre is situated next to the O(1A) atom. Selected bond distances are listed in Table 2.

The bond distances and angles observed in the  $[\text{V}_{10}\text{O}_{28}]^{6-}$  unit indicate that the geometry is quite similar to that found in previously reported structures of decavanadate salts [7,20–23], namely  $[\text{V}3\text{a–A } 2.318(3) \text{ \AA}$ ,  $\text{V}3\text{a–B1 } 1.894(2) \text{ \AA}$ ,  $\text{V}3\text{a–C1 } 1.808(2) \text{ \AA}$ ,  $\text{V}2\text{a–D}$

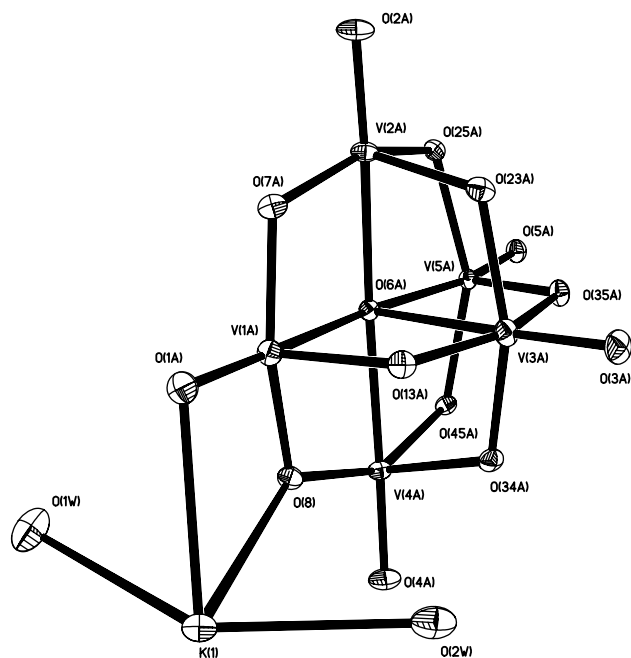


Fig. 1. An ORTEP diagram of the half anion of  $[V_{10}O_{28}]^{6-}$  in **1**, showing the interaction with the  $K^+$  ion. The hydrogen atoms have been omitted for clarity.

1.820(2) Å, V1a–E1 1.687(2) Å, and V3a–F1 1.614(2) Å, see Scheme 1 and Table 2]. The structure shows a three-dimensional array in which the four components interact with each other. Each cape is hydrogen bonded to water molecules and  $H_2en^{2+}$  ions to afford a layered structure (see Fig. 2 and section SM2 in Supplemental Material).

In the asymmetric unit each  $K^+$  ion interacts with four O atoms, (see Fig. 1) two from water molecules and two from O atoms of the decavanadate. The terminal oxygen atom O(1A) (doubly bonded to the vanadium atom) acts as the bridging atom between two  $K^+$  ions. In the crystal packing (see Fig. 2) each  $K^+$  interacts with three different decavanadate anions and two water molecules, forming a complex coordination polyhedron. The polyhedron can be described as a very distorted square antiprism with a deviation from planarity of the two faces of the polyhedron of 0.0711 Å for O(2A), O(4A), O(1W) and O(1AA) (upper pseudo-plane, [vs(j)]) and 0.2561 Å for O(3A), O(2W), O(8) and O(1A) (lower pseudo-plane, [vi(j)]) (see section SM1).

The  $H_2en^{2+}$  cations are involved in H-bonding interactions. They interact with the waters of crystallisation and can act as hydrogen acceptors [O(1W)–N(1) 2.866 Å, H(1H)–N(1) 1.99 Å, and N(2)–H(2A)–N(2S) 165.2°], or donors [N(1)–O(2W) 2.815 Å, H(3N)–O(2W) 2.01 Å, and N(1)–H(3N)–O(2W) 128.5°]. There are also H-bonds between the  $H_2en^{2+}$  and the oxygen atoms of the decavanadate anions, for example [N(1)–

