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

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Key indicators

Single-crystal X-ray study
$T = 180$ K
Mean σ(C–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, $(C_3H_{12}N_2)$-$[V_3O_3(OH)_2(PO_4)_2]\cdot 2H_2O$, 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 N^+—H$\cdots$O and O—H$\cdots$O interactions. One vanadyl (V=O) bond and the central –CH_2– group of 1,3-diammoniopropane are located on a mirror plane.

Comment

Large crystals of the title compound, (I), $H_3N(CH_2)_3$-$NH_3[(VO)_3(OH)_2(PO_4)_2]\cdot(H_2O)_2$, 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.

(I)
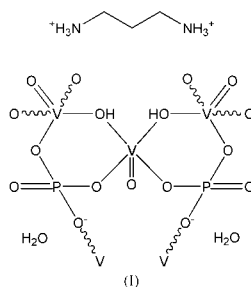
The compound contains two crystallographically unique vanadium centres, each coordinated by five O atoms in a geometry which is best described as a square pyramid (Figs. 1 and 2, and Table 1). The basal planes are formed by three phosphate ions and a μ_2-OH group, with the V—O bonds ranging between 1.95 and 2.02 Å (Table 1). The apical position of each square pyramid is occupied by a V=O bond with the
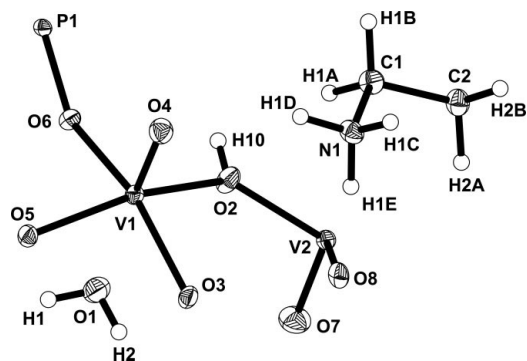
Figure 1
The asymmetric unit of (I), showing the labelling scheme for all atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres.
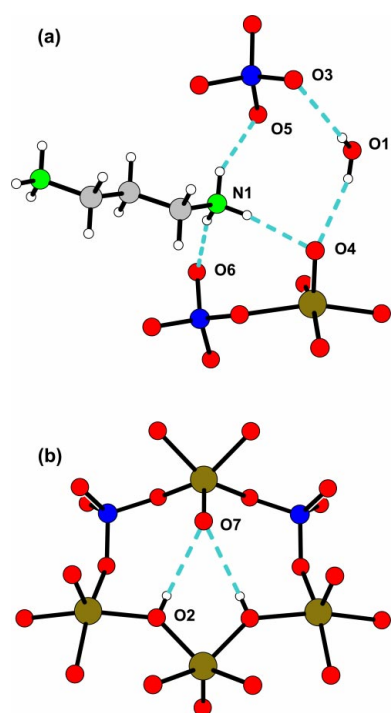

Figure 2
View of the N^+—H···O and O—H···O hydrogen bonds (dashed light blue lines). For hydrogen-bonding details, see Table 2.

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

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 & Fér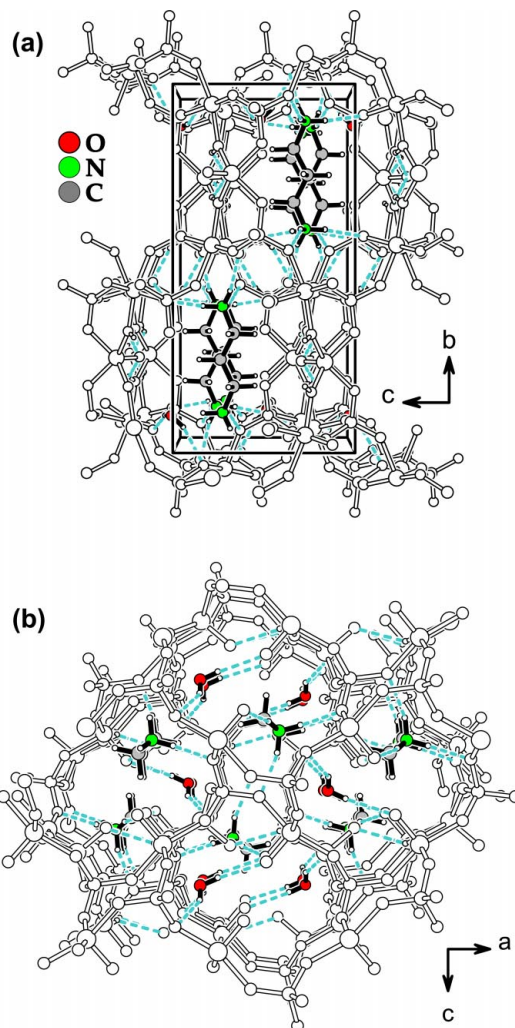ey (1994), we believe that the separation of the V and O centres is very large for a typical dative coordinative bond to form.

