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Key indicators

Single-crystal X-ray study

$T = 293$ K

Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å

R factor = 0.037

wR factor = 0.090

Data-to-parameter ratio = 15.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

**Butane-1,4-diammonium decavanadate(V)
 hexahydrate**

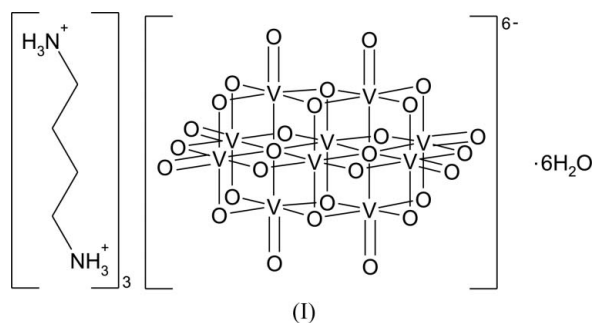
The asymmetric unit cell of the title compound, $(\text{C}_4\text{H}_{14}\text{N}_2)_3[\text{V}_{10}\text{O}_{28}] \cdot 6\text{H}_2\text{O}$, consists of one half-decavanadate anion of C_i symmetry, three water molecules, one butane-1,4-diammonium cation in a general position and one half-butane-1,4-diammonium cation in a special position of C_i symmetry. Water molecules are located within cavities of a framework formed by the anions and cations. All molecules are connected via hydrogen bonds into a three-dimensional network.

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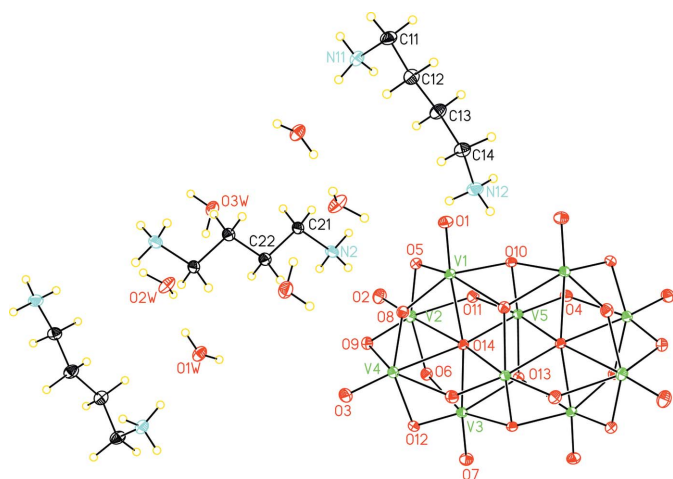
Comment

This article is a continuation of our previous work on salts of polyoxovanadates with organic cations (Rakovský & Gyepes, 2006). We are studying the influence of different cations on such properties of polyoxovanadate species as protonation mode, IR spectrum and crystal structure. The supramolecular chemistry of polyoxovanadates has potential application in catalysis and materials science. Until now, these studies have been mostly focused on the synthesis, IR spectra and thermal properties of n -alkanediammonium oxovanadates (Žúrková *et al.*, 1998, 1999, 2000).



The asymmetric unit of the title compound, (I), consists of one half-decavanadate anion of C_i symmetry, three water molecules of crystallization, one butane-1,4-diammonium cation in a general position and one half-butane-1,4-diammonium cation on a special position of C_i symmetry. All molecules are involved in hydrogen bonding, forming a three-dimensional network.

The counter-ions, water molecules, hydrogen bonds or protonation state have only a slight influence on the geometry of the decavanadate anions which are rigid species and, as such, can be uniquely identified by IR spectroscopy. However, even though the possibility of distinguishing between different protonation states of the $\text{H}_n\text{V}_{10}\text{O}_{28}^{(6-n)-}$ anion on the basis of the IR spectra has been claimed (Román *et al.*, 1995), currently an increased number of reports on the structural and spectroscopic data on decavanadates negate such a possibility (Rakovský & Žúrková, 1998).