Table 2  
Selected internuclear distances for **1**

| Bond     | Length (Å) |
|----------|------------|
| N1–C2    | 1.479(4)   |
| C1–N2    | 1.451(5)   |
| C1–C2    | 1.525(5)   |
| K1–O2A   | 2.719(2)   |
| K1–O4A   | 2.781(2)   |
| K1–O1A   | 2.783(2)   |
| K1–O3A   | 2.828(2)   |
| K1–O8    | 2.851(2)   |
| K1–O2W   | 2.857(3)   |
| K1–O1W   | 2.876(2)   |
| K1–O1A'  | 2.915(2)   |
| V1A–O1A  | 1.609(2)   |
| V1A–O13A | 1.843(2)   |
| V1A–O7A  | 1.856(2)   |
| V1A–O8   | 1.883(2)   |
| V1A–O5A  | 2.051(2)   |
| V1A–O6A  | 2.319(2)   |
| V2A–O2A  | 1.618(2)   |
| V2A–O23A | 1.795(2)   |
| V2A–O7A  | 1.835(2)   |
| V2A–O25A | 1.991(2)   |
| V2A–O45A | 2.029(2)   |
| V2A–O6A  | 2.2329(19) |
| V3A–O3A  | 1.606(2)   |
| V3A–O13A | 1.834(2)   |
| V3A–O23A | 1.873(2)   |
| V3A–O34A | 1.878(2)   |
| V3A–O35A | 2.040(2)   |
| V3A–O6A  | 2.3171(19) |
| V4A–O4A  | 1.614(2)   |
| V4A–O8   | 1.819(2)   |
| V4A–O34A | 1.821(2)   |
| V4A–O45A | 2.011(2)   |
| V4A–O25A | 2.013(2)   |
| V4A–O6A  | 2.2501(19) |
| V5A–O5A  | 1.686(2)   |
| V5A–O35A | 1.693(2)   |
| V5A–O45A | 1.899(2)   |
| V5A–O25A | 1.953(2)   |
| V5A–O6A  | 2.107(2)   |
| V5A–O6A  | 2.1232(19) |

O(4A) 3.190 Å, H(2N)–O(4A) 2.36 Å, N(1)–H(2N)–O(4A) 161.3° and N(1)–O(25A) 2.777 Å, H(1N)–O(25A) 1.92 Å, N(1)–H(1N)–O(25A) 168.1°] (see Table SM4 in section SM2).

In order to evaluate the possibility of protonation sites in the decavanadate anion, we used the empirical bond length/bond number calculation, which finds valence-deficiency for the O atoms. We used the function  $s = (R/1.791)^{-5.1}$  developed by Brown [24], where  $R$  is the V–O distance and  $s$  the bond number.  $\sum s$  values were obtained for the vanadium atoms, which confirmed the oxidation state +5, for all of them. For all the oxygen atoms the calculated  $\sum s$  values are between 1.7 and 1.86, confirming the  $[V_{10}O_{28}]^{6-}$  formulation (data included in section SM3).

