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A second polymorph of $[H_3N(CH_2)_3NH_3][V_4O_{10}]$

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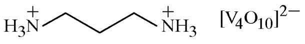
The title compound, propane-1,3-diammonium tetravanadate, $(C_3H_{12}N_2)[V_4O_{10}]$, represents a second polymorph of composition β-$[H_3N(CH_2)_3NH_3][V_4O_{10}]$. It differs from the α polymorph [Riou & Ferey (1995). *J. Solid State Chem.* **120**, 137–145] in the conformation of the propane-1,3-diammonium dication which, in the present example, lies on a twofold axis and adopts a *syn–syn* rather than a *syn–anti* conformation. The twofold symmetry of this conformation thus co-operates with the vanadium oxide framework to result in a higher symmetry for the resultant crystal, *viz*. $C2/c$ *versus* $P2_1/n$. The overall unit-cell parameters for the two polymorphs are similar, and the inorganic layer within each is topologically identical, comprising edge-sharing $V^{IV}O_5$ square pyramids linked together *via* corner-sharing with V^VO_4 tetrahedra. A key difference between the two polymorphs is a 'head-to-head' *versus* 'head-to-tail' stacking of the vanadyl groups in adjacent layers.

Comment

The title compound, β-$[H_3N(CH_2)_3NH_3][V_4O_{10}]$, (I), was prepared during a more general survey of the hydrothermal chemistry of vanadium in the presence of organic templating agents and HF (Aldous *et al.*, 2006). Specifically, it arose from an attempt to prepare a structural analogue of an interesting polar material, $[H_3N(CH_2)_2NH_3][VOF_4(H_2O)]$ (Stephens & Lightfoot, 2005). An α polymorph of the same composition has been reported previously (Riou & Ferey, 1995). The different polymorphs arise from quite similar hydrothermal reactions, both employing HF, but the α polymorph also included SiO_2 in the reaction mixture and the synthesis being carried out at a higher temperature of 453 K and a lower pH of 4–5.



(I)

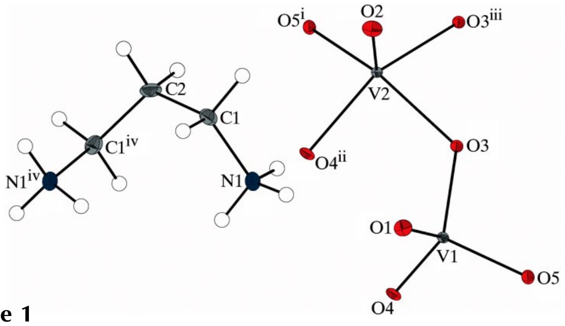


Figure 1
The asymmetric unit of compound (I), with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $-\frac{1}{2}+x, \frac{1}{2}+y, z$; (ii) $-\frac{1}{2}-x, \frac{1}{2}-y, -z$; (iii) $-x, 1-y, -z$; (iv) $-1-x, y, \frac{1}{2}-z$.]

