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**Key indicators**

Single-crystal X-ray study  
 T = 150 K  
 Mean  $\sigma(C-C)$  = 0.002 Å  
 R factor = 0.021  
 wR factor = 0.056  
 Data-to-parameter ratio = 19.6

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

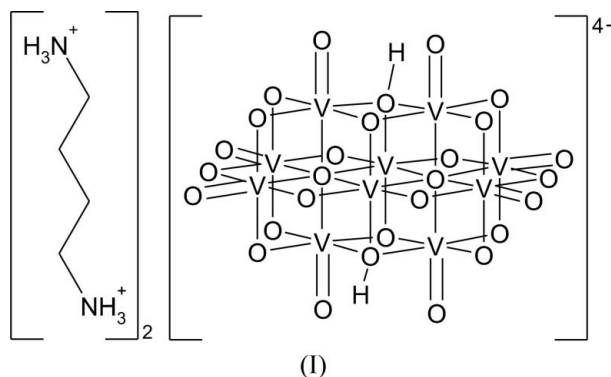
**Butane-1,4-diammonium dihydrogendecavanadate(V)**

The crystal structure of  $(C_4H_{14}N_2)_2[H_2V_{10}O_{28}]$  consists of a dihydrogendecavanadate anion with  $C_i$  symmetry lying on a centre of symmetry, and two butane-1,4-diammonium cations per anion for charge compensation. The anion is protonated on centrosymmetrically related  $\mu-OV_3$  groups; this is a less common protonation mode for dihydrogendecavanadates. Anions are involved in a two-dimensional hydrogen-bonding network, forming a layered structure.

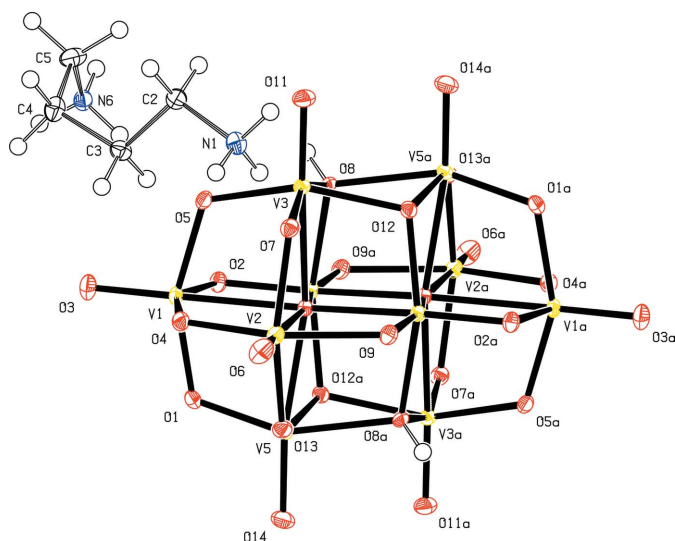
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**Comment**