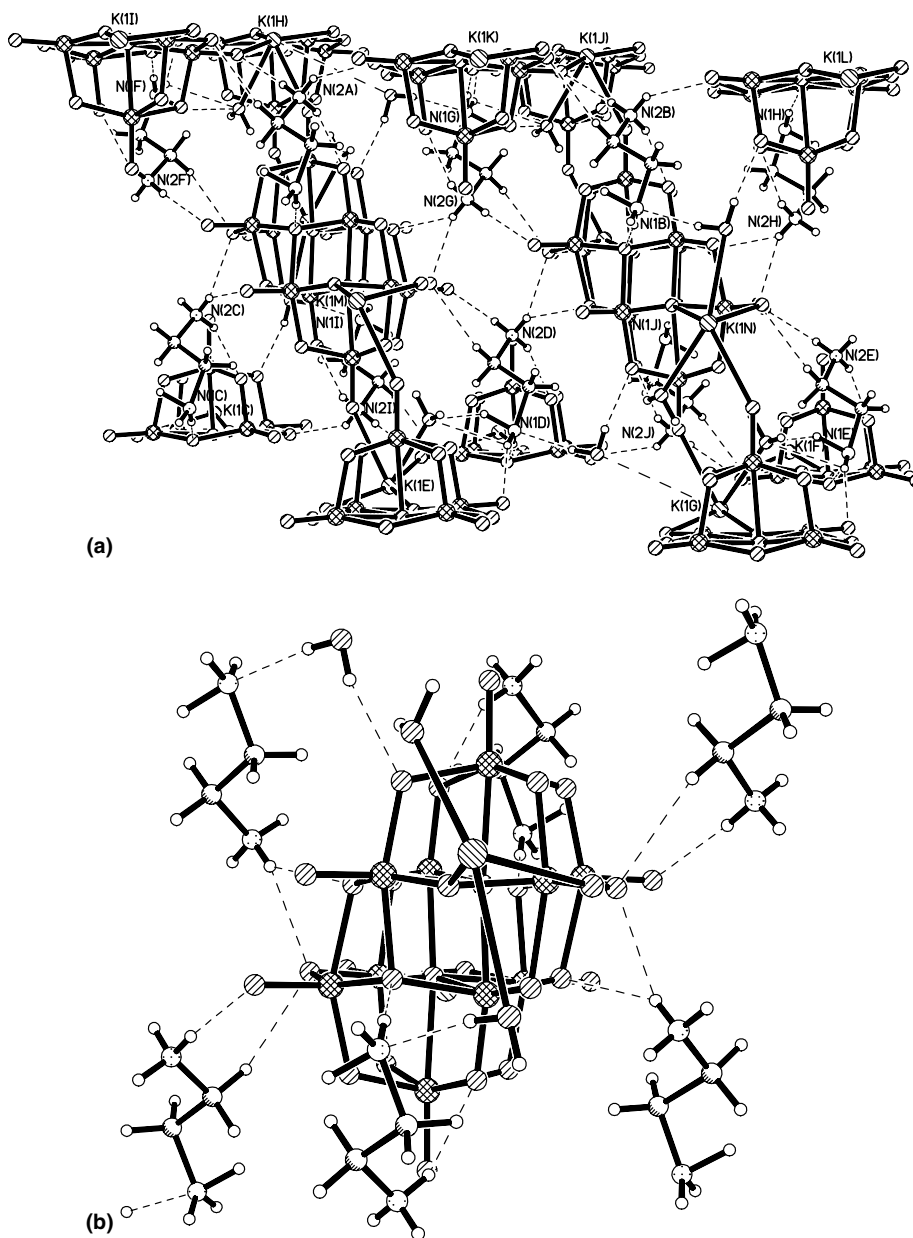


Fig. 2. View of the three-dimensional structure of  $(\text{H}_2\text{en})_2\text{K}_2[\text{V}_{10}\text{O}_{28}] \cdot 4\text{H}_2\text{O}$  (**1**) showing the interactions between the components, which form a three-dimensional array of monomers.

Considering the supramolecular structure, the decavanadates can be classified as monomers in a three-dimensional array. The presence of the small  $\text{K}^+$  ions and the absence of protons in the decavanadate anions preclude the assembly between decavanadates, which do not interact directly with each other. There is a layer containing the decavanadate anions, connected through the  $\text{K}^+$  ions (each  $\text{K}^+$  bonds two anions of the layer). Then, each layer is bonded through H-bonds with the ethylenediamine cations and water molecules, which occupy the interlayer space. The  $\text{K}^+$  ions also establish connections between the layers.

### 3.2.2. $(\text{H}_2\text{en})_3(\text{en})[\text{H}_3\text{V}_{10}\text{O}_{28}]_2 \cdot 7\text{H}_2\text{O}$ (**2**)

In the crystal structure obtained for **2** the  $\text{K}^+$  ions are absent, and this conditions/determines the crystal packing. The asymmetric unit contains four ethylenediamine molecules (three  $\text{H}_2\text{en}^{2+}$  and one en, see below), two decavanadate anions and seven water molecules, which are shown in Fig. 3. Selected bond distances are listed in Table 3.

The structure consists of triprotonated decavanadates,  $[\text{H}_3\text{V}_{10}\text{O}_{28}]^{3-}$ , in one-dimensional chains, linked by interdecavanadate H-bonds and separated by a region populated by ethylenediamine and  $\text{H}_2\text{O}$  molecules

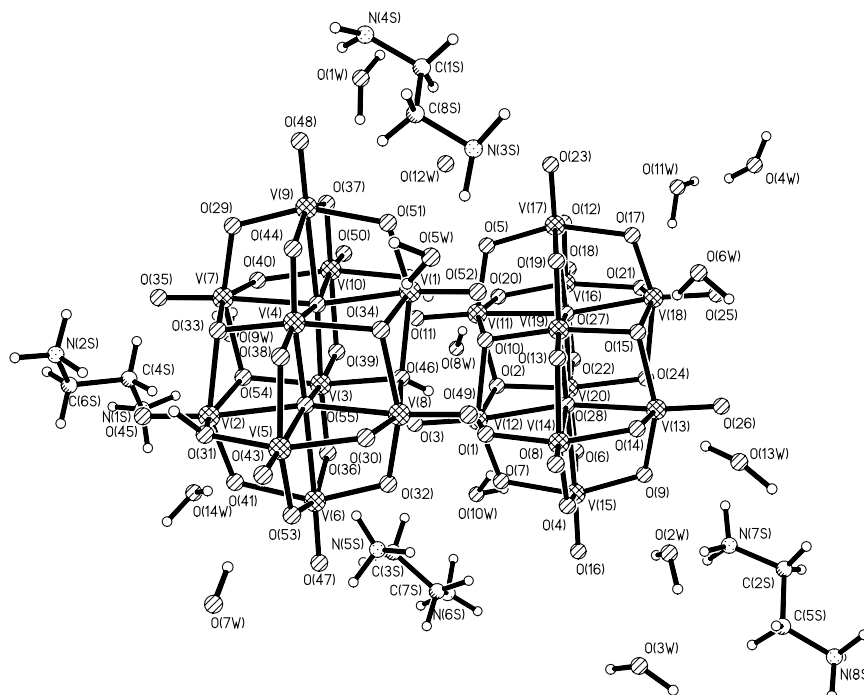


Fig. 3. Components of the asymmetric unit in  $(\text{H}_2\text{en})_3(\text{en})[\text{H}_3\text{V}_{10}\text{O}_{28}]_2 \cdot 7\text{H}_2\text{O}$  (**2**) and atom labelling scheme. Figure SM3 in section SM2 shows the H-bonds between the several moieties present in the crystal structure.