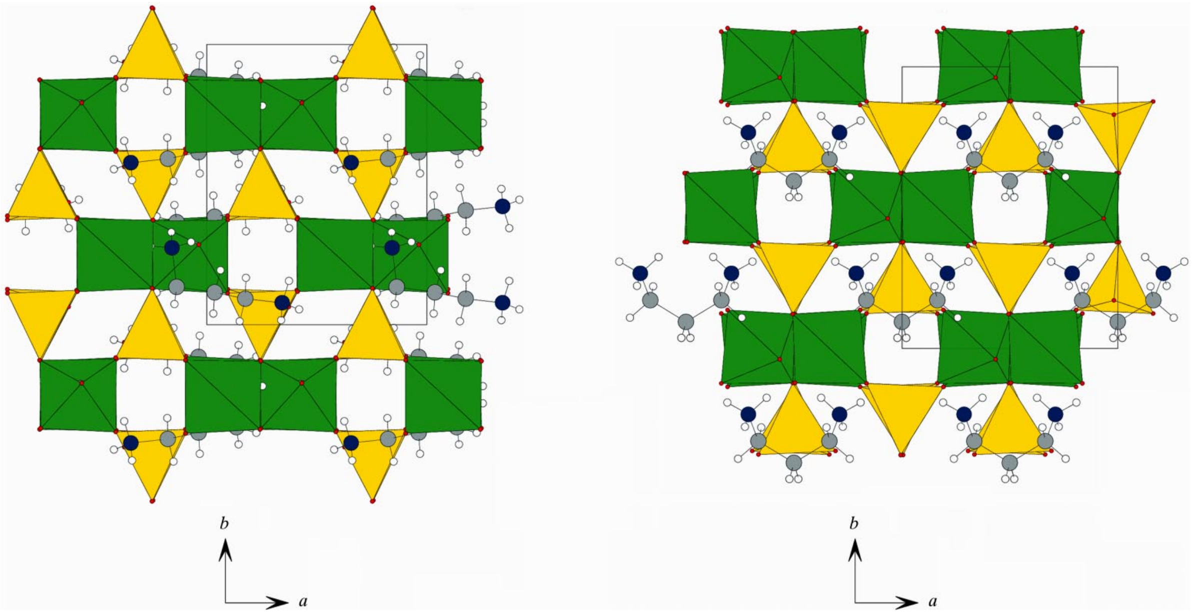


Figure 2
Projections of the structures of the α form (left) and the β form (right) down [001]. Note the relative positions and conformations of the organic cation.

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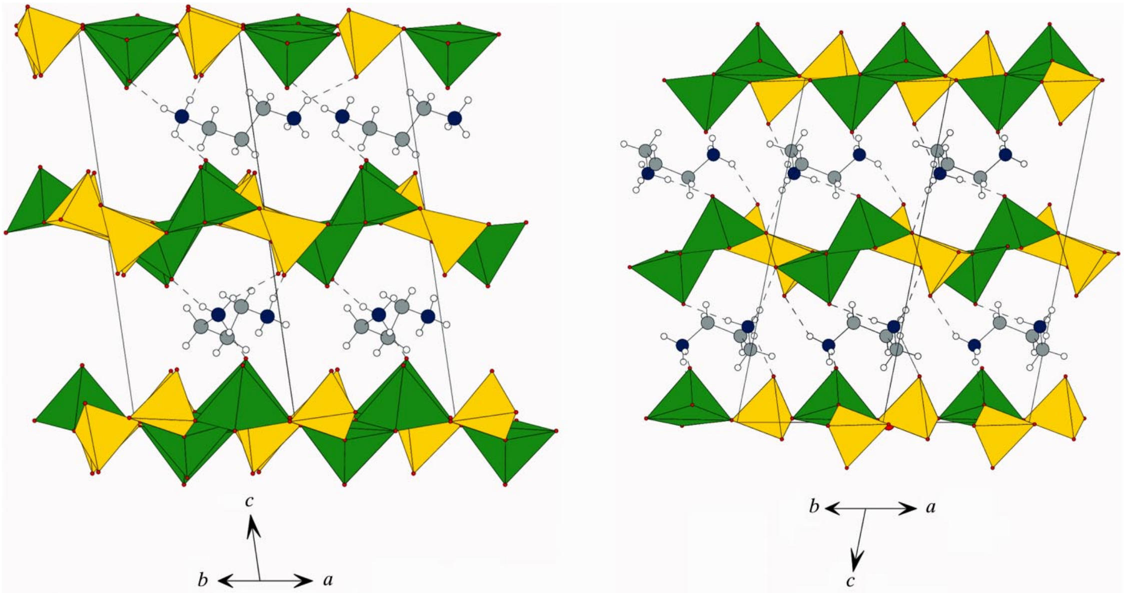

Figure 3
Projections of the structures perpendicular to the c axis, showing the α form along $[\overline{1}\overline{1}0]$ (left) and the β form along [110] (right).

The α form has similar unit-cell parameters to (I) [$P2_1/n$, a = 7.9991 (1) Å, b = 10.001 (1) Å and c = 15.703 (1) Å, and β = 100.49 (1)° at 298 K]. Although the structural units are the same in each case, the higher symmetry in (I) is perhaps encouraged by the additional symmetry within the organic dication, which lies on a twofold axis in the β form (Fig. 1). A projection of the unit cell of (I) along the c axis, together with the corresponding view for the α form, is shown in Fig. 2.