Figure 1

The structure of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Symmetry operations relating labelled atoms to unlabelled ones: for the anion ($1-x, -y, 1-z$); for the cations and water molecules ($1-x, 1-y, 1-z$).

The decavanadate anion exhibits the usual crystallographic C_i symmetry; however, its symmetry is close to the D_{2h} point group. Bond lengths, $d(V-O_T)$, of the terminal $V-O$ bonds lie in the range 1.604 (2)–1.611 (2) Å, with an average value of 1.608 (3) Å. Bond lengths to the remaining O atoms with different coordination numbers, $d(\mu-OV_2)$, $d(\mu-OV_3)$ and $d(\mu-OV_6)$ have mean values of 1.85 (11), 1.99 (4) and 2.23 (10) Å, respectively (Table 1).

Intermolecular interactions are based predominantly on cation–anion, cation–water, water–anion, water–water $O-H \cdots O$ and $N-H \cdots O$ hydrogen bonds, as shown in Table 2 and Fig. 2. There are also less significant $C-H \cdots O$ interactions between cations, anion and water molecules.

Experimental

Compound (I) was prepared by continuous addition of aqueous solution of butane-1,4-diamine (0.09 g; 1 mmol in 3 ml) to a stirred aqueous suspension of V_2O_5 (0.23 g, 1.3 mmol in 40 ml) over a period of 30 min. The reaction mixture was incubated at 343–353 K. The orange solution was filtered, cooled and its volume completed to 50 ml giving the value of pH = 6.0. Orange crystals of the title compound appeared after 24 h in a refrigerator. The solution was filtered and the crystals were air-dried in the dark (Žúrková *et al.*, 2000).

Crystal data

$(C_4H_{14}N_2)_3[V_{10}O_{28}] \cdot 6H_2O$
 $M_r = 1336.01$
 Monoclinic, $P2_1/n$
 $a = 10.6504$ (4) Å
 $b = 17.6351$ (4) Å
 $c = 10.9644$ (4) Å
 $\beta = 92.0375$ (16)°
 $V = 2058.04$ (12) Å³

$Z = 2$
 $D_x = 2.156$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 2.27$ mm⁻¹
 $T = 293$ (2) K
 Prism, orange
 $0.50 \times 0.13 \times 0.08$ mm

Data collection

Nonius KappaCCD diffractometer
 ω and φ scans
 Absorption correction: analytical
 numeric absorption correction
 (PLATON; Spek, 2003), using a
 multifaceted crystal model based
 on de Meulenaer & Tompa (1965)
 $T_{\min} = 0.698$, $T_{\max} = 0.841$

15546 measured reflections
 4706 independent reflections
 3665 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.047$
 $\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.090$
 $S = 1.04$
 4706 reflections
 302 parameters
 H atoms treated by a mixture of
 constrained and restrained
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0319P)^2 + 2.7675P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.43$ e Å⁻³
 $\Delta\rho_{\min} = -0.52$ e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0010 (3)

Table 1

Selected bond lengths (Å).

V1–O1	1.609 (2)	V3–O12	1.819 (2)
V1–O5	1.812 (2)	V3–O13	2.024 (2)
V1–O8	1.822 (2)	V3–O14	2.2558 (19)
V1–O10	2.013 (2)	V4–O3	1.609 (2)
V1–O13 ⁱ	2.0080 (19)	V4–O4 ⁱ	2.106 (2)
V1–O14	2.2377 (19)	V4–O8	1.864 (2)
V2–O2	1.604 (2)	V4–O9	1.810 (2)
V2–O5	1.910 (2)	V4–O12	1.890 (2)
V2–O6	1.853 (2)	V4–O14	2.292 (2)
V2–O9	1.861 (2)	V5–O4	1.675 (2)
V2–O11	1.998 (2)	V5–O10	1.944 (2)
V2–O14	2.3429 (19)	V5–O11	1.6998 (19)
V3–O6	1.837 (2)	V5–O13	1.917 (2)
V3–O7	1.611 (2)	V5–O14	2.171 (2)
V3–O10 ⁱ	1.9939 (19)	V5–O14 ⁱ	2.0713 (19)