(see Fig. 4). The spacing between the atoms of different decavanadate anions in chains, estimated from the spacing between their respective least-squares planes, is comparable with the values obtained for  $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$  protonated decavanadates (2.55 and 2.64 Å) [25]. The distances between oxygen atoms of different decavanadates in chains are, e.g., O(42)–O(10) 2.841(4) Å and O(46)–O(1) 2.838(5) Å. These distances suggest the presence of H-bonds between the oxygen atoms. The organic ethylenediamine and the water molecules are also involved in H-bonding interactions between the chains. There is a network of intermolecular H-bonds between the three units of the three-dimensional structure and these are shown in Fig. 4 and listed in Table SM5 in section SM2. The protonation sites agree with those predicted analysing the several  $\text{V}_4\text{O}_4$  rings and the oxygen layers, as described by Day et al. [26].

Hydrogen atoms are very difficult to localise on the Fourier maps. Considering the residual density, but also the distances between the oxygen atoms of the two decavanadate anions in the unit cell, the protonation of O(21), O(24), O(42), and O(46) is proposed. However, the formulation given for **2** is also based on bond valence calculations. The  $\sum s$  values for all oxygen atoms except six of them, in the two decavanadate ions, are between 1.67 and 2.27. The exceptions are O(42)–1.14, O(36)–1.41 and O(46)–1.63 in one of the decavanadates of the asymmetric unit, and O(15)–1.27, O(24)–1.31 and O(21)–1.16 in the other one (see section SM3). All these oxygen atoms are doubly or triply [O(46) and O(24)]

bonded to vanadium. This is in agreement with the observed in several other protonated decavanadate anions, as the doubly and triply bonded oxygens are expected to have a higher basicity and therefore to be the more favourable protonation sites. Moreover, the protonation of an oxygen atom is expected to lengthen the related V–O distances, as it removes negative charge from the oxygen, and to induce some *trans* effect. In fact, this is observed for all V–O distances of the suggested protonated oxygens, e.g., the V–O distances of the triply bonded O(46) are longer when compared to the related O(54). The *trans* effect is also observed as the VO distances *trans* to the V–O(protonated) are smaller than the *trans* V–O bonds corresponding to the VO(unprotonated), e.g., the V–O bonds *trans* to V–O(42) average 1.88 Å and the bonds *trans* to VO(31) average 1.97 Å.

Therefore, there is considerable amount of information indicating the protonation of three oxygen atoms in each decavanadate. In order to have zero net charge, two of the ethylenediamine molecules must be mono-protonated, or one of them unprotonated. Unfortunately, it was not possible to localise with certainty the hydrogen atoms in the ethylenediamine molecules, however, one of the molecules does not take part in the H-bonding network of the crystal packing, suggesting that it is unprotonated. So, we propose the following formulation for the resolved structure:  $(\text{H}_2\text{en})_3(\text{en})(\text{H}_3\text{V}_{10}\text{O}_{28})_2 \cdot 7\text{H}_2\text{O}$ .

The supramolecular array shows vertical one-dimensional chains of the type b [7]. This may be seen in Fig. 4

