Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

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

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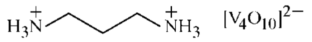
Received 29 September 2006
Accepted 3 October 2006
Online 31 October 2006

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*. *C*2/*c versus P*2$_1$/*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)

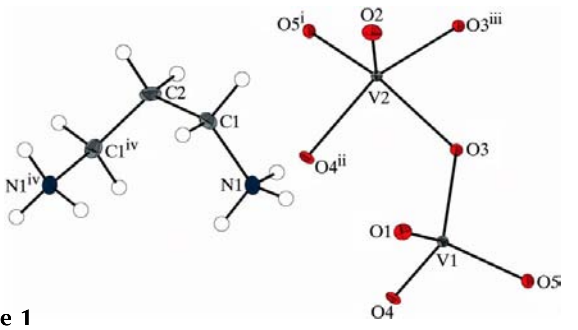


Figure 1
The asymmetric unit of compound (I), with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $-\frac{1}{2} + x, \frac{1}{2} + y, z$; (ii) $-\frac{1}{2} - x, \frac{1}{2} - y, -z$; (iii) $-x, 1 - y, -z$; (iv) $-1 - x, y, \frac{1}{2} - z$.]

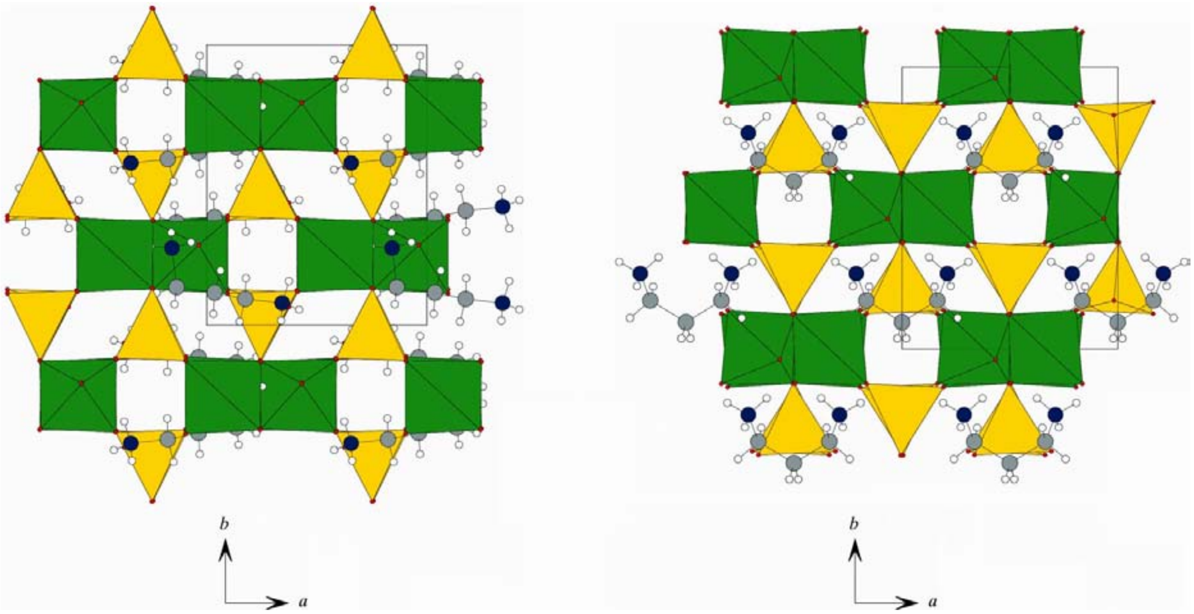


Figure 2
Projections of the structures of the α form (left) and the β form (right) down [001]. Note the relative positions and conformations of the organic cation.

DOI: 10.1107/S0108270106040777

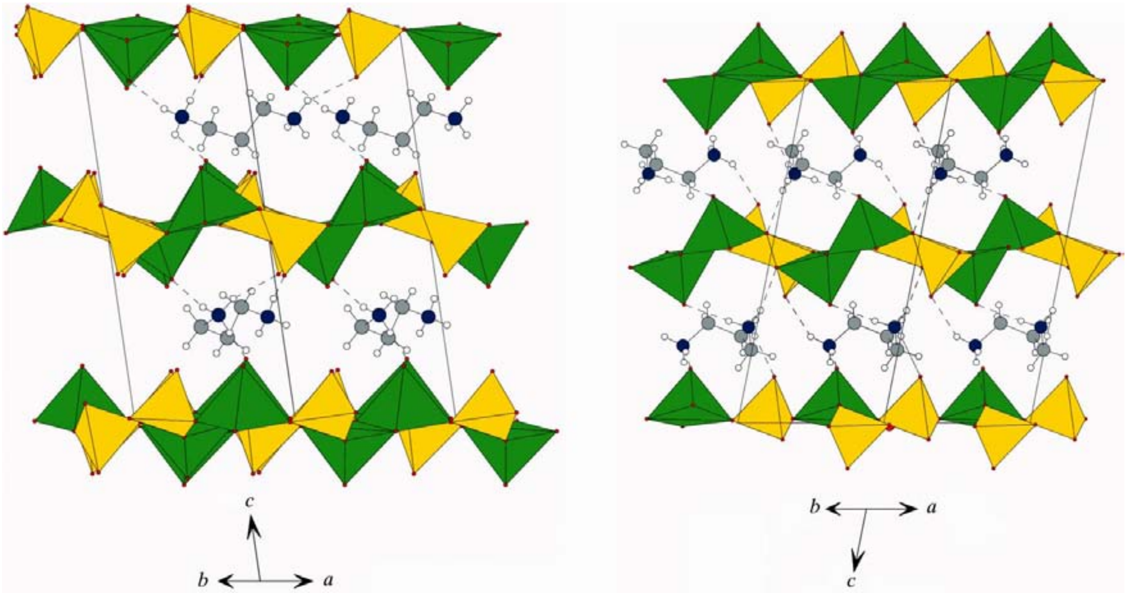


Figure 3
Projections of the structures perpendicular to the c axis, showing the α form along $[\overline{1}\overline{1}0]$ (left) and the β form along [110] (right).

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).

The authors thank Professor Alex Slawin for assistance in data collection, and the University of St Andrews for funding.

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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