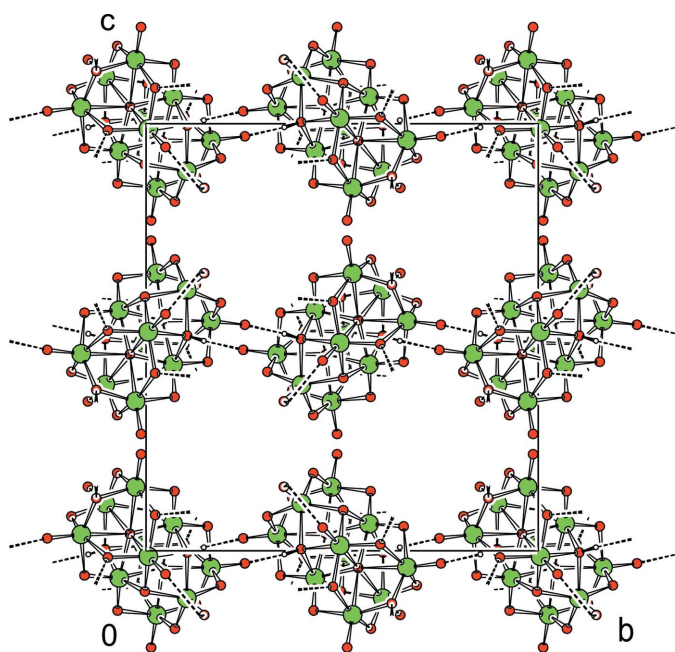
In recent years, the preparation and structural studies of different polyoxovanadates with organic cations have attracted our attention. We wish to obtain a better understanding of the role of the counter-ion in the formation of  $H_nV_{10}O_{28}^{(6-n)-}$  species, and the effect of the chain length of the  $n$ -alkanediammonium cations on structural features of the polyoxovanadates. This is interesting because of possible applications of these compounds in materials science and catalysis, and the influence of the cation and the decavanadate anion protonation mode on the IR spectra. We have prepared and recently published papers on compounds of composition  $(HdaH_2)H_2V_{10}O_{28} \cdot 2H_2O$  (Rakovský *et al.*, 2001),  $(HdaH_2)H_2V_{10}O_{28}$  (Rakovský *et al.*, 2002),  $(BdaH_2)_3V_{10}O_{28} \cdot 6H_2O$ ,  $(BdaH_2)_2H_2V_{10}O_{28} \cdot 4H_2O$  and  $(BdaH_2)_2H_2V_{10}O_{28}$  (Hda is hexane-1,6-diamine and Bda is butane-1,4-diamine), with synthesis, IR spectra and thermoanalytical properties, but without crystallographic studies (Žúrková *et al.*, 2000).



The asymmetric unit of the title compound, (I), contains one butane-1,4-diammonium cation and one half of the dihydrogendecavanadate anion of symmetry  $C_i$ , which is protonated on the  $\mu-OV_3$  bridging atom O8 (Fig. 1). The protonation site of the anion was determined in the difference electron density map and confirmed by performing empirical bond-length/bond-number calculations in order to find the



**Figure 1**  
The cation and anion, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (a)  $1 - x, 1 - y, 1 - z$ .]



**Figure 2**  
View of the packing along the *a* axis. Dashed lines indicate hydrogen bonds inside anionic layers.

valence-deficient O atoms using the power function  $s = (R/1.791)^{-5.1}$  which relates the V–O distance *R* and the bond number *s* (Brown, 1981). We obtained  $\Sigma s$  values for all O atoms in the range from 1.73 (O3) to 2.01 (O12), apart from O8. The  $\Sigma s$  value for O8 (1.38) is comparable with the  $\Sigma s$  values for protonation sites in other  $H_nV_{10}O_{28}^{(6-n)-}$  ( $n = 1-4$ ) anions, which are typically in the range 1.1–1.4 Å bond-length comparison for the protonated (O8) and non-protonated (O12)  $\mu$ -OV<sub>3</sub> groups is given in Table 1. This protonation mode is less obvious than the protonation on centrosym-

metrically related  $\mu$ -OV<sub>2</sub> groups and is observed only in dihydrogendecavanadates with organic cations. There is one example known of a dihydrogendecavanadate with protonation on neighbouring  $\mu$ -OV<sub>2</sub> and  $\mu$ -OV<sub>3</sub> groups (Lapshin *et al.*, 1997).

The interionic hydrogen-bond interactions are mainly based on strong anion–anion (O–H...O) and cation–anion (N–H...O) interactions, with some influence of less significant C–H...O interactions (Table 2). The dihydrogendecavanadate anions are involved in a two-dimensional hydrogen-bonding network, forming layers parallel to the (001) plane (Fig. 2). Cationic layers bind anionic layers together; the positions of cations in the layer are determined by electrostatic repulsion of  $-\text{NH}_3^+$  groups.