Table 3  
Selected bond lengths for 2

| Bond    | Length (Å) |
|---------|------------|
| V1–O52  | 1.602(3)   |
| V1–O51  | 1.724(3)   |
| V1–O34  | 1.940(3)   |
| V1–O42  | 1.975(4)   |
| V1–O46  | 2.132(3)   |
| V1–O56  | 2.254(3)   |
| V2–O45  | 1.620(3)   |
| V2–O41  | 1.761(3)   |
| V2–O31  | 1.822(3)   |
| V2–O54  | 2.025(3)   |
| V2–O33  | 2.069(3)   |
| V2–O55  | 2.285(3)   |
| V3–O39  | 1.683(3)   |
| V3–O36  | 1.691(3)   |
| V3–O54  | 1.865(3)   |
| V3–O46  | 2.072(3)   |
| V3–O56  | 2.095(3)   |
| V3–O55  | 2.107(3)   |
| V4–O38  | 1.687(3)   |
| V4–O44  | 1.690(3)   |
| V4–O33  | 1.927(3)   |
| V4–O34  | 1.965(3)   |
| V4–O55  | 2.087(3)   |
| V4–O56  | 2.145(3)   |
| V5–O43  | 1.599(3)   |
| V5–O53  | 1.801(3)   |
| V5–O31  | 1.860(3)   |
| V5–O30  | 1.914(3)   |
| V5–O38  | 2.047(3)   |
| V5–O55  | 2.356(3)   |
| V6–O47  | 1.602(3)   |
| V6–O32  | 1.808(3)   |
| V6–O53  | 1.859(3)   |
| V6–O41  | 1.959(3)   |
| V6–O36  | 2.035(3)   |
| V6–O55  | 2.342(3)   |
| V7–O35  | 1.592(3)   |
| V7–O29  | 1.838(3)   |
| V7–O40  | 1.858(3)   |
| V7–O33  | 1.972(3)   |
| V7–O54  | 1.983(3)   |
| V7–O56  | 2.308(3)   |
| V8–O49  | 1.599(3)   |
| V8–O30  | 1.766(3)   |
| V8–O32  | 1.852(3)   |
| V8–O34  | 1.987(3)   |
| V8–O46  | 2.114(3)   |
| V8–O55  | 2.271(3)   |
| V9–O48  | 1.606(3)   |
| V9–O29  | 1.823(3)   |
| V9–O37  | 1.824(3)   |
| V9–O51  | 1.968(3)   |
| V9–O44  | 2.028(3)   |
| V9–O56  | 2.331(3)   |
| V10–O50 | 1.585(3)   |
| V10–O40 | 1.815(3)   |
| V10–O37 | 1.833(3)   |
| V10–O42 | 2.025(4)   |
| V10–O39 | 2.029(3)   |
| V10–O56 | 2.316(3)   |
| V11–O11 | 1.591(3)   |
| V11–O20 | 1.834(3)   |
| V11–O27 | 2.303(3)   |

Table 3 (continued)

| Bond    | Length (Å) |
|---------|------------|
| V11–O2  | 1.970(3)   |
| V11–O5  | 1.860(3)   |
| V11–O10 | 1.976(3)   |
| V12–O28 | 2.275(3)   |
| V12–O3  | 1.601(3)   |
| V12–O7  | 1.781(3)   |
| V12–O10 | 2.054(3)   |
| V13–O15 | 1.988(3)   |
| V13–O24 | 2.123(3)   |
| V13–O28 | 2.257(3)   |
| V13–O9  | 1.845(3)   |
| V13–O26 | 1.604(3)   |
| V13–O14 | 1.773(3)   |
| V14–O13 | 2.052(3)   |
| V14–O14 | 1.915(3)   |
| V14–O28 | 2.367(3)   |
| V14–O1  | 1.843(3)   |
| V14–O4  | 1.816(3)   |
| V14–O8  | 1.605(3)   |
| V15–O16 | 1.594(3)   |
| V15–O28 | 2.353(3)   |
| V15–O4  | 1.868(3)   |
| V15–O6  | 2.041(3)   |
| V15–O7  | 1.910(3)   |
| V15–O9  | 1.818(3)   |
| V16–O12 | 1.798(3)   |
| V16–O18 | 1.597(3)   |
| V16–O20 | 1.836(3)   |
| V16–O21 | 2.018(3)   |
| V16–O22 | 2.047(3)   |
| V16–O27 | 2.281(3)   |
| V17–O12 | 1.855(3)   |
| V17–O23 | 1.592(3)   |
| V17–O17 | 1.969(3)   |
| V17–O19 | 1.991(3)   |
| V17–O27 | 2.329(3)   |
| V17–O5  | 1.814(3)   |
| V18–O25 | 1.595(3)   |
| V18–O21 | 1.967(4)   |
| V18–O24 | 2.141(3)   |
| V18–O27 | 2.265(3)   |
| V19–O19 | 1.696(3)   |
| V19–O28 | 2.068(3)   |
| V19–O27 | 2.166(3)   |
| V19–O10 | 1.914(3)   |
| V20–O24 | 2.066(3)   |
| V20–O27 | 2.087(3)   |
| V20–O28 | 2.119(3)   |
| V20–O2  | 1.874(3)   |
| V20–O6  | 1.687(3)   |
| C1S–C8S | 1.507(6)   |
| N2S–C6S | 1.467(6)   |
| C2S–N7S | 1.473(6)   |
| C2S–C5S | 1.501(6)   |
| N3S–C8S | 1.508(6)   |
| C3S–N5S | 1.486(6)   |
| C3S–C7S | 1.518(6)   |
| C4S–C6S | 1.511(6)   |
| C5S–N8S | 1.474(6)   |
| N6S–C7S | 1.474(6)   |

as the interactions between the oxygen atoms are of the type Ob···Ob, Oc···Oc and Oe···Of. This type of arrangement has also been found for two other triprot-