The open three-dimensional anionic framework is templated by 1,3-diaminopropane, which appears in the crystal structure as 1,3-diammoniopropane 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%), $YCl_3.6H_2O$ (0.54 g, Aldrich, 99.9% purity), adipic acid [$HO_2C(CH_2)_4CO_2H$, 0.95 g, Aldrich, 99% purity] and 1,3-diaminopropape ($C_3H_{10}N_2$, 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
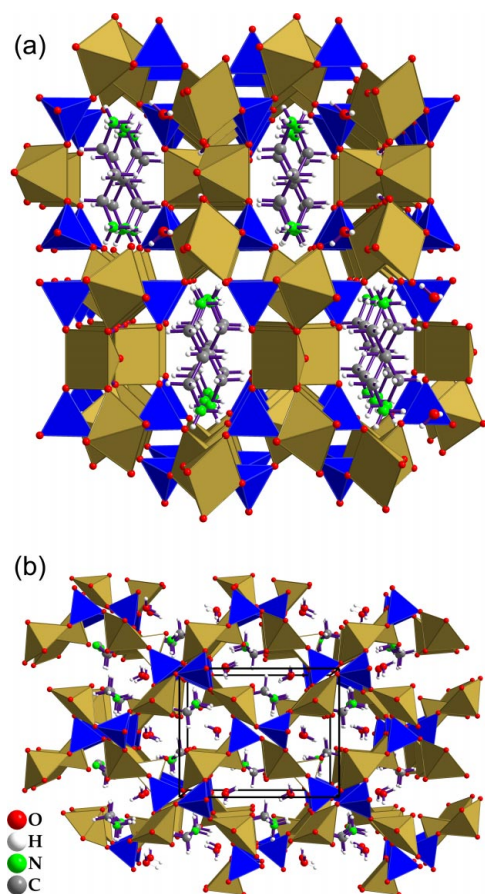
Refinement

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

$w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 1.8P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.69$ e Å^{-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—H1$C\cdots$O6^{iv}	0.91	1.97	2.846 (3)	161
N1—H1$D\cdots$O4^{v}	0.91	2.09	2.985 (3)	168
N1—H1$E\cdots$O5^{vi}	0.91	2.01	2.842 (3)	152
O1—H2$\cdots$O4^{vi}	0.79 (3)	2.25 (3)	3.009 (3)	161 (4)
O1—H1$\cdots$O3^{vii}	0.79 (3)	2.23 (4)	2.935 (3)	150 (6)
O2—H10$\cdots$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 $U_{iso}(H) = xU_{eq}(C)$, where $x = 1.2$ for —CH$_2$ and $x = 1.5$ for —CH$_3$ groups. Water and —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 –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: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXTL* (Bruker, 2001); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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.

O — O
H — H
N — N
C — C

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
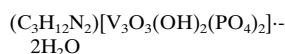
(C$_3$H$_{12}$N$_2$)[V$_3$O$_3$(OH)$_2$(PO$_4$)$_2$]·2H$_2$O
$M_r = 536.95$
Orthorhombic, $Pnma$
$a = 10.464$ (2) Å
$b = 17.142$ (3) Å
$c = 8.4481$ (17) Å
$V = 1515.4$ (5) Å^3
$Z = 4$

$D_x = 2.354$ 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 $I > 2\sigma(I)$
$R_{int} = 0.064$
$\theta_{max} = 27.5°$
$h = -11 \rightarrow 13$
$k = -22 \rightarrow 22$
$l = -10 \rightarrow 10$

metal-organic papers

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