

# catena-[1,3-Diammoniopropane di- $\mu_2$ -hydroxo-di- $\mu_4$ -phosphato-trioxotri vanadium dihydrate]: a redetermination at 180 (2) K

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## Key indicators

Single-crystal X-ray study

$T = 180$  K

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

$R$  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.

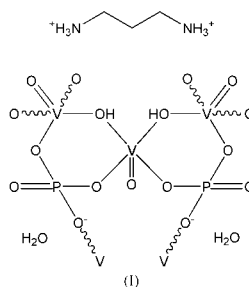
Received 7 March 2003

Accepted 13 March 2003

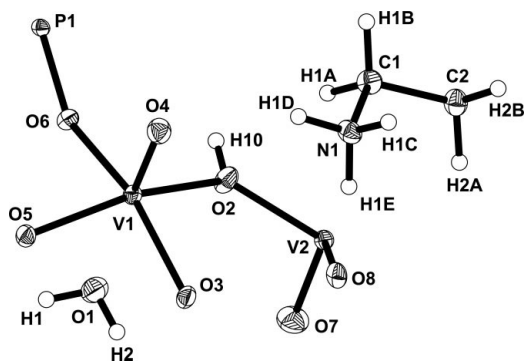
Online 21 March 2003

## Comment

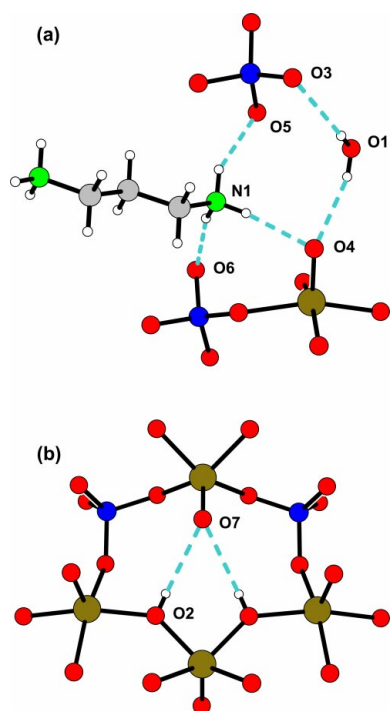
Large crystals of the title compound, (I),  $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3^+[(\text{VO})_3(\text{OH})_2(\text{PO}_4)_2] \cdot (\text{H}_2\text{O})_2$ , were obtained in quantitative yields during our syntheses of novel hybrid materials containing vanadium centres. The crystal structure of (I) was originally reported by Soghomonian *et al.* (1993), and found to contain vanadium centres showing penta- (square-pyramidal geometry,  $\text{VO}_5$ ) and hexacoordination geometries (distorted  $\text{VO}_6$  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  $\text{VO}_6$  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  $\mu_2$ -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

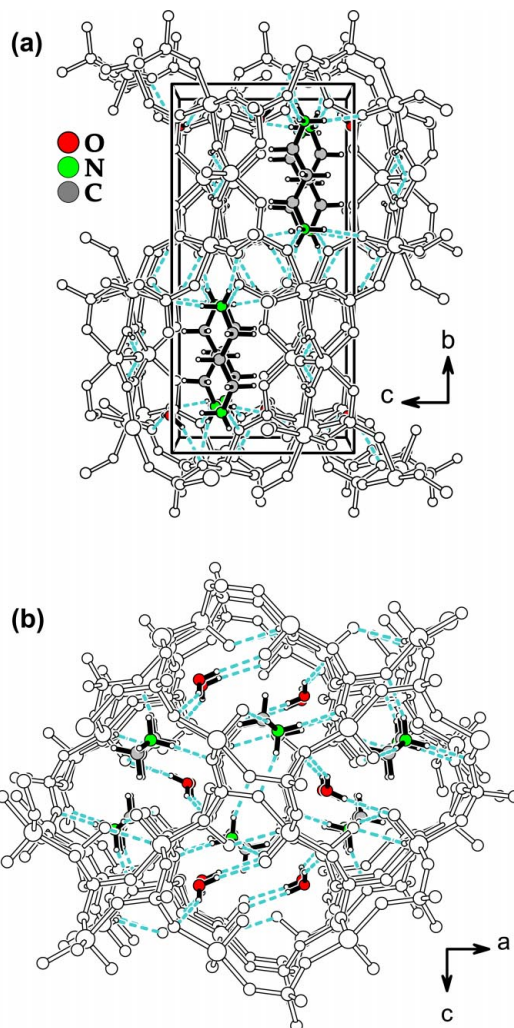


**Figure 1**  
The asymmetric unit of (I), showing the labelling scheme for all atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres.