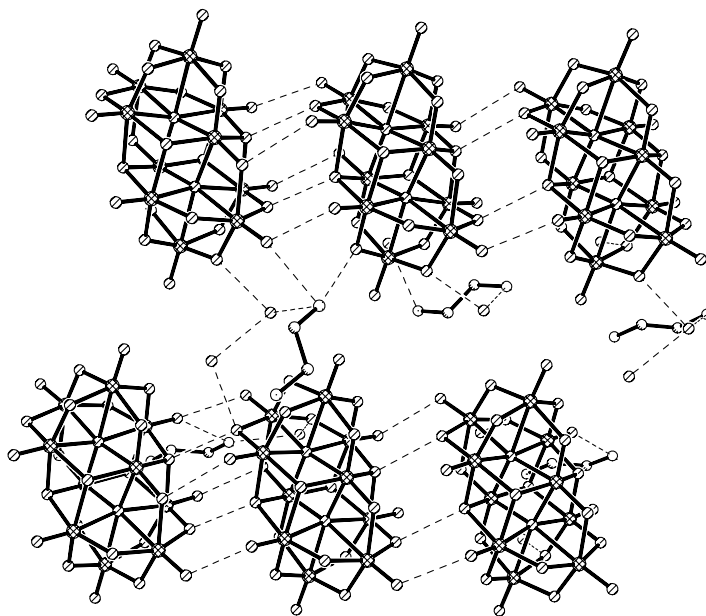


Fig. 4. Schematic drawing emphasising the H-bonding pattern between the decavanadates in chains in  $(\text{H}_2\text{en})_3(\text{en})[\text{H}_3\text{V}_{10}\text{O}_{28}]_2 \cdot 7\text{H}_2\text{O}$  (**2**).

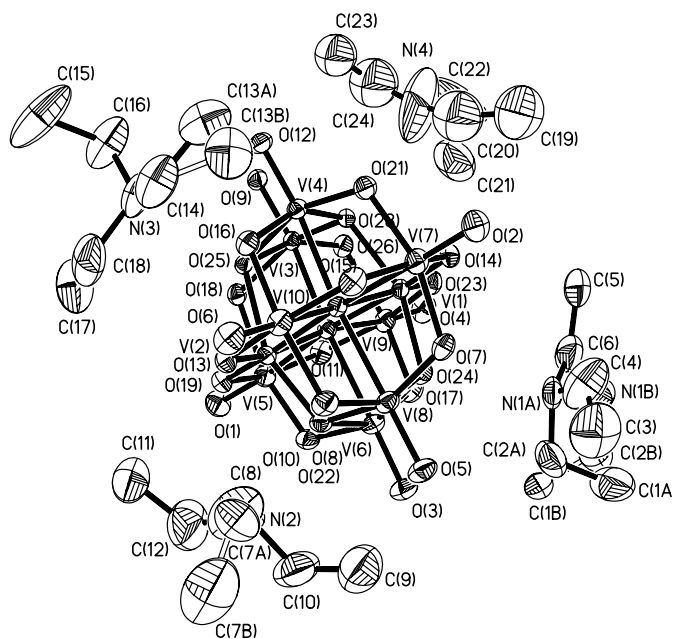


Fig. 5. Components of asymmetric unit in  $[(\text{C}_2\text{H}_5)_3\text{NH}]_4[\text{H}_2\text{V}_{10}\text{O}_{28}]$  (**3**) and atom labelling scheme. The thermal ellipsoids were drawn at 30% level. The disorder in the organic molecules is emphasised.

onated decavanadate structures (compounds with CCDC codes BAYBUY01 and GASROH in [7]).

### 3.2.3. $[(\text{C}_2\text{H}_5)_3\text{NH}]_4[\text{H}_2\text{V}_{10}\text{O}_{28}]$ (**3**)

Fig. 5 shows the structure and atom-labelling scheme of the four triethylammonium cations and the decavanadate anion  $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$  present in the asymmetric unit of **3**. Table 4 contains selected bond distances. The structure consists of diprotonated decavanadate anions,

$[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$ , bonded by interdecavanadate hydrogen bonds and separated by a region populated by  $[(\text{C}_2\text{H}_5)_3\text{NH}]^+$  cations, which form large cavities.

