

catena-[1,3-Diammoniopropane di- μ_2 -hydroxo-di- μ_4 -phosphato-trioxotri vanadium dihydrate]: a redetermination at 180 (2) K

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Key indicators

Single-crystal X-ray study

$T = 180\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

R factor = 0.029

wR factor = 0.073

Data-to-parameter ratio = 13.7

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

The crystal structure of the title compound, $(\text{C}_3\text{H}_{12}\text{N}_2)[\text{V}_3\text{O}_3(\text{OH})_2(\text{PO}_4)_2]\cdot 2\text{H}_2\text{O}$, has been reported by Soghomonian *et al.* [*Chem. Mater.* (1993), **5**, 1690–1691]. We present here a redetermination of greatly improved precision and at a low temperature of 180 (2) K. The H atoms connected to oxygen have been successfully located and the coordination environments of the two crystallographically independent vanadium centres have been properly elucidated. Large channels, running along the a direction, contain water molecules and 1,3-diammoniopropane cations that are strongly hydrogen bonded to the anionic framework through $\text{N}^+ - \text{H} \cdots \text{O}$ and $\text{O} - \text{H} \cdots \text{O}$ interactions. One vanadyl ($\text{V}=\text{O}$) bond and the central $-\text{CH}_2-$ group of 1,3-diammoniopropane are located on a mirror plane.

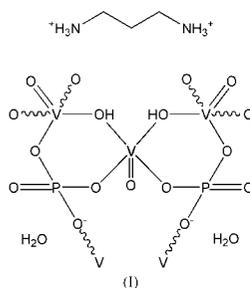
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Comment

Large crystals of the title compound, (I), $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3^+[(\text{VO})_3(\text{OH})_2(\text{PO}_4)_2]\cdot(\text{H}_2\text{O})_2$, were obtained in quantitative yields during our syntheses of novel hybrid materials containing vanadium centres. The crystal structure of (I) was originally reported by Soghomonian *et al.* (1993), and found to contain vanadium centres showing penta- (square-pyramidal geometry, VO_5) and hexacoordination geometries (distorted VO_6 octahedra). A very closely related crystal structure containing mixed IV and V oxidation states for the vanadium centres has also been reported by Loiseau & Férey (1994). The unusual very long V–O bonds to water molecules reported (Soghomonian *et al.*, 1993) for the VO_6 octahedra [2.363 (5) and 2.355 Å, respectively] and the unavailability of three-dimensional atomic coordinates for (I) motivated us to reinvestigate the crystal structure at low temperature.



The compound contains two crystallographically unique vanadium centres, each coordinated by five O atoms in a geometry which is best described as a square pyramid (Figs. 1 and 2, and Table 1). The basal planes are formed by three phosphate ions and a μ_2 -OH group, with the V–O bonds ranging between 1.95 and 2.02 Å (Table 1). The apical position of each square pyramid is occupied by a V=O bond with the

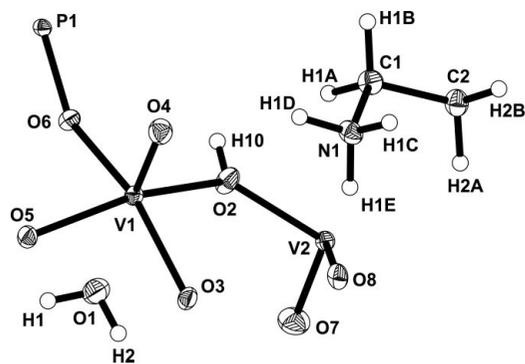


Figure 1
The asymmetric unit of (I), showing the labelling scheme for all atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres.

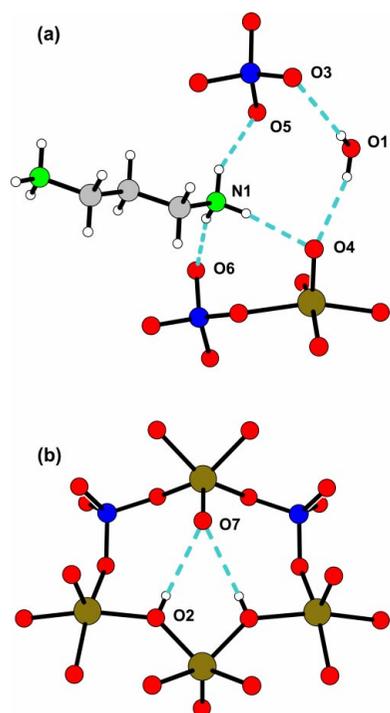


Figure 2
View of the $N^+—H \cdots O$ and $O—H \cdots O$ hydrogen bonds (dashed light blue lines). For hydrogen-bonding details, see Table 2.

corresponding bond distances being, as expected, much smaller than for the single bonds. Bridges between consecutive V centres are established by the phosphate and the μ_2 -OH groups, with the V1—OH and V2—OH bond distances being comparable to the distances reported in the first crystal structure determination (Soghomonian *et al.*, 1993), but slightly shorter, as was also expected. The μ_2 -OH groups are also involved in hydrogen bonding, with O7 acting as a bifurcated acceptor as shown in Fig. 2 (Table 2). Although our calculated distance between V1 and the O atom from the molecule of water of crystallization [2.3203 (19) Å] is also comparable to that reported by Soghomonian *et al.* (1993) and Loiseau & Férey (1994), we believe that the separation of the