**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  $\mu_2$ -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  $\mu_2$ -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



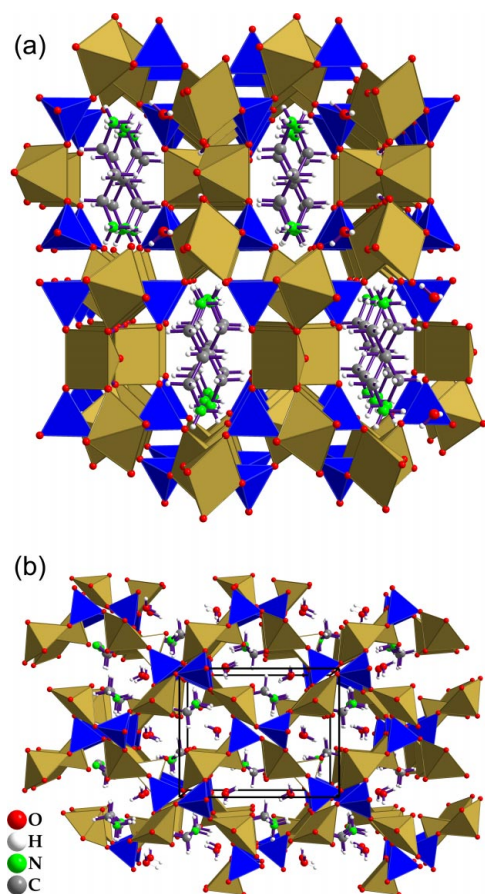
**Figure 3**  
Perspective view of (I) along the *a* (top) and *b* (bottom) directions, showing the  $N^+ - H \cdots O$  and  $O - H \cdots O$  hydrogen-bonding network (light blue dashed lines). The anionic three-dimensional inorganic framework is represented by hollow bonds.

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-diammoniumpropane 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

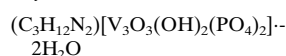
All chemicals were obtained from commercial sources and were used as received. A mixture containing  $V_2O_5$  (0.40 g, Aldrich, 99.6% purity),  $H_3PO_4$  (0.43 g, Merck, minimum 85%),  $YCl_3 \cdot 6H_2O$  (0.54 g, Aldrich, 99.9% purity), adipic acid [ $HO_2C(CH_2)_4CO_2H$ , 0.95 g, Aldrich, 99% purity] 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) Å<sup>3</sup>

$Z = 4$

$D_x = 2.354$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

Cell parameters from 14014 reflections

$\theta = 1.0$ – $27.5^\circ$

$\mu = 2.11$  mm<sup>-1</sup>

$T = 180$  (2) K

Block, green

$0.25 \times 0.18 \times 0.12$  mm

#### Data collection

Nonius KappaCCD diffractometer

Thin-slice  $\omega$  and  $\varphi$  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 <sup>i</sup>	1.5407 (16)
V1—O3	1.9972 (16)	P1—O8 <sup>i</sup>	1.5409 (17)
V1—O5	2.0184 (16)	P1—O6	1.5413 (16)
V2—O7	1.598 (3)	P1—O5 <sup>ii</sup>	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 <sup>iii</sup>	107.77 (9)
O2—V1—O3	89.69 (7)	O2—V2—O2 <sup>iii</sup>	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 <sup>iii</sup> —V2—O8	145.87 (8)
O6—V1—O5	89.96 (6)	O7—V2—O8 <sup>iii</sup>	106.35 (8)
O3—V1—O5	87.09 (6)	O2—V2—O8 <sup>iii</sup>	145.87 (8)
O4—V1—O1	178.33 (8)	O2 <sup>iii</sup> —V2—O8 <sup>iii</sup>	85.44 (7)
O2—V1—O1	81.10 (8)	O8—V2—O8 <sup>iii</sup>	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 $\cdots$ O6 <sup>iv</sup>	0.91	1.97	2.846 (3)	161
N1—H1D $\cdots$ O4 <sup>v</sup>	0.91	2.09	2.985 (3)	168
N1—H1E $\cdots$ O5 <sup>vi</sup>	0.91	2.01	2.842 (3)	152
O1—H2 $\cdots$ O4 <sup>vi</sup>	0.79 (3)	2.25 (3)	3.009 (3)	161 (4)
O1—H1 $\cdots$ O3 <sup>vii</sup>	0.79 (3)	2.23 (4)	2.935 (3)	150 (6)
O2—H10 $\cdots$ O7 <sup>i</sup>	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 $\cdots$ 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.

We are grateful to FEDER, POCTI (Portugal) and also to the Portuguese Foundation for Science and Technology (FCT) for their general financial support and the PhD scholarship, No. SFRH/BD/3024/2000, to FAAP.

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