In the crystal, the distances between oxygen atoms of different decavanadates are, e.g., O(12)–O(18) 2.778(4) Å and O(9)–O(25) 2.716(3) Å. The decavanadate ion is diprotonated at the doubly bridged oxygen atom O(18) and triply bridged O(25) to give a total charge of  $-4$ . The protonation sites are consistent with the

Table 4  
Selected bond lengths for **3**

| Bond     | Length (Å) |
|----------|------------|
| V1–O14   | 1.683(2)   |
| V1–O23   | 1.689(2)   |
| V1–O24   | 1.920(2)   |
| V1–O28   | 1.959(2)   |
| V1–O20   | 2.084(2)   |
| V1–O27   | 2.121(2)   |
| V2–O13   | 1.674(2)   |
| V2–O19   | 1.682(2)   |
| V2–O22   | 1.863(2)   |
| V2–O25   | 2.056(2)   |
| V2–O20   | 2.097(2)   |
| V2–O27   | 2.110(2)   |
| V3–O9    | 1.613(2)   |
| V3–O26   | 1.716(2)   |
| V3–O28   | 1.915(2)   |
| V3–O18   | 1.946(3)   |
| V3–O25   | 2.123(2)   |
| V3–O27   | 2.205(2)   |
| V4–O12   | 1.619(3)   |
| V4–O21   | 1.747(2)   |
| V4–O16   | 1.836(2)   |
| V4–O28   | 2.006(2)   |
| V4–O25   | 2.117(2)   |
| V4–O20   | 2.224(2)   |
| V5–O10   | 1.813(3)   |
| V5–O11   | 1.830(3)   |
| V5–O18   | 1.978(3)   |
| V5–O19   | 2.042(3)   |
| V5–O27   | 2.299(2)   |
| V5–O1    | 1.590(3)   |
| V6–O17   | 1.833(3)   |
| V6–O10   | 1.836(3)   |
| V6–O24   | 1.978(3)   |
| V6–O22   | 1.978(2)   |
| V6–O27   | 2.343(2)   |
| V6–O3    | 1.587(3)   |
| V7–O15   | 1.825(3)   |
| V7–O7    | 1.833(3)   |
| V7–O21   | 1.935(3)   |
| V7–O14   | 2.027(3)   |
| V7–O20   | 2.394(2)   |
| V7–O2    | 1.594(3)   |
| V8–O8    | 1.817(3)   |
| V8–O24   | 2.013(2)   |
| V8–O22   | 2.022(3)   |
| V8–O20   | 2.310(2)   |
| V10–O8   | 1.875(3)   |
| V9–O11   | 1.813(3)   |
| V9–O17   | 1.824(3)   |
| V9–O26   | 1.981(3)   |
| V9–O23   | 2.011(3)   |
| V9–O27   | 2.345(2)   |
| V9–O4    | 1.592(3)   |
| V10–O16  | 1.863(3)   |
| V10–O13  | 2.074(3)   |
| V10–O20  | 2.310(2)   |
| V10–O15  | 1.822(3)   |
| C13A–C14 | 1.481(18)  |
| C15–C16  | 1.506(9)   |
| C17–C18  | 1.472(11)  |
| C19–C20  | 1.374(16)  |
| C21–C22  | 1.50(2)    |
| C23–C24  | 1.496(14)  |

Table 4 (continued)

| Bond     | Length (Å) |
|----------|------------|
| N1A–C4   | 1.376(9)   |
| N1A–C2A  | 1.482(12)  |
| N1A–C6   | 1.482(9)   |
| C1A–C2A  | 1.462(15)  |
| N1B–C2B  | 1.426(14)  |
| N1B–C6   | 1.446(10)  |
| N1B–C4   | 1.451(11)  |
| C1B–C2B  | 1.445(17)  |
| N2–C12   | 1.484(9)   |
| N2–C10   | 1.488(8)   |
| N2–C8    | 1.506(9)   |
| N3–C16   | 1.435(7)   |
| N3–C14   | 1.438(8)   |
| N3–C18   | 1.591(9)   |
| C3–C4    | 1.450(12)  |
| N4–C20   | 1.198(16)  |
| N4–C24   | 1.292(16)  |
| N4–C22   | 1.61(3)    |
| C5–C6    | 1.473(10)  |
| C7A–C8   | 1.54(2)    |
| C7B–C8   | 1.584(16)  |
| C9–C10   | 1.468(10)  |
| C11–C12  | 1.460(11)  |
| C13B–C14 | 1.484(14)  |

Fourier density maps and with the bond valence calculations. The oxygen atoms O(18) and O(25) possess  $\sum_s$  values of 1.26 and 1.34, respectively.  $\sum_s$  values for all other oxygen atoms are between 1.7 and 2.0 (see section SM3). This is in agreement with previously reported structures, which indicated the doubly and triply bonded oxygen atoms as the more basic sites, [21,22,27], with those predicted analysing the several  $V_4O_4$  rings and oxygen layers, as described by Day et al. [26].

The structure of **3** presents disorders in the  $C_2H_5$  groups of the triethylammonium cations. These disorders were resolved in some cases, and several atomic sites were observed and refined with anisotropic atomic displacement parameters. Disorder was also observed for the organic cations in  $[(C_2H_5)_4N]_3[H_3V_{10}O_{28}] \cdot 2H_2O$  [9] and the authors suggested that this was due to the fact that the cations did not have sufficient volume to occupy the void space between the anions. This might be also the case in compound **3**.