## Experimental

(BdaH<sub>2</sub>)<sub>2</sub>H<sub>2</sub>V<sub>10</sub>O<sub>28</sub> was prepared as the kinetically frozen product of thermal dehydration of the tetrahydrate at 393 K on a Derivatograph Q 1500 D thermoanalytical apparatus (MOM Budapest, Hungary) under the following conditions: sample mass 100 mg, heating rate 5 K min<sup>-1</sup>, Pt crucibles, air atmosphere (Žúrková *et al.*, 2000). The microcrystalline yellow product obtained was surprisingly suitable for X-ray structure analysis.

### Crystal data

(C<sub>4</sub>H<sub>14</sub>N<sub>2</sub>)<sub>2</sub>[H<sub>2</sub>V<sub>10</sub>O<sub>28</sub>]  
*M<sub>r</sub>* = 1139.76  
 Orthorhombic, *Pbca*  
*a* = 10.2268 (1) Å  
*b* = 16.7196 (2) Å  
*c* = 18.2311 (2) Å  
*V* = 3117.30 (6) Å<sup>3</sup>

*Z* = 4  
*D<sub>x</sub>* = 2.429 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 $\mu$  = 2.96 mm<sup>-1</sup>  
*T* = 150 (2) K  
 Prism, yellow  
 0.30 × 0.28 × 0.10 mm

### Data collection

Enraf–Nonius KappaCCD  
 diffractometer  
 $\omega$  scans  
 Absorption correction: analytical  
 (PLATON; Spek, 2003), using a  
 multifaceted crystal model based  
 on de Meulenaer & Tompa

(1965).  
*T<sub>min</sub>* = 0.423, *T<sub>max</sub>* = 0.742  
 59189 measured reflections  
 4555 independent reflections  
 4375 reflections with  $I > 2\sigma(I)$   
*R<sub>int</sub>* = 0.092  
 $\theta_{\text{max}}$  = 30.0°

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.021  
*wR*(*F*<sup>2</sup>) = 0.056  
*S* = 1.23  
 4555 reflections  
 232 parameters  
 H atoms treated by a mixture of  
 independent and constrained  
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.018P)^2 + 3.0702P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.00128 (13)

**Table 1**

Selected bond lengths (Å).

O8–V3	2.0956 (11)	O12–V3	1.9607 (11)
O8–V4 <sup>i</sup>	2.0562 (11)	O12–V4	1.8679 (11)
O8–V5	2.1072 (11)	O12–V5	1.9946 (11)

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

**Table 2**  
Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O8—H8···O3 <sup>ii</sup>	0.82 (3)	1.86 (3)	2.6844 (16)	175 (3)
N1—H1A···O11 <sup>iii</sup>	0.91	2.25	3.0655 (18)	148
N1—H1A···O14 <sup>iii</sup>	0.91	2.35	2.9531 (18)	123
N1—H1B···O4 <sup>iv</sup>	0.91	2.00	2.8471 (18)	153
N1—H1C···O7	0.91	1.89	2.7829 (17)	168
N6—H6A···O5	0.91	1.91	2.8158 (17)	171
N6—H6B···O1 <sup>ii</sup>	0.91	1.86	2.7567 (17)	170
N6—H6C···O13 <sup>v</sup>	0.91	1.95	2.8074 (17)	156
C2—H2B···O2 <sup>vi</sup>	0.99	2.41	3.334 (2)	155
C3—H3A···O11 <sup>iii</sup>	0.99	2.45	3.3007 (19)	143
C3—H3B···O5	0.99	2.48	3.407 (2)	157
C4—H4A···O6 <sup>vii</sup>	0.99	2.57	3.068 (2)	111
C4—H4B···O9 <sup>vi</sup>	0.99	2.51	3.274 (2)	133

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

H atoms of the cation were located in difference syntheses and refined in geometrically idealized positions (C—H = 0.99 Å and N—H = 0.91 Å), and constrained to ride on their parent atoms with  $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C,N})$ , where  $x = 1.2$  for methylene H and  $x = 1.5$  for  $\text{NH}_3^+$  H (which were treated as rigid rotors). The H atom of the anion was found in a difference map and refined freely, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ .

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:

*PLATON* (Spek, 2003); software used to prepare material for publication: *pubCIF* (Westrip, 2006).

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