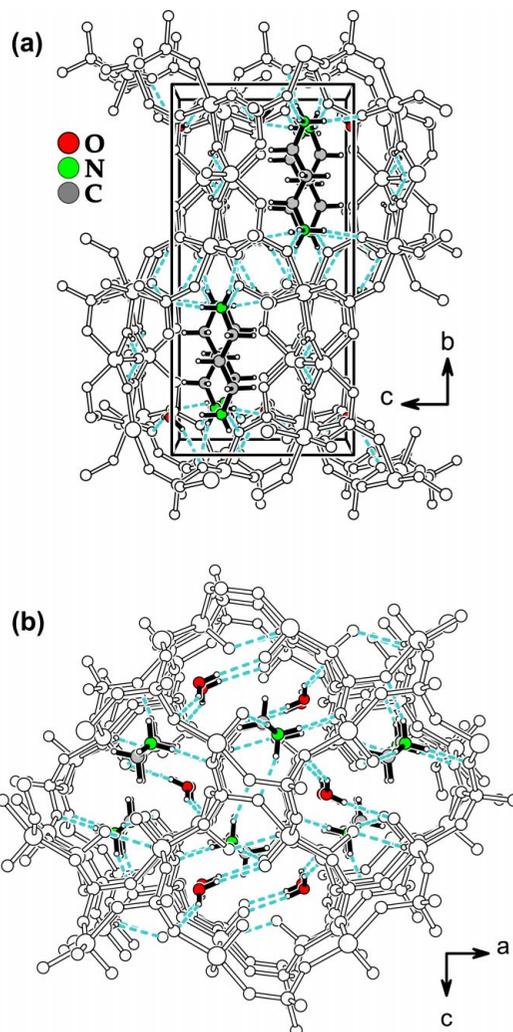


Figure 3
Perspective view of (I) along the *a* (top) and *b* (bottom) directions, showing the $N^+—H \cdots O$ and $O—H \cdots O$ hydrogen-bonding network (light blue dashed lines). The anionic three-dimensional inorganic framework is represented by hollow bonds.

V and O centres is very large for a typical dative coordinative bond to form.

The open three-dimensional anionic framework is templated by 1,3-diaminopropane, which appears in the crystal structure as 1,3-diammonio propane cations. These ions, along with the water molecules, are involved in the complex and extensive hydrogen-bonding network present in the crystal structure (Figs. 2 and 3, and Table 2), and occupying the large channels which run in the *a* direction (Figs. 3 and 4).

Experimental

All chemicals were obtained from commercial sources and were used as received. A mixture containing V_2O_5 (0.40 g, Aldrich, 99.6% purity), H_3PO_4 (0.43 g, Merck, minimum 85%), $YCl_3 \cdot 6H_2O$ (0.54 g, Aldrich, 99.9% purity), adipic acid [$HO_2C(CH_2)_4CO_2H$, 0.95 g, Aldrich, 99% purity] and 1,3-diaminopropane ($C_3H_{10}N_2$, 0.32 g, Fluka, 99% purity) in *ca* 16 ml of distilled water was stirred thoroughly for 15 min at ambient temperature. The suspension was

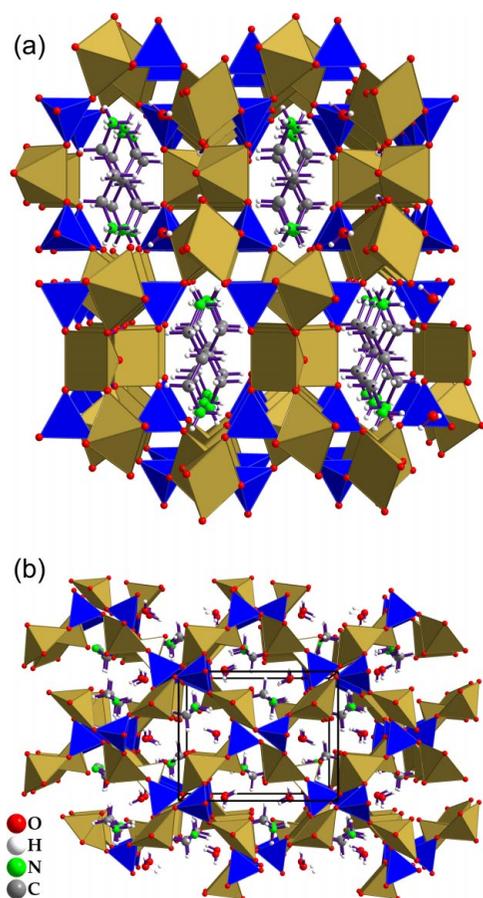
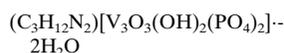


Figure 4

Polyhedral representation of the crystal structure of (I) along the *a* (top) and *b* (bottom) directions. V centres are represented as brown square pyramids, while the phosphate ions are drawn as blue tetrahedra. Water molecules and 1,3-diammoniopropane cations are drawn in ball-and-stick mode.

transferred to a Parr stainless steel Teflon-lined reaction vessel (40 ml, 70% full), which was placed inside an oven at 433 K. The reaction took place under autogeneous pressure and static conditions over a period of 7 d, after which the vessel was slowly cooled to ambient temperature before opening. Large dark green crystals of the title compound were formed; these were collected by vacuum filtration and then air-dried.