The protonation of the decavanadate anions allows the establishment of four H-bonds between each two anions, forming dimeric aggregates. These are of the vertical type [7], as the interactions occur between the  $Of \cdots Oc$  and  $Of \cdots Ob$  oxygen atoms. Interactions between the dimers are not possible due to the presence of the organic cations, which occupy the space between the dimers. The organic cations are H-bonded to the anions through the protonated nitrogen atom N(2) and N(3) [N(2)–O(8) 2.888 Å, H(2N)–O(8) 1.87 Å, N(2)–H(2N)–O(8) 157.0° and N(3)–O(16) 2.704 Å, H(2N)–O(16) 1.79 Å, N(3)–H(2N)–O(8) 173.1°]. The

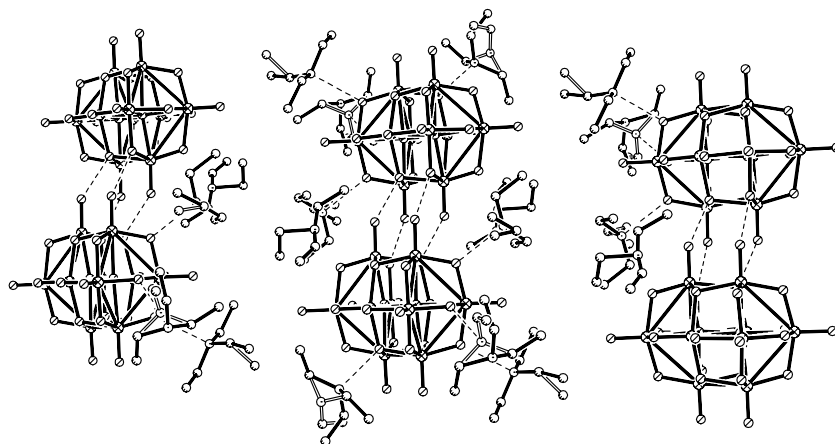


Fig. 6. Crystal packing in **3** showing the hydrogen bonds between the vertical dimers and with the triethylammonium cations.

crystal packing showing the H-bonding pattern is shown in Fig. 6 (see also section SM2).

#### 4. Conclusions

Three decavanadates in different protonation states were obtained and their structures determined by X-ray diffraction. The structure of **1** consists of  $[V_{10}O_{28}]^{6-}$  monomers, forming a three-dimensional array, due to the Coulombic interactions with the inorganic cations and the H-bonds with the organic cations and water molecules. In **1**, all the interactions between the anions are mediated by the other components of the crystal structure. The structure of **2** consists of vanadium triprotonated decavanadates  $[H_3V_{10}O_{28}]^{3-}$  in one-dimensional chains, due to the formation of six interdecavanadate H-bonds. The chains are joined together by H-bonds with ethylenediamine cations and water molecules, which occupy the interchain region. In **3** the diprotonated decavanadates  $[H_2V_{10}O_{28}]^{4-}$  form vertical dimers, connected through four interdecavanadate H-bonds and due to the presence of the large cations,  $[(C_2H_5)_3NH]^+$ , the interaction between dimers is precluded.

Comparing the supramolecular motifs in compounds **1** and **2** we can conclude that when the decavanadate anion is not protonated and small cations are present (as in **1**) the Coulombic forces are important in generating a compact structure, in which there is no possibility of aggregation between the anionic units. In **2** the protonation of the decavanadate anions allows the direct interaction between the anions, forming a one-dimensional vertical array, in which the hydrogen bonds are the main cement. This structure is less compact.

We can therefore conclude that the organic molecules and inorganic cations condition the crystal packing in the solid state, which is determined by the interactions

between the components. H-bonding and Coulombic forces seem to be the most important of these contributions.

This work emphasises the nature and importance of H-bonding interactions involving the  $H_2en^{2+}$  and  $(C_2H_5)_3NH^+$  cations with the  $V_{10}O_{28}$  core. Moreover, the procedures where water-soluble Schiff base ligands stabilise  $V^V$ - and/or  $V^{IV}$ -species in solution, thereby slowing down the formation of the  $V_{10}O_{28}$  units, in the presence of organic compounds capable of H-bonding, may be promising to prepare crystals containing decavanadates and organic cations as counter ions, and is being presently explored in our lab.

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#### Appendix A. Supplementary material

The crystallographic data of the structures described in this paper were deposited in the Cambridge Crystallographic Data Center with the following deposition numbers: CCDC 234266, 234267 and 234268. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2004.06.055](https://doi.org/10.1016/j.ica.2004.06.055).

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