There are two unique V sites in the structure of (I), atom V1 being five-coordinated by O and atom V2 being four-coordinate. Bond-valence sum analysis (Brown & Altermatt, 1985) shows these sites to be V^{IV} and V^{V}, respectively. The compound exhibits a layered crystal structure comprised of edge-sharing $V1O_5$ square pyramids linked together via corner-sharing $V2O_4$ tetrahedra to form continuous inorganic sheets in the ab plane. These are separated by hydrogen-bonded organic cations along the c axis. Similar structural building units are known in vanadium oxide chemistry (Zavalij & Whittingham, 1999).

The most significant difference in the unit-cell parameters of the two forms is the considerable reduction in the c axis of the β form. A comparative view perpendicular to the c axis is shown in Fig. 3, and the difference in c dimensions may be explained by the more extensive hydrogen bonding in the β form (Table 2), whereby each N—H bond acts as a donor. This difference in interlayer hydrogen bonding is co-operative, with a different stacking of adjacent vanadium oxide layers, such that the vanadyl bonds of the VO_5 pyramids take up a 'head-to-head' arrangement in the β polymorph, in contrast with a 'head-to-tail' configuration in the α polymorph. This leads to a short interlayer $O5\cdots O5(-x, y, \frac{1}{2} - z)$ contact of 2.770 (3) Å in (I), which does not occur in the α polymorph. We note that polymorphism has also been observed in two closely related compositions incorporating dications of ethylenediamine and piperazine (Zhang *et al.*, 1996).

Experimental

Vanadium pentoxide (0.1819 g), water (5 ml) and a 48% solution of HF (0.5 ml) were heated in a polypropylene bottle at 373 K for 1 h. To the resulting yellow solution was added ethylene glycol (5 ml). Finally, propane-1,3-diamine (0.5 ml) was added to give a green solution of pH 10. This was heated in a polypropylene bottle at 373 K for 5 d. The pH remained constant over this time. The final product was isolated as dark-blue crystals, filtered off, washed in water and allowed to dry overnight at room temperature. Elemental analysis confirmed phase purity; found: C 8.34, H 2.21, N 6.41%; $(C_3H_{12}N_2)[V_4O_{10}]$ requires: C 8.19, H 2.75, N 6.37%. Additionally, powder X-ray diffraction of the product at room temperature confirmed that the bulk material was the new β polymorph, with no indication of the presence of the α polymorph.

Crystal data

$(C_3H_{12}N_2)[V_4O_{10}]$
M_r = 439.91
Monoclinic, $C2/c$
a = 7.977 (3) Å
b = 10.099 (3) Å
c = 15.210 (5) Å
β = 104.075 (11)°
V = 1188.6 (7) $Å^3$
Z = 4
D_x = 2.458 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 3.10 mm^{-1}
T = 93 (2) K
Needle, blue
0.15 × 0.01 × 0.01 mm

Data collection

Rigaku Mercury70 (2 × 2 bin mode) CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.84, T_{max} = 0.97
3674 measured reflections
1075 independent reflections
997 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 25.3°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.059
S = 1.13
1075 reflections
87 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0213P)^2 + 5.2306P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.37 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.36 e $Å^{-3}$

Table 1
Selected bond lengths (Å).

V1—O1	1.635 (2)	V2—O2^{i}	1.921 (2)
V1—O2	1.705 (2)	V2—O3^{ii}	1.952 (2)
V1—O3	1.737 (2)	V2—O4	1.969 (2)
V1—O4	1.838 (2)	V2—O4^{iii}	1.982 (2)
V2—O5	1.607 (2)		

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1^{iv}	0.91	2.13	2.932 (3)	147
N1—H2$\cdots$O3^{ii}	0.91	2.02	2.911 (3)	164
N1—H3$\cdots$O5^{v}	0.91	2.04	2.947 (3)	176

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

Space group $C2/c$ was chosen on the basis of the systematic absences and successful refinement of the structure. No unusual problems occurred during the refinement. H atoms were refined as riding on their carrier atoms, with C—H = 0.99 Å and N—H = 0.91 Å, and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ or $1.5U_{\rm eq}({\rm N})$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3063). Services for accessing these data are described at the back of the journal.

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