Crystal data



$M_r = 536.95$

Orthorhombic, *Pnma*

$a = 10.464$ (2) Å

$b = 17.142$ (3) Å

$c = 8.4481$ (17) Å

$V = 1515.4$ (5) Å³

$Z = 4$

$D_x = 2.354$ Mg m⁻³

Mo $K\alpha$ radiation

Cell parameters from 14014 reflections

$\theta = 1.0$ – 27.5°

$\mu = 2.11$ mm⁻¹

$T = 180$ (2) K

Block, green

$0.25 \times 0.18 \times 0.12$ mm

Data collection

Nonius KappaCCD diffractometer

Thin-slice ω and φ scans

Absorption correction: multi-scan (SORTAV; Blessing, 1995)

$T_{\min} = 0.621$, $T_{\max} = 0.786$

12781 measured reflections

1789 independent reflections

1568 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.064$

$\theta_{\text{max}} = 27.5^\circ$

$h = -11 \rightarrow 13$

$k = -22 \rightarrow 22$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.073$

$S = 1.03$

1789 reflections

131 parameters

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 1.8P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\text{max}} = 0.001$$

$$\Delta\rho_{\text{max}} = 0.49 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\text{min}} = -0.69 \text{ e \AA}^{-3}$$

Table 1

Selected geometric parameters (Å, °).

V1—O4	1.6142 (16)	V2—O2	1.9554 (18)
V1—O2	1.9548 (18)	V2—O8	1.9602 (16)
V1—O6	1.9908 (16)	P1—O3 ⁱ	1.5407 (16)
V1—O3	1.9972 (16)	P1—O8 ⁱ	1.5409 (17)
V1—O5	2.0184 (16)	P1—O6	1.5413 (16)
V2—O7	1.598 (3)	P1—O5 ⁱⁱ	1.5446 (16)
O4—V1—O2	99.66 (9)	O3—V1—O1	80.12 (7)
O4—V1—O6	100.48 (8)	O5—V1—O1	81.33 (7)
O2—V1—O6	87.52 (7)	O7—V2—O2	107.77 (9)
O4—V1—O3	98.38 (8)	O7—V2—O2 ⁱⁱⁱ	107.77 (9)
O2—V1—O3	89.69 (7)	O2—V2—O2 ⁱⁱⁱ	83.59 (11)
O6—V1—O3	161.14 (7)	O7—V2—O8	106.35 (8)
O4—V1—O5	97.90 (8)	O2—V2—O8	85.44 (7)
O2—V1—O5	162.43 (8)	O2 ⁱⁱⁱ —V2—O8	145.87 (8)
O6—V1—O5	89.96 (6)	O7—V2—O8 ⁱⁱⁱ	106.35 (8)
O3—V1—O5	87.09 (6)	O2—V2—O8 ⁱⁱⁱ	145.87 (8)
O4—V1—O1	178.33 (8)	O2 ⁱⁱⁱ —V2—O8 ⁱⁱⁱ	85.44 (7)
O2—V1—O1	81.10 (8)	O8—V2—O8 ⁱⁱⁱ	85.80 (10)
O6—V1—O1	81.02 (7)		

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1C ^{iv} ···O6 ^{iv}	0.91	1.97	2.846 (3)	161
N1—H1D ^v ···O4 ^v	0.91	2.09	2.985 (3)	168
N1—H1E ^{vi} ···O5 ^{vi}	0.91	2.01	2.842 (3)	152
O1—H2 ^{vi} ···O4 ^{vi}	0.79 (3)	2.25 (3)	3.009 (3)	161 (4)
O1—H1 ^{vii} ···O3 ^{vii}	0.79 (3)	2.23 (4)	2.935 (3)	150 (6)
O2—H10 ⁱ ···O7 ⁱ	0.74 (3)	2.41 (3)	3.015 (3)	140 (4)

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

H atoms bound to C atoms were placed in calculated positions and allowed to ride during subsequent refinement, with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, where $x = 1.2$ for $-\text{CH}_2$ and $x = 1.5$ for $-\text{CH}_3$ groups. Water and $-\text{OH}$ H atoms were located in difference Fourier maps and refined with independent isotropic displacement parameters. The O—H and N—H bonds for the hydroxyl and $-\text{NH}_3$ groups were restrained to 0.82 (3) and 0.89 (3) Å, respectively, and the O—H and H···H distances for the water were also restrained in order to ensure a reasonable geometry for these molecules.

Data collection: COLLECT (Nonius, 1998); cell refinement: HKL SCALEPACK (Otwinowski & Minor, 1997); data reduction: HKL DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: SHELXTL (Bruker, 2001); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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