Symmetry code: (i) $-x + 1, -y, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N11–H1A ⁱⁱ ···O8 ⁱⁱ	0.89	1.89	2.785 (3)	178
N11–H1B ⁱⁱⁱ ···O1W ⁱⁱⁱ	0.89	2.05	2.817 (4)	144
N11–H1C ^{iv} ···O1W ^{iv}	0.89	1.97	2.845 (4)	167
N12–H2A ^v ···O3W ^v	0.89	1.84	2.729 (4)	173
N12–H2B ^{vi} ···O10	0.89	1.93	2.810 (3)	168
N12–H2C ^{vii} ···O3 ^{vii}	0.89	2.58	3.308 (4)	140
N12–H2C ^{vii} ···O5	0.89	2.54	2.938 (4)	108
N2–H21N ^{viii} ···O12 ^{viii}	0.89	1.92	2.815 (3)	179
N2–H22N ^{ix} ···O1 ^{ix}	0.89	2.34	2.890 (3)	120
N2–H22N ^{ix} ···O7 ^{vii}	0.89	2.24	3.076 (3)	156
N2–H23N ^x ···O2	0.89	2.15	3.019 (4)	164
O1W–H11W ^x ···O13 ^{vii}	0.826 (18)	1.893 (19)	2.716 (3)	175 (4)
O1W–H12W ^x ···O2W	0.832 (18)	1.95 (2)	2.748 (3)	161 (3)
O2W–H21W ^x ···O6 ^{vii}	0.838 (18)	2.01 (2)	2.774 (3)	152 (4)
O2W–H22W ^x ···O5 ^{iv}	0.852 (18)	1.95 (2)	2.780 (3)	165 (4)
O3W–H31W ^x ···O9 ^{iv}	0.837 (18)	1.94 (2)	2.744 (3)	162 (4)
O3W–H32W ^x ···O2W	0.826 (18)	2.05 (2)	2.833 (4)	157 (4)

Symmetry codes: (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $x - 1, y, z$; (iv) $-x + 1, -y + 1, -z + 1$; (v) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (vi) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (vii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.

H atoms of the cations were placed in geometrically idealized positions ($C-H = 0.97$ Å and $N-H = 0.89$ Å), and constrained to ride on their parent atoms, with $U_{\text{iso}}(H) = xU_{\text{eq}}(C,N)$, where $x = 1.2$ for methylene and $x = 1.5$ for NH_3^+ H atoms (these groups were

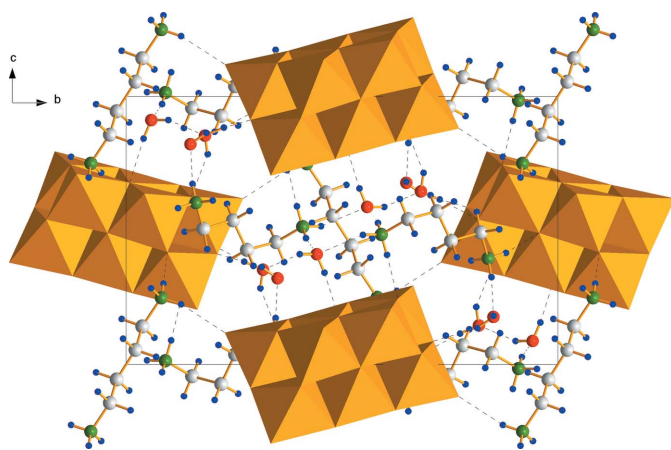


Figure 2
Packing diagram viewed along the *a* axis (dashed lines indicate hydrogen bonds).

treated as rigid rotors). H atoms of the water molecules were located in a difference map and refined with interatomic distances restrained [$O-H = 0.85(2)$ and $H \cdots H = 1.37(2)$ Å] to hold near-optimal geometry, with an $H-O-H$ angle of about 107.7° (Nardelli, 1999) and $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *COLLECT* (Hooft, